VI.—On *Bromophenoldisulphonic Acid: its behaviour towards Nitric Acid and Bromine.*

By HENRY E. ARMSTRONG.

EXPERIMENT shows, as indeed appeared probable from the beginning, that the first action of bromine on phenoldisulphonic acid is to substitute hydrogen, and so to form a monobromophenoldisulphonic acid, which by the further action of bromine is converted successively into dibromophenolsulphonic acid and into tribromophenol.

In preparing potassium phenoldisulphonate, the slight modification of Kekulé's method described by Engelhardt and Latschinoff (*Zeitschr. f. Chem.* [2], iv, 270) was adopted.

Action of Bromine.—A cold moderately dilute solution of potassium phenoldisulphonate was treated with bromine in the proportion requisite to form the monobrominated derivative: the solution is at first coloured yellow, but the bromine disappears rapidly on shaking. After standing for some hours, crystals are deposited, and a further quantity is obtained on evaporating the solution.

That the product is the expected potassium bromophenoldisulphonate is shown by the following analysis :—

·3196 grm. gave ·1477 grm. AgBr and ·397 grm. BaSO₄.

·2406 grm. gave ·0994 grm. K₂SO₄.

	Theory.	I.
Br	19·55	19·66
S	15·64	17·05
K	19·07	18·49 *

This salt is very soluble in hot, and moderately soluble in cold water. Barium chloride produces no precipitate with it, except in very concentrated solutions. It crystallises either in needles or in tufts of short flat blades, which rapidly disintegrate to a snow-white anhydrous powder on exposure to the air.

It is violently acted upon by nitric acid (sp. gr. 1·36) and unless precaution be taken, is for the greater part converted into trinitrophenol. By gradually adding the dry salt to the well cooled acid, it is converted into bromodinitrophenol, identical with the product of the action of bromine on dinitrophenol, as was proved by the identity of melting point (117°) and crystalline form of the phenols from the two sources; by the appearance of the potassium derivative; and more especially by the characteristic separation of the calcium derivative from a hot saturated solution in orange coloured rhombic plates, and from the cold dilute solution in yellow needles.

·3429 grm. gave ·2456 grm. AgBr.

	Theory.	I.
Br	30·41	30·47

By the action of carefully cooled nitric acid somewhat less concentrated than the above, the bromophenoldisulphonate is only partially converted into bromodinitrophenol; a considerable portion is so acted upon that KSO₃ is replaced by NO₂, thus forming a potassium bromonitrophenolsulphonate. This is readily separated, after removing the excess of nitric acid by filtration and washing on a vacuum-filter with cold water, by digesting the mixed product with hot water, which dissolves the sulpho-salt and but very little bromodinitrophenol. It crystallises in short pale yellow needles, quite different in appearance from the potassium α -bromonitrophenolsulphonate obtained by nitration of potassium dibromophenolparasulphonate. It is also, I believe, *isomeric* with the potassium β -bromonitrophenolsulphonate, and may therefore be termed provisionally potassium γ -bromonitrophenolsulphonate.

A complete analysis of this salt was not made. Judging from the bromine and sulphur determinations, however, it contains one molecule of water of crystallisation—

·3675 grm. gave ·2182 grm. AgBr and ·259 grm. BaSO₄.

$C_6H_2BrNO_2OH(SO_3K) + aq.$		I.
Br	25·31	25·26
S.	10·12	9·67

The dipotassium salt crystallises in short bright-red needles.

A small quantity of a dibromonitrophenol (melting point 117·5°) yielding a deep red potassium derivative was always obtained, together with the above-mentioned nitro-products. The formation of this body appeared to show that potassium bromophenoldisulphonate was converted by the further action of bromine into potassium dibromophenolsulphonate.

This proves on examination to be the case. A weighed quantity (409 parts) of pure potassium bromophenoldisulphonate was dissolved in water, and the well cooled solution treated with bromine (160 parts) which disappeared rapidly on shaking. On standing, a small quantity of *tribromophenol* separated; this was removed by filtration, the solution evaporated to dryness, and the residue at once acted upon by nitric acid. The nitro-product consisted chiefly of dibromonitrophenol (melting point, 117°·5) yielding the characteristic red potassium salt, together with a small quantity of dinitrobromophenol (melting point, 117°), evidently the nitro-product of the bromodisulpho-salt which, owing to the formation of some tribromophenol, had escaped the action of bromine.

In the previous communication the conclusion has been drawn that the dibromonitrophenol in question is the nitration-product of dibromophenol*metasulphonic* acid: consequently the above observation shows that bromophenoldisulphonic acid is converted into dibromophenol*metasulphonic* acid by the action of bromine, and it is therefore probable that the potassium γ -bromonitrophenolsulphonate above described is also a *phenolmetasulphonic* acid derivative.

Many instances are known of the conversion of isomeric substitution-compounds into the same higher substitution-compounds by the action of the same agent; and it may fairly be asked, can no rule be given which shall enable us to predict the nature of the product which results when in such a case the higher substitution-compound is submitted to a reverse action, and is reduced to the lower—will the compound C, into which the isomeric bodies A and B are alike convertible, yield A or B when reconverted?

Although we have comparatively little evidence on this point, all that which we possess tends, I believe, in the same direction, as shown by the following examples:—

1. On nitration of toluene, two isomeric mononitrotoluenes are

obtained, viz., *orthonitrotoluene** (liquid) and *paranitrotoluene* (melting point, 54°), both of which yield the same dinitrotoluene on further nitration. By partially reducing this dinitrotoluene with ammonium sulphide, converting the nitrate of the amidonitrotoluene into diazonitrotoluene nitrate, and acting upon this by absolute alcohol, it is reconverted into *orthonitrotoluene* (Beilstein and Kuhlberg, *Ann. Chem. Pharm.*, clv, 13).

2. The two modifications of nitrophenol, *orthonitrophenol* (melting point, 110°) and *metanitrophenol* (melting point, 45°) are convertible into the same dinitrophenol; if this be reduced to amidonitrophenol, and the diazonitrophenol obtained from the latter be acted upon by hydriodic acid, an iodonitrophenol is produced, identical with the product of the action of iodine on *orthonitrophenol* (Körner, *Zeitschr. f. Chem.* [2] iv, 324).

3. Dinitrophenol and chlorine give chlorodinitrophenol (melting point, 110°–111°), from which, by the above series (Example 2) of reactions, NO₂ may be removed and replaced by H; the chloronitrophenol thus obtained is identical with the product of the action of chlorine on *orthonitrophenol*. (Faust, this *Journal* [2] x, 62; Armstrong, *ibid.* x, 14).

If the existence of three series of isomeric di-derivatives of benzene—and of isomerides generally—be regarded as a consequence of the expenditure of different amounts of force in the reactions by which the isomerides are formed, and if for the nonce it be assumed that least force is expended in the formation of compounds of the ortho-series, the greatest amount in that of para-derivatives, and an intermediate amount in the case of meta-derivatives, or, in other words, that the so-called ortho-derivatives are bodies of higher potential energy than either the corresponding meta- or para-derivatives, then the above quoted reactions appear to show that, given a compound C, capable of being formed from either of two isomerides A and B, this compound C will be reconverted on reduction into the body A, if A be an ortho- and B a meta- or para-derivative, or if A be a meta- and B a para-derivative: that is to say, that the body A will be obtained on reduction if in the formation of A less force has been expended than in the formation of B.†

The conversion of bromophenoldisulphonic acid into dibromophenol-metasulphonic acid previously described is obviously in accordance with

* Usually termed *metanitrotoluene*; v. Meyer's experiments (*Ann. Chem. Pharm.* clvi, 265, and cliv, 1), show, however, that the so-called meta-derivatives of toluene are really members of the phthalic acid, or *ortho*-series. Compare also Fittig, *Zeitschr. f. Chem.* [2], vii, 179 and 587.

† I propose to discuss this subject, and my reasons for adopting the above explanation of isomerism, fully in a future communication, so soon as a series of experiments bearing on the question are completed.

this statement. The conditions under which phenol is converted into phenolmeta- and phenolpara-sulphonic acids show that there is a greater expenditure of force in the formation of the latter.

Two classes of reactions only have been discussed in the foregoing: the reduction of nitro-compounds by Griess's method, and the reduction of sulpho-acids by bromine; it is possible that in other classes of reactions, the relation, if that above pointed out be not apparent only, may be of a different order.

It is hoped that the further investigation of the disulpho-acids will lead to useful results bearing on this question. I propose in the first place to examine the phenoldisulphonic acid which, according to Mr. Duppa, is obtained by heating salicylic acid with an excess of sulphuric acid to 180° .

My acknowledgment is due to my friend Mr. Elltoft, for the manner in which he has interested himself in preparing many of the above described compounds.