XXIV.—*Researches on the Laws of Substitution in the Naphthalene Series.* No. I.

By HENRY E. ARMSTRONG, F.R.S.

THE product of the action of sulphuric acid in excess on naphthalene at a somewhat elevated temperature consists, according to Ebert and Merz (*Ber.*, **10**, 592), of *two* isomeric disulphonic acids, which furnish lead metallic salts, chloride, and amide, differing considerably in crystalline form, solubility, amount of water of crystallisation, &c. They are also sharply distinguished by their behaviour on fusion with potassium hydroxide, the one—the so-called α -disulphonic acid—yielding a corresponding dihydroxynaphthalene, $C_{10}H_6(OH)_2$; the other, betanaph-

* Ammonia was also formed in many experiments, when mixed nitrogen and hydrogen were passed over heated freshly reduced *copper*. The production always ceased when the nitrogen was passed *alone* through the apparatus, till all hydrogen had been expelled.

tholsulphonic acid, $C_{10}H_6(OH)(SO_3H)$. This latter acid was regarded by Ebert and Merz as identical with that produced on treating betanaphthol with sulphuric acid.

In the latter part of the year 1879, when preparing an article on Naphthalene for the forthcoming new supplement to *Watts's Dictionary of Chemistry*, I had occasion to discuss the constitution of the naphthalene derivatives, including these disulphonic acids. The following passage from the article in question may be here cited, as the conclusions then arrived at led to the experiments to be described in this communication :—

“ δ - and ϵ -dichloronaphthalene, which are derived from the isomeric naphthalenedisulphonic acids, are probably, one or both, $\beta\beta$ -derivatives. Both the disulphonic acids are probably derived from the β -monosulphonic acid (being formed at an elevated temperature); but supposing this to be the case, and that the β -disulphonic acid contains both sulpho-groups in β -positions, there are still three formulæ which may be applied to it, viz.:

“According to Ebert and Merz, the naphtholsulphonic acid formed on fusing the β -disulphonate with potassium hydroxide is identical with that produced from betanaphthol and sulphuric acid; if this be the case, the first of the above formulæ would appear to be the most probable, for as the action of sulphuric acid and bromine on the phenols is similar, in so far as the constitution of the resulting compounds is concerned, as betanaphthol yields a bromo-derivative in which both bromine and the OH-group are in the same C_6 -group (Smith, *Chem. Soc. Trans.*, 1879, 789), it is probable that the sulphonic acid derived from betanaphthol would contain both the OH- and the sulpho-group in the same C_6 -group. If, however, the β -disulphonic acid were thus constituted, the dicarboxylic acid derived from it should be identical with naphthophthalic acid, $C_{10}H_6(COOH)_2$, which is not the case. It is therefore a question whether the naphtholsulphonic acid from the β -disulphonic acid and that from betanaphthol are identical, as Ebert and Merz have stated, or whether isomeric change does not take place in some of the reactions above referred to. The fact that it is the C_6 -group which does not contain the sulpho-group that is attacked when naphthalene- α - and β -sulphonic chlorides are submitted to the action of chlorine, or when naphthalene- α -sulphonic acid is treated with nitric acid, renders it probable that the naphthalenedisulphonic acids also contain the sulpho-groups in distinct hexagons (this expression, of course, merely has reference to the

symbols), and such a conclusion would appear to harmonise well with their general behaviour and that of the compounds derived from them. On this assumption the second and third of the formulæ given above are the most probable expressions of the constitution of the α - and β -disulphonic acids respectively."

As a first step towards the solution of the problem here indicated, it appeared desirable to verify the conclusion arrived at by Ebert and Merz, who do not appear to have themselves compared the betanaphtholsulphonic acid they obtained with that previously prepared by Schaeffer (*Annalen*, 152, 296) from betanaphthol, but to have concluded that the two products were identical on the grounds that their acid crystallised in plates melting at 122°, that obtained by Schaeffer being described as crystallising in plates melting at 125°; and that it exhibited the same reactions with ferric chloride and with nitric acid as Schaeffer's product. The only salt they describe is the potassium salt, which was not prepared by Schaeffer.

In conjunction with Mr. N. C. Graham, I therefore commenced experiments having this end in view. Subsequently we directed our attention to the investigation of the betanaphtholsulphonic acids, as it was to be expected that results of interest would accrue from the examination of derivatives of a phenol which in some respects behaves as no other known phenol, the determination of the constitution of the β -naphthaquinone of Stenhouse and Groves being a problem of peculiar interest. Lastly, the dihydroxynaphthalene described by Ebert and Merz claimed our attention. The results we have obtained are in part so remarkable, and necessitate so large an extension of the investigation as originally planned, that it appears to me desirable to publish them as a preliminary communication.

Betanaphthol- α -sulphonic Acid from Betanaphthol and from Naphthalenedisulphonic Acid.

By HENRY E. ARMSTRONG, and N. C. GRAHAM.

We have found that instead of neutralising the crude product of the action of sulphuric acid on betanaphthol at 100° with lead carbonate, &c., as recommended by Schaeffer, it is preferable to employ calcium carbonate. The calcium betanaphthol- α -sulphonate readily crystallises from the properly concentrated solution, and may without difficulty be purified by recrystallisation and the aid of animal charcoal. A much smaller proportion of sulphuric acid than is recommended by Schaeffer may with advantage be employed, but we reserve further particulars for a future communication.

Calcium Betanaphthol- α -sulphonate, $[C_{10}H_6(OH)(SO_3)]_2Ca + 5OH_2$. This salt ordinarily crystallises in the manner described by Schaeffer;

it may also be obtained in massive, but most irregularly formed prismatic crystals by allowing the cold saturated solution to evaporate spontaneously. Although it becomes slightly brown on heating at 100° , no sensible amount of decomposition takes place at this temperature, and the water of crystallisation may safely be determined in the usual manner. The results of our analyses agree with Schaeffer's formula given above.

Potassium Betanaphthol- α -sulphonate, $C_{10}H_6(OH)(SO_3K)$.—This salt is readily prepared from the calcium salt and potassium carbonate. It crystallises with varying amounts of water and in various forms, according to the conditions. By allowing not too small a quantity of a hot saturated solution to cool slowly, it may usually be obtained in groups of transparent, well-defined, elongated prisms, pointed at the end, and apparently square in section; these crystals contain about 3 per cent. of water, but on exposure to the air they gradually become opaque from loss of water. More frequently it separates in less well-defined, more plate-like prismatic forms, which appear always to contain less water—a little over 1 per cent.—and these remain unaltered on exposure to air. Potassium betanaphthol- α -sulphonate is less soluble than the calcium salt, dissolving only to the extent of about 2 parts in 100 of water at 15° . An aqueous solution exhibits a faint blue fluorescence, which is much intensified by the addition of ammonia. As commercial betanaphthol was employed in the preparation of the acid, we were at first inclined to regard this fluorescence as accidental, but as the salt which has been several times crystallised also exhibits it, and as all other salts we have prepared of the acid are also fluorescent, there can be little doubt that it is a specific character of the betanaphthol- α -sulphonates. According to Griess (*Ber.*, 13, 1959), the betanaphtholdisulphonates are also fluorescent, especially in presence of ammonia.

Barium Betanaphthol- α -sulphonate, $[C_{10}H_6(OH)(SO_3)]_2Ba + 6OH_2$.—This is by far the most characteristic of the betanaphthol- α -sulphonates. It is readily prepared by precipitating a hot saturated solution of the calcium salt with barium chloride. If the boiling saturated solution be allowed to cool very slowly, it separates in transparent well-developed long narrow prisms. Like the calcium salt, it parts with its water of crystallisation when introduced into hot water, and the anhydrous salt then dissolves with extreme difficulty.

Betanaphtholsulphonic Acid from Naphthalene- β -disulphonic Acid.—Following Ebert and Merz's directions, naphthalene was heated with five times its weight of sulphuric acid at 180° during about 24 hours. The least soluble portion of the mixture of calcium salts obtained on neutralising with calcium carbonate was converted into potassium salt, and the latter fused with 2–3 times its weight of potassium

hydroxide. The naphtholsulphonate obtained did not, however, agree in appearance with that from betanaphthol, and always crystallised in less well-defined forms; but its solubility in cold water was the same, and all doubt as to the identity of the two products was removed on treating it with bromine. The salt obtained had the same composition as the bromobetanaphtholsulphonate prepared from betanaphthol described later on. It crystallised in the same unmistakeable forms; it had the same solubility; and, lastly, the calcium salt produced by precipitating its solution with calcium chloride crystallised from water in the thin micaceous plates characteristic of calcium bromobetanaphthol- α -sulphonate.

On the Action of Bromine, Chlorine and Nitric Acid on Potassium Betanaphthol- α -sulphonate. By the Same.

Potassium Bromobetanaphthol- α -sulphonate, $C_{10}H_5Br(OH)(SO_3K) + 2OH_2$.—This salt is readily prepared by adding the calculated amount of bromine to a cold saturated solution of potassium betanaphthol- α -sulphonate. The bromine is rapidly absorbed on agitating the liquid, and the greater part of the bromo-salt at once separates in glistening scales; it is readily purified by recrystallisation from boiling water. It crystallises from a hot saturated solution in broad, transparent, well developed prisms and plates of considerable thickness; usually a number of isolated rhombus-shaped plates form on the side of the beaker. Although very sparingly soluble in cold water, 100 parts of which at 15° dissolve only about 0.4 part anhydrous salt, it is moderately soluble in water at 100° . It does not manifest any tendency to effloresce on exposure to air. When heated with dilute nitric acid, it yields a yellow solution. By boiling with nitric acid and subsequent evaporation on the water-bath, it is oxidised to phthalic acid.

Calcium Bromobetanaphthol- α -sulphonate, $[C_{10}H_5Br(OH)(SO_3)]_2Ca + xOH_2$.—This salt was prepared in the same way as the potassium salt. It is very slightly soluble in cold water, and not much more so in boiling water; nevertheless it separates with remarkable slowness from a hot saturated solution, crystallising in aggregates of extremely thin micaceous plates. These aggregates mostly exhibit a characteristic serrated outline, and a broad spear-shaped termination. On removal from the liquid the crystals rapidly become opaque from loss of water of crystallisation.

If potassium betanaphthol- α -sulphonate be submitted to the action of bromine in the proportion of 1 mol. of the former to 2 mols. of the latter, a dibromosulpho-salt is produced, but it is somewhat difficult when operating in aqueous solution to avoid the formation of coloured products. This salt is more soluble than the monobromo-salt, and

crystallises in a less characteristic manner, but it may be obtained perfectly colourless.

We have not succeeded in preparing a tribromosulpho-salt by the action of bromine in the proportion of 3 mols. to 1 mol. of betanaphthol- α -sulphonate. The product is apparently a mixture of the products of the action of 2 mols. and of 4 mols. of bromine.

If an acetic acid solution of potassium betanaphtholsulphonate be treated with bromine in the proportion of 1 mol. to 4 mols., a deep yellow-coloured solution is obtained which remains clear on the addition of water; if the acid be evaporated off on the water-bath and the residue be boiled with water, it dissolves with the exception of a relatively small amount of a yellow substance soluble in acetic acid, and as the solution cools a potassium sulpho-salt crystallises out in glistening dark-yellow plates not unlike chloranil in appearance, but of darker colour. This substance forms a deep blood-red coloured solution; it is readily soluble in boiling water, but only moderately in cold water. Bromine and potassium determinations coincide with the formula $C_{10}H_4BrSO_3K$; the air-dry salt contains in addition the elements of a molecule of water. The only probable formulæ for a body of this composition produced in such a manner are the following:

The first is that of a *potassium bromoxynaphthaquinonesulphonate*, and is, we think, to be preferred, as there is no evidence of the production of a tribromobetanaphthol- α -sulphonate, as should be the case if the second formula were a correct expression of the constitution of our salt.

Bromine has no further action on this salt at 100° in presence of water.

A corresponding chloro-compound is obtained on saturating an acetic acid solution of potassium betanaphthol- α -sulphonate with chlorine. It very closely resembles the bromo-compound in appearance and properties. The action of iodine does not appear to extend so far as that of chlorine or bromine.

No effect is produced on adding nitric acid to a cold solution of a betanaphthol- α -sulphonate, but on the application of heat the liquid assumes a magnificent carmine-red colour, as already noticed by Schaeffer. A small amount of a red crystalline substance is gradually deposited from the solution, and a further small amount is precipitated on the addition of common salt solution; it has little tinctorial power and is very unstable. The chief product remains in solution. If a solution of potassium betanaphthol- α -sulphonate be mixed with nitric acid in the proportion of 1 mol. to 4 mols. and evaporated to dryness on the water-bath, vigorous action ensues, and a dark-coloured residue

finally remains which is almost entirely soluble in water but very difficult to crystallise. Its solution has an intense red colour similar to, but much deeper in shade than, that of the bromo-salt above described, and it is highly probable that it is an allied substance; that, in fact, it is a hydroxynaphthaquinonesulphonate of the formula $C_{10}H_4(O_2)(OH).SO_3K$. We hope either to obtain this body from hydroxy- α -naphthaquinone (naphthalic acid), or to succeed in converting it into this latter compound.

We have also prepared the barium betanaphtholdisulphonates recently described by Griess (*Ber.*, **13**, 1956), and submitted them to the action of bromine. In the first instance, they yield monobromo-derivatives, but, apparently, they ultimately furnish the same product as a betanaphthol- α -sulphonate. It is noteworthy that neither of the disulphonates exhibits a characteristic reaction with nitric acid, their solutions being merely coloured yellow when warmed with the acid.

On Dihydroxynaphthalene from Naphthalene- α -disulphonic Acid.

By the Same.

Ebert and Merz are so specific in their statement that naphthalene yields two disulphonic acids, and that only one of these is convertible into a corresponding dihydroxynaphthalene, that we did not consider it necessary to prepare pure naphthalene- α -disulphonate, but fused the potassium salt from the more soluble portion of the mixture of calcium salts obtained by neutralising the crude mixture of acids formed on heating 1 pt. of naphthalene with 5 pts. of sulphuric acid at 160° for about four hours. The product, although moderately soluble in boiling water, was very slightly soluble in cold water; it crystallised in fine white needles.

On warming it with twice its weight of sulphuric acid on the water-bath for a few minutes, it was completely converted into sulphonic acid, the mixture, which was liquid at first, solidifying to a but slightly coloured mass of crystals almost entirely soluble in water. The solution was neutralised with calcium carbonate and evaporated to a small bulk; on cooling, it solidified to a mycelium-like mass of extremely fine long prismatic crystals very easily soluble in water. The barium salt, prepared in a similar manner, is also very soluble, but crystallises on slow evaporation of the solution in well-defined prisms. Both salts contain water of crystallisation; the anhydrous salts gave numbers on analysis indicating that they are *tetrasulphonates*. On treatment with an excess of bromine, a solution of the calcium salt furnishes a precipitate consisting of fine white needles precisely similar to tribromophenol. The product is free from sulphur, and is evidently a highly brominated derivative of the parent phenol, as it contains over 70 per

cent. of bromine. By the employment of less bromine, bromosulpho-salts are obtained which, on treatment with nitric acid, yield several bromonitro-derivatives closely resembling those obtained in a similar manner from the bromophenolsulphonates. Nitric acid also converts the original sulpho-salt into nitrosulpho-salt, or a nitro-derivative of the parent phenol, according to the proportion employed. In short, the dihydroxynaphthalene in question exhibits precisely the behaviour of phenol itself. The amount of material at our disposal has been too small to admit of the complete elucidation of the nature of the reactions here indicated, but we trust soon to be in a position to continue their examination.

Dr. Griess has recently described (*Ber.*, 13, 1959) a dihydroxynaphthalenedisulphonic acid, prepared from a commercial product obtained from Dr. Caro. As, according to Ebert and Merz, only one of the two disulphonic acids from naphthalene yields a dihydroxynaphthalene on fusion with potassium hydroxide, we at first supposed that we were operating with the same substance, but it soon became obvious that this could not be the case, and on sending a specimen of our product to Dr. Griess, he at once informed us that it was quite different from the dihydroxynaphthalene he had used. We were thus led to contrast Ebert and Merz's statements with those of previous workers in the same field more carefully than we had previously done, and soon came to the conclusion that the observations of Dusart (*Compt. rend.*, 64, 859), and of Darmstädter and Wichelhaus (*Annalen*, 152, 306), could not be reconciled with those of Ebert and Merz. Two explanations were possible, (1) that by the action of sulphuric acid on naphthalene, not two, but three, isomeric disulphonic acids are produced, two of which are convertible into corresponding dihydroxynaphthalenes, the third yielding betanaphthol- α -sulphonate on fusion with potassium hydroxide; (2) that only two disulphonic acids are produced, and that both may be converted into corresponding dihydroxynaphthalenes, *i.e.*, the sulpho-group in the betanaphthol- α -sulphonates *may* be displaced by OH. We believe that we are justified in regarding the first and the latter part of the second of these propositions as true.

By submitting the potassium salt prepared from the portion of medium solubility of the crude mixture of calcium naphthalenedisulphonates to the action of fused potassium hydroxide, we have succeeded in obtaining a product in all respects identical with that employed by Griess, and entirely different from the dihydroxynaphthalene which we had previously prepared, but agreeing fairly well in properties with the descriptions given by Dusart, and Darmstädter and Wichelhaus, of their products.

Secondly, we find that it *is* possible to decompose potassium beta-

naphthol- α -sulphonate by fused potassium hydroxide, although great care is necessary in conducting the operation. If the melt be dissolved in water, and the solution mixed with an excess of hydrogen chloride, much sulphur dioxide is evolved, and a small quantity of resinous matter separates out; if the hot liquid be rapidly filtered and then left to cool, a considerable quantity of a grey precipitate is deposited. On digesting this precipitate with warm ether, filtering, and evaporating the solution, a brown crystalline residue is obtained, which dissolves with considerable difficulty in hot water; the solution is decolorised by digestion with animal charcoal, filtered boiling hot, and then allowed to cool slowly. Two substances ultimately crystallise out: the one in the form of minute glistening scales, the other in the form of brownish, transparent, prismatic crystals, which often present a peculiar dagger-shaped outline. They may be almost entirely separated by levigation. We have not yet determined the composition of either of these substances, the quantity at our disposal being too small.

The dihydroxynaphthalene first prepared by us crystallises from water in long fine needles, melting at 158° ; its alkaline solution remains colourless, even after long exposure to the air. That employed by Griess is more soluble, especially in cold water, and crystallises in thin glistening plates of considerable size; when heated in a fine tube, it blackens without melting, at a temperature below 200° , but melts when heated quickly on platinum foil; its alkaline solution remains colourless on exposure to the air, but acquires a magnificent red colour on the addition of a minute quantity of orthodiazophenolsulphonate, this last reaction being remarkably characteristic,* and not exhibited by the isomeride, which is unaffected by the diazo-body in question; lastly, on the addition of bromine-water to its aqueous solution, a brilliant yellow precipitate is thrown down, which, however, gradually darkens in colour.

The two products from potassium betanaphthol- α -sulphonate possess somewhat different properties. That crystallising in small scales appears to be much less soluble in water than the substance employed by Griess; it dissolves in alkali, forming a brown solution, which darkens on exposure to the air. That crystallising in prisms is characterised by a magnificent blue fluorescence produced on adding alkali to its aqueous solution; at the same time, the liquid becomes brown. By this reaction we have ascertained that the substance resembling that employed by Griess, which we prepared, was distinctly contaminated with this particular product of the action of potassium hydroxide on potassium betanaphtholsulphonate. The alkaline solutions of both products from the betanaphthol- α -sulphonate are coloured red on the addition of orthodiazophenolsulphonate, but the colour is fugitive.

* We are indebted to Dr. Griess for acquainting us with this reaction.

Cleve has stated (*Bull. Soc. Chim.*, **25**, 244), that naphthalene- β -disulphonic acid yields a dichloronaphthalene, melting at 135° , when distilled with phosphorus pentachloride. In order further to confirm the relation between naphthalene- β -disulphonic acid and betanaphthol- α -sulphonic acid, we treated a small quantity of the potassium salt of the latter acid in like manner, and obtained a product possessing the properties assigned by Cleve to the dichloronaphthalene in question.

Theoretical Considerations. By HENRY E. ARMSTRONG.

The facts brought to light by the experiments above described are not without interest with reference to the problems indicated in the commencement of this communication.

Betanaphtholsulphonic acid and the naphthalenedisulphonic acid from which it may be formed by displacement of one of the SO_3H groups by OH obviously are similar in constitution, unless indeed isomeric change take place in the conversion of the one into the other, which is improbable. As I have already stated, our prior knowledge appears to warrant the conclusion that the OH and SO_3H groups are both contained in the one C_6 -group, and this is shown to be the case by the formation of phthalic acid from bromobetanaphthol- α -sulphonate, and from nitrosobetanaphthol- α -sulphonate (Meldola, this Journal, **39**, 46). Regarding the relative position of the OH and SO_3H groups, the last of the three formulæ ($\text{S} = \text{SO}_3\text{H}$):

may be pronounced quite out of question, as the group SO_3H in all cases tends to occupy either the ortho- or the para-position relatively to an OH-group; and No. 1 I am inclined to regard as the far more probable of the two remaining formulæ, as there appears to be a special tendency in the naphthalene series for bodies having symmetrical formulæ to be produced. The formation of a compound which there can be little doubt is an α -naphthaquinone derivative by the action of bromine on potassium betanaphtholsulphonate, lends considerable support to this view. If the conclusion thus arrived at be correct, naphthalene- β -disulphonic acid is represented by formula I, p. 134.

The constitution of the dihydroxynaphthalene of Ebert and Merz, and of the corresponding naphthalenedisulphonic acid, has yet to be finally determined, but judging from its general behaviour, it can hardly be doubted that the former is an $\alpha\alpha$ -derivative of naphthalene,

and that the disulphonic acid in question has the constitution represented by one or other of the following formulæ :

The dihydroxynaphthalene of Dusart and of Darmstädter and Wichelhaus (that employed by Griess) probably has one or both of its OH-groups in the β -position, as it readily furnishes coloured derivatives with diazo-compounds, in which respect it resembles betanaphthol.

Assuming the two bodies obtained on fusing potassium betanaphthol- α -sulphonate with potassium hydroxide to be dihydroxynaphthalenes, one—perhaps that characterised by the blue fluorescence—is probably formed by the direct displacement of the SO_3H -group by OH. On this view, it appeared not unlikely that it was identical with β -naphthaquinol, but on dissolving a small quantity of β -naphthaquinone in sulphurous acid, and then adding alkali, not the slightest fluorescence was visible. It is possible, however, that the action of nitrous acid on betanaphthol does not strictly correspond with that of bromine and sulphuric acid, and that the nitrosobetanaphthol, from which β -naphthaquinone is formed is an $\alpha\beta$ -derivative. The formation of a second dihydroxynaphthalene from betanaphthol- α -sulphonate would involve a reaction more than once observed in the anthracene series, viz., the direct introduction of an OH-group in place of an atom of hydrogen, and the displacement of the SO_3H -group by hydrogen. It is noteworthy that hydrogen is slowly evolved, almost from the beginning of the fusion process.