CCXLI.—*The Synthesis and Orientation of Trichloroanthraquinones and Amino-disulphonates of Anthraquinone. Part I.*

By Alan August Goldberg.

Of the fourteen theoretically possible trichloroanthraquinones, only three are known and the constitution of one of these has not been satisfactorily established.

Ullmann and Conzetti (*Ber.*, 1920, **53**, 826) obtained from phthalic anhydride and 2 : 4-dichlorophenol a dichlorohydroxybenzoylbenzoic acid which, after closure of the anthraquinone ring and replacement of the hydroxyl group by chlorine, gave a trichloroanthraquinone, m. p. 186°; they obtained the same substance by the chlorination of 1-chloro-4-hydroxyanthraquinone and replacement of hydroxyl by chlorine in the dichlorohydroxyanthraquinone formed. This substance must therefore be 1 : 2 : 4-trichloroanthraquinone. The authors of the French patent 384471 state that chlorine at high temperatures reacts with both anthraquinone-α- and -β-monosulphonate to give dichloroanthraquinone-α- and -β-monosulphonate respectively. Fusion of the latter with boric acid, it is claimed, gave a "quinizarinmonosulphonic acid," but their method of identifying this product and also *which* monosulphonic acid of quinizarin they obtained are not stated. They are, however, subsequently designated "chloranthraquinone-α-monosulphonate" and "1 : 4-dichloranthraquinone-β-monosulphonate." Later, the patentees of D.R.-P. 214714 replaced the sulpho-groups in the above substances, which they refer to as "1 : 4-dichloranthraquinone-α- and -β-monosulphonates," by chlorine and obtained two trichloroanthraquinones, m. p. 254° and 236° respectively. No mention is made in the German specification concerning the positions occupied by the chlorine substituent in these trichloroanthraquinones, but Houben ("Das Anthracen und die Anthra-

chinone," p. 278) refers to them, and apparently correctly, as 1 : 4 : 5- and 1 : 4 : 6-trichloroanthraquinone respectively. Later, Meyer and Egerer (*Monatsh.*, 1913, **34**, 69) condensed 4-chlorophthalic anhydride with *p*-dichlorobenzene and obtained a trichloroanthraquinone, m. p. 236°, which must be 1 : 4 : 6-trichloroanthraquinone.

The present work describes the synthesis of 1 : 2 : 3-, 1 : 2 : 5-, 1 : 2 : 6-, 1 : 2 : 7-, 1 : 3 : 6-, 1 : 3 : 7-, 1 : 4 : 5-, and 1 : 4 : 6-trichloroanthraquinones and the determination of their orientation by a method which it is believed is superior to the benzoylbenzoic acid synthesis, because of the limited applicability of the latter and the tendency to halogen migration during the fusion of the phthaloyl and the benzene residue (Heller, *Ber.*, 1912, **45**, 792). Although chlorine atoms substituted in the α-positions in anthraquinone may be caused to shift to the adjacent β-positions under the influence of sulphuric acid at high temperatures (Atack and Clough, Eng. Pat. 169732) and the α-halogen atoms in homonuclear halogenoaminoanthraquinones migrate to the β-position contiguous to the amino-group if this position is unoccupied (D.R.-P. 275299), no such wandering of halogen takes place under the experimental conditions of the present work.

It is highly desirable to have available a set of trisubstituted anthraquinones of known constitution to serve as standards in the examination of new substances and of derivatives of anthraquinone of uncertain constitution. The trichloroanthraquinones are ideal in this respect, for not only are they well-defined, sharp-melting substances, but also many substituents in the anthraquinone nucleus may with ease be replaced by chlorine—nitro- and amino-groups by

The Trichloroanthraquinones.

Position of substituents	1 : 2 : 3-	*1 : 2 : 4-	1 : 2 : 5-	1 : 2 : 6-	1 : 2 : 7-
Melting point	194—195°	186°	235—236°	222—223°	225—226°

Position of substituents	1 : 3 : 6-	1 : 3 : 7-	1 : 4 : 5-	1 : 4 : 6-
Melting point	212—213°	216—217°	258°	236°

* Ullmann, *loc. cit.*

the usual methods, hydroxyl by the action of phosphorus pentachloride, which does not attack the ketonic groups (D.R.-P. 290879; Ullmann, *Ber.*, 1920, **53**, 826), and sulpho-groups by the action of nascent chlorine.

The synthetic method employed consists essentially in sulphonating α-chloroanthraquinone and selected dichloroanthraquinones, separating isomeric chloroanthraquinonedisulphonates and dichloro-

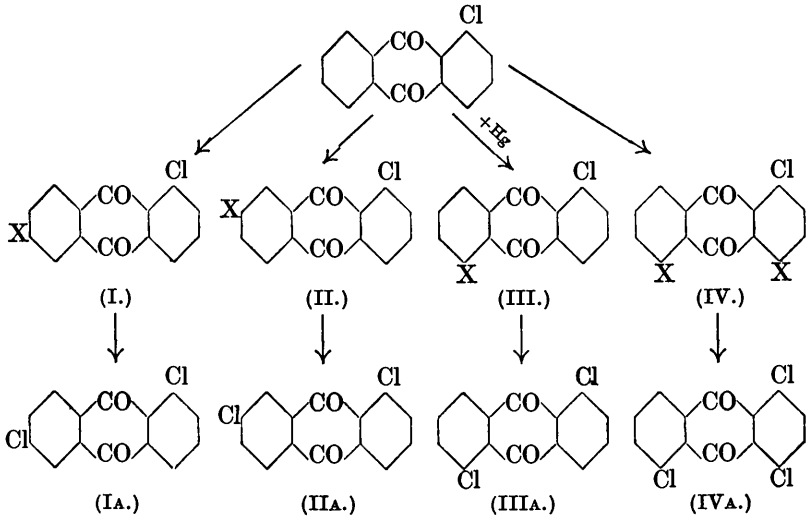
anthraquinonemonosulphonates, and replacing the sulpho-groups in these by chlorine.

According to Schilling (*Ber.*, 1913, **46**, 1066) the sulphonation of chloroanthraquinones gives chloroanthraquinonemonosulphonic acids in the absence of mercury and only chloroanthraquinonedisulphonic acids in its presence. He made no attempt to orient his products, or indeed to separate the isomeric compounds which would be expected to be formed in a reaction of this nature, but assumed that the entrance of the sulpho-group or groups follows the laws of Schmidt and Iljinsky—an assumption which ignores the directive influence exerted by the chlorine substituents and, moreover, has been shown to be erroneous by the present work. The sulphonation of α-chloroanthraquinone and selected dichloroanthraquinones was therefore investigated from first principles. The results show that the sulphonating agent first attacks both β-positions in the chlorine-free nucleus, giving rise to two isomeric heteronuclear chloroanthraquinonemonosulphonic acids; this also happens in the sulphonation of the homonuclear dichloroanthraquinones. In the presence of mercury, however, only the α-position in the chlorine-free nucleus, which is 5 to the chlorine atom, is attacked, giving an α-chloroanthraquinone-α-monosulphonic acid. The mercury therefore exerts its usual α-directing influence. On further sulphonation of these heteronuclear chloroanthraquinonemonosulphonates, a second sulpho-group enters the molecule in the chlorine-containing ring in position 2 or 4 or both, *i.e.*, respectively β- and α-positions which are 2- and 4- to the chlorine substituent. The presence of mercury inhibits entrance at the 2-position. The sulphonation of the two heteronuclear dichloroanthraquinones bears resemblance to this. Hence it can be deduced that the para-directing influence of chlorine is greater than the meta-directing influence of the carbonyl groups, and the α-directing influence of the catalyst, mercury, is more powerful than the combined β-directive influence of carbonyl and chlorine. It is of interest to compare with this the sulphonation of mono- and di-hydroxyanthraquinones.

Sulphonation of α-chloroanthraquinone gives two isomeric chloroanthraquinonemonosulphonic acids which are easily separable through their sodium salts; the less soluble is *sodium 1-chloroanthraquinone-6-sulphonate* (I) (*sulphonyl chloride*, m. p. 205°), and the more soluble is *sodium 1-chloroanthraquinone-7-sulphonate* (II) (*sulphonyl chloride*, m. p. 200—201°). Neither of these reacts with alkyl mercaptans, a reaction diagnostic of α-sulpho-groups (Reid, Mackall, and Miller, *J. Amer. Chem. Soc.*, 1921, **43**, 2104). The constitutions of (I) and (II) are shown by replacement of the sulpho-

group by chlorine, 1 : 6- and 1-7-dichloroanthraquinones (IA and IIA) respectively being produced, identical with those obtained from Claus's α- and β-nitroanthraquinonesulphonic acids (Claus, *Ber.*, 1882, **15**, 1514; Schmidt, *Ber.*, 1904, **37**, 66; Fierz-David, *Helv. Chim. Acta*, 1927, **10**, 209).

Sulphonation of α-chloroanthraquinone in the presence of mercury gives only one monosulphonic acid (III) (*sulphonyl chloride*, m. p. 244°). Replacement of the sulpho-group by chlorine yields 1 : 5-dichloroanthraquinone; it is therefore 1-chloroanthraquinone-5-sulphonic acid. No trace of 1-chloroanthraquinone-8-sulphonic acid is formed. The mercury catalyst not only exerts its specific α-directive influence but also facilitates the entrance of the sulpho-group into the molecule, since under the same conditions under which only monosulphonic acids are formed in its absence, a considerable amount of 1-*chloroanthraquinone*-4 : 5-*disulphonic acid* (as IV) is produced in its presence.

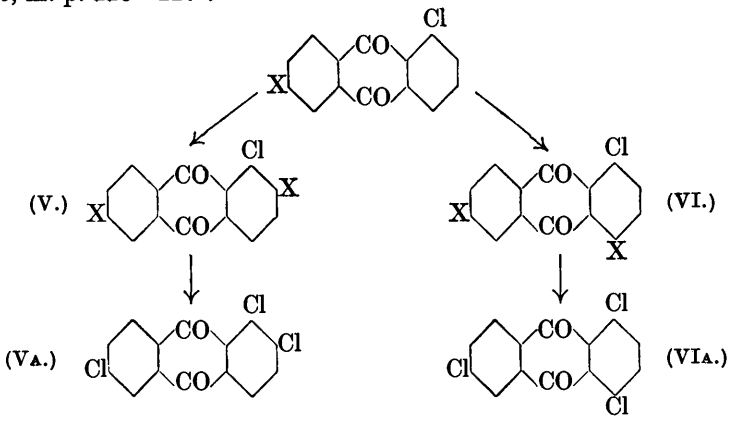


(X = SO_3Na or SO_3H)

Sulphonation of sodium 1-chloroanthraquinone-6-sulphonate yields two isomeric chloro-disulphonates of anthraquinone, (V) and (VI), which have been shown to be *sodium* 1-*chloroanthraquinone*-2 : 6-*disulphonate* and *sodium* 1-*chloroanthraquinone*-4 : 6-*disulphonate* respectively. Nascent chlorine reacts with these to give 1 : 2 : 6-*trichloroanthraquinone* (VA), m. p. 222—223°, and 1 : 4 : 6-trichloroanthraquinone (VIA), m. p. 236°.

Sulphonation of sodium 1-chloroanthraquinone-7-sulphonate (II) gives *sodium* 1-*chloroanthraquinone*-2 : 7-*disulphonate*, which on

treatment with nascent chlorine yields 1 : 2 : 7-*trichloroanthraquinone*, m. p. 226—227°.



Sulphonation of sodium 1-chloroanthraquinone-5-sulphonate gives a product which apparently contains more than one substance but from which only *sodium* 1-*chloroanthraquinone*-2 : 5-*disulphonate* can be isolated in quantity. An appreciable amount of *sodium* 1-*chloroanthraquinone*-4 : 5-*disulphonate* is simultaneously produced, but owing to the insolubility of its barium salt this is almost completely lost during the process of isolation. It is, however, obtained with ease by the prolonged catalytic sulphonation of α-chloroanthraquinone. Replacement of the sulpho-groups in sodium 1-chloroanthraquinone-2 : 5- and -4 : 5-disulphonates gives 1 : 2 : 5-*trichloroanthraquinone*, m. p. 237°, and 1 : 4 : 5-*trichloroanthraquinone*, m. p. 258° (IVA).

Orientation : Proof of the position taken up by the second sulpho-group. The second sulpho-group—the only group in the above chloroanthraquinonedisulphonates whose position is unknown—must enter the chlorine-containing nucleus for the following reasons. A review of the chemistry of the sulphonates of anthraquinone shows that the presence of a sulpho-group enhances the stability of the ring that contains it to such an extent that further entrance of substituents into that ring is inhibited or (more usually) completely suppressed. No homonuclear disulphonates of anthraquinone are known; both anthraquinone-α- and -β-monosulphonate are nitrated and chlorinated only in the unsubstituted nucleus (Claus, *Ber.*, 1882, **15**, 1514; Fierz-David, *Helv. Chim. Acta*, 1927 **10**, 206; French Pat. 384471) and neither chlorine nor the nitro-group can enter the molecule of any of the disulphonates of anthraquinone (Houben, *op. cit.*, p. 298; see pp. 1779, 1793). By the sulphonation of selected dichloroanthraquinones, and treatment of the dichloro-

anthraquinonemonosulphonates produced with nascent chlorine, various new trichloroanthraquinones have been synthesised. The establishment of an identity between one of these and one obtained from the above chloroanthraquinonedisulphonates supplies the necessary information to prove its structure. The orientation of the trichloroanthraquinones consequently shows the positions occupied by all the substituents in the chloroanthraquinonedisulphonates and in the aminoanthraquinonedisulphonates derived from them.

1 : 2-*Dichloroanthraquinone and its Sulphonation.*—The preparation of 1 : 2-dichloroanthraquinone from 3 : 4-dichlorophthalic anhydride and benzene (Ullmann and Billig, *Annalen*, 1909, **381**, 11) is attended with difficulties.

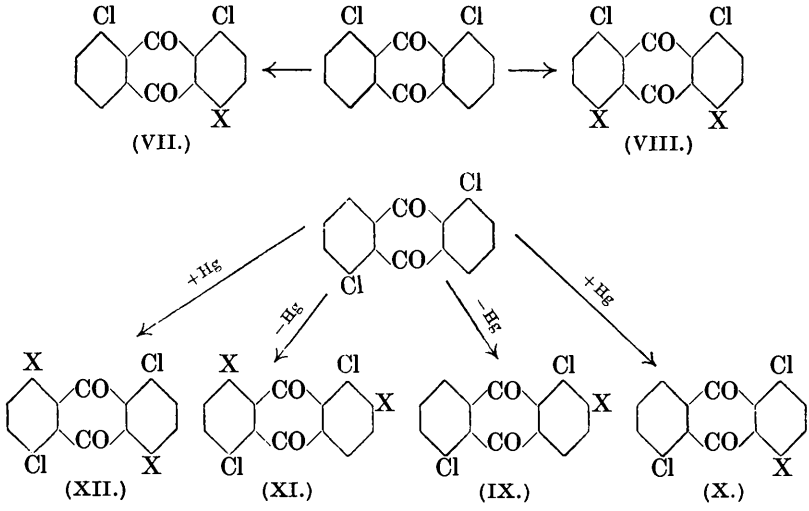
Condensation of phthalic anhydride and *o*-chlorophenol yields a chlorohydroxybenzoylbenzoic acid (D.R.-P. 148110; Tanaka, *Proc. Imp. Acad. Tokio*, 1927, **3**, 82; Hayashi, J., 1930, 1521) which on closure of the anthraquinone ring gives a chlorohydroxyanthraquinone. This is, as assumed by Hayashi, 2-chloro-3-hydroxyanthraquinone, for 2 : 3-dichloroanthraquinone has now been obtained from it by the action of phosphorus pentachloride.

1 : 2-Dichloroanthraquinone can be prepared rapidly and in large quantities from 2-aminoanthraquinone. Sulphonation gives two isomeric sulphonates : these are *sodium* 1 : 2-*dichloroanthraquinone*-6- and -7-*sulphonates*, for these are converted on treatment with chlorine into 1 : 2 : 6- and 1 : 2 : 7-*trichloroanthraquinone* respectively.

1 : 3-Dichloro-2-aminoanthraquinone on deamination gives 1 : 3-dichloroanthraquinone (Junghaus, *Annalen*, 1913, **399**, 316); by the Sandmeyer reaction it is converted almost quantitatively into 1 : 2 : 3-*trichloroanthraquinone*, m. p. 194—195°. Sulphonation of 1 : 3-dichloroanthraquinone gives likewise two isomeric dichloroanthraquinonemonosulphonic acids, the sodium salt of one of which is considerably less soluble than that of the other. Because of this analogy between these products and those obtained from the sulphonation of both α-chloroanthraquinone and 1 : 2-dichloroanthraquinone (also compare the sulphonation of 1 : 4-dichloroanthraquinone), the acids are probably 1 : 3-*dichloroanthraquinone*-6- and -7-*sulphonic acids* respectively. Hence the trichloroanthraquinone derived from the less soluble acid, m. p. 213°, is 1 : 3 : 6-*trichloroanthraquinone* and that from the more soluble acid, m. p. 216—217°, is 1 : 3 : 7-*trichloroanthraquinone*.

Sulphonation of 1 : 4-dichloroanthraquinone, in accordance with the views expressed above, yields only one dichloroanthraquinonemonosulphonate. As this gives 1 : 4 : 6-trichloroanthraquinone, m. p. 236°, on treatment with chlorine, it is *sodium* 1 : 4-*dichloroanthraquinone*-6-*sulphonate*.

The Sulphonation of Heteronuclear Dichloroanthraquinones.—Sulphonation of 1 : 8-dichloroanthraquinone gives only one monosulphonic acid (VII), which yields 1 : 4 : 5-trichloroanthraquinone (IVA). Sulphonation in the presence of mercury gives, besides this monosulphonic acid, a dichloroanthraquinonedisulphonic acid (VIII), which yields 1 : 4 : 5 : 8-tetrachloroanthraquinone, m. p. 341°. Sulphonation of 1 : 5-dichloroanthraquinone, on the other hand, gives two isomeric dichloroanthraquinonemonosulphonic acids, the sodium salt of one of which (IX) is less soluble than that of the other (X). The less soluble salt gives a trichloroanthraquinone, m. p. 237°, and the more soluble salt yields 1 : 4 : 5-trichloroanthraquinone. Consequently (X) is *sodium* 1 : 5-*dichloroanthraquinone*-4-*sulphonate*; the compound (VII) is *sodium* 1 : 8-*dichloroanthraquinone*-4-*sulphonate*, and the structure of (IV) is as before stated. Hence the monosulphonic acid with the less soluble sodium salt (IX) must be 1 : 5-*dichloroanthraquinone*-2- or -3-*sulphonic acid*, and in consideration of the views expressed above, it is accorded the former constitution. The trichloroanthraquinone derived from it is therefore 1 : 2 : 5-*trichloroanthraquinone*. Since the trichloroanthraquinone of m. p. 237° (p. 1775) is identical with this, the structure of the chloroanthraquinonedisulphonic acid from which it is obtained is established. Besides these two monosulphonic acids, a dichloroanthraquinonedisulphonic acid (XI) is simultaneously produced which yields a tetrachloroanthraquinone, m. p.



280—282°. Sulphonation of 1 : 5-dichloroanthraquinone in the presence of mercury not only suppresses the formation of the

monosulphonic acid with the less soluble sodium salt (IX) but also gives rise to another dichloroanthraquinonedisulphonic acid (XII), which yields the tetrachloroanthraquinone of m. p. 340—341°. It therefore appears that (VIII) and (XII) are *sodium* 1 : 8-*dichloroanthraquinone*-4 : 5-*disulphonate* and 1 : 5-*dichloroanthraquinone*-4 : 8-*disulphonate* respectively, and the tetrachloroanthraquinone derived from them is 1 : 4 : 5 : 8-tetrachloroanthraquinone, which is apparently identical with that obtained by Schilling (*loc. cit.*). To the substance (XI) is assigned the constitution *sodium* 1 : 5-*dichloroanthraquinone*-2 : 8-*disulphonate*, and the tetrachloroanthraquinone derived from it is considered to be 1 : 2 : 5 : 8-*tetrachloroanthraquinone*.

The Semi-chlorination of Anthraquinonedisulphonic Acids.—The chlorination of potassium anthraquinone-2 : 6- and -2 : 7-disulphonates gives potassium 2-chloroanthraquinone-6- and -7-sulphonates respectively (Fierz-David, *loc. cit.*), both of which are very sparingly soluble and resistant to further attack by nascent chlorine. Also, according to Fierz-David, the partial chlorination of both potassium anthraquinone-1 : 6- and -1 : 7-disulphonates gives rise to the corresponding intermediates, potassium 1-chloroanthraquinone-6- and -7-sulphonates. This is to be expected, since it has been found during the present work that an α-sulpho-group is approximately 20 times as easily replaced by chlorine as a β-sulpho-group. It is, however, stated both in the English patent 1822/08 and by Fierz-David that by the partial chlorination of potassium anthraquinone-1 : 5-disulphonate the intermediate potassium 1-chloroanthraquinone-5-sulphonate can be isolated in nearly theoretical yield; this is surprising, since the solubility of the intermediate is of the same order as that of the parent and, moreover, there is no reason to suppose that the chlorine will attack one of the α-sulpho-groups in the parent substance in preference to the α-sulpho-group in the intermediate potassium 1-chloroanthraquinone-5-sulphonate, which, presumably, is initially formed. The partial chlorination of potassium anthraquinone-1 : 5-disulphonate has been carried out several times, but the product, after separation of considerable amounts of 1 : 5-dichloroanthraquinone, invariably was a mixture of potassium 1-chloroanthraquinone-5-sulphonate and unchanged parent material, which do not admit of easy separation. It is accordingly believed that the catalytic sulphonation of α-chloroanthraquinone is the only satisfactory method for synthesising 1-chloroanthraquinone-5-sulphonic acid.

The Amino-mono- and -di-sulphonic Acids of Anthraquinone.—The mono- and di-sulphonates of α-chloroanthraquinone resemble certain negatively substituted halogenobenzenes, notably picryl chloride, dinitrochlorobenzene, etc., inasmuch as the α-chlorine atom

is reactive and can be replaced with ease by amino- and by substituted amino-groups. This is effected by heating, at temperatures which are not necessarily high, with ammonia or the requisite primary or secondary amines in the presence of a catalyst. The reaction serves as a more convenient method of obtaining heteronuclear aminoanthraquinonemonosulphonic acids which have previously been described (Claus, *Ber.*, 1882, **15**, 1514; Schmidt, *Ber.*, 1904, **37**, 66; Ullmann, *Ber.*, 1919, **52**, 545) and for synthesising *aminoanthraquinonedisulphonic acids*, none of which has hitherto been known. The amino-disulphonic acids of anthraquinone, as are the amino-monosulphonic acids, are intensely coloured substances, and although they are extremely soluble in water—in some cases in less than their own weight—they attach themselves directly to animal fabric and cannot then be removed by the agency of water. The *n*-alkylamino-mono- and -di-sulphonic acids are more deeply coloured, *i.e.*, their colour tends more towards the violet end of the spectrum, than the parent amino-compound, a fact in accordance with the views of structure and colour of Hartley. It is believed that it is not possible to obtain aminoanthraquinonedisulphonic acids by nitration of disulphonates of anthraquinone and reduction of the product. Claus and Schneider (*Ber.*, 1883, **16**, 907) claim to have nitrated sodium anthraquinone-2 : 6-disulphonate and to have isolated a mononitro-compound. Later, Iljinsky (Houben, *op. cit.*, p. 298) stated that both sodium anthraquinone-2 : 6- and -2 : 7-disulphonates are too stable to be nitrated, an observation which is in agreement with the author's repeated experiments and moreover also applies to the sodium 1 : 5- and 1 : 8-disulphonates.

Experimental.

The Sulphonation of α-Chloroanthraquinone. Sodium 1-Chloroanthraquinone-6- and -7-sulphonates.—Pure α-chloroanthraquinone (200 g.) was heated with 20% fuming sulphuric acid (160 c.c.) at 160° for 4 hours. The dark red melt, after cooling, was poured into ice-water (3000 c.c.), and the unchanged α-chloroanthraquinone (*ca.* 40 g.) removed. The dark filtrate was boiled for a short time with nitric acid (50 c.c.) until it was light orange, and a solution of sodium hydroxide (160 g. in 400 c.c. of water) then added. The canary-yellow precipitate produced was collected after some time and extracted with boiling water (1000 c.c.). The residue, after being washed with boiling water (1000 c.c.), was *sodium 1-chloroanthraquinone-6-sulphonate* (96 g.). It required about 300 parts of boiling water for complete solution, and crystallised in pale yellow spangles (Found in dehydrated salt : S, 9·5. $C_{14}H_6O_5ClSNa$ requires S, 9·3%). The combined filtrate and washings were con-

siderably evaporated and the hot liquid was filtered from a little sodium 1-chloroanthraquinone-6-sulphonate, well concentrated, and cooled. The thick glutinous precipitate obtained was crystallised twice from the minimum amount of boiling water (*ca.* 400 c.c.), small head fractions being rejected each time. The product (112 g.), *sodium 1-chloroanthraquinone-7-sulphonate*, was soluble in about 4 parts of boiling water and crystallised in long, silky, deep yellow needles of gelatinous appearance (Found in anhydrous salt : S, 9·7%).

Salts. The barium, calcium, and lead salts of 1-chloroanthraquinone-6-sulphonic acid are precipitated almost quantitatively in white flocks when the ions of these metals are added to a solution of the sodium salt. The first is insoluble and the others are difficultly soluble in mineral acids. Barium 1-chloroanthraquinone-7-sulphonate is similarly insoluble, but the calcium and lead salts crystallise well from water and dilute nitric acid respectively.

Sulphonyl chlorides. An intimate mixture of sodium 1-chloroanthraquinone-6-sulphonate (10 g.) and phosphorus pentachloride (10 g.) was heated with phosphoryl chloride (40 c.c.) at 110—115° for 4—5 hours, the phosphoryl chloride distilled off, the residue ground, kept under cold water for 1 hour, dried, and dissolved in benzene (charcoal), and the filtered solution evaporated. The *1-chloroanthraquinone-6-sulphonyl chloride* (7 g.) obtained crystallised from ligroin (b. p. 110—120°) in pale yellow prisms, m. p. 207—208° (decomp.) (Found : Cl, 20·7. $C_{14}H_6O_4Cl_2S$ requires Cl, 20·8%).

The *7-sulphonyl chloride*, similarly obtained, crystallised from benzene in lemon-yellow plates, m. p. 200—201° (decomp.) (Found : Cl, 20·6%). A mixture of the two chlorides melted below 180°.

The Chlorination of Sodium 1-Chloroanthraquinone-6- and -7-sulphonates. 1 : 6- and 1 : 7-Dichloroanthraquinones.—The 6-sodium salt (6 g.), suspended in water (1500 c.c.) containing hydrochloric acid (30 c.c.) and potassium chlorate (6 g.), when heated on the water-bath for 15—20 hours, gradually dissolved and 1 : 6-dichloroanthraquinone was deposited as a yellow microcrystalline flocculent precipitate. This crystallised from glacial acetic acid in long, pale citron needles, m. p. 203—204° (yield, almost theoretical) (Found : Cl, 25·7. Calc. for $C_{14}H_6O_2Cl_2$: Cl, 25·6%). Depressions in m. p. were observed in admixture with 1 : 2-, 1 : 3-, 1 : 4-, 1 : 5-, 1 : 7-, and 1 : 8-dichloroanthraquinones but not with 1 : 6-dichloroanthraquinone obtained from Claus's α-nitro-sulphonic acid (Fierz-David, *loc. cit.*).

1 : 7-Dichloroanthraquinone, similarly obtained from a solution of sodium 1-chloroanthraquinone-7-sulphonate (10 g.) in water (800 c.c.) containing hydrochloric acid (50 c.c.) and potassium chlorate

(10 g.), crystallised from acetic acid in stellate clusters of small feathery needles, m. p. 213—214° (Found: Cl, 25·6%). Depressions in m. p. in admixture with 1 : 2-, 1 : 3-, 1 : 4-, 1 : 5-, 1 : 6-, and 1 : 8-dichloroanthraquinones were observed but not with 1 : 7-dichloroanthraquinone (Fierz-David, *loc. cit.*).

Reduction to 1 : 6- *and* 1 : 7-*dichloroanthracenes.* Either dichloroanthraquinone (4 g.) was heated on the water-bath with zinc dust (16 g.), aqueous ammonia (160 c.c.; *d* 0·880) and an equal quantity of water until the blood-red colour which developed was discharged (3—4 hours). The liquor was then evaporated to dryness, the residue extracted with boiling absolute alcohol, and the extract evaporated. 1 : 6-*Dichloroanthracene* crystallised from acetic acid in golden rectangular plates, m. p. 149—150° (Found: Cl, 28·5. $C_{14}H_8Cl_2$ requires Cl, 28·7%), and 1 : 7-*dichloroanthracene* in deep yellow, feathery needles, m. p. 160—161° (Found: Cl, 28·5%).

The Catalytic Sulphonation of α-*Chloroanthraquinone. Sodium* 1-*Chloroanthraquinone-5-sulphonate and* -4 : 5-*disulphonate.*—A solution of α-chloroanthraquinone (100 g.) in 20% fuming sulphuric acid (80 c.c.) containing mercuric sulphate (12 g.) or red mercuric oxide (14—15 g.) was heated at 155—160° for 4½ hours, being shaken at intervals. When cold, the dark melt was decanted from the red sediment (mercuric oxide) into water (1500 c.c.), and the solution was filtered from a little unchanged α-chloroanthraquinone and decolorised by boiling for a short time with a little nitric acid. Sodium hydroxide (80 g. in 200 c.c. of water) was added, the still clear solution (contrast the non-catalytic sulphonation) was evaporated to small bulk and cooled, and the yellow precipitate (*ca.* 150 g.) collected (the filtrate, which was rejected, had a volume of 300 c.c.). This was dissolved in the minimum amount of boiling water, and the solution evaporated slightly, and kept after removal of the first small precipitate. The yellow precipitate now obtained, on recrystallisation from the minimum volume of boiling water, gave *sodium* 1-*chloroanthraquinone-5-sulphonate* (40 g.), soluble in about 6 parts of water at 100° and crystallising in yellow leaves (Found: S, 9·7. $C_{14}H_6O_5ClSNa$ requires S, 9·3%). The combined filtrates from the two previous crystallisations were well concentrated and cooled. The precipitate thus obtained, on recrystallising twice from water, small head fractions being removed each time, gave *sodium* 1-*chloroanthraquinone*-4 : 5-*disulphonate* (38 g.) (Found: S, 14·2. $C_{14}H_5O_8ClS_2Na_2$ requires S, 14·4%).

Barium 1-chloroanthraquinone-5-sulphonate is a white gelatinous substance almost insoluble in dilute mineral acids, and the calcium and lead salts are soluble with difficulty. Barium 1-chloroanthraquinone-4 : 5-disulphonate is insoluble in water and mineral acids.

1-*Chloroanthraquinone-5-sulphonyl chloride* crystallises from toluene in small yellow lustrous plates, m. p. 243—244° (decomp.) (Found: Cl, 20·5. $C_{14}H_6O_4Cl_2S$ requires Cl, 20·8%).

Chlorination of Sodium 1-*Chloroanthraquinone-5-sulphonate and -4 : 5-disulphonate.* 1 : 5-*Dichloro- and* 1 : 4 : 5-*Trichloro-anthraquinones.*—A solution of sodium 1-chloroanthraquinone-5-sulphonate (10 g.) in water (800 c.c.) containing potassium chlorate (10 g.) and acidified with hydrochloric acid (45 c.c.) was gently boiled. The precipitation of 1 : 5-dichloroanthraquinone was complete in 1½ hours (contrast 1 : 6- and 1 : 7-dichloroanthraquinones). It crystallised from acetic acid in elongated, pale yellow needles, m. p. 244° alone and in admixture with an authentic specimen (Found: Cl, 25·7. Calc. for $C_{14}H_6O_2Cl_2$: Cl, 25·6%).

A dilute solution of sodium 1-chloroanthraquinone-4 : 5-disulphonate, heated in the same manner with double the quantities of acid and chlorate, gave 1 : 4 : 5-*trichloroanthraquinone*, which crystallised from acetic acid in long needles, m. p. 254° (Found: Cl, 33·8. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%).

1-*Aminoanthraquinone-6-sulphonic Acid.*—Sodium 1-chloroanthraquinone-6-sulphonate (12 g.), hydrated copper sulphate (2 g.), aqueous ammonia (60 c.c.; *d* 0·880), and water (300 c.c.) were heated in a closed vessel at 100° for 30 hours. The intensely red product was evaporated to remove the excess of ammonia and heated with just more than sufficient sodium hydroxide solution to decompose the ammonium chloride formed during the reaction. (Without this procedure the product is contaminated with ammonium chloride and gives high nitrogen analyses.) After acidification of the solution with dilute hydrochloric acid the copper was removed as sulphide, and the filtered solution evaporated to small bulk. On cooling, *sodium* 1-*aminoanthraquinone-6-sulphonate* separated in lustrous black micro-needles. Crystallisation from water, in which it was very soluble, gave the pure salt (7 g.) [Found: loss at 150°/20 mm., 2·7; S (in anhydrous salt), 9·6; N, 4·0. $C_{14}H_8O_5NSNa,\frac{1}{2}H_2O$ requires loss, 2·7%. $C_{14}H_8O_5NSNa$ requires S, 9·8; N, 4·3%]. The free *acid* crystallises in carmine spangles when concentrated hydrochloric acid is added to a concentrated solution of the sodium salt (Found: S, 10·3. $C_{14}H_9O_5NS$ requires S, 10·6%). There was no residue on ignition on platinum. Both the free acid and the sodium salt, in aqueous solution, have an intense blood-red colour and are directly substantive to animal fabric.

1-*Diethylaminoanthraquinone-6-sulphonic Acid.*—Sodium 1-chloroanthraquinone-6-sulphonate (8 g.), suspended in water (200 c.c.) containing hydrated copper sulphate (1 g.), was heated with diethylamine (20 c.c.) at 100° for 40 hours. The purple solution produced

was evaporated to dryness, the residue taken up in water, and the insoluble copper–diethylamine complex removed. The filtrate was rendered slightly acid with hydrochloric acid, freed from the last trace of copper as sulphide, and well concentrated. Addition of a little saturated sodium chloride solution precipitated *sodium* 1-*diethylaminoanthraquinone*-6-*sulphonate* (6 g.). The salt crystallises from its purple aqueous solution in dark violet, micro-needles [Found: loss at 140°/20 mm., 2·7; (in anhydrous salt) Na, 6·3; N, 3·9. $C_{18}H_{16}O_5NSNa,\frac{1}{2}H_2O$ requires loss, 2·3%. $C_{18}H_{16}O_5NSNa$ requires Na, 6·0; N, 3·7%]. The free acid is precipitated in violet leaves when a concentrated aqueous solution of the sodium salt is rendered strongly acid.

1-*Piperidinoanthraquinone*-6-*sulphonic acid*, obtained as above by using piperidine (20 c.c.) instead of diethylamine, was precipitated by hydrochloric acid (25 c.c.) in almost theoretical yield. It was dissolved in dilute sodium hydroxide solution (the sodium salt is very soluble) and precipitated with hydrochloric acid (Found: N, 4·3; S, 7·8. $C_{19}H_{17}O_5SN$ requires N, 3·8; S, 8·6%) (see footnote on p. 1785).

1-*Aminoanthraquinone*-7-*sulphonic acid* was prepared in the same manner as the 1 : 6-isomeride and obtained as a dark red, microcrystalline powder very soluble in water, giving a blood-red solution (Found: S, 10·1; N, 4·6. $C_{14}H_8O_5NSNa$ requires S, 9·8; N, 4·3%).

1-*Diethylaminoanthraquinone*-7-*sulphonic acid* is a dark violet, microcrystalline substance very soluble in water with an intense purple colour (Found: N, 3·9. $C_{18}H_{16}O_5NSNa$ requires N, 3·7%).

Sulphonation of Sodium 1-*Chloroanthraquinone*-6-*sulphonate. Sodium* 1-*Chloroanthraquinone*-4 : 6- *and* -2 : 6-*disulphonates.*—Anhydrous sodium 1-chloroanthraquinone-6-sulphonate (80 g.) was heated at 155—160° with 20% fuming sulphuric acid (250 c.c.) for 11 hours. The red liquid was then poured into ice-water (1000 c.c.) and heated with a little nitric acid until its colour faded to a light orange. Hot water (4000 c.c.) was added, and the sulphuric acid removed by the slow addition of barium carbonate (800 g., made into a milk with water). After standing on the steam-bath for some time, the yellow supernatant liquor was separated from the barium sulphate, which was thoroughly extracted with boiling water containing a little dilute sulphuric acid until it was white. The combined mother-liquor and washings were evaporated to dryness, the yellow residue (98 g.) dissolved in boiling water (*ca.* 400 c.c.), a solution of sodium hydroxide (20 g.) added, and the solution concentrated and cooled. The yellow precipitate was filtered off (volume of filtrate, 300 c.c.), dissolved in the minimum amount of boiling water, and, after the addition of a saturated

solution of sodium chloride (10 g.), allowed to stand. The precipitate (40 g.) was *sodium* 1-*chloroanthraquinone*-4 : 6-*disulphonate*. It crystallised from water in long yellow leaves (Found in dehydrated salt : S, 14·8; Na, 10·0. $C_{14}H_5O_8ClS_2Na_2$ requires S, 14·4; Na, 10·3%). From hydrochloric acid (1 : 1), the *sodium hydrogen* salt separates in small needles (Found : Na, 6·0. $C_{14}H_6O_8ClS_2Na$ requires Na, 5·5%). The combined mother-liquors were evaporated and the first precipitate was removed and rejected. When well concentrated, the filtrate set, on cooling, to a mass of *sodium* 1-*chloroanthraquinone*-2 : 6-*disulphonate*. This was drained and recrystallised (28 g.) (Found in the dehydrated salt : S, 14·9%. $C_{14}H_5O_8ClS_2Na_2$ requires S, 14·4%). The barium and calcium salts of both sulphonic acids are easily soluble in water. Calcium carbonate may be substituted for barium carbonate for the removal of sulphuric acid : it has the advantage that less has to be used and calcium sulphate is much more easily removed by filtration than barium sulphate, but its use suffers from the serious defect that calcium 1-chloroanthraquinone-6-sulphonate, which is appreciably soluble, finds its way into the final product. This is also the case with the sulphonation of the isomeric sodium chloroanthraquinonesulphonates.

Chlorination of Sodium 1-*Chloroanthraquinone*-4 : 6- *and* -2 : 6-*disulphonates*. 1 : 4 : 6- *and* 1 : 2 : 6-*Trichloroanthraquinones*.—A solution of sodium 1-chloroanthraquinone-4 : 6-disulphonate (10 g.) in water (1000 c.c.) containing potassium chlorate (20 g.) and acidified with hydrochloric acid (80 c.c.) was heated on the steam-bath until a test portion, on filtration, gave a colourless filtrate (10 hours). The precipitated 1 : 4 : 6-trichloroanthraquinone crystallised from glacial acetic acid in long golden needles, m. p. 236° (Found : Cl, 34·2. Calc. for $C_{14}H_5O_2Cl_3$: Cl, 34·1%). Reduction with zinc dust and ammonia gave 1 : 4 : 6-*trichloroanthracene*, which crystallised from acetic acid in plates, m. p. 158—159° (Found : Cl, 37·8. $C_{14}H_7Cl_3$ requires Cl, 37·9%).

1 : 2 : 6-*Trichloroanthraquinone* was obtained in an identical manner from sodium 1-chloroanthraquinone-2 : 6-disulphonate. It crystallised from acetic acid in lustrous, attenuated, pale yellow needles, m. p. 222—223°; this m. p. was considerably depressed in admixture with 1 : 4 : 6-trichloroanthraquinone (Found : Cl, 34·2%).

Sodium 1-*Aminoanthraquinone*-4 : 6-*disulphonate*.—This was obtained from the 4 : 6-disulphonate (20 g.) (water 500 c.c., hydrated copper sulphate 2·5 g., aqueous ammonia 100 c.c.; 100°; 48 hours), in the same way as 1-aminoanthraquinone-6-sulphonic acid (p. 1782), as a mass of dark micro-needles (14 g.). The anhydrous salt is brick-red and is very soluble in water with a fine crimson colour;

it crystallises in small black needles containing water of crystallisation which is not removed even by prolonged heating at 100° [Found: loss at 140°/20 mm., 9·6. Found in anhydrous salt (two preparations): S, 15·3, 14·7; Na, 10·7, 10·9; N, 3·5, 3·4. $C_{14}H_7O_8NS_2Na_2,2\frac{1}{2}H_2O$ requires loss, 9·5%. $C_{14}H_7O_8NS_2Na_2$ requires S, 15·0; Na, 10·8; N, 3·3%]. The *monosodium* salt crystallises from strongly acidified solutions of the disodium salt (Found: S, 15·9. $C_{14}H_8O_8NS_2Na$ requires S, 15·8%).

1-*Diethylaminoanthraquinone*-4 : 6-*disulphonic Acid.*—A solution of sodium 1-chloroanthraquinone-4 : 6-disulphonate (8 g.) in water (180 c.c.) containing copper sulphate (1·5 g.) was heated with diethylamine (20 c.c.) at 100° for 50 hours. The purple solution produced was filtered from the copper–diethylamine complex, heated with sodium hydroxide (4 g.) to remove the excess of diethylamine, slightly acidified, and well concentrated. The dark violet, crystalline mass which separated (6 g.) was taken up in a small volume of water and rendered strongly acid with hydrochloric acid; 1-*diethylaminoanthraquinone*-4 : 6-*disulphonic acid* then separated in violet-brown leaves (4 g.). It was recrystallised from dilute hydrochloric acid, in which it was not very soluble [Found: N, 3·6, 3·8; S, 11·6, 10·9 (alkali fusions), 10·2 (micro-Carius). $C_{18}H_{17}O_8NS_2$ requires N, 3·2; S, 14·6%].*

Sodium 1-*aminoanthraquinone*-2 : 6-*disulphonate* was obtained in the same manner as its isomeride from the chloro-2 : 6-disulphonate. It is much more soluble than the 1 : 4 : 6-isomeride and is obtained in the pure state with great difficulty (Found: S, 16·4; N, 4·0. $C_{14}H_8O_8NS_2Na$ requires S, 15·8; N, 3·5%).

The Sulphonation of Sodium 1-*Chloroanthraquinone*-7-*sulphonate. Sodium* 1-*Chloroanthraquinone*-2 : 7-*disulphonate.*—Sodium 1-chloroanthraquinone-7-sulphonate (80 g.) was heated with 20% fuming sulphuric acid (240 c.c.) for 10 hours at 155—160°. The liquor was poured into water, decolorised by boiling with a little nitric acid, its volume made up to about 3 litres, and the sulphuric acid removed by addition of milk of barium carbonate (850 g.). The mother-liquor and washings from the barium sulphate were concentrated and sodium hydroxide (10 g.) was added. The solution was evaporated to very small bulk; on cooling, it had the consistency of glue. An excess of absolute alcohol was added and after a considerable time the precipitate was collected and dissolved in the minimum amount of boiling water, and the solution evaporated, the head fractions being removed. The filtrate on evaporation to dryness

* Better sulphur analyses could not be obtained; moreover, consistent results were not given by the alkali-fusion method even with the same specimen. Carius's method invariably gives low results with anthraquinone derivatives.

gave an ochreous residue of *sodium* 1-*chloroanthraquinone*-2 : 7-*disulphonate* (70 g.). The substance is extremely soluble even in cold water and cannot be crystallised; for analysis it was precipitated from its concentrated aqueous solution with alcohol (Found for the anhydrous salt: S, 15·6. $C_{14}H_6O_8ClS_2Na$ requires S, 15·1%. $C_{14}H_5O_8ClS_2Na_2$ requires S, 14·4%).

Chlorination of Sodium 1-*Chloroanthraquinone*-2 : 7-*disulphonate.* 1 : 2 : 7-*Trichloroanthraquinone.*—A dilute aqueous solution of sodium 1-chloroanthraquinone-2 : 7-disulphonate was treated with nascent chlorine at 100° in the manner previously described for isomeric substances. 1 : 2 : 7-*Trichloroanthraquinone*, which was completely precipitated in about 20 hours, crystallised from glacial acetic acid in small feathery needles, m. p. 225—226° after several crystallisations (Found: Cl, 34·0. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%). Reduction with zinc dust and ammonia gave 1 : 2 : 7-*trichloroanthracene*, which crystallised from acetic acid in long needles, m. p. 208—209° (Found: Cl, 37·3. $C_{14}H_7Cl_3$ requires Cl, 37·8%).

Sodium 1-*aminoanthraquinone*-2 : 7-*disulphonate*, obtained by condensing the corresponding sodium chloro-disulphonate with ammonia, was an amorphous carmine powder soluble in less than its own weight of cold water with a fine red colour. It could not be obtained in the pure form (Found: S, 16·5. $C_{14}H_9O_8NS_2$ requires S, 16·7. $C_{14}H_8O_8NS_2Na$ requires S, 15·8%).

Sulphonation of Sodium 1-*Chloroanthraquinone*-5-*sulphonate. Sodium* 1-*Chloroanthraquinone*-2 : 5-*disulphonate.*—The 5-sulphonate (30 g.) was heated for 11 hours at 155° with 20% fuming sulphuric acid (100 c.c.). The product was treated as for previous sulphonations, 400 g. of barium carbonate being used. The mother-liquor, combined with the washings, was well concentrated, sodium hydroxide (5 g.) added, and the solution evaporated to very small bulk. *Sodium* 1-*chloroanthraquinone*-2 : 5-*disulphonate* slowly separated in yellow leaves (17 g. after recrystallisation) (Found: S, 13·9. $C_{14}H_5O_8ClS_2Na_2$ requires S, 14·4%).

Treatment of a boiling aqueous solution of the salt with nascent chlorine gave 1 : 2 : 5-*trichloroanthraquinone*, which crystallised from acetic acid in needles, m. p. 228—230°, and was shown by the usual method to be identical with the 1 : 2 : 5-trichloroanthraquinone obtained from 1 : 5-dichloroanthraquinone (Found: Cl, 33·8. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%).

*3′-*Chloro*-4′-*hydroxybenzoylbenzoic Acid.*—To phthalic anhydride (20 g.) and *o*-chlorophenol (20 g.) in dry acetylene tetrachloride

* This condensation, together with the subsequent closure of the anthraquinone ring, was carried out a considerable time before the appearance of Hayashi's paper.

(100 c.c.), anhydrous aluminium chloride (50 g.) was added in three portions at ½-hour intervals, and the mixture was then heated at 80° for 1 hour and at 105—110° for 1 hour and poured into dilute hydrochloric acid. The heavy white precipitate produced was pressed on a tile and dissolved in dilute caustic soda solution, and concentrated hydrochloric acid added; *3'-chloro-4'-hydroxybenzoylbenzoic acid* was then obtained in almost theoretical yield. It is exceedingly soluble in methyl alcohol; when this solvent is removed in a vacuum the substance is deposited in large hard white cubes, m. p. 224—225° [Found: Cl, 12·8; *M*, by titration (dibasic), 280. $C_{14}H_9O_4Cl$ requires Cl, 12·8%; *M*, 276·5].

2-Chloro-3-hydroxyanthraquinone.—3'-Chloro-4'-hydroxybenzoylbenzoic acid (40 g.) was dissolved in sulphuric acid (400 c.c.) and heated with pulverised anhydrous zinc chloride (40 g.) at 130° for 5½ hours. The mixture was poured into an excess of water and, after being coagulated on the steam-bath, the precipitated *2-chloro-3-hydroxyanthraquinone* (30 g.) was filtered off and crystallised from dry xylene, forming silky yellow needles, m. p. 267—268° (Found: Cl, 13·7. $C_{14}H_7O_3Cl$ requires Cl, 13·7%). It is soluble in hot aqueous sodium bicarbonate, from which solution blood-red needles are deposited.

2 : 3-*Dichloroanthraquinone.*—2-Chloro-3-hydroxyanthraquinone (3 g.) was dissolved in anhydrous xylene (50 c.c.) and refluxed with phosphorus pentachloride (3 g.), more of which (3 g.) was added after 2 hours. After being heated for another 2 hours, the xylene was distilled off and the crystalline residue extracted with several small quantities of glacial acetic acid. The extracts were oxidised with chromic acid, and the 2 : 3-dichloroanthraquinone precipitated with water (0·2 g.). It crystallised from acetic acid in lemon needles, m. p. 258—259°.

1 : 2-*Dichloroanthraquinone.*—To a solution of 1-chloro-2-aminoanthraquinone (15 g.) (Junghaus, *Annalen*, 1913, **399**, 316) in sulphuric acid (75 c.c.) at 0°, sodium nitrite (5·1 g.) was added during 5 minutes, followed after 15 minutes by ice (150 g.); a grey-yellow precipitate of 1-chloroanthraquinone-2-diazonium sulphate was thrown down. The sulphate gives in water a scarlet stable solution which decomposes slowly at the boiling point; it crystallises in brick-red micro-needles. In aqueous solution it couples with sodium β-naphthoxide with the production of a carmine dye completely insoluble in, and fast to, acids and alkalis. With R-salt it gives a soluble red compound which dyes animal fabric mordanted with ferric salts a bright red.

The above suspension of the diazonium sulphate was poured into a solution of cuprous chloride (30 g.) in hydrochloric acid (150 c.c.),

and the whole stirred vigorously at the ordinary temperature for 15 minutes and at 90° for a further 15 minutes (this is essential to obtain a good yield). It was then poured into water (600 c.c.) and heated on the steam-bath for 1½ hours with stirring. The precipitate was collected, dissolved in acetic acid, and treated at the boiling point with chromic acid; addition of water precipitated 1 : 2-dichloroanthraquinone, which crystallised from acetic acid (charcoal) in long stout yellow needles (9·2 g.), m. p. 203° (Found : Cl, 25·5. Calc. for $C_{14}H_6O_2Cl_2$: Cl, 25·6%).

Sulphonation of 1 : 2-*Dichloroanthraquinone. Sodium* 1 : 2-*Dichloroanthraquinone*-6- *and* -7-*sulphonates.*—1 : 2-Dichloroanthraquinone (5 g.) dissolved in 20% fuming sulphuric acid (7 c.c.) was heated at 155—160° for 5¼ hours. The dark red melt was poured into water (200 c.c.), in which it was completely soluble, and its dark colour was discharged by heating with a little nitric acid. Sodium hydroxide (15 g. in 45 c.c. of water) was added and after some time the yellow precipitate was filtered off and dissolved in the minimum amount of boiling water, and the solution evaporated; golden spangles then began to separate. When the liquor was reduced to about half its volume, it was cooled and the crystalline precipitate of *sodium* 1 : 2-*dichloroanthraquinone*-6-*sulphonate* was collected (1·9 g.). This substance is sparingly soluble in water, from which it separates in golden spangles (Found : S, 8·7. $C_{14}H_5O_5Cl_2SNa$ requires S, 8·45%). The filtrate was further evaporated and the first small precipitate was removed. When the filtered solution was concentrated to small bulk and kept, *sodium* 1 : 2-*dichloroanthraquinone*-7-*sulphonate* came down in golden leaves (2 g.). Crystallised from water, in which it was very soluble, it gave the pure salt (Found : S, 8·9%).

Chlorination of Sodium 1 : 2-*Dichloroanthraquinone*-6- *and* -7-*sulphonate.* 1 : 2 : 6- *and* 1 : 2 : 7-*Trichloroanthraquinones.*—Sodium 1 : 2-dichloroanthraquinone-6-sulphonate (2 g.), suspended in water (800 c.c.) containing potassium chlorate (2 g.) and acidified with hydrochloric acid (10 c.c.), gradually dissolved when heated on the steam-bath, with the simultaneous precipitation of 1 : 2 : 6-*trichloroanthraquinone* in microcrystalline flocks. These, collected after 20 hours and crystallised from acetic acid, formed long lemon needles, m. p. 221—223° alone and in admixture with the trichloroanthraquinone obtained from sodium 1-chloroanthraquinone-2 : 6-disulphonate (Found : Cl, 34·1. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%). The m. p. was depressed in admixture with specimens of 1 : 2 : 7-trichloroanthraquinone obtained from sodium 1 : 2-dichloroanthraquinone-7-sulphonate and from sodium 1-chloroanthraquinone-2 : 7-disulphonate.

A dilute aqueous solution of sodium 1 : 2-dichloroanthraquinone-7-sulphonate, treated in the same manner with nascent chlorine, gave 1 : 2 : 7-*trichloroanthraquinone*, which crystallised from acetic acid in long pale needles, m. p. 224°, which did not depress the m. p. of 1 : 2 : 7-trichloroanthraquinone obtained from sodium 1-chloroanthraquinone-2 : 7-disulphonate (Found : Cl, 34·0%).

1 : 3-*Dichloro- and* 1 : 2 : 3-*Trichloro-anthraquinone*.—2-Aminoanthraquinone was chlorinated by the two methods described by Ullmann and Junghaus (*loc. cit.*), but their high yields of 1 : 3-dichloro-2-aminoanthraquinone could not be obtained. The crude products melted below 185° and required to be recrystallised 4 or 5 times to raise the m. p. to 224°, the figure given by these authors.

A solution of 1 : 3-dichloro-2-aminoanthraquinone (20 g.) in sulphuric acid (100 c.c.) was slowly treated at 0° with sodium nitrite (7 g.). When a test portion was completely soluble in an excess of water (*ca.* 20 minutes), the mixture was poured into ice-water (200 g.). The diazonium sulphate was thrown down as a grey-brown precipitate. This substance is easily soluble in water, giving a pink solution which is moderately stable at the boiling point. The sulphate couples with sodium β-naphthoxide, yielding a crimson dye. For the deamination, it was suspended together with dry cuprous oxide (4 g.) in absolute alcohol (800 c.c.) and gently heated. When the vigorous reaction was over (2 hours), the alcohol was removed by evaporation, the residue heated with nitric acid to remove copper oxide, and the 1:3-dichloroanthraquinone dissolved in acetic acid, treated with chromic acid, and precipitated with water. After crystallising twice from acetic acid, it was obtained in long, stout, yellow needles (8 g.), m. p. 208° (Junghaus gives 203°).

For the synthesis of 1 : 2 : 3-trichloroanthraquinone, 1 : 3-dichloro-2-aminoanthraquinone (20 g.) was diazotised as above, and ice (100 g.) added to the sulphuric acid solution. The whole was poured with stirring into a solution of cuprous chloride (40 g.) in hydrochloric acid (200 c.c.). The frothy mass was stirred vigorously for 15 minutes at room temperature and at 90° for ½ hour, water (160 c.c.) added, and the mixture heated on the steam-bath for 1½ hours. The 1 : 2 : 3-*trichloroanthraquinone* was then filtered off, treated in boiling acetic acid with chromic acid, and precipitated by the addition of water. After crystallising twice from acetic acid, it was obtained in long, lustrous, pale yellow needles (7·4 g.), m. p. 194—195° (Found : Cl, 34·0. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%).

Sulphonation of 1 : 3-*Dichloroanthraquinone. Sodium* 1 : 3-*Dichloroanthraquinone*-6- *and* -7-*sulphonates*.—1 : 3-Dichloroanthraquinone (10 g.) was sulphonated in the same way as 1 : 2-dichloro-

anthraquinone (p. 1788), and the product treated as there described. The solution of the product (19·1 g.) in the minimum amount of boiling water (700 c.c.), on cooling, set to a transparent jelly, which became opaque but still unfilterable on the addition of a little hydrochloric acid. The solution was therefore evaporated considerably (volume *ca.* 300 c.c.) at 100°, and the granular precipitate of *sodium* 1 : 3-*dichloroanthraquinone*-6-*sulphonate* (5·6 g.) removed from the hot liquor (Found in recrystallised salt: S, 8·8. $C_{14}H_5O_5Cl_2SNa$ requires S, 8·45%). The filtrate was further evaporated, and the first precipitate (nearly 2 g.) removed; the filtered solution on evaporation to small bulk gave a crystalline precipitate of *sodium* 1 : 3-*dichloroanthraquinone*-7-*sulphonate* (2·4 g.), which was obtained pure after one recrystallisation (Found: S, 9·0%).

Chlorination of Sodium 1 : 3-*Dichloroanthraquinone*-6- *and* -7-*sulphonates.* 1 : 3 : 6- *and* 1 : 3 : 7-*Trichloroanthraquinones.*—A solution of sodium 1 : 3-dichloroanthraquinone-6-sulphonate (4 g.) in water (500 c.c.) containing potassium chlorate (4 g.) and acidified with hydrochloric acid (20 c.c.) was heated on the steam-bath until a test portion, on filtration, gave a colourless filtrate. The 1 : 3 : 6-*trichloroanthraquinone* was collected, washed with dilute sodium hydroxide solution, and crystallised from acetic acid, forming long yellow needles (1·7 g.), m. p. 212—213° (Found: Cl, 34·1. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%).

Chlorination of sodium 1 : 3-dichloroanthraquinone-7-sulphonate (1 g.) in the same manner gave 1 : 3 : 7-*trichloroanthraquinone*, which crystallised from acetic acid in starry clusters of lemon needles, m. p. 216—217° (Found: Cl, 33·83%).* A mixture of the two trichloroanthraquinones melted below 195°.

Sulphonation of 1 : 4-*Dichloroanthraquinone. Sodium* 1 : 4-*Dichloroanthraquinone*-6-*sulphonate.*—1 : 4-Dichloroanthraquinone (3 g.) (Ullmann and Conzetti, *loc. cit.*) was heated with 20% fuming sulphuric acid (3 c.c.) at 160° for 4 hours. After cooling, the dark liquor was poured into water (75 c.c.), in which it dissolved completely, the dark colour was removed with nitric acid, and a solution of sodium hydroxide (4 g.) added. When the solution was evaporated to small bulk and cooled, *sodium* 1 : 4-*dichloroanthraquinone*-6-*sulphonate* separated in small yellow leaves (Found in the anhydrous salt: S, 8·8. $C_{14}H_5O_5Cl_2SNa$ requires S, 8·45%).

Chlorination of Sodium 1 : 4-*Dichloroanthraquinone*-6-*sulphonate.* 1 : 4 : 6-*Trichloroanthraquinone.*—A solution of sodium 1 : 4-dichloroanthraquinone-6-sulphonate (2 g.) in water (300 c.c.) containing potassium chlorate (2 g.) and hydrochloric acid (10 c.c.) was heated

* Micro-analysis by Dr. Schoeller, Berlin.

at 100° until precipitation of the 1 : 4 : 6-trichloroanthraquinone was complete. This crystallised from acetic acid in long golden needles, m. p. 236° alone and in admixture with the specimen obtained from sodium 1-chloroanthraquinone-4 : 6-disulphonate. The m. p. was depressed by the addition of 1 : 4 : 5-trichloroanthraquinone (Found : Cl, 34·3. Calc. for $C_{14}H_5O_2Cl_3$: Cl, 34·1%).

Sulphonation of 1 : 8-*Dichloroanthraquinone. Sodium* 1 : 8-*Dichloroanthraquinone*-4-*sulphonate.*—1 : 8-Dichloroanthraquinone was prepared by the chlorination of the corresponding potassium anthraquinone disulphonate (Fierz-David, *loc. cit.*). It was found preferable to use this salt in a state of high purity, as then the 1 : 8-dichloroanthraquinone was precipitated in pale lemon needles, nearly 1 cm. in length, m. p. 201°. A solution of technical sodium anthraquinone-1 : 8-disulphonate was treated with concentrated potassium chloride solution and the relatively insoluble potassium salt, which separated in golden spangles, was recrystallised from a large volume of water.

1 : 8-Dichloroanthraquinone (50 g.) was dissolved in 20% fuming sulphuric acid (75 c.c.) and heated for 8 hours at 155—160°. The product was poured into water (1000 c.c.) and, after the unchanged 1 : 8-dichloroanthraquinone (8 g.) had been removed, the filtrate was decolorised with nitric acid (50 c.c.). Sodium hydroxide (50 g. in 200 c.c. of water) was added, and the solution evaporated to small volume (*ca.* 300 c.c.) and cooled. The bulky precipitate was collected and on crystallisation from the minimum amount of boiling water gave 24 g. of pure *sodium* 1 : 8-*dichloroanthraquinone*-4-*sulphonate* (Found : S, 8·7. $C_{14}H_5O_5Cl_2SNa$ requires S, 8·45%). The filtrate, after removal of a further crop of the above monosulphonate, was well concentrated and cooled; yellow leaves of sodium 1 : 8-dichloroanthraquinone-4 : 5-disulphonate were precipitated (5 g.).

Chlorination of Sodium 1 : 8-*Dichloroanthraquinone*-4-*sulphonate and* -4 : 5-*disulphonate.* 1 : 4 : 5-*Trichloro- and* 1 : 4 : 5 : 8-*Tetrachloro-anthraquinones.*—A dilute aqueous solution of sodium 1 : 8-dichloroanthraquinone-4-sulphonate (4 g.) was treated with nascent chlorine at 100°, in the manner previously described, until precipitation of 1 : 4 : 5-*trichloroanthraquinone* was complete. This crystallised from acetic acid in long yellow needles, m. p. 258° alone and in admixture with the specimen obtained from sodium 1-chloroanthraquinone-4 : 5-disulphonate (Found : Cl, 34·3. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%).

In the same manner, double the quantities of potassium chlorate and hydrochloric acid being used, sodium 1 : 8-dichloroanthraquinone-4 : 5-disulphonate gave 1 : 4 : 5 : 8-tetrachloroanthraquinone,

which crystallised from acetic acid in very pale, small needles, m. p. 341—342° (Maquenne block) (Found : Cl, 40·3. Calc. for $C_{14}H_4O_2Cl_4$: Cl, 41·0%).

Sulphonation of 1 : 5-*Dichloroanthraquinone. Sodium* 1 : 5-*Dichloroanthraquinone*-2- *and* -4-*sulphonates.*—1 : 5-Dichloroanthraquinone was prepared by the chlorination of the highly purified sodium salt of the corresponding disulphonic acid; it was precipitated in long needles, m. p. 245°. 50 G. were dissolved in 20% fuming sulphuric acid (50 c.c.) and heated at 155—160° for 4 hours. The liquor was poured into water, the unchanged 1 : 5-dichloroanthraquinone removed (28 g.), and the filtrate, after being decolorised with a little nitric acid, treated with a solution of sodium hydroxide (40 g.). The solution was evaporated to small bulk and cooled, and the yellow precipitate was collected and dissolved in the minimum amount of boiling water, a saturated solution of sodium chloride (5 g.) added, and the solution allowed to cool. The precipitated *sodium* 1 : 5-*dichloroanthraquinone*-2-*sulphonate* (9 g.) crystallised from water in small pointed leaves (Found : S, 8·9. $C_{14}H_5O_5Cl_2SNa$ requires S, 8·45%). The filtrate from the above had deposited after 12 hours a thick glutinous yellow precipitate which, after crystallising twice from water, gave *sodium* 1 : 5-*dichloroanthraquinone*-4-*sulphonate* in the pure form (10·5 g.). It crystallised from water, in which it was very soluble, in long needles which had a gelatinous appearance (Found : S, 9·0%). The filtrate was well concentrated and cooled; sodium 1 : 5-dichloroanthraquinone-2 : 8-disulphonate then came down. This, treated with nascent chlorine in boiling aqueous solution, gave 1 : 2 : 5 : 8-*tetrachloroanthraquinone*, which, after two crystallisations from acetic acid, was obtained in long felted needles, m. p. 282—283° (Found : Cl, 40·6. $C_{14}H_4O_2Cl_4$ requires Cl, 41·0%).

1 : 2 : 5- *and* 1 : 4 : 5-*Trichloroanthraquinones.*—A dilute solution of sodium 1 : 5-dichloroanthraquinone-2-sulphonate (6 g.) was heated overnight at 100° with potassium chlorate (6 g.) and hydrochloric acid (28 c.c.). The 1 : 2 : 5-*trichloroanthraquinone* obtained crystallised from acetic acid in long stout yellow needles, m. p. 235—236° (Found : Cl, 34·0. $C_{14}H_5O_2Cl_3$ requires Cl, 34·1%).

In the same manner, sodium 1 : 5-dichloroanthraquinone-4-sulphonate gave 1 : 4 : 5-*trichloroanthraquinone*, which was precipitated very rapidly. It crystallised from acetic acid in yellow needles, the m. p. of which was raised by several recrystallisations to 256—257° (Found : Cl, 34·4%). In admixture, it depresses considerably the m. p. of 1 : 2 : 5-trichloroanthraquinone, but not that of 1 : 4 : 5-trichloroanthraquinone obtained from sodium 1 : 8-dichloroanthraquinone-4-sulphonate.

Catalytic Sulphonation of 1 : 5-*Dichloroanthraquinone.*—The above sulphonation was carried out with the addition of red mercuric oxide (5—6 g.). The product was worked up as before, and the yellow substance obtained crystallised in fractions from water. The first fraction (11 g.) was pure sodium 1 : 5-dichloroanthraquinone-4-sulphonate; on treatment with nascent chlorine it gave 1 : 4 : 5-trichloroanthraquinone, m. p. 256° after one crystallisation from acetic acid. The last fraction (3 g.) was sodium 1 : 5-dichloroanthraquinone-4 : 8-disulphonate; treatment with nascent chlorine gave 1 : 4 : 5 : 8-tetrachloroanthraquinone, m. p. 337°, which did not depress the m. p. of that obtained from sodium 1 : 8-dichloroanthraquinone-4 : 5-disulphonate.

Attempted Chlorination of Sodium Anthraquinone-1 : 5-*disulphonate.*—The disulphonate (10 g.) was dissolved in sulphuric acid (35 c.c.), a crystal of iodine added, and the mixture heated at 160° for 3 hours while dry chlorine was passed in (from 60 g. of potassium permanganate and 440 c.c. of hydrochloric acid). The product was poured into water and salted out with sodium chloride. The yellow precipitate (10 g.) was separated by fractional crystallisation from water into 4 portions, each of which was separately treated with nascent chlorine in boiling aqueous solution. They all gave precipitates of 1 : 5-dichloroanthraquinone, m. p. 244°. The same negative result was obtained when 20% fuming sulphuric acid was used as solvent.

The Attempted Nitration of Sodium Anthraquinone-1 : 5-*disulphonate.*—The following is a typical experiment. Anhydrous sodium anthraquinone-1 : 5-disulphonate (20 g.), dissolved in sulphuric acid (60 c.c.), was heated to 100°, fuming nitric acid (20 c.c.) slowly dropped in with shaking, and the mixture heated on the water-bath over-night. The liquid was cooled and filtered through asbestos. The residue on the filter was dissolved in water, a little sodium hydroxide added, and the substance in solution separated into 3 portions by fractional crystallisation. All these fractions when treated in boiling aqueous solution with nascent chlorine precipitated 1 : 5-dichloroanthraquinone in the pure state. The same result was obtained when 20% fuming sulphuric acid or 40% oleum was used as solvent in place of ordinary sulphuric acid. Sodium anthraquinone-1 : 8-sulphonate was treated similarly with negative results; moreover, although repeated experiments were made, no nitrogenous substance could be detected in the product obtained by treating either sodium anthraquinone-2 : 6- or -2 : 7-disulphonate with fuming nitric acid.

The Semi-chlorination of Potassium Anthraquinone-1 : 5-*disulphonate.*—The following is a typical experiment. Potassium anthra-

quinone-1 : 5-disulphonate (30 g.) was dissolved in water (1125 c.c.), acidified with hydrochloric acid (150 c.c.), and heated on the steam-bath to 90°. A solution of sodium chlorate (15 g.) in water (150 c.c.) was slowly dropped in during 15 minutes, and the temperature maintained at 90° for a further 1½ hours. The precipitated 1 : 5-dichloroanthraquinone (7·9 g.) was filtered off, the filtrate evaporated slightly, a saturated aqueous solution of potassium chloride (80 g.) added, and, after standing, the yellow precipitate collected (12 g.). This was converted into sulphonyl chloride, an excess of the reagents being used. The crude sulphonyl chloride melted below 100° (contrast that obtained from the catalytic preparation which had crude m. p. above 200°). On treatment with benzene, part was soluble with ease, leaving a residue (*ca.* one-third of the whole) which was soluble only with great difficulty in benzene. This residue after several recrystallisations had m. p. 230—235°, which was depressed in admixture with authentic 1-chloroanthraquinone-5-sulphonyl chloride but not by anthraquinone-1 : 5-disulphonyl chloride (Found: S, 15·2. Calc. for $C_{14}H_6O_6Cl_2S_2$: S, 15·8%). It was therefore impure anthraquinone-1 : 5-disulphonyl chloride. The portion easily soluble in benzene was recrystallised several times from this solvent and obtained (1·8 g.) in small crystals, m. p. 204—215° (Found : S, 10·5. Calc. for $C_{14}H_6O_4Cl_2S$: S, 9·4%). It was therefore impure 1-chloroanthraquinone-5-sulphonyl chloride.

In another experiment the reaction was arrested when only 2 g. of 1 : 5-dichloroanthraquinone had been formed. The filtered solution was salted out, and the product treated with phosphorus pentachloride; anthraquinone-1 : 5-disulphonyl chloride was then obtained, which crystallised from nitrobenzene in dark yellow tablets, m. p. 260—262°.

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