CCLXXIX.—*The Dinitration of Monosulphonated* m-*Chlorophenol and the Sulphonation and Subsequent Further Nitration of 3-Chloro-2- and -6-nitrophenols.*

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ALTHOUGH sulphonation of 3-chlorophenol takes place mainly in the 6-position (Hodgson and Kershaw, this vol., p. 1419), it would appear from the present investigation that a sulphonic acid group tends to wander from the 4- to the 6-position, since the ratio of 3-chloro-2 : 4-dinitrophenol to 3-chloro-2 : 6-dinitrophenol produced by the dinitration and subsequent hydrolysis of the sulphonation mixture is larger when the sulphonation is carried out at 100° than when it is carried out below 15°. This result is to be anticipated, since the 6-position is the most active in 3-chlorophenol, whereas n phenol the 4-position has the maximum reactivity, with consequent reversed wandering of the sulphonic acid group from the 6- to the 4-position.

Although 3-chloro-2-nitrophenol is nitrated preferentially in the 6-position (Hodgson and Moore, J., 1925, **127**, 1599), it is sulphonated rather more readily in the 4-position, possibly owing to steric effects associated with the proximity of so many oxygen atoms.

3-Chloro-6-nitrophenol is nitrated or sulphonated in the 4-position; the sulphonic acid produced in the latter case gives on nitration 3-chloro-2 : 6-dinitrophenol-4-sulphonic acid, hydrolysis of the *potassium* salt of which yields 3-chloro-2 : 6-dinitrophenol.

3-Chloro-4-nitrophenol is completely destroyed during attempted sulphonation (compare Hodgson and Moore, *loc. cit.*).

EXPERIMENTAL.

The Dinitration of the Monosulphonation Products of m-*Chlorophenol.*—(a) *Cold sulphonation.* *m*-Chlorophenol (12·8 g.; 1/10 mol.), dissolved in pure concentrated sulphuric acid (10 c.c.), was cooled with ice, treated gradually with oleum (32 g.; 25% SO_3) below 15°, and, after 1 hour, dinitrated below 20° by the very gradual addition of a solution of nitric acid (8·8 c.c.; *d* 1·5) in oleum (30 c.c.; 25% SO_3). The product was kept over-night, diluted with water (30 c.c.), and hydrolysed in a current of steam; a mixture of 3-chloro-2 : 4- and -2 : 6-dinitrophenols then passed over. The soluble products in the distillate were extracted with ether and added to the solid products. The isomerides were dissolved in a hot mixture of glacial acetic acid (60 c.c.) and water

(10 c.c.); on cooling, most of the 3-chloro-2 : 6-dinitrophenol slowly crystallised (3·1 g.; 67%). The filtrate was treated hot with an excess of ammonia; the ammonium salt of 3-chloro-2 : 4-dinitrophenol (10·2 g.) was deposited on cooling. The mother-liquor yielded a further crop of 3-chloro-2 : 6-dinitrophenol (1·5 g.).

(b) *Hot sulphonation.* *m*-Chlorophenol (12·8 g.) and pure concentrated sulphuric acid (20 g.) were heated together on the water-bath for 10 hours, and after the mixture had been diluted with sulphuric acid (8 c.c.; 100%) the operations of dinitration, hydrolysis, and separation were carried out as in (a). The yields of 3-chloro-2 : 4- and -2 : 6-dinitrophenols were 14 g. and 2·4 g. respectively.

Sulphonation of 3-*Chloro*-2-*nitrophenol*.—The phenol (8·7 g.) was added to oleum (11 g.; 30% SO_3) maintained below 20°, the mixture, after being kept over-night, poured on ice (100 g.), and the resulting solution diluted to 1 litre. After exact removal of the free sulphuric acid by means of barium carbonate (about 18 g.), the solution was filtered, neutralised (Congo-red) with potassium carbonate, and evaporated so that crystals of *potassium* 3-*chloro*-2-*nitrophenol*-4-*sulphonate dihydrate* separated in light yellow, flat needles on cooling (Found: N, 4·4; Cl, 10·7; K, 11·7. $C_6H_3O_6NClSK,2H_2O$ requires N, 4·3; Cl, 10·8; K, 11·9%). The constitution of this was settled by conversion through further nitration and subsequent hydrolysis into 3-chloro-2 : 6-dinitrophenol.

Sulphonation and Further Nitration of 3-*Chloro*-2-*nitrophenol*.—The phenol (8·7 g.) was sulphonated as above and the product was kept over-night and then nitrated below 20° (external cooling) with a mixture of nitric acid (2·2 c.c.; 97%) and oleum (6 c.c.; 30% SO_3). After 12 hours, the reaction products were converted into potassium salts as above and the less soluble *potassium* 3-*chloro*-2 : 6-*dinitrophenol*-4-*sulphonate* (Found: N, 8·5; Cl, 10·4; K, 11·4. $C_6H_2O_8N_2ClSK$ requires N, 8·3; Cl, 10·5; K, 11·6%) was separated from the isomeric *potassium* 3-*chloro*-2 : 4-*dinitrophenol*-6-*sulphonate* (Found: N, 8·5; Cl, 10·6; K, 11·7%) by fractional crystallisation. They formed yellow plates and deeper yellow needles. Approximate relative yields were obtained by hydrolysis of the nitration mixture and separation of the resulting 3-chloro-2 : 6-dinitrophenol (4·1 g.) and 3-chloro-2 : 4-dinitrophenol (2·7 g.) by procedure (a) above.

Sulphonation of 3-*Chloro*-6-*nitrophenol*.—This was carried out by the method used for the sulphonation of 3-chloro-2-nitrophenol (above). The *potassium* 3-*chloro*-6-*nitrophenol*-4-*sulphonate dihydrate* eventually obtained crystallised in pale fawn prisms (Found: N, 4·4; Cl, 10·8; K, 11·8. $C_6H_3O_6NClSK,2H_2O$ requires

N, 4·3; Cl, 10·8; K, 11·9%). It was dinitrated, and the product hydrolysed to give 3-chloro-2 : 6-dinitrophenol, but was partly destroyed during the process.

Sulphonation and Further Nitration of 3-*Chloro*-6-*nitrophenol.*—The further nitration of the sulphonation mixture above, unlike that in the case of 3-chloro-2-nitrophenol, was accompanied by considerable decomposition with evolution of chlorine, especially if the temperature was allowed to rise. The *potassium* 3-*chloro*-2 : 6-*dinitrophenol*-4-*sulphonate* (Found : N, 8·1; S, 9·7; K, 11·9. $C_6H_2O_8N_2ClSK$ requires N, 8·3; S, 9·5; K, 11·6%) was obtained in yellow plates in about 50% yield. Like its isomeride, it decomposed with great violence, attended by flame and a heavy deposit of carbon, when heated. On hydrolysis, only 3-chloro-2 : 6-dinitrophenol was obtained.

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