

### 314. The Direct Nitration of 5-Chloro-3-hydroxy- and of 5-Chloro-3-nitro-anisole.

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NITRATION of 5-chloro-3-hydroxyanisole in a dilute aqueous medium appears to give first 5-chloro-4-nitro-3-hydroxyanisole (isolated in small quantity by Hodgson and Wignall, J., 1928, 329), which then undergoes further nitration to give 5-chloro-4:6-dinitro-3-hydroxyanisole. More severe nitration conditions afford the 2:4:6-trinitro-compound.

The constitution of the dinitro-compound has been established by the fact that, on treatment with diazomethane, it gives 5-chloro-4:6-dinitroresorcinol dimethyl ether (m. p. 216°), not identical with the 2:4-dinitro-isomeride (m. p. 110°) prepared by nitration of 5-chloro-2-nitroresorcinol dimethyl ether. Further, the 5-chloro-4:6-dinitroresorcinol dimethyl ether is converted by alcoholic potash into the known 5-hydroxy-4:6-dinitroresorcinol dimethyl ether, and by ammonia under pressure into the known 4:6-dinitro-5-aminoresorcinol dimethyl ether (both prepared by Blanksma, *Rec. trav. chim.*, 1908, 27, 254), the latter product being deaminated to the well-known 4:6-dinitroresorcinol dimethyl ether.

5-Chloro-4:6-dinitroresorcinol dimethyl ether is also obtained by the dinitration of 5-chlororesorcinol dimethyl ether and by the action of sodium methoxide under suitable conditions upon 1:3:5-trichloro-2:4-dinitrobenzene. It is noteworthy that, though all three chlorine atoms are reactive towards sodium methoxide, the two which occupy *op*-positions to both nitro-groups, *i.e.*, the 1- and the 5-chlorine atom, are the more labile.

Nitration of 5-chloro-3-nitroanisole gives 5-chloro-3:4:6-trinitroanisole, no dinitro-compound having been isolated, and the constitution follows from its conversion into 5-chloro-4:6-dinitroresorcinol dimethyl ether by means of sodium methoxide.

When 3:5-dichloro-2-nitroanisole was heated with alcoholic potash, the 3-chlorine atom was displaced to give 5-chloro-2-nitro-3-hydroxyanisole. Under the same conditions, the chlorine atom in 3-chloro-2-nitroanisole resists displacement.

#### EXPERIMENTAL.

*Nitration of 5-Chloro-3-hydroxyanisole.*—The compound (6 g.) was added gradually to a well-stirred solution of sodium nitrate (6 g.) in concentrated sulphuric acid (4.2 c.c.) and water (15 c.c.) at 30°, the mixture kept over-night, and the separated product washed free from acid prior to steam distillation, whereby the volatile 5-chloro-4-nitro-3-hydroxyanisole was removed;

it crystallised from dilute alcohol in almost colourless needles, m. p. 106° (Hodgson and Wignall, *loc. cit.*, give m. p. 105°). The non-volatile residue (0.3 g.) of 5-chloro-4 : 6-dinitro-3-hydroxyanisole crystallised from light petroleum in colourless needles, m. p. 126° (Found : N, 11.4; Cl, 14.2.  $C_7H_5O_6N_2Cl$  requires N, 11.3; Cl, 14.3%).

*5-Chlororesorcinol Dimethyl Ether.*—5-Chloro-3-hydroxyanisole (5 g.), dissolved in 20% aqueous sodium hydroxide (50 c.c.) was stirred for  $\frac{1}{2}$  hour at 30° with methyl sulphate (5 g.). The precipitated dimethyl ether crystallised from carbon tetrachloride in stout colourless prisms, m. p. 38° (Found : Cl, 20.5.  $C_8H_9O_2Cl$  requires Cl, 20.6%).

*Nitration of 5-Chlororesorcinol Dimethyl Ether.*—(a) *Mononitration.* The ether (2.4 g.), dissolved in acetic anhydride (8 c.c.), was treated with a solution of nitric acid (1 c.c.; *d* 1.5) in acetic anhydride (4 c.c.) at room temperature, the mixture kept over-night and then poured on ice, and the precipitated 5-chloro-4-nitroresorcinol dimethyl ether crystallised from methyl alcohol; it formed light yellow needles, m. p. 123° (Found : Cl, 16.2. Calc. : Cl, 16.3%), identical with an authentic specimen (Hodgson and Wignall, *loc. cit.*).

(b) *Dinitration.* When the preceding nitration was carried out with 2 c.c. of nitric acid in 8 c.c. of acetic anhydride, stellate clusters (m. p. 210°) of 5-chloro-4 : 6-dinitroresorcinol dimethyl ether separated after 12 hours; this crystallised from methyl alcohol in short prisms, m. p. 216° (Found : N, 10.7; Cl, 13.3.  $C_8H_7O_6N_2Cl$  requires N, 10.6; Cl, 13.5%), identical with the product obtained from 5-chloro-4 : 6-dinitro-3-hydroxyanisole by treatment with diazomethane in ether.

*Action of Sodium Methoxide on 2 : 4 : 6-Trichloronitrobenzene.*—(a) The nitro-compound (2.25 g.) was dissolved in methyl alcohol (35 c.c.) containing sodium (0.3 g.), and the mixture refluxed for 4 hours and steam-distilled; unchanged material came over at first, but the later fractions contained 3 : 5-dichloro-2-nitroanisole, which crystallised from methyl alcohol in colourless needles, m. p. and mixed m. p. with an authentic specimen 75° (Found : Cl, 31.9. Calc. : Cl, 32.0%).

(b) The nitro-compound (2.25 g.), dissolved in methyl alcohol (20 c.c.) containing sodium (0.5 g.), was heated in a sealed tube for  $1\frac{1}{2}$  hours at 120°. After distillation of the alcohol, the residue was steam-distilled until 3 : 5-dichloro-2-nitroanisole ceased to come over. The non-volatile 5-chloro-2-nitroresorcinol dimethyl ether crystallised from acetic anhydride, to which one drop of fuming nitric acid had been added, in short colourless prisms, m. p. 184° (Hodgson and Wignall, *loc. cit.*, give m. p. 171°) (Found : Cl, 16.2. Calc. : Cl, 16.3%).

(c) The mixture as in (b), but with 0.75 g. of sodium, was heated for 5 hours at 150°; the non-volatile product, after steam distillation, was nitrophenolglucinol trimethyl ether, which crystallised from methyl alcohol in stout micro-prisms, m. p. 153° (Found : N, 6.7; OMe, 43.5.  $C_9H_{11}O_5N$  requires N, 6.6; OMe, 43.7%). This product (1 g.), dissolved in acetic anhydride (2 c.c.) and treated with a solution of nitric acid (0.3 c.c.; *d* 1.5) in acetic anhydride (1.5 c.c.) at room temperature, gave dinitrophenolglucinol trimethyl ether, which was precipitated when the reaction mixture was poured on ice; it crystallised from methyl alcohol in colourless needles, m. p. 166° (*lit.* 165°) (Found : N, 10.9. Calc. : N, 10.8%).

*Nitration of 5-Chloro-2-nitroresorcinol Dimethyl Ether.*—The ether (2.2 g.) was added to a solution of nitric acid (4 c.c.; *d* 1.5) in acetic anhydride (8 c.c.) and the mixture was heated to 50°, kept over-night, and poured on ice; the precipitated 5-chloro-2 : 4-dinitroresorcinol dimethyl ether crystallised from alcohol in almost colourless needles, m. p. 110° (Found : N, 10.7; Cl, 13.4.  $C_8H_7O_6N_2Cl$  requires N, 10.6; Cl, 13.5%).

*Action of Sodium Methoxide on 1 : 3 : 5-Trichloro-2 : 4-dinitrobenzene.*—The compound (3 g.), dissolved in benzene (5 c.c.) and methyl alcohol (10 c.c.), was treated gradually in the cold with a solution of sodium (1 g.) in methyl alcohol (5 c.c.). The mixture was kept for 10 days, dinitrophenolglucinol trimethyl ether separating; after crystallisation from methyl alcohol, this had m. p. and mixed m. p. with the previous specimen, 166°. The filtrate from the above product yielded 5-chloro-4 : 6-dinitroresorcinol dimethyl ether on acidification.

*Nitration of 5-Chloro-3-nitroanisole.*—The anisole (3 g.) was boiled for 15 mins. with a solution of nitric acid (20 c.c.; *d* 1.4) in concentrated sulphuric acid (20 c.c.), the cooled mixture poured on ice, and the precipitated 5-chloro-3 : 4 : 6-trinitroanisole crystallised from alcohol, forming orange-yellow prisms, m. p. 128° (Found : N, 15.3; Cl, 12.6.  $C_7H_4O_7N_3Cl$  requires N, 15.1; Cl, 12.8%). Milder conditions failed to effect nitration.

*Action of Sodium Methoxide on 5-Chloro-3 : 4 : 6-trinitroanisole.*—The anisole (1.0 g.), dissolved in methyl alcohol (3 c.c.) and benzene (6 c.c.), was heated on the water-bath for 10 mins. with a solution of sodium (0.15 g.) in methyl alcohol (3 c.c.); water was then added, and the benzene layer separated and allowed to evaporate slowly; 5-chloro-4 : 6-dinitroresorcinol

dimethyl ether crystallised. Recrystallised from methyl alcohol, it formed colourless prisms, m. p. 216° (Found : Cl, 13.4%).

*5-Chloro-2-nitro-3-hydroxyanisole.*—3 : 5-Dichloro-2-nitroanisole (1 g.) was heated with excess of 20% alcoholic potash in a sealed tube for 2 hours at 130°. The mixture was diluted with water, filtered from unchanged material, and acidified with hydrochloric acid; the precipitated *5-chloro-2-nitro-3-hydroxyanisole* crystallised from methyl alcohol in almost colourless needles, m. p. 88° (depressed by the 4-nitro-isomeride) (Found : Cl, 17.2.  $C_7H_6O_4NCl$  requires Cl, 17.4%), which were volatile in steam.

*5-Chloro-2 : 4 : 6-trinitro-3-hydroxyanisole.*—5-Chloro-3-hydroxyanisole (1 g.) was added to well-stirred nitric acid (10 c.c.; *d* 1.47) at room temperature during 15 minutes, and the mixture then heated slowly to the b. p., cooled, and poured on ice. The precipitated *5-chloro-2 : 4 : 6-trinitro-3-hydroxyanisole* crystallised from water in almost colourless micro-prisms, m. p. 147° (Found : N, 14.4; Cl, 12.0.  $C_7H_4O_8N_3Cl$  requires N, 14.3; Cl, 12.1%).

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