

possible in a hot needle flame. The glass stem remaining is then bent into a hook, using the tiny gas flame. The wax is then melted off and the bulb cleaned with an appropriate solvent. A bituminous base wax, such as Picein, is recommended over a shellac wax, such as deKhotinsky, because it is readily removed with carbon disulfide or carbon tetrachloride.

Buckets prepared in this manner may be made in any desired size. The author has prepared a number which are more than 1 cm. in diameter and which weigh less than 0.1 g. The weight of such buckets is usually about 0.07 g. These buckets will withstand a baking-out temperature of 450°.

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## ALPHA-NAPHTHOLSULFONIC ACIDS AND DERIVATIVES. II

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In a series of articles it has been shown that phenols can be converted in phenolpolysulfonyl chlorides<sup>1</sup> by the action of chlorosulfonic acid. It also was noticed that the reagent caused four distinct types of reaction: namely, sulfonation, sulfochlorination, chlorination and oxidation. In certain cases the hydroxyl group of the phenol was found to be esterified prior to sulfonation, while in other instances condensation products such as the sulfonylides were isolated. The predominance of any one of the above-mentioned reaction types will depend on the time, temperature, quantity of reagent and the nature of the phenols.

The most striking aspect of the reaction between unsubstituted phenols and chlorosulfonic acid is the fact that so far it has been impossible to obtain the respective monosulfonyl chlorides.

From these facts a reaction mechanism for the action of chlorosulfonic acid on phenols (and phenolsulfonic acids) was postulated comprising as the first step the primary formation of the phenolsulfonic acid ester, and as the second step its rearrangement to form a phenolsulfonic acid; this is followed by reesterification of the hydroxy group and a second rearrangement to form the phenoldisulfonic acid in presence of sufficient amounts of the reagent.<sup>2</sup> Only when the phenoldisulfonic acid is formed and further

<sup>1</sup> J. Pollak and E. Gebauer-Fuelnegg, *Monatsh.*, **46**, 383 (1925); **46**, 499 (1925); **47**, 109 (1926); **47**, 511 (1926); **49**, 187 (1928); O. Litvay, E. Riesz and L. Landau, *Ber.*, **62**, 1863 (1929); E. Katscher, *Monatsh.*, **56**, 381 (1930).

<sup>2</sup> E. Gebauer-Fuelnegg and A. Schlesinger, *Ber.*, **61**, 781 (1928).

sulfonation of the aromatic ring is more difficult, is chlorination of the phenolpolysulfonic acid accomplished with the formation of phenolpolysulfonyl chlorides. Therefore the action of the chlorosulfonic acid on phenols must be regarded as primarily a sulfonation. The chlorination of the sulfonic acid group does not occur until later. It is possible, however, to prepare phenolmonosulfonyl chlorides<sup>2</sup> when the phenolic hydroxy group is carbethoxylated. Other protective groups failed to give the expected results.<sup>3</sup>

The field which thus presented itself seemed interesting from three points of view. (I) Phenolpolysulfonyl chlorides became easily accessible, while their preparation was successful only in special cases before the experiments with chlorosulfonic acid mentioned above. Due to their reactivity they might prove to be interesting intermediates for dyestuff preparation, as well as for certain pharmaceutical purposes.

(II) The isolation and purification of the phenolsulfonyl chlorides as well as the separation of isomers, as compared to the corresponding sulfonic acids, are greatly facilitated on account of their solubility in organic solvents and the ease with which they are crystallized. Their purity can be tested by melting point determination.

(III) The relative ratio of isomeric sulfo derivatives obtained with chlorosulfonic acid is sometimes altered as compared to sulfonations with sulfuric acid.

While in previous papers a method was developed for the sulfochlorination of various phenols<sup>1</sup> and naphtholmonosulfonic<sup>4</sup> acids, the present report will deal with results obtained with isomeric 1-naphtholdisulfonic acids.

The sulfochlorination of the isomeric  $\alpha$ -naphtholmonosulfonic acids had resulted in the isolation of five isomeric 1-naphtholtrisulfonyl chlorides, in which the position of only one of the sulfo groups was known. The position of the newly introduced sulfo radicals remained to be determined.

The 1-naphthol-2-sulfonic acid yielded a trisulfonyl chloride with a melting point of 174°. From 1-naphthol-3-sulfonic acid a product was obtained which is not yet identified but which is also believed to be a trisulfonyl chloride. The 1-naphthol-4-sulfonic acid was found to form the same trisulfonyl chloride as the isomeric-2-sulfonic acid whose melting point is 174°. Upon treating the 1-naphthol-5-sulfonic acid in a similar manner, a trisulfonyl chloride with a melting point of 140° was obtained. From the 1-naphthol-6-sulfonic acid, a trisulfonyl chloride having a melting point of 203° resulted. The 1-naphthol-7-sulfonic acid yielded again the trisulfonyl chloride with a melting point of 174° and the isomeric

<sup>3</sup> E. Gebauer-Fuelnegg and F. v. Meissner, *Monatsh*, 50, 531 (1928).

<sup>4</sup> E. Gebauer-Fuelnegg and A. Glueckmann, *ibid.*, 53-54, 100 (1929).

8-sulfonic acid was found to give a trisulfonylchloride with a melting point of  $217^{\circ}$ . From this series of experiments the constitution of only one trisulfonyl chloride could be established: namely, that of melting point  $174^{\circ}$  which was obtained from the 1-naphthol-2, -4- and -7-acids. It therefore is the 1-naphthol-2,4,7-trisulfonyl chloride.

The present report will deal with attempts to establish the constitution of some of the other trisulfonyl chlorides described above.

Since the isomeric 1-naphtholtrisulfonic acids were not sufficiently reliable for the present study, the isomeric disulfonic acids were used. When two of them upon treatment with chlorosulfonic acid will form only one trisulfonyl chloride, the position of the three sulfonic groups is determined. This scheme was successful with the 1-naphthol-2,4- and -4,7-disulfonic acids, which both yielded the 1-naphthol-2,4,7-trisulfonyl chloride.

The constitution of a second trisulfonyl chloride was established when both the 1-naphthol-4,6- and -6,8-disulfonic acids were found to yield only one trisulfonyl chloride, which therefore has the structure of a 1-naphthol-4,6,8-trisulfonyl chloride. This was identical with the compound obtained from 1-naphthol-8-sulfonic acid.

With the given data the position of the sulfonyl groups in the trisulfonyl chloride with a melting point of  $203^{\circ}$  can be either that of a 1-naphthol-2,6,8- or 3,6,8-trisulfonyl derivative. From other indications we conclude that the 2,3,6-position probably represents its actual structure. Two other isomers theoretically equally possible are excluded because of the fact that its anilide does not condense with diazotized bases (elimination of 2,4,6-position) while the 4,6,8-position was found to belong to the trisulfonyl chloride with a melting point of  $217^{\circ}$  as stated above.

The constitution of the trisulfonyl chloride of m. p.  $140^{\circ}$  for which the positions 3,5,7- or 2,5,7- *a priori* are most probable, is not yet definitely settled.

In the course of the present work, a number of new derivatives of 1-naphtholdisulfonic acids were encountered.

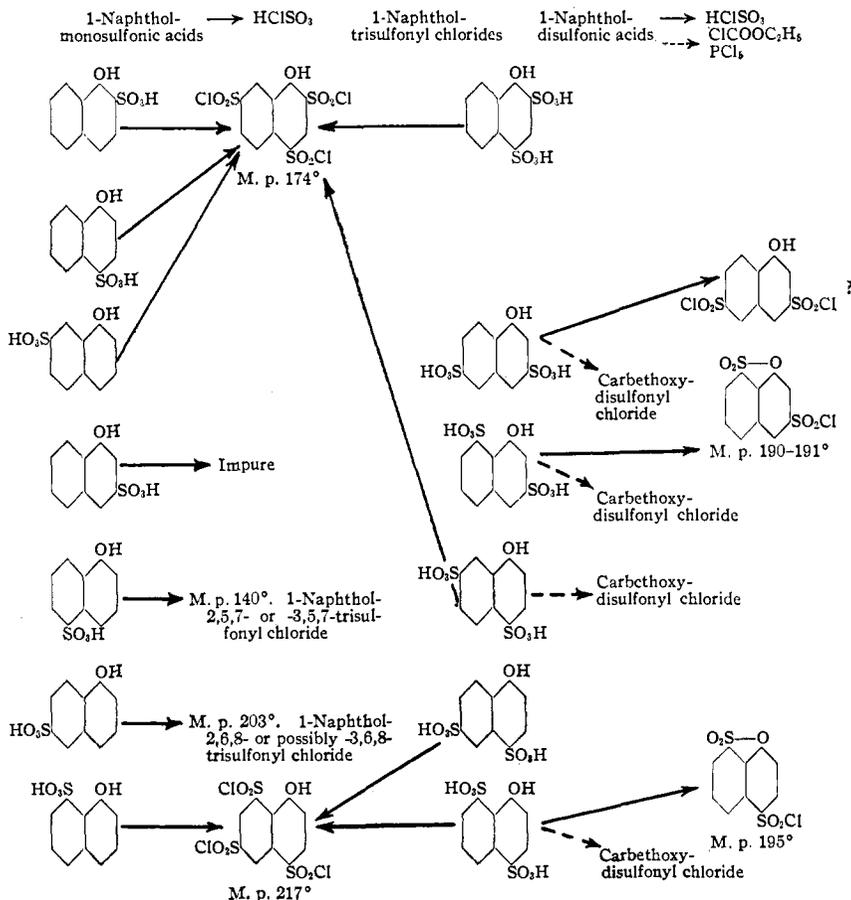
Upon treatment of the 1-naphthol-3,8-disulfonic acid with chlorosulfonic acid, the naphthsultone-3-sulfonyl chloride was obtained. From this acid no trisulfonyl chloride was obtained. The isomeric naphthsultone-4-sulfonyl chloride resulted under analogous conditions from the 1-naphthol-4,8-disulfonic acid.

When treated with aniline a reaction takes place, but the products obtained do not seem to be the expected naphthsultone sulfanilides. They will be studied and reported upon later.

The carbethoxy-1-naphtholdisulfonyl chlorides and some of the anilides of 1-naphthol-3,6-, -3,8-, -4,7- and -4,8-disulfonic acid have also been prepared. From the 4,6-disulfonic acid we were unable to isolate the

corresponding chloride or anilide. Special care was necessary in the case of the 4,8-disulfonic acid, which was found to be easily converted by the presence of moisture into the corresponding naphthsultonesulfonyl chloride.

The chart shows the relation of the different 1-naphtholsulfonic acids and their derivatives.



## Experiments

**1-Naphthol Trisulfonyl Chlorides.**—Ten grams of 1-naphthol-2,4-disulfonic acid was added to 100 g. of chlorosulfonic acid in small portions. After this had stood at room temperature for three days, crystals had formed. The yield did not seem to increase after ten days. They were filtered by suction through a funnel with a porous glass bottom, finally washed with water and dried in a vacuum. The substance was first crystallized from benzene and finally from carbon disulfide and yielded crystals melting at 174°.

The same substance may be obtained after three hours, when the reaction mixture

is cautiously poured on crushed ice, carefully dried and crystallized as above. A mixture melting point proved the identity of the two preparations.

Ten grams of sodium salt of 1-naphthol-4,7-disulfonic acid were slowly added to 100 g. of chlorosulfonic acid. After fourteen days the crop of crystals was isolated and purified as above. The melting point of  $174^{\circ}$  and mixed melting point with the preparations obtained from the 1-naphthol-2,4-disulfonic acid as well as from 1-naphthol-2,4- and -7-monosulfonic acids, proved the identity of the substances. This compound also is formed after a three-hour reaction period from 1-naphthol-4,7-disulfonic acid with chlorosulfonic acid at room temperature.

Ten grams of 1-naphthol-4,8-disulfonic acid is added to 100 g. of chlorosulfonic acid, and the mixture is heated in an oil-bath for one hour at  $150^{\circ}$ . (The reaction which takes place under milder conditions will be described in a following paragraph.) After repeatedly crystallizing from carbon disulfide, the constant melting point of  $217^{\circ}$  is reached.

If 1-naphthol-4,6-disulfonic acid is treated analogously at 100 or  $150^{\circ}$  and the reaction product poured into concd. hydrochloric acid, filtered, completely dried, dissolved in benzene and crystallized from carbon disulfide to a constant melting point, crystals are obtained which melt at  $217^{\circ}$ , identical with those obtained above as well as with the compound previously obtained from 1-naphthol-8-sulfonic acid.

*Anal.* Calcd. for  $C_{10}H_6O_7S_2Cl_3$ : Cl, 24.20. Found: Cl, 24.48.

The corresponding anilide is obtained when an ether solution is refluxed with an excess of aniline on the water-bath.

**Naphthsultonesulfonyl Chlorides.**—Ten grams of sodium salt of 1-naphthol-3,8-disulfonic acid is added in small portions to 100 g. of chlorosulfonic acid at room temperature. The reaction mixture is cooled in the ice box, poured on crushed ice, filtered and completely dried *in vacuo*. The residue is first dissolved in benzene, crystallized and finally recrystallized from carbon disulfide, whereby crystals with a constant melting point of  $190$ – $191^{\circ}$  are obtained. The same substance was isolated with better yields, when the reaction was prolonged for thirty days or the mixture heated to  $150^{\circ}$ .

*Anal.* Calcd. for  $C_{10}H_6O_5S_2Cl$ : Cl, 11.64; S, 21.06. Found: Cl, 11.65; S, 20.96.

Ten grams of sodium salt of 1-naphthol-4,8-disulfonic acid is slowly added to 100 g. of chlorosulfonic acid, isolated as before, m. p.  $195^{\circ}$  (a mixed melting point with the naphthsultone-3-sulfonyl chloride, m. p.  $190$ – $191^{\circ}$ , gave a depression). The same product is obtained after prolongation of the reaction for thirty days.

*Anal.* Calcd. for  $C_{10}H_6O_8S_2Cl$ : C, 39.39; H, 1.65; Cl, 11.64. Found: C, 39.53; H, 2.11; Cl, 11.67.

The two isomeric naphthsultonesulfonyl chlorides do not react with aniline in ether solution to form the corresponding anilides. Only when boiled with aniline does a reaction ensue with the formation of products which are not the expected anilides. They will be discussed elsewhere.

**Carbethoxy-1-naphtholdisulfonyl Chlorides.**—Twenty grams of sodium salt of 1-naphthol-4,7-disulfonic acid is dissolved in a concd. solution of 15 g. of potassium hydroxide and well cooled, 20 g. of ethyl ester of chlorocarbonic acid is added drop by drop and the reaction mixture mechanically shaken for five to six hours. Alcohol was added to complete the precipitation and to dissolve any excess of reagent and filtered. The well dried substance was finely powdered and mixed with 1.5 molar proportions of phosphorus pentachloride and heated for one hour in an oil-bath at  $130$ – $150^{\circ}$ . The reaction mixture was cooled to room temperature, poured on crushed ice, filtered and well washed with water. The completely dried residue was crystallized from carbon disulfide, finally giving crystals with a constant melting point of  $120^{\circ}$ .

*Anal.* Calcd. for  $C_{13}H_{10}O_7Cl_2S_2$ : Cl, 17.17. Found: Cl, 17.10.

The preparation of the carbethoxy-1-naphthol-3,8-disulfonyl chloride was analogous with the experiments described above, m. p. 180–181°.

*Anal.* Calcd. for  $C_{13}H_{10}O_7S_2Cl_2$ : C, 37.76; H, 2.44; Cl, 17.17. Found: C, 38.05; H, 2.81; Cl, 17.46.

Carbethoxy-1-naphthol-4,8-disulfonyl chloride was prepared in the same way. The substance was finally obtained from carbon disulfide and melted from 177–179°. The analysis also indicates that the product is not entirely pure.

Care must be taken to avoid even traces of moisture during the reaction as well as recrystallization since the carbethoxy group is easily split off and as a result the naphth-sultone-4-sulfonyl chloride, m. p. 195°, is obtained.

*Anal.* Calcd. for  $C_{13}H_{10}O_7S_2Cl_2$ : C, 37.76; H, 2.44; Cl, 17.17. Found: C, 38.52; H, 2.21; Cl, 17.80.

The carbethoxy-1-naphthol-3,6-disulfonyl chloride melted at 95° after crystallization from ether.

*Anal.* Calcd. for  $C_{13}H_{10}O_7S_2Cl_2$ : C, 37.76; H, 2.44; S, 15.52; Cl, 17.17. Found: C, 37.44; H, 2.77; S, 15.69; Cl, 17.21.

Some of the anilides of the isomeric carbethoxy-1-naphtholdisulfochlorides were prepared by boiling them with 2.5 molar proportions of aniline in ether solution for three hours. After evaporation the residue is washed with dilute hydrochloric acid and water. The carbethoxydisulfanilides were purified by carefully dissolving in dilute potassium hydroxide and precipitating with dilute hydrochloric acid.

We are indebted to the I. G. Farbenindustrie A.-G. for furnishing us with the 1-naphtholsulfonic acids.

### Summary

The value of chlorosulfonic acid as a sulfochlorinating agent for phenols is emphasized.

1-Naphthol-2,4-, -2,7-, -3,6-, -3,8-, -4,6- and -4,8-disulfonic acids were sulfochlorinated with chlorosulfonic acid. 1-Naphthol-2,4- and -2,7-disulfonic acid yielded the same trisulfonyl chloride, the constitution of which therefore is determined as the 1-naphthol-2,4,7-trisulfonyl chloride. 1-Naphthol-4,6- and -6,8- also gave only one trisulfonyl chloride, which therefore must be the 1-naphthol-4,6,8-trisulfonyl chloride. Previously it had been obtained by sulfochlorination of the 1-naphthol-8-sulfonic acid. The constitution of the trisulfonyl chloride previously obtained from the 1-naphthol-6-sulfonic acid is believed to be the 1-naphthol-2,6,8- or possibly -3,6,8- derivative, while the structure of the trisulfonyl chloride derived from 1-naphthol-5-sulfonic acid is either that of a 1-naphthol-2,5,7- or -3,5,7- derivative.

From the 1-naphthol-3,8- and -4,8-disulfonic acids the respective naphth-sultonemonosulfonyl chlorides were obtained under proper conditions.

The carbethoxynaphtholdisulfonyl chlorides and a number of their anilides also have been prepared from the above acids.