

9. *The Synthesis and Orientation of Trichloroanthraquinones and Amino-disulphonates of Anthraquinone. Part II.*

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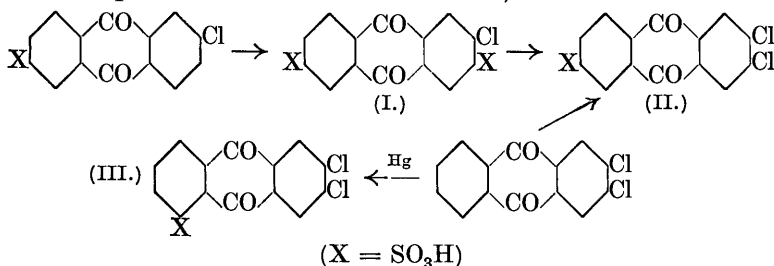
OF the fourteen theoretically possible trichloroanthraquinones, nine have been synthesised and their orientations determined (compare Part I, J., 1931, 1771). The unknown isomerides are the 2:3:5-, 2:3:6-, 1:2:8-, 1:3:5-, and 1:3:8-trichloro-compounds.

The present work deals principally with derivatives of β -chloroanthraquinone; of the five unknown trichloroanthraquinones, three have been obtained and the constitutions of two of these definitely established, namely, the 2:3:5-, 2:3:6-, and 1(?) : 2:8-compounds, m. p. 227—228°, 245°, and 190—192° respectively.

The sulphonation of β -chloroanthraquinone has not been studied because, according to the rules already established in Part I concerning the entrance of the sulpho-group into the molecule of a chloroanthraquinone, it would produce a mixture of the known 2-chloroanthraquinone-6- and -7-sulphonic acids: since their alkali salts are almost completely insoluble in water, no method presents itself for their separation and, in consequence, for the determination of the constitutions of the products. These compounds are,

however, readily obtained by the chlorination of the corresponding alkali anthraquinone-2 : 6- and -2 : 7-disulphonates.

Sulphonation of potassium 2-chloroanthraquinone-6-sulphonate yields a homogeneous product which has been shown to be *potassium 2-chloroanthraquinone-3 : 6-disulphonate* (I) : the action of nascent chlorine upon this replaces the sulpho-group adjacent to the halogen, giving insoluble *potassium 2 : 3-dichloroanthraquinone-6-sulphonate* (II) (*sulphonyl chloride*, m. p. 229—230°). The sulpho-group in this substance completely resists replacement by chlorine by the reaction either of the nascent element with the potassium salt, or of thionyl chloride with the sulphonyl chloride at a high temperature (compare and contrast the behaviour of 2-chloroanthraquinone-6- and -7-sulphonates under similar conditions).



Orientation. The second-entering sulpho-group in the chloroanthraquinonedisulphonate, for reasons already set out (Part I), must occupy a position in the chlorine-containing nucleus, and accordingly there are but three structures which may be assigned to this substance. Two of the possibilities are untenable, for, if the sulphonating agent attacked either the 1- or the 4-position, it would be this α -sulpho-group which is replaced by chlorine, since no case is known in which an α -sulpho-group can resist removal by this element : in consequence, the chlorination product would be either the 1 : 2-dichloroanthraquinone-6-sulphonate or the 1 : 3-dichloroanthraquinone-7-sulphonate, both of which react normally with chlorine, giving the corresponding trichloroanthraquinone (Part I). Hence the second sulpho-group must occupy the 3-position—a conclusion which might have been deduced from the ortho- and meta-directive influences of chlorine and carbonyl respectively. The chlorination product (II) may therefore have one of two possible constitutions, and in view of the stability of the 6- and the 7-sulpho-group in anthraquinone-2 : 6- and -2 : 7-disulphonates it would appear highly probable that it is the same sulpho-group which is unreactive in potassium 2-chloroanthraquinone-3 : 6-disulphonate. That this is the case is proved by the study of the sulphonation of 2 : 3-dichloroanthraquinone.

As anticipated, 2 : 3-dichloroanthraquinone on sulphonation yields a homogeneous product consisting of 2 : 3-dichloroanthraquinone-6-sulphonic acid, which is, as are the alkali salts, insoluble in water and completely resistant to attack by chlorine. The sulphonyl chloride, m. p. 229—230°, is identical with that of (II). This identity supplies the necessary information to prove that both these substances possess the constitution assigned to them and, moreover, independently establishes the structure of (I).

The catalytic sulphonation of 2 : 3-dichloroanthraquinone gives a dichloroanthraquinonemonosulphonic acid (III) which is different from the non-catalytic product not only because both the free acid and the alkali salts are easily soluble in water but also because it reacts rapidly with nascent chlorine—a reaction diagnostic of α -sulpho-groups (Part I)—giving a trichloroanthraquinone, m. p. 227—228°. Since the sulphonating agent undoubtedly attacks the unsubstituted nucleus of the dichloroanthraquinone, and moreover the trichloroanthraquinone is not the 1 : 2 : 3-compound, the parent substance must be *potassium* 2 : 3-dichloroanthraquinone-5-sulphonate and the product derived from it, m. p. 228°, is 2 : 3 : 5-trichloroanthraquinone. More prolonged catalytic sulphonation gives *potassium* 2 : 3-dichloroanthraquinone-1 : 5(or 8)-disulphonate, since this yields a compound, m. p. 208°, which must be 1 : 2 : 3 : 5-(or 8)-tetrachloroanthraquinone.

2 : 3 : 6-Trichloroanthraquinone.—Sulphonation of 2 : 7-dichloroanthraquinone yields 2 : 7-dichloroanthraquinone-3-sulphonic acid, m. p. above 300°, the sulpho-group in which is replaceable by chlorine, although with difficulty, giving 2 : 3 : 6-trichloroanthraquinone, m. p. 245°. The directive influences at work within the molecule of the parent dichloroanthraquinone and the enhanced stability of the sulphonation product towards chlorine strongly indicate the presence of a β -sulpho-group, and this is proved by the fact that the trichloroanthraquinone, m. p. 246°, which, *a priori*, must be 1 : 2 : 7-, 1 : 3 : 6-, or 2 : 3 : 6-trichloroanthraquinone, is neither of the first two. Moreover the constitution of this trichloroanthraquinone is independently proved by its rational synthesis from 4 : 5-dichlorophthalic anhydride and chlorobenzene; these condense to give 4' : 4 : 5-trichloro-2-benzoylbenzoic acid, m. p. 196—197°, which on closure of the anthraquinone ring yields a trichloroanthraquinone, m. p. 245°, identical with that obtained from 2 : 7-dichloroanthraquinone-3-sulphonic acid.

It is remarkable that 2 : 6-dichloroanthraquinone, when sulphonated under the same conditions as its 2 : 7-isomeride, gives only a disulphonic acid, m. p. above 300°, believed, by analogy, to be 2 : 6-dichloroanthraquinone-3 : 7-disulphonic acid. This is not

converted into the corresponding tetrachloroanthraquinone by the action of nascent chlorine.

Sulphonation of potassium 2-chloroanthraquinone-7-sulphonate gives *potassium 2-chloroanthraquinone-3 : 7-disulphonate*, the action of chlorine upon which replaces only one sulpho-group with the production of potassium 2 : 3-dichloroanthraquinone-6-sulphonate, identified as such by means of its sulphonyl chloride. There appears, however, a peculiar tendency for chlorine, besides replacing the 3-sulpho-group in the above chloroanthraquinonedisulphonate, to enter the nucleus—a tendency which has no analogue in the large number of similar chlorinations previously described. This may be coupled with the extreme readiness with which 2 : 6-dichloroanthraquinone undergoes disulphonation, since that may be ascribed to the enhanced reactivity of the intermediate 2 : 6-dichloroanthraquinone-3-sulphonic acid which presumably is initially formed.

The Sulphonation of 1 : 7-Dichloroanthraquinone.—It is considered highly probable that in the presence of mercury a sulpho-group would enter the molecule of 1 : 7-dichloroanthraquinone in the α -position which is ortho to the β -chlorine substituent. The product obtained in this reaction exhibits the property of an α -sulphonate in reacting rapidly with nascent chlorine, to give a trichloroanthraquinone, m. p. 190—192°. This is accordingly believed to be 1 : 2 : 8-trichloroanthraquinone, but this view must be accepted with reserve until substantiated by further evidence.

The Reactivity of Chloroanthraquinone-mono- and -di-sulphonates towards Ammonia.—It has been shown that the mono- and disulphonates of α -chloroanthraquinone resemble certain negatively substituted halogenobenzenes, notably picryl chloride and chlorodinitrobenzene, inasmuch as the halogen substituent is mobile, these substances readily condensing at temperatures which are not necessarily high with ammonia to form amino-mono- and -disulphonic acids of anthraquinone. The β -chlorine substituent in potassium 2-chloroanthraquinone-6- and -7-sulphonates, however, is not mobile, but the entrance of the strongly negative sulpho-group in the β -position contiguous to the halogen confers the necessary mobility upon the latter : both potassium 2-chloroanthraquinone-3 : 6- and -3 : 7-disulphonates readily condense with ammonia with the formation of the corresponding *aminoanthraquinonedisulphonates*. These substances possess powerful tinctorial properties and are substantive to animal fabric.

The Colour of the Chloroanthraquinones.—The capacity displayed by the chloroanthraquinones for the selective absorption of light depends entirely upon the position of the halogen substituents. The chloroanthraquinones possessing one or more substituents in

α -positions have a pronounced yellow colour, as also do their solutions in acetic acid, in which they all readily dissolve. The three $\beta\beta$ -dichloroanthraquinones and the $\beta\beta\beta$ -compound, however, are but feebly coloured and dissolve in acetic acid with difficulty with the production of almost colourless solutions.

The Identification of the Disulphonates of Anthraquinone.—Since the disulphonyl chlorides of anthraquinone decompose at or below the melting point, they are undesirable as reference compounds for the identification of the corresponding disulphonates. The chlorination products, on the other hand, are in all cases well-defined sharp-melting substances and accordingly are ideal for this purpose; moreover they are usually more easily obtained than are the disulphonyl chlorides. The two $\alpha\alpha$ -disulphonates are rapidly and directly converted by the action of nascent chlorine into the corresponding dichloroanthraquinones; the $\beta\beta$ -disulphonates yield as sole products the chlorosulphonates, identifiable as such by means of the chlorosulphonyl chlorides; whereas the $\alpha\beta$ -disulphonates give as intermediates the α -chloro- β -sulphonates, which may be converted either into the sulphonyl chlorides or, by the further action of chlorine, into the $\alpha\beta$ -dichloroanthraquinones.

EXPERIMENTAL.

Potassium 2-Chloroanthraquinone-6- and -7-sulphonates.—A solution of sodium anthraquinone-2:6-disulphonate (100 g.) in water (3500 c.c.) containing hydrochloric acid (500 c.c.) was heated on the steam-bath, and a saturated solution of potassium chlorate (200 g.) slowly added. The heating was continued all night and the precipitated potassium 2-chloroanthraquinone-6-sulphonate was then separated from the hot liquor, washed with much boiling water, dried, pulverised, and extracted with an excess of rectified spirit to remove a small quantity of 2:6-dichloroanthraquinone (yield, 61 g.).

The sulphonyl chloride, prepared in the manner described for isomeric compounds (Goldberg, J., 1931, 1780), crystallised from benzene in pale yellow leaves, m. p. 202—203° (Found: Cl, 20.7. Calc. for $C_{14}H_6O_4Cl_2S$: Cl, 20.8%).

Sodium anthraquinone-2:7-disulphonate (100 g.), dissolved in water (3000 c.c.) containing hydrochloric acid (250 c.c.) and potassium chlorate (100 g.), was heated at 100° for 12 hours. A further quantity of hydrochloric acid (250 c.c.) and potassium chlorate (100 g.) in aqueous solution was then added, heating continued for 30—35 hours, and the precipitated potassium 2-chloroanthraquinone-7-sulphonate collected. After being washed with boiling water and extracted with alcohol, it was obtained as a light yellow powder (25 g.).

The sulphonyl chloride crystallised from benzene in stellate clusters of elongated, pale yellow needles, m. p. 200—201° (Fierz-David, *Helv. Chim. Acta*, 1927, **10**, 209, gives 176°); this m. p. was considerably depressed in admixture with 2-chloroanthraquinone-6-sulphonyl chloride (Found : Cl, 20·9%).

Both potassium 2-chloroanthraquinone-6- and -7-sulphonates are insoluble in water and are not acted upon by nascent chlorine.

Sulphonation of Potassium 2-Chloroanthraquinone-6-sulphonate. Potassium 2-Chloroanthraquinone-3 : 6-disulphonate.—A solution of potassium 2-chloroanthraquinone-6-sulphonate (200 g.) in 20% fuming sulphuric acid (600 c.c.) was heated at 155—160° for 10 hours. The red melt was poured into an excess of ice-water, and the finely divided precipitate of unchanged 2 : 6-chloro-sulphonate removed by filtration. The combined filtrate and washings, after the addition of a solution of potassium hydroxide (400 g.), were evaporated to ca. 3000 c.c. and after some time the bulky precipitate was collected; a further crop was obtained by concentrating the mother-liquor. The combined precipitates were crystallised twice from water, small head fractions being rejected each time. The *potassium 2-chloroanthraquinone-3 : 6-disulphonate* (180 g.) thus obtained is soluble in about 10 parts of boiling water and crystallises in slender lemon-yellow needles (Found in dehydrated salt : S, 13·3. $C_{14}H_5O_8ClS_2K_2$ requires S, 13·4%). The calcium, lead, and barium salts are precipitated when the ions of these metals are added to a solution of the potassium salt. The first is soluble in boiling water, the lead salt almost insoluble in water but soluble in dilute nitric acid, and the barium salt insoluble in both these solvents.

Chlorination of Potassium 2-Chloroanthraquinone-3 : 6-disulphonate. Potassium 2 : 3-Dichloroanthraquinone-6-sulphonate.—A solution of potassium 2-chloroanthraquinone-3 : 6-disulphonate (80 g.) in water (3000 c.c.) was treated with hydrochloric acid (600 c.c.) and potassium chlorate (150 g.) and heated on the steam-bath for 48—60 hours. The precipitated *potassium 2 : 3-dichloroanthraquinone-6-sulphonate* was collected, washed with boiling water, and lixiviated with rectified spirit; it was then obtained as a pale yellow, amorphous powder (49 g.), insoluble in water (Found in anhydrous salt : S, 8·5. $C_{14}H_5O_5Cl_2SK$ requires S, 8·1%). Nascent chlorine has no action upon an aqueous suspension of the substance.

2 : 3-Dichloroanthraquinone-6-sulphonyl chloride crystallises from xylene in microcrystalline tablets, m. p. 227—229° (Found : Cl, 28·7. $C_{14}H_5O_4Cl_3S$ requires Cl, 28·4%).

Potassium 2-Aminoanthraquinone-3 : 6-disulphonate.—A solution of potassium 2-chloroanthraquinone-3 : 6-disulphonate (25 g.) in water (300 c.c.) containing hydrated copper sulphate (3 g.) was

heated with aqueous ammonia (120 c.c.; d 0.880) in a sealed tube at 100° for 60 hours. The product was evaporated to dryness, redissolved, and warmed with the minimum amount of aqueous potassium hydroxide to decompose the ammonium chloride that was formed. After acidification with dilute hydrochloric acid the copper was removed as sulphide, and the solution evaporated; *potassium 2-aminoanthraquinone-3:6-disulphonate* (18 g.) then slowly separated in a microcrystalline form. It is easily soluble in boiling water, giving an intensely red solution even at great dilutions, and crystallises in dark red micro-needles (Found in dehydrated salt: S, 13.7; N, 3.4. $C_{14}H_7O_8NS_2K_2$ requires S, 13.9; N, 3.1%).

Sulphonation of 2:3-Dichloroanthraquinone. Potassium 2:3-Dichloroanthraquinone-6-sulphonate.—2:3-Dichloroanthraquinone was prepared by the condensation of phthalic anhydride with *o*-dichlorobenzene (Phillips, *J. Amer. Chem. Soc.*, 1927, **49**, 473) and by the condensation of 4:5-dichlorophthalic anhydride (Villiger, *Ber.*, 1909, **42**, 3529) with benzene (Ullmann and Billig, *Annalen*, 1911, **381**, 11). It crystallised from acetic acid, in which it was difficultly soluble, in needles, *m. p.* 267° .

2:3-Dichloroanthraquinone (20 g.) was dissolved in 20% fuming sulphuric acid (25 c.c.) and heated at 155 – 160° for 4 hours. The semi-solid product was poured into ice-water (400 c.c.), a large dark grey precipitate being thrown down. Nitric acid (10 c.c.) was added, and the mixture heated on the steam-bath until the dark colour was discharged. The insoluble 2:3-dichloroanthraquinone-6-sulphonic acid was separated and suspended in water, and potassium hydroxide added until the mixture was alkaline; it was then heated for some time on the steam-bath. The solid was washed with water, dried, and refluxed with an excess of acetic acid to remove unchanged 2:3-dichloroanthraquinone. On filtration, *potassium 2:3-dichloroanthraquinone-6-sulphonate* was obtained as a yellowish-grey amorphous powder insoluble in water (Found in anhydrous salt: S, 8.4. $C_{14}H_5O_5Cl_2SK$ requires S, 8.1%). The *sulphonyl chloride* crystallised from xylene in microcrystalline yellow-grey tablets, *m. p.* 228 – 229° alone and in admixture with the dichloroanthraquinonesulphonyl chloride obtained by the chlorination of potassium 2-chloroanthraquinone-3:6-disulphonate (Found: Cl, 28.2. $C_{14}H_5O_4Cl_3S$ requires Cl, 28.4%).

Catalytic Sulphonation of 2:3-Dichloroanthraquinone. Potassium 2:3-Dichloroanthraquinone-5-sulphonate.—A solution of 2:3-dichloroanthraquinone (10 g.) in 20% fuming sulphuric acid (7 c.c.) was heated with yellow mercuric oxide (1.5 g.) for $2\frac{1}{2}$ hours, with shaking at frequent intervals. The product was poured into water, and the liquid filtered from unchanged dichloroanthraquinone and a

small quantity of the 6-sulphonate which was formed. After decolorisation of the filtrate with nitric acid an aqueous solution of potassium hydroxide (5 g.) was added, and the yellow solution concentrated to small bulk; *potassium 2 : 3-dichloroanthraquinone-5-sulphonate* then crystallised in small yellow leaves. Recrystallisation from water, in which it was easily soluble, gave the pure salt (Found in dehydrated salt : S, 8.4. $C_{14}H_5O_5Cl_2SK$ requires S, 8.1%).

Chlorination of Potassium 2 : 3-Dichloroanthraquinone-5-sulphonate. 2 : 3 : 5-Trichloroanthraquinone.—A dilute aqueous solution of potassium 2 : 3-dichloroanthraquinone-5-sulphonate was treated with nascent chlorine at 100° in a manner previously described (Part I). Precipitation of 2 : 3 : 5-trichloroanthraquinone was very rapid, being complete in several hours. It crystallised from acetic acid in stellate clusters of lemon-yellow needles, m. p. 227—228°, which depressed the m. p. of 1 : 2 : 3-trichloroanthraquinone (Found : Cl, 34.2. $C_{14}H_5O_2Cl_3$ requires Cl, 34.1%).

Catalytic Disulphonation of 2 : 3-Dichloroanthraquinone. Potassium 2 : 3-Dichloroanthraquinone-1(or 4) : 5-disulphonate and 1 : 2 : 3 : 5(or 8)-Tetrachloroanthraquinone.—2 : 3-Dichloroanthraquinone (10 g.) was agitated with 20% fuming sulphuric acid (10.5 c.c.) and yellow mercuric oxide (2 g.) for 4 hours at 155—160°. The product was poured into water and treated in the same manner as the catalytic monosulphonation product. After the addition of potassium hydroxide (10 g.) the solution was concentrated and cooled and the first crop of crystals (ca. 3 g.) rejected. The filtered solution was further concentrated; on standing, potassium 2 : 3-dichloroanthraquinone-1(or 4) : 5-disulphonate came down in small leaves, which were obtained pure after one crystallisation.

A dilute aqueous solution of the salt was treated with nascent chlorine, the quantities being the same as those already recorded for isomeric substances. 1 : 2 : 3 : 5(or 8)-Tetrachloroanthraquinone was rapidly precipitated and on crystallisation from acetic acid was obtained in tufted, small, pale yellow needles, m. p. 208° (Found : Cl, 41.2. $C_{14}H_4O_2Cl_4$ requires Cl, 41.0%).

Sulphonation of 2 : 7-Dichloroanthraquinone. 2 : 7-Dichloroanthraquinone-3-sulphonic Acid.—2 : 7-Dichloroanthraquinone was obtained from the corresponding diaminoanthraquinone by the method of D.R.-P. 197,554. A solution of 2 : 7-dichloroanthraquinone (40 g.) in 20% fuming sulphuric acid (50 c.c.) was heated at 155—160° for 4 hours. The semi-solid product was poured into water, and the mixture heated on the steam-bath over-night in order to coagulate the precipitate and render it filterable. The filtered solution was decolorised with nitric acid and concentrated

until crystallisation began. On cooling, 2 : 7-dichloroanthraquinone-3-sulphonic acid separated in attenuated yellow needles (13 g.), m. p. above 300°. The acid is readily soluble in boiling water and is precipitated in the crystalline form by the addition of mineral acids (Found in anhydrous acid : S, 9.3. $C_{14}H_6O_5Cl_2S$ requires S, 9.0%).

Chlorination of 2 : 7-Dichloroanthraquinone-3-sulphonic Acid. 2 : 3 : 6-Trichloroanthraquinone.—A solution of 2 : 7-dichloroanthraquinone-3-sulphonic acid (10 g.) in water (500 c.c.) containing hydrochloric acid (45 c.c.) and sodium chlorate (15 g.) was heated on the steam-bath over-night. The gelatinous precipitate was then collected, suspended in water (2500 c.c.) containing hydrochloric acid (100 c.c.) and sodium chlorate (10 g.), and heated on the steam-bath for a further 36 hours. The 2 : 3 : 6-trichloroanthraquinone (7 g.) crystallised from acetic acid, in which it dissolved with difficulty, giving an almost colourless solution, in long, pale yellow needles, m. p. 245°, which depressed the m. p. of 2 : 3 : 5-trichloroanthraquinone (Found : Cl, 34.1. $C_{14}H_5O_2Cl_3$ requires Cl, 34.1%).

Sulphonation of 2 : 6-Dichloroanthraquinone. 2 : 6-Dichloroanthraquinone-3(?) : 7(?)-disulphonic Acid.—2 : 6-Dichloroanthraquinone (40 g.) was sulphonated in the same way as the 2 : 7-isomeride. The decolorised dilute sulphuric acid solution was evaporated to ca. 220 c.c. and allowed to cool; 2 : 6-dichloroanthraquinone-3(?) : 7(?)-disulphonic acid then crystallised in long, lemon-yellow needles (19 g.), m. p. above 300°. It is very soluble in boiling water and is precipitated from its aqueous solution by the addition of mineral acids (Found in anhydrous acid : S, 14.9, 14.6; Cl, 15.8. $C_{14}H_6O_8Cl_2S_2$ requires S, 14.65; Cl, 16.3%).

Condensation of 4 : 5-Dichlorophthalic Anhydride with Chlorobenzene. 4' : 4 : 5-Trichloro-2-benzoylbenzoic Acid.—Finely divided aluminium chloride (80 g.) was stirred with 40 g. of 4 : 5-dichlorophthalic anhydride in chlorobenzene (300 g.) at 105–110° for 7½ hours with exclusion of moisture. The product was poured into water, the chlorobenzene distilled off in steam, and the residual solid separated, pulverised, and extracted thoroughly with boiling dilute aqueous sodium carbonate. The filtered extract was acidified with hydrochloric acid, and the precipitate dissolved by boiling with a large volume of aqueous ammonia (charcoal). Acidification of the cold solution precipitated 4' : 4 : 5-trichloro-2-benzoylbenzoic acid in white flocks (56 g.). The acid was dissolved in alcohol, and water added until a faint turbidity was produced; on cooling, the acid was precipitated quantitatively as a mass of long white needles, m. p. 196–197° (Found : Cl, 32.5. $C_{14}H_7O_3Cl_3$ requires Cl, 32.4%). The acid is very soluble in alcohol but insoluble in water; the

ammonium salt crystallises from water, in which it is soluble with difficulty, in white tablets.

2 : 4 : 6-Trichloroanthraquinone.—The above trichlorobenzoylbenzoic acid (10 g.) was dissolved in 5% fuming sulphuric acid (40 c.c.) and heated at 155–160° for 3½ hours. The product was poured into water, and the precipitate collected and digested with dilute aqueous sodium hydroxide to remove unchanged trichlorobenzoylbenzoic acid. The washed residue was dissolved in a large volume of acetic acid and treated at the boiling point with chromic acid. The addition of water precipitated 2 : 4 : 6-trichloroanthraquinone in flocks; it crystallised from acetic acid, in which it was difficultly soluble, in long, pale yellow needles, m. p. 245° alone and in admixture with the trichloroanthraquinone obtained from 2 : 7-dichloroanthraquinone-3-sulphonic acid (Found : Cl, 34.0. Calc. for $C_{14}H_5O_2Cl_3$: Cl, 34.1%).

Sulphonation of Potassium 2-Chloroanthraquinone-7-sulphonate.
Potassium 2-Chloroanthraquinone-3 : 7-disulphonate.—Potassium 2-chloroanthraquinone-7-sulphonate (100 g.) was sulphonated in the same way as the 2 : 6-isomeride. The yellow product, on recrystallising twice from boiling water, small head fractions being rejected each time, gave *potassium 2-chloroanthraquinone-3 : 7-disulphonate* (110 g.) as a mass of long yellow needles (Found in dehydrated salt : S, 12.9. $C_{14}H_5O_8ClS_2K_2$ requires S, 13.4%). The calcium salt is soluble in boiling water, but the barium and lead salts are insoluble.

Chlorination of Potassium 2-Chloroanthraquinone-3 : 7-disulphonate.
Potassium 2 : 3-Dichloroanthraquinone-6-sulphonate.—Potassium 2-chloroanthraquinone-3 : 7-disulphonate (40 g.) was chlorinated in the same manner as the 2 : 3 : 6-isomeride. Precipitation of the potassium 2 : 3-dichloroanthraquinone-6-sulphonate, however, was more rapid, and was complete in 12 hours (23 g.). The *sulphonyl chloride* had m. p. 210–212° after one crystallisation (Found : Cl, 30.9%), but after many crystallisations the m. p. was 222–223° : the mixed m. p. with the sulphonyl chloride obtained from the sulphonation product of 2 : 3-dichloroanthraquinone was 224–227° (Found : Cl, 29.2. $C_{14}H_5O_4Cl_3S$ requires Cl, 28.4%).

Potassium 2-Aminoanthraquinone-3 : 7-disulphonate.—Condensation of potassium 2-chloroanthraquinone-3 : 7-disulphonate with aqueous ammonia in the presence of copper sulphate in the manner described above gave *potassium 2-aminoanthraquinone-3 : 7-disulphonate* as a dark micro-crystalline powder soluble in water with an intense fine red colour (Found in anhydrous salt : S, 13.4; N, 3.0. $C_{14}H_7O_8NS_2K_2$ requires S, 13.9; N, 3.1%).

Sulphonation of 1 : 7-Dichloroanthraquinone.
Potassium 1 : 7-Dichloroanthraquinone-8(?)sulphonate.—A solution of 1 : 7-dichloro-

anthraquinone (24 g.) (Goldberg, *loc. cit.*) in 20% fuming sulphuric acid (20 c.c.) was heated for $3\frac{1}{2}$ hours, with shaking, with yellow mercuric oxide (6 g.). The product was poured into water, the solution filtered to remove unchanged dichloroanthraquinone and mercuric oxide, and potassium hydroxide (20 g.) added. The solution was evaporated, an early fraction of crystals rejected, and the final solution concentrated to small bulk. On standing, a yellow precipitate (23 g.) was obtained which, on recrystallising twice from boiling water, gave *potassium 1 : 7-dichloroanthraquinone-8(?) -sulphonate* as a canary-yellow crystalline mass (11 g.) (Found in anhydrous salt : S, 8.5. $C_{14}H_5O_5Cl_2SK$ requires S, 8.1%).

Chlorination of Potassium 1 : 7-Dichloroanthraquinone - 8(?) -sulphonate. 1(?) : 2 : 8-Trichloroanthraquinone.—A dilute aqueous solution of potassium 1 : 7-dichloroanthraquinone-8(?) -sulphonate was treated with nascent chlorine; precipitation of 1(?) : 2 : 8-*trichloroanthraquinone* in a micro-crystalline form began in 10 minutes and was complete in a few hours. It crystallised from acetic acid in small, tufted, yellow needles, m. p. 190—192° (Found : Cl, 34.2. $C_{14}H_5O_2Cl_3$ requires Cl, 34.1%).

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