CLXXXVI.—*The Iodobenzenemonosulphonic Acids. Part I.*

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ALTHOUGH a large number of chloro- and bromo-derivatives of benzenesulphonic acid and of the homologous acids have been prepared, little is known of the corresponding iodo-compounds, the *o*-, *m*-, and *p*-iodo-derivatives alone being known in the case of benzenesulphonic acid.

The investigation, of which the first part is described in this communication, has for its object the preparation and study of the higher iodo-derivatives of benzenesulphonic acid, and an account is given of 2:4-, 2:5-, 3:4-, and 3:5-di-iodo-, and 2:3:5-, 2:4:5-, and 3:4:5-tri-iodo-benzenesulphonic acids.

Historical.

p-Iodobenzenesulphonic acid was first described in 1872 by Körner and Paterno (*Gazzetta*, **2**, 448), who prepared it from iodobenzene and fuming sulphuric acid; it was subsequently prepared by Lenz in 1877 (*Ber.*, **10**, 1135) by displacing the amino-group of aniline-*p*-sulphonic acid by iodine.

The ortho-acid was prepared by Bahlmann in 1877 (*Annalen*, **186**, 325) by the action of fuming hydriodic acid on the diazo-salt of aniline-*o*-sulphonic acid; the meta-acid was prepared in like manner from aniline-*m*-sulphonic acid by Langmuir in 1895 (*Ber.*, **28**, 93). Iodo-derivatives of several sulphonic acids of the

homologues of benzene have also been prepared, namely, *o*-iodotoluenesulphonic acid by Mabery and Palmer (*Amer. Chem. J.*, 1884, **6**, 170); the para-derivative by Glassner (*Ber.*, 1875, **8**, 560) and de Roode (*Amer. Chem. J.*, 1891, **13**, 233); a disulphonic acid of *p*-iodotoluene by Richter (*Annalen*, 1885, **230**, 325); an iodoxylenesulphonic acid by Hammerich (*Ber.*, 1890, **23**, 1635); a di-iodoxylenesulphonic and an iodomesitylenesulphonic acid by Töhl (Töhl and Bauch, *Ber.*, 1893, **26**, 1107; Töhl and Eckel, *Ber.*, 1893, **26**, 1101), besides others of a more complex nature.

Theoretical.

The sulphonation of iodo-compounds in all cases involves the formation of compounds richer in iodine, the sulphuric acid acting to a certain extent as a carrier of halogen, and causing the transfer of iodine from one molecule to another. Such sulphonating experiments, therefore, result in the production of at least three substances, namely, (1) a compound containing more iodine in the nucleus than the original substance; (2) an iodosulphonic acid; (3) a sulphonic acid free from iodine, the molecule which has lost the iodine being, as a rule, readily attacked by the sulphonating agent. Such was observed to be the case by Hammerich (*loc. cit.*), who subjected iodo-*m*-xylene to the action of concentrated sulphuric acid, also by Neumann (*Annalen*, 1887, **241**, 47) during his investigation of the action of sulphuric acid on iodobenzene.

The latter observer studied the conditions under which sulphonation of the iodo-compound is possible, and arrived at the conclusion that strength of acid, proportions of the interacting substances, and temperature are all important factors to be taken into consideration. As a rule, concentrated acid favours sulphonation, high temperatures the production of di-iodobenzene.

My first attempts to prepare 2:5-di-iodobenzenesulphonic acid were made on the lines of these experiments, since it was evident that if *p*-iodoaniline or *p*-iodoacetanilide could be directly sulphonated, the conversion of either product into the required acid would be a matter of little difficulty. The results were very unsatisfactory.

In the case of iodoaniline hydrochloride, no sulphonation was effected at low temperatures, and, on gently heating the mixture, iodine was copiously evolved; in the case of iodoacetanilide, when the conditions were such as to render sulphonation possible, a considerable amount of iodine was evolved, and the sulphonic acid obtained did not contain the halogen.

It may be noted that similar results have been obtained with

iodophenolic compounds by Neumann (*loc. cit.*), his attempts to prepare an iodophenolsulphonic acid by direct sulphonation of the iodophenol having resulted, at the ordinary temperature, in the elimination of iodine, and, at low temperatures, in the formation of a di-iodo-derivative unaccompanied by any sulphonic acid.

The action of sulphonating agents on *p*-di-iodobenzene was next studied, but with not much more satisfactory results.

The di-iodobenzene was treated both with the calculated amount and with excess of concentrated sulphuric acid, with fuming acid of various strengths, and with sulphur trioxide at many different temperatures. At the ordinary temperature, no action took place with either concentrated or fuming acid; at the temperature of the water-bath, fuming acid caused the formation of tri- and tetra-iodobenzene and a trace of a sulphonic acid. The vapour of sulphur trioxide, when passed over dry and slightly warm di-iodobenzene, caused the formation of small quantities of the higher iodo-derivatives of benzene, but when the experiment was carried out at higher temperatures, the proportion of unchanged material became much less, and a small amount of a crystalline di-iodobenzenesulphonic acid was isolated.

The yield, however, was so extremely poor, being, under the most favourable conditions, less than 10 per cent., and becoming much less when large quantities were dealt with, that the method, as a means of preparing a large amount of the acid, was seen to be hopeless, and was abandoned.

The possibility of introducing iodine into substances already containing a sulphonic group was next considered. A patent by Kalle and Co. (D.R.-P. 129808), describing the preparation of iodo-substituted derivatives of aniline-*m*- and -*p*-sulphonic acids, indicated that success in that direction had already been achieved. A brief description of the preparation of the iodo-derivatives of these acids is given in the patent, but, as far as can be gathered from a study of subsequent literature, they have not been investigated with a view to the determination of their structure; and others, prepared by myself, which form the starting point for the preparation of several iodobenzenesulphonic acids described in this paper, are not mentioned.

Of these sulphonic acids, 3:4-di-iodobenzenesulphonic acid, prepared from the moniodoaniline-*p*-sulphonic acid described by Kalle and Co., which is readily obtained in large amount, was first studied; the preparation of 2:5-di-iodobenzenesulphonic acid, which involves the production of aniline-*o*-sulphonic acid, and is a more lengthy operation, was undertaken later.

Of the six theoretically possible di-iodobenzenesulphonic acids, the following four:

and, of the six theoretically possible tri-iodobenzenesulphonic acids, the following three:

have been prepared and examined by the author.

Only two of these acids, namely, 2: 5- and 3: 4-di-iodobenzene-sulphonic acids, have been thoroughly investigated with regard to the properties of the acids, their derivatives and salts; derivatives and salts of the other acids have been prepared, but have not as yet been studied.

Indirectly, during the course of the work, several iodoaniline-sulphonic acids, isomeric with that described by Kalle and Co., and some iodonitrobenzenesulphonic acids in the form of their potassium salts, have been prepared but not subjected to examination.

It is stated in the specification of the patent referred to that mono- and di-iodoaniline-*p*-sulphonic acids are produced from aniline-*p*-sulphonic acid by the action of one and two molecular proportions of iodine monochloride respectively, and that a di-iodoaniline-*m*-sulphonic acid is formed under very similar conditions. On carrying out experiments with aniline-*m*-sulphonic acid under the conditions described by Kalle and Co., the statement that a di-iodo-acid is produced was confirmed, but it was found that under carefully regulated conditions a monoiodoaniline-*m*-sulphonic acid may also be prepared, and, as the constitution of this acid is readily determined, its formation is of service in the elucidation of the constitution of the more highly iodinated product. Judging from the results obtained with aniline-*m*- and -*p*-sulphonic acids, it was to be expected that aniline-*o*-sulphonic acid should also give rise to iodo-substituted derivatives; experiments in this direction have been attended with marked success, well-defined crystalline mono-iodo- and di-iodo-aniline-*o*-sulphonic acids having been obtained.

The constitutions of these six iodoanilinesulphonic acids are, in most cases, quite clear, and rigid proofs of structure have been obtained in the case of four of them.

Monoiodoaniline-p-sulphonic Acid.—In the case of monoiodo-

aniline-*p*-sulphonic acid, the formation of *m*-iodobenzenesulphonic acid (identified in the form of its amide) on the removal of the amino-group by the diazo-method, is proof that the iodine atom occupies the ortho-position with respect to the amino-group; consequently, the di-iodo-acid, obtained by directly displacing the amino-group by iodine, is 3:4-di-iodobenzenesulphonic acid.

Monoiodoaniline-m-sulphonic Acid.—As this acid is convertible into a di-iodosulphonic acid identical with that obtained from monoiodoaniline-*p*-sulphonic acid, the ortho-position with respect to the amino- and the para-position with respect to the sulphonic group must be occupied by iodine, as 6-iodoaniline-*m*-sulphonic acid is alone capable of giving rise to 3:4-di-iodobenzenesulphonic acid. Recent work by Brenans (*Compt. rend.*, 1904, **138**, 1503; **139**, 63) and by Körner and Contardi (*Atti R. Accad. Lincei.*, 1908, [v], **17**, i, 465) on the iodination and bromination of *m*-nitroaniline is of interest in connexion with the iodination of aniline-*m*-sulphonic acid, inasmuch as it admits of a comparison being made between the influences exerted by the negative nitro- and sulphonic groups on the position assumed by the entering halogen atom. Brenans states that the action of iodine chloride on *m*-nitroaniline dissolved in acetic acid results in the production of 6-iodo-3-nitroaniline, 2:4-di-iodo-3-nitroaniline, and 2:6-di-iodo-3-nitroaniline.

That is to say, the first atom of iodine assumes the same position relatively to the amino- and nitro-groups as it does in aniline-*m*-sulphonic acid with respect to the amino- and sulphonic groups, thus:

but the second atom of iodine seems (according to Brenans) to be as readily introduced into the second ortho-position as it is into that para- with respect to the amino-group; I find, however, in the case of aniline-*m*-sulphonic acid, that the second atom of iodine, as will be shown later, enters only into the para-position.

The results of Körner and Contardi's observations on the bromination of *m*-nitroaniline dissolved in acetic acid are not in harmony with the above, bromine entering into the para-position by preference, and only to a small extent into the ortho-position with respect to the amino-group, which is that assumed in the first instance by iodine, thus:

It is further stated that, if the para-position is occupied, the bromine atom enters either ortho-position indifferently, thus:

In the case of aniline-*m*-sulphonic acid, only one di-iodo-derivative has been isolated, and it has not yet been found possible to displace the hydrogen in the position between the amino- and sulphonic groups by the halogen, so that there is an essential difference between the nitro- and sulphonic groups as regards their directive influence, the latter in conjunction with the amino-group forming, as it were, a screen which prevents all interaction with the enclosed hydrogen atom. The impregnability of this second ortho-position was clearly manifested in an experiment with *p*-nitroaniline-*m*-sulphonic acid, a solution of which, in very dilute hydrochloric acid, was treated with a considerable excess of iodine chloride. It was thought that, as the para-position was occupied, the second atom of iodine would enter the second ortho-position, but under no conditions could a di-iodo-derivative of any kind be obtained, the monoiodo-compound of the following constitution being alone produced:

The failure to introduce iodine into this position and the non-formation of a tri-iodoaniline-*m*-sulphonic acid is the more remarkable in that a tribromoaniline-*m*-sulphonic acid has been obtained by Berendsen (*Annalen*, 1874, **174**, 84) and by Reinke (*Annalen*, 1877, **186**, 286) by the action of bromine on aniline-*m*-sulphonic acid. This failure may be due to the very sparing solubility of the di-iodo-acid, which is rapidly removed from the further action of the iodine chloride, but such a suggestion will not serve to explain the results obtained with *p*-nitroaniline-*m*-sulphonic acid which remained in solution throughout.

Monoiodoaniline-o-sulphonic Acid.—The action of iodine chloride on a solution of aniline-*o*-sulphonic acid gives an excellent yield of the monoiodo-derivative. Further action under specially regulated conditions which are discussed in the experimental part of this paper, gives rise to a di-iodo-derivative; under no conditions, as was to be expected, can a third iodine atom be introduced into the nucleus.

The monoiodoaniline-*o*-sulphonic acid is the pure para-compound,

free from any admixture of the ortho-isomeride; if produced at all, the latter must be present in such small amount as to escape detection; the second iodine atom enters the free ortho-position. That the iodine atoms occupy the positions stated has been clearly demonstrated. As it was clear that the iodine atom in the mono-iodo-derivative was in either the para- or the ortho-position with respect to the amino-group, the displacement of the latter by hydrogen, leading, as it would, to *m*-iodobenzenesulphonic acid in both cases, could give no definite information as to the constitution of the acid. The amino-group was therefore displaced by iodine, and attempts were made to remove the sulphonic group and obtain a di-iodobenzene. These attempts, as might be expected, proved unsuccessful. The acid proved to be perfectly stable when heated in superheated steam; and when a mixture of the potassium salt with sulphuric acid was heated in the same way, although the sulphonic group was removed, the product became further iodinated in the presence of the sulphuric acid; tri- and tetra-iodobenzenes were isolated, but no trace of a di-iodobenzene could be detected.

Finally, the relative positions of the amino-group and the iodine atom in monoiodoaniline-*o*-sulphonic acid were demonstrated by the preparation of the latter from *p*-nitroaniline-*m*-sulphonic acid:

The constitution of the di-iodobenzenesulphonic acid prepared directly from this acid is therefore definitely settled:

Di-iodoaniline-o- and -p-sulphonic Acids.—Although the monoiodo-derivatives of aniline-*o*- and -*p*-sulphonic acids may theoretically each give rise to three isomeric di-iodo-derivatives, taking into account the well-known fact that halogens always act on amino-compounds in such a manner that the halogen enters into either the ortho- or the para-position, the only two derivatives to be considered are the following:

On displacement of the amino-group by hydrogen, these two acids should yield one and the same di-iodosulphonic acid; this was found actually to be the case:

The two tri-iodo-acids prepared directly from these amino-acids must be therefore 2:3:5-tri-iodobenzenesulphonic acid and 3:4:5-tri-iodobenzenesulphonic acid respectively:

It was thought that independent confirmation of the position of the iodine atoms in the two di-iodoamino-acids would be afforded if the series of changes could be effected which is indicated in the two following schemes, the first having in view the determination of the position assumed by the first iodine atom:

the relative positions of the iodine atoms in the last acid being known; and the second, the proof of the constitution of 2:6-di-iodoaniline-*p*-sulphonic acid:

If the tri-iodo-acid finally obtained, the constitution of which is definitely settled by the method of its production, is identical with the one obtained from di-iodoaniline-*p*-sulphonic acid, the constitution of the latter is also clear. An unexpected difficulty, however, arose in attempting to carry out the experiment. The nitroaniline-*p*-sulphonic acid readily absorbed iodine under the usual conditions, but when this iodo-derivative was diazotised and treated

with potassium iodide, a crystalline potassium salt was obtained, which proved to be a salt, not of the expected di-iodonitrosulphonic acid, but of the tri-iodobenzenesulphonic acid of the second scheme, the nitro-group having been displaced by an iodine atom.

A similar displacement of a nitro-group by iodine was not observed in the case of the isomeric 4-nitroaniline-*m*-sulphonic acid, which exhibited normal behaviour throughout, so that it seems that the proximity to the nitro-group of the amino-group which is subjected to the action of nitrous acid, is an important factor in determining the nature of the interaction.

As regards the problem under consideration, although, owing to the abnormal character of the change, the result scarcely affords decisive proof, the formation of the tri-iodosulphonic acid from a monoiodo-derivative, in which the iodine is undoubtedly in the ortho-position with respect to the amino-, and in the meta-position with respect to each of two negative groups, is convincing evidence of the constitution of the acid.

Di-iodoaniline-m-sulphonic Acid.—That this acid is the 4:6-di-iodo-acid, and that the tri-iodo-acid formed from it is the 2:4:5-tri-iodo-acid, is quite clear from the following considerations.

1. The removal of the amino-group from di-iodoaniline-*m*-sulphonic acid involves the production of a di-iodobenzene-sulphonic acid which, from other modes of preparation, must be regarded as, 2:4-di-iodobenzenesulphonic acid. Two possible configurations of the amino-acid could give rise to this substance, namely:

This di-iodo-acid can be prepared from 5-nitroaniline-*o*-sulphonic acid in such a way as to establish its constitution by the following series of changes:

One iodine atom in di-iodoaniline-*m*-sulphonic acid therefore occupies the para-, the second the ortho-position, with respect to the sulphonic group.

2. If 4-nitroaniline-*m*-sulphonic acid is treated with iodine chloride, it yields a monoiodo-derivative, from which a tri-iodo-acid

may be obtained by carrying out the changes expressed in the following scheme:

In this manner, the same tri-iodosulphonic acid is obtained as may be produced directly from di-iodoaniline-*m*-sulphonic acid. The constitution of the original nitroamino-acid requires that the tri-iodo-acid finally obtained shall possess two iodine atoms in para-positions with respect to each other.

Since, therefore, one iodine atom must be in the para-position with respect to the sulphonic group and two others in para-positions with respect to each other, the constitution of the tri-iodo-acid is settled beyond question as being 2:4:5-tri-iodobenzenesulphonic acid.

The following table shows at a glance how the seven acids under discussion may be obtained from the anilinesulphonic acids:

The iodobenzenesulphonic acids are all extremely soluble in water, much less so in mineral acids; they all crystallise well from mineral acid solutions; the 2:5-di-iodo- and the 2:4:5-tri-iodo-benzenesulphonic acids crystallise extremely well from water alone.

The chlorides crystallise in well-defined forms; the amides are white powders insoluble even in hot water, but, in the case of the tri-iodo-compounds, crystallise well from alcohol; the two anilides

which have been prepared can also be crystallised from alcohol. The acids are characterised by forming beautifully crystalline salts and esters.

The diazo-anhydrides of the iodoaminosulphonic acids considered in this paper are all coloured, the colour varying from the palest yellow, almost cream colour, in the case of *p*-iodoaniline-*o*-sulphonic acid, to bright yellow in the case of all the di-iodoamino-acids. They are only sparingly soluble in sulphuric acid, and are comparatively stable in the dry state.

Melting Points of the Acids and of their Derivatives.

Benzene-sulphonic acids.	Anhydrous acid.	Chloride.	Amide.	Ethyl ester.	Anilide.
3:4-Di-iodo	122—125°	82°	227°	81°	—
2:5-Di-iodo	132°	131—132°	211—230°	112·5°	—
3:5-Di-iodo	146	92·5	210—218	—	—
2:4-Di-iodo	167	78	230	—	—
3:4:5-Tri-iodo ..	211	145	above 250	—	201°
2:4:5-Tri-iodo ..	230	135	„ 288	155	194—196
2:3:5-Tri-iodo ..	210—215	122·5	„ 280	110	—

EXPERIMENTAL.

3:4-Di-iodobenzenesulphonic Acid.

The material used for preparing this acid is the monoiodoaniline-*p*-sulphonic acid described by Kalle and Co. (*loc. cit.*). 17·3 Grams of aniline-*p*-sulphonic acid are dissolved in about 2 litres of hot water, the solution cooled and mixed with 30 c.c. of concentrated hydrochloric acid; after cooling the mixture to about 10°, a molecular proportion of iodine chloride (16·3 grams) is drawn into it, the flask containing the chloride being heated on a water-bath kept at 70—80°, and the exit tube from the flask containing the acid solution being attached to the pump.

The dark brown mixture was kept for twelve hours, and then evaporated to crystallisation; the long, white needles which separated were purified by crystallisation from water. The yield of monoiodoaniline-*p*-sulphonic acid approximated to 50 per cent. of the theoretical:

Found, C=23·84; H=1·92; N=4·71; I=42·54.

C₆H₄O₃NIS requires C=24·08; H=2·00; N=4·68;

I=42·47 per cent.

Constitution of Monoiodoaniline-p-sulphonic Acid.—Although there could be little doubt that the iodine occupied the position ortho- with respect to the amino-, and meta- with respect to the sulphonic group, in order completely to verify the point, the amino-

group was displaced by hydrogen and the resulting *m*-iodobenzene-sulphonic acid was converted into its amide and identified.

The displacement of the amino-group by hydrogen was effected by boiling the *diazo-anhydride* (Found, $N=9.14$. $C_6H_3O_3N_2IS$ requires $N=9.03$ per cent.) with methylated spirit or with 95 per cent alcohol under a pressure slightly above the ordinary. Under the atmospheric pressure, using absolute alcohol, the amino-group was also partly displaced by the ethoxy-group. The flask containing the mixture was attached to a reflux condenser, and a tube bent twice at right angles was inserted through the tightly-fitting cork closing the top of the condenser; the whole length of the further limb of this tube, about 400 mm. long, was immersed in mercury (compare Schmitt, *Annalen*, 1861, **120**, 152; Ador and Meyer, *ibid.*, 1871, **159**, 10). After some time, a vigorous evolution of gas occurred and the diazo-compound passed into solution, a deep red colour being developed. On evaporating the liquid on the water-bath, a dark red, pasty mass remained; on diluting this slightly, and pouring it into a saturated solution of common salt, a copious, brownish-yellow precipitate of *sodium iodobenzene-m-sulphonate* was obtained. This salt was shaken with animal charcoal, and a portion further purified and freed from all traces of chloride by dissolving it in absolute alcohol:

Found, $C=23.93$; $I=41.31$.

$C_6H_4O_3ISNa$ requires $C=23.53$; $I=41.50$ per cent.

The purified salt was then treated with the requisite amount of phosphorus pentachloride, the liquid mixture heated for some time on the water-bath, and then added to concentrated ammonia. On gently warming, a voluminous, white precipitate was obtained, which, after crystallisation from water, separated in needles melting at $150-151^\circ$. The recorded melting point of iodobenzene-*m*-sulphonamide is $151-152^\circ$. The original amino-acid was thus proved to be *o*-iodoaniline-*p*-sulphonic acid.

To prepare 3:4-di-iodobenzenesulphonic acid, a solution of 20 grams of *o*-iodoaniline-*p*-sulphonic acid was rendered faintly alkaline with sodium carbonate, and mixed with 4.7 grams of sodium nitrite; the mixture was then poured gradually into 300 c.c. of dilute sulphuric acid cooled to 2° .

After about three hours, 15 grams of potassium iodide were added, and the mixture heated on the water-bath until all the nitrogen was evolved, and a clear red solution was obtained. Practically no evolution of gas took place below 15° ; at that point vigorous effervescence began, the diazo-compound passing rapidly into solution.

In many experiments, when crude iodoaniline-*p*-sulphonic acid

was employed, and a slight excess of iodine chloride had been used in its preparation, fine, sparkling crystals made their appearance at this stage even in the hot solution; these, on examination, proved to be potassium 3: 4: 5-tri-iodobenzenesulphonate, a salt which is almost insoluble in water and is readily formed from di-iodo-aniline-*p*-sulphonic acid by displacement of the amino-group by iodine.

This acid and its derivatives are described on p. 1711.

When pure recrystallised iodoaniline-*p*-sulphonic acid was used, no crystals separated until the red solution had been considerably concentrated; on cooling, a mass of glistening, pale yellow crystals separated, which became colourless on recrystallisation, crystallising from water in small needles and from alcohol in shining scales. Concentration of the mother liquor yielded a further crop of the same crystals, which proved to be *potassium 3: 4-di-iodobenzene-sulphonate*. The yield of potassium salt was in some cases 70 per cent. of the theoretical:

Anhydrous salt: Found, I=56.39; K=8.58.

$C_6H_3O_3I_2SK$ requires I=56.69; K=8.70 per cent.

Hydrated salt: Found, C=15.55; H=1.01.

$C_6H_3O_3I_2SK \cdot H_2O$ requires C=15.45; H=1.07 per cent.

3: 4-Di-iodobenzenesulphonic acid was prepared from the potassium salt by converting the latter into the barium salt, and decomposing this with excess of dilute sulphuric acid; the acid solution was evaporated on the water-bath until, on cooling, masses of shining flakes separated. These were collected, dissolved in a little water, and precipitated with concentrated hydrochloric acid. The white crystals obtained were washed free from sulphuric acid with concentrated hydrochloric acid, dried on a porous plate, and freed from hydrochloric acid in a desiccator containing potassium hydroxide.

3: 4-Di-iodobenzenesulphonic acid is a white, crystalline substance, extremely soluble in water, but is precipitated from the aqueous solution by acids. It does not crystallise well from water, attempts to purify it in this way giving a paste which filters extremely slowly, and, when pressed on a porous plate and left in the desiccator, dries to a hard cake. The dry acid is soluble in ether, and, when recovered from ether or when precipitated from a solution by hydrochloric acid, is extremely deliquescent. The crystals obtained from water, when dried in the air on a porous plate, melt irregularly from 80° onwards; when dried at 100° they melt at 122—125°; if the dried acid is once more exposed to moist air for a short time, the melting point is rapidly lowered to 80°.

There is no doubt, therefore, that the acid contains water of

crystallisation; the actual number of molecules has not yet been determined, owing to the difficulty of obtaining it in a sufficiently defined crystalline form.

Analysis of a specimen dried on porous plate in the desiccator seems to point to one molecule of water of crystallisation, but as there is every probability that partial dehydration had occurred, the point must be left undecided for the present:

Found, C=16.69; I=58.75.

$C_6H_4O_3I_2S \cdot H_2O$ requires C=16.82; I=59.34 per cent.

Salts of 3: 4-Di-iodobenzenesulphonic Acid.—The salts of this acid crystallise well from water. Many have been prepared, but of these only the sodium, barium, and lead salts have been thoroughly investigated with regard to their solubility and water of crystallisation; it is proposed to study the others similarly, and to communicate the results in a later paper.

Sodium 3: 4-Di-iodobenzenesulphonate.—This salt was prepared from the pure acid by neutralisation with sodium hydroxide and recrystallisation from water. It crystallises in beautiful, white, glistening plates. For the determination of the water of crystallisation, the pure air-dried salt was heated to 160°:

Hydrated salt: Found, Na=5.05; H_2O =3.95.

$C_6H_3O_3I_2SNa \cdot H_2O$ requires Na=5.11; H_2O =4.00 per cent.

Anhydrous salt: Found, C=16.82; H=0.93; I=59.28; Na=5.18.

$C_6H_3O_3I_2SNa$ requires C=16.66; H=0.69; I=58.79;

Na=5.32 per cent.

Solubility.—One hundred grams of water dissolve 3.47 grams of the anhydrous salt at 22.5°.

Barium 3: 4-Di-iodobenzenesulphonate.—The barium salt was prepared from the pure acid by neutralisation with barium carbonate, and also by precipitation from the ammonium salt.

It crystallises in very small, white needles containing one molecule of water of crystallisation. For the determination of the water, about 1 gram of material was heated during several hours at 125°, two hours at 135°, and finally three hours at 140°; heating at 155° during another hour caused no further decrease in weight, but, on raising the temperature to 210°, decomposition, accompanied by darkening and considerable loss in weight, occurred:

Found, I=52.44; Ba=13.58; H_2O =1.68.

$C_{12}H_6O_6I_4S_2Ba \cdot H_2O$ requires I=52.20; Ba=13.65;

H_2O =1.84 per cent.

Solubility.—One hundred grams of water dissolve 0.27 gram of the anhydrous salt at 21.5°.

Lead 3: 4-Di-iodobenzenesulphonate.—The lead salt separates

from water in very fine, white needles containing two molecules of water of crystallisation. The water was determined at two different temperatures, 170° and 250° , but identical results were obtained in the two cases:

Found, $C=13.72$; $H=0.85$; $H_2O=3.38$.

$C_{12}H_6O_6I_4S_2Pb \cdot 2H_2O$ requires $C=13.57$; $H=0.94$; $H_2O=3.50$ per cent.

Ammonium Salt.—This salt is extremely soluble in water, and it was not possible to obtain it in a crystalline condition.

Silver Salt.—This was obtained by precipitation from the ammonium salt; it crystallises from water in transparent needles, and darkens on exposure to light.

The nickel, cobalt, manganese, cerium and copper salts have all been prepared in small amount by precipitation from a fairly concentrated solution of the ammonium salt; they may be described roughly as follows.

Nickel salt: beautiful, long, green plates; *cobalt salt*: long, flat, pink crystals; *manganese salt*: small, white, sparkling crystals; *cerium salt*: thick, white nodules; *copper salt*: small, blue plates.

3: 4-Di-iodobenzenesulphonyl Chloride.—The chloride was prepared in some cases from the dry potassium salt, in others from the pure anhydrous acid by the action of phosphorus pentachloride. The potassium salt (5.3 grams) and phosphorus pentachloride (2.8 grams) were mixed, and heated on a water-bath during one hour. After cooling, water was added gradually, and, after one hour, the chloride was isolated by extraction with ether. Small, transparent needles, in many cases white nodules, separated, which, when recrystallised from ether, or, better, from a mixture of equal parts of benzene and light petroleum, separated in very long, transparent needles, melting at 82° , which, however, became white and opaque when left in the desiccator over sulphuric acid:

Found, $C=17.11$; $H=0.83$.

$C_6H_3O_2ClI_2S$ requires $C=16.80$; $H=0.74$ per cent.

3: 4-Di-iodobenzenesulphonamide.—The amide was prepared from the crude chloride by adding it gradually to excess of cooled, concentrated ammonia, a white mass being at once precipitated. This was collected and well washed with cold water. It is insoluble in cold, and only sparingly soluble in hot, water, but is readily soluble in alcohol, from which, however, no separation of crystals takes place. For purification, it was either dissolved in 95 per cent. alcohol, and a few drops of water added to the warm solution until a turbidity was produced, or boiled repeatedly with water. It is a fine, white powder, which burns with a luminous, smoky flame, giving off iodine, and evolves alkaline fumes when heated with sodium hydroxide. Its melting point is 227° :

Found, C=17.56; H=1.28; I=62.13.

$C_6H_5O_2NI_2S$ requires C=17.60; H=1.22; I=62.10 per cent.

Ethyl 3:4-Di-iodobenzenesulphonate.—This was prepared by warming the sulphonyl chloride with twice its volume of absolute alcohol in the presence of excess of sodium hydroxide. On cooling, the mass was extracted with ether, and the ethereal solution, on evaporation, left white needles, melting at 81°.

2:5-Di-iodobenzenesulphonic Acid.

To obtain this acid, aniline-*o*-sulphonic acid was prepared by sulphonating *p*-bromoacetanilide with concentrated sulphuric acid (Kreis, *Annalen*, 1895, **286**, 377), and then removing the bromine by means of zinc dust and sodium hydroxide. It may be mentioned, however, that six hours' boiling with these agents, the time prescribed, was in all cases totally insufficient to reduce the bromo-compound.

As the strongly alkaline liquid was found to attack Jena flasks, a large open porcelain dish was used and the water renewed at intervals, boiling being continued during ten to eleven hours. Excellent yields of the acid in the form of grey, rhombic crystals were obtained in this way.

*Action of Iodine Chloride on Aniline-*o*-sulphonic Acid*.—The iodine chloride was passed into the solution of the acid under conditions very similar to those adopted in the corresponding experiments with aniline-*p*-sulphonic acid. It is essential to use a dilute solution of the acid in preparing the pure iodo-compound.

17.3 Grams of aniline-*o*-sulphonic acid were dissolved in about 1.75 litres of warm water. After cooling, 30 c.c. of concentrated hydrochloric acid were added, the solution cooled to 10°, and 16.3 grams of iodine chloride drawn through as in earlier experiments. From the reddish-violet solution, silky, grey crystals slowly separated; by the end of the experiment, a semi-solid mass was obtained.

After several hours, the crystals were collected and well washed with water. On concentrating the mother liquor, more crystals were obtained, but accompanied by beautiful, long, violet needles, which were very heavy, and could be separated to some extent mechanically from the grey plates; they consisted of di-iodo-aniline-*o*-sulphonic acid, a product which accompanies the mono-iodo-compound to a very slight extent under every condition so far tried.

In one experiment, when 4 grams in excess of the theoretical quantity of iodine chloride had been passed into the solution of the amino-acid, about 1.5 grams of these purple needles were extracted

in a fairly pure condition from the final mother liquor; analysis pointed to a slight admixture of the monoiodo-derivative:

Found, C=17.67; H=1.41; I=59.09.

$C_6H_5O_3NI_2S$ requires C=16.94; H=1.17; I=59.76 per cent.

Iodoaniline-o-sulphonic acid crystallises in shining plates from much hot water; it is almost insoluble in cold water. It is noteworthy that the colour of the crystals varies in a rather arbitrary way, being sometimes buff, often very pale violet, but usually of a dull grey colour; it has not been found possible to determine what conditions favour the production of any particular coloured variety, but there is no doubt of the identity of the differently coloured substances:

Found, C=24.35; H=2.08; I=42.41.

$C_6H_5O_3NIS$ requires C=24.08; H=2.00; I=42.47 per cent.

The yield of pure iodoaniline-*o*-sulphonic acid amounted to 91 per cent. of the theoretical.

Constitution of Iodoaniline-o-sulphonic Acid.—It was pointed out in the theoretical part of this paper that attempts to remove the sulphonic group from the di-iodo-acid obtained from the iodoamino-acid by displacement of the amino-group by iodine were all unsuccessful, and that the relative positions of the iodo- and amino- or of the two iodo-groups were finally demonstrated by the preparation of the substance under investigation from a nitroamino-compound containing these two groups in the para-positions with respect to each other.

The attempts to remove the sulphonic group consisted in distilling either the dry acid or a mixture of its potassium salt with sulphuric acid in superheated steam; a third method consisting in heating a mixture of the acid with concentrated hydriodic acid in sealed tubes to 170°. In the first experiment, the unchanged acid was recovered intact; in the second, iodine was evolved, and tri- and tetra-iodobenzenes were separated from the distillate; in the third, very little action took place, the white solid, which separated from water and melted irregularly from 80° to 130°, being produced in too small quantities for accurate investigation. (*p*-Di-iodobenzene melts at 129°.)

The *p*-nitroaniline-*m*-sulphonic acid necessary for the determination of the constitution of iodoaniline-*o*-sulphonic acid was prepared from aniline-*m*-sulphonic acid by Eger's method (*Ber.*, 1888, **21**, 2581), by acetylating the barium salt and nitrating the crude product with a mixture of nitric and sulphuric acids. A yield corresponding with 56 per cent. of the aniline-*m*-sulphonic acid was finally obtained.

Conversion of p-Nitroaniline-m-sulphonic Acid into 5-Iodo-
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2-nitrobenzenesulphonic Acid.—The amino-compound (1.8 grams) was dissolved in warm water, together with a little sodium carbonate. The clear solution was poured into about 200 c.c. of dilute sulphuric acid, and the mixture cooled to 0°. One gram of sodium nitrite dissolved in water was then added gradually, when a yellow diazo-compound slowly separated. After the addition of a solution of 5 grams of potassium iodide, the mixture was warmed on the water-bath until the evolution of nitrogen was at an end.

On cooling the concentrated solution, *potassium 5-iodo-2-nitrobenzenesulphonate* separated in yellow plates. The yield was theoretical. The corresponding acid has so far been only very cursorily examined; its chloride and amide have been prepared, but no analyses have been made.

Conversion of 5-Iodo-2-nitrobenzenesulphonic Acid into p-Iodoaniline-o-sulphonic Acid.—It was anticipated that difficulty would be experienced in reducing the nitro-group without at the same time displacing iodine from the nucleus; in point of fact, in many experiments, the two actions proceeded simultaneously, a mixture of the amino- and of the iodoamino-compounds being obtained. The method eventually used was that described by Claisen and Thompson (*Ber.*, 1879, **12**, 1946), which consists in reducing the barium salt of the acid with the requisite amount of ferrous sulphate in the presence of barium hydroxide. It was found, however, to be more convenient to use the potassium salt of the iodonitrosulphonic acid, and to reduce this by means of ferrous sulphate and potassium hydroxide. The nitro-group was reduced almost quantitatively, the iodine being unaffected. Curiously enough, in one experiment, when the barium salt was digested with ferrous sulphate and barium hydroxide, not only was the nitro-group reduced, but the iodine was also displaced.

Five grams of the potassium salt were dissolved in hot water, and the solution was mixed with 22 grams of crystallised ferrous sulphate dissolved in about 250 c.c. of water; the mixture was then heated on the water-bath, and a solution of 8.9 grams of potassium hydroxide was added. The black precipitate, which first formed, was gradually oxidised to the red hydrated ferric oxide; after two hours' heating on the water-bath and a few minutes over an ordinary flame, reduction was complete. Concentrated hydrochloric acid precipitated from the filtered solution a mass of grey crystals of *p*-iodoaniline-*o*-sulphonic acid. This acid was identified with that obtained by the action of iodine chloride on aniline-*o*-sulphonic acid by displacing the amino-group in both acids by iodine, and comparing the melting point of the *p*-di-iodosulphonic acid produced from the former, and also that of its chloride with

similar compounds formed from the latter acid. The melting points of the two acids were identical ($130\text{--}131^\circ$), as were also those of the chlorides ($131\text{--}132^\circ$), so that there is no doubt that when iodine chloride is passed into a solution of aniline-*o*-sulphonic acid, iodine enters into the para-position with respect to the amino-group:

2: 5-Di-iodobenzenesulphonic acid was prepared in the usual way from *p*-iodoaniline-*o*-sulphonic acid by the diazo-process. Unlike the other iodoaminosulphonic acids, which yield bright yellow diazo-compounds, this acid gives rise to a greyish-white or purplish-white substance, differing very slightly in appearance from the original amino-compound.

After adding potassium iodide, the reddish-yellow liquid was evaporated to crystallisation; on cooling, potassium 2: 5-di-iodobenzenesulphonate separated in golden-yellow needles which became cream-coloured on recrystallisation. The yield of potassium salt amounted to 84 per cent. of the theoretical. Again, as in the case of iodoaniline-*p*-sulphonic acid, when excess of iodine chloride is passed into the ortho-acid and no care taken to purify the resulting iodoaminosulphonic acid, diazotisation involves the production of a mixture of the potassium salts of the di-iodo- and tri-iodo-sulphonic acids; it is not difficult to separate the two, the latter being practically insoluble in cold, and very sparingly soluble in hot, water. These potassium salts were recrystallised and dried at 110° for analysis:

Potassium 2: 5-Di-iodobenzenesulphonate:

Found, C=16.07; H=0.67.

$\text{C}_6\text{H}_3\text{O}_3\text{I}_2\text{SK}$ requires C=16.07; H=0.67 per cent.

Potassium Tri-iodobenzenesulphonate: Found, C=12.48.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}$ requires C=12.54 per cent.

When a solution of potassium 2: 5-di-iodobenzenesulphonate is mixed with lead acetate, silver nitrate, or barium chloride, thick, white precipitates of the lead, silver, and barium salts are respectively produced. The acid was prepared by boiling the barium salt with a slight excess of dilute sulphuric acid; on evaporation of the filtrate, radiating masses of the acid were obtained in theoretical yield.

2: 5-Di-iodobenzenesulphonic acid crystallises in the above way from water containing a little sulphuric acid; from water alone, it crystallises in colourless, transparent plates, which become white

and opaque when left in the desiccator over sulphuric acid. Of the di-iodosulphonic acids prepared, this is the only one that separates from water in well-defined crystals. The crystals appear to contain water of crystallisation, for the air-dried substance begins to melt at about 80° , but the fusion is not complete until above 100° , whilst, when dried at 95 — 100° , the melting point is 132° . Further, when dried for some days at 100° , or for a shorter time at 130° , the material melts approximately at 195° . It is clear, then, that the acid melting at 80° contains water of crystallisation; that either this water is lost partly at 100° and completely at 130° , or that it is lost completely at 100° , and the high melting point of 195° is due to partial decomposition, or more probably to the formation of an anhydride. The correctness of the latter view has been manifested by the preparation of the anhydride, by treating the acid either with an excess of phosphorus pentachloride or with a mixture of this and phosphoryl chloride. It is a white substance, which melts irregularly at 235 — 245° . On exposure of the anhydrous acid to air, hydration rapidly occurs, with a consequent lowering of the melting point to 80° . On analysis:

Air-dried material, melting at 80° :

Found, C=15.53; H=2.36; H_2O =11.88.

$C_6H_4O_3I_2S \cdot 3H_2O$ requires C=15.51; H=2.15; H_2O =11.63 per cent.

Acid dried in desiccator over sulphuric acid:

Found, C=17.03; H=1.84.

Acid melting at 132° : Found, C=17.25; H=1.40.

Acid heated during several hours at 130° :

Found, C=17.76; H=1.02.

$C_6H_4O_3I_2S$ requires C=17.56; H=0.87 per cent.

The water of crystallisation was determined (1) by noting the loss in weight after application of heat; (2) by neutralising the acid with standard sodium hydroxide.

2: 5-Di-iodobenzenesulphonic acid dissolves very readily in water, moderately in ether, and is almost insoluble in mineral acids. Its salts all crystallise well.

Sodium 2: 5-di-iodobenzenesulphonate crystallises from water in cream-coloured plates, which are anhydrous:

Found, Na=5.21.

$C_6H_3O_3I_2SNa$ requires Na=5.32 per cent.

Solubility.—One hundred grams of water dissolve 6.82 grams of the salt at 22.5° .

Lead 2: 5-di-iodobenzenesulphonate crystallises in clusters of white, feathery needles. No absolutely satisfactory determinations of the water of crystallisation have been made; heating at 147°

during two hours caused a loss in weight corresponding with four molecules, but on heating to 200° , further loss, which may possibly be due to slight decomposition, occurred:

Found, $\text{H}_2\text{O} = 6.58$.

$\text{C}_{12}\text{H}_6\text{O}_6\text{I}_4\text{S}_2\text{Pb}, 4\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.56$ per cent.

Solubility.—One hundred grams of water dissolve 0.77 gram of the anhydrous salt at 20° .

Ammonium 2:5-di-iodobenzenesulphonate is at once precipitated on the addition of ammonia to a solution of the acid; on recrystallisation, it separates in long, cream-coloured needles. A comparison of the ammonium salts of the 3:4-di-iodo- and the 2:5-di-iodosulphonic acids shows that the two differ enormously in solubility, the former being so soluble that it is impossible to isolate any crystals from the aqueous solution, the latter being even less soluble than the sodium salt.

Solubility.—One hundred grams of water at 20° dissolve 4.35 grams of the salt.

Barium 2:5-di-iodobenzenesulphonate crystallises from much water in long, transparent needles, containing $4\frac{1}{2}$ molecules of water of crystallisation. The salt may be dehydrated by heating to 170° :

Found, $\text{Ba} = 13.20$; $\text{H}_2\text{O} = 7.69$.

$\text{C}_{12}\text{H}_6\text{O}_6\text{I}_4\text{S}_2\text{Ba}, 4\frac{1}{2}\text{H}_2\text{O}$ requires $\text{Ba} = 13.22$; $\text{H}_2\text{O} = 7.81$ per cent.

Solubility.—One hundred grams of water at 20° dissolve 0.522 gram of the anhydrous salt.

Potassium 2:5-di-iodobenzenesulphonate crystallises in long, colourless needles, containing one molecule of water of crystallisation:

Found, $\text{C} = 15.36$; $\text{H} = 1.36$; $\text{K} = 8.27$; $\text{H}_2\text{O} = 3.99$.

$\text{C}_6\text{H}_3\text{O}_3\text{I}_2\text{SK}, \text{H}_2\text{O}$ requires $\text{C} = 15.45$; $\text{H} = 1.12$; $\text{K} = 8.36$;
 $\text{H}_2\text{O} = 3.86$ per cent.

The *silver* salt is only sparingly soluble in water, crystallising in fine, woolly needles; the *copper* salt crystallises in small, pale blue needles; the *cobalt* in small, pink, glistening plates; the *nickel* in pale green, sparkling plates; the *manganese* and the *cerium* in small, white plates.

2:5-Di-iodobenzenesulphonyl Chloride.—The chloride, prepared from the potassium salt, and also from the anhydrous acid, separates from ether in white needles, melting at 131 — 132° :

Found, $\text{C} = 17.00$; $\text{H} = 0.81$.

$\text{C}_6\text{H}_3\text{O}_2\text{ClI}_2\text{S}$ requires $\text{C} = 16.80$; $\text{H} = 0.70$ per cent.

A mixture of the sulphonyl chloride with the anhydride is obtained when excess of phosphorus pentachloride or a mixture of phosphorus pentachloride and phosphoryl chloride is used in its preparation;

the anhydride being insoluble in ether, the separation of the two is easily effected. The *anhydride* is a white, amorphous powder, melting at 235—245°; it is stable in air, insoluble in cold water, partly soluble in hot water, giving an acid solution, and is hydrolysed on boiling vigorously with alkali; on boiling with absolute alcohol, an ester, melting at 113°, is obtained.

2: 5-Di-iodobenzenesulphonamide.—This is prepared by boiling the chloride with ammonia; it is practically insoluble in hot or cold water, and soluble in alcohol, but it does not crystallise from this solvent, so that, in order to purify it for analysis, it was boiled repeatedly with water and dried, first on a porous plate, and then at 100°:

Found, C=17.71; H=1.14.

$C_6H_5O_2NI_2S$ requires C=17.60; H=1.22 per cent.

Ethyl 2: 5-Di-iodobenzenesulphonate.—This was prepared by the action of alcohol on the chloride in presence of sodium hydroxide, or by treating an ethereal solution of the chloride with sodium ethoxide in alcoholic solution; after the addition of water, the ester was extracted by ether, which, on evaporation, yielded colourless needles, melting at 112.5°.

2: 5-Di-iodobenzenesulphonyl Chloride Dichloride.—On passing a rapid stream of dry chlorine into a solution of the chloride in chloroform, a yellow colour is first developed, and after an interval yellow crystals begin to separate. These form stout, glistening, yellow needles, melting at 128—129°; they liberate iodine from potassium iodide. On comparing the behaviour of the dichlorides of *o*-, *m*-, and *p*-iodobenzenesulphonyl chloride, it is obvious that the ortho- is much less readily formed than the meta- and para-compounds; in the present instance, therefore, it may be assumed that it is the iodine in the meta-position relatively to the sulphonyl group that becomes tervalent.

0.3872 Gram liberated iodine equivalent to 15.3 c.c. of 0.0997*N*-sodium thiosulphate:

Found, Active chlorine=13.70.

$C_6H_3O_2Cl_3I_2$ requires Active chlorine=14.21 per cent.

3: 5-Di-iodobenzenesulphonic Acid.

In order to obtain evidence as to the position occupied by the second iodine atom in di-iodoaniline-*p*-sulphonic acid, it was necessary to remove the amino-group, and to investigate the nature of the di-iodobenzenesulphonic acid so produced. This acid was found to differ from the two which have already been described, and to be 3: 5-di-iodobenzenesulphonic acid.

Both the methods generally used in removing the amino-group, namely, that of boiling the diazo-compound with alcohol, and that of oxidising the hydrazine derivative, have been applied satisfactorily.

Method I.—The amino-acid was diazotised in presence of very slight excess of dilute sulphuric acid, and the diazo-compound, after being collected and washed with alcohol, boiled with a large quantity of methylated spirit under the ordinary pressure; vigorous evolution of nitrogen occurred, and during the course of two or three hours the diazo-compound passed completely into solution, with the production of a deep red colour. After removing the excess of alcohol, sodium chloride was added, and the crude product was boiled with animal charcoal and recrystallised; a good yield of *sodium di-iodobenzenesulphonate* was obtained. It gave an acid melting at 146° , and a chloride melting in the crude state at $87-88^{\circ}$.

Method II.—The diazo-compound of di-iodoaniline-*p*-sulphonic acid is readily reduced by stannous chloride, a yield of the hydrazine compound amounting to 76 per cent. of the amino-acid being obtained.

The crude amino-acid (40 grams) suspended in a very slight excess of hydrochloric acid was diazotised by the requisite amount of sodium nitrite (6.9 grams). In experiments with small quantities of material, it was found more convenient to add slowly to the cooled acid the mixture of nitrite with the sodium salt of the substance to be diazotised, but when larger quantities were employed, it was found impossible sufficiently to dilute the solution of the sodium salt, so as to prevent the latter from crystallising out, without producing a rather unmanageable bulk of liquid. The warm solution of the sodium salt was therefore poured at once into hydrochloric acid, the amino-acid being precipitated in a fine state of division. After diazotisation, the solution of the diazo-salt was poured slowly into a cooled solution of stannous chloride in concentrated hydrochloric acid, when a thick, white precipitate at once separated, which, after several hours, was collected, well washed with cold water, and dried. Examination showed it to consist of an iodohydrazinobenzenesulphonic acid, probably containing water of crystallisation. It is practically insoluble in cold water, but crystallises from much hot water in small, white needles, which, on being exposed to air during several hours, acquire a slight pink tinge; it is insoluble in alcohol, reduces Fehling's solution on warming, reduces an ammoniacal solution of silver nitrate, and is decomposed by copper sulphate, nitrogen being evolved even in the cold, and violently on heating.

Four agents, namely, copper sulphate, ferric chloride, potassium

chromate, and potassium permanganate, have been used to oxidise the hydrazine, but only potassium permanganate is quite satisfactory. Copper sulphate causes removal of the iodine, ferric chloride gives rise to a substance which still contains nitrogen, but which has not been further investigated, and potassium chromate causes removal of part of the iodine with formation of a mixture of monoiodo- and di-iodo-benzenesulphonic acids.

Potassium Chromate as Oxidising Agent.—The recent work of Chattaway on the oxidation of aromatic hydrazines (Trans., 1908, **93**, 270) seems to show that the best agents to employ for displacing the hydrazino-group by hydrogen are potassium chromate and potassium permanganate in alkaline solution; both of these have been employed successfully. In the case of the former, the following experiment was carried out.

Fifty grams of potassium chromate and 5.7 grams of potassium hydroxide were dissolved in water, and the solution was heated almost to the boiling point; 10 grams of the hydrazino-derivative were then gradually added to the hot liquid, and the heating was continued until the action, which was at first very vigorous and was accompanied by much frothing, ceased. After a time, green, hydrated chromic oxide was precipitated, and the clear, yellow filtrate deposited crystals of potassium 3:5-di-iodobenzenesulphonate on cooling. On concentrating the mother liquor, crystals of potassium *m*-iodobenzenesulphonate were obtained. The first crop of crystals gave rise ultimately to a di-iodosulphonic acid, melting at 146°; the second, to an acid which could not be crystallised, and to an amide which crystallised from hot water in colourless needles, melting at 148°; it proved, on analysis, to be *m*-iodobenzene-sulphonamide:

Found, C=25.47; H=2.22.

$C_6H_6O_2NIS$ requires C=25.48; H=2.12 per cent.

The melting point of *m*-iodobenzenesulphonamide is given as 152° by Langmuir, but repeated recrystallisations of the amide obtained in this experiment did not raise it above 148°.

Potassium Permanganate as Oxidising Agent.—A dilute solution of 2.4 grams of potassium permanganate and 5 grams of potassium hydroxide was heated to about 60–70°, and 10 grams of the hydrazine were gradually added; the addition was continued until the green colour, which was first developed, disappeared, and hydrated manganese dioxide made its appearance. The mixture was then heated until no other solid than manganese dioxide was present, filtered hot, and the pale yellow filtrate concentrated; impure crystals of potassium 3:5-di-iodobenzenesulphonate (6 grams) were obtained. A second crop from the mother liquor

proved identical with the first. The yield amounted to 70 per cent. of the theoretical. Fractional crystallisation of the product separated it into two distinct sets of crystals, namely, less soluble crystals which have not yet been investigated, and more soluble ones identical with those obtained in method I:

Found, C=16.16; H=0.66.

$C_6H_3O_3I_2SK$ requires C=16.07; H=0.67 per cent.

The same di-iodobenzenesulphonic acid may be obtained from di-iodoaniline-*o*-sulphonic acid by a similar series of changes.

Di-iodoaniline-*o*-sulphonic acid gives rise to a hydrazine closely resembling in appearance that obtained from the para-acid. It is insoluble in cold, and very sparingly soluble in hot, water; it gives the ordinary reactions of a hydrazine. When oxidised by alkaline permanganate, it yields a potassium di-iodobenzenesulphonate, from which an acid, melting at 146° , the melting point of 3:5-di-iodobenzenesulphonic acid, is readily obtained.

3:5-Di-iodobenzenesulphonic acid crystallises from faintly acid solutions in long, radiating crystals, which in the dry state are almost white. It is very soluble in water, moderately soluble in ether, from which it separates in white, soapy crystals, and almost insoluble in mineral acids; it is freed from adhering sulphuric acid by precipitation with concentrated hydrochloric acid, the latter being subsequently removed without difficulty. The crystals from water melt irregularly, beginning at 70° ; when dried at 98° , they melt at 138 — 146° .

Salts of 3:5-Di-iodobenzenesulphonic Acid.—Salts of this acid have been prepared, but only cursorily examined; the *potassium* salt crystallises in large, white plates, the *sodium* in white needles, the *ammonium* and the *barium* in fine, colourless needles.

3:5-Di-iodobenzenesulphonyl Chloride separates from ether in small needles, and from a mixture of ether and light petroleum in clusters of needles, melting at 93° :

Found, C=16.76; H=0.71.

$C_6H_3O_2ClI_2S$ requires C=16.80; H=0.70 per cent.

3:5-Di-iodobenzenesulphonamide is a white powder, insoluble in hot or cold water; it is extremely difficult to purify, and melts irregularly from 205 — 218° :

Found, C=17.58; H=1.36; I=62.00.

$C_6H_5O_2NI_2S$ requires C=17.60; H=1.22; I=62.10 per cent.

2:4-Di-iodobenzenesulphonic Acid.

Two distinct methods have been used in preparing this acid, the first consisting in preparing 5-nitroaniline-*o*-sulphonic acid and

successively displacing the amino- and nitro-groups by iodine, the second in removing the amino-group from di-iodoaniline-*m*-sulphonic acid by the diazo-reaction. The first method fixes the constitution of the acid, the second affords some evidence as to the constitution of di-iodoaniline-*m*-sulphonic acid; of the two, the former, although involving more operations, is the more convenient, and gives rise to better yields and purer products.

Method I: Preparation of o-Iodo-p-nitrobenzenesulphonic Acid.—The 5-nitroaniline-*o*-sulphonic acid was prepared from *m*-nitroaniline by Post and Hardtung's method (*Ber.*, 1880, **13**, 40; *Annalen*, 1880, **205**, 102), which consists in heating *m*-nitroaniline with fuming sulphuric acid during several hours. As the authors point out, there is much difficulty in so regulating the conditions of temperature and strength of acid that carbonisation shall not occur; in many experiments, when quantities given by the authors (nitroaniline with five times its weight of fuming acid) were gradually heated in an oil-bath, the whole mass decomposed at a temperature far below that given as the temperature of sulphonation. It has been found, however, that if the mixture be kept well shaken, and the oil-bath be gradually heated to 160°, allowed to cool, and again heated to 160° with constant agitation, the heating being continued during two or three hours, sulphonation is complete; a shorter time than two hours leaves some nitroaniline unattacked. The acid mixture is neutralised with barium carbonate, the brown barium salt collected, purified, and decomposed with dilute sulphuric acid; the sulphonic acid crystallises out from the clear filtrate.

21.8 Grams of this nitroaminosulphonic acid were dissolved in water with the addition of a little sodium carbonate, the solution being kept hot and sufficiently dilute to prevent the precipitation of the sodium salt, which tends to separate as a bright yellow precipitate; the clear, hot solution was then poured into excess of dilute sulphuric acid and the mixture well cooled; on the gradual addition of 7 grams of sodium nitrite, the dark yellow colour of the nitro-compound became much paler, and, on complete diazotisation, a very pale yellow diazo-compound separated from the acid mixture. After adding 25 grams of potassium iodide, the mixture was heated on the water-bath until the evolution of nitrogen was at an end; the cooled filtrate, after concentration, deposited crystals. These were collected and recrystallised, separating from water in orange-yellow, shining rhombs, which consisted of potassium *o*-iodo-*p*-nitrobenzenesulphonate. The yield amounted to 30 grams, which is approximately 90 per cent. of the theoretical.

Preparation of m-Iodoaniline-p-sulphonic Acid.—A solution of 15 grams of potassium *o*-iodo-*p*-nitrobenzenesulphonate, with 90 grams of crystallised ferrous sulphate, was heated on the water-bath, and potassium hydroxide (35.5 grams) was slowly added to the hot mixture. After two hours' digestion on the water-bath, reduction was complete; hydrochloric acid then precipitated a white, crystalline mass of the iodoanilinesulphonic acid from the concentrated filtrate.

m-Iodoaniline-p-sulphonic acid crystallises from water in white, feathery needles; it closely resembles, in appearance and properties, the iodoaminosulphonic acids which have been already described. It is much less soluble in water than the iodonitro-acid from which it is produced, the addition of mineral acid to a solution of the potassium salt of the latter causing no precipitation of the corresponding acid.

The appearance, therefore, of a white precipitate on the addition of mineral acid may be taken to indicate that reduction has proceeded satisfactorily; separation of the amino-acid from any unchanged nitro-acid is thus easily effected.

Preparation of 2:4-Di-iodobenzenesulphonic Acid.—*m*-Iodoaniline *p*-sulphonic acid yields a very pale yellow diazo-compound; the addition of potassium iodide to a solution of the latter causes evolution of nitrogen and formation of a reddish solution, from which potassium 2:4-di-iodobenzenesulphonate separates on concentration; this salt crystallises in cream-coloured, shining plates. The yield is about 70 per cent. of the theoretical. Addition of barium chloride causes precipitation of the barium salt, and the latter, when decomposed with sulphuric acid, yields, on concentration of the solution, the sulphonic acid in shining needles.

Method II.—The second method of preparing the acid involves the use of di-iodoaniline-*m*-sulphonic acid, which is easily obtained in a pure condition from aniline-*m*-sulphonic acid.

Attempts to remove the amino-group by boiling the diazo-compound with alcohol proved unsuccessful; oxidation of the hydrazine by alkaline chromate yielded, however, satisfactory results. The hydrazine is obtained as a thick, white precipitate, which, on keeping, becomes slightly coloured. It is practically insoluble in hot or cold water and attempts to purify it by recrystallisation from hot water resulted in the production of a slightly coloured solution, from which no crystals could be obtained; the substance was purified, therefore, by boiling it several times with water, after which it was collected and dried. It gives all the reactions of a hydrazine. Attempts to oxidise the hydrazine with copper sulphate resulted in the production of cuprous iodide;

oxidation with alkaline chromate gave, however, the desired result. The same proportions as before were used, and the hydrazine was added gradually to the hot alkaline solution of potassium chromate; violent evolution of nitrogen occurred, and hydrated chromic oxide was gradually precipitated; the cooled, concentrated filtrate deposited crystals of potassium 2:4-di-iodobenzenesulphonate.

2:4-Di-iodobenzenesulphonic acid is very soluble in water. It separates from concentrated solutions in small needles which contain water of crystallisation; this is lost after several hours' exposure in a desiccator, or after a few minutes at 98° . The anhydrous acid melts at 167° to an opaque liquid, which becomes transparent at 172° . The dry acid dissolves readily in ether; the crystals which separate on evaporation of the solvent are very deliquescent, becoming, however, dry and powdery, and melting at 167° , when dried for a few minutes at 98° . The acid is precipitated from its aqueous solution by concentrated hydrochloric acid; use is made of this property in its purification.

Salts of 2:4-Di-iodobenzenesulphonic Acid.—The sodium salt crystallises from water in glistening, white scales, the potassium salt in sparkling, plate-like needles, the ammonium and the barium salts in small, white needles. Solubility determinations have not yet been made, but, owing to the considerable loss entailed in the preparation of the pure barium salt from the potassium salt, there is no doubt that the former is considerably more soluble than the corresponding salts of the isomeric acids.

2:4-Di-iodobenzenesulphonyl Chloride separates from ether in white scales, melting at $77-78^{\circ}$; from a mixture of benzene and light petroleum, it crystallises in rhombic plates:

Found, C=16.90; H=0.98.

$C_6H_3O_2ClI_2S$ requires C=16.80; H=0.70 per cent.

The amide prepared (1) from the potassium salt obtained after removing the amino-group from di-iodoaniline-*m*-sulphonic acid, (2) from the acid obtained directly from 5-nitroaniline-*o*-sulphonic acid, melts at 230° .

3:4:5-Tri-iodobenzenesulphonic Acid.

On passing two molecular proportions of iodine chloride into a dilute solution of aniline-*p*-sulphonic acid, di-iodoaniline-*p*-sulphonic acid, described by Kalle and Co. (*loc. cit.*) as a brown substance rather insoluble in water, is obtained. No difficulty has been experienced in obtaining it free from the monoiodo-derivative; it is an advantage to use a slight excess of iodine chloride, since, as it is impossible to introduce a third atom of iodine into the nucleus, the excess simply ensures complete iodination of the acid. It

crystallises from much hot water; a more convenient method of purification, however, consists in converting the crude substance into its sodium salt, and precipitating the amino-acid from a solution of the latter by the addition of mineral acid. The displacement of the amino-group by iodine, with formation of potassium tri-iodobenzenesulphonate, is readily brought about. The diazo-anhydride of di-iodoaniline-*p*-sulphonic acid is bright yellow, and is decomposed by potassium iodide at 30°. At that temperature, nitrogen begins to be evolved, and a fine, silky precipitate takes the place of the somewhat granular diazo-compound, the precipitate forming a thick scum on the surface of the liquid. A yield of 13 grams from 10 grams of the amino-acid, amounting to 97 per cent. of the theoretical, was obtained.

Potassium 3:4:5-tri-iodobenzenesulphonate is insoluble in cold, and very sparingly soluble in hot, water, from which it crystallises in small, yellowish-white needles; these were dried at 100° for analysis:

Found, C=12.69; H=0.39; I=66.43; K=6.76.

$C_6H_2O_3I_3SK$ requires C=12.54; H=0.34; I=66.38;
K=6.79 per cent.

The barium, lead, and silver salts are all very sparingly soluble in water and in hydrochloric, acetic, and nitric acids respectively. When the barium salt is boiled with excess of concentrated hydrochloric acid, it dissolves to a slight extent, and is at once precipitated if the solution is cooled; it is therefore difficult to detect traces of sulphuric acid or of sulphate in this substance, since the difference in solubility between barium tri-iodobenzenesulphonate and barium sulphate is not very marked. As a whole, sparing solubility may be regarded as characteristic of the salts of this and of the isomeric tri-iodosulphonic acids. The great stability and insolubility of the lead salt was demonstrated by an attempt to prepare the sulphonic acid from it by decomposition with hydrogen sulphide.

The lead salt was suspended in water, and hydrogen sulphide was passed through to saturation; after passing the gas during two or three hours the major portion of the iodo-salt was still unattacked, and it was not until it had been passed into the mixture, which was heated at intervals, for two or three days, that the lead was completely precipitated as lead sulphide, and a clear solution of the sulphonic acid was obtained on filtration. On concentrating the solution, needle-like crystals of the acid, melting at 150—157°, were obtained.

In a second attempt to isolate the sulphonic acid, the calcium salt was heated with the requisite amount of oxalic acid; no change in appearance and practically no decomposition occurred.

A third series of experiments involved the preparation of the barium salt and its decomposition with sulphuric acid, and in this case the acid was obtained without much difficulty. The main difficulty lies in the preparation of the barium salt, the great insolubility of the potassium salt rendering its decomposition by barium chloride a difficult matter when large quantities are being manipulated. The most satisfactory results were obtained when the potassium salt was suspended in much water, excess of barium chloride added, and the mixture boiled during many hours until the yellow scum of potassium salt had entirely disappeared, and until the white precipitate collected after repeated washings by decantation with hot water gave no test for potassium. The barium salt was then boiled with excess of dilute sulphuric acid until the crystalline salt had given place to the heavy barium sulphate; on cooling the concentrated filtrate, a mass of glistening crystals of the sulphonic acid separated.

The acid is extremely soluble in water, moderately so in ether, and insoluble in acids; it is best freed from any adhering sulphuric acid by adding concentrated hydrochloric acid to its aqueous solution, and treating the precipitated acid as described in the case of 3:4-di-iodobenzenesulphonic acid; from acid solutions it crystallises in cream-coloured plates. On account of the difficulty of obtaining good crystals from water, no attempt has yet been made to determine whether or not it contains water of crystallisation, but, judging from analogy to the two isomeric tri-iodobenzenesulphonic acids, and considering the variation in the melting point as the acid is dried under varying conditions, there is little doubt that it does. The melting point of the acid (1) precipitated by mineral acids, (2) separated from ether, (3) crystallised from water and air-dried, or (4) dried at 95° , is 158° ; after being dried at 125° , it melts at 221° . The latter may therefore be regarded as the melting point of the anhydrous acid.

Salts of 3:4:5-Tri-iodobenzenesulphonic Acid.—The sodium salt crystallises from water in fine, cream needles, the potassium salt in small needles, the ammonium salt in long, colourless needles; the barium, lead, and silver salts have all been obtained by precipitation, but have not been prepared in a crystalline condition.

3:4:5-Tri-iodobenzenesulphonyl Chloride separates from ether in small, white needles, and from a mixture of light petroleum and ether in rhombic plates, melting at 145° :

Found, C=13.19; H=0.54.

$C_6H_2O_2ClI_3S$ requires C=12.98; H=0.36 per cent.

The amide is a yellowish-white substance, insoluble in hot or cold water; it crystallises from methylated spirit in fine, transparent needles, melting above 250° .

The *anilide* crystallises from alcohol in short, transparent needles, melting at 201° :

Found, C = 23.73; H = 1.42.

$C_{12}H_8O_2NI_3S$ requires C = 23.57; H = 1.30 per cent.

2 : 3 : 5-*Tri-iodobenzenesulphonic Acid*.

It has already been stated that when one molecular proportion of iodine chloride is passed into a solution of aniline-*o*-sulphonic acid, *p*-iodoaniline-*o*-sulphonic acid is produced, which, being insoluble in water, separates in purplish-grey crystals as it is formed. Owing to the sparing solubility of this monoiodo-acid great difficulty was to be expected, and has been experienced, in preparing the di-iodo-derivative in a state of purity.

Although the preparation of the tri-iodosulphonic acid does not necessitate the production of a pure amino-acid, the potassium di-iodo- and tri-iodo-sulphonates formed from a mixture of monoiodo- and di-iodo-amino-acids by displacement of the amino-groups by iodine being readily separated by fractional crystallisation, it was thought advisable to determine the conditions favouring the formation of the more highly iodinated product and to obtain it, if possible, in a pure state.

The best method of preparing di-iodoaniline-*o*-sulphonic acid is to pass excess of iodine chloride into a dilute solution of the monoiodo-acid. On adding hydrochloric acid to the solution of the monoiodo-acid, the latter began to separate out, but, as iodine chloride was passed through, this suspended acid gradually dissolved; a clear, reddish-brown solution was obtained, which yielded, after concentration, a large amount of the desired di-iodo-acid. This method of preparation involved the use of small quantities of material; to prepare the acid on the large scale, it was found advisable to precipitate the monoiodo-acid in a fine state of division, and then to pass iodine chloride through the suspended material, with frequent agitation, until the grey crystals of the monoiodo-gave place to the heavy, violet needles of the di-iodo-acid; these were collected and dried.

The acid yields a bright yellow diazo-compound, which is decomposed by potassium iodide, with the production of flaky crystals of potassium 2 : 3 : 5-tri-iodobenzenesulphonate. The yield of potassium salt is theoretical.

The barium, lead and silver salts, obtained by precipitation from the potassium salt, are all very sparingly soluble in water; the same difficulty, therefore, attends the preparation of the pure barium salt and of the acid from the barium salt as in the case of 3 : 4 : 5-tri-iodobenzenesulphonic acid. The potassium salt must be boiled for a long time with excess of barium chloride before

complete decomposition occurs; the barium salt must then be boiled with excess of sulphuric acid until, on evaporating the clear filtrate, an acid is obtained which leaves no residue when heated on platinum foil.

From a mineral acid solution, the sulphonic acid separates in shining crystals, which dissolve readily in water, less readily in ether, and are almost insoluble in mineral acids; from water alone, they crystallise in colourless plates, which become rather coloured when exposed to air. The melting point of the air-dried material was found to vary somewhat irregularly; it was usually $166-170^{\circ}$, sometimes 183° , and once above 200° . One can only account for these variations by assuming that the acid, which contains water of crystallisation, loses this gradually; consideration of the melting points obtained when the acid is dried at different temperatures confirms this assumption. When recrystallised from water and examined at once, the melting point is $166-170^{\circ}$; when dried at 95° , it is 183° ; and when dried at 135° , it is $210-215^{\circ}$. Analyses showed that it probably crystallises with three molecules of water; $166-170^{\circ}$ is therefore the melting point of the hydrated, and $210-215^{\circ}$ that of the anhydrous material:

1.2191 lost $0.1137 \text{ H}_2\text{O}$ when heated during several hours at 135° . $\text{H}_2\text{O}=9.32$.

$\text{C}_6\text{H}_3\text{O}_3\text{I}_3\text{S}, 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=9.15$ per cent.

Salts of 2:3:5-Tri-iodobenzenesulphonic Acid.—The sodium, potassium, and ammonium salts obtained by neutralisation, and the lead, barium, silver, copper, manganese, nickel, and cobalt salts obtained by precipitation have all been prepared. The sodium salt crystallises in transparent needles, the ammonium salt in white needles, and the potassium salt in shining plates; of the others, the barium and silver salts are extremely difficult to crystallise, the lead salt separates in small, woolly needles, the copper salt in pale blue plates, the nickel salt in small, green needles, the cobalt salt in pink plates, and the manganese salt in fine, white, feathery needles.

2:3:5-Tri-iodobenzenesulphonyl Chloride separates from ether in small, white needles, and from a mixture of benzene and light petroleum in long, transparent needles, melting at $122-123^{\circ}$:

Found, $\text{C}=13.01$; $\text{H}=0.42$.

$\text{C}_6\text{H}_2\text{O}_2\text{ClI}_3\text{S}$ requires $\text{C}=12.98$; $\text{H}=0.36$ per cent.

The amide is a white powder, insoluble in hot or cold water, and very sparingly soluble in alcohol; it does not melt below 280° .

Ethyl 2:3:5-tri-iodobenzenesulphonate was prepared from the sulphonyl chloride by treating it with absolute alcohol in the presence of excess of sodium hydroxide. It separates from ether in clusters of needles, melting at 110° :

Found, C=16.91; H=1.35.

$C_8H_7O_2I_3S$ requires C=17.02; H=1.24 per cent.

2:4:5-Tri-iodobenzenesulphonic Acid.

In Kalle and Co.'s patent (*loc. cit.*), it was stated that the passage of two molecular proportions of iodine chloride into a solution of aniline-*m*-sulphonic acid containing a little hydrochloric acid resulted in the formation of di-iodoaniline-*m*-sulphonic acid, which separated out as it was formed. No mention was made of any monoiodoaniline-*m*-sulphonic acid, and the conclusion was therefore drawn that such a substance could not be isolated under these conditions. It was not, therefore, until quite recently, after the di-iodo-derivative had been converted into the tri-iodosulphonic acid and subjected to investigation, that any attempt was made to discover whether the mono-derivative could be obtained, and, if so, what conditions favoured its production. It will be seen from the theoretical part of this paper that a knowledge of the constitution of monoiodoaniline-*m*-sulphonic acid is useful in fixing the constitution of the di-iodo-derivative, and, consequently, of the tri-iodosulphonic acid formed from it; it seems advisable, therefore, to give experimental details of its preparation here when substances prepared from aniline-*m*-sulphonic acid are being discussed.

In one experiment, slightly less than one molecular proportion of iodine chloride was passed into a very dilute solution of aniline-*m*-sulphonic acid (8.6 grams in 2 litres of water), and the dark brown liquid was kept for several hours; a violet colour was gradually developed, and, on cooling the concentrated solution, yellowish-brown crystals separated; these, after being diazotised and treated with potassium iodide, yielded crystals of potassium 3:4-di-iodobenzenesulphonate in an impure condition. The acid obtained from this salt melted irregularly at 115–117° (3:4-di-iodobenzenesulphonic acid melts at 122–125°), the low melting point indicating that some amino-acid had probably escaped iodination in the first instance, and that the final product was therefore a mixture of the di-iodo- with some monoiodo-sulphonic acid. The conversion of a fresh quantity of the potassium salt, dried at 100°, into the chloride, afforded convincing evidence of its constitution; the chloride crystallised from a mixture of light petroleum and benzene in transparent needles, which became white and opaque when left in a desiccator over sulphuric acid, and melted sharply at 82°, the melting point of 3:4-di-iodobenzenesulphonyl chloride.

There is no doubt, therefore, that when iodine chloride acts on aniline-*m*-sulphonic acid, a monoiodo-derivative is formed, in which the iodine atom occupies the position ortho- and para- to the amino- and sulphonic groups respectively; the second iodine atom, as has

already been shown, enters the para-position with respect to the amino-group. Di-iodoaniline-*m*-sulphonic acid yields a yellow diazo-compound, which is decomposed by potassium iodide, with formation of 2:4:5-tri-iodobenzenesulphonic acid, which separates from the hot solution in shining crystals of the potassium salt. The preparation of the barium salt and of the acid from the barium salt are matters of little difficulty, the acid separating on evaporation of its aqueous solution in shining plates. It dissolves very readily in water, more sparingly in ether, and is almost insoluble in mineral acids; the crystals from water melt sharply at 182° ; when dried at 100° , or at 125° , they melt at 230° . Analysis showed that the acid melting at 182° contains three molecules of water of crystallisation:

Found, $C=12.32$; $H=1.69$; $H_2O=9.14$.

$C_6H_3O_3I_3S \cdot 3H_2O$ requires $C=12.20$; $H=1.50$; $H_2O=9.15$ per cent.

Salts of 2:4:5-Tri-iodobenzenesulphonic Acid.—The sodium and potassium salts crystallise in long, white needles; the ammonium salt in small, white nodules; the potassium salt crystallises with one molecule of water:

Found, $C=12.34$; $H=0.66$; $H_2O=3.34$.

$C_6H_2O_3I_3SK \cdot H_2O$ requires $C=12.16$; $H=0.67$; $H_2O=3.04$ per cent.

2:4:5-Tri-iodobenzenesulphonyl Chloride crystallises from ether in small needles, and from a mixture of light petroleum and ether in small, sparkling crystals, melting at 135° :

Found, $C=12.96$; $H=0.40$.

$C_6H_2O_2ClI_3S$ requires $C=12.98$; $H=0.36$ per cent.

The amide is a yellowish-white powder, insoluble in water, but soluble in methylated spirit; it does not melt below 260° :

Found, $C=13.45$; $H=0.70$; $I=71.21$; $N=2.37$.

$C_6H_4O_2I_3NS$ requires $C=13.45$; $H=0.74$; $I=71.21$;

$N=2.61$ per cent.

The anilide crystallises from alcohol in small, needle-shaped crystals, melting at 194 — 196° :

Found, $C=23.67$; $H=1.49$.

$C_{12}H_8O_2I_3NS$ requires $C=23.27$; $H=1.31$ per cent.

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