THE FORMATION OF DINAPHTHYL SULPHONIC ACIDS AND THEIR DERIVATIVES.

by

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ABBREVIATIONS.

Annalen	Liebig's Annalen der Chemie.
Berichte.	Berichte der deutschen Chemischen Gesellschaft.
Brit.Assoc.Report.	Report of the British Association for the Advancement of Science.
Bull.Soc.Chim.	Bulletin de la Société Chimique de France.
Chem.Zentral.	Chemisches Zentralblatt.
Compt.rend.	Comptes Rendus.
D.R.P.	Deutsches Reichs-Patent.
E.P.	English Patent.
J.Amer.C.S.	Journal of the American Chemical Society.
J.C.S.	Journal of the Chemical Society, London.
J.prakt.Chem.	Journal für praktische Chemie.
J.Roy.Tech.College.	Journal of the Royal Technical College, Glasgow.
Proc.Chem.Soc.	Proceedings of the Chemical Society of London.
Z.phys.Chem.	Zeitschrift für physikalische Chemie.

INTRODUCTORY REVIEW.

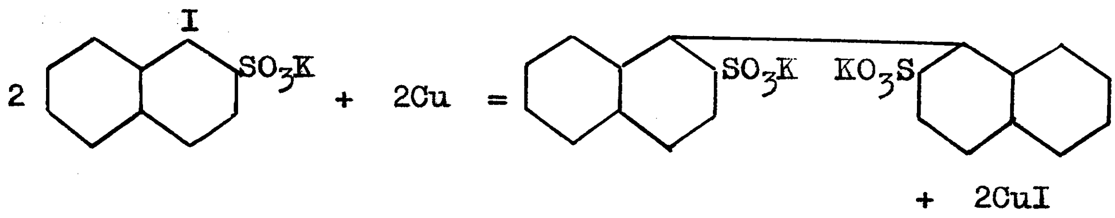
The preparation of dinaphthyl sulphonic acids from readily available starting materials would open the way to the preparation of a series of hydroxy- and amino-dinaphthyls of considerable potential value as dyestuffs intermediates.

The problem of preparing these acids - to which this investigation has been confined - may be approached in at least three different ways.

In the first place, there is the obvious method involving the preparation and subsequent sulphonation of the isomeric dinaphthyls. Such a procedure was employed by Smith and Takamatsu (J.C.S., 1881, 551) who isolated a number of calcium, barium and lead salts of ββ-dinaphthyl mono-, di- and tetra- sulphonic acids, obtained by sulphonating ββ-dinaphthyl with varying concentrations of sulphuric acid. The principal objection to such a method is that the determination of the orientation of the substituted sulphonic acid groups (which Smith and Takamatsu did not attempt) is a matter of great difficulty without previous knowledge of the properties of definitely constituted dinaphthyl sulphonic acids. A second objection to approaching the problem in this way is that the dinaphthyls themselves are not readily prepared in good yield from suitable starting materials.

This method was therefore rejected as unsuitable, and premature from the point of view of preparing dinaphthyl sulphonic acids of known constitution.

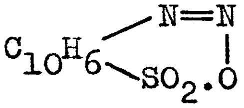
A second method of approach is afforded by the well-known Ullmann reaction. Halogeno-naphthalene sulphonic acids, as their salts or derivatives, may be treated with copper powder (or other powdered metals) with the object of bringing about diaryl-formation by removal of halogen as cuprous halide. The only dinaphthyl sulphonic acid of established constitution to which a reference has been found in the literature, was prepared by Barber and Smiles (J.C.S., 1928, 1148) in this manner. These workers obtained a small yield of dipotassium 1:1'-dinaphthyl-2:2'-disulphonate by boiling an aqueous solution of potassium 1:2-iodonaphthalene sulphonate, containing a little cupric sulphate, with excess of copper powder, the reaction being -



The reaction has also been employed with success in the preparation of dinaphthyls and other dinaphthyl derivatives. Ullmann and co-workers (Berichte, 1901, 34, 2184; Annalen, 1904, 332, 50) prepared αα- and ββ-dinaphthyls from α- and β-iodonaphthalenes, and Schoepfle (J.Amer.C.S., 1923, 45(i), 1567) prepared αα-dinaphthyl from α-bromonaphthalene by treatment with copper powder; while Cumming and Howie (J.C.S., 1931, 3176), and later Hodgson and Elliott (J.C.S., 1937, 123), obtained dinitrodinaphthyls from iodonitronaphthalenes in the same way. The observation made by Ullmann (Annalen, 1904, 332, 60) in his work on the condensation of halogen compounds with copper powder, that halogeno-acetylphenylamines failed to condense unless an acidic group (e.g. sulphonic acid) was present, lent encouragement to the proposed investigation of this reaction applied to halogeno-naphthalene sulphonic acids.

From the point of view of devising convenient economical methods for preparing dinaphthyl sulphonic acids, the Ullmann reaction possesses inherent disadvantages. It involves the intermediate step of preparing halogeno-naphthalene sulphonic acids – generally the iodo- or bromo- compounds, since iodine in the naphthalene nucleus has been shown to be more reactive than bromine which, in turn, is more reactive than chlorine (Cumming and Howie, loc. cit.). On objections similar to those raised against the direct sulphonation of dinaphthyls, the preparation of halogeno-naphthalene sulphonic acids by sulphonating the halogeno-naphthalenes was rejected as impracticable. Accordingly, the halogeno-acids employed were prepared from diazonaphthalene sulphonic acids by the Sandmeyer and

Gattermann reactions (or modifications thereof). Diazonaphthalene sulphonic acids are prepared, of course, by diazotizing the naphthylamine sulphonic acids, a considerable range and supply of which are available as starting materials. The diazo-compounds obtained from naphthylamine sulphonic acids all have the "inner diazo-sulphonate" structure -



- but, for simplicity, are described as "diazonaphthalene sulphonic acids" in the text.

But elimination of this intermediate stage of preparing halogeno-naphthalene sulphonic acids would effect economy in material and time, and therefore a more direct method of preparation was also sought.

Vorländer and Meyer (Annalen, 1901, 320, 122) obtained high yields of diphenyl-2:2'-dicarboxylic acid by treating diazotized anthranilic acid with "ammoniacal cuprous oxide solutions". A still more promising suggestion was afforded by E.P. 278,100 (I.G. 6/7/26) in which the preparation of dinaphthyl dicarboxylic acids by treating diazonaphthoic acids with similar "ammoniacal cuprous oxide solutions" is described. Although Vorländer and Meyer applied the reaction to a large number of substituted benzene diazonium salts (e.g. containing the groups $-CH_3$, $-O.CH_3$, $-Cl$, $-NO_2$, $-COOH$ and $-COO.CH_3$), they do not describe its application to diazobenzene sulphonic acids, nor has any reference been found to its application to diazonaphthalene sulphonic acids.

The two practicable methods of attempting to prepare dinaphthyl sulphonic acids which have just been considered, both involve the use of naphthylamine sulphonic acids as starting materials and, since only naphthylamine monosulphonic acids were available, investigations were necessarily limited to attempts to prepare the dinaphthyl disulphonic acids.

1:2-, 1:4-, 1:5-, 1:7-, 1:8-, 2:1- and 2:6-naphthylamine sulphonic acids were employed as starting materials throughout and, broadly speaking, it may be said that the object of the research has been to convert the diazo-compounds obtained from these acids into the corresponding dinaphthyl disulphonic acids, either indirectly through the halogeno-naphthalene sulphonic acids or directly by treatment with reducing agents.

One or two interesting side-lines emerged in the course of the work, and these have been followed up to the extent warranted by their apparent importance.

This introduction is now divided into appropriate sections the aim of which is to review comparitively the results obtained by each type of reaction or treatment as applied to the various diazonaphthalene sulphonic acids, or halogeno-naphthalene sulphonic acids derived from them.

(1) Preparation of Halogeno-naphthalene Sulphonic Acids.

It was found that, while practically all the isomeric chloronaphthalene sulphonic acids were referred to in the literature, not very many bromonaphthalene sulphonic acids, and rather fewer iodonaphthalene sulphonic acids, had been prepared.

Since iodine in the naphthalene nucleus has been shown to be more reactive than chlorine and bromine, most attention was devoted to the preparation of the iodo-acids. Of those which had been prepared before, 1:2-, 1:5- and 2:6-iodonaphthalene sulphonic acids were obtained (and isolated as their sodium or potassium salts) in the orthodox manner by heating the corresponding diazonaphthalene sulphonic acids with hydriodic acid. 1:4-Iodonaphthalene sulphonic acid had only been obtained previously by sulphonating α-iodonaphthalene (Armstrong, Brit.Assoc.Report, 1887, 231), and this was now prepared by treating a suspension of the 1:4-diazo-compound in potassium iodide solution with copper powder. Naphthalene-α-sulphonic acid was a by-product of this reaction, and two new derivatives of it were prepared, viz. naphthalene-α-sulpho-o-toluidide and -α-sulpho-p-nitroanilide. The melting point of naphthalene-α-sulphoanilide (152°C.) was found to be 40 degrees higher than that recorded by Carleson (Bull.Soc.Chim., 1877, <u>27</u>, 360).

1:7-, 1:8- and 2:1-iodonaphthalene sulphonic acids were not recorded in the literature. The 1:7- and 2:1-

compounds were obtained by the usual method of heating the diazo-compounds with hydriodic acid, but the 1:8-compound required a modified method owing to the facility with which 1:8-diazonaphthalene sulphonic acid decomposed on heating to form naphthasultone. This modification consisted of allowing a suspension of 1:8-diazonaphthalene sulphonic acid in potassium iodide solution, containing a little pyridine or acetone, to stand at laboratory temperature until nitrogen evolution ceased. The pyridine or acetone served to accelerate the evolution of nitrogen and reduced the quantity of naphthasultone formed.

It should be noted that in his book "The Aromatic Diazo-Compounds and Their Technical Applications", K. H. Saunders misinterprets a section of "Substituted Naphthalene Sulphonic Acids and their Derivatives" (Cumming and Muir, J.Roy.Tech.College, 1936, 3, 562), in referring to the general method of preparing iodo-compounds by treating diazo-compounds with hydriodic acid. He writes, "An exception to this very general reaction has been recently reported by Cumming and Muir, who found that 1-diazonaphthalene-8-sulphonic acid when treated with potassium iodide in pyridine solution affords not the iodo-compound but naphthalene-1:8-sultone."

Derivatives of the halogeno- (and other) sulphonic acids with definite melting points were required for identification purposes and, in some cases, for subjection to treatment with copper powder. It was customary to treat the various sulphonates obtained with phosphorus pentachloride, converting them to the sulphonyl chlorides from which sulphonamides, sulphoanilides, etc. could be prepared by the action of ammonia and amines. In this way, the following new derivatives were prepared:-

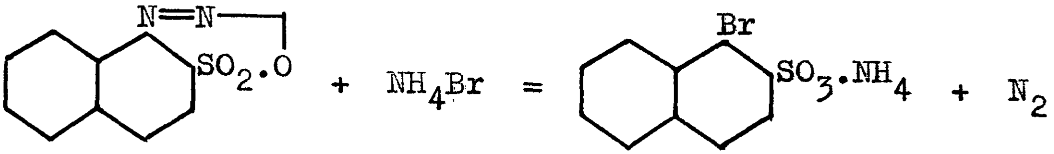
1:2-Iodonaphthalene sulphonamide; 1:4-iodonaphthalene sulphonamide, sulphoanilide and sulpho-o-toluidide; 1:7-iodonaphthalene sulphonyl chloride and sulphonamide; 1:8-iodonaphthalene sulphonyl chloride, sulphonamide and sulphoanilide; 2:1-iodonaphthalene sulphonyl chloride and sulphonamide. An interesting point concerning 1:8-iodonaphthalene sulponamide and sulphoanilide was the readiness with which they were converted into 1:8-naphthasultam and phenyl-1:8-naphthasultam by heating in aqueous solution alone, and with copper powder in alcoholic solution, respectively.

1:4- and 1:8-chloronaphthalene sulphonic acids had both been prepared previously, but an improved method of preparing the latter was devised, taking into account the readiness with which 1:8-diazonaphthalene sulphonic acid is converted into naphthasultone. New derivatives of 1:4-chloronaphthalene sulphonic acid were prepared, viz. the sulphoanilide, sulpho-o-toluidide, sulpho-p-nitroanilide and sulpho-α-naphthylamide.

Three new bromonaphthalene sulphonic acids - the 1:2-, 1:8- and 2:1- compounds - were prepared by an interesting reaction encountered more or less accidentally in the course of a search for suitable reducing agents to apply to the diazo-compounds in the hope of obtaining direct diaryl formation. Cuprous oxide was boiled with ammonium bromide solution in which it dissolved forming a bluish solution from which a complex salt, believed to be diammino-cuprous bromide, separated on cooling -

$$Cu_2O + 2NH_4Br = Cu_2(NH_3)_2Br_2 + H_2O .$$

When 1:2-, 1:8- and 2:1-diazonaphthalene sulphonic acids were added to a suspension of a small amount of this complex in ammonium bromide solution at room temperature, nitrogen was evolved and salts of the corresponding bromonaphthalene sulphonic acids obtained - in good yield except in the case of the 1:8-compound. The part played by diammino-cuprous bromide appears to be catalytic since only a small quantity of the complex was necessary to facilitate nitrogen evolution, which did not occur in its absence. Increasing the quantity of the complex in the reagent accelerated the reaction, which is believed to take the following course -



The following new derivatives were prepared:- 1:2-bromonaphthalene sulphonyl chloride and sulphonamide; 1:8-bromonaphthalene sulphonyl chloride; 2:1-bromonaphthalene sulphonyl chloride and sulphonamide.

This reaction has several advantages over the orthodox Sandmeyer reaction for the preparation of bromo-compounds, e.g. the ease with which the reagent is prepared, the economy in materials, the absence of large amounts of secondary inorganic substances (such as sulphuric acid) which may interfere with the isolation or purification of the product, and the fact that it is carried out at ordinary temperature. The author intends to apply it to other diazo-compounds not possessing the "inner diazo-sulphonate" structure, since the latter may render the diazonaphthalene sulphonic acids particularly amenable to such a reaction. In a single experiment conducted by a student in the Royal Technical College, a small yield of bromobenzene was obtained when benzene diazonium chloride solution was treated in the manner described, but no attempt was made to adjust conditions to improve the yield.

(2) Application of the Ullmann Reaction to Salts and Derivatives of Halogeno-naphthalene Sulphonic Acids.

The first attempts to effect diaryl-formation by means of the Ullmann reaction were made with salts and derivatives of 1:4-chloronaphthalene sulphonic acid. Potassium, sodium and copper salts of this acid were refluxed in aqueous solution with powdered copper, zinc and magnesium, but in no case was the chlorine displaced. Nor was there any reaction when fused 1:4-chloronaphthalene sulphoanilide was heated with copper powder or zinc dust.

When an aqueous solution of potassium 1:4-iodonaphthalene sulphonate, containing a little cupric sulphate, was refluxed with copper powder, the iodine was gradually replaced by hydrogen with formation of naphthalene-α-sulphonic acid (potassium salt), but there was no evidence of diaryl-formation. A similar reaction occurred when the potassium iodo-sulphonate was refluxed with zinc or magnesium. The iodine was not replaced when 1:4-iodonaphthalene sulphonamide was refluxed with zinc dust in pyridine or with magnesium in nitrobenzene solution. In quinoline solution, however, the iodine was replaced by refluxing with zinc dust (doubtless owing to the higher reflux temperature), an unidentifiable resinous product being isolated. In similar experiments with the iodo-sulphoanilide, the iodine was unaffected by boiling with zinc dust or copper powder in pyridine solution. Copper powder and zinc dust both reacted with the iodine in the sulphoanilide in boiling quinoline, but only resinous products were isolated.

Many attempts were made to confirm the work of Barber and Smiles (J.C.S., 1928,1148) who obtained the potassium salt and disulphonyl chloride derived from 1:1'-dinaphthyl-2:2'-disulphonic acid by refluxing a solution of potassium 1:2-iodonaphthalene sulphonate, containing a little cupric sulphate (catalyst), with copper powder. But in all the early experiments, potassium naphthalene-α-sulphonate was identified as the sole product, the replacement of iodine by hydrogen occurring readily.

Professor Smiles kindly supplied additional information regarding this reaction when the author wrote to him of the trouble encountered. He stated in his reply that the addition of a little cupric sulphate had been found essential, but that the yield of 1:1'-dinaphthyl-2:2'-disulphonyl chloride had been small since it had required 300 gm. of potassium 1:2-iodonaphthalene sulphonate to produce sufficient of this to yield 2 gm. of dinaphthyl disulphide on reduction - the second stage normally giving good results.

Hurtley (J.C.S., 1929, 1870) records that an aqueous solution of 2-bromobenzoic acid, when heated with copper powder, was converted mainly into benzoic acid with a secondary 7% yield of diphenic acid. The yield of diphenic acid was apparently increased greatly by adding a little water to an intimate mixture of potassium o-bromobenzoate and copper powder heated to 100°C. Accordingly, an experiment on these lines was carried out with potassium 1:2-iodonaphthalene sulphonate, but no reaction occurred at all, the salt being recovered unchanged.

In the same paper, Hurtley refers to the use of cupric acetate as a catalyst in the Ullmann reaction. In a final last minute endeavour, the author succeeded in isolating a small yield of the 1:1'-dinaphthyl-2:2'-disulphonyl chloride obtained by Barber and Smiles by employing this, instead of cupric sulphate, to promote the reaction.

An aqueous solution of sodium 1:2-bromonaphthalene sulphonate was refluxed with copper powder in the hope that it might show a greater tendency than the iodo-sulphonate to yield the dinaphthyl disulphonate, but in this case the halogen proved quite unreactive.

When the potassium salts or sodium salts of 1:5-, 1:7- and 2:6-iodonaphthalene sulphonic acids were refluxed in aqueous solution, containing a little cupric sulphate, with copper powder for several hours, no reaction took place, the salts being recovered unchanged. When zinc dust was used instead of copper powder, the iodine in potassium 1:5-iodonaphthalene sulphonate was replaced by hydrogen with formation of potassium naphthalene-α-sulphonate.

However, with 1:8- and 2:1-iodonaphthalene sulphonates, iodine was readily replaced by treatment with copper powder in aqueous solution, with formation of the corresponding dinaphthyl disulphonates. Considerable difficulty was encountered in preparing a derivative of the supposed 1:1'-dinaphthyl-8:8'-disulphonic acid since treatment with phos-

phosphorus pentachloride apparently ruptured the diaryl bond with formation of 1:8-chloronaphthalene sulphonyl chloride, and fusion with caustic potash to obtain the dinaphthol resulted in an unidentified resinous product; but by heating with fused aniline hydrochloride, a compound believed to be 1:1'-dinaphthyl-8:8'-sultone was isolated. On the other hand, there was no difficulty in identifying 2:2'-dinaphthyl-1:1'-disulphonic acid which readily yielded the disulphonyl chloride, and gave both ββ-dinaphthyl and 1:1'-dihydroxy-2:2'-dinaphthyl on fusion with caustic potash.

The activating influence of a sulphonic group in the 1-position ortho to halogen was further confirmed when it was found that potassium 2:1-bromonaphthalene sulphonate also reacted readily with copper powder yielding dipotassium 2:2'-dinaphthyl-1:1'-disulphonate - in contrast to the inactivity of the 1:2-bromo-compound.

From these results, two generalizations which have been shown elsewhere to apply to other halogeno-compounds, are confirmed:-

(a) Iodine in the naphthalene nucleus is more reactive than chlorine or bromine. This was shown by the observations that copper displaced iodine from the 1:2-, 1:4-, 1:8- and 2:1- iodo-sulphonates, bromine from the 2:1- but not the 1:2-bromo-sulphonate, and did not react with the chlorine in the 1:4-chloro-sulphonates.

(b) Halogen in the naphthalene nucleus is activated by the close proximity of an acidic group. In support of this, it has been shown that when the sulphonate group was ortho or peri to iodine (1:2-, 2:1- or 1:8-) in the iodonaphthalene sulphonates, the iodine was readily displaced with formation of either a dinaphthyl disulphonic acid (1:2-, 2:1- and 1:8-) or a naphthalene sulphonic acid (1:2-). When the substituents were oriented in the 1:4-position, the iodine was gradually replaced by hydrogen on treatment with copper powder, but with the more "remote" orientations, viz. 1:5-, 1:7- and 2:6-, no reaction occurred.

What does not emerge from the experimental results obtained is any generalization governing the disposition of the more reactive iodonaphthalene sulphonic acids (1:2-, 1:4-, 1:8- and 2:1-) to form either naphthalene sulphonic acids or dinaphthyl disulphonic acids on treatment with copper powder. While the 2:1-compound gave good yields of dinaphthyl disulphonate, and no replacement of iodine by hydrogen was detected, the 1:2-compound was converted mainly to naphthalene-β-sulphonic acid. It can probably be said that the factors favouring replacement of iodine by hydrogen or diaryl bond are mainly experimental, i.e. the course of reaction is controlled largely by the concentration and nature of the solution (acidity, etc.) and the form of catalyst employed.

(3) The Reaction of Diazonaphthalene Sulphonic Acids with "Ammoniacal Cuprous Oxide Solution".

Vorländer and Meyer (Annalen, 1901, 320, 122), who employed "ammoniacal cuprous oxide solution" to prepare substituted diphenyls and azobenzenes from substituted benzene diazonium salts, usually obtained this reagent by reducing ammoniacal cupric sulphate solution with hydroxylamine, though they state that the latter may be replaced by sulphurous acid or ferrous hydroxide. These three reducing agents are also employed to prepare the reagents used in E.P. 278,100 for converting diazonaphthoic acids into dinaphthyl dicarboxylic acids, though in addition sodium bisulphite is mentioned. But neither of these sources indicates any distinction between the forms of "ammoniacal cuprous oxide solution" obtained by the action of the respective reducing agents. It is presumed, therefore, that identical or similar results were obtained irrespective of the manner in which the ammoniacal cupric sulphate was reduced.

The two forms of ammoniacal cuprous solution generally used by the author were those obtained by reduction with sulphur dioxide and hydroxylamine. Since the results obtained by treating diazonaphthalene sulphonic acids with these two forms of "ammoniacal cuprous oxide solution" were entirely different, it is advisable to divide this section into two parts, considering the reactions of each form separately.

(a) Reduction by means of sulphur dioxide.

When sulphur dioxide is passed into ammoniacal cupric sulphate solution (deep blue), the sulphur dioxide is rapidly absorbed and, ultimately, when excess of sulphurous acid is present, the colour of the solution is pale red and a colourless crystalline salt separates. Addition of excess of ammonia to this reduced solution dissolves the crystalline salt and a pale greenish-blue solution is obtained.

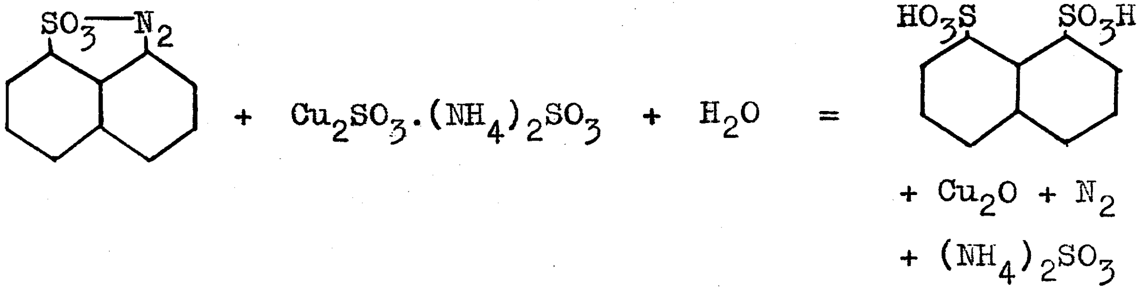
Before considering the nature of the crystalline salt and its ammoniacal solution, it is advisable to survey the results of the reaction between this "ammoniacal cuprous oxide solution" (prepared as in Example 1 of E.P. 278,100) and the diazonaphthalene sulphonic acids.

Nitrogen was rapidly evolved in all cases when the diazo-compounds were added to the reagent, and isolation of the product had generally to be performed by evaporation and treatment of the total solute with phosphorus pentachloride, since salting out proved ineffective. The first three diazo-compounds to be treated in this way were those derived from 1:4-, 1:5- and 1:8-naphthylamine sulphonic acids, and the substances obtained by phosphorus pentachloride treatment of the product were believed at first to be derivatives of the desired dinaphthyl disulphonic acids. This was disproved by analysis, which showed that they were actually derivatives of naphthalene disulphonic acids (naphthalene-1:4- and -1:5-disulphonyl chlorides and naphthalene-1:8-disulphonic anhydride respectively). Subsequently 1:2- and 2:6-diazonaphthalene sulphonic acids were found to react in the same manner with this reagent, yielding naphthalene-1:2-disulphonic anhydride and -2:6-disulphonyl chloride respectively, although in the case of the 2:6-compound a small quantity of azonaphthalene disulphonate was also obtained.

These results do not lead to the belief that "ammoniacal cuprous oxide" is the reactive constituent in the reagent prepared by reduction with sulphur dioxide.

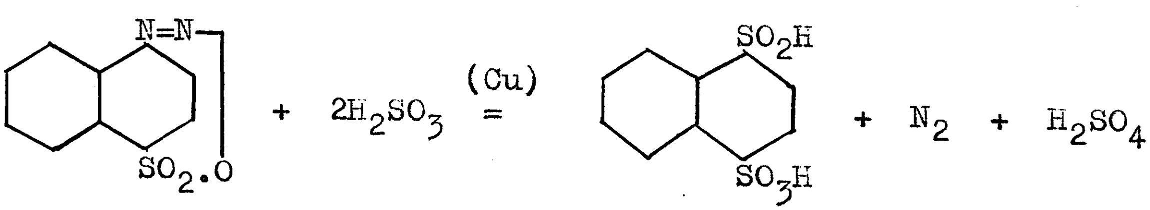
Another experiment with 1:8-diazonaphthalene sulphonic acid throws some light on the matter. Instead of rendering the reduced cupric sulphate solution ammoniacal and adding the diazo-compound, the crystalline salt (which separated when excess of sulphurous acid was present) was filtered off, suspended in water and the solid diazo-compound added. Nitrogen was evolved as before and cuprous oxide separated, naphthalene-1:8-disulphonic anhydride being isolated subsequently in better yield than that obtained by the previous treatment in ammoniacal solution.

From a paper by Ramberg (Z.phys.Chem., 1909, 69, 512), it appears that this crystalline salt is cuprous ammonium sulphite, $Cu_2SO_3.(NH_4)_2SO_3$, and it is therefore suggested that the course of the reaction may be illustrated by the equation -



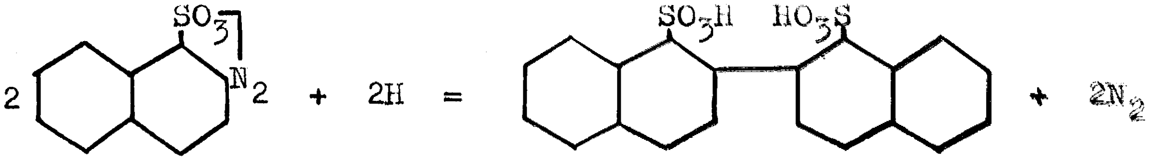
Dissolved in ammonia, the double sulphite would doubtless give rise to complex ammino-cuprous ions, $[Cu_2(NH_3)_n]^{++}$, which, since the ammoniacal reagent gave the same product, probably catalyse the evolution of nitrogen and reaction of sulphite ion to form naphthalene disulphonic acids.

Gattermann (Berichte, 1899, 32, 1156) prepared naphthalene-1:4-disulphonic acid by adding copper powder to an aqueous suspension of 1:4-diazonaphthalene sulphonic acid saturated with sulphur dioxide, and oxidizing the sulphonic-sulphinic acid formed with potassium permanganate. The first stage of the reaction appears to take this course;-



In a single experiment, this method was compared with that involving ammoniacal cuprous sulphite solution, and a higher yield of naphthalene-1:4-disulphonyl chloride was obtained. It is possible, however, that the second method of preparing the 1:8-disulphonic acid (aqueous suspension of $Cu_2SO_3.(NH_4)_2SO_3$) would also result in an improved yield of the 1:4-disulphonic acid when applied to the 1:4-diazo-compound.

While all the other diazonaphthalene sulphonic acids yielded naphthalene disulphonic acids on treatment with this ammoniacal cuprous sulphite solution, 2:1-diazonaphthalene sulphonic acid reacted (like the diazonaphthoic acids in E.P. 278,100) to form 2:2'-dinaphthyl-1:1'-disulphonic acid. The reaction is thus essentially a reduction with simultaneous nitrogen evolution and diaryl-formation :-



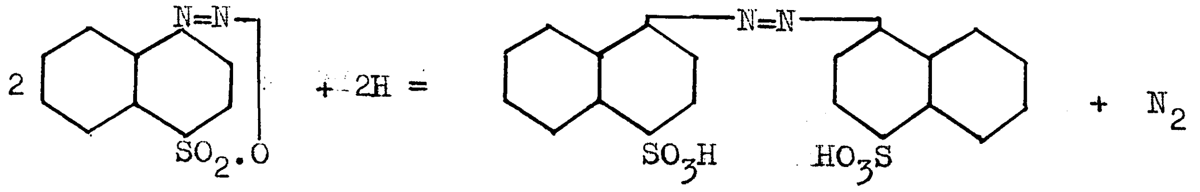
Mainly with the object of ascertaining if the presence of cuprous copper was essential to the conversion of diazonaphthalene sulphonic acids to naphthalene disulphonic acids by sulphite treatment, several experiments were performed involving the treatment of diazo-sulphonic acids with sodium sulphite solution. The results of these are reviewed in section (5).

(b) Reduction by means of hydroxylamine.

The preparation of tetrammino-cuprous sulphate by reducing ammoniacal cupric sulphate solution with hydroxylamine is described by Péchard (Compt. rend., 1903, 136, 505). It is inferred therefore that an ammoniacal solution of this complex is that described by Vorländer and Meyer, and referred to in Example 6 of E.P. 278,100, as "ammoniacal cuprous oxide solution", since the latter is prepared in a similar manner.

When treated with such a solution, diazonaphthalene sulphonic acids were found to react with brisk evolution of nitrogen. Only in the case of 2:1-diazonaphthalene sulphonic acid was a dinaphthyl disulphonic acid identified as the product. As in the treatment with ammoniacal cuprous sulphite solution (a), the reaction is a reduction with simultaneous evolution of nitrogen and diaryl-formation, being represented by the equation shown above.

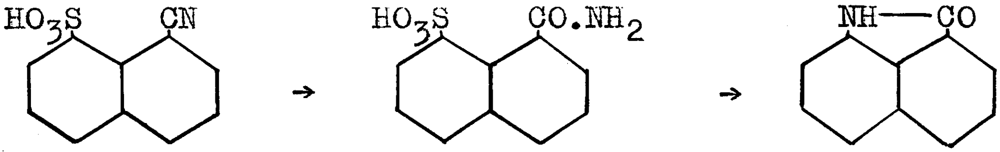
The only products identified in the reactions of the 1:2-, 1:4-, 1:5-, 1:8- and 2:6-diazo-sulphonic acids with this reagent, were salts of the corresponding azonaphthalene disulphonic acids. The reaction here might be described as a reduction with partial elimination of nitrogen:-



Although reference is made in D.R.P.343,149 (20/7/16) to 1:1'-azonaphthalene-2:2'- and -5:5'-disulphonic acids as starting materials in the preparation of diaminodinaphthyl sulphonic acids, only 1:1'-azonaphthalene-4:4'-disulphonic acid appears to be recorded in other than Patent literature.

The results obtained by this treatment with tetra-ammino-cuprous sulphate solution conflict with an interesting generalization made by Vorländer and Meyer (loc. cit.), in so far as it might apply to the naphthalene series. It emerged from their study of the reactions of substituted benzene diazonium salts with "ammoniacal cuprous oxide solution". They state that the course of the reaction of simple diazotized aromatic amines with this solution depends not upon the positive or negative, strongly or weakly acidic, character of the substituent groups, but upon their saturated or unsaturated nature. Thus, they showed that o-substituted benzene diazonium salts yielded <u>diphenyl</u> derivatives if the substituent group was <u>unsaturated</u> (e.g. $-NO_2$, -COOH, $-COO.CH_3$) while if the substituent group was <u>saturated</u> (e.g. $-CH_3$, -Cl, $-O.CH_3$) <u>azo-compounds</u> were formed. It is evident that this generalization does not hold for the diazonaphthalene sulphonic acids (containing an unsaturated substituent) since, with one exception, azonaphthalene disulphonic acids were produced.

It should be noted that in E.P. 278,100 only unsubstituted diazo-naphthoic acids of ortho or peri orientation are claimed to yield dinaphthyl dicarboxylic acids. At an early stage in the research, before 2:2'-dinaphthyl-1:1'-disulphonic acid had been prepared by this direct treatment, it was considered advisable to examine the conditions under which 1:1'-dinaphthyl-8:8'-dicarboxylic acid was obtained by the method described in E.P. 278,100 (Example 1). To do this, a good deal of preliminary work was necessary, since the starting material, 1:8-aminonaphthoic acid, had to be prepared from peri acid. 1:8-Diazonaphthalene sulphonic acid was first converted into 1:8-cyanonaphthalene sulphonic acid (of which two new derivatives, the sulphonyl chloride and sulphonamide, were prepared). This was then subjected to alcoholic alkaline hydrolysis according to a method described in E.P. 276,126, which resulted in the interesting transformation to naphthostyril -



Sodium 1:8-aminonaphthoate was obtained from naphthostyril by hydrolysis with caustic soda. It was found that on diazotization and treatment with ammoniacal cuprous sulphite, 1:8-aminonaphthoic acid yielded 1:1'-dinaphthyl-8:8'-dicarboxylic acid as claimed in the Patent under the conditions recorded.

Further investigations with the aminonaphthoic acids were abandoned after 2:2'-dinaphthyl-1:1'-disulphonic acid had been prepared by the direct methods.

1:5- and 1:8-diazonaphthalene sulphonic acids were treated with an ammoniacal cuprous solution prepared by reducing ammoniacal cupric sulphate with ferrous sulphate in the manner described in Example 5 of E.P. 278,100, but no identified products were isolated.

(4) Other Attempts to Effect Direct Diaryl-Formation.

Numerous experiments with various reducing agents were carried out with the object of converting diazonaphthalene sulphonic acids (particularly the 1:4- and 1:8- compounds) directly into the correponding dinaphthyl disulphonic acids. In most cases, no definite products were isolated, but several treatments resulted in the formation of naphthalene-α-sulphonic acid. Examples of the latter were - treatment of the 1:4-diazo-sulphonic acid with (a) sulphurous acid in the presence of pyridine and (b) sodium meta-bisulphite solution; and treatment of the 1:8-diazo-sulphonic acid with (a) a suspension of copper powder in concentrated hydrochloric acid, (b) a suspension of copper powder in a concentrated hydrochloric acid solution of cuprous chloride, (c) an aqueous suspension of zinc dust, and (d) an ammoniacal suspension of stannous hydroxide.

Reactions in which no definite products were identified included the following - treatment of the 1:4-diazo-sulphonic acid with (a) an ammoniacal suspension of ferrous hydroxide, (b) ferrous sulphate solution to which pyridine had been added, (c) zinc dust and copper powder in caustic soda solution, (d) an aqueous suspension of cuprous oxide and (e) strong ammonium sulphite solution with subsequent addition of copper powder; and treatment of the 1:8-diazo-sulphonic acid with (a) an aqueous suspension of cuprous chloride, (b) an aqueous suspension of cuprous oxide, (c) an ammoniacal suspension of cuprous oxide, (d) copper powder in aqueous suspension, (e) an ammoniacal solution of cupric sulphate reduced by stannous chloride, (f) sodium ethoxide in alcoholic solution, and (g) ammoniacal sodium sulphite solution.

When it was found that none of the treatments applied to 1:4-diazonaphthalene sulphonic acid resulted in the formation of the dinaphthyl disulphonic acid, it was decided to try to prepare sulpho-derivatives of 1:4-naphthylamine sulphonic acid (naphthionic acid), with the object of investigating the reactions of the diazo-compounds derived from them with reducing agents.

Naphthionic acid does not react with phosphorus pentachloride to form the sulphonyl chloride, but E.P.331,596 (10/4/29) describes a process for manufacturing amino-sulphonyl chlorides by treating amino-sulphonic acids with chlorosulphonic acid. When the author applied this reaction to naphthionic acid, it was further sulphonated, no sulphonyl chloride being isolated. Attempts were therefore made to prepare the amino-sulphoanilide and amino-sulpho-α- and -β-naphthylamides by heating naphthionic acid with aniline and α- and β-naphthylamines. In the reaction between boiling aniline and naphthionic acid, phenyl-α-naphthylamine was formed, and aniline naphthionate was the product when aniline was boiled in water with naphthionic acid. When α- and β-naphthylamines were refluxed with naphthionic acid in nitrobenzene solution, only naphthylamine naphthionates were formed. On destructive distillation, β-naphthylamine naphthionate was partly converted into ββ-dinaphthylamine.

Thus, no sulpho-derivatives of naphthionic acid were obtained, and this line of investigation was discontinued.

(5) Reaction of Diazo-Compounds with Sodium Sulphite.

The purpose of this secondary investigation is described at the end of section (3)(a), and the theoretical conclusions which emerged are discussed in considerable detail in the Experimental Sections I.(12) and VI.(12), and in the Appendix.

Briefly, the diazo-compounds derived from 1:4- and 2:1-naphthylamine sulphonic acids and sulphanilic acid were treated with sodium sulphite solution (neutral, acid or alkaline). Naphthalene (or benzene) disulphonic acids were not obtained, but in each case, under suitably adjusted conditions, azo-disulphonates were formed. The intermediate products in these reactions were investigated and proved to be stable diazo-sulphonates in the case of diazotized 2:1-naphthylamine sulphonic acid and sulphanilic acid.

Bucherer and Schmidt (J.prakt.Chem., 1909, 79(ii), 389) converted 1:4-hydrazino-naphthalene sulphonic acid into 1:1'-azonaphthalene-4:4'-disulphonic acid by treatment with sodium sulphite, but this reaction was tested and shown to be much too slow to infer that the hydrazino-sulphonic acid was an intermediate product in the conversion of diazotized naphthionic acid into the disodium azo-disulphonate (Cuba Orange), which occurred rapidly. No diazo-sulphonate was isolated as intermediate product in the latter reaction, but it seems probable that it is present in solution when the diazo-compound first dissolves in the sodium sulphite solution

Notes.

At the end of Section V. (Experimental) the nitration of 1:8-naphthasultone and the hydrolysis of the nitro-derivative are recorded. In the Appendix, the formation of ββ-azonaphthalene by treating naphthalene-β-diazonium chloride with tetrammino-cuprous sulphate solution is described.

A Summary, in which the chief experimental findings of the research are surveyed very briefly, is included after the Appendix.

EXPERIMENTAL SECTION

STARTING MATERIALS.

The starting materials employed throughout the investigations were naphthylamine sulphonic acids of varying purity, with the exception of o-naphthionic acid which was available as the pure sodium salt.

DIAZOTIZATION TECHNIQUE

The stability of the diazo-compounds derived from the naphthylamine sulphonic acids made it possible for diazotization to be carried out at room temperature except in the case of Cleve acid, where cooling was necessary.

The general procedure adopted for diazotization was to dissolve the sodium naphthylamine sulphonate in a suitable quantity of water (usually hot) and add an amount of dilute sulphuric or hydrochloric acid equivalent to 2¼ molecules of the sulphonate. The cooled suspension of naphthylamine sulphonic acid so formed was diazotized by gradually introducing the requisite amount of sodium nitrite solution (equivalent to 1 molecule of the sulphonate) through a dropping funnel dipping beneath the surface of the suspension. Mechanical agitation was supplied by a water motor and glass stirrer.

For convenience, large volumes of solutions of dilute sulphuric and hydrochloric acids and sodium nitrite were prepared containing definite quantities of the reagents.

At first, the entire diazo-suspension was employed as reagent in the reactions which are to be described; but when the stability of the diazo-compounds was fully recognized, it was found considerably more effective to filter the suspensions and use the solid diazo-compounds, either in a moist state or as aqueous suspensions. This procedure cut down the amount of secondary inorganic product in the various reactions and eliminated the necessity for taking into consideration the excess of mineral acid present in the diazo-suspensions.

ARRANGEMENT OF RESULTS.

The results are most conveniently classified and recorded according to the starting material employed. The reactions involving naphthionic acid as starting material were those first investigated and are therefore given precedence, but the other acids are dealt with according to the order of their substituent groups, viz. 1:2-, 1:5-, 1:7-, 1:8-, 2:1- and 2:6- naphthylamine sulphonic acids.

As far as practicable, the reactions of the various acids are recorded in the same order in each case.

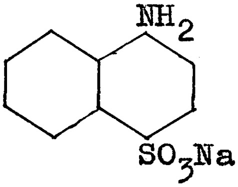
I. 1-NAPHTHYLAMINE-4-SULPHONIC ACID. (Naphthionic Acid).

(1) Preparation of Sodium 1-Naphthylamine-4-Sulphonate.

The crude naphthionic acid (samples provided varied in purity) was dissolved in hot dilute caustic soda solution, so that a slight excess of alkali remained. A little decolourizing carbon was added and the hot solution filtered. On cooling, fine almost colourless crystals of sodium 1-naphthylamine-4-sulphonate (hereafter referred to as sodium naphthionate) separated, further crops being obtained by concentrating the mother liquor.

The sodium naphthionate obtained thus was generally sufficiently pure to serve as starting material, though recrystallization was sometimes necessary.

Sodium naphthionate crystallizes with five molecules of water of crystallization -



$\cdot 5H_2O$ M.W. 335.

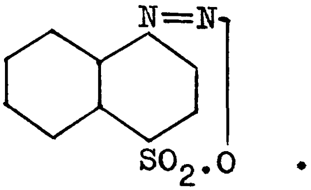
(2) Diazotization of Naphthionic Acid.

Some attention was devoted to various methods of diazotizing naphthionic acid. In initial experiments with the direct method outlined above, the naphthionic acid was not precipitated in a sufficiently fine state of division for even moderately rapid diazotization, and other methods were attempted. A mixture of sodium naphthionate and sodium nitrite was added to dilute hydrochloric acid and, although diazotization occurred, it was attended by a certain amount of coupling which gave the diazo-suspension a deep red colour. In the same way, diazotization by adding dilute hydrochloric acid to a mixed solution of sodium naphthionate and sodium nitrite resulted in some coupling between the diazo-compound and unchanged sodium naphthionate.

Adopting the following procedure, a clean yellow diazo-suspension was obtained by direct diazotization:-

10 gm. (1 mol.) of sodium naphthionate were dissolved in about 400 c.c. of water and 12 gm. of concentrated hydrochloric acid (3¼ mol.), diluted to 30 c.c., were added with mechanical agitation. The finely divided suspension of naphthionic acid so formed was diazotized quite rapidly at room temperature by slowly adding a solution of 2.4 gm. (1 mol.) of sodium nitrite in 25 c.c. of water, with mechanical agitation.

The quantity of hydrochloric or sulphuric acid added was subsequently reduced to the equivalent of 2¼ mol. of sodium naphthionate - all that is necessary in view of the ring structure of the diazo-compound -



(3) Properties of the Diazo-Compound.

A few preliminary tests were carried out to ascertain the properties of the diazo-compound:-

(a) On heating the diazo-suspension alone, nitrogen was not evolved until a temperature of about 80°C. was reached. Above this temperature, nitrogen evolution was rapid and a deep red solution was formed; the result, no doubt, of coupling between undecomposed diazo-compound and N.W. acid (1-naphthol-4-sulphonic acid) which is likely to be formed.

(b) When copper powder was added to the cold diazo-suspension, nitrogen was evolved rapidly and a deep red solution obtained. No nitrogen was evolved on similar treatment with powdered zinc, aluminium or magnesium.

(c) The dry diazo-compound did not explode on warming, but decomposed rapidly with sintering. No organic solvents for the diazo-compound were found.

(d) The diazo-compound was readily soluble in sodium hydroxide solution and, on heating a strongly alkaline solution, no nitrogen was evolved. This solution, orange in colour, only coupled with β-naphthol on warming. From its comparative stability, it seems probable that the anti-diazotate is formed in the presence of excess of alkali.

On dissolving as much diazo-compound as possible in weak caustic soda solution, a point was reached when nitrogen was suddenly evolved and a deep red solution produced. The less stable syn-diazotate is probably formed when there is little excess of alkali present.

Similar results were observed when the diazo-compound was dissolved in ammonia.

(e) The diazo-compound dissolved in stannous chloride solution on warming without evolution of nitrogen and, almost immediately, a white flocculent precipitate separated which was soluble in alkali.

(f) The diazo-compound dissolved in neutral sodium sulphite solution in the cold, with slow evolution of nitrogen. Pyridine or ammonia hastened nitrogen evolution.

(g) When sulphur dioxide was passed through the diazo-suspension, nitrogen was not evolved until ammonia or pyridine was added.

(4) Preparation of Copper, Sodium and Potassium 1:4-Chloronaphthalene Sulphonates.

Both the Sandmeyer reaction, using cuprous chloride, and the Gattermann reaction, using copper powder in hydrochloric acid solution, were employed successfully in preparing salts of chloronaphthalene sulphonic acid (1:4-).

Sandmeyer reaction:- The diazo-suspension prepared from 20 gm. of sodium naphthionate was poured into a solution of 6 gm. of cuprous chloride in fairly strong hydrochloric acid, maintained near boiling point. Nitrogen was rapidly evolved and a clear deep green solution obtained. This solution was evaporated to about a quarter of its original bulk and, on cooling, a crop of yellowish spangles separated. This was filtered off and recrystallized from hot water after adding a little decolourizing carbon and filtering. The almost colourless spangles obtained were identified as the cupric salt of 1:4-chloronaphthalene sulphonic acid obtained by Arnell (Dissert., Upsala, 1889) - $Cu(C_{10}H_6ClSO_3)_2,6H_2O$ (Found Cu, 9.7%; theory requires Cu, 9.7%).

Gattermann reaction:- Several trial preparations were carried out by this method, but in no case was a good yield of the copper salt obtained. The method consisted of adding copper powder to a 1:4-diazonaphthalene sulphonic acid suspension made strongly acid with hydrochloric acid, in the cold. Nitrogen was evolved fairly rapidly and, after filtering off excess of copper powder, the filtrate was worked up in a manner similar to that described for the Sandmeyer reaction.

Atmospheric oxidation during the process of working up probably accounts for the formation of the cupric salt in both of these reactions.

The potassium salt (Arnell, loc. cit.) was prepared by boiling a solution of the copper salt with potassium hydroxide solution, filtering and concentrating the filtrate. It separated as colourless hexagonal spangles; (found Cl, 12.7%; $C_{10}H_6Cl.SO_3K$ requires Cl, 12.7%). The sodium salt, prepared in a similar manner from the copper salt and sodium hydroxide, crystallizes from hot water as colourless spangles. (Found Cl, 12.4%; $C_{10}H_6Cl.SO_3Na,H_2O$ requires Cl, 12.5%).

(5) Derivatives of 1:4-Chloronaphthalene Sulphonic Acid.

To establish further the identity of the acid and to gain experience in methods of preparing sulpho-derivatives, a considerable number of 1:4-chloronaphthalene sulpho-derivatives were prepared:-

(a) 1:4-Chloronaphthalene Sulphonyl Chloride.

A quantity of potassium 1:4-chloronaphthalene sulphonate was triturated with excess of phosphorus pentachloride in a mortar. When the reaction had ceased, a large volume of cold water was added to decompose excess phosphorus pentachloride, and the sulphonyl chloride separated as a yellow sticky mass which soon solidified. It crystallized from acetone as colourless prisms, m.p. 95°C. Arnell (loc. cit.) gives m.p. 95°C. (Found Cl, 26.9%; $C_{10}H_6Cl.SO_2Cl$ requires Cl, 27.1%).

(b) 1:4-Chloronaphthalene Sulphonamide.

The sulphonyl chloride was boiled with concentrated ammonia solution until it dissolved. After concentrating the solution slightly and cooling, the sulphonamide crystallized. It separated from water as colourless prisms, m.p. 185°C. Arnell (loc. cit.) gives m.p. 187°C. This derivative was also prepared by treating an alcoholic solution of the sulphonyl chloride with concentrated ammonia, this technique being also applicable to the derivatives which follow.

(c) 1:4-Chloronaphthalene Sulphoanilide.

The sulphonyl chloride was boiled in water with a slight excess of aniline until the pasty mass solidified. The sulphoanilide crystallized from alcohol, after decolourizing with carbon, as very pale yellow plates, m.p. 143°C. (Found Cl, 11.0%; $C_{10}H_6Cl.SO_2NH.C_6H_5$ requires Cl, 11.2%).

(d) 1:4-Chloronaphthalene Sulpho-o-toluidide.

The sulphonyl chloride was treated as in (c) with a slight excess of o-toluidine. The sulpho-o-toluidide crystallized from alcohol as colourless prisms, m.p. 151°C. (Found Cl, 10.6%; $C_{10}H_6Cl.SO_2NH.C_6H_4.CH_3$ requires Cl, 10.7%).

(e) 1:4-Chloronaphthalene Sulpho-p-nitroanilide.

By boiling the sulphonyl chloride with a slight excess of p-nitroaniline in water for 2-3 hours and crystallizing the resultant solid from alcohol-water, the sulpho-p-nitroanilide was obtained as pale yellow prisms, m.p. 188°C. (Found Cl, 9.5%; $C_{10}H_6Cl.SO_2NH.C_6H_4.NO_2$ requires Cl, 9.8%).

(f) 1:4-Chloronaphthalene Sulpho-α-naphthylamide.

The sulphonyl chloride was treated with α-naphthylamine as in (c), and the sulpho-α-naphthylamide crystallized from alcohol (after repeated treatments with decolourizing carbon) from which it separated as mauve prisms, m.p. 162°C. (Found Cl, 9.5%; $C_{10}H_6Cl.SO_2NH.C_{10}H_7$ requires Cl, 9.6%).

The sulphoanilide, sulpho-o-toluidide, sulpho-p-nitroanilide and sulpho-α-naphthylamide are not referred to in the literature.

(6) Attempts to Prepare 1:1'-Dinaphthyl-4:4'-Disulphonic Acid from salts and derivatives of 1:4-Chloronaphthalene Sulphonic Acid.

The method employed in attempts to convert 1:4-chloronaphthalene sulphonates into the corresponding 1:1'-dinaphthyl-4:4'-disulphonates was to dissolve a quantity of the former in water and boil the solution under reflux with an excess of powdered metal for several hours. In this manner, neutral solutions of the potassium, sodium and copper salts of the acid were refluxed with powdered copper (also in the presence of $CuSO_4$, cf. Barber and Smiles, J.C.S., 1928, 1148), zinc, aluminium and magnesium. In one or two cases, the reaction was also attempted in slightly acid or slightly alkaline solution. After 2-3 hours boiling, excess of the metal was filtered off, and the solution either tested for chloride or concentrated and the sulphonate obtained converted into the sulphonyl chloride by treatment with phosphorus pentachloride. In no case did any reaction appear to have occurred - chloride tests were negative and 1:4-chloronaphthalene sulphonyl chloride was obtained when the isolated sulphonate was treated with phosphorus pentachloride.

An attempt to effect diaryl formation by heating the finely powdered anhydrous potassium salt with sodium amalgam, and again with sodium itself, proved unsuccessful.

Two attempts were made to bring about diaryl formation through derivatives of the acid. 1:4-chloronaphthalene sulphoanilide was heated almost to boiling point with zinc dust for about half an hour, but was recovered unchanged. A similar result was obtained when the sulphoanilide was heated with copper powder.

It was therefore inferred that, in the 1:4-oriented compound, the nuclear chlorine is too firmly held to participate in a reaction of this kind.

(7) Preparation of Potassium 1:4-Iodonaphthalene Sulphonate.

The only method of preparing 1:4-iodonaphthalene sulphonic acid found in the literature was that of Armstrong (Brit. Assoc. Report, 1887, 231) who isolated it from the sulphonation products of α-iodonaphthalene. As this method is cumbersome, involving initial preparation of α-iodonaphthalene, attention was given to methods of preparing the acid from 1:4-diazonaphthalene sulphonic acid.

The first method employed to prepare the iodo-acid (as the potassium salt) consisted in pouring the diazo-suspension gradually into excess of a boiling solution of hydriodic acid, prepared by acidifying potassium iodide solution with hydrochloric acid, with stirring. A very deep red solution resulted and, after nitrogen ceased to be evolved, this was neutralized with potassium hydroxide and evaporated to small bulk. On cooling, a dark brown solid separated which, on repeated crystallization from hot water using decolourizing carbon, yielded a very small crop of pink crystals subsequently identified as potassium 1:4-iodonaphthalene sulphonate. The yield being rather less than 1% theoretical, this method was rejected as unsuitable. Several attempts to modify this method, e.g. by adding the diazo-suspension to the hydriodic acid in the cold and heating up gradually, were unsuccessful.

As has been noted, nitrogen is not evolved from the diazo-suspension (nor in the presence of hydriodic acid) until it is heated to about 80°C. At this temperature it appears that the tendency for formation of 1:4-naphthol sulphonic acid, and consequent coupling with undecomposed diazo-compound, is much greater than the tendency for replacement by iodine.

With the object of bringing about nitrogen evolution at ordinary temperatures, a modification of the Gattermann reaction was employed and found to be effective.

In this modification, the diazo-suspension from 20 gm. of sodium naphthionate was added, in the cold, to a solution of 15 gm. of potassium iodide in 300 c.c. of water. 5 gm. of copper powder were then added with mechanical agitation. Nitrogen was evolved rapidly and, after filtering off excess copper powder and cuprous iodide, the solution was evaporated to small bulk and neutralized with potassium hydroxide. The copper hydroxide formed was removed by boiling with a little decolourizing carbon and filtering. Pinkish crystals separated from the cooled filtrate, the yield of potassium salt being now approximately 17% theoretical. The product was recrystallized from hot water using decolourizing carbon, and separated as very pale yellow prisms. (Found I, 33.6%; $C_{10}H_6I.SO_3K$ requires I, 34.1%).

On concentrating the mother liquor after separating the potassium iodo-sulphonate in the above preparation, a large quantity of a very soluble yellow salt was obtained. This was identified, by the melting points of the sulphonyl chloride and sulphonamide derived from it (65°C. and 149°C. respectively), as the potassium salt of naphthalene α-sulphonic acid. Derivatives of this acid are described in sub-division (9) of this section.

(8) Derivatives of 1:4-Iodonaphthalene Sulphonic Acid.

(a) 1:4-Iodonaphthalene Sulphonyl Chloride.

The sulphonyl chloride is the only derivative referred to in the literature. It was prepared like that of the 1:4-chloro-acid by triturating the potassium salt with phosphorus pentachloride and then adding a large excess of cold water. It crystallized from acetone or alcohol as pale yellow prisms, m.p. 121°C. Armstrong (Brit. Assoc. Report, 1887, 231) gives m.p. 123°C.

(b) 1:4-Iodonaphthalene Sulphonamide.

This was obtained by boiling the sulphonyl chloride with strong ammonia solution until it dissolved and cooling the solution after considerable evaporation. On recrystallization from water, the sulphonamide separated as pale yellow prisms, m.p. 202°C. An identical product was obtained by treating an alcoholic solution of the sulphonyl chloride with ammonia. (Found I, 37.2%; $C_{10}H_6I.SO_2.NH_2$ requires I, 38.1%).

(c) 1:4-Iodonaphthalene Sulphoanilide.

The sulphoanilide was prepared by adding a slight excess of aniline to an alcoholic solution of the sulphonyl chloride and evaporating until the solid separated on cooling. Recrystallized from alcohol, it separated as pale yellow prisms, m.p. 133°C. (Found I, 30.5%; $C_{10}H_6I.SO_2.NH.C_6H_5$ requires I, 31.0%).

(d) 1:4-Iodonaphthalene Sulpho-o-toluidide.

This was prepared in a similar manner to the sulphoanilide, from the sulphonyl chloride and o-toluidine. Crystallized from alcohol as pale yellow prisms, m.p. 138°C.

(Found I, 29.9%; $C_{10}H_6I.SO_2NH.C_6H_4.CH_3$ requires I, 30.0%).

Barium, calcium and lead 1:4-iodonaphthalene sulphonates are precipitated by adding solutions of soluble barium, calcium and lead salts to a solution of the potassium iodo-sulphonate. They are colourless salts, practically insoluble in hot or cold water. The calcium and lead salts are soluble in hot dilute hydrochloric acid, but the barium salt is not. They have not been analysed.

(9) Derivatives of Naphthalene-α-Sulphonic Acid.

It has been noted that potassium naphthalene-α-sulphonate was a secondary product in the preparation of potassium 1:4-iodonaphthalene sulphonate. Naphthalene-α-sulphonates were formed as the main products in one or two of the reactions to be described, and a number of reference compounds by which they might be identified were therefore prepared.

(a) Naphthalene-α-Sulphonyl Chloride.

Prepared in the usual manner by treating the potassium salt with phosphorus pentachloride, the sulphonyl chloride crystallized from acetone as colourless prisms, m.p. 65°C. Various authorities give 65-67°C. as the melting point.

(b) Naphthalene-α-Sulphonamide.

Prepared by boiling the sulphonyl chloride with ammonia solution, the sulphonamide crystallized from water as colourless prisms, m.p. 149°C. Kimberly (Annalen, 1860, 114, 135) gives m.p. 150°C.

(c) Naphthalene-α-Sulphoanilide.

When the sulphonyl chloride derived from the "by-product" potassium naphthalene-α-sulphonate was boiled in water with a slight excess of aniline, and the solid product crystallized from alcohol, the latter was found to melt at 152°C. (Found S, 11.2%; $C_{10}H_7.SO_2NH.C_6H_5$ requires S, 11.3%). Carleson (Bull. Soc. Chim., 1877, 27, 360), however, gives the melting point of the α-sulphoanilide as 112°C. An identical product was obtained, m.p. 152°C., when an alcoholic solution of the sulphonyl chloride was treated with aniline.

When the sulphoanilide was prepared from a pure specimen of naphthalene-α-sulphonic acid through the sulphonyl chloride, it was found to melt at 153°C., a mixed melting point with the product obtained above showing no depression.

(d) Naphthalene-α-Sulpho-o-toluidide.

This was prepared in a similar manner to the sulphoanilide from the sulphonyl chloride and o-toluidine. It separated from alcohol as colourless plates, m.p. 134°C. (Found S, 10.9%; $C_{10}H_7.SO_2NH.C_6H_4.CH_3$ requires S, 10.8%).

(e) Naphthalene-α-Sulpho-p-nitroanilide.

Prepared in a similar manner to the corresponding 1:4-chloro derivative from the sulphonyl chloride and p-nitroaniline, the sulpho-p-nitroanilide separated from alcohol as pale yellow prisms, m.p. 205°C. (Found S, 9.7%; $C_{10}H_7.SO_2NH.C_6H_4.NO_2$ requires S, 9.7%).

The sulpho-o-toluidide and sulpho-p-nitroanilide are not recorded in the literature.

(10) Attempts to Prepare 1:1'-Dinaphthyl-4:4'-Disulphonic Acid from Salts and Derivatives of 1:4-Iodonaphthalene Sulphonic Acid.

The potassium salt and derivatives of 1:4-iodonaphthalene sulphonic acid, whose preparation is described in (7) and (8) of this section, were employed in these attempts to effect diaryl-formation by means of the Ullmann reaction using powdered metals.

(a) Employing Potassium 1:4-Iodonaphthalene Sulphonate.

5 gm. of potassium 1:4-iodonaphthalene, together with a small crystal of cupric sulphate, were dissolved in about 100 c.c. of water and the solution boiled under reflux with excess (1.5 gm.) of copper powder for an hour. After filtering, concentrating and cooling, the crystalline salt which separated was removed and treated with phosphorus pentachloride in the usual manner. From the melting point of the sulphonyl chloride obtained (121°C.) it was evident that no reaction had occurred.

When, however, the experiment was repeated giving three hours of reflux, the product isolated (much more soluble than the potassium iodo-sulphonate) yielded a sulphonyl chloride melting at 64°C. and a sulphonamide melting at 149°C. These melting points prove that the product obtained was potassium naphthalene-α-sulphonate. Thus, on boiling with copper powder, the iodine was gradually replaced by hydrogen. There was no evidence of diaryl-formation having occurred even to a small extent.

In a similar fashion, iodine was replaced by hydrogen when an aqueous solution of the potassium iodo-sulphonate was refluxed with zinc dust or magnesium powder. The replacement was more rapid than in the case of copper, however.

(b) <u>Employing 1:4-Iodonaphthalene Sulphonamide</u>.

When the sulphonamide was refluxed in nitrobenzene with magnesium powder for about two hours, it was recovered unchanged, after steam distilling the nitrobenzene. Nor was the iodine replaced when it was refluxed with zinc dust in pyridine solution.

In boiling quinoline solution (236°C.), however, the iodine was replaced on refluxing with zinc dust for 3-4 hours. The quinoline was steam distilled after filtering from excess of zinc, and the aqueous residue in the flask was proved to contain zinc iodide. The insoluble gummy substance in the residue was dissolved in alcohol, and the solution treated several times with decolourizing carbon, but only a resinous solid, which would not crystallize, was obtained. It was shown to contain no iodine, however.

(c) Employing 1:4-Iodonaphthalene Sulphoanilide.

As with the sulphonamide, the iodine in the sulphoanilide was unaffected on refluxing with zinc dust in pyridine. Nor did copper powder in the same solvent react with it.

The iodine was replaced, as in the sulphonamide, when a solution of the sulphoanilide in quinoline was refluxed with copper powder or zinc dust for several hours, but again only a gummy resinous product was isolated after steam distillation. This resisted all attempts to purify it by crystallization from alcohol.

(11) Reaction of 1:4-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cupric Sulphate Reduced by means of Sulphur Dioxide.

In E.P.278,100, "ammoniacal solutions of cuprous oxide" are employed to prepare dinaphthyl dicarboxylic acids from diazonaphthoic acids. In Example 1 of this Patent, the reducing cuprous solution is prepared by passing sulphur dioxide through strongly ammoniacal cupric sulphate solution until the deep blue colour is discharged, and then adding sufficient ammonia to keep the liquor ammoniacal until the reaction is complete. The diazonaphthoic acid is added slowly to this solution and, when nitrogen ceases to be evolved, the dinaphthyl dicarboxylic acid is isolated by acidifying the resulting solution. In this way, 1:1'-8:8'-, 1:1'-2:2'-, and 2:2'-3:3'- dinaphthyl dicarboxylic acids are obtained.

Following the procedure suggested, an "ammoniacal solution of cuprous oxide" was prepared;-

30 c.c. of ammonia (sp. gr. 0.88) were added to a solution of 20 gm. of hydrated cupric sulphate in 300 c.c. of water. Sulphur dioxide was passed through this solution until the deep blue colour was discharged. The resulting solution was reddish in colour and contained a considerable deposit of colourless crystalline substance, inferred to be cuprous ammonium sulphite. Sufficient dilute ammonia (equivalent to 20 c.c. of the 0.88 solution) was now added to keep the solution alkaline throughout the subsequent reaction, and it was noted that the crystalline deposit dissolved to form a pale bluish-green solution.

The diazo-suspension obtained from 10 gm. of sodium naphthionate was then added to the ammoniacal cuprous solution, with mechanical agitation. After nitrogen had ceased to be evolved, the solution was concentrated to small bulk and a number of crops of mixed crystals obtained by exhaustive evaporation. These were dried and triturated with phosphorus pentachloride. A large volume of cold water was added to decompose excess of phosphorus pentachloride and dissolve inorganic salts, and a sulphonyl chloride, separating as a brownish solid, was filtered off and dried. It was crystallized from acetone, after several treatments with decolourizing carbon, and separated as colourless plates, m.p. 158°C.

It was thought at first that 1:1'-dinaphthyl-4:4'-disulphonyl chloride had been obtained, but subsequent analysis disproved this (found S, 19.5% and Cl, 21.4%). The high sulphur and chlorine contents forced the conclusion that a second sulphonyl chloride group must be attached to each naphthalene residue. Melting point and analysis point to the substance being naphthalene-1:4-disulphonyl chloride; Armstrong and Wynne (Proc. Chem. Soc., 1893, 166) give m.p. 160°C. ($C_{10}H_6(SO_2Cl)_2$ requires S, 19.7% and Cl, 21.8%). In support of this, the sulphonamide prepared by boiling the sulphonyl chloride with ammonia solution, was found to melt at 269°C. Gattermann (Berichte, 1899, <u>32</u>, 1156) states that naphthalene-1:4-disulphonamide melts at 273°C.

In the hope that a simple method for isolating the disulphonic acid as a sparingly soluble salt might be found, the disulphonyl chloride was hydrolysed by means of caustic soda solution and the readily soluble sodium salt obtained. On treating a solution of this with solutions of calcium and barium chlorides, however, no precipitates were obtained. The yield of pure disulphonyl chloride obtained by this method was only about 3% theoretical, but it is believ-

believed that this low figure is due to the inefficiency of the method of isolation. It should be noted that no other sulphonyl chloride-forming sulphonic acid was detected in the product.

To compare this method of preparing naphthalene-1:4-disulphonic acid with that used by Gattermann (Berichte, loc. cit.), the following experiment was performed:-

The diazo-suspension obtained from 5 gm. of sodium naphthionate was saturated with sulphur dioxide. Copper powder was now added, with mechanical agitation, until no more nitrogen was evolved. After filtering from excess of copper, the solution was shaken with common salt to salt out the acid sodium naphthalene-1:4-sulphinic-sulphonate, which appeared to separate in good yield. After filtering, this salt was redissolved in water and oxidized with acid potassium permanganate. A little carbon was now added and the solution boiled, filtered and cooled. Sodium 1:4-naphthalene disulphonate was obtained from the filtrate by salting out with common salt. The disulphonate was filtered, dried and treated with phosphorus pentachloride, etc. in the usual manner. The pure disulphonyl chloride, crystallized from acetone (m.p. 158.5°C.), was obtained in approximately 20% yield.

<u>Note on "Salting Out"</u>.

In many cases in the course of this research, salting out with sodium or potassium chloride has proved effective for isolating sulphonates. But in some instances, e.g. in the isolation of naphthalene-1:4-disulphonic acid prepared by the method described first in this section, it has proved useless unless considerable preliminary treatment was applied to the product-bearing solution. When copper or ammonium salts are present in the latter, they may have to be removed before salting-out is effective. Cupric copper appears to have an inhibitory effect upon the process, while ammonium salts are frequently salted out prior to the desired sulphonate. For these reasons, the somewhat unsatisfactory process of exhaustive evaporation and subsequent treatment with phosphorus pentachloride was resorted to in several experiments.

(12) Reaction of 1:4-Diazonaphthalene Sulphonic Acid with Sodium Sulphite Solution.

Interest in the formation of naphthalene-1:4-disulphonic acid by the reactions described in (11) led to an investigation of the reaction between alkaline sulphite solution and 1:4-diazonaphthalene sulphonic acid to find out if it were possible to prepare the disulphonic acid in the absence of cuprous salts.

In a preliminary experiment, a diazo-suspension obtained from sodium naphthionate was added to a solution containing a large excess of sodium sulphite to which sufficient ammonia had been added to keep the solution alkaline until about half of the suspension had been introduced. As the solution approached neutrality during the addition, nitrogen was evolved in small quantity and, when it was acid, sulphur dioxide was evolved. When the addition was nearly complete, a fine shimmering crystalline suspension appeared in the red solution. After settling, this was filtered off and recrystallized from hot water in which it was moderately soluble.

The fine orange-red crystals so obtained were found to contain N, S and Na. The red colour of an aqueous solution of the substance was discharged on reduction with zinc and hydrochloric acid. Woollen patterns were dyed in an acid bath with the substance, and shades ranging from pale yellow to deep orange-red obtained in the fabric.

For a long time there was doubt as to the composition of the substance. It was thought at one time that 1-naphthol-4-sulphonic acid had been formed by decomposition of the diazo-compound, and that this had coupled with undecomposed diazo-compound to form the dyestuff. But when the diazo-compound was added to an alkaline solution of N.W. acid, a deep reddish violet solution was obtained which dyed wool from pink to magenta according to concentration. It was also suggested that the substance might be a stable diazo-sulphonate. The question was settled by elementary analysis which showed the substance to be disodium 1:1'-azonaphthalene-4:4'-disulphonate. (Found C, 47.6%; H, 3.1%; N, 5.5% and S, 12.7%; $(:N.C_{10}H_6.SO_3Na)_2,H_2O$ requires C, 47.6%, H, 2.8%; N, 5.6% and S, 12.7%).

This compound was now found to be described in the Colour Index (p. 178) under the name "Cuba Orange". There, its preparation by the action of sodium sulphite in sodium acetate solution upon 1:4-diazonaphthalene sulphonic acid is outlined, and a characteristic colour reaction mentioned. When Cuba Orange is added to concentrated sulphuric acid, an intense blue solution is obtained which reverts to an orange colour on dilution; this reaction was shown by the compound isolated.

An interesting property of an aqueous solution of Cuba Orange was its reaction with moderately concentrated solutions of potassium, sodium, barium, calcium and lead salts. Silky precipitates of varied and unusual crystalline forms were obtained, and it was noted that this did not occur with solutions of other metallic salts such as those of magnesium, aluminium and zinc. It is intended to examine the possibilities of using Cuba Orange as a reagent in qualitative, and perhaps quantitative, analysis in the near future.

Bucherer and Schmidt (J. prakt. Chem., 1909, 79(ii), 389) prepared 1:1'-azonaphthalene-4:4'-disulphonic acid by treating 1-hydrazinonaphthalene-4-sulphonic acid with sodium sulphite. Interest in the mechanism of the various reactions resulting in the formation of Cuba Orange justified a short series of experiments, varying the conditions under which the diazo-compound and sodium sulphite react:-

(a) <u>Diazo-suspension added to neutral sodium sulphite with subsequent acidification</u>.

The diazo-suspension obtained from 10 gm. of sodium naphthionate was poured into a cold solution of 20 gm. of crystallized sodium sulphite in 200 c.c. of water. The diazo-compound dissolved without marked evolution of gas to form an orange-red solution, and to this was added about 50 c.c of dilute hydrochloric acid. Sulphur dioxide, and presumably nitrogen, were evolved with simultaneous separation of Cuba Orange. Yield approximately 60%.

(b) <u>Diazo-compound added to sodium sulphite in sodium acetate solution</u>.

The solid diazo-compound (suspension filtered) from 10 gm. (1 mol.) of sodium naphthionate was added slowly to a solution of 13 gm. (1 mol.) of $Na_2SO_3.7H_2O$ and 10 gm. of sodium acetate in 100 c.c. of water. The diazo-compound appeared to dissolve and then an orange-red solid separated. A small amount of gas, probably nitrogen, was evolved, but there was no trace of sulphur dioxide. After keeping overnight the solid was filtered off and proved to be Cuba Orange. Yield approximately 35%.

(c) <u>Diazo-compound added to sodium sulphite in sodium acetate solution, with subsequent acidification</u>.

The solid diazo-compound from 10 gm. of sodium naphthionate was added to a solution of 13 gm. of $Na_2SO_3.7H_2O$ and 10 gm. of crystalline sodium acetate in 100 c.c. of water, with vigorous agitation. A slight evolution of nitrogen occurred, and an orange suspension was formed. On acidifying with dilute hydrochloric acid, copious evolution of sulphur dioxide, presumably mixed with nitrogen, took place and Cuba Orange separated. In this case the yield was approximately 65%.

(d) 1-Hydrazinonaphthalene-4-sulphonic acid prepared and treated with sodium sulphite.

6 gm. of 1:4-diazonaphthalene sulphonic acid were suspended in 50 c.c. of water and added to 25 gm. of stannous chloride in 100 c.c. of concentrated hydrochloric acid and 10 c.c. of water. The mixture was stirred vigorously for three hours and then heated on a water bath for one hour, the colour changing from yellow to white. A complex stannichloride was obtained which was filtered, dissolved and decomposed in boiling dilute caustic soda solution, the free hydrazine sulphonic acid being precipitated as a micro-crystalline white solid on addition of concentrated hydrochloric acid. (Found S, 13.3%; $NH_2.NH.C_{10}H_6.SO_3H$ requires S, 13.4%).

This hydrazine sulphonic acid, on heating with aqueous sodium sulphite, did not undergo any immediate change, and though Bucherer and Schmidt stated that the azo-compound is formed on heating with sodium sulphite for eight hours, the reaction appears to be much too slow to be intermediate in the formation of Cuba Orange from the diazo-compound and sodium sulphite.

(e) Other tests.

It has been noted (sub-division 3g) that the diazo-compound is unaffected by SO_2 in acid solution.

When the diazo-compound was suspended in dilute hydrochloric acid and treated with sodium sulphite, there was no apparent change, but if dilute acetic acid was used instead, reaction took place on the addition of sodium sulphite, and Cuba Orange was formed with evolution of nitrogen and sulphur dioxide.

The foregoing experiments indicate that for the formation of Cuba Orange, the sodium sulphite should be alkaline, neutral or only mildly acidic before addition of the diazo-compound; and that it is desirable to render the solution distinctly acid after the addition of diazo-compound to obtain good yields.

Rejecting the idea that the hydrazine sulphonic acid is an intermediate product in the formation of Cuba Orange because of observations made in (d), it seems likely that the intermediate compound is a diazo-sulphonate, stable under alkaline or mildly acidic conditions but converted into the azo-compound by excess of acid.

Attempts were made to isolate such a diazo-sulphonate by conducting the reaction at low temperatures, but no product other than Cuba Orange was obtained. The suggestion is, however, amply supported by the results of experiments with 2:1-diazonaphthalene sulphonic acid (described later), and by the findings of Hantzsch and Schmiedel (Berichte, 1897, 30, 81) who isolated a diazo-sulphonate as intermediate product in the preparation of 1:1'-azonaphthalene from diazotized α-naphthylamine and potassium sulphite solution.

(13) Reaction of 1:4-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cuprous Sulphate.

A second form of "ammoniacal cuprous oxide solution" described in E.P.278,100 (Example 6) is prepared by reducing ammoniacal cupric sulphate solution with hydroxylamine, and doubtless contains the complex, $Cu_2(NH_3)_4SO_4$, tetrammino-cuprous sulphate. Such a solution was prepared in the following manner:-

20 gm. of hydrated cupric sulphate were dissolved in 150 c.c. of water, and 20 gm. of 0.88 ammonia added to the solution. A mixture of 9 gm. of hydroxylamine hydrochloride and 7 gm. of potassium hydroxide in 100 c.c. of water was now added, the resulting solution, after effervescence had ceased, being pale green in colour.

The solid diazo-compound obtained from 10 gm. of sodium naphthionate was added gradually, with stirring, to this solution at lab temperature. Nitrogen was evolved, but an orange-red micro-crystalline solid separated from the solution almost simultaneously in considerable yield. This product was filtered off and recrystallized from hot water, separating as minute diamond-shaped plates of similar form to those obtained when a potassium salt was added to a solution of Cuba Orange. The substance gave the same colour change as Cuba Orange on dissolving in concentrated sulphuric acid and subsequent dilution. It was found to contain nitrogen, potassium and water of crystallization. (Found S, 11.6% and H_2O at 145°C., 7.3%; $(:N.C_{10}H_6SO_3K)_2,2H_2O$ requires S, 11.6% and H_2O, 6.9%).

The principal product of this reaction was therefore dipotassium 1:1'-azonaphthalene-4:4'-disulphonate. No sulphonyl chloride-forming products were isolated on evaporating the filtrate.

(14) Reaction of 1:4-Diazonaphthalene Sulphonic Acid with Sulphurous Acid in the Presence of Pyridine.

In an attempt to effect direct diaryl-formation, sulphur dioxide was passed into a suspension of the 1:4-diazo-compound containing pyridine. Nitrogen was evolved and, after making alkaline with potassium hydroxide and concentrating, a yellowish salt was isolated which proved to be potassium naphthalene-α-sulphonate (yielding a sulphonyl chloride and sulphonamide melting at 63° and 147°C. respectively).

In a similar experiment with sodium meta-bisulphite solution, but without addition of pyridine, the same reaction occurred the diazo-group being replaced by hydrogen with formation of naphthalene-α-sulphonic acid.

(15) Various Experiments without Conclusive Results.

The following attempts to effect direct diaryl-formation with 1:4-diazonaphthalene sulphonic acid are recorded very briefly since no identified products were isolated:-

(a) Dilute ammonia was added to a suspension of the diazo-compound in ferrous sulphate solution. Nitrogen evolved and ferrous hydroxide precipitated in deep-red solution - boiled with carbon, filtered and filtrate concentrated - brown tarry semi-crystalline product obtained yielding no sulphonyl chloride with phosphorus pentachloride.

(b) Diazo-suspension poured into ferrous sulphate solution containing pyridine - nitrogen evolution slow, accelerated by warming. Highly coloured product isolated as in (a), yielding no sulphonyl chloride.

(c) Diazo-suspension poured into aqueous suspension of cuprous oxide - nitrogen evolved slowly - allowed to stand until complete - concentrated, treated with caustic potash and filtered. On further concentration, water-soluble tar obtained which did not yield sulphonyl chloride.

(d) Zinc dust added to solution of stable diazotate in caustic soda in cold - nitrogen not evolved. Copper powder then added - slow nitrogen evolution. Filtered and concentrated, obtaining highly coloured product which did not yield a sulphonyl chloride.

(e) Diazo-suspension poured into strong aqueous solution of ammonium sulphite. Nitrogen not evolved so copper powder added. Nitrogen now evolved, but no sulphonyl chloride obtained after filtering, concentrating and treating isolated solute with phosphorus pentachloride.

(16) Attempts to Prepare Sulpho-Derivatives of Naphthionic Acid.

Treatment of 1:4-diazonaphthalene sulphonic acid with various reducing reagents had failed to yield the dinaphthyl disulphonic acid, and it was therefore decided to investigate the possibilities of applying similar treatments to diazotized 1:4-aminonaphthalene sulpho-derivatives (none of which are recorded in the literature).

E.P. 331,596 describes a method for preparing aromatic amino-sulphochlorides by the action of chlorosulphonic acid on amino-sulphonic acids.

The procedure adopted in an attempt to prepare 1:4-aminonaphthalene sulphonyl chloride from naphthionic acid was that employed in the patent for preparing 4:3-chloroaniline sulphonyl chloride:-

10 gm. of naphthionic acid were added gradually, with mechanical agitation, to 50 gm. of redistilled chlorosulphonic acid in a flask cooled in ice. After standing for an hour, the flask was heated on a water bath for six hours, and the contents, after cooling, were poured on to ice. No solid separated and the dark coloured solution was evaporated until acid fumes were evolved. On slight dilution with water, a greyish crystalline precipitate was formed which was collected and recrystallized from hot water after treatment with decolourizing carbon. The colourless spangles obtained were found to contain no chlorine. No sulphonyl chloride was obtained on treatment with phosphorus pentachloride, and the substance could be diazotized and coupled with alkaline β-naphthol. It was obtained in good yield, and is probably an α-naphthylamine disulphonic acid.

In an endeavour to prepare the sulphoanilide and sulphonaphthylamides of naphthionic acid, the latter was treated in various ways with aniline and α- and β-naphthylamines. The desired products were not obtained, however, the following reactions taking place:-

(a) Formation of Phenyl-α-Naphthylamine.

An excess of aniline was refluxed with naphthionic acid for about three hours and the excess then removed by extraction with dilute hydrochloric acid. By extracting the residue with alcohol, decolourizing with carbon and recrystallizing several times from the same solvent, a compound containing no sulphur, which had properties similar to diphenylamine, was isolated, m.p. 58°C. (Found N, 6.4%). It was noted that sulphur dioxide was produced during reflux, and the odour of α-naphthylamine was also detected.

The substance appears to be phenyl-α-naphthylamine which is generally prepared by heating α-naphthylamine with aniline salts at about 250°C. (Requires N, 6.4%). Friedlander (Berichte, 1883, <u>16</u>, 2085) states that this compound melts at 60°C. A bromo-derivative was prepared by adding bromine water in slight excess to a glacial acetic acid solution of the compound, and was found to melt at 145°C., though Streiff (Annalen, 1881, <u>209</u>, 155) records m.p. 137°C. for the tribromo-derivative obtained in the same way. The nitroso-derivative, after three crystallizations, gave m.p. 86°C.; Fischer (Berichte, 1887, <u>20</u>, 1247) records m.p. 92°C.

(b) Formation of Aniline Naphthionate.

By treating an excess of naphthionic acid with aniline in boiling water, a solution of aniline naphthionate was obtained from which, after filtering, the salt crystallized on cooling as greyish clusters. It did not melt, but gave off water on heating. (Found N, 7.6%; $C_6H_5.NH_3.SO_3.C_{10}H_6.NH_2,3H_2O$ requires N, 7.6%). On destructive distillation, the only product identified was α-naphthylamine.

(c) Formation of β-Naphthylamine Naphthionate.

Equivalent quantities of naphthionic acid and β-naphthylamine were refluxed in nitrobenzene for about 4 hours, and the residual solid (after cooling) was extracted with hot water. A salt, resembling aniline naphthionate, was isolated which did not melt and contained water of crystallization. It appeared to be β-naphthylamine naphthionate. (Found, N, 6.6%; $C_{10}H_7.NH_3.SO_3.C_{10}H_6.NH_2,3H_2O$ requires N, 6.7%). This salt was also obtained by adding a solution of β-naphthylamine hydrochloride to sodium naphthionate solution.

(d) Formation of ββ-Dinaphthylamine.

When β-naphthylamine naphthionate was distilled destructively, a considerable quantity of distillate, which quickly solidified, was collected and a product also sublimed in the neck of the flask. The odours of sulphur dioxide and naphthylamine were detected during the distillation. The distillate, when crystallized from alcohol, yielded a small crop of yellowish crystals. On recrystallization from alcohol, after treatment with decolourizing carbon, this product was found to melt at 169°C., and to contain no sulphur.

The nature of the decomposition suggested that the product was either ββ-dinaphthylcarbazole, for which melting point 169-170°C. is recorded, or ββ-dinaphthylamine, m.p. 170.5°C. The picrate was therefore prepared, and found to melt at 160°C. Since the picrate of the carbazole is stated to melt at 221°C., and that of the dinaphthylamine at 164-65°C., it was inferred that ββ-dinaphthylamine was one of the decomposition products. Both α- and β-naphthylamines were also found in the distillate.

(e) Formation of α-Naphthylamine Naphthionate.

This salt was obtained by the two treatments which yielded the β-salt, and had similar properties. (Found N, 6.6%; $C_{10}H_7.NH_3.SO_3.C_{10}H_6.NH_2,3H_2O$ requires N, 6.7%).

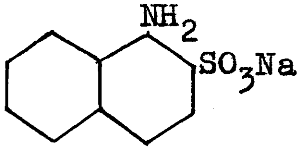
On destructive distillation, only α-naphthylamine was identified in the distillate.

It was apparent therefore that if these naphthionates were converted at one stage by heat to sulphoarylamides with loss of water, the latter are liable to decompose at higher temperatures, forming secondary amines.

II. 1-NAPHTHYLAMINE-2-SULPHONIC ACID. (o-Naphthionic Acid).

(1) Sodium 1-Naphthylamine-2-Sulphonate.

The sample of sodium o-naphthionate supplied was 99.5% pure, and was used without further purification. The salt is anhydrous -

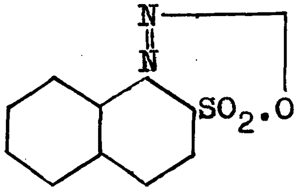


M.W. 245.

(2) Diazotization of o-Naphthionic Acid.

o-Naphthionic acid was readily diazotized by the direct method:-

10 gm. of the sparingly soluble sodium salt were dissolved in 300 c.c. of hot water, and the necessary volume of dilute sulphuric acid (equivalent to 2¼ mol. of the salt) added. The fine suspension of o-naphthionic acid obtained was cooled and diazotized by the addition of sodium nitrite solution (containing 3.0 gm. $NaNO_2$) at room temperature with mechanical agitation. Diazotization was rapid, and the sparingly soluble diazo-compound was easily filtered. It has the structure -



(3) Preparation of Sodium and Potassium 1:2-Iodonaphthalene Sulphonates.

1:2-Iodonaphthalene sulphonic acid was prepared according to the method of Barber and Smiles (J.C.S., 1928, 1148) by heating 1:2-diazonaphthalene sulphonic acid with hydriodic acid:-

The solid diazo-compound from 10 gm. of sodium o-naphthionate was added to a solution of 15 gm. of potassium iodide in 100 c.c. of dilute sulphuric acid (3N). The mixture was heated gradually, with constant stirring, until nitrogen was being evolved at a moderate rate, at which temperature it was maintained until the reaction was complete (considerable quantity of iodine liberated). On cooling, a large crop of crystals (free iodo-acid) separated in the deeply coloured solution. This was filtered off, suspended in about 100 c.c. of water and neutralized with sodium hydroxide. After heating to effect solution, some carbon was added and the hot solution filtered, the sodium salt crystallizing from the filtrate on cooling.

When the potassium salt was required, it was usual to neutralize the hot solution containing the free acid with potassium hydroxide, the latter serving to remove the liberated iodine. The potassium salt which is sparingly soluble in cold water, separated in large yield. It was recrystallized from hot water. The two salts were identified by conversion to the derivatives described below.

(4) Derivatives of 1:2-Iodonaphthalene Sulphonic Acid.

(a) 1:2-Iodonaphthalene Sulphonyl Chloride.

Prepared by treating the sodium or potassium salt obtained above with phosphorus pentachloride, etc., the sulphonyl chloride crystallized from acetone-water as pale yellow needles, m.p. 94°C. Barber and Smiles also record m.p. 94°C.

(b) 1:2-Iodonaphthalene Sulphonamide.

A quantity of the sulphonyl chloride was dissolved in acetone and excess of dilute ammonia solution added. The solution was evaporated to small bulk and cooled, the sulphonamide separating as colourless prisms, which were recrystallized from acetone-water, m.p. 247°C. No reference to this derivative was found in the literature. (Found I, 38.1%; $C_{10}H_6I.SO_2NH_2$ requires I, 38.1%).

(5) Reaction of Sodium and Potassium 1:2-Iodonaphthalene Sulphonates in Aqueous Solution with Copper Powder.

In "The Formation of Dinaphthyl Disulphonic Acids" (J.Roy.Tech.College, 1937, 4(i), 62) the author recorded his failure to corroborate Barber and Smiles' method of preparing 1:1'-dinaphthyl-2:2'-disulphonic acid by refluxing potassium 1:2-iodonaphthalene sulphonate with copper powder in aqueous solution (containing a little cupric sulphate). One of the numerous attempts (using both the potassium and sodium iodo-sulphonates) to repeat the preparation, the quantitative aspect of which is not referred to in Barber and Smiles' paper, was recorded as follows:-

7 gm. of sodium 1:2-iodonaphthalene sulphonate were dissolved in 150 c.c. of water, along with a few crystals of cupric sulphate, and the solution refluxed for an hour with excess of copper powder. After filtering from cuprous iodide and excess of copper powder, hydrogen sulphide was passed through the solution for a few minutes, the solution then being boiled and filtered through carbon. The filtrate was now saturated with sodium chloride and the white crystalline salt which separated was filtered off, dried and treated with phosphorus pentachloride. The sulphonyl chloride obtained was recrystallized from acetone-water, m.p. 76°C. The sulphonamide derived from this sulphonyl chloride by treating an acetone solution with aqueous ammonia was found to melt at 212°C. These two melting points agree exactly with those recorded in the literature for naphthalene-β-sulphonyl chloride and β-sulphonamide respectively. Barber and Smiles give the melting point of 1:1'-dinaphthyl-2:2'-disulphonyl chloride as 202-203°C.

Many modifications of this treatment were employed - e.g. the quantity of cupric sulphate added was altered, a different form of copper bronze employed, the period of reflux and concentration of the solution were varied, the product was isolated by evaporation instead of salting out, etc. - but in all cases, naphthalene-β-sulphonates were the only products identified.

When Professor Smiles wrote of the small yield of dinaphthyl disulphide (2 gm.) obtained by reducing the dinaphthyl disulphonyl chloride prepared from 300 gm. of the potassium iodo-sulphonate, it was apparent that only a very small yield of dinaphthyl disulphonate was to be expected, and that the failures recorded above were probably due to inadequate quantities of starting material. However, in his letter, he referred the author to a paper by Hurtley (J.C.S., 1929, 1870) who adopted a special method for improving the yield of diphenic acid obtained by heating potassium o-bromobenzoate with copper powder. On identical lines, the following experiment was therefore performed:-

An intimate mixture of 8 gm. of dry finely-powdered potassium 1:2-iodonaphthalene sulphonate and 10 gm. of copper powder was heated to 100°C. on a water bath, and 6 c.c. of water added, with stirring. The water evaporated in a short time, but heating was continued for two hours. The mixture was then extracted with hot water and filtered. No reaction had occurred, as the iodo-sulphonate was recovered unchanged, no other product being identified on treating the solute with phosphorus pentachloride.

In the same paper, Hurtley mentions the use of cupric acetate as a catalyst in the Ullmann reaction and, thanks to this hint, an eleventh hour experiment yielded confirmation of Barber and Smiles' work, using a reasonably small quantity of starting material:-

30 gm. of potassium 1:2-iodonaphthalene sulphonate were dissolved in 300 c.c. of water and two or three drops of a saturated cupric acetate solution solution added, along with 20 gm. of copper powder. The mixture was refluxed for five hours, after which it was filtered and salted out with sodium chloride. A large quantity of colourless salt separated, which was filtered off, dried and triturated with phosphorus pentachloride. The oily sulphonyl chloride which separated on addition of cold water was allowed to solidify, and was then filtered off, dried and dissolved in acetone in which it was very soluble. By the careful addition of water to the acetone solution, a small quantity of colourless sulphonyl chloride separated (solid), which was filtered off and recrystallized several times from acetone-water - colourless needles, m.p. 203°C. (starting to soften at 200°C.). This melting point agrees with that recorded by Barber and Smiles for 1:1'-dinaphthyl-2:2'-disulphonyl chloride. The yield of pure disulphonyl chloride (0.6 gm.) was approximately 5% theoretical.
The sulphonyl chloride in the filtrate from the dinaphthyl derivative was separated by the addition of more water, and

was shown to be naphthalene-β-sulphonyl chloride, m.p. 76°C., after recrystallization from acetone-water.

It is possible that the slight acidity imparted to the solution by cupric sulphate (used as catalyst in earlier attempts) may have influenced the course of the reaction with copper powder in favour of complete replacement by hydrogen, when relatively small quantities of starting material were employed. By using cupric acetate instead, acidity would be kept to a minimum.

(6) Preparation of Sodium 1:2-Bromonaphthalene Sulphonate.

No reference was found to 1:2-bromonaphthalene sulphonic acid in the literature. The method by which it, and the 1:8- and 2:1-bromo-acids, were prepared emerged from a search for new cuprous reducing agents to apply to diazonaphthalene sulphonic acids in the hope of bringing about direct diaryl formation.

When cuprous oxide is boiled with ammonium bromide solution, a sparingly soluble cuprous complex, believed to be diammino-cuprous bromide, is formed. It was noted that when diazonaphthalene sulphonic acids were added to a suspension of a small amount of this complex in ammonium bromide solution, nitrogen was evolved at room temperature. The action of the complex was apparently catalytic, and the rate of nitrogen evolution was increased when larger quantities of the complex were present. The products of the reaction proved to be bromonaphthalene sulphonic acids (as ammonium salts):-

A solution of 24 gm. of ammonium bromide in 200 c.c. of water was boiled with 1 gm. of cuprous oxide for about five minutes, and the solution then filtered and cooled. The solid diazo-compound obtained from 20 gm. of sodium o-naphthionate was added gradually to the filtrate, in the form of an aqueous paste, with mechanical agitation. Nitrogen was evolved rapidly and a pink shimmering substance separated immediately. When all the diazo-compound had been added and the reaction had ceased, this substance was filtered off. It was proved to be ammonium 1:2-bromonaphthalene sulphonate (by subsequent analysis of derivatives), and was obtained in approximately 85% yield.

Sodium 1:2-bromonaphthalene sulphonate was obtained from the ammonium salt by boiling the latter with caustic soda solution. It crystallized from hot water as colourless hexagonal plates.

(7) <u>Derivatives of 1:2-Bromonaphthalene Sulphonic Acid</u>.

(a) <u>1:2-Bromonaphthalene Sulphonyl Chloride</u>.

The sodium or ammonium salt prepared above, on treatment with phosphorus pentachloride, etc., yielded a sulphonyl chloride which was recrystallized once or twice from acetone-water (using decolourizing carbon), separating as almost colourless elongated prisms (containing bromine), m.p. 93°C. (Found S, 10.5%; $C_{10}H_6Br.SO_2Cl$ requires S, 10.5%).

(b) 1:2-Bromonaphthalene Sulphonamide.

A quantity of the sulphonyl chloride was dissolved in acetone and the solution warmed with aqueous ammonia. The sulphonamide separated readily, being insoluble in cold water, acetone and alcohol, and only slightly soluble in hot aqueous ammoniacal alcohol from which it was crystallized. It separated from this solvent as colourless prisms, m.p. 271°C. (Found S, 11.2%; $C_{10}H_6Br.SO_2NH_2$ requires S, 11.2%).

(8) Attempt to Prepare 1:1'-Dinaphthyl-2:2'-Disulphonic Acid from Sodium 1:2-Bromonaphthalene Sulphonate.

6 gm. of sodium 1:2-bromonaphthalene sulphonate were dissolved in 150 c.c. of hot water containing a little cupric sulphate, and the solution was refluxed with 3 gm. of copper powder for two hours. It was then filtered hot and, on cooling, the sodium bromo-sulphonate separated unchanged from the filtrate (shown by formation of sulphonyl chloride, m.p. 93°C.). No other product was isolated from the filtrate, nor was there any sign of cuprous bromide-formation during reflux.

(9) Reaction of 1:2-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cupric Sulphate Reduced by means of Sulphur Dioxide.

The reagent employed (Example 1 of E.P. 278,100) was prepared by passing sulphur dioxide through an ammoniacal solution of 40 gm. of hydrated cupric sulphate, and adding excess of ammonia to the reduced solution, as described in section I.(11).

An aqueous suspension of the solid diazo-compound obtained from 20 gm. of sodium o-naphthionate was added to this solution gradually through a dropping funnel dipping beneath the surface, with mechanical agitation. Nitrogen was evolved rapidly and, when this had ceased, the solution was acidified with hydrochloric acid and evaporated to about one third of its original volume. On cooling, a crop of crystals separated, which were filtered off, dried and treated with phosphorus pentachloride. The insoluble residue, after addition of cold water, was found to consist mainly of cuprous chloride, but a small portion dissolved in acetone and proved, on purification, to be naphthalene-β-sulphonyl chloride, m.p. 76°C.

The mother liquor from the first crop was evaporated to obtain the total solute, which was dried and treated with phosphorus pentachloride. A considerable insoluble residue was left after addition of water, and this was found to be almost completely soluble in acetone. It would not crystallize from either acetone-water or acetone, however, and chloroform was used. Recrystallized from the latter, after treatment with decolourizing carbon, it was found to melt at 200°C. (colourless parallelograms), but to contain no chlorine - showing that it could not be the dinaphthyl disulphonyl chloride. Analysis proved it to be naphthalene-1:2-disulphonic anhydride. (Found 23.0% S; $C_{10}H_6(SO_2)_2O$ requires S, 23.6%). Armstrong and Wynne (Proc.Chem.Soc.,1893, 166) give m.p. 198°C. for this derivative.

(10) Reaction of 1:2-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cuprous Sulphate.

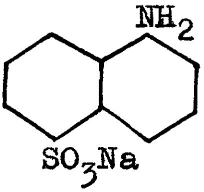
The tetrammino-cuprous sulphate solution (Example 6 of E.P. 278,100) was prepared in the manner described in section I.(13) by reducing an ammoniacal solution of 20 gm. of hydrated cupric sulphate with hydroxylamine.

To this solution, the solid diazo-compound from 10 gm. of sodium o-naphthionate was added as a thin aqueous paste. Nitrogen was rapidly evolved and a deep red solution resulted. Sodium hydroxide was then added and the solution boiled to eliminate ammonia and precipitate the copper. After filtering through carbon, the filtrate was salted out with sodium chloride and a bright red compound separated in large yield. This compound gave an intense blue colour with concentrated sulphuric acid, the normal red colour being restored when the solution was diluted (similarity to Cuba Orange). Readily soluble in water, it was crystallized from aqueous alcohol, separating as a red micro-crystalline meal of curious crystalline form. It was shown to contain nitrogen and sodium, and analysis proved it to be disodium 1:1'-azonaphthalene-2:2'-disulphonate. (Found S, 13.2%; $(:N.C_{10}H_6.SO_3Na)_2$ requires S, 13.2%).

III. 1-NAPHTHYLAMINE-5-SULPHONIC ACID. (Laurent Acid).

(1) Preparation of Sodium 1-Naphthylamine-5-Sulphonate.

Almost pure Laurent acid was available, and the sodium salt was prepared by dissolving it in hot caustic soda solution, filtering through carbon, concentrating the filtrate considerably and allowing to crystallize. The sodium salt crystallizes with one molecule of water -



.H_2O M.W. 263.

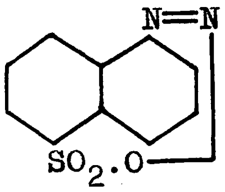
(2) Diazotization of Laurent Acid.

Laurent acid was effectively diazotized by both the direct and indirect methods.

Direct:- 10 gm. of the sodium salt were dissolved in 300 c.c. of water and Laurent acid precipitated in a fine form by adding dilute sulphuric acid (equivalent to 2¼ mol. of the salt). The suspension was then diazotized by adding sodium nitrite solution (containing 2.6 gm. $NaNO_2$) during the course of 1½ hours, with mechanical agitation.

Indirect:- 5 gm. of the sodium salt were dissolved in 200 c.c. of water with 1.3 gm. of sodium nitrite. This solution was poured, with mechanical agitation, into dilute hydrochloric acid containing 7 gm. concentrated acid, at room temperature.

The stable greyish diazo-suspension filtered readily. The diazo-compound has the structure -



(3) Preparation of Potassium 1:5-Iodonaphthalene Sulphonate.

The preparation of 1:5-iodonaphthalene sulphonic acid from 1:5-diazonaphthalene sulphonic acid is described by Mauzelius (Berichte, 1889, 22, 2823).

The diazo-suspension (indirect method) from 10 gm. of sodium 1-naphthylamine-5-sulphonate was added to a hot solution of 15 gm. of potassium iodide acidified with about 100 c.c. of 5N sulphuric acid. When the reaction had ceased, the potassium iodo-sulphonate was isolated by neutralizing with potassium hydroxide and concentrating.

On treatment with phosphorus pentachloride, the potassium salt yielded a sulphonyl chloride, m.p. 113°C., from which a sulphonamide, m.p. 236°C., was prepared by the action of ammonia. Mauzelius (loc. cit.) records m.ps. 114° and 239°C. respectively for 1:5-iodonaphthalene sulphonyl chloride and sulphonamide.

(4) Reaction of Potassium 1:5-Iodonaphthalene Sulphonate in Aqueous Solution with Copper Powder and Zinc Dust.

A solution of 5 gm. of potassium 1:5-iodonaphthalene sulphonate and a few small crystals of cupric sulphate in 100 c.c. of water was refluxed with excess of copper powder for four hours. No reaction was apparent and on recovering the solute after filtration it was found to be unchanged potassium iodo-sulphonate (by preparing the sulphonyl chloride).

When a similar experiment was carried out using zinc dust in place of copper powder, the product isolated was shown to be potassium naphthalene-α-sulphonate, identified by preparing the sulphonyl chloride and sulphonamide (m.p. 65°C. and 149°C. respectively). The iodine had thus been replaced by hydrogen.

(5) <u>Reaction of 1:5-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cupric Sulphate Reduced by means of Sulphur Dioxide</u>.

The ammoniacal cuprous solution employed (Example 1 of E.P. 278,100) was prepared in the manner recorded in section I.(11) by reducing an ammoniacal solution of 10 gm. of hydrated cupric sulphate by means of sulphur dioxide, adding finally an adequate excess of ammonia.

To this was added, with mechanical agitation, the diazo-suspension (indirect diazotization) obtained from 5 gm. of sodium 1-naphthylamine-5-sulphonate. Nitrogen was evolved, and the total solute was obtained by evaporation of the resulting solution. After drying, the mixed solute was triturated with phosphorus pentachloride, and a sulphonyl chloride isolated by adding a large volume of cold water. This was crystallized from acetone, separating as colourless needles, m.p. 182°C. Analysis showed that, as in the case of the 1:4-diazo-compound, the reaction had resulted in the formation of a naphthalene disulphonic acid, this product being naphthalene-1:5-disulphonyl chloride. (Found S, 19.7%; and Cl, 21.4%; $C_{10}H_6(SO_2Cl)_2$ requires S, 19.7% and Cl, 21.8%). The melting point recorded by Armstrong (Berichte, 1882, <u>15</u>, 205) for this derivative is 183°C.

The yield of pure disulphonyl chloride obtained was approximately 11% theoretical.

(6) <u>Reaction of 1:5-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cuprous Sulphate</u>.

An ammoniacal solution of tetrammino-cuprous sulphate (Example 6 of E.P. 278,100) was prepared by reducing an ammoniacal solution of 20 gm. of hydrated cupric sulphate by means of hydroxylamine, in the manner described in section I.(13).

The diazo-compound (obtained by direct diazotization) from 10 gm. of sodium 1-naphthylamine-5-sulphonate was added in the form of an aqueous suspension, to this solution, with mechanical agitation.. Nitrogen was evolved and, when about half of the diazo-suspension had been added, a bright red compound separated. After allowing to stand for half an hour the suspension obtained was filtered, and the red crystalline product washed with a little dilute ammonia. On recrystallization from hot water, the product separated in a shimmering micro-crystalline state. With concentrated sulphuric acid it formed a rich purple solution, which reverted to orange-red on dilution (resemblance to Cuba Orange). It was shown to contain nitrogen and potassium and proved on analysis to be dipotassium 1:1'-azonaphthalene-5:5'-disulphonate. (Found S, 12.0%, and H_2O at 145°C., 3.9%; $(:N.C_{10}H_6.SO_3K)_2H_2O$ requires S, 11.9% and H_2O, 3.4%). The yield of azo-disulphonate was approximately 75% theoretical.

No sulphonyl chloride-forming product was found in the filtrate from the azo-disulphonate on evaporating and treating with phosphorus pentachloride.

Like Cuba Orange, this azo-disulphonate, in dilute aqueous solution, gave interesting crystalline precipitates with solutions of various metallic salts, those of the alkaline earth and alkali metals in particular being readily formed from quite dilute solutions. The crystalline form of these precipitates was extremely varied, for example with a solution of -

Sodium chloride - spherical nodules.
Ammonium chloride - leaflets.
Lithium chloride - elongated hexagonal plates.
Calcium chloride - fernlike clusters.
Nickel chloride - rosettes.
Hydroxylamine hydrochloride - clusters of needles.

It is interesting to note that quite dilute solutions of potassium salts also give a crystalline precipitate (of rather indefinite form), and it is assumed that in this case the process is one of "salting out."

As with Cuba Orange, it is intended to investigate the possibilities of this azo-disulphonate as an analytical reagent.

(7) Two Reactions of 1:5-Diazonaphthalene Sulphonic Acid without Definite Results.

(a) Example 5 of E.P. 278,100 describes the preparation of a third form of "ammoniacal cuprous oxide solution", in which ammoniacal cupric sulphate solution is reduced by means of ferrous sulphate.

Such a solution was prepared by dissolving 1.2 gm. of hydrated cupric sulphate in 50 c.c. of water and adding first 6.2 gm. of 25% ammonia and then a solution of 2 gm. of ferrous sulphate in 50 c.c. of water.

The diazo-suspension from 5 gm. of sodium 1-naphthylamine-5-sulphonate was added to this solution with mechanical agitation. When nitrogen ceased to be evolved, the suspension (containing ferric hydroxide) was filtered, and the filtrate boiled and treated with caustic potash to eliminate ammonia and copper. After filtering once more, the filtrate was evaporated to obtain the solute, which was highly coloured. This yielded no sulphonyl chloride on treatment with phosphorus pentachloride.

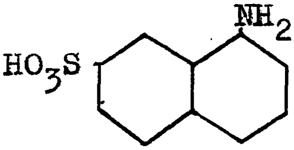
(b) A diazo-suspension was poured into an ammoniacal solution of glucose. Nitrogen was slowly evolved and a deep red solution obtained, but on working up the solute and treating it with phosphorus pentachloride, no sulphonyl chloride was isolated.

IV. 1-NAPHTHYLAMINE-7-SULPHONIC ACID. (Cleve Acid).

(1) Purification of Cleve Acid.

The Cleve acid available was a moist technical sample containing 37% of the acid, and was greyish purple in colour. Some difficulty was encountered in purifying it, partly owing to the readiness with which it undergoes atmospheric oxidation in a moist state. It was not found advantageous to isolate it as the sodium salt, and the following method of purifying it was adopted:-

The acid was dissolved in hot 3N caustic soda solution and sulphur dioxide passed through it to reprecipitate the acid. After filtering, this operation was repeated once or twice and a quantity of the acid - light grey in colour - was obtained, of sufficient purity for diazotization. Cleve acid is anhydrous -

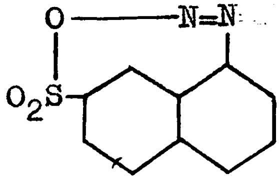


M.W. 223.

(2) Diazotization of Cleve Acid.

Owing to the tendency for coupling to occur between the diazo-compound and unchanged Cleve acid, the direct method of diazotization is unsuitable. The following method was therefore employed:-

22.3 gm. (1 mol.) of Cleve acid were dissolved in a solution of 4 gm. of caustic soda (1 mol.) in 400 c.c. of hot water. After cooling to about 3°C. by the addition of ice and adding a solution of 6.9 gm. of sodium nitrite (1 mol.), 25 gm. of concentrated hydrochloric acid (2¼ mol.) were added all at once, with vigorous stirring. There was some evolution of nitrous fumes, and a certain amount of coupling appeared to take place as the solution was deeply coloured. The diazo-solution was kept below 5°C. for half an hour by which time the solid diazo-compound had partly separated, and a little more sodium nitrite was added to complete the diazotization. It was found very difficult to filter the diazo-suspension which was almost gelatinous in consistency. The diazo-compound (dark brown) has the "inner diazo-sulphonate" structure -



(3) Preparation of Sodium 1:7-Iodonaphthalene Sulphonate.

No reference to 1:7-iodonaphthalene sulphonic acid was found in the literature.

The diazo-suspension obtained from 10 gm. of Cleve acid was added to a solution of 15 gm. of potassium iodide in 80 c.c. of 5N sulphuric acid. The mixture was heated to 50-60°C., when nitrogen was evolved fairly rapidly, and finally boiled. On cooling and standing, a quantity of deeply coloured solid separated (containing free iodine). (Note:- in a subsequent preparation, using larger quantities, it was found necessary to salt out this product). Since it was found very difficult to purify otherwise, the solid was filtered off, dried and treated with phosphorus pentachloride. The crude sulphonyl chloride isolated was purified (described below), the yield being approximately 25% theoretical. By hydrolysing with hot caustic soda solution, the sulphonyl chloride was converted into the sodium salt, which was then recrystallized from hot water (sparingly soluble in cold).

(4) Derivatives of 1:7-Iodonaphthalene Sulphonic Acid.

(a) 1:7-Iodonaphthalene Sulphonyl Chloride.

Crystallized from acetone-water, after one or two treatments with decolourizing carbon, the sulphonyl chloride separated as almost colourless needles, m.p. 141°C. (Found S, 8.9%; $C_{10}H_6I.SO_2Cl$ requires S, 9.1%).

(b) 1:7-Iodonaphthalene Sulphonamide.

The sulphonyl chloride was dissolved in acetone and strong aqueous ammonia added. The precipitate formed at first redissolved. The solution was evaporated considerably and cooled, whereupon the sulphonamide crystallized. It was recrystallized from acetone-water after one treatment with decolourizing carbon, separating as colourless needles (containing iodine), m.p. 199°C. (Found S, 9.7%; $C_{10}H_6I.SO_2.NH_2$ requires S, 9.6%).

(5) Attempt to Prepare 1:1'-Dinaphthyl-7:7'-Disulphonic Acid from Sodium 1:7-Iodonaphthalene Sulphonate.

5 gm. of sodium 1:7-iodonaphthalene sulphonate, prepared by hydrolysing the sulphonyl chloride, were dissolved, together with a small crystal of cupric sulphate, in 50 c.c. of hot water, and the solution refluxed for four hours with excess of copper powder (3 gm.). After filtering, unchanged sodium 1:7-iodo-sulphonate separated on cooling the filtrate (identified by converting to sulphonyl chloride, m.p. 141°C.), and no other product was identified when the remaining solute was isolated and treated with phosphorus pentachloride.

(6) Reaction of 1:7-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cupric Sulphate Reduced by means of Sulphur Dioxide.

The ammoniacal cuprous sulphite solution was prepared in the manner described in section I.(11), by saturating an ammoniacal solution of 25 gm. of hydrated cupric sulphate with sulphur dioxide, finally rendering the solution ammoniacal once more.

The diazo-suspension obtained from 10 gm. of Cleve acid was gradually added to this solution at room temperature, with mechanical agitation. Nitrogen was evolved and, when this had ceased, the highly coloured solution was concentrated to obtain the total solute which was then dried and triturated with phosphorus pentachloride. On the addition of excess of cold water, no insoluble sulphonyl chloride separated.

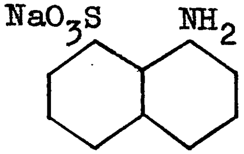
Had a soluble azo-disulphonate been the product of this reaction, it would have been very difficult to isolate it owing to the presence of secondary products of coupling which always seemed to occur during diazotization.

V. 1-NAPHTHYLAMINE-8-SULPHONIC ACID. (Peri Acid).

(1) Preparation of Sodium 1-Naphthylamine-8-Sulphonate.

The supplies of technical Peri acid available varied considerably in purity. The sodium salt (referred to hereafter as sodium periate), which is not very soluble in cold water, was prepared by dissolving the technical acid in hot dilute caustic soda solution, filtering through carbon and cooling the filtrate. In preparing large quantities of the salt, it was found useful to add dilute caustic soda solution to the filtrate after cooling as this had the effect of salting out a larger quantity of sodium periate than was otherwise obtained; and the mother liquor was then sufficiently alkaline to dissolve more peri acid, so effecting an economy in time and materials.

The sodium periate was then recrystallized from hot water. It was greyish in colour, even after treatment with decolourizing carbon, but was considered of sufficient purity. Sodium periate is anhydrous -



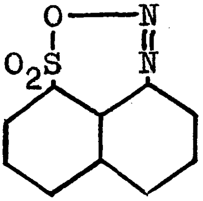
M.W. 245.

(2) Diazotization of Peri Acid.

To begin with, peri acid was diazotized by the indirect method, i.e. a solution of 5 gm. of sodium periate and 1:4 gm. of sodium nitrite in about 400 c.c. of water was added to dilute hydrochloric acid (containing 7.5 gm. of the concentrated acid), with mechanical agitation. The large volume of water was necessary because of the slight solubility of sodium periate in cold water, and as a result the diazo-compound remained in solution.

The above method was discarded later in favour of the direct method, which enabled the solid diazo-compound to be isolated. Direct method:-

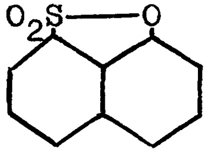
From a solution of 10 gm. of sodium periate in 200 c.c. of boiling water, peri acid was precipitated in a fine state of division by adding dilute sulphuric acid (equivalent to 2¼ mol. of the periate). After cooling to room temperature, the suspension was diazotized by gradually adding a slight excess of sodium nitrite solution (containing 3.0 gm. $NaNO_2$). The brownish diazo-compound crystallized out and was further separated by salting out with common salt. It could then be filtered quite readily and used in the solid form. It has the structure -



(3) Properties of the Diazo-Compound.

The following preliminary tests were carried out on the diazo-compound:-

(a) When completely dry (i.e. after washing with alcohol several times), the diazo-compound is quite stable at ordinary temperatures. If, however, a thick aqueous paste of the compound is left to stand for a little, heat is evolved and decomposition is quite rapid. When heated, the dry compound sinters with evolution of nitrogen. A small quantity of the dry compound was "ignited" by touching it with a hot wire, whereon it decomposed with slight charring leaving a grey residue. The residue dissolved almost completely in acetone, from which it separated as colourless needles on concentration, m.p. 156°C. The residue thus consisted mainly of naphthasultone -



Schultz (Berichte, 1887, <u>20</u>, 3162) gives m.p. 154°C.

(b) When a diazo-suspension was heated up gradually, nitrogen started to come off at about 65°C. and naphthasultone separated.

(c) When a large excess of caustic soda or ammonia was added to the diazo-compound, nitrogen was not evolved - stable anti-diazotate probably formed. When only a slight excess of alkali was added, nitrogen was evolved in the cold - unstable anti-diazotate probably formed.

(d) When copper powder was added to the diazo-suspension, nitrogen was evolved and a deeply coloured solution formed.

(4) Preparation of Sodium 1:8-Iodonaphthalene Sulphonate.

No reference to 1:8-iodonaphthalene sulphonic acid in the literature could be found. Considerable difficulty was encountered in obtaining a salt of the acid, since the orthodox methods of replacing a diazo-group by iodine proved unsucessful.

In a first attempt to prepare the acid, the diazo-solution (by indirect diazotization) from 5 gm. of sodium periate was poured into excess of boiling hydriodic acid solution. Nitrogen was rapidly evolved and naphthasultone separated almost immediately in large yield. The naphthasultone was filtered off and the filtrate concentrated to obtain the solute. When the latter was treated with phosphorus pentachloride, etc., no sulphonyl chloride was isolated, however.

Naphthasultone was again the only product identified when the diazo-solution was added to hydriodic acid in the cold and the mixture gradually heated until all nitrogen had been evolved.

The necessity for carrying out the reaction at low temperatures was evident from the readiness with which naphthasultone is formed when the diazo-compound is heated. The modification of the Gattermann reaction found effective in the preparation of 1:4-iodonaphthalene sulphonic acid, was accordingly applied to the diazo-compound:-

The diazo-solution was added to excess of potassium iodide solution in the cold. Copper powder was then added with stirring, nitrogen being evolved, and when this had ceased the solution was filtered and concentrated. The crystalline product isolated was dried and treated with phosphorus pentachloride. The sulphonyl chloride so obtained, after recrystallization from acetone, was found to melt at 66°C., and the sulphonamide and sulphoanilide derived from it at 148°C. and 152°C. respectively. The diazo-group had thus been replaced by hydrogen, with formation of naphthalene-α-sulphonic acid, a secondary product in the preparation of 1:4-iodonaphthalene sulphonic acid by a similar treatment.

Pyridine has been shown (E.P. 248,230 and E.P. 287,232) to activate diazo-compounds, increasing their "coupling energy", and it has been noted in connection with 1:4-diazonaphthalene sulphonic acid, that it increases the rate of nitrogen evolution in certain treatments. Employing pyridine to facilitate nitrogen evolution, sodium 1:8-iodonaphthalene sulphonate was successfully prepared in good yield in the following manner:-

In a trial experiment, the diazo-compound obtained from 5 gm. of sodium periate was added to a cold solution of 10 gm. of potassium iodide in about 100 c.c. of water to which one drop of pyridine had been added. The suspension was stirred mechanically for some time, but as nitrogen evolution was very slow it was merely left to stand for three days at lab temperature, by which time there was no further reaction. The bluish suspension so formed was boiled for a few minutes and filtered. The residue, after crystallizing from acetone using decolourizing carbon, was identified as naphthasultone (m.p. 156°C.). After boiling with carbon, the filtrate was saturated with common salt. In this way, a pinkish crystalline solid separated from the deeply coloured solution and, after filtering off, this was redissolved in water and crystallized out slowly by almost saturating the hot solution with pure sodium chloride and allowing to cool. The pink crystalline plates so obtained were found to contain sulphur, iodine and sodium, and analysis of derivatives prepared subsequently showed that the salt was sodium 1:8-iodonaphthalene sulphonate.

The method was tested under various conditions; the quantities affording the best yield were found to be 15 gm. of potassium iodide, the diazo-compound from 10 gm. of sodium periate, and one c.c. of pyridine in 150 c.c. of water. With these quantities, the yield of sodium salt (anhydrous) was approximately 70% theoretical. Fair yields were also obtained using 10 gm. of potassium iodide (per 10 gm. sodium periate) and smaller or larger amounts of pyridine; but much pyridine caused difficulties in salting out, a gummy product separating with the iodo-sulphonate. It was found that temperature, even over a 10° to 20°C. range, had a marked effect upon the speed of the reaction. A quantity of pyridine which effected complete liberation of nitrogen in two days during the summer was inadequate to produce the same result during cold spells in the winter, when standing for five or six days was necessary.

An experiment was performed, omitting pyridine. The diazo-compound from 5 gm. of sodium periate in an aqueous solution of potassium iodide was allowed to react at lab temperature (during warm weather). After seven days, practically all the diazo-compound had decomposed, but the yield of iodo-sulphonate was poor (approximately 20%).

It was found that acetone could be used in place of pyridine to facilitate nitrogen evolution. The diazo-compound from 20 gm. of sodium periate was added to a solution of 25 gm. of potassium iodide in 200 c.c. of water containing 10 c.c. of acetone. The suspension was allowed to stand for several days until nitrogen evolution had ceased. It was noted that the resulting suspension had a very irritating odour, resembling that of formic acid. After boiling and filtering the suspension (small yield of naphthasultone), the filtrate was salted out with common salt. An almost black product separated which was found extremely difficult to purify by recrystallization from water even after repeated treatments with decolourizing carbon. This must have been due to the concurrent separation of a highly coloured secondary product, since the iodo-sulphonyl chloride obtained by treatment with phosphorus pentachloride was readily purified. The yield of pure sulphonyl chloride (described in 5) obtained from the product of salting out, was approximately 28% theoretical.

(5) Derivatives of 1:8-Iodonaphthalene Sulphonic Acid.

(a) 1:8-Iodonaphthalene Sulphonyl Chloride.

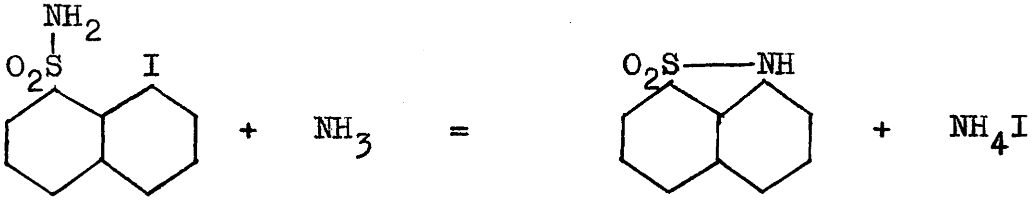
The sulphonyl chloride obtained by treating the sodium iodo-sulphonate prepared above with phosphorus pentachloride, was crystallized several times from acetone-water, after treatment with decolourizing carbon. It separated as pale yellow plates, m.p. 115°C. (Found S, 9.1%; $C_{10}H_6I.SO_2Cl$ requires S, 9.1%).

(b) I:8-Iodonaphthalene Sulphonamide.

Dilute ammonia was added gradually, with stirring, to a cold solution of the sulphonyl chloride in acetone. Colourless crystalline plates of the sulphonamide gradually separated out, m.p.(decomp.) 187°C. (Found I, 37.9%; $C_{10}H_6I.SO_2NH_2$ requires I, 38.1%).

(c) Formation of 1:8-Naphthasultam.

In an attempt to prepare 1:8-iodonaphthalene sulphonamide by boiling an acetone solution of the sulphonyl chloride with ammonia solution, a product containing no iodine was isolated which, after recrystallizing from acetone-water, melted at 176°C. According to Dannerth (J.Amer.C.S., 1907, 29, 1319), peri-naphthasultam melts at 177°C. It appears that the iodonaphthalene sulphonamide first formed is readily converted at higher temperatures, in the presence of ammonia, to peri-naphthasultam with elimination of hydriodic acid, thus -

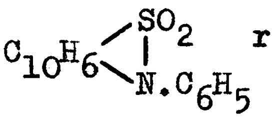


(d) 1:8-Iodonaphthalene Sulphoanilide.

Slight excess of aniline was added to an acetone solution of the sulphonyl chloride, the solution being slowly evaporated to small bulk on the water bath. A yellow semi-solid product separated on the addition of water, and excess of aniline was removed by dissolving it in acetone and reprecipitating with dilute hydrochloric acid. After recrystallizing several times from acetone-water, the sulphoanilide was obtained as pale yellow plates, m.p. 140°C. (Found I, 29.8%; $C_{10}H_6I.SO_2NH.C_6H_5$ requires I, 31.0%).

(e) Formation of Phenyl-1:8-Naphthasultam.

A solution of 3 gm. of 1:8-iodonaphthalene sulphoanilide in 50 c.c. of alcohol was refluxed with copper powder for about three hours. After filtering, the solution was evaporated to half its original bulk and a colourless product separated. This was crystallized from alcohol (prisms),m.p.

165°C., and was found to contain no iodine. (Found Mol. Wt. (Rast), 293 and S, 11.3%;  $C_{10}H_6\langle{}^{SO_2}_{N.C_6H_5}$ requires Mol. Wt., 281 and S, 11.4%).

König and Wagner (Berichte, 1924, <u>57</u>(ii), 1059), who obtained peri-phenylnaphthasultam from N-phenyl-1-naphthylamine-8-sulphonate by treatment with phosphoryl chloride, state that it melts at 158°C.

(6) Reaction of Sodium 1:8-Iodonaphthalene Sulphonate in Aqueous Solution with Copper Powder.

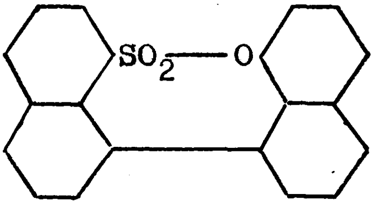
5 gm. of sodium 1:8-iodonaphthalene sulphonate were dissolved in 150 c.c. of water together with a few small crystals of cupric sulphate, and the solution refluxed with excess of copper powder for an hour. The formation of cuprous iodide was apparent after boiling for a few seconds. Cuprous iodide and copper powder (excess) were then filtered off, and the filtrate treated to isolate the solute. It was found that direct salting out was ineffective, probably owing to the presence of copper salts, and in initial treatments the very soluble product was isolated by evaporation to dryness. Subsequently it was found that the product could be separated by first saturating the filtrate with hydrogen sulphide, filtering through carbon, boiling off excess of hydrogen sulphide, and finally salting out with common salt.

The colourless product, believed to be disodium 1:1'-dinaphthyl-8:8'-disulphonate, was filtered, dried and triturated with phosphorus pentachloride. On adding a large volume of cold water, a sulphonyl chloride separated which was recrystallized from acetone-water, m.p. 101°C. (Found Mol. Wt. 271-278). The sulphonamide, prepared by treating an acetone solution of the sulphonyl chloride with ammonia, was found to melt at 198°C., and to contain chlorine. The preparation of 1:8-chloronaphthalene sulphonyl chloride (m.p. 101°C.) and 1:8-chloronaphthalene sulphonamide (m.p. 198°C.) is recorded in the next part (7) of this section, and mixed melting points were accordingly determined with these and the corresponding derivatives obtained above. No depression was noted in either case.

Sodium 1:8-chloronaphthalene sulphonate is different in both appearance and solubility from the salt isolated above; and, moreover, the mode of formation of the latter could not result in the substitution of iodine by chlorine. It was inferred therefore that phosphorus pentachloride, in addition to effecting the conversion to a sulphonyl chloride, had ruptured the diaryl linkage, substituting chlorine.

There was some difficulty in obtaining a derivative of the supposed 1:1'-dinaphthyl-8:8'-disulphonic acid. The very soluble disulphonate could not be purified sufficiently for analysis, and only resinous products were isolated when attempts were made to prepare 1:1'-8:8'-dinaphthol by fusing it with caustic potash. What is believed to be a derivative was obtained in the following manner:-

About 4 gm. of aniline hydrochloride were fused in a small flask and 1 gm. of the supposed dinaphthyl disulphonate added to the melt (it was hoped that the disulphoanilide might be formed). This was heated at about 250°C. for 15 minutes in the course of which evolution of sulphur dioxide was detected. After cooling, the product was extracted with water to dissolve excess of aniline hydrochloride, and the residue crystallized from alcohol using decolourizing carbon. The small yield of colourless product, m.p. (decomp.) 252°C., was found to contain sulphur but no nitrogen or chlorine. It is believed to be 1:1'-dinaphthyl-8:8'-sultone -



(Found S, 9.55%; $C_{20}H_{12}O_3S$ requires S, 9.63%).

(7) Reaction of 1:8-Diazonaphthalene Sulphonic Acid with Cuprous Chloride under Varying Conditions.

(a) The diazo-compound from 10 gm. of sodium periate was added with stirring to a solution of 5 gm. of cuprous chloride in about 100 c.c. of concentrated hydrochloric acid heated to about 80°C. Nitrogen was evolved and a large bulk of solid separated which was subsequently proved to be naphthasultone. This was filtered off and the filtrate concentrated to small bulk. On cooling, crystalline needles separated (cuprous salt of chloro-acid), and these were filtered and boiled with caustic soda solution to eliminate copper. After filtering through carbon, the sodium chloro-sulphonate was salted out with common salt, dried and treated with phosphorus pentachloride, etc. in the usual manner. Only a small yield of the sulphonyl chloride was obtained compared with that of naphthasultone. After recrystallization from acetone-water, the sulphonyl chloride melted at 101°C. The sulphonamide derived from this by treating an acetone solution with aqueous ammonia melted at 199°C. Cleve (Berichte, 1890, 23, 962) records m.p. 101°C. and 196-197°C. for 1:8-chloronaphthalene sulphonyl chloride and sulphonamide respectively.

(b) Results similar to the above were obtained when the solid diazo-compound was added to a concentrated hydrochloric acid solution of cuprous chloride and the suspension heated up gradually, the yield of 1:8-chloronaphthalene sulphonyl chloride beimg low.

(c) The solid diazo-compound was added to a suspension of copper powder in a concentrated hydrochloric acid solution of cuprous chloride in the cold. Nitrogen was rapidly evolved and when this ceased the solution was boiled. On cooling, a large crop of greenish crystals separated, and these were filtered off along with excess of copper powder and boiled with dilute caustic soda solution. A little carbon was added and, after filtering, the clear green filtrate was salted out with common salt. The colourless sulphonate obtained was dried and converted into the sulphonyl chloride by treatment with phosphorus pentachloride. On crystallization from acetone, this was found to melt at 66°C. On treatment with aqueous ammonia, a sulphonamide melting at 151°C. was obtained. These melting points agree quite closely with those recorded for naphthalene-α-sulphonyl chloride and -α-sulphonamide respectively, showing that the diazo-group had been replaced by hydrogen. No naphthasultone was produced in this treatment, and the yield of naphthalene-α-sulphonyl chloride was good.

(d) The solid diazo-compound from 5 gm. of sodium periate was added, with mechanical agitation, to a cold suspension of 3 gm. of cuprous chloride in 200 c.c. of water. Nitrogen evolution was slow and after about four hours the suspension was heated up gradually to boiling. Naphthasultone and cuprous chloride were filtered off and, on cooling the filtrate, some more cuprous chloride separated. After removing this, the deep red filtrate was saturated with common salt, but no sulphonyl chloride-forming product was isolated.

(e) This treatment was suggested by that employed with success in the preparation of sodium 1:8-iodonaphthalene sulphonate:-

The solid diazo-compound from 10 gm. of sodium periate was added to a cold solution of 3 gm. of cuprous chloride in about 40 c.c. of concentrated hydrochloric acid. The suspension was allowed to stand for several days at room temperature, with intermittent stirring, until the gradual evolution of nitrogen had ceased. After diluting slightly and boiling, the solution was treated with caustic soda solution to neutralize and eliminate copper, and filtered through carbon. By saturating the filtrate with common salt, sodium 1:8-chloronaphthalene sulphonate was obtained. This was converted into the sulphonyl chloride, m.p. 101°C., by the usual treatment with phosphorus pentachloride. The yield of pure sulphonyl chloride was 45% theoretical - very much better than that obtained in experiments (a) and (b).

(8) Preparation of 1:8-Bromonaphthalene Sulphonyl Chloride.

1:8-Bromonaphthalene sulphonic acid is not referred to in the literature, and two attempts to prepare it by methods similar to those used for preparing 1:8-iodo- and 1:8-chloro-naphthalene sulphonic acids were made without success. These consisted of maintaining for several days at room temperature (a) a suspension of diazotized peri acid in potassium bromide solution containing pyridine, and (b) a suspension of diazotized peri acid in a solution of cuprous bromide in sulphuric acid. Nitrogen evolution was very slow and naphthasultone was the only product identified in both cases.

The acid has been isolated as the sulphonyl chloride, however, in the following manner:-

1 gm. of cuprous oxide was boiled with a solution of 12 gm. of ammonium bromide in 150 c.c. of water for five minutes and the solution filtered hot. To the cold suspension of diammino-cuprous bromide in ammonium bromide solution so produced was added, with stirring, the solid diazo-compound from 10 gm. of sodium periate. This suspension was kept for 24 hours at lab temperature, after which nitrogen evolution had ceased, and was then boiled, filtered through carbon, and the filtrate salted out with potassium chloride. The dark-coloured product which separated was filtered, dried and treated with phosphorus pentachloride, etc., and the crude sulphonyl chloride so formed was recrystallized once or twice from acetone-water, using decolourising carbon. A small yield (0.5 gm.) of pale yellow hexagonal plates, m.p. 110°C., containing bromine and chlorine, was obtained. (Found S, 10.6%; $C_{10}H_6Br.SO_2Cl$ requires S, 10.5%).

By increasing the quantity of diammino-cuprous bromide in the above treatment, the evolution of nitrogen was accelerated, but no increase of yield was obtained.

Side reactions were indicated by the intense colour of the suspension obtained.

(9) Reaction of 1:8-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cupric Sulphate Reduced by means of Sulphur Dioxide.

The ammoniacal cuprous solution (Example 1 of E.P.278,100) employed was prepared in the manner recorded in section I.(11) by dissolving 10 gm. of hydrated cupric sulphate in water, adding ammonia, reducing by means of sulphur dioxide and adding finally an adequate excess of ammonia.

The diazo-solution (by indirect diazotization) from 5 gm. of sodium periate was poured slowly, with mechanical agitation, into this ammoniacal cuprous solution. Nitrogen was evolved and, when this had ceased, the solution was concentrated exhaustively to obtain crops of dark-coloured crystals comprising the total substance in solution. These crops were thoroughly dried and treated with phosphorus pentachloride in the usual manner. After decomposing excess pentachloride with water, a small insoluble residue remained which, after crystallizing from acetone-water, was found to melt at 225°C. and to contain no chlorine. Believed at first to be 1:1'-dinaphthyl-8:8'-disulphonic anhydride, it was shown by analysis and mol. wt. determinations to be naphthalene-1:8-disulphonic anhydride. (Found Mol. Wt., 210 and S, 23.3% $C_{10}H_6(SO_2)_2O$ requires Mol. Wt. 270 and S, 23.6%). Armstrong and Wynne (Proc. Chem. Soc., 1893, 166) state that the disulphonic anhydride melts at 227°C. The yield of pure anhydride was approximately 8% theoretical.

A compound, m.p. 282°C., obtained by boiling the anhydride with aqueous ammonia, appears to be the ammonium salt of the disulphonic acid (Found N, 8.8% and S, 21.0%; $C_{10}H_6(SO_3NH_4)_2$ requires N, 8.7% and S, 19.9%).

In the preparation of the ammoniacal cuprous solution, it has been noted in section 1.(11) that a deposit of colourless crystalline substance (suggested to be cuprous ammonium sulphite) was obtained after saturating the ammoniacal cupric sulphate solution with sulphur dioxide. With the object of testing whether or not this substance was the reactive constituent of the solution, the following experiment was carried out :-

10 gm. of hydrated cupric sulphate were dissolved in about 100 c.c. of water and sufficient dilute ammonia solution added just to redissolve the hydroxide formed at first. This solution was then saturated with sulphur dioxide and the colourless needle-shaped crystals which separated on cooling were rapidly filtered off and suspended in 100 c.c. of water in which they were insoluble. The solid diazo-compound from 5 gm. of sodium periate was then

added gradually to this suspension in the cold. Nitrogen was evolved rapidly and, after boiling the resultant solution (in the course of which cuprous oxide separated) and filtering, the filtrate was salted out with common salt. A considerable quantity of brownish crystalline solid separated which was filtered off, dried and treated with phosphorus pentachloride. The product obtained, after addition of water, was crystallized several times from acetone and found to melt at 226°C. As by the first method, naphthalene-1:8-disulphonic anhydride had been isolated, but the yield of pure product was considerably better - approximately 16% theoretical.

The principal interest of this experiment was that it showed that cuprous ammonium sulphite was the active constituent in this particular of "ammoniacal cuprous exide solution", the presence of excess of ammonia being inessential to the formation of the napthalene disulphonic acid.

(10) Reaction of 1:8-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cuprous Sulphate.

An ammoniacal solution of tetrammino-cuprous sulphate (Example 6 of E.P.278,100) was prepared from 10 gm.of hydrated cupric sulphate in the manner described in section I.(13), by reducing an ammoniacal solution with hydroxylamine.

To this solution, cooled in ice to 4°C., was gradually added the solid diazo-compound obtained from 5 gm. of sodium periate, with mechanical agitation. Nitrogen was evolved and a deep red solution produced. The solution was heated to boiling and sodium hydroxide solution added to eliminate ammonia and precipitate the copper. Carbon was added and the solution filtered. The filtrate was saturated with sodium chloride, whereupon a bright yellow substance separated. This was redissolved in water in which it was very soluble, the solution filtered with a little carbon, and reprecipitated by the careful addition of pure sodium chloride.

The yellow salt, obtained in fair yield, was found very difficult to purify by crystallization. It contained nitrogen, sulphur, sodium and water of crystallization, and gave a deep purple solution and precipitate on acidifying an aqueous solution with hydrochloric acid. Since, in most other cases, diazonaphthalene sulphonic acids reacted with tetrammino-cuprous sulphate solution to form azo-disulphonates, the salt was believed to be disodium 1:1'-azonaphthalene-8:8'-disulphonate. The following reduction test tends to support this inference:-

A quantity of the yellow salt was dissolved in water and dilute hydrochloric acid added, followed by zinc dust. The purple colour produced by the hydrochloric acid was gradually discharged leaving a fine greyish suspension from which excess of zinc dust was dissolved by warming with more acid. This suspension was diazotized directly by adding excess of sodium nitrite solution, and the diazo-suspension formed was heated to boiling. Nitrogen was evolved and the yellowish substance which separated was filtered off, dried and crystallized from acetone using decolourizing carbon. Containing S but no N, it was readily shown to be naphthasultone (m.p. 156°C.) by carrying out a mixed melting point determination, which showed no depression. This means that on reduction the compound yielded peri acid, the product which would be obtained by reducing a 1:1'-azo-naphthalene-8:8'-disulphonate.

(11) Preparation of Naphthostyril and Its Conversion to 1:1'-Dinaphthyl-8:8'-Dicarboxylic Acid.

The purpose of this piece of work was to confirm the claims made in E.P.278,100 and ascertain the conditions under which good yields of 1:1'-dinaphthyl-8:8'-dicarboxylic acid are obtained. It was discontinued, however, when 2:1-diazonaphthalene sulphonic acid was successfully converted directly to 2:2'-dinaphthyl-1:1'-disulphonic acid by treatment with "ammoniacal cuprous oxide solution".

The reactions involved can be divided into three stages:-

(a) Conversion of 1:8-diazonaphthalene sulphonic acid to 1:8-cyanonaphthalene sulphonic acid (D.R.P. 444,325).

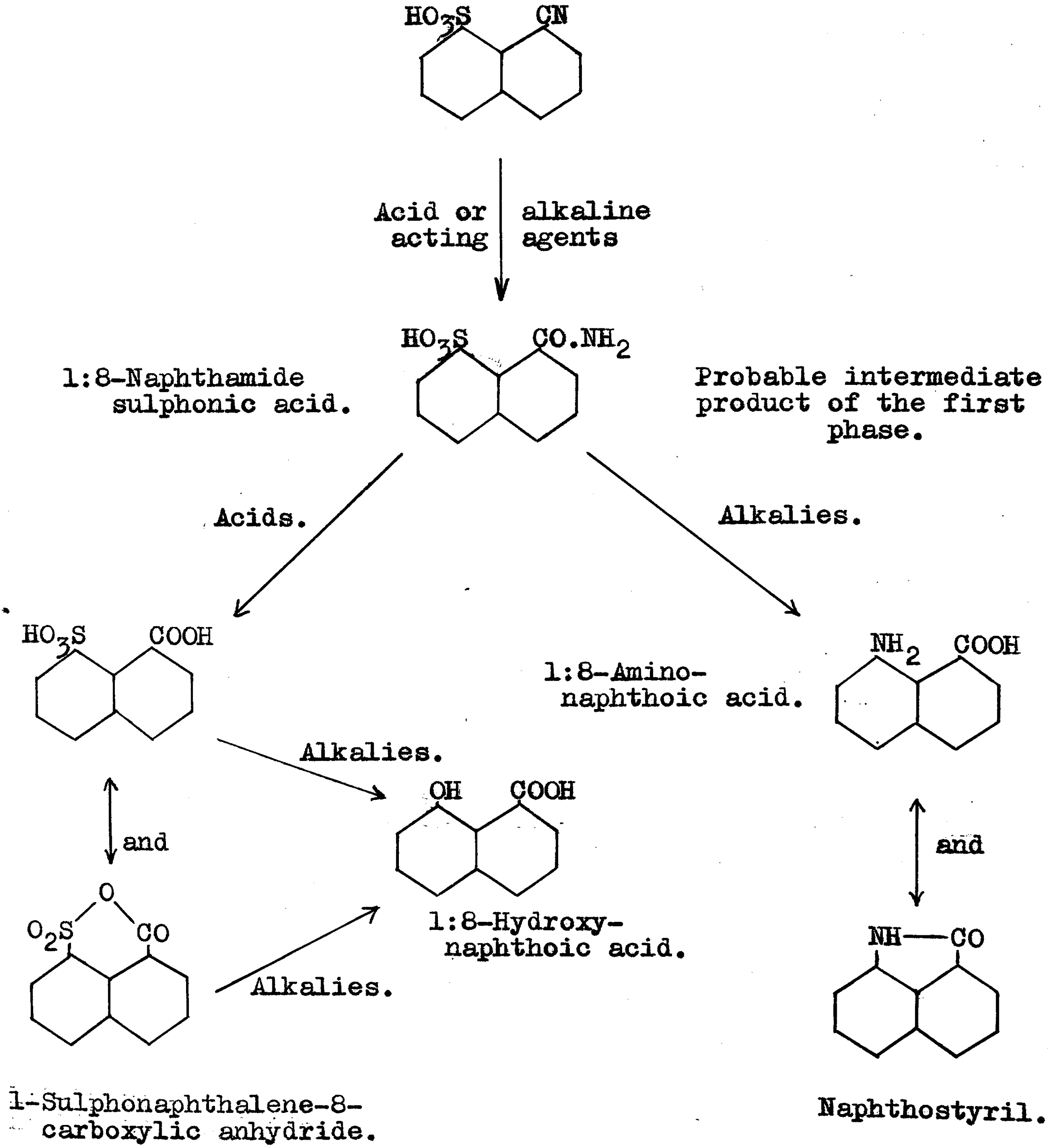
(b) Conversion of 1:8-cyanonaphthalene sulphonic acid to naphthostyril and 1:8-aminonaphthoic acid (E.P. 276,126).

(c) Conversion of 1:8-aminonaphthoic acid to 1:1'-dinaphthyl-8:8'-dicarboxylic acid (E.P. 278,100).

In E.P. 276, 126 (stage b), the course of acid and alkaline hydrolysis of 1:8-cyanonaphthalene sulphonic acid is represented graphically in the manner shown on the next page -

Over.

Hydrolysis of 1:8-Cyanonaphthalene Sulphonic Acid.



(a) Preparation of 1:8-Cyanonaphthalene Sulphonic Acid.

E.P. 276,126 does not mention any method for the preparation of 1:8-cyanonaphthalene sulphonic acid, and information on the subject was gathered from a paper by Royle and Schedler (J.C.S., 1923, 1643) on the preparation of 1:3-, 1:6- and 1:7-cyanonaphthalene sulphonic acids, and from an abstract of D.R.P. 444,325 (Chem. Zentral., 1927,(3), 742).

According to the former, the solid diazo-compound is added to a cuprous cyanide solution at 50-60°C., and the mixture subsequently warmed on the steam-bath for an hour. Concentrated hydrochloric acid is then added to the hot solution, the precipitated cuprous cyanide filtered off and washed with a little hot water, the washings and filtrate evaporated to dryness, and the residue extracted several times with 90-95% alcohol. The alcohol is evaporated and the nitrile crystallized from a small bulk of water, animal charcoal being used if necessary.

In a trial experiment, this method proved ineffective, no nitrile being extracted by the alcohol, and the following procedure, embodying the main features of D.R.P. 444,325, was adopted:-

12 gm. of hydrated cupric sulphate were dissolved in about 200 c.c. of water in a conical flask. To this solution at about 40°C. was added 13 gm. of potassium

cyanide with shaking. Dilute hydrochloric acid was added to the clear solution obtained until a faint opalescence was produced, thus decomposing any excess of potassium cyanide.

The solid diazo-compound from 10 gm. of sodium periate was gradually added in small quantities to the cuprous cyanide solution prepared above (heated to 50-60°C.) with continual shaking. The flask was then heated on the water bath for an hour, and the cuprous cyanide precipitated with concentrated hydrochloric acid and filtered off. The filtrate was made alkaline with caustic soda solution and evaporated to about half of its original volume. It was then saturated with common salt and sodium 1:8-cyanonaphthalene sulphonate separated as a pale pink solid. The pure salt (colourless needles) was obtained by decolourizing an aqueous solution of the crude product with carbon and salting out from a hot solution. No derivatives of 1:8-cyanonaphthalene sulphonic acid are referred to in the literature, so the sulphonyl chloride and sulphonamide were prepared.

1:8-Cyanonaphthalene Sulphonyl Chloride.

The sodium salt was treated with phosphorus pentachloride in the usual manner and the crude sulphonyl chloride, crystallized from acetone using decolourizing carbon, yielded colourless leaflets, m.p. 139°C. (Found Cl, 14.3%; $C_{10}H_6CN.SO_2Cl$ requires Cl, 14.1%).

1:8-Cyanonaphthalene Sulphonamide.

An acetone solution of the sulphonyl chloride was treated with excess of aqueous ammonia and evaporated to small volume. The sulphonamide crystallized on cooling and, after recrystallization from dilute ammonia, was found to melt at 334-336°C. (Found N, 11.6%; $C_{10}H_6CN.SO_2NH_2$ requires N, 12.0%).

(b) Hydrolysis of 1:8-Cyanonaphthalene Sulphonic Acid.

Acid Solution. 5 gm. of sodium 1:8-cyanonaphthalene sulphonate were dissolved in 30 gm. of concentrated sulphuric acid and ice was added until the concentration of the acid was reduced to approximately 60%, the temperature rising meanwhile to about 35°C. The temperature of the solution was now raised to 70°C. on the water bath and kept there for some time, after which the mixture was allowed to cool. In this way, the inner anhydride of 1-sulphonaphthalene-8-carboxylic acid separated out and was filtered off, dried and crystallized from benzene. The pure anhydride was obtained as colourless plates, m.p. 152°C., similar to that described in E.P. 276,126 (m.p. 152-153°C.).

This inner anhydride was also prepared readily by evaporating a dilute hydrochloric acid solution of sodium 1:8-cyanonaphthalene sulphonate to small bulk and allowing to cool. It separated as greyish crystals which were easily purified by recrystallization from acetone.

Alkaline Solution. Of the four methods described in E.P. 276,126 for preparing naphthostyril by alkaline hydrolysis of 1:8-cyanonaphthalene sulphonic acid, the one outlined in Example 8 was selected as the most suitable for laboratory investigation.

20 gm. of potassium hydroxide were added to 30 gm. of methyl alcohol in a small flask and heated between 80° and 100°C. until solution was obtained. With the temperature maintained at this range, 5 gm. of sodium 1:8-cyanonaphthalene sulphonate were introduced gradually with stirring. The methyl alcohol was slowly distilled off until the temperature reached 135°C., when heating was continued for about two hours under reflux. The mixture was then transferred while hot to a beaker containing four times its volume of water.. This was heated for a short time to dissolve excess of potassium hydroxide and, after cooling, was acidified with concentrated hydrochloric acid. In this way, naphthostyril was precipitated. It was filtered, dried and crystallized once or twice from methyl alcohol from which it separated as yellow needles, m.p. 179°C. The melting point is given as 181°C. in E.P. 276,126, but Bamberger and Philip (Berichte, 1887, 20, 243) found it to be 178-179°C. The percentage yield calculated from the initial weight of sodium periate used was approximately 45% theoretical.

Sodium 1:8-aminonaphthoate was obtained by boiligg naphthostyril with caustic soda solution until it dissolved, decolourizing with carbon, evaporating to small bulk and cooling. The salt crystallized as colourless needles. Several derivatives of naphthostyril were prepared:-

Acetonaphthostyril. Naphthostyril was warmed with excess of acetic anhydride until it dissolved. Acetonaphthostyril separated from the solution on adding excess of water, and was readily recrystallized from alcohol. Colourless needles, m.p. 123°C. Ekstrand (Berichte, 1886, 19, 1135) gives m.p. 125°C.

Dichloronaphthostyril. An aqueous suspension of naphthostyril was warmed to about 60°C. and chlorine passed through it until chlorination was considered complete. The bright yellow product was filtered off and crystallized from alcohol. Yellow needles, m.p. 263°C. Ekstrand (loc. cit.) gives m.p. 264-265°C.

Dibromonaphthostyril. A small quantity of naphthostyril was suspended in water and heated with a slight excess of bromine. When the reaction was considered complete, sulphur dioxide was passed through the solution to remove excess of bromine, and the product filtered off and crystallized from alcohol. Yellow needles, m.p. 270°C. Ekstrand (loc. cit.) gives m.p. 268-270°C.

Dibromoacetonaphthostyril. Dibromonaphthostyril obtained as above was heated with excess of acetic anhydride until it dissolved. On cooling, yellow needles separated and these were filtered off and recrystallized from alcohol, m.p. 186°C. Ekstrand (loc. cit.) gives m.p. 185°C.

(c) Diazotization of 1:8-Aminonaphthoic Acid. Reaction of the Diazo-compound with Ammoniacal Cuprous Oxide Solution.

2 gm. of naphthostyril were boiled with a slight excess of dilute caustic soda solution until saponified. After cooling, just sufficient dilute hydrochloric acid was added to precipitate the aminonaphthoic acid. 13 c.c. of concentrated hydrochloric acid were now added to the suspension and an excess of sodium nitrite run in slowly with mechanical agitation.

The orange diazo-compound so obtained was filtered off and added to an ammoniacal cuprous solution prepared in the following manner (Example 1 of E.P.278,100):-

5.4 gm. of hydrated cupric sulphate were dissolved in 100 c.c. of water and 25 gm. of 25% ammonia added. Sulphur dioxide was passed through the solution until it was colourless, and a further 10 gm. of dilute ammonia were added.

When all the nitrogen had evolved, the solution was filtered and the solution acidified with dilute hydrochloric acid. A small precipitate was formed which was filtered off. This substance was found to melt above 300°C. and, as described in Example 1 of the Patent, it gave a red colouration, turning to green on warming, with concentrated sulphuric acid. Thus 1:1'-dinaphthyl-8:8'-disulphonic acid had been prepared.

None of the other treatments recorded in the Patent were given a trial.

(12) Reactions of 1:8-Diazonaphthalene Sulphonic Acid Resulting in the Formation of Naphthalene-α-Sulphonic Acid.

The following three experiments, which were attempts to effect direct diaryl formation through 1:8-diazonaphthalene sulphonic acid, all resulted in the formation of naphthalene-α-sulphonic acid in good yield.

(a) Action of Copper Powder on a Concentrated Hydrochloric acid Suspension of the Diazo-compound.

When copper powder was added to a suspension of the solid diazo-compound in concentrated hydrochloric acid, nitrogen was rapidly evolved in the cold. The solution obtained was boiled for a short time, allowed to cool, and the crystals which separated were filtered off along with excess of copper powder. By boiling a solution of the crystals and adding caustic soda solution, copper was precipitated as the hydrated oxide. After filtering, the filtrate was salted out, and the product isolated was coverted into the sulphonyl chloride in the usual manner. Crystallized from acetone-water, the sulphonyl chloride melted at 65°C., no depression being noted when a mixed melting point with naphthalene-α-sulphonyl chloride was determined.

(b) Action of Zinc Dust on an Aqueous Suspension of the Diazo-compound.

Excess of zinc dust was added, with mechanical agitation, to a cold aqueous suspension of the diazo-compound. Nitrogen was evolved very rapidly and after boiling with a little carbon and filtering, sodium naphthalene-α-sulphonate was isolated directly by salting out the filtrate with sodium chloride. Identification by preparing the sulphonyl chloride (m.p. 66°C.) in the usual way.

(c) Action of an Ammoniacal Suspension of Stannous Hydroxide on the Diazo-compound.

The solid diazo-compound was added gradually, with stirring, to an ammoniacal suspension of stannous hydroxide prepared by adding excess of dilute ammonia to stannous chloride solution. When nitrogen was no longer evolved, the suspension was boiled with a little carbon and filtered. Sodium naphthalene-α-sulphonate was isolated by salting out and identified by preparing the sulphonyl chloride.

(13) Various Experiments Without Conclusive Results.

The experiments which follow are recorded very briefly since no definite products were isolated. They were all attempts to convert 1:8-diazonaphthalene sulphonic acid into 1:1'-dinaphthyl-8:8'-disulphonic acid by direct reduction.

(a) Cuprous oxide added to aqueous suspension of diazo-compound - nitrogen evolution slow - deep red solution. Efforts to salt out or otherwise precipitate product were fruitless.

(b) Diazo-compound added gradually to aqueous suspension of cuprous oxide - nitrogen evolution slow - filtered, concentrated and treated with KOH. Filtered again and evaporated almost to dryness - water soluble tar (red) obtained. Treated with PCl_5 after drying - no sulphonyl chloride.

(c) Diazo-compound added to suspension of cuprous oxide in dilute ammonia - nitrogen evolution brisk - deeply coloured solution boiled and treated with NaOH to eliminate Cu and NH_3. Filtered and salted out - brown substance which did not yield sulphonyl chloride, but gave deep purple solution in HCl - indicates azo-disulphonate present.

(d) Copper powder added to aqueous suspension of diazo-compound alone - brisk evolution of nitrogen - deep red solution from which no product was isolated by salting out.

(e) Solid diazo-compound added to solution of sodium ethoxide in alcohol - nitrogen evolved and very deep red solution formed. On evaporation, red-brown solid obtained - very soluble in water - solution gives yellow colour in alkali, purple colour in acid.

(f) Ammoniacal copper sulphate solution reduced with $SnCl_2$ and diazo-compound added - nitrogen evolved briskly - filtered, boiled and eliminated Cu and NH_3 by means of NaOH - no product on salting out.

(g) Ammoniacal copper sulphate solution reduced by means of ferrous sulphate and diazo-suspension added - nitrogen evolved - boiled, filtered and treated with KOH to eliminate Cu and NH_3. Filtered again and evaporated to obtain solute - treated with PCl_5, but no sulphonyl chloride obtained.

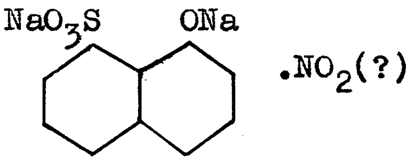
(h) Diazo-solution added to ammoniacal sodium sulphite solution - nitrogen not evolved, nor when pyridine added. Copper powder added and nitrogen was evolved. Filtered and evaporated to obtain solute - brown solid yielding no sulphonyl chloride with PCl_5.

(14) Nitration of 1:8-Naphthasultone.

No nitro derivatives of naphthasultone are referred to in the literature, and since it was found to be easily nitrated, the product was isolated and analysed:-

8 gm. of naphthasultone were heated with 50 c.c. of concentrated nitric acid in a flask until solution was effected. On cooling, pale yellow needles crystallized out which were filtered through sintered glass and washed with water. The nitro derivative, recrystallized from acetone-water, melted at 223°C. (Found S, 12.7%; $C_{10}H_5SO_3(NO_2)$ requires S, 12.7%).

In order to try to ascertain the position of the nitro group, the sultone ring was first ruptured by refluxing a quantity of the derivative with dilute caustic soda solution until it dissolved. On cooling, orange prisms separated, presumably of the structure -



This salt was redissolved in hot water and acidified with dilute hydrochloric acid. Pale yellow crystals (in the form of "indented pyramids") separated on cooling the solution. These were recrystallized from hot water, and found to leave a small sodium salt residue on ignition. (Found S, 10.9%; sodium ?-nitro-1-naphthol-8-sulphonate, $C_{10}H_6O_6NSNa$, requires S, 11.0%).

In the hope of splitting off the sulphonic group, and identifying the remaining nitronaphthol, this salt was dissolved in 60% sulphuric acid and the solution distilled.

No volatile product came over with the vapour, however, and when the solution had become fairly concentrated charring occurred.

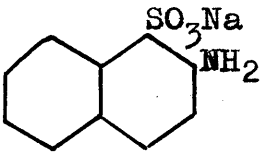
The position of the nitro group remains undetermined.

VI. 2-NAPHTHYLAMINE-1-SULPHONIC ACID. (Tobias Acid).

(1) Preparation of Sodium 2-Naphthylamine-1-Sulphonate.

The Tobias acid supplied was of 97.7% purity. The sodium salt was readily prepared by dissolving the acid in a slight excess of hot dilute caustic soda solution, boiling with a little carbon, filtering and allowing the filtrate to cool. Almost colourless nacreous plates crystallized in quantity, the sodium salt being much less soluble in cold than in hot water.

The sodium salt crystallizes with one molecule of water of crystallization -

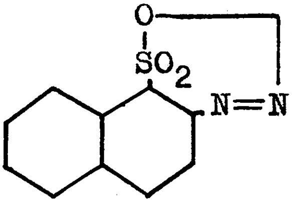


$.H_2O$ M.W. 263.

(2) Diazotization of Tobias Acid.

It was found that Tobias acid was readily diazotized by the direct method:-

10 gm. of sodium 2-naphthylamine-1-sulphonate were dissolved in 300 c.c. of warm water and dilute sulphuric acid, equivalent to 2¼ mol. of the salt, added. The suspension of Tobias acid obtained was cooled rapidly and diazotized by gradually adding slight excess of sodium nitrite solution (containing 2.8 gm. $NaNO_2$), with mechanical agitation. The yellow diazo-compound was crystalline in form and easily filtered; it has the structure -



The diazo-compound was remarkably stable. An aqueous suspension, on heating, was not decomposed until boiling point was reached. The diazo-compound dissolved in excess of alkali without decomposition forming a pale yellow solution from which it was reprecipitated unchanged on the addition of acid.

(3) Preparation of Potassium 2:1-Iodonaphthalene Sulphonate.

No reference was found in the literature to 2:1-iodonaphthalene sulphonic acid or its derivatives.

Difficulty was anticipated in the preparation of the acid, although this was shown later to be unjustified, and the methods first employed for preparing it were modelled on those used to prepare the 1:4- and 1:8- iodo-acids.

Briefly, these first methods consisted of (a) adding copper powder to a cold suspension of the diazo-compound in potassium iodide solution, subsequently heating to 80°C. to promote reaction, and isolation of the potassium salt by salting out with potassium chloride; and (b) adding the diazo-compound to potassium iodide solution containing pyridine, subsequently heating to 80°C. to promote reaction, and isolation of the potassium salt as before.

Moderate yields of the potassium salt, identified by analysis and formation of derivatives, were obtained by these methods, but the straightforward method of heating the diazo-compound with hydriodic acid was found much more effective:-

The solid diazo-compound obtained from 10 gm. of sodium 2-naphthylamine-1-sulphonate was added to a solution of 15 gm. of potassium iodide in 150 c.c. of 5N sulphuric acid. The suspension was slowly heated, with stirring, until nitrogen evolution commenced. All the nitrogen was given off between 70° and 80°C., and a clear orange-red solution resulted. The hot solution was neutralized with potassium hydroxide, and pale yellow leaflets of potassium 2:1-iodonaphthalene sulphonate crystallized on cooling, this being sparingly soluble in cold water. The salt gave up its water of hydration on heating at 145°C. for two hours, without decomposition. (Found I, 32.5% and H_2O, 4.5%; $C_{10}H_6I.SO_3K,H_2O$ requires I, 32.5% and H_2O, 4.6%). The yield of salt was approximately 65% theoretical.

(4) Derivatives of 2:1-Iodonaphthalene Sulphonic Acid.

(a) 2:1-Iodonaphthalene Sulphonyl Chloride.

The potassium salt obtained above was treated in the usual manner with phosphorus pentachloride, the crude sulphonyl chloride being separated by the addition of excess of cold water. After crystallizing several times from acetone-water, pale yellow crystals, m.p. 109.5°C., were obtained. (Found S, 9.2%; $C_{10}H_6I.SO_2Cl$ requires S, 9.1%).

(b) 2:1-Iodonaphthalene Sulphonamide.

A solution of the sulphonyl chloride in alcohol was warmed with excess of aqueous ammonia. On cooling, the sulphonamide separated and was recrystallized from alcohol, forming colourless needles, m.p. 154°C. (Found S, 9.6%; $C_{10}H_6I.SO_2NH_2$ requires S, 9.6%).

(5) Reaction of Potassium 2:1-Iodonaphthalene Sulphonate in Aqueous Solution with Copper Powder.

20 gm. of potassium 2:1-iodonaphthalene sulphonate were dissolved in 300 c.c. of hot water along with a few small crystals of cupric sulphate. 5 gm. of copper powder were added to the solution which was then boiled under reflux for half an hour, the formation of cuprous iodide being apparent after a few moments. After filtering hot through carbon, the filtrate was cooled and saturated with potassium chloride. The colourless crystalline salt which separated was used to prepare the derivatives described below, which served to identify it as dipotassium 2:2'-dinaphthyl-1:1'-disulphonate.

(6) Derivatives of 2:2'-Dinaphthyl-1'-Disulphonic Acid.

(a) 2:2'-Dinaphthyl-1:1'-Disulphonyl Chloride.

A quantity of the dipotassium disulphonate obtained above was intimately mixed with excess of phosphorus pentachloride and warmed gently until the reaction was complete. Excess of phosphorus pentachloride was removed by pouring into a large volume of cold water, and the insoluble disulphonyl chloride which remained was filtered off, dried and crystallised from acetone-water, from which it separated as colourless fern-like crystals, m.p. 245°C. (with decomposition, after starting to darken at 170°C.) (Found S, 13.7%, Cl, 15.0% and Mol. Wt. 429; $C_{20}H_{12}(SO_2Cl)_2$ requires S, 14.2%, Cl, 15.7% and Mol. Wt. 451).

(b) Diammonium 2:2'-Dinaphthyl-1:1'-Disulphonate.

1.5 gm. of the disulphonyl chloride were mixed with 50 c.c. of alcohol and 20 c.c. of strong ammonia, and the mixture boiled until solution was effected. After evaporating considerably the solution was allowed to cool whereupon colourless crystals, m.p. 303-304°C. (with decomposition, and darkening at about 250°C.). This substance appears to be diammonium 2:2'-dinaphthyl-1:1'-disulphonate. (Found S, 14.4%; $(C_{10}H_6SO_3NH_4)_2$ requires S, 14.3%).

(c) ββ-Dinaphthyl.

With the object of preparing 1:1'-dihydroxy-2:2'-dinaphthyl, potassium 2:2'-dinaphthyl-1:1'-disulphonate was fused with caustic potash in the following manner:-

2 gm. of the disulphonate were gradually introduced with stirring, into a solution of 15 gm. of potassium hydroxide in 5 c.c. of water contained in an iron crucible heated to 110°C. The temperature of the melt was gradually raised, with constant stirring, and from time to time small portions were removed, dissolved in water and tested for dinaphthol-formation by acidifying with hydrochloric acid. Before there was any indication of this, however, a dark oily substance separated on the surface of the melt, and an odour similar to that of naphthalene was detected. Portions of the melt were now found to be insoluble in water. The contents of the crucible were now transferred hot to a beaker of cold water and, after cooling, the insoluble portion was filtered off, washed and dried. This was found to be moderately soluble in hot alcohol from which it crystallized after treatment with decolourizing carbon, as hexagonal plates. It was purified by recrystallization from acetone, separating again as colourless hexagonal plates, m.p. 185.5°C. (Found C, 94.2%, H, 5.8% and Mol. Wt., 236-246).

It was apparent from the analysis and melting point of the product that it was ββ-dinaphthyl, m.p. 187°C. ($C_{10}H_7.C_{10}H_7$ requires C, 94.5%; H, 5.5% and Mol. Wt. 254).

This result is interesting when compared with that obtained in the next experiment in which a nickel crucible and copper stirrer were used in place of the iron crucible and stirrer.

(d) 1:1'-Dihydroxy-2:2'-Dinaphthyl.

2 gm. of potassium 2:2'-dinaphthyl-1:1'-disulphonate were added gradually, using a copper stirrer, to a hot solution of 7 gm. of potassium hydroxide in 1 c.c. of water contained in a nickel crucible. The temperature was gradually raised in the course of an hour's heating until a thick brown paste was produced. This was found to be entirely soluble in water and, on acidifying with dilute sulphuric acid, a precipitate was formed and sulphur dioxide evolved from the solution. After filtering and washing, the precipitate was dried and crystallized from alcohol using decolourizing carbon. The colourless product was found to melt at 213°C. (Found C, 83.1%; H, 4.8% and Mol. Wt. 289-297). According to Clemo, Cockburn and Spence (J.C.S., 1931, 1272), 1:1'-dihydroxy-2:2'-dinaphthyl melts at 212°C. (requiring C, 83.9%; H, 4.8% and Mol. Wt. 286).

(It may be mentioned here that in the course of a discussion with an industrial chemist, the author was informed that large scale fusions of this type quite frequently give high hydrocarbon yields when performed in iron pots.)

(7) Preparation of Potassium 2:1-Bromonaphthalene Sulphonate.

No record of 2:1-bromonaphthalene sulphonic acid was found in the literature. Since the potassium 2:1-iodo-sulphonate had readily yielded a dinaphthyl disulphonate, it was of interest to know whether the bromo-compound would also respond to the Ullmann reaction. Potassium 2:1-bromonaphthalene sulphonate was therefore prepared by the method used for the preparation of sodium 1:2-bromonaphthalene sulphonate:-

0.2 gm. of cuprous oxide was boiled with a solution of 6 gm. of ammonium bromide in 100 c.c. of water for several minutes and filtered. To the cold suspension of diammino-cuprous bromide in ammonium bromide solution so formed was added, with stirring, the solid diazo-compound from 5 gm. of sodium 2-napthylamine-1-sulphonate in the form of an aqueous paste. Nitrogen was evolved fairly rapidly at first and then the reaction slowed down, being complete after keeping for 24 hours. In subsequent preparations, the original amount of cuprous oxide was increased to about 1 gm., so reducing the reaction period to a matter of a few minutes. The resulting solution was boiled for a few minutes with decolourizing carbon, filtered and the filtrate salted out with potassium chloride, whereby the potassium bromo-sulphonate was isolated in good yield (of the order 70% theoretical).

(8) Derivatives of 2:1-Bromonaphthalene Sulphonic Acid.

(a) 2:1-Bromonaphthalene Sulphonyl Chloride.

Potassium 2:1-bromonaphthalene sulphonate was treated with phosphorus pentachloride, and the crude sulphonyl chloride isolated and crystallized from acetone-water in the usual manner. It consisted of pale yellow prisms. m.p. 97°C., shown to contain bromine. (Found S, 10.5%; $C_{10}H_6Br.SO_2Cl$ requires S, 10.5%).

(b) 2:1-Bromonaphthalene Sulphonamide.

Dilute ammonia in excess was added to an acetone solution of the sulphonyl chloride and the solution evaporated considerably. On cooling, the sulphonamide separated as colourless needles - recrystallized from acetone-water, m.p. 140°C. (Found Br, 27.4%; $C_{10}H_6Br.SO_2NH_2$ requires Br, 27.9%).

(9) Reaction of Potassium 2:1-Bromonaphthalene Sulphonate in Aqueous Solution with Copper Powder.

15 gm. of potassium 2:1-bromonaphthalene sulphonate (purified by recrystallization from water) were dissolved, with a little cupric sulphate, in 150 c.c. of hot water, and the solution boiled with 8 gm. of copper powder for half an hour. The formation of cuprous bromide was noted after boiling for a few minutes. After filtering, the solution was saturated with potassium chloride. A

substance separated, first as a syrupy liquid which subsequently solidified to a colourless crystalline mass, and this was filtered off, dried and treated with phosphorus pentachloride in the usual manner. The crude sulphonyl chloride was recrystallized from acetone-water, yielding colourless crystals, m.p. 246°C. (with decomp.), identical in form with the dinaphthyl disulphonyl chloride obtained from the potassium iodo-sulphonate. Considerable loss in yield is incurred through recrystallization, but the yield of crude washed disulphonyl chloride obtained by this reaction was approximately 40% theoretical.

(10) Reaction of 2:1-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cupric Sulphate Reduced by means of Sulphur Dioxide.

The reagent employed (Example 1 of E.P. 278,100) was prepared by passing sulphur dioxide through an ammoniacal solution of 20 gm. of hydrated cupric sulphate, and adding excess of ammonia to the reduced solution, as described in section I.(11).

An aqueous suspension of the diazo-compound obtained from 10 gm. of sodium 2-naphthylamine-1-sulphonate was added gradually through a dropping funnel, with mechanical agitation, to this solution at lab temperature. Nitrogen was evolved rapidly and the solution obtained was filtered once, after boiling, through decolourizing carbon and evaporated to isolate, as a series of crystalline crops, the total solute present. The latter was dried and triturated with phosphorus pentachloride, with subsequent addition of a large volume of cold water. The sulphonyl chloride obtained was filtered, washed with some concentrated hydrochloric acid (to remove any cuprous chloride) and then with water, and finally dried and crystallized twice from acetone-water after treatment with decolourizing carbon. It was found to melt at 245°C. (with decomp.) and to be identical in other respects with the 2:2'-dinaphthyl-1:1'-disulphonyl chloride obtained by the Ullmann reactions applied to the potassium 2:1-iodo- and bromo-sulphonates. The yield of crude disulphonyl chloride in this case was approximately 55% theoretical.

This is the only case in which a dinaphthyl disulphonic acid was identified as the product of the reaction between the diazonaphthalene sulphonic acids and this reagent, the general rule being the formation of naphthalene disulphonic acids.

(11) Reaction of 2:1-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cuprous Sulphate.

The tetrammino-cuprous sulphate solution (Example 6 of E.P. 278,100) was prepared in the manner described in section I.(13) by reducing an ammoniacal solution of 20 gm. of hydrated cupric sulphate with hydroxylamine.

To this solution was added the solid diazo-compound obtained from 10 gm. of sodium 2-naphthylamine-1-sulphonate, in the form of an aqueous suspension, with mechanical agitation. Nitrogen was rapidly evolved and, when this ceased, dilute sulphuric acid was added to precipitate the remaining cuprous compounds, and the solution filtered. Hydrogen sulphide was now passed through the filtrate to precipitate cupric copper, which was removed by filtering through carbon. After considerable evaporation the filtrate was salted out with potassium chloride. The salt which separated was filtered and dried, one half of it being converted into the sulphonyl chloride by treatment with phosphorus pentachloride, and the other half fused with caustic potash in a nickel crucible. The two derivatives obtained were shown, after purification, to be 2:2'-dinaphthyl-1:1'-disulphonyl chloride, m.p. 245°C.(with decomp.), and 1:1'-dihydroxy-2:2'-dinaphthyl, m.p. 213°C. respectively.

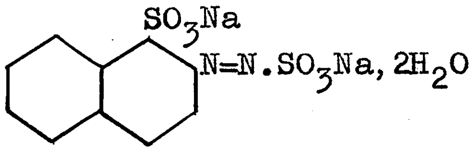
Thus treatment with this form of "ammoniacal cuprous oxide solution", which in the case of the other diazo-sulphonic acids had yielded azo-disulphonates, had converted 2:1-diazonaphthalene sulphonic acid directly into the correponding dinaphthyl disulphonic acid.

(12) Reaction of 2:1-Diazonaphthalene Sulphonic Acid with Sodium Sulphite Solution.

The two experiments now described were performed with the object of ascertaining whether 2:1-diazonaphthalene sulphonic acid reacted with sodium sulphite in a manner similar to the 1:4-diazo-compound, yielding an azo-disulphonate; and if so, to determine the course of the reaction.

(a) Diazo-compound added to neutral sodium sulphite.

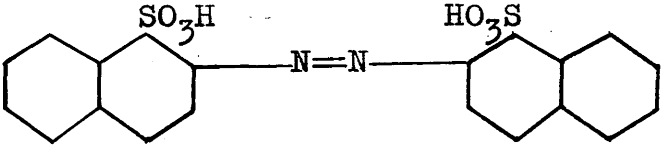
The solid diazo-compound obtained from 10 gm. of sodium 2-naphthylamine-1-sulphonate was added to a solution of 10 gm. of hydrated sodium sulphite ($7H_2O$) in 20 c.c. of water. The diazo-compound dissolved completely without evolution of gas to give an orange-red solution from which a yellow solid separated on standing. This substance was sufficiently stable to be recrystallized from warm water. On heating alone, it was found to sinter and to contain both water of crystallization and inorganic matter. On heating with 50% (by vol.) sulphuric acid, sulphur dioxide and probably nitrogen were evolved. Analysis, and the properties just described, indicated that this substance was a stable diazo-sulphonate of the formula -



(Found S, 15.7%; above diazo-sulphonate requires S, 16.0%).

(b) Diazo-compound added to neutral sodium sulphite with subsequent acidification.

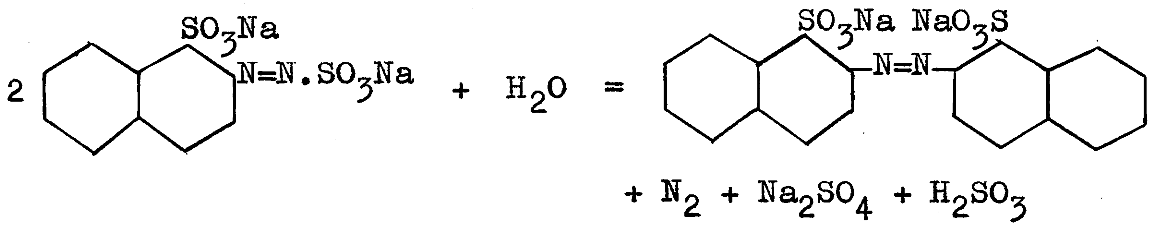
The solid diazo-compound obtained from 10 gm. of sodium 2-naphthylamine-1-sulphonate was dissolved, as in (a), in a solution of 13 gm. of hydrated sodium sulphite in 50 c.c. of water. A little dilute hydrochloric acid was added to the orange-red solution, producing an immediate precipitate which redissolved on shaking. The solution was then heated to 70°C. and made distinctly acid by addition of dilute hydrochloric acid, whereupon sulphur dioxide and probably nitrogen were evolved. No immediate precipitation occurred, but on cooling and allowing to stand an orange solid separated. This was recrystallized from hot water (slight evolution of gas) separating as minute red octahedra. It gave an acid reaction with litmus, and was found to contain no inorganic matter. No gas was evolved on heating it with sulphuric acid. Analysis, and the properties described, showed that the substance was the free azo-disulphonic acid -



(Found S, 14.5%; the azo-disulphonic acid requires S, 14.5%).

These two experiments show that a stable diazo-sulphonate is an intermediate product in the conversion of the 2:1-diazo-sulphonic acid to the corresponding azo-disulphonic acid by treatment with sodium sulphite followed by mineral acid.

It seems improbable that there is any other intermediate product in the reaction since the decomposition of the diazo-sulphonate by heating with acid apparently involved simultaneous evolution of sulphur dioxide.and nitrogen. As in the case of the reactions of other diazo-compounds with tetrammino-cuprous sulphate solution to form azo-disulphonates, there must be also a simultaneous reduction. The reaction is probably represented (approximately) by the equation -

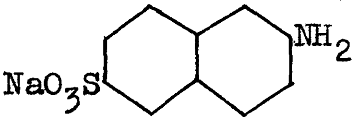


The mineral acid doubtless promotes the decomposition of the diazo-sulphonate, and liberates the free disulphonic acid.

VII. 2-NAPHTHYLAMINE-6-SULPHONIC ACID. (Brönner Acid).

(1) Preparation of Sodium 2-Naphthylamine-6-Sulphonate.

Sodium 2-naphthylamine-6-sulphonate was prepared from 78% Brönner acid by dissolving the latter in dilute caustic soda solution (hot), filtering through decolourizing carbon and rapidly cooling the filtrate. In this way the salt was obtained as a fine, almost colourless, crystalline meal which did not require further purification. It crystallizes from water with two molecules of water of crystallization -

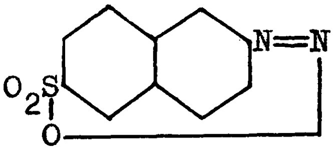


$.2H_2O$ M.W. 281.

(2) Diazotization of Brönner Acid.

Brönner acid is readily diazotized by the normal direct method:-

10 gm. of the sodium salt were dissolved in 300 c.c. of hot water and a quantity of dilute sulphuric acid equivalent to 2¼ mol. of the salt added. After cooling to room temperature, sodium nitrite solution (containing 2.6 gm. of $NaNO_2$) was introduced slowly with mechanical agitation. The diazotization was rapid, a curdy pale yellow suspension being formed which could be easily filtered. The diazo-compound has the structure -



(3) <u>Preparation of Potassium 2:6-Iodonaphthalene Sulphonate</u>.

Potassium 2:6-iodonaphthalene sulphonate was prepared according to the method of Houlding (Berichte, 1891, <u>24</u>(ii), 706) by heating 2:6-diazonaphthalene sulphonic acid with hydriodic acid:-

The solid diazo-compound from 20 gm. of sodium 2-naphthylamine-6-sulphonate was added, with stirring, to a solution of 25 gm. of potassium iodide in dilute sulphuric acid, and the suspension heated up gradually. The temperature was maintained at 55°C until nitrogen ceased to be evolved, and was then raised to boiling point for a few minutes. The hot solution was neutralized with caustic potash and cooled whereupon potassium 2:6-iodonaphthalene sulphonate separated in good yield as a pale yellow crystalline meal; recrystallized from hot water.

To establish its identity, some of the potassium salt was treated with phosphorus pentachloride, etc. and 2:6-iodonaphthalene sulphonyl chloride obtained. This crystallized from acetone-water as pale yellow needles, m.p. 140°C. - the figure given by Houlding (loc. cit.). The sulphonamide, m.p. 222°C., was prepared by treating an acetone solution of the sulphonyl chloride with ammonia; Houlding (loc. cit.) gives m.p. 220°C.

An aqueous solution of the potassium salt was now treated with copper powder in the usual manner.

(4) Attempt to Prepare 2:2'-Dinaphthyl-6:6'-Disulphonic Acid from Potassium 2:6-Iodonaphthalene Sulphonate.

10 gm. of potassium 2:6-iodonaphthalene sulphonate were dissolved in about 150 c.c. of hot water along with a little cupric sulphate, and the solution boiled under reflux for three hours with 4 gm. of copper powder.

There was no evidence of cuprous iodide being formed and, after filtering, the only substance identified in the solution was unchanged potassium 2:6-iodonaphthalene sulphonate which separated out readily on cooling owing to its sparing solubility in cold water. This was proved by conversion to the sulphonyl chloride and sulphonamide, whose melting points coincided with those recorded above.

(5) Reaction of 2:6-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cupric Sulphate Reduced by means of Sulphur Dioxide.

The reagent used is decribed in Example 1 of E.P.278,100, and was prepared in the manner recorded in section I.(11), by passing sulphur dioxide through ammoniacal cupric sulphate solution and adding excess of ammonia to the reduced solution.

To such a solution, prepared from 20 gm. of hydrated cupric sulphate, was added the diazo-compound from 10 gm. of sodium 2-naphthylamine-6-sulphonate in the form of an aqueous suspension. The addition was made slowly through a dropping funnel at room temperature, with mechanical agitation. Nitrogen was evolved rapidly and when this had ceased it was noticed that there was a slight suspension in the solution. On filtering, a very small quantity of orange solid was obtained, resembling in appearance and properties the product formed in the next experiment. It is believed to be an azo-disulphonate.

Concentrated hydrochloric acid in excess was added to the filtrate from the above, and the solution evaporated to about one third of its original volume. It was now saturated with hydrogen sulphide until all the copper was precipitated, carbon was added and, after warming, the solution was filtered. The filtrate was saturated with common salt, whereupon a large crop of crystalline solid separated. This appeared to consist mainly of ammonium salts, but after drying and treating with phosphorus pentachloride in the usual manner, a small quantity of sulphonyl chloride was isolated. After decolourizing an acetone solution with carbon, the sulphonyl chloride was recrystallized several times from acetone-water and found to melt at 223°C. Since Armstrong and Wynne (Proc. Chem. Soc., 1890, 127) state that naphthalene-2:6-disulphonyl chloride melts at 225°C., it was inferred that the above reaction has followed the general course observed with other diazo-sulphonic acids, and resulted partly in the formation of a naphthalene disulphonic acid.

(6) Reaction of 2:6-Diazonaphthalene Sulphonic Acid with an Ammoniacal Solution of Tetrammino-Cuprous Sulphate.

An ammoniacal solution of tetrammino-cuprous sulphate (Example 6, E.P.278,100) was prepared from 20 gm. of hydrated cupric sulphate in the manner described in section I.(13), by reducing an ammoniacal solution with hydroxylamine.

The diazo-compound obtained from 10 gm. of sodium 2-naphthylamine-6-sulphonate was gradually added in the form of an aqueous paste to this solution, at room temperature and with mechanical agitation. Nitrogen was rapidly evolved and a deeply coloured solution formed. On standing, a reddish microcrystalline substance separated slowly. The solution was filtered and the solid (about 1 gm.) recrystallized from hot water from which it separated as small orange hexagonal plates. On ignition, no inorganic residue was left and, on boiling with caustic soda solution, ammonia was evolved. On treating an aqueous solution with zinc and hydrochloric acid, the colour was discharged, and with concentrated sulphuric acid the solid formed a deep red solution, reverting to a paler shade on dilution. The substance was concluded to be diammonium 2:2'-azonaphthalene-6:6'-disulphonate. (Found S, 13.2%; $(:N.C_{10}H_6SO_3NH_4)_2$ requires S, 13.4%).

The filtrate from the above was boiled and dilute caustic soda solution added to eliminate copper and ammonia.

After boiling for about an hour, adding more caustic soda when necessary, some carbon was added and the solution filtered. On salting out the deeply coloured solution with common salt, a greyish substance separated which was then filtered off and subjected to the usual phosphorus pentachloride treatment. Attempts to isolate a sulphonyl chloride were fruitless however, and efforts to identify any other product of the reaction met with failure.

APPENDIX.

(1) Reaction of Naphthalene-β-Diazonium Chloride with an Ammoniacal Solution of Tetrammino-Cuprous Sulphate.

Another worker in the Royal Technical College obtained ββ-azonaphthalene (yield of pure product, 38%) and αα-azonaphthalene by treating the corresponding naphthalene diazonium chlorides with ammoniacal cuprous sulphite solution (sulphur dioxide reduction). (Private communication).

In a single experiment, the author treated naphthalene-β-diazonium chloride with ammoniacal cuprous sulphate solution (hydroxylamine reduction), to find out if the reaction took a similar course with this reagent.

The diazo-suspension obtained by diazotizing 10 gm. of β-naphthylamine was added gradually, with stirring, to an ammoniacal tetrammino-cuprous sulphate solution prepared in the following manner:-

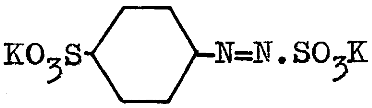
35 gm. of hydrated cupric sulphate were dissolved in 200 c.c. of water and 35 gm. of 0.88 ammonia added. To this was added the solution obtained by dissolving 8 gm. of hydroxylamine hydrochloride and 6 gm. of potassium hydroxide in 100 c.c. of water.

On the addition of the diazo-suspension, nitrogen was rapidly evolved and a deep red compound separated. After warming to 60°C. on a water bath to complete the reaction, the suspension was cooled and filtered. The crude product was crystallized from hot benzene and found to melt at 205°C., showing that it was ββ-azonaphthalene. No other substance was identified in the product. The yield of crude azonaphthalene was approximately 60% theoretical.

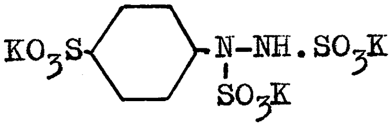
(2) Reaction between Diazotized Sulphanilic Acid and Sodium Sulphite Solution.

These experiments are recorded with the kind permission of Dr. T. Love, who followed up the author's initial work on reactions with sodium sulphite applying them to other diazo-compounds. This work was also supervised by Professor Cumming.

The action of potassium sulphite on diazotized sulphanilic acid has been investigated by Pechmann (Berichte, 1895, 28, 867), Hantzsch and Schmidt (Berichte, 1897, 30, 79), Strecher (Berichte, 1871, 4, 785) and Fischer (Annalen, 190, 76). It was found that on treatment with an equivalent of potassium sulphite, the potassium salt of benzene-1-sulphonic-4-diazo-sulphonic acid was formed -



With excess of potassium sulphite, the potassium salt of 4(αβ-disulphohydrazino)-benzene sulphonic acid was formed -

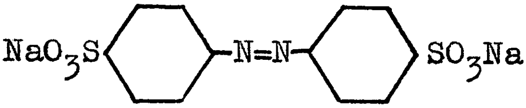


In addition, Fischer (loc. cit.) found that a weakly alkaline solution of diazotized sulphanilic acid treated with potassium sulphite and then boiled with hydrochloric acid yielded phenylhydrazine-4-sulphonic acid.

Dr. Love performed the following experiments with diazotized sulphanilic acid and sodium sulphite:-

(a) The solid diazo-compound obtained from 10 gm. of sodium sulphanilate was added to 10 gm. of hydrated sodium sulphite (equivalent to 0.77 mol.) in 15 c.c. of water. It dissolved giving a clear orange-yellow solution, with evolution of sulphur dioxide and possibly nitrogen. The solution was made alkaline and nitrogen was evolved. On concentrating a yellow solid separated (6 gm.). This solid did not decompose when heated with dilute sulphuric acid, but gave a clear yellow solution. When heated with 60% sulphuric acid, sulphur dioxide was evolved. It was found to contain water of crystallization, and was believed to be a hydrated form of the sodium azobenzene-4:4'-disulphonate obtained in (b). (Found S, 15.3%; $(:N.C_6H_4.SO_3Na)_2,2H_2O$ requires S, 15.2%).

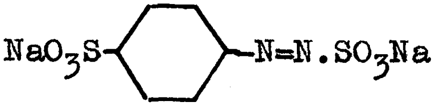
(b) The solution obtained by adding the solid diazo-compound from 10 gm. of sodium sulphanilate to 10 gm. of hydrated sodium sulphite in 15 c.c. of water was warmed and made alkaline so that no sulphur dioxide was evolved. A gas, probably nitrogen, was given off and, on cooling, a reddish brown solid separated. The deep red filtrate was discarded and the solid dissolved in water and precipitated by the addition of alcohol. This gave an orange-yellow solid which was recrystallized from water-alcohol, giving yellow needles (4 gm.). The product did not evolve sulphur dioxide on heating with dilute sulphuric acid, but did so with more concentrated acid. The product is apparently disodium azobenzene-4:4'-disulphonate -



(requiring S, 16.6%; found S, 16.6%).

(c) The solid diazo-compound from 10 gm. of sodium sulphanilate was added in small quantities to a solution of 30 gm. of hydrated sodium sulphite (2.31 mol.) in 40 c.c. of water. On addition of the first portions of the diazo-compound, an orange-red solution was formed, and this changed to yellow finally becoming colourless. Successive additions behaved similarily except that the solution did not finally become colourless but remained orange-yellow having changed from an initial reddish-orange. When all the diazo-compound had been added, the solution was warmed to 30°C. A small amount of gas was evolved and, on stirring vigorously, a yellow solid (elongated prisms) separated. This solid was recrystallized from water. It sintered on heating, but did not appear to contain water of crystallization. It is believed to be the sodium salt of benzene-1-sulphonic-4-

diazo-sulphonic acid corresponding to the potassium diazosulphonate obtained by Pechmann (loc. cit.) -



requires S, 20.6%;
found S, 19.9%.

The behaviour of diazotized sulphanilic acid with sodium sulphite is thus somewhat similar to that of 1:4- and 2:1-diazonaphthalene sulphonic acids; particularly the 2:1-compound which yielded both a stable diazotate and an azo-compound.

SUMMARY.

The more important experimental results of this investigation are now summarized in tabular form.

TABLE I. Preparation of Halogenonaphthalene Sulphonic Acids.

These were isolated as salts and derivatives. Those acids or derivatives to which no reference was found in the literature are underlined.

Halogeno-Sulphonic Acid.	Method of Preparation:- Diazonaphthalene Sulphonic Acid treated with -	Sulpho-Derivatives.
1:2-Bromo-	Suspension of diammino-cuprous bromide in ammonium bromide solution.	Chloride. Amide.
1:2-Iodo-	Hot solution of hydriodic acid.	Chloride. Amide.
1:4-Chloro-	Hot solution of cuprous chloride in concentrated hydrochloric acid.	Chloride. Amide. Anilide. o-Toluidide. p-Nitroanilide. α-Naphthylamide.
1:4-Iodo-	Potassium iodide solution and copper powder in the cold. (New method of preparation).	Chloride. Amide. Anilide. o-Toluidide.
1:5-Iodo-	Hot solution of hydriodic acid.	Chloride. Amide.
1:7-Iodo-	Hot solution of hydriodic acid.	Chloride. Amide.

Continued on next page.

TABLE I. - continued.

Halogeno-Sulphonic Acid.	Method of Preparation:- Diazonaphthalene sulphonic acid treated with -	Sulpho-Derivatives.
1:8-Chloro-	Cold solution of cuprous chloride in concentrated hydrochloric acid.	Chloride. Amide.
1:8-Bromo-	Suspension of diammino-cuprous bromide in ammonium bromide solution.	Chloride.
1:8-Iodo-	Cold solution of potassium iodide containing pyridine or acetone.	Chloride. Amide. Anilide.
2:1-Bromo-	Suspension of diammino-cuprous bromide in ammonium bromide solution.	Chloride. Amide.
2:1-Iodo-	Hot solution of hydriodic acid.	Chloride. Amide.
2:6-Iodo-	Hot solution of hydriodic acid.	Chloride. Amide.

Two new derivatives of naphthalene-α-sulphonic acid were also prepared, the o-toluidide and p-nitroanilide, while the melting point of the anilide was found to be 152°C. as against 112°C. recorded in the literature.

The chloride and amide of 1:8-cyanonaphthalene sulphonic acid, which are not recorded in the literature, were also obtained.

TABLE II. Reactions of Salts and Derivatives of Halogenonaphthalene Sulphonic Acids with Copper and Other Powdered Metals.

Halogeno-Sulphonic Acid.	Salt or Derivative Employed.	Metal and Reflux Medium.	Reaction.
1:2-Bromo-	Na salt.	Cu in H_2O.	None.
1:2-Iodo-	K salt.	Cu in H_2O.	Iodine rapidly replaced with formation of 1:1'-Dinaphthyl-2:2'-disulphonic acid and naphthalene-β-sulphonic acid.
1:4-Chloro-	Cu, Na or K salt.	Cu, Zn, Mg or Al in H_2O.	None.
	Anilide.	Fused with Cu or Zn.	None.
1:4-Iodo-	K salt.	Cu in H_2O	Iodine gradually replaced with formation of naphthalene-α-sulphonic acid.
		Zn or Mg in H_2O.	As with Cu, but replacement more rapid.
	Amide.	Zn in pyridine.	None.
		Mg in $C_6H_5.NO_2$.	None.
		Zn in quinoline.	Iodine replaced but no identifiable product.
	Anilide.	Cu or Zn in pyridine.	None.
		Cu or Zn in quinoline.	Iodine replaced but no identifiable product.
1:5-Iodo-	K salt.	Cu in H_2O.	None.
		Zn in H_2O	Iodine replaced. Naphthalene-α-sulphonic acid formed.

TABLE II. - continued.

Halogeno-Sulphonic Acid.	Salt or Derivative Employed.	Metal and Reflux Medium.	Reaction.
1:7-Iodo-	Na salt.	Cu in H_2O.	None.
1:8-Iodo-	Na salt.	Cu in H_2O.	Iodine replaced rapidly with formation of 1:1'-dinaphthyl-8:8'-disulphonic acid.
	Anilide.	Cu in $C_2H_5.OH$.	Iodine replaced with formation of N-phenyl-1:8-naphthasultam.
2:1-Bromo-	K salt.	Cu in H_2O.	Bromine readily replaced with formation of 2:2'-dinaphthyl-1:1'-disulphonic acid.
2:1-Iodo-	K salt.	Cu in H_2O.	Iodine replaced rapidly with formation of 2:2'-dinaphthyl-1:1'-disulphonic acid.
2:6-Iodo-	K salt.	Cu in H_2O	None.

TABLE III. Reaction of Diazonaphthalene Sulphonic Acids with Ammoniacal Cuprous Sulphite Solution.

Diazo-Sulphonic Acid.	Product. Derivative of -
1:2-	Naphthalene-1:2-disulphonic acid.
1:4-	Naphthalene-1:4-disulphonic acid.
1:5-	Naphthalene-1:5-disulphonic acid.
1:7-	No identifiable product.
1:8-	Naphthalene-1:8-disulphonic acid.
2:1-	2:2'-Dinaphthyl-1:1'-disulphonic acid.
2:6-	Naphthalene-2:6-disulphonic acid and a small quantity of a 2:2'-azonaphthalene-6:6'-disulphonate.

TABLE IV. Reaction of Diazonaphthalene Sulphonic Acids with Tetrammino-Cuprous Sulphate Solution.

Diazo-Sulphonic Acid.	Product. Salt or derivative of -
1:2-	1:1'-Azonaphthalene-2:2'-disulphonic acid.
1:4-	1:1'-Azonaphthalene-4:4'-disulphonic acid.
1:5-	1:1'-Azonaphthalene-5:5'-disulphonic acid.
1:8-	1:1'-Azonaphthalene-8:8'-disulphonic acid.
2:1-	2:2'-Dinaphthyl-1:1'-disulphonic acid.
2:6-	2:2'-Azonaphthalene-6:6'-disulphonic acid.

Notes on Tables III and IV.

A few inferences may be drawn from the combined results shown in Tables III and IV, but their value is necessarily limited by the fact that the reactions of all the diazonaphthalene sulphonic acids have not been investigated.

(1) When the diazo-group is in the α-position, ammoniacal cuprous sulphite solution yields naphthalene-disulphonic acids, whereas ammoniacal cuprous sulphate solution yields azo-compounds.

(2) When the diazo-group is in the β-position, both reagents yield azo-compounds, or formation of a dinaphthyl disulphonic acid or naphthalene disulphonic acid takes place.

(3) When the sulphonic acid group is in the same half of the nucleus as the diazo-group in the β-diazo-compounds, diaryl-formation occurs with both reagents.

(4) When the sulphonic acid group is in the other half of the nucleus from the diazo-group in the β-diazo-compounds, an azo-compound or naphthalene disulphonic acid is formed.

(5) The relative positions of the sulphonic acid group apparently does not influence the results when the diazo-group is in the α-position.

TABLE V. Reactions of Diazonaphthalene Sulphonic Acids in which the Diazo-Group was Replaced by Hydrogen.

Diazo-Sulphonic Acid.	Reagent.
1:4-	(1) Suspension containing pyridine saturated with sulphur dioxide.
	(2) Sodium meta-bisulphite solution.
1:8-	(1) Suspension of copper powder in concentrated hydrochloric acid.
	(2) Suspension of copper powder in concentrated hydrochloric acid solution of cuprous chloride.
	(3) Aqueous suspension of zinc dust.
	(4) Ammoniacal suspension of stannous hydroxide.

Miscellaneous Results.

(a) The claim made in E.P. 278,100, that 1:1'-dinaphthyl-8:8'-dicarboxylic acid was formed by the reaction between 1:8-diazonaphthoic acid and "ammoniacal cuprous oxide solution" was confirmed. The preparation of naphthostyril by alkaline hydrolysis of 1:8-cyanonaphthalene sulphonic acid, as claimed in E.P. 276,126, was also confirmed.

(b) Attempts to prepare sulpho-derivatives of naphthionic acid resulted in the formation of other bodies, viz. phenyl-α-naphthylamine, aniline naphthionate, α- and β-naphthylamine naphthionates, and ββ-dinaphthylamine.

(c) 1:4- and 2:1-diazonaphthalene sulphonic acids reacted with sodium sulphite, under suitable conditions, to form azonaphthalene disulphonic acids (or salts thereof). A diazo-sulphonate was shown to be an intermediate product in the formation of 2:2'-azonaphthalene-1:1'-disulphonic acid.

(d) A nitro derivative and sodium nitro-1-naphthol-8-sulphonate were prepared from 1:8-naphthasultone.

(e) ββ-Azonaphthalene was obtained by treating naphthalene-β-diazonium chloride with ammoniacal tetrammino-cuprous sulphate solution.

SUBSTITUTED NAPHTHALENE SULPHONIC ACIDS AND THEIR DERIVATIVES

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Substituted Naphthalene Sulphonic Acids and their Derivatives.

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ABSTRACT.

The acids and derivatives described herein have been prepared in the course of work which has been a continuation of that recorded in a previous paper.[1] That paper contained an account of the preparation of 1 : 4- and 1 : 8-chloronaphthalene sulphonic acids, 1 : 4- and 1 : 5-iodonaphthalene sulphonic acids and a number of their derivatives, and some new derivatives of naphthalene-α-sulphonic acid and naphthionic acid. Attempts to prepare 1 : 8-iodonaphthalene sulphonic acid were also described.

1 : 8-iodo- and 1 : 8-bromo-naphthalene sulphonic acids, 2 : 1-iodo- and 2 : 1-bromonaphthalene sulphonic acids have now been prepared as their potassium or sodium salts, and derivatives obtained. An improved method for the preparation of 1 : 8-chloronaphthalene sulphonic acid, reactions in which naphthalene-α-sulphonic acid has been obtained from diazo-peri acid, and the preparation of 1 : 8-cyanonaphthalene sulphonic acid and derivatives, are recorded. An interesting reaction which resulted in the conversion of 1 : 4-, 1 : 5- and 1 : 8-diazonaphthalene sulphonic acids to the corresponding naphthalene disulphonic acids is also noted.

I. 1 : 8-*Iodonaphthalene Sulphonic Acid and Derivatives.*

From a solution of 10 gm. of sodium periate (1-naphthylamine-8-sulphonate) in 200 c.c. of boiling water, peri acid was precipitated in a fine form by the addition of dilute sulphuric acid (equivalent to 2¼ mol.). After cooling to room temperature, the suspension was diazotized by gradual addition of slight excess of sodium nitrite yielding a solid diazo-compound which was further separated by salting out with common salt. After filtration, this was suspended in a solution of 15 gm. of potassium iodide in 150 c.c. of water containing 1 c.c. of pyridine. The suspension was kept, with intermittent stirring, for two days at room temperature, by which time the gradual evolution of nitrogen had ceased. After boiling for a few minutes, the resultant suspension was filtered ; the residue, crystallized from acetone, was identified as 1 : 8-naphthasultone (m.p. 156° C.). The pinkish crystalline plates obtained by saturating the filtrate with salt were recrystallized from water, using decolourizing carbon, and were subsequently identified as sodium 1 : 8-iodonaphthalene sulphonate by analysis of derivatives obtained. (Yield, 70 per cent.).

The acid was also produced in absence of pyridine under the above conditions, but the duration of nitrogen evolution was much longer and the yield of naphthasultone higher with a correspondingly poor yield of iodo-salt. The duration of nitrogen evolution was considerably diminished by slight increases in temperature. While increase of pyridine also effected more rapid nitrogen evolution, large quantities resulted in the separation of a highly-coloured gummy product on salting out.

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[1] This Journal, 1934, 223.

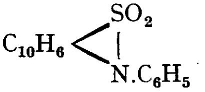
It was found that acetone could be used in place of pyridine to facilitate nitrogen evolution, fairly good yields of the iodo-sulphonate being obtained.

(*a*) *Preparation of* 1 : 8-*Iodonaphthalene Sulphonyl Chloride.*—The sulphonyl chloride was prepared by treating the sodium salt obtained above with phosphorus pentachloride, the crude product being isolated by addition of excess of cold water. After two or three recrystallizations from acetone-water, using decolourizing carbon, the pure derivative was obtained as pale yellow plates, m.p. 115° C. (Found S, 9·1 per cent. ; $C_{10}H_6I.SO_2Cl$ requires S, 9·1 per cent.).

(*b*) *Preparation of* 1 : 8-*Iodonaphthalene Sulphonamide.*—Dilute ammonia was added gradually, with stirring, to a cold solution of the pure sulphonyl chloride in acetone. In this way, colourless crystalline plates of the sulphonamide separated out gradually, m.p. (decomp.) 187° C. (Found I, 37·9 per cent. ; $C_{10}H_6I.SO_2NH_2$ requires I, 38·1 per cent.).

(*c*) *Formation of* 1 : 8-*Naphthasultam.*—In an attempt to prepare 1 : 8-iodonaphthalene sulphonamide by boiling an acetone solution of the sulphonyl chloride with aqueous ammonia, a product containing no iodine was obtained which, after recrystallization from acetone-water, gave m.p. 176° C. Peri-naphthasultam melts at 177° C. according to Dannerth.[2] Thus it appears that the iodonaphthalene sulphonamide first formed is readily converted at higher temperatures, in the presence of ammonia, to peri-naphthasultam, ring closure being effected by the elimination of hydriodic acid.

(*d*) *Preparation of* 1 : 8-*Iodonaphthalene Sulphoanilide.*—Slight excess of aniline was added to an acetone solution of the sulphonyl chloride, the solution being slowly evaporated on the water bath to small bulk. A yellow semi-solid product separated on the addition of water which, after removal of excess aniline by redissolving in acetone and re-precipitation with dilute hydrochloric acid, was recrystallized several times from acetone-water, giving pale yellow plates, m.p. 140° C. (Found I, 29·8 per cent. ; $C_{10}H_6I.SO_2NH.C_6H_5$ requires I, 31·0 per cent.).

(*e*) *Formation of Phenyl*-1 : 8-*Naphthasultam.*—A solution of 3 gm. of 1 : 8-iodonaphthalene sulphoanilide in 50 c.c. of alcohol was refluxed with copper powder for about three hours and, after filtering, was concentrated to half its original bulk. On cooling, colourless prism-shaped crystals, recrystallized from alcohol and containing no iodine, separated, m.p. 165° C. (Found S, 11·3 per cent. ;  $C_{10}H_6\left<\begin{array}{l}SO_2\\ |\\ N.C_6H_5\end{array}\right.$ requires S, 11·4 per cent. Found Mol. Wt., 293 ; requires Mol. Wt., 281).

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[2] J.A.C.S., 1907, *29*, 1319.

König and Wagner,[3] who obtained peri-phenylnaphthasultam from N-phenyl-1-naphthylamine-8-sulphonate by treatment with phosphoryl chloride, give m.p. 158° C.

II. 1 : 8-*Chloronaphthalene Sulphonic Acid.*

It was found that while methods of preparing 1 : 8-chloronaphthalene sulphonic acid from diazo-peri acid by treatment with hot solutions of cuprous chloride in concentrated hydrochloric acid result in a poor yield of the chloro-acid and a correspondingly high yield of naphthasultone, a treatment similar to that employed in the preparation of 1 : 8-iodonaphthalene sulphonic acid gave greatly improved yields.

The solid diazo-compound from 10 gm. of sodium periate was added to a cold solution of cuprous chloride in about 40 c.c. of concentrated hydrochloric acid. The suspension was allowed to stand for several days at room temperature, with intermittent stirring, until the gradual evolution of nitrogen had ceased. After diluting slightly and boiling, the solution was treated with sodium hydroxide solution to neutralize and eliminate copper, and filtered through carbon. By salting out, sodium 1 : 8-chloronaphthalene sulphonate was obtained, this being converted by treatment with phosphorus pentachloride into the sulphonyl chloride, m.p. 101° C. (Yield 45 per cent.). The sulphonamide was derived by treating an acetone solution of the sulphonyl chloride with ammonia solution, m.p. 199° C.

Cleve[4] records m.p. 101° C. and 196-197° C. respectively for these derivatives.

III. 1 : 8-*Bromonaphthalene Sulphonic Acid and Derivative.*

Two attempts to prepare this acid by means similar to those employed in the preparation of 1 : 8-iodo- and 1 : 8-chloro-naphthalene sulphonic acids were made without success. They consisted of maintaining for several days at room temperature (*a*) a suspension of diazo-peri acid in potassium bromide solution containing pyridine, and (*b*) a suspension of diazo-peri acid in a sulphuric acid solution of cuprous bromide. Nitrogen evolution was very slow and naphthasultone was the only product identified in both cases.

The acid has been isolated as the sulphonyl chloride, however, in the following manner :—

1 gm. of cuprous oxide was boiled with a solution of 12 gm. of ammonium bromide in 150 c.c. of water for five minutes, and filtered hot. To the cold suspension of diammino-cuprous bromide in ammonium bromide so formed was added, with stirring, the solid diazo-compound obtained from 10 gm. of sodium periate. This suspension was kept for 24 hours at room temperature,

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[3] Ber., 1924, *57* (ii), 1059.

[4] Ber., 1890, *23*, 962.

when nitrogen evolution had ceased, and was then boiled, filtered through carbon, and the filtrate salted out with potassium chloride. The dark-coloured product which separated was filtered, dried and treated with phosphorus pentachloride, the crude sulphonyl chloride being recrystallized once or twice from acetone-water, using decolourizing carbon. A small yield of pale yellow hexagonal plates containing bromine, m.p. 110° C., was obtained. (Found S, 10·6 per cent. ; $C_{10}H_6Br.SO_2Cl$ requires S, 10·5 per cent.).

Increasing the quantity of diammino-cuprous bromide, the function of which appears to be catalytic, facilitates more rapid nitrogen evolution but does not increase the yield, which was poor, side reactions being indicated by the intense colour of the suspension obtained.

IV. 1 : 8-*Cyanonaphthalene Sulphonic Acid Derivatives.*

The method adopted for preparing the sodium salt of 1 : 8-cyanonaphthalene sulphonic acid is outlined in D.R.P. 444,325[5].

To 12 gm. of crystallized cupric sulphate in 200 c.c. of water, at about 40° C., were added with shaking 13 gm. of potassium cyanide. To the clear solution was added dilute hydrochloric acid until a faint opalescence was produced, thus removing excess of potassium cyanide.

The solid diazo-compound obtained from 10 gm. of sodium periate was gradually added in small quantities to this cuprous cyanide solution at 50-60° C., with continual shaking. The product was then heated on the water-bath for an hour, and the cuprous cyanide precipitated with concentrated hydrochloric acid. The filtrate, after removal of cuprous cyanide, was made alkaline with caustic soda and evaporated to half its original volume. Sodium 1 : 8-cyanonaphthalene sulphonate separated as a pale pink solid on saturating this solution with sodium chloride. The pure salt (colourless needles) was obtained by decolourizing an aqueous solution of the crude product with carbon and salting out from a hot solution.

(*a*) *Preparation of* 1 : 8-*Cyanonaphthalene Sulphonyl Chloride.*—The sodium salt was treated with phosphorus pentachloride in the usual manner, and the crude sulphonyl chloride, crystallized from acetone, using decolourizing carbon, gave colourless leaflets, m.p. 139° C. (Found Cl, 14·3 per cent. ; $C_{10}H_6CN.SO_2Cl$ requires Cl, 14·1 per cent.).

(*b*) *Preparation of* 1 : 8-*Cyanonaphthalene Sulphonamide.*—An acetone solution of the sulphonyl chloride was treated with excess of aqueous ammonia and evaporated to small volume. The sulphonamide crystallized out on cooling and, after recrystallization from dilute ammonia, gave m.p. 334-336° C. (Found N, 11·6 per cent. ; $C_{10}H_6CN.SO_2NH_2$ requires N, 12·0 per cent.).

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[5] Chem. Zent., 1927, *3*, 742.

V. *Naphthalene-α-Sulphonic Acid from Diazo-Peri Acid.*

Brief mention may be made here of four reactions of diazo-peri acid, all of which resulted in the formation of naphthalene-α-sulphonic acid in good yield :—

(*a*) Treatment of the solid diazo-compound with a suspension of copper powder in concentrated hydrochloric acid, in the cold.

(*b*) Treatment of the solid diazo-compound with a suspension of copper powder in a solution of cuprous chloride in concentrated hydrochloric acid, in the cold.

(*c*) Action of an ammoniacal suspension of stannous hydroxide on the solid diazo-compound, in the cold.

(*d*) Action of zinc dust on an aqueous suspension of the solid diazo-compound, in the cold.

In each case the formation of naphthalene-α-sulphonic acid was verified by preparing the sulphonyl chloride, m.p. 65-66° C. and the sulphonamide, m.p. 150-151° C.

VI. 2 : 1-*Iodonaphthalene Sulphonic Acid and Derivatives.*

2 : 1-iodonaphthalene sulphonic acid, to which no reference has been found in the literature, has been prepared as its potassium salt in the following manner :—

10 gm. of sodium 2-naphthylamine-1-sulphonate were dissolved in 250 c.c. of warm water and the requisite volume of dilute sulphuric acid ($2\frac{1}{4}$ mol.) added. The fine suspension of Tobias acid so produced was diazotized at room temperature in the usual manner, with agitation. The solid yellow crystalline diazo-compound obtained was filtered and added to a solution of 15 gm. of potassium iodide in 150 c.c. of dilute sulphuric acid (approximately 5N). This suspension was slowly heated with stirring until nitrogen evolution commenced. All the nitrogen was evolved between 70° and 80° C., and a clear orange-red solution resulted. The hot solution was neutralized with potassium hydroxide, and pale yellow plates (leaf-shaped) of the potassium iodo-sulphonate separated on cooling, this being sparingly soluble in cold water. The compound gave up its water of hydration on heating at 145° C. for two hours, without decomposition. Yield, 65 per cent. (Found I, 32·5 per cent. ; $C_{10}H_6I.SO_3K.H_2O$ requires I, 32·5 per cent. Found H_2O, 4·5 per cent. ; requires H_2O, 4·6 per cent.).

(*a*) *Preparation of* 2 : 1-*Iodonaphthalene Sulphonyl Chloride.*—The potassium salt obtained above was treated in the usual manner with phosphorus pentachloride, the crude sulphonyl chloride being separated by the addition of excess of cold water. After crystallizing several times from acetone-water, pale yellow crystals, m.p. 109·5° C., were obtained. (Found S, 9·2 per cent. ; $C_{10}H_6I.SO_2Cl$ requires S, 9·1 per cent.).

(*b*) *Preparation of* 2 : 1-*Iodonaphthalene Sulphonamide.*—A solution of the sulphonyl chloride in alcohol, after warming with dilute aqueous ammonia, was allowed to cool and the crystals which readily separated were recrystallized from alcohol giving colourless needles, m.p. 154° C. (Found S, 9·6 per cent. ; $C_{10}H_6I.SO_2NH_2$ requires S, 9·6 per cent.).

VII. 2 : 1-*Bromonaphthalene Sulphonic Acid and Derivatives.*

0·2 gm. of cuprous oxide was boiled with a solution of 6 gm. of ammonium bromide in 100 c.c. of water for several minutes and filtered. To the cooled filtrate was added, with stirring, the solid diazo-compound from 5 gm. of sodium 2-naphthylamine-1-sulphonate. Nitrogen was evolved fairly rapidly at first and then the reaction slowed down, being complete after keeping for 24 hours. Increasing the amount of diammino-cuprous bromide, however, reduced the reaction period to a few minutes. The resultant solution was boiled for a few moments with carbon, filtered, and the filtrate salted out with potassium chloride, whereby the potassium bromo-sulphonate was isolated in good yield.

(*a*) *Preparation of* 2 : 1-*Bromonaphthalene Sulphonyl Chloride.*—The potassium bromo-sulphonate was treated with phosphorus pentachloride, and the crude sulphonyl chloride isolated and recrystallized from acetone-water in the usual manner. Very pale yellow prisms, containing bromine, m.p. 97° C., were obtained. (Found S, 10·5 per cent. ; $C_{10}H_6Br.SO_2Cl$ requires S, 10·5 per cent.).

(*b*) *Preparation of* 2 : 1-*Bromonaphthalene Sulphonamide.*—Dilute ammonia in excess was added to an acetone solution of the sulphonyl chloride and the solution evaporated considerably. On cooling, the sulphonamide separated as colourless needles, recrystallized from acetone-water, m.p. 140° C. (Found Br, 27·4 per cent. ; $C_{10}H_6Br.SO_2NH_2$ requires Br, 27·9 per cent.).

VIII. *Naphthalene Disulphonic Acids.*

Naphthalene -1 : 4-, -1 : 5-, and -1 : 8- disulphonic acids have been identified among the products of reaction between the diazo-compounds from the corresponding 1 : 4-, 1 : 5-, and 1 : 8- aminonaphthalene sulphonic acids and an ammoniacal solution of cuprous oxide prepared in the following manner :—

30 c.c. of 0·88 ammonia solution were added to a solution of 20 gm. crystallized cupric sulphate in 300 c.c. of water, and sulphur dioxide was passed through until the deep blue colour was discharged.

Sufficient ammonia solution was now added to keep the solution alkaline until the completion of the reaction, and the suspension obtained by diazotizing 10 gm. of the sodium aminonaphthalene sulphonate added gradually, with agitation. After nitrogen evolution had ceased, the solution was evaporated to small bulk and, by cooling and further evaporation, most of the solute was isolated. After drying thoroughly, the crystalline product mixed with inorganic salts was treated with phosphorus pentachloride in the usual manner.

In the case of diazo-naphthionic acid, naphthalene-1 : 4-disulphonyl chloride, m.p. 158° C., was isolated. (Found S, 19·5 per cent., Cl, 21·4 per cent.; $C_{10}H_6(SO_2Cl)_2$ requires S, 19·7 per cent., Cl, 21·8 per cent.). The sulphonamide prepared from this gave m.p. 269° C. The melting points recorded by Armstrong and Wynne,[6] and Gattermann,[7] for these derivatives are 160° C. and 273° C. respectively.

In the case of diazo-Laurent acid, naphthalene-1 : 5-disulphonyl chloride, m.p. 182° C., was isolated. (Found S, 19·7 per cent., Cl, 21·4 per cent.; requires S, 19·7 per cent., Cl, 21·8 per cent.). The m.p. recorded by Armstrong [8] is 183° C.

In the case of diazo-peri acid, however, naphthalene-1 : 8-disulphonic anhydride was obtained, m.p. 225° C. (Found S, 23·3 per cent.; $C_{10}H_6:(SO_2)_2O$ requires S, 23·6 per cent.). Armstrong and Wynne[6] record m.p. 227° C.

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[6] Proc. Chem. Soc., 1893, 166.
[7] Ber., 1899, *32*, 1156.
[8] Ber., 1882, *15*, 205.

THE FORMATION OF DINAPHTHYL DISULPHONIC ACIDS

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The Formation of Dinaphthyl Disulphonic Acids.

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ABSTRACT.

In two previous papers [1] [2] we have recorded the preparation of a number of halogen substituted naphthalene sulphonic acids and their derivatives. These were prepared with the object of converting them to dinaphthyl disulphonic acids by means of the Ullmann reaction with copper powder. Barber and Smiles [3] obtained 1 : 1′-dinaphthyl-2 : 2′-disulphonic acid by this reaction, though apparently in very small yield, but we have so far failed to confirm their results. We have, however, applied the reaction successfully to 2 : 1- and 1 : 8-iodonaphthalene sulphonic acids, and shown that it does not result in diaryl formation when 1 : 4-, 1 : 5- and 2 : 6-iodonaphthalene sulphonic acids are used. Experiments on the application of the Ullmann reaction to bromonaphthalene sulphonic acids are recorded, and a method for the preparation of 1 : 2-bromonaphthalene sulphonic acid is described.

In our last paper [2] (Section VIII) a reaction was described whereby diazonaphthalene sulphonic acids were converted into naphthalene disulphonic acids by treatment with an ammoniacal solution of cuprous oxide prepared by reducing tetrammino-cupric sulphate solution with sulphur dioxide. A similar reaction applied to diazonaphthoic acids is claimed in a Patent [4] to yield dinaphthyl dicarboxylic acids. Other reactions suggested by this Patent have been applied to diazonaphthalene sulphonic acids with interesting results. When the " ammoniacal cuprous oxide solution " took the form of tetrammino-cuprous sulphate solution, 2 : 1-diazonaphthalene sulphonic acid yielded 2 : 2′-dinaphthyl-1 : 1′-disulphonic acid, but when subjected to the same treatment, 1 : 2-, 1 : 4-, 1 : 8- and 2 : 6-diazonaphthalene sulphonic acids gave azonaphthalene disulphonates of the Cuba Orange type.

The results recorded are classified according to the dinaphthyl disulphonic acids which we hoped to prepare.

I. 1 : 1′-*Dinaphthyl*-2 : 2′-*Disulphonic Acid.*

(*a*) *Reaction of Sodium* 1 : 2-*Iodonaphthalene Sulphonate with Copper Powder.*—Sodium 1 : 2-iodonaphthalene sulphonate was prepared according to the method of Barber and Smiles [3] in the following manner :—

The solid diazo-compound from 10 gm. of sodium *o*-naphthionate was added to a solution of 15 gm. of potassium iodide in 100 c.c. of dilute sulphuric acid (3N). The mixture was heated gradually, with constant stirring, until nitrogen was being evolved at a moderate rate, at which temperature it was maintained until the reaction was complete. On cooling, a large crop of crystals separated in the deeply coloured solution. This was filtered off,

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[1] This Journal, 1934, p. 223.

[2] This Journal, 1936, p. 562.

[3] J. C. S., 1928, 1148.

[4] E.P., 278,100.

suspended in about 100 c.c. of hot water and neutralized with sodium hydroxide solution. After filtering hot, sodium 1 : 2-iodonaphthalene sulphonate crystallized from the filtrate on cooling.

On treatment with phosphorus pentachloride, this yielded 1 : 2-iodonaphthalene sulphonyl chloride, m.p. 94° C. (Barber and Smiles give 94° C.). 1 : 2-iodonaphthalene sulphonamide (hitherto unrecorded) was prepared from the sulphonyl chloride by dissolving a quantity of the latter in acetone and adding excess of aqueous ammonia. The sulphonamide separated as colourless prisms on evaporating the solution to small bulk ; recrystallized from acetone-water, m.p. 247° C. (Found I, 38·1 per cent. ; $C_{10}H_6I.SO_2NH_2$ requires I, 38·1 per cent.).

7 gm. of pure sodium 1 : 2-iodonaphthalene sulphonate were dissolved in 150 c.c. of water, along with a few crystals of cupric sulphate, and the solution refluxed for an hour with excess of copper powder. After filtering from cuprous iodide and excess of copper powder, hydrogen sulphide was passed through the solution for a few minutes, the solution then being boiled and filtered through carbon. The filtrate was now saturated with sodium chloride and the white crystalline salt which separated was filtered off, dried and treated with phosphorus pentachloride. The sulphonyl chloride obtained was recrystallized from acetone-water, m.p. 76° C. Barber and Smiles give the melting point of 1 : 1′-dinaphthyl-2 : 2′-disulphonyl chloride as 202-203° C. The sulphonamide derived from the sulphonyl chloride prepared above by treating an acetone solution with aqueous ammonia was found to melt at 212° C. The two melting points observed agree exactly with those recorded in the literature for naphthalene-β-sulphonyl chloride and naphthalene-β-sulphonamide respectively.

Various modifications in the treatment and method of isolating the product have been carried out, but in no case was there evidence of diaryl-formation having taken place. We have been in communication with Professor Smiles who states that 300 gm. of the iodo-sulphonate were required to produce sufficient of the dinaphthyl disulphonate to yield 2 gm. of the dinaphthyl disulphide on reduction. Our failure to confirm his results is probably due to the very much smaller quantities of starting material we have employed.

(*b*) *Preparation of Sodium* 1 : 2-*Bromonaphthalene Sulphonate and its Treatment with Copper Powder.*—The solid diazo-compound obtained from 20 gm. of sodium *o*-naphthionate was added gradually in the form of an aqueous paste, with mechanical agitation, to a solution of 24 gm. of ammonium bromide in 200 c.c. of water which had been previously boiled with about 1 gm. of cuprous oxide, filtered and cooled. Nitrogen was rapidly evolved and a pink shimmering crystalline substance separated immediately. When all the diazo-compound had been added and the reaction was complete, this substance was filtered off. Assuming it to be the ammonium salt of 1 : 2-bromonaphthalene sulphonic acid, the yield was approximately 85 per cent.

A portion of the salt was treated with phosphorus pentachloride in the usual manner and the crude sulphonyl chloride recrystallized from acetone-water after decolourizing with carbon, yielding almost colourless elongated prisms, m.p. 93° C. (Found S, 10·5 per cent.; $C_{10}H_6Br.SO_2Cl$ requires S, 10·5 per cent.).

Part of this sulphonyl chloride was converted into the sulphonamide by dissolving in acetone and warming the solution with aqueous ammonia. The sulphonamide separated out readily, being insoluble in cold water, acetone and alcohol, and only slightly soluble in hot aqueous ammoniacal alcohol from which it was crystallized (prisms), m.p. 271° C. (Found S, 11·2 per cent.; $C_{10}H_6Br.SO_2NH_2$ requires S, 11·2 per cent.).

Sodium 1 : 2-bromonaphthalene sulphonate was obtained from the ammonium salt by boiling the latter with caustic soda solution. It separated, on cooling the solution, as hexagonal plates. 6 gm. of the recrystallized salt were dissolved in 150 c.c. of hot water containing a little cupric sulphate, and the solution was refluxed with 3 gm. of copper powder for two hours. It was then filtered hot and, on cooling, the sodium bromo-sulphonate separated unchanged from the filtrate (proved by formation of sulphonyl chloride). No other product was isolated from the filtrate, and there was no evidence of cuprous bromide being formed during the treatment with copper powder.

It appears, therefore, that the bromine in the 1 : 2-bromonaphthalene sulphonic acid is not so reactive as the iodine in the corresponding iodo-sulphonic acid, which had been replaced by hydrogen on boiling with copper powder in aqueous solution.

(*c*) *Action of Ammoniacal Tetrammino-Cuprous Sulphate Solution on Diazo-o-Naphthionic Acid.*—An ammoniacal solution of tetrammino-cuprous sulphate was prepared in the following manner:—

20 gm. of hydrated cupric sulphate were dissolved in 150 c.c. of water, and to this was added 20 gm. of 0·88 ammonia solution. A mixture of 9 gm. of hydroxylamine hydrochloride and 7 gm. of potassium hydroxide in 100 c.c. of water was now added, the resulting solution, after effervescence had ceased, being pale green in colour.

To this solution, the solid diazo-compound from 10 gm. of sodium *o*-naphthionate was added as a thin aqueous paste. Nitrogen was rapidly evolved and a deep red solution resulted. Sodium hydroxide was then added and the solution boiled to eliminate ammonia and precipitate the copper. After filtering through carbon, the filtrate was salted out with sodium chloride and a bright red compound separated in large yield. This compound gave an intense blue colour with concentrated sulphuric acid, the normal red colour being restored when the solution was diluted. This colour change is characteristic of the dye, Cuba Orange (disodium 1 : 1′-azonaphthalene-4 : 4′-disulphonate) to which we refer later (Section II). The readily soluble compound was recrystallized from aqueous alcohol, separating as a red microcrystalline meal of curious crystalline form. (Found S, 13·2 per cent.; $(N.C_{10}H_6.SO_3Na)_2$ requires S, 13·2 per cent.). The product obtained is therefore disodium 1 : 1′-azonaphthalene-2 : 2′-disulphonate.

II. 1 : 1′-*Dinaphthyl*-4 : 4′-*Disulphonic Acid.*

(*a*) *Reaction of Potassium* 1 : 4-*Iodonaphthalene Sulphonate with Copper Powder.*—The preparation of potassium 1 : 4-iodonaphthalene sulphonate is described in Section II of our first paper.[1]

When an aqueous solution of this salt containing a little cupric sulphate was refluxed with excess of copper powder the iodine was gradually replaced by hydrogen as in the case of the 1 : 2-iodo-acid. The reaction was much slower, and the result was established by concentrating the filtrate and treating the product isolated with phosphorus pentachloride. The sulphonyl chloride so formed melted at 64° C. and the sulphonamide at 149° C., these melting points agreeing closely with those of the corresponding derivatives of naphthalene-α-sulphonic acid.

In a similar fashion, the iodine was replaced by hydrogen when an aqueous solution of the salt was refluxed with powdered zinc or magnesium. Experiments were also performed with various salts of 1 : 4-chloronaphthalene sulphonic acid, which were refluxed with powdered copper, aluminium, magnesium and zinc in aqueous solution, but in no case was the chlorine replaced by hydrogen or in the course of diaryl-formation.

(*b*) *Reaction between Diazo-Naphthionic Acid and Sodium Sulphite Solution.*—Our interest in the formation of naphthalene disulphonic acids by treatment of diazo-naphthalene sulphonic acids with an " ammoniacal solution of cuprous oxide " prepared by reducing tetrammino-cupric sulphate with sulphur dioxide (Section VIII[2]) led us to investigate the reaction between alkaline sulphite solution and diazo-naphthionic acid to ascertain if it were possible to prepare naphthalene-1 : 4-disulphonic acid in the absence of cuprous salts.

A diazo-naphthionic acid suspension was added to a solution containing excess of sodium sulphite to which sufficient ammonia was added to keep the solution alkaline until about half of the suspension had been introduced. As the solution approached neutrality during the addition, nitrogen was evolved in small quantity and, when it was acid, sulphur dioxide was evolved. It was noted that, when the addition was nearly complete, a fine shimmering crystalline suspension appeared in the red solution. This was allowed to settle, filtered off and recrystallized from hot water in which it was fairly readily soluble.

Elementary analysis showed that the substance was Cuba Orange,[5] normally

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[5] Colour Index, 178.

prepared by the action of sodium sulphite in sodium acetate solution on diazonaphthionic. When it is added to concentrated sulphuric acid, an intense blue solution is obtained, which reverts to an orange colour on dilution. When solutions of potassium, sodium, calcium, barium, and lead salts are added to an aqueous solution of the dye, silky precipitates of varied crystalline form are obtained, and it was noted that this did not occur with solutions of salts of magnesium, aluminium or zinc.

(*c*) *Action of Ammoniacal Tetrammino-Cuprous Sulphate Solution on Diazo-Naphthionic Acid.*—The solid diazo-compound from 10 gm. of sodium naphthionate was added, with stirring, to an ammoniacal solution of tetrammino-cuprous sulphate prepared according to the method described under Section I (*c*) of this paper.

Nitrogen was evolved, and an orange-red substance separated simultaneously from the solution. This product was filtered off and recrystallized from hot water, separating as minute crystals similar in form to those obtained when a potassium salt was added to a solution of Cuba Orange. It also gave a colour reaction with concentrated sulphuric acid identical to that obtained with Cuba Orange. In view of these properties and the fact that disodium 1 : 1′-azonaphthalene-2 : 2′-disulphonate was obtained by a similar reaction, it was concluded that this product was dipotassium 1 : 1′-azonaphthalene-4 : 4′-disulphonate.

III. 1 : 1′-*Dinaphthyl*-5 : 5′-*Disulphonic Acid.*

(*a*) *Reaction of Potassium* 1 : 5-*Iodonaphthalene Sulphonate with Copper Powder and Zinc Dust.*—The method for the preparation of potassium 1 : 5-iodonaphthalene sulphonate is outlined in our first paper [1] (Section IV).

When an aqueous solution of this salt was refluxed with excess of copper powder for several hours, the nuclear iodine was not attacked, the salt being recovered unchanged. If zinc dust was used, however, instead of copper, the iodine was replaced by hydrogen, naphthalene-α-sulphonic acid being identified as the resulting product.

IV. 1 : 1′-*Dinaphthyl*-8 : 8′-*Disulphonic Acid.*

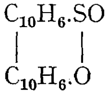
(*a*) *Reaction of Sodium* 1 : 8-*Iodonaphthalene Sulphonate with Copper Powder*—The preparation of sodium 1 : 8-iodonaphthalene sulphonate is described in Section I of our last paper.[2]

5 gm. of this salt were dissolved in 150 c.c. of water together with a few crystals of cupric sulphate, and the solution refluxed with excess of copper powder for an hour. The formation of cuprous iodide was soon apparent and this, along with excess of copper powder, was filtered off. The filtrate was cooled, saturated with hydrogen sulphide and, after adding a little carbon, was filtered once more. After boiling to remove hydrogen sulphide, the solution was saturated with sodium chloride. What was apparently sodium 1 : 1′-dinaphthyl-8 : 8′-disulphonate separated as a colourless, readily soluble salt. It was filtered, dried and treated with phosphorus pentachloride, yielding

a sulphonyl chloride, recrystallized from acetone-water, m.p. 101° C., M.W. (Rast), 271-278.

The sulphonamide, prepared by treating an acetone solution of the sulphonyl chloride with ammonia, was found to melt at 198° C., and to contain chlorine. It has already been noted in our first paper[1] (Section V) that 1 : 8-chloronaphthalene sulphonyl chloride (M.W., 261) melts at 101° C., and the sulphonamide at 198° C., and mixed melting point determinations were accordingly carried out with these and the corresponding derivatives obtained above. No depression was noted in either case. However, sodium 1 : 8-chloronaphthalene sulphonate is quite different in its appearance and solubility from the salt isolated above. Moreover, its mode of preparation could scarcely result in the substitution of iodine by chlorine. It is inferred, therefore, that phosphorus pentachloride, in addition to effecting the conversion to a sulphonyl chloride, has served to rupture the diaryl linkage, substituting chlorine. This conjecture is supported by the formation of the derivative described below.

About 4 gm. of aniline hydrochloride were fused in a small flask, and 1 gm. of the supposed disodium 1 : 1′-dinaphthyl-8 : 8′-disulphonate added to the melt. This was heated at about 250° C. for 15 minutes, in the course of which evolution of sulphur dioxide was detected. After cooling, the product was extracted with water to dissolve excess of aniline hydrochloride, and the residue crystallized from alcohol using decolourizing carbon. The small yield of colourless product, m.p. 252° C. (with decomp.), was found to contain sulphur, but no nitrogen. It is believed to be 1 : 1′-dinaphthyl-8 : 8′-sultone. (Found S, 9·55 per cent. ; $C_{10}H_6.SO_2$ requires S, 9·63 per cent.).



$$\begin{array}{c} C_{10}H_6.SO_2 \\ |\qquad\ | \\ C_{10}H_6.O \end{array}$$

(*b*) *Action of Ammoniacal Tetrammino-Cuprous Sulphate Solution on Diazo-Peri Acid.*—The solid diazo-compound from 5 gm. of sodium periate was gradually added, with stirring, to an ammoniacal solution of tetrammino-cuprous sulphate, prepared as in Section I (*c*) of this paper, cooled in ice.

Nitrogen was evolved and a deep red solution obtained. This solution was heated to boiling and sodium hydroxide solution added to eliminate ammonia and precipitate the copper. Carbon was added and the solution filtered. The filtrate was saturated with sodium chloride, whereupon a bright yellow substance separated. This was extremely soluble in water, and difficult to purify by recrystallization. It contained sulphur, nitrogen, sodium and water of crystallization, and gave a deep purple solution and precipitate on acidifying its aqueous solution with hydrochloric acid. When reduced with zinc dust and hydrochloric acid, it yielded peri acid, shown by the fact that when the product was diazotized and warmed with water, 1 : 8-naphthasultone was formed. Because of its mode of formation, and this product of reduction, the salt is believed to be disodium 1 : 1′-azonaphthalene-8 : 8′-disulphonate, corresponding to the products obtained by a similar treatment applied to diazo-*o*-naphthionic and diazo-naphthionic acids.

V. 2 : 2′-*Dinaphthyl*-1 : 1′-*Disulphonic Acid.*

(*a*) *Reaction of Potassium* 2 : 1-*Iodonaphthalene Sulphonate with Copper Powder.*—20 gm. of potassium 2 : 1-iodonaphthalene sulphonate (for preparation, see Section VI of our last paper [2]) were dissolved in 300 c.c. of hot water along with a little cupric sulphate. 5 gm. of copper powder were added to the solution which was then boiled under reflux for half an hour, the formation of cuprous iodide being apparent after a few moments. After filtering hot through carbon, the filtrate was cooled and saturated with potassium chloride. The colourless crystalline salt which separated was used to prepare the derivatives described below, which served to identify it as dipotassium 2 : 2′-dinaphthyl-1 : 1′-disulphonate.

A quantity of the disulphonate was converted into the disulphonyl chloride in the usual manner by treatment with phosphorus pentachloride. Recrystallized from acetone-water, it separated as colourless fern-shaped crystals, m.p. 245° C. (with decomp.). (Found S, 13·7 per cent. ; Cl, 15·0 per cent. ; M.W. 429 ; $C_{20}H_{12}(SO_2Cl)_2$ requires S, 14·2 per cent. ; Cl, 15·7 per cent. ; M.W. 451).

1·5 gm. of the disulphonyl chloride in 50 c.c. of alcohol and 20 c.c. of strong ammonia solution was boiled until solution was effected. After evaporating considerably, the solution was allowed to cool, whereupon colourless crystals, m.p. 303-304° C. separated. This appears to be the diammonium disulphonate. (Found S, 14·4 per cent. ; $(C_{10}H_6.SO_3NH_4)_2$ requires S, 14·3 per cent.).

With the object of preparing 1 : 1′-dihydroxy-2 : 2′-dinaphthyl, a portion of the dipotassium 2 : 2′-dinaphthyl-1 : 1′- disulphonate was fused with caustic potash in the following manner :—

2 gm. of the potassium disulphonate were gradually introduced, with stirring, into a solution of 15 gm. of potassium hydroxide in 5 c.c. of water in an iron crucible heated to about 110° C. The temperature of the melt was gradually raised, with constant stirring, and from time to time small portions of it were removed, dissolved in water and tested for dinaphthyl formation. Before there was any indication of this, however, a dark oily substance separated on the surface of the melt, this being insoluble in water. The contents of the crucible were transferred hot to a beaker of cold water and, after cooling, the insoluble portion was filtered off, washed and dried. This crystallized from hot alcohol, after decolourizing with carbon, in hexagonal plates. It was recrystallized from hot acetone, m.p. 185·5° C. (Found C, 94·2 per cent. ; H. 5·8 per cent. ; M.W. 236-246 ; $(C_{10}H_7)_2$ requires C, 94·5 per cent. ; H. 5·5 per cent., and M.W. 254). It is apparent from this analysis and melting point that the product obtained was $\beta\beta$-dinaphthyl, m.p. 187° C., and the result is interesting when compared with that obtained in the following experiment in which a nickel crucible and copper stirrer were used in place of the iron crucible and stirrer.

In this experiment, 2 gm. of the dipotassium disulphonate were added gradually to a hot solution of 7 gm. of potassium hydroxide in 1 c.c. of water contained in a nickel crucible. The temperature was gradually raised during an hour's heating, until a thick brown paste was produced. This was found to be entirely soluble in water, and, on acidifying the solution, a precipitate was formed and sulphur dioxide evolved. After filtering and drying, the precipitate was crystallized from alcohol after treatment with decolourizing carbon, m.p. 213° C. (Found C, 83·1 per cent.; H, 4·8 per cent.; M.W. 289-297; $(C_{10}H_6.OH)_2$, requires C, 83·9 per cent.; H, 4·8 per cent. and M.W. 286). According to Clemo, Cockburn and Spence,[6] 1 : 1′-dihydroxy-2 : 2′-dinaphthyl melts at 212° C.

(*b*) *Reaction of Potassium* 2 : 1-*Bromonaphthalene Sulphonate with Copper Powder.*—The preparation of potassium 2 : 1-bromonaphthalene sulphonate is described in Section VII of our last paper.[2]

15 gm. of the salt were dissolved, with a little cupric sulphate, in 150 c.c. of hot water, and the solution boiled with 8 gm. of copper powder for half an hour. After filtering, it was saturated with potassium chloride, and the product which separated was treated with phosphorus pentachloride in the usual manner. The sulphonyl chloride, on crystallization from acetone-water, was found to melt at 246° C. (with decomp.). Thus, this reaction had also resulted in diaryl-formation, the final product being 2 : 2′-dinaphthyl-1 : 1′-disulphonyl chloride as in the case of the 2 : 1-iodo-sulphonate treatment.

(*c*) *Action of Ammoniacal Tetrammino-Cuprous Sulphate Solution on Diazo-Tobias Acid.*—The solid diazo-compound obtained from 10 gm. of sodium 2-naphthylamine-1-sulphonate was added in the form of a thin aqueous paste to an ammoniacal solution of tetrammino-cuprous sulphate prepared as in Section I (*c*) of this paper.

Nitrogen was rapidly evolved and, when this ceased, dilute sulphuric acid was added to precipitate remaining cuprous compounds, and the solution filtered. Hydrogen sulphide was now passed through the filtrate to precipitate cupric copper, which was removed by filtering through carbon. After considerable evaporation, the filtrate was salted out with potassium chloride. As in the treatments of the 2 : 1-iodo- and 2 : 1-bromo-sulphonates with copper powder, recorded above, this product was shown to be dipotassium 2 : 2′-dinaphthyl-1 : 1′-disulphonate by converting it into the disulphonyl chloride, m.p. 245° C. (with decomp.). Its identity was further established in this case by converting it into 1 : 1′-dihydroxy-2 : 2′-dinaphthyl, m.p. 213° C., by fusion with potassium hydroxide.

VI. 2 : 2′-*Dinaphthyl*-6 : 6′-*Disulphonic Acid.*

(*a*) *Reaction of Potassium* 2 : 6-*Iodonaphthalene Sulphonate with Copper Powder.*—Potassium 2 : 6-iodonaphthalene sulphonate was prepared according

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[6] J.C.S., 1931, 1272.

to the method described by Houlding[7] by diazotizing Brönner acid and heating the diazo-compound with hydriodic acid.

10 gm. of the potassium salt were dissolved in 150 c.c. of hot water together with a little cupric sulphate, and the solution boiled under reflux with 4 gm. of copper powder for three hours. There was no evidence of cuprous iodide formation and, after filtering, the only substance identified in solution was unchanged potassium 2 : 6-iodonaphthalene sulphonate. This was identified by preparing its sulphonyl chloride, m.p. 140° C., and the sulphonamide, m.p. 222° C. (Houlding gives 140° C. and 220° C. respectively).

(*b*) *Action of an Ammoniacal Solution of Tetrammino-Cuprous Sulphate on Diazo-Brönner Acid.*—On adding the solid diazo-compound obtained by diazotizing Brönner acid to ammoniacal tetrammino-cuprous sulphate solution, nitrogen was evolved and a small quantity of an orange-red compound separated. From appearance and reduction tests it was concluded to be the ammonium salt of 2 : 2′-azonaphthalene-6 : 6′-disulphonic acid. It gave a deep red solution in concentrated sulphuric acid, reverting to a paler shade on dilution. It was recrystallized from water, separating as small orange hexagonal plates. (Found S, 13·2 per cent. ; $(N.C_{10}H_6.SO_3NH_4)_2$ requires S, 13·4 per cent.)

SUMMARY.

The results of these attempts to form dinaphthyl disulphonic acids are summarized in tabular form below :—.

TABLE I.

Reagent. Copper powder.

Sulphonic Acid Salt	Result
1 : 2-Bromonaphthalene,	No reaction.
1 : 2-Iodonaphthalene,	Iodine readily replaced by hydrogen.
1 : 4-Chloronaphthalene,	No reaction.
1 : 4-Iodonaphthalene,	Iodine replaced by hydrogen with difficulty.
1 : 5-Iodonaphthalene,	No reaction.
1 : 8-Iodonaphthalene,	Diaryl formation occurs readily.
2 : 1-Bromonaphthalene,	Diaryl formation occurs readily.
2 : 1-Iodonaphthalene,	Diaryl formation occurs readily.
2 : 6-Iodonaphthalene,	No reaction.

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[7] Ber., 1891, 24 [2] 706; Proc. Chem. Soc., 1889, 74.

TABLE II.[2]

Reagent. Tetrammonium cupric sulphate solution reduced by sulphur dioxide.

Sulphonic Acid	Result.
1 : 4-Diazonaphthalene, ...	Formation of naphthalene disulphonic acid.
1 : 5-Diazonaphthalene, ...	Formation of naphthalene disulphonic acid.
1 : 8-Diazonaphthalene, ...	Formation of naphthalene disulphonic acid.

TABLE III.

Reagent. Tetrammino-cuprous sulphate solution prepared by reducing tetrammino-cupric sulphate with hydroxylamine.

Sulphonic Acid	Result.
1 : 2-Diazonaphthalene, ...	Formation of azonaphthalene disulphonic acid.
1 : 4-Diazonaphthalene, ...	Formation of azonaphthalene disulphonic acid.
1 : 8-Diazonaphthalene, ...	Formation of azonaphthalene disulphonic acid.
2 : 1-Diazonaphthalene, ...	Diaryl formation occurs.
2 : 6-Diazonaphthalene, ...	Formation of azonaphthalene disulphonic acid.

The reactions recorded for the halogenonaphthalene sulphonic acids confirm the observations made by Cumming and Howie[8] that the order of replaceability of halogen in the naphthalene series is I>Br>Cl, and that the halogen is activated by the close proximity of an acidic group. Thus, when the sulphonic acid group is ortho or peri to the iodo- group, *e.g.*, 1 : 2-, 2 : 1- or 1 : 8-, the halogen is readily replaceable, whereas it is less readily replaceable in the 1 : 4- acid. With the 1 : 5- and 2 : 6- acids no replacement takes place.

No generalization is possible as yet regarding the reactions of diazonaphthalene sulphonic acids with ammoniacal cuprous solutions, but it is interesting to note that, with the exception of the reaction between diazo-Tobias acid and tetrammino-cuprous sulphate solution, either naphthalene

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[8] J.C.S., 1931, 3176.

disulphonic acids or azonaphthalene disulphonic acids are formed. This does not lend support to the generalization of Vörlander and Meyer,[9] who studied the reactions of substituted benzene diazonium salts with ammoniacal cuprous oxide solutions, in so far as it might apply to the naphthalene series. They noted that the presence of a saturated substituent group (*e.g.*, $-CH_3$, $-O.CH_3$ or—Cl) favoured the formation of an azo-compound (*i.e.*, *o*-azotoluene, etc., while an unsaturated substituent group (*e.g.*, $-NO_2$, $-COOH$, or $-COO.CH_3$) favoured diaryl-formation (*i.e.*, *o*-dinitrodiphenyl, etc.).

The authors again record their thanks to Imperial Chemical Industries for a grant towards the cost of this work and for the gift of materials, and desire to thank Professor Smiles for kindly supplying further information *re* the paper quoted.

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[9] Annalen, 1901, *122*, 319-320.

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α-SULPHONIC ACID DERIVATIVES OF NAPHTHALENE

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ABSTRACT.

The derivatives described herein were prepared in the course of work on certain sulphonic acids of naphthalene, and were of assistance in determining the constitution of these compounds.

I. 1 : 4–*Chloronaphthalene Sulphonic Acid.*

(*a*) *Diazotisation of Naphthionic Acid* (1 : 4–naphthylamine sulphonic acid).—Methods of diazotisation in which the necessary volume of hydrochloric acid (3¼ mol.) is added to the mixed sodium nitrite (1 mol.) and sodium naphthionate (1 mol.) solutions, and in which the mixed sodium nitrite and naphthionate is added to the hydrochloric acid, were both found to be unsatisfactory as a certain amount of coupling takes place resulting in a red colouration.

The method finally adopted was as follows :—10 gm. of sodium naphthionate were dissolved in about 400 c.c. of water and 12 gm. of concentrated hydrochloric acid, diluted to about 30 c.c., were added to the solution with mechanical agitation. The finely divided naphthionic acid suspension so formed was readily diazotised at room temperature by the gradual introduction of a solution of 2·4 gm. of sodium nitrite in water, with mechanical agitation. The yellow diazo-suspension produced was found to be remarkably stable, no appreciable evolution of nitrogen taking place under 80°C.

(*b*) *Preparation of Copper, Sodium, and Potassium* 1 : 4–*Chloronaphthalene Sulphonates.*—In the preparation of the salts of 1 : 4–chloronaphthalene sulphonic acid, both the Sandmeyer reaction, using cuprous chloride, and the Gattermann reaction, using copper powder, were employed successfully, but the former gave the better yields.

Sandmeyer reaction.—The yellow diazo-suspension obtained by diazotising naphthionic acid was poured into excess of a hydrochloric acid solution of cuprous chloride, maintained near the boiling point. Nitrogen was rapidly evolved and a clear deep green solution obtained from which, after evaporation to about a quarter of its initial volume and cooling, a crop of yellowish spangles separated which were then recrystallized from water, using decolourizing carbon. On analysis and subsequent formation of derivatives (see below), the colourless spangles were identified as a copper salt of 1 : 4–chloronaphthalene sulphonic acid.[1]

The *sodium* salt was prepared from a solution of the cupric salt by boiling with sodium hydroxide solution, filtering and concentrating the filtrate.

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[1] Arnell, Dissert., Upsala, 1889.

The salt separated in colourless spangles (found Cl, 12·4 per cent.; $C_{10}H_6Cl.SO_3Na, H_2O$ requires Cl, 12·5 per cent.).

The *potassium* salt[1], prepared in a similar manner from the copper salt and potassium hydroxide, separated as colourless hexagonal spangles (found Cl, 12·7 per cent.; $C_{10}H_6Cl.SO_3K$ requires Cl, 12·7 per cent.).

(*c*) *Preparation of* 1 : 4–*Chloronaphthalene Sulphonic Chloride.*—A quantity of the potassium salt obtained was ground in a mortar with excess of phosphorus pentachloride. When the reaction had ceased, a large volume of cold water was added to decompose the excess phosphorus pentachloride, and the sulphonic chloride separated as a sticky yellow mass which soon solidified. It crystallized from acetone in colourless prisms melting at 95°C. (Arnell[1] gives 95°C.) (found Cl, 26·9 per cent.; $C_{10}H_6Cl.SO_2Cl$ requires Cl, 27·1 per cent.).

(*d*) *Preparation of* 1 : 4–*Chloronaphthalene Sulphonamide.*—The sulphonic chloride was boiled with concentrated ammonia solution until it dissolved. After concentration and cooling, the sulphonamide separated and was recrystallized from water (colourless prisms), m.p. 185°C. (Arnell[1] gives 187°C.). This derivative may also be prepared by treating an alcoholic solution of the sulphonic chloride with concentrated ammonia solution. This latter method is also applicable to the derivatives which follow.

(*e*) *Preparation of* 1 : 4–*Chloronaphthalene Sulphoanilide.*—The sulphonic chloride was boiled in water with a slight excess of aniline until the pasty mass solidified. The sulphoanilide crystallized from alcohol in very pale yellow plates, m.p. 143°C. (found Cl, 11·0 per cent.; $C_{10}H_6Cl.SO_2NH.C_6H_5$ requires Cl, 11·2 per cent.).

(*f*) *Preparation of* 1 : 4–*Chloronaphthalene Sulpho–o–toluidide.*—The sulphonic chloride was treated as in (*e*) with a slight excess of *o*-toluidine. The sulpho-*o*-toluidide separated from alcohol as colourless prisms, m.p. 151°C. (found Cl, 10·6 per cent.; $C_{10}H_6Cl.SO_2NH.C_6H_4CH_3$ requires Cl, 10·7 per cent.).

(*g*) *Preparation of* 1 : 4–*Chloronaphthalene Sulpho–p–nitroanilide.*—By boiling the sulphonic chloride with a slight excess of *p*-nitroaniline in water for 2-3 hours, and crystallizing the resultant solid from alcohol-water, the sulpho-*p*-nitroanilide was obtained as pale yellow prisms, m.p. 188°C. (found Cl, 9·5 per cent.; $C_{10}H_6Cl.SO_2NH.C_6H_4NO_2$ requires Cl, 9·8 per cent.).

(*h*) *Preparation of* 1 : 4–*Chloronaphthalene Sulpho–α–naphthylamide.*—The sulphonic chloride was treated with α-naphthylamine as in (*e*), and the sulpho-α-naphthylamide crystallized from alcohol from which it separated as mauve prisms (after repeated treatments with decolourizing carbon), m.p. 162°C. (found Cl, 9·5 per cent.; $C_{10}H_6Cl.SO_2NH.C_{10}H_7$ requires Cl, 9·6 per cent.).

II. 1 : 4–*Iodonaphthalene Sulphonic Acid.*

The only method found in the literature for preparing this acid consists in sulphonating α-iodonaphthalene[2], but this is an involved process, and was not employed.

(*a*) *Isolation of Potassium* 1 : 4–*Iodonaphthalene Sulphonate.*—The first method attempted for preparing 1 : 4-iodonaphthalene sulphonic acid (isolated as the potassium salt) gave an extremely poor yield. It consisted in pouring the diazo-naphthionic acid suspension into boiling potassium iodide solution acidified with excess hydrochloric acid. A very deep red solution resulted, and after nitrogen ceased to be evolved, this was neutralized with potassium hydroxide and concentrated to small bulk. On cooling, a dark brown solid separated which, on repeated crystallization using decolourizing carbon, yielded a very small crop of pink crystals identified as being potassium 1 : 4-iodonaphthalene sulphonate.

As has been noted, nitrogen is not evolved from the diazo-suspension (also in the presence of hydriodic acid) unless the solution is heated to about 80°C., and at this temperature it appears that the tendency for hydrolysis of the diazo-compound to 1 : 4-hydroxynaphthalene sulphonic acid, and consequent coupling with undecomposed diazo-compound, is much greater than the tendency for replacement by iodine.

Several attempts to modify the above method, e.g., by adding the diazo-suspension to hydriodic acid solution in the cold and heating up gradually, proved unsuccessful.

With the object of bringing about nitrogen evolution at ordinary temperatures, a modification of the Gattermann reaction was employed and found to be effective.

In this method, the diazo-suspension was added, in the cold, to a solution of rather more than the theoretical quantity of potassium iodide, and copper powder added with mechanical agitation. Nitrogen was rapidly evolved and, after filtering off excess copper powder and cuprous iodide, the solution was evaporated to small bulk and neutralized with potassium hydroxide. By boiling with a little decolourizing carbon, the copper hydroxide formed was readily filtered off and, on cooling, the solution yielded pinkish crystals. These were recrystallized from water using decolourizing carbon, and separated as very pale yellow curiously shaped prisms. The yield is approximately 17 per cent. theoretical (found I, 33·6 per cent.; $C_{10}H_6I.SO_3K$ requires I, 34·1 per cent.).

From the mother liquor, after separation of the iodo-salt, a large quantity of a very soluble yellow salt was obtained which was identified by the melting points of the sulphonic chloride and sulphonamide (65°C. and 149°C. respectively) derived from it, as the potassium salt of naphthalene α-sulphonic acid (see section on naphthalene α-sulphonic acid).

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[2] Armstrong, Brit. Assoc. Report, 1887, 231.

(*b*) *Preparation of* 1 : 4*–Iodonaphthalene Sulphonic Chloride.*—The sulphonic chloride is the only derivative of 1 : 4-iodonaphthalene sulphonic acid referred to in the literature. It was prepared like that of the 1 : 4-chloro-acid by treating the potassium salt with phosphorus pentachloride. It crystallized from alcohol or acetone as pale yellow prisms, m.p. 121°C. (Armstrong[2] [redacted] gives m.p. 123°C.).

(*c*) *Preparation of* 1 : 4*–Iodonaphthalene Sulphonamide.*—By boiling the sulphonic chloride with concentrated ammonia solution until it dissolved and concentrating the solution, the sulphonamide was obtained which, on recrystallization from water, separated as pale yellow prisms, m.p. 202°C. (found I, 37·2 per cent. ; $C_{10}H_6I.SO_2NH_2$ requires I, 38·1 per cent.). It was also obtained by treating an alcoholic solution of the sulphonic chloride with ammonia, m.p. 202°C.

(*d*) *Preparation of* 1 : 4*–Iodonaphthalene Sulphoanilide.*—This derivative was prepared in exactly the same manner as that of the chloro-acid, and separated from alcohol as pale yellow prisms, m.p. 133°C. (found I, 30·5 per cent. ; $C_{10}H_6I.SO_2NH.C_6H_5$ requires I, 31·0 per cent.).

(*e*) *Preparation of* 1 : 4*–Iodonaphthalene Sulpho–o–toluidide.*—Prepared in the same manner as the 1 : 4-chloro-acid derivative. Pale yellow prisms from alcohol, m.p. 138°C. (found I, 29·9 per cent. ; $C_{10}H_6I.SO_2NH.C_6H_4CH_3$ requires I, 30·0 per cent.).

III. *Naphthalene α–Sulphonic Acid.*

(*a*) *Isolation from Mother Liquor in Preparation of Iodo-acid.*—As has already been noted, potassium naphthalene α-sulphonate was obtained from the mother liquor in the preparation of 1 : 4-iodonaphthalene sulphonic acid after separation of the potassium iodo-sulphonate.

By treatment with phosphorus pentachloride, the sulphonic chloride was derived from this salt. It crystallized from acetone as colourless prisms, m.p. 65°C. Various authorities give 65–67°C. as the m.p. of naphthalene α-sulphonic chloride. This was boiled with ammonia solution and yielded the sulphonamide which crystallized from water as colourless prisms, m.p. 149°C. (Kimberly[4] gives m.p. 150°C.).

(*b*) *Preparation of Naphthalene α–Sulphoanilide.*—When the naphthalene α-sulphonic chloride obtained from the above source was boiled in water with a slight excess of aniline and the solid product crystallized from alcohol (colourless prisms), it was found to melt at 152°C. (found S, 11·2 per cent. ; $C_{10}H_7.SO_2NH.C_6H_5$ requires S, 11·3 per cent.). Carleson,[5] however, gives

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[redacted]

[4] Annalen, 1860, *114*, 135.

[5] Bull. Soc. Chim., [redacted], *27*, 360.
1877,

m.p. of the α-sulphoanilide as 112°C. An exactly similar product was obtained when an alcoholic solution of the sulphonic chloride was treated with aniline.

When the sulphoanilide was prepared from a pure specimen of naphthalene α-sulphonic acid through the sulphonic chloride, it was found to melt at 153°C., a mixed melting point with the product obtained above showing no depression.

(*c*) *Preparation of Naphthalene α–Sulpho–o–toluidide.*—Prepared in a similar manner to the sulphoanilide from the sulphonic chloride and *o*-toluidine, the sulpho-*o*-toluidide separated from alcohol as colourless crystalline plates, m.p. 134°C. (found S, 10·9 per cent.; $C_{10}H_7.SO_2NH.C_6H_4CH_3$ requires S, 10·8 per cent.).

(*d*) *Preparation of Naphthalene α–Sulpho–p–nitroanilide.*—Prepared in a similar manner to the 1 : 4–chloro derivative from the sulphonic chloride and *p*-nitroaniline, the α-sulpho-*p*-nitroanilide separated from alcohol as pale yellow prisms, m.p. 205°C. (found S, 9·7 per cent.; $C_{10}H_7.SO_2NH.C_6H_4NO_2$ requires S, 9·7 per cent.).

IV. 1 : 5–*Iodonaphthalene Sulphonic Acid.*

(*a*) *Diazotisation of Laurent Acid* (1 : 5-naphthylamine sulphonic acid).—The following was found to be the most effective method of diazotising Laurent acid:—

5 gm. of sodium Laurentate were dissolved in water (about 200 c.c.) with 1·3 gm. of sodium nitrite. This solution was poured, with mechanical agitation, into dilute hydrochloric acid containing 7 gm. concentrated acid, at room temperature. The greyish diazo-suspension is stable at ordinary temperatures.

(*b*) *Preparation of Potassium* 1 : 5–*Iodonaphthalene Sulphonate and Identification of the Acid.*—The diazo-suspension obtained as above was added to an excess of hot hydriodic acid solution, as described by Mauzelius,[6] and the iodo-acid isolated as the potassium salt by treatment with potassium hydroxide followed by concentration.

The acid was identified by preparing the sulphonic chloride, m.p. 113°C., and thence the sulphonamide, m.p. 236°C. (Mauzelius gives 114°C, and 239°C. respectively).

V. 1 : 8–*Iodonaphthalene Sulphonic Acid.*

No reference could be found in the literature to a preparation of 1 : 8-iodonaphthalene sulphonic acid.

(*a*) *Diazotisation of Peri Acid* (1 : 8-naphthylamine sulphonic acid).—Peri acid was effectively diazotised in a similar manner to Laurent acid by adding mixed sodium periate (5 gm.) and sodium nitrite (1·4 gm.) solutions

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[6] Berichte, 1889, *22*, 2823.

to dilute hydrochloric acid (containing 7·5 gm. concentrated acid), with mechanical agitation, but employing in this case a larger volume of solution since sodium periate is not very soluble in water. The diazo-compound remains in solution.

(*b*) *Isolation of Naphthalene* 1 : 8–*Sultone.*—The following attempt was made to prepare 1 : 8-iodonaphthalene sulphonic acid :—

The solution obtained by diazotising 5 gm. of sodium periate was poured into boiling hydriodic acid, whereupon nitrogen was rapidly evolved and a greyish precipitate separated almost immediately. This precipitate did not contain iodine nor did it yield a sulphonic chloride on treatment with phosphorus pentachloride. It was recrystallized from acetone (colourless prisms) and found to melt at 156°C. It appears that 1 : 8-hydroxynaphthalene sulphonic acid had been produced in solution by replacement of the diazo-group by hydroxyl, and that this had lost water during boiling to form naphthalene 1 : 8-sultone. Schultz[7] gives m.p. 154°C. No sulphonic chloride-forming sulphonic acid was isolated in the remaining solution.

This inner-anhydride was also produced when the mixed hydriodic acid and diazo solutions were heated up slowly or when the diazo-solution was heated alone.

(*c*) *Isolation of Naphthalene α–Sulphonic Acid.*—In another attempt to prepare 1 : 8-iodonaphthalene sulphonic acid, a diazo-peri acid solution was treated with potassium iodide and copper powder in the cold. Nitrogen was evolved, but on working up the acid in solution as the potassium salt and treating with phosphorus pentachloride, the sulphonic chloride obtained was found to melt at 66°C. The sulphonamide and sulphoanilide derived from this melted at 148°C. and 152°C. respectively. Naphthalene α-sulphonic acid had thus been formed by replacement of the diazo-group by hydrogen. Evidently this tendency is more marked with peri than with naphthionic acid, since a considerable portion of the diazo-naphthionic acid was converted into the iodo-acid by a similar treatment. This may be due to the proximity of the sulphonic acid group in the case of peri acid.

(*d*) *Isolation of Potassium* 1 : 8–*Chloronaphthalene Sulphonate and Identification of the Acid.*—When diazo-peri acid was poured into a hot solution of cuprous chloride in concentrated hydrochloric acid, the inner-anhydride was not formed to such an extent as with hydriodic acid. On working up the product in solution as the potassium salt after filtering off the sultone, it was found to give a sulphonic chloride, m.p. 101°C. and thence a sulphonamide, m.p. 198°C. The figures recorded in the literature for 1 : 8-chloronaphthalene sulphonic chloride and 1 : 8-chloronaphthalene sulphonamide are 101°C. and 196-197°C.[8] respectively.

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[7] Berichte, 1887, *20*, 3162.

[8] Cleve, Berichte, 1890, *23*, 962.

VI. *Naphthionic Acid.*

(*a*) *Isolation of Phenyl–α–Naphthylamine.*—In an attempt to obtain the sulphoanilide of naphthionic acid, an excess of aniline was refluxed with naphthionic acid for about 3 hours. By removing the excess of aniline with hydrochloric acid, extracting the residue with alcohol, decolourizing with carbon and recrystallizing several times, a compound free from sulphur was isolated, m.p. 58°C. (found N, 6·4 per cent.), which had properties similar to diphenylamine.

It was noted that sulphur dioxide was produced during reflux, and the odour of α-naphthylamine was also detected. The substance appears to be phenyl-α-naphthylamine (Friedlander[9] gives m.p. 60°C.; $C_6H_5.NH.C_{10}H_7$ requires N, 6·4 per cent.), which is generally prepared by heating α-naphthylamine with aniline salts at about 250°C.

A bromo-derivative was prepared by adding bromine water in slight excess to a glacial acetic acid solution of the substance, and found to melt at 145°C. (Streiff[10] gives 137°C. for the tribromo-compound). The nitroso-compound, after three crystallizations, gave m.p. 86°C. (Fischer[11] gives 92°C.).

(*b*) *Preparation of Aniline Naphthionate.*—This salt was prepared by treating an excess of naphthionic acid with aniline in boiling water. It is fairly soluble in hot water and crystallizes out readily in greyish clusters. It does not melt, but gives off water on heating (found N, 7·6 per cent.; $C_{10}H_6NH_2.SO_3H$, $C_6H_5NH_2$, $3H_2O$ requires N, 7·6 per cent.).

(*c*) *Preparation of β–Naphthylamine Naphthionate.*—In trying to prepare the sulpho-β-naphthylamide of naphthionic acid by refluxing the latter with β-naphthylamine in nitrobenzene, a substance was isolated which resembles aniline naphthionate in properties. It was slightly soluble in hot water, contained water of crystallization (after recrystallization from water) and did not melt (found N, 6·6 per cent.; $C_{10}H_6NH_2.SO_3H$, $C_{10}H_7NH_2$, $3H_2O$ requires N, 6·7 per cent.).

This naphthionate was also prepared by adding a solution of β-naphthlyamine hydrochloride to sodium naphthionate solution.

(*d*) *Isolation of ββ–Dinaphthylamine.*—When β-naphthylamine naphthionate was distilled destructively, the odours of sulphur dioxide and α-naphthylamine were noted. A considerable quantity of distillate, which quickly solidified, was collected and a portion of the products also sublimed in the neck of the flask. The distillate, when crystallized from alcohol, yielded a small crop of yellowish crystals which, on recrystallization using decolourizing carbon, gave m.p. 169°C. Sulphur was found to be absent.

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[9] Berichte, 1883, *16*, 2085.

[10] Annalen, 1881, *209*, 155; BERICHTE, 1880, 13, 1852.

[11] Berichte, 1887, *20*, 1247.

The nature of the decomposition suggested that this compound was probably either ββ-dinaphthylcarbazole (m.p. 169-170°C.) or ββ-dinaphthylamine (m.p. 170·5°C.). The picrate was prepared and gave m.p. 160°C. That of the carbazole is recorded as 221°C., and of the dinaphthylamine as 164-165°C. It was concluded that ββ-dinaphthylamine had been formed in the decomposition; α- and β-naphthylamines were also found in the distillate.

(*e*) *Preparation of α–Naphthylamine Naphthionate.*—This salt was obtained by the two methods employed with the β-salt, and had similar properties (found N, 6·6 per cent.; $C_{10}H_6NH_2.SO_3H$, $C_{10}H_7NH_2$, $4H_2O$ requires N, 6·4 per cent.).

On distillation, only α-naphthylamine was identified in the distillate.

Note.—In spite of the formation of these naphthionates, it appears that sulphoanilide or sulphonaphthylamide formation with loss of water does not take place on heating, but rather does secondary amine formation tend to occur, presumably with loss of ammonia.

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