CLXXXIV.—*The Sulphonation of* m-*Chlorophenol and Some New Halogenophenols.*

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THE monosulphonation of *m*-chlorophenol, whether hot or cold, gives almost entirely 3-chlorophenol-6-sulphonic acid. On the current electronic theory this result was to be anticipated, since the normally less intensely activated 4-position is deactivated by the general effect of the 3-chloro-substituent (compare Hodgson and Jenkinson, J., 1929, 469). With the more powerful kationoid reagent, oleum, disulphonation takes place in the 4- and 6-positions.

The solubilities of the salts of 3-chlorophenol-6-sulphonic acid resemble those of the corresponding sulphates, *viz.*, $Ca>Sr>Ba$, and $Na>K$, and the calcium salt is unique in forming a hydrate.

The tetrahydrated barium salts of the 4 : 6-disulphonic acid and of its 2-halogeno-derivatives are of interest from the co-ordination standpoint, and it is suggested that two of the molecules of water are co-ordinated with the barium atom by means of oxygen atoms and that each sulphonic acid group is co-ordinated by means of its negatively charged oxygen atoms with the hydrogen atoms of a molecule of water (compare Sidgwick, "Electronic Theory of Valency," 1927, pp. 192 and 195).

3-Chloro-2 : 4-dibromo-6-nitrophenol is obtained in two crystalline forms according to the method of preparation, *viz.*, elongated needles by the dibromination of 6-nitro-3-chlorophenol, and stout prisms by the nitration of 3-chloro-2 : 4-dibromophenol. Though interconvertible, each form could be recrystallised from alcohol without change of habit. It is tentatively suggested that the two forms are an example of Kekulé's ortho-isomerism.

EXPERIMENTAL.

Monosulphonation of 3-Chlorophenol at 100° and at the Ordinary Temperature.—3-Chlorophenol (12 g.) and concentrated sulphuric acid (20 g.) were heated together for 8 hours on the water-bath, the mixture was then poured into water (1000 c.c.), and the solution was heated on the water-bath while it was being made neutral to Congo-red by addition of barium carbonate. The residue after filtration was extracted several times with boiling water (1000 c.c. in all) and the solution obtained, combined with the filtrate above, was evaporated to dryness, leaving the barium salt (26 g.) of the sulphonic acid (yield, theoretical). The salt was decomposed by dilute sulphuric acid, the solution evaporated to small bulk, and the remainder of the water removed in a vacuum desiccator containing calcium chloride; colourless prisms of 3-chlorophenol-6-sulphonic acid were obtained containing a variable quantity of water of hydration. The constitution of the acid has already been deduced by the authors (J., 1929, 2923). The same results were also obtained when the sulphonation was conducted at room temperature.

The following salts are prepared by adding the corresponding carbonates to solutions of the acid until these are neutral to Congo-red: The *potassium* salt forms anhydrous prisms (Found: C, 28·9; H, 1·7; Cl, 14·4; K, 16·0. $C_6H_4O_4ClSK$ requires C, 29·2; H, 1·7; Cl, 14·4; K, 15·9%). The *sodium* salt is much more soluble in water than the potassium salt, and separates from this solvent in anhydrous, minute, elongated prisms (Found: Cl, 15·6; Na, 10·2. $C_6H_4O_4ClSNa$ requires Cl, 15·4; Na, 10·0%). The *ammonium* salt crystallises in large stout prisms (Found: Cl, 15·9; S, 14·5. $C_6H_4O_4ClSNH_4$ requires Cl, 15·7; S, 14·2%). The *barium* salt forms anhydrous, short, stout prisms which are sparingly soluble in water [Found: C, 26·2; H, 1·6; Ba, 24·6. $(C_6H_4O_4ClS)_2Ba$ requires C, 26·1; H, 1·4; Ba, 24·8%]. The *strontium* salt separates from water, in which it is more soluble than the barium salt, in anhydrous flat prisms [Found: Sr, 17·1. $(C_6H_4O_4ClS)_2Sr$ requires Sr, 17·3%. 0·2195 G. gave 0·3339 g. of mixed silver chloride and strontium sulphate; required, 0·3291 g.). The *lead* salt crystallises in anhydrous prisms which are easily soluble in water [0·2490 g. gave 0·2991 g. of mixed precipitates (see below); required, 0·3016 g.]. The monohydrated *calcium* salt separates from water, in which it is readily soluble, in flat rectangular prisms [Found: C, 30·0; H, 2·4; Cl, 15·0; Ca, 8·6. $(C_6H_4O_4ClS)_2Ca,H_2O$ requires C, 30·4; H, 2·1; Cl, 15·0; Ca, 8·5%].

Analytical Note.—The above salts were analysed for carbon and hydrogen by admixture with lead chromate and combustion in a stream of oxygen in a tube packed with lead chromate. Very few gave stoicheiometric results, but those obtained are recorded. In other cases the amounts of mixed silver halides and insoluble sulphates obtained by the Carius method are given, and also the percentage of metal estimated as sulphate.

Halogenation of 3-Chlorophenol-6-sulphonic Acid.—(a) *Dichlorination.* Barium 3-chlorophenol-6-sulphonate (14 g.) was dissolved in water (1000 c.c.), and the theoretical amount of a freshly prepared solution of barium hypochlorite added. After 12 hours, the mixture was neutralised with sulphuric acid, and the filtered liquid evaporated to small bulk; *barium* 2 : 3 : 4-*trichlorophenol*-6-*sulphonate* then separated in good yield as flat rhombs sparingly soluble in water [Found: Ba, 20·1. $(C_6H_2O_4Cl_3S)_2Ba$ requires Ba, 20·2%]. The *dihydrate* of this salt separated on one occasion in very long prisms [Found: Ba, 19·25. $(C_6H_2O_4Cl_3S)_2Ba,2H_2O$ requires Ba, 19·0%. 0·1225 G. gave 0·1849 g. of mixed precipitates (see above); required, 0·1849 g.].

2 : 3 : 4-*Trichlorophenol* is obtained by heating the above salt in aqueous sulphuric acid (80%) during the passage of steam, in which it is volatile; it crystallises from light petroleum in elongated needle-like prisms, m. p. 79° (Found: Cl, 53·7. $C_6H_3OCl_3$ requires Cl, 53·9%).

2 : 3 : 4-*Trichloroanisole*, obtained from the phenol by the action of methyl sulphate and sodium hydroxide solution, crystallises from alcohol in long, flat, rectangular prisms, m. p. 69·5° (Found: Cl, 50·3. $C_7H_5OCl_3$ requires Cl, 50·3%).

(b) *Dibromination. Barium* 3-*chloro*-2 : 4-*dibromo*-6-*sulphonate dihydrate* was obtained by the action of bromine (2·5 c.c.; 8 g.) on barium 3-chlorophenol-6-sulphonate (7 g.) dissolved in water (500 c.c.). The solution obtained was made neutral to Congo-red with barium carbonate, filtered, and evaporated to small bulk; the product then crystallised in very long prisms sparingly soluble in water [Found: Ba, 15·1. $(C_6H_2O_4ClBr_2S)_2Ba,2H_2O$ requires Ba, 15·2%. 0·1225 G. gave 0·2260 g. of mixed precipitates; required, 0·2338 g.].

The *potassium* salt separates from water, in which it is sparingly soluble, in anhydrous, thin, flat plates (Found: C, 17·8. $C_6H_2O_4ClBr_2SK$ requires C, 17·8%. 0·1116 G. gave 0·1430 g. of mixed silver halides; required, 0·1432 g.).

The *sodium* salt was obtained in clusters of anhydrous flat plates (Found: Na, 6·0. $C_6H_2O_4ClBr_2SNa$ requires Na, 5·9%. 0·2542 G. gave 0·3400 g. of mixed silver halides; required, 0·3320 g.).

The above salts are extremely stable and very difficult to hydrolyse, as they crystallise unchanged from hot concentrated sulphuric acid; the free acid, however, is easily hydrolysed under the same conditions.

3-*Chloro*-2 : 4-*dibromophenol* was prepared by heating for 8 hours on the water-bath a mixture of 3-chlorophenol (65 g.) and concentrated sulphuric acid (12 g.), then pouring it on ice (30 g.) and adding bromine (16 g.). After 4 hours, a small quantity (less than 1 g.) of 3-chloro-2 : 4 : 6-tribromophenol which had separated was removed and the filtrate was hydrolysed in steam; the 3-chloro-2 : 4-dibromophenol (9·5 g.) which passed over crystallised from light petroleum in long colourless prisms, m. p. 88° (0·2228 g. gave 0·4062 g. of mixed silver halides; required, 0·4039 g.). Its constitution was established by nitration to 3-*chloro*-2 : 4-*dibromo*-6-*nitrophenol* as follows: the phenol (9 g.), dissolved in glacial acetic acid (20 c.c.), was treated gradually, whilst ice-cold, with a solution of nitric acid (1·8 c.c.; *d* 1·5) in glacial acetic acid (7 c.c.). The mixture was kept over-night and the 3-chloro-2 : 4-dibromo-6-nitrophenol was then precipitated by the addition of water (500 c.c.), and crystallised from alcohol (yield, 8·0 g.; 76%); m. p. 90° (0·2143 g. gave 0·3470 g. of mixed silver halides; required, 0·3504 g.). The product was identical (m. p. and mixed m. p.) with that obtained by treating 3-chloro-6-nitrophenol (3 g.), dissolved in glacial acetic acid (15 c.c.), with bromine (2·4 g.).

3-*Chloro*-2 : 4-*dibromoanisole*, prepared by the usual method, crystallises from alcohol in very long, flat prisms, m. p. 92° (0·2312 g. gave 0·4019 g. of mixed silver halides; required, 0·3996 g.).

3-*Chloro*-2 : 4 : 6-*tribromoanisole* is obtained by bromination of the previous product in glacial acetic acid, and also by methylation of the corresponding phenol (see above). It crystallises from alcohol or acetic acid in long needles, m. p. 92° (0·1409 g. gave 0·2643 g. of mixed silver halides; required, 0·2620 g.).

(c) *Di-iodination.* 3-*Chloro*-2 : 4-*di-iodophenol*-6-*sulphonic acid trihydrate* is obtained from the corresponding barium salt (see below) by treatment with dilute sulphuric acid, the solution being then evaporated to small bulk and the acid precipitated by means of concentrated hydrochloric acid; it forms long flat prisms, m. p. 167° (slight decomp.) (Found: S, 6·7. $C_6H_3O_4ClI_2S,3H_2O$ requires S, 6·2%. 0·2328 G. gave 0·2764 g. of mixed silver halides; required, 0·2774 g.).

The tetrahydrated *barium* salt was obtained when barium 3-chlorophenol-6-sulphonate (10 g.), powdered iodine (20 g.), precipitated mercuric oxide (8 g.), alcohol (60 c.c.), and water (20 c.c.) were shaken together for 30 minutes. After removal of the excess iodine by the gradual addition of sodium bisulphite solution, the whole mixture was evaporated to dryness, the residue extracted with boiling water (300 c.c.), and barium chloride (2 g.) added to the filtered extract; when this was then evaporated to 100 c.c., the sparingly soluble salt was obtained in long thin prisms. Any mercuric iodide which may separate with the product may be removed by extraction with boiling alcohol [Found : Ba, 12·1. $(C_6H_2O_4ClI_2S)_2Ba,4H_2O$ requires Ba, 12·17%]. (Mercuric iodide is definitely soluble in hot water, and may be steam-distilled from hot sulphuric acid, passing over in the yellow form which subsequently becomes red.)

3-*Chloro*-2 : 4-*di-iodophenol,* obtained from its 6-sulphonic acid (above) by hydrolysis, crystallises from light petroleum in long prisms, m. p. 111·5° (0·1329 g. gave 0·2161 g. of mixed silver halides; required, 0·2144 g.).

3-*Chloro*-2 : 4-*di-iodoanisole,* readily obtained in the usual way, crystallises from alcohol in somewhat stout prisms, m. p. 105° (0·1715 g. gave 0·2701 g. of mixed silver halides; required, 0·2667 g.).

Disulphonation of 3-*Chlorophenol.*—*Barium* 3-*chlorophenol*-4 : 6-*disulphonate tetrahydrate* is obtained when 3-chlorophenol (12·8 g.) is added gradually to oleum (75 g.; 27% SO_3) with cooling, the mixture kept over-night, then heated for 2 hours on the water-bath, poured into water (1000 c.c.), rendered neutral to Congo-red by addition of barium carbonate (about 10 g.), and the filtered solution evaporated to dryness. It is a white powder, which, like the salts of the other sulphonic acids described later, is very soluble in water, in marked contrast to the sparing solubility of the barium salts of the 6-monosulphonic acids described above. The product crystallises from water in clusters of minute short prisms (Found : Ba, 27·4. $C_6H_3O_7ClS_2Ba,4H_2O$ requires Ba, 27·7%).

Halogenation of the above Barium Salt and Preparation of the 2-*Halogeno*-3-*chlorophenols.*—(a) *Chlorination. Barium* 2 : 3-*dichlorophenol*-4 : 6-*disulphonate tetrahydrate* is obtained when the foregoing barium salt (24 g.), dissolved in water (500 c.c.), is treated with the theoretical quantity of freshly prepared barium hypochlorite solution, the mixture kept over-night and neutralised with sulphuric acid, and the solution filtered and evaporated to dryness. It crystallises from water in clusters of long prisms (Found : Ba, 26·2. $C_6H_2O_7Cl_2S_2Ba,4H_2O$ requires Ba, 25·9%).

2 : 3-Dichlorophenol, prepared from the above product in 70% yield by the usual procedure for the elimination of sulphonic acid groups, forms a mass of prisms on solidification after distillation, m. p. 58°, b. p. 206° (Found : Cl, 43·5. Calc.: Cl, 43·6%).

2 : 3-*Dichloro*-4 : 6-*dibromophenol* is readily obtained by direct dibromination of the above phenol and separates from glacial acetic acid in colourless needles which rapidly become opaque; m. p. 90° (0·1581 g. gave 0·3230 g. of mixed silver halides; required, 0·3266 g.).

2 : 3-*Dichloro*-4 : 6-*dibromoanisole* crystallises from alcohol in long needle-like prisms, m. p. 82° (0·1324 g. gave 0·2623 g. of mixed silver halides; required, 0·2621 g.).

(b) *Bromination.* 3-Chlorophenol (12·8 g.) was disulphonated as above, the solution diluted with water (100 c.c.) and treated with bromine (16 g.), and the resulting solution hydrolysed to give the corresponding phenol or diluted to 1000 c.c. and neutralised with barium carbonate, etc., as above.

Barium 3-*chloro*-2-*bromophenol*-4 : 6-*disulphonate tetrahydrate* crystallises from water in small prisms (Found: Ba, 24·0. $C_6H_2O_7ClBrS_2Ba,4H_2O$ requires Ba, 23·8%. 0·1615 G. gave 0·1541 g. of mixed precipitates; required, 0·1558 g.).

3-*Chloro*-2-*bromophenol* is obtained in 75% yield as above and crystallises from light petroleum in large stout prisms, m. p. 55·5°, b. p. 225° (0·2438 g. gave 0·3892 g. of mixed silver halides; required, 0·3910 g.).

3-*Chloro*-2-*bromoanisole*, obtained by the action of methyl sulphate and sodium hydroxide on the above phenol, crystallises from alcohol in long colourless plates, m. p. and mixed m. p. with a specimen prepared from 3-chloro-2-aminoanisole (Hodgson and Kershaw, *loc. cit.*), 50°.

A solution of 3-chloro-2-bromophenol (7 g.) in ice-cold glacial acetic acid (7 c.c.) was treated with nitric acid (3·5 c.c.; *d* 1·5) in glacial acetic acid (4 c.c.). After 12 hours, steam distillation removed the volatile 3-*chloro*-2-*bromo*-6-*nitrophenol*, which crystallised from light petroleum in small yellow prisms, m. p. 98·5° (0·0755 g. gave 0·0990 g. of mixed silver halides; required, 0·0991 g.), leaving behind the non-volatile 3-*chloro*-2-*bromo*-4-*nitrophenol*, which crystallised from dilute alcohol in fine, almost colourless, needles, m. p. 136° (0·1949 g. gave 0·2601 g. of mixed silver halides; required, 0·2569 g.).

(c) *Iodination.* *Barium* 3-*chloro*-2-*iodophenol*-4 : 6-*disulphonate tetrahydrate* was prepared by stirring for 1 hour a mixture of barium 3-chlorophenol-4 : 6-disulphonate (13 g.), finely powdered iodine (7·6 g.), precipitated mercuric oxide (3·3 g.), alcohol (50 c.c.), and water (50 c.c.), during which period most of the iodine disappeared. The alcohol was then boiled off, and the residue extracted with boiling water (200 c.c.); the filtered extract on slow evaporation gave the product in small rectangular prisms (Found: Ba, 22·4. $C_6H_2O_7ClIS_2Ba,4H_2O$ requires Ba, 22·1%. 0·1814 G. gave 0·1745 g. of mixed precipitates; required, 0·1783 g.).

3-*Chloro*-2-*iodophenol* was prepared by hydrolysis of the above disulphonate and also by the action of potassium iodide on diazotised 3-chloro-2-aminophenol. It crystallises from light petroleum in colourless needles, m. p. 56° (Found: 0·1107 g. gave 0·1692 g. of mixed silver halides, required, 0·1646 g.).

Colour Reactions of the Sulphonic Acids with Ferric Chloride.—An aqueous solution of 3-chlorophenol-6-sulphonic acid gives a violet colour with ferric chloride, and the salts give similar but deeper colours. The colours are not produced in concentrated acid solutions.

The halogeno-derivatives of the above acid give bluer colours than the parent acid, all the halogens having approximately the same effect : the nitro-derivatives give brownish-red colours.

3-Chlorophenol-4 : 6-disulphonic acid and its salts give red colours : the halogeno- and nitro-derivatives have similar effects on the shades as in the case of the monosulphonic acids and salts.

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