PAPERS READ BEFORE THE CHEMICAL SOCIETY.

IV.—COMMUNICATIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

No. IV.—*The Nitration-products of the Dichlorophenolsulphonic Acids.*

By HENRY E. ARMSTONG.

I HAVE previously stated that when ordinary dichlorophenol is converted into sulpho-acid by digestion with sulphuric acid, and the product is submitted to the action of nitric acid, Stenhouse's dinitrochlorophenol (melting point 103°) is obtained. This observation seemed necessarily to lead to the conclusion that the dichloro-sulpho-acid so formed is isomeric with those obtained by direct chlorination of Kekulés meta- and para-phenolsulphonic acids, which yield dichloronitrophenols, melting respectively at 121·5° and 125°, corresponding to dinitrochlorophenols melting at 80·5° and 111°.

The action of sulphuric acid on dichlorophenol had furnished but a poor yield of sulpho-acid, and as I required a considerable quantity of the latter, in order to study its transformations, I was led to substitute chlorhydric sulphate, SO_2OHCl, for dihydric sulphate, $SO_2(OH)_2$, hoping thereby to obtain an increased, if not theoretical, yield of sulpho-acid.

SO_3HCl (1 mol.) was added gradually to dichlorophenol (1 mol.) diluted with a small quantity of carbon bisulphide. The action was immediate, and volumes of hydrochloric acid escaped. The carbon bisulphide was subsequently distilled off, the product digested for about an hour on the water-bath, and after cooling poured into cold water. Nearly the whole dissolved, a proof that the conversion into sulpho-acid was almost complete. Sufficient potassic carbonate was then added to form the potassic salt, and the solution was evaporated to dryness. The potassic salt so obtained, though readily soluble in hot, is difficultly soluble in cold water, from which it separates in groups of short, opaque, white needles.

The dry sulpho-salt was then acted on by nitric acid (1·36) in the *cold*, and the nitro-product subsequently converted into potassium derivative, and fractionally crystallised. Thus was obtained, as sole product of the reaction, nitrodichlorophenol melting at 121·5°, viz., the same body that is obtained by direct nitration of the dichlorophenol from which the sulpho-acid operated upon was prepared. The introduction of the SO_3H group into the complex has, therefore, in this instance, had no influence in the subsequent nitration.

I now proceeded to treat a portion of the same potassic salt with acid at a temperature of 40°—50°, expecting to obtain, as by the nitration of the sulpho-acid prepared by the action of sulphuric acid on dichlorophenol, dinitrochlorophenol, melting point 103°; this proved not to be the case, however, the same dichloronitrophenol, melting point 121·5°, as before was obtained, and under no circumstances, even by the action of a much stronger acid, and at higher temperatures, was I able to determine the formation of any other than this

I mentioned in a previous paper that when a mixture of phenolmeta- and phenolpara-sulphonic acids was chlorinated, and the mixed product nitrated, there was obtained—besides the nitro-compounds which could be fixed as derived from the dichlorophenolparasulphonic acid—dichloronitrophenol melting at 121·5°, which was probably the *sole* nitration-product of the dichlorophenolmetasulphonic acid, since no corresponding dinitrochlorophenol was formed. There is now no doubt, I believe, that the above described dichlorophenolsulphonic acid, obtained by the intervention of SO_3HCl, is this same dichlorophenol*meta*sulphonic acid. I hope to effect its reduction to phenolmetasulphonic acid by nascent hydrogen, and also intend to compare it directly with the chlorination product of pure phenolmetasulphonic acid.

The only possible interpretation of the above anomalous result is, in my opinion, that the sulpho-acids obtained respectively by the action of SO_4H_2 and SO_3HCl on dichlorophenol, are *isomeric*, and I am the more persuaded of this by the following facts:—In a former communication, "On the formation of Sulpho-acids," I described the action of SO_3HCl on several benzene derivatives, and stated how in some cases the substituted sulpho-acid was the sole product, whilst in others a mixture of substituted sulpho-acid and substituted sulphobenzid was obtained. I have since extended this investigation to a number of mono- and di-benzene substitution-derivatives, and have obtained, for instance, from chlorobenzene, dichlorosulphobenzid and chlorobenzenesulphonic acid, from cyanobenzene (benzonitril) dicyanosulphobenzid, &c., &c., reactions of which I hope shortly to bring a detailed description before the Society. On examining the salts, however, more especially of the chloro- and bromo-benzenesulphonic acids so obtained, I have observed that they all differ somewhat in the amounts of water of crystallisation, &c., from the corresponding salts of the acids obtained by the action of SO_4H_2, as described by Glutz, Otto, Garrick, and others, and without having yet directly compared the bodies from the two sources, or submitted my product to the crucial test of fusion with potassic hydrate, I believe there is sufficient evidence to show that, in many cases at least, the acids obtained by the action of SO_3HCl are isomeric with those formed by SO_4H_2, the above described difference in comportment of the acids from dichlorophenol being confirmatory of this view. Again, Petersen has described at great length the conversion of monochlorophenol into sulpho-acid by the action of SO_4H_2, and the nitration-products of this sulpho-acid, which are mainly dinitrochlorophenol melting at 80·5°; ditto, melting at 69·5°; ditto melting at 114°; and dichloronitrophenol melting at 106°; the two latter being formed in small quantity only; in no case was a nitro-chloro-sulpho acid detected, although specially sought for. By converting the same monochlorophenol into sulpho-acid by the action of SO_3HCl, and nitrating, I have obtained totally different products, viz., (1) a nitro-chlorosulpho-acid, distinguished by the insolubility of its potassic salt; (2) dinitrochlorophenol melting at 103°. I have not yet examined this reaction in detail, so reserve further description for the present; it seems, however, to leave no doubt as to the isomerism of my product with Petersen's.

I believe the isomerism of the sulpho-acids formed in the above two ways might almost have been theoretically predicted, when the conditions under which the various substituted phenols are formed are considered. Let us compare the action of the halogens and of nitric acid on phenol, with that of sulphuric acid. The "reactive energy," if I may use the term, of the latter agent is feeble compared with that of chlorine and bromine; by its action on phenol we obtain two sulpho-acids, the so-called *meta*- and *para*-phenolsulphonic acids; by the action of chlorine (Br) on phenol in the cold, two monochlorophenols are formed, by far the larger quantity, however, consists of *ortho*chlorophenol. Similarly by the action of nitric acid, an extremely powerful agent, ortho- and meta-derivatives are formed simultaneously. The "reactive energy" of the chlorhydric sulphate is far greater than that of sulphuric acid, and it may rather be compared in its action to chlorine than to sulphuric acid, and it seems to me, therefore, that it should give rise to derivatives belonging to a different series to those obtained by the aid of sulphuric acid. In all probability, however, there is a direct relation between the amount of heat evolved in the formation of a substitution-derivative and the position it assumes in the isomeric series. I believe, moreover, that, in the formation of compounds of the so-called ortho-series, less heat is evolved than in the production of para-derivatives, the meta-derivatives probably occupying an intermediate position. On this assumption we can readily understand how it is that such bodies as Cl, Br, HNO_3, &c., which effect the replacement of hydrogen with such ease, should preferably form ortho- and meta-derivatives, whilst I, H_2SO_4, &c., less energetic reagents, should form meta- and para-derivatives. A direct study of the heat evolved in the formation of *isomeric* bodies will doubtless throw great light on this subject, and I intend, at the earliest possible opportunity, to prosecute such a series of experiments. It will first be necessary to ascertain the "thermic" relations of the three isomeric series—ortho, meta, and para—and this I propose to do by determining the heats of combustion of the three isomeric dihydroxylbenzols, the three phthalic acids, and the three oxybenzoic acids.*

I have observed that on nitrating crude dichlorophenol, and purifying the resulting nitrodichlorophenol by recrystallisation of the potassium derivative, the mother-liquors always deposit a small quantity of an orange-yellow salt, also the potassium salt of a nitrodichlorophenol, according to analysis, but differing from either of the three already known. The same was obtained on nitration of the sulpho-acid from dichlorophenol by SO_3HCl. This salt crystallises with one molecule of water, and yields, on decomposition with dilute acid, a nitrodichlorophenol melting at about 95°, almost insoluble in water, from which it separates in short pale yellow needles. The quantity hitherto obtained has been so small that I have not been able to characterise it further by the preparation of salts.

Dinitrochlorophenol—melting point 103°.

This body has been obtained by Dr. Stenhouse by the action of chloride of iodine on picric acid.† Dr. Griess,‡ by the action of nitric acid on crude chlorinated phenol, prepared by passing a moderately strong stream of chlorine into about 1 lb. of phenol for 15 hours, obtained, among other products, a dinitrochlorophenol melting at 103°, which Stenhouse has assumed to be identical with his product. I believe the following facts, taken together, prove that Griess's product is identical, not with that of Stenhouse, but with the so called β-dinitrochlorophenol melting at 110°—111°.

1. β-dinitrochlorophenol was obtained by Faust and Saame by nitration of crude monochlorophenol, but neither did they nor Fischer ever observe the formation of the 103° melting-point body on nitration of either mono- di- or tri-chlorophenol, nor have I been more successful.

---

* The two isomeric succinic acids may be quoted as an extremely interesting case of isomerism proper. Whereas the ordinary acid (from ethylene dicyanide) volatilises when heated, and is finally converted into the anhydride, the isosuccinic acid (from cyanopropionic acid) splits up at quite a low temperature into propionic acid and carbonic anhydride. The amount of heat evolved in the combustion of the latter acid will no doubt be found to be much greater than that evolved by combustion of the extremely stable ordinary acid.

† Journ. Chem. Soc. [2], v, 433.

‡ Ann. Ch. Pharm., cix, 286.

2. β-dinitrochlorophenol, when reduced, yields amido-nitrochlorophenol, crystallising in long *brass*-yellow needles, which contain half a molecule of water, and become *brick-red* when dried at 100°, then melt at about 160°. Griess's description of the amido-product from his dinitrochlorophenol agrees literally with the above, whereas, as I have found, the amido-product from Stenhouse's phenol forms *bronze*-yellow needles, which also contain half a molecule of water, but become *cinnamon-brown* on drying at 100°, and then melt at about 158°.

3. The salts obtained from β-dinitrochlorophenol, and from the 103° body, differ so slightly, that little weight can be attached to the description given by Dr. Griess of the salts he obtained, as a means of determining the identity of one or the other of the above. On the other hand, he says that the silver salt forms crimson laminæ; neither the 111° nor 103° melting-point phenol gives such a salt; both are yellow; but this discrepancy at once disappears when the assumption is made that Griess's product contained dinitrochlorophenol melting at 80·5°, which yields a crimson salt.

4. On application to Dr. Griess, he kindly gave me his small specimen (a fraction of a gram) of his product. I was able to recrystallise this from water, and take its melting-point. In appearance the crystals are not distinguishable from those of β-dinitrochlophenol, but distinctly *lighter* in colour, and more laminated than the 103° body. The melting point was about 109°, the same thermometer giving 110° and 103° respectively as the melting points of β-dinitro- and Stenhouse's dinitro-chlorophenol. The low melting point observed by Griess is readily accounted for by the above assumption that the specimen employed by him contained traces of the isomeride melting at 80·5°. This latter being the end-product of the nitration of ordinary monochlorophenol, as shown by Faust and Saame, must have been present in Griess's crude product, inasmuch as, according to my experience, "a moderately strong stream of chlorine" would not suffice to dichlorinate "about 1 lb. of phenol in 15 hours." If then my conviction be true, Dr. Stenhouse discovered a new dinitrochlorophenol, and not merely a new method of describing one already known.

Trichlorophenolsulphonic Acid.—Trichlorophenol is readily acted upon by chlorhydric sulphate, with evolution of hydrochloric acid. The product dissolves for the greater part in cold water, but the aqueous solution of the sulpho-acid becomes decomposed on standing, with separation of trichlorophenol.