

TABLE V(continued).

Reagent.	Fibroin.	Nitrofibroin.
Glacial acetic acid	Soluble in hot solution	Insoluble
Conc. HCl	Soluble	Soluble
Conc. H ₂ SO ₄	Soluble	Soluble
Conc. HNO ₃	Soluble	Soluble
Application of heat (Melting point)	Disintegrates at about 170°. No definite decomposition point	Begins to turn brown at about 240° and at 300° is almost black. No definite decomposition point
Copper oxide in am- moniacal solution (Schweitzer's re- agent)	Soluble in hot solution	Insoluble
Nickel oxide in am- moniacal solution	Soluble in hot solution	Insoluble
Biuret reaction	Positive	Color does not develop on account of orange color of the alkaline solution
Strong KOH solution (50%)	Soluble with evolution of ammonia	Soluble in hot solution with slight evolution of ammonia

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

THE SEPARATION OF MONO- β -, 2,6- AND 2,7-SULFONIC ACIDS OF ANTHRAQUINONE.

By M. L. CROSSLEY.

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Mono- β -, 2,6- and 2,7-sulfonic acids of anthraquinone, the products of direct sulfonation, are said to be easily separated as calcium salts which ultimately can be converted into the acids.¹ In preparing these acids, I have observed that when the lime treatment is used a considerable portion of the calcium salts of mono- β - and 2,6-acid is thrown out of solution and discarded with the calcium sulfate. As a result a poor yield of these acids is obtained. Especially is this true when the sulfonation is intended to give the 2,6- and 2,7-acids as the chief products.

After considerable experimentation with different methods, I find that the best yields are obtained on separating the acids as their sodium salts by the direct neutralization of the sulfonated mixture with sodium hydroxide. By careful concentration of the solution of sodium sulfonates the mono- β - and 2,6-salts can be separated together, leaving the bulk of the sodium sulfate in the filtrate with the 2,7-salt, from which it can be precipitated by ethyl alcohol. The first two salts are separated from each other by their different solubilities in water. In addition to the three salts already mentioned, I have obtained a new substance which has not previously been described.

¹ Beilstein's *Handbuch der Organische Chemie*, 2, 406.

50 g. of best anthraquinone, recrystallized from benzene, and 18 g. of concentrated H_2SO_4 were mixed to a uniform paste in a casserole, 82 g. of fuming H_2SO_4 (60% SO_3) were then added. The casserole was covered with a watch glass and heated in an oil bath to 170° (thermometer in the oil) for two hours. A dark red pasty product was obtained. This was poured carefully into a liter of water and the mixture boiled for half an hour. It was then filtered while hot to remove unchanged anthraquinone. The filtrate was treated with a concentrated solution of sodium hydroxide until almost neutral and then evaporated to a thick paste. This was filtered and then pumped free of liquid. The solid was a mixture of mono- β - and 2,6-sodium sulfonates. These were separated from each other by their different solubilities in water and recognized by their sulfone chlorides, amides, and esters. The 2,6-sodium sulfonate is extremely sensitive to sunlight and changes from a light plum color to almost black.

The dark ruby-red filtrate from the pasty mixture was treated with 95% ethyl alcohol until no further precipitate of sodium sulfate formed. This was filtered and the filtrate evaporated over a water bath almost to dryness. The residue was then taken up in a very small amount of distilled water and to this solution was added a large excess of 95% ethyl alcohol, whereupon, a salmon-pink substance separated. This has very striking properties and is different from any of the anthraquinone derivatives thus far studied. It was filtered and dried at 150° . It dissolves readily in distilled water, giving a golden-yellow solution which changes to pink on adding a small amount of tap water.¹ This color change is not permanent and when the pink solution is exposed to sunlight for about twenty-four hours it completely changes back to the original golden-yellow color. The pink color can be again developed by the addition of tap water. If the exposure to sunlight is continued for two or three days no amount of tap water will re-establish the pink color. If a drop of dilute sodium hydroxide is added to the pink solution and it is then exposed to sunlight, the pink color is not discharged but instead it darkens to permanent ruby-red. The substance behaves as a very sensitive indicator, being reddish pink in alkaline solution and golden-yellow in acid solution. The pink color is not discharged by carbon dioxide. The compound is practically insoluble in acetone, acetic acid, benzene, ethyl alcohol, ether, ethyl acetate, aniline, ligroin, nitrobenzene, and pyridine. It is slightly soluble in methyl alcohol. Chloroform changes it to a dark red oil which is not soluble in an excess of the solvent. On standing this oil solidifies to a mass of beautiful red needle-shaped crystals. It also forms a dark red oil with toluene and this solidifies to a mass of rod-

¹ The tap water referred to was the City of Providence water and also Middletown water.

shaped crystals. When the substance, suspended in 95% ethyl alcohol, is exposed to sunlight, it changes to a beautiful dark green compound. This, when filtered and dried, slowly reverts back to the original salmon-pink substance. The transformation takes place very slowly when the substance is protected from sunlight. The change, however, is sufficiently rapid to prevent accurate information being accumulated with regard to the exact composition of the green compound. I have not felt certain that any one of the analyses of this substance represented a compound of uniform composition. No concordant results have been obtained. It appears to be a loose addition product of the salmon-pink compound. I reserve judgment in regard to the constitution of these substances until some later date when more evidence has been established from the continuation of the work in this laboratory.

The alcohol filtrate from the salmon-pink compound was again evaporated to dryness and the residue taken up in distilled water. To the solution was added about ten times its volume of 95% ethyl alcohol. There was no precipitate formed. The alcohol solution was evaporated to dryness and the residue shown to be 2,7-sodium sulfonate.

Yields: Mono- β -sodium sulfonate, 2 grams; 2,6-sodium sulfonate, 60 grams; 2,7-sodium sulfonate, 28 grams; new substance, 9 grams.

By the calcium treatment only 40 g. of 2,6 were obtained. None of the new substance was isolated. The yield of 2,7 averaged 29 g. and only a trace of mono- β or "silver salt" was obtained.

In order to produce the "silver salt" as the chief product of the reaction, 50 g. of best¹ anthraquinone and 9 g. of concentrated sulfuric acid were mixed to a uniform paste, to which were then added 41 g. of fuming sulfuric acid (60% SO₃). The reaction was carried out in a casserole. This was covered with a watch glass and heated in an oil-bath to 160° for two hours. The sulfonated product was then poured into water and boiled for half an hour. It was then filtered to remove the unchanged anthraquinone. The filtrate was treated with sodium hydroxide until almost neutral and then evaporated over a water bath to about one-third of its volume. On cooling, the mono- β -sodium sulfonate or silver salt separated. It was filtered and dried. The average yield obtained in this way was 38 g. The calcium treatment by the same method of sulfonation only yielded an average of 29 g. In the course of this work it was found that the "silver salt" separates best in mildly acid solution.

Summary.

The mono- β -, 2,6- and 2,7-sulfonic acids of anthraquinone are most advantageously separated as sodium salts by the direct neutralization

¹ Merck's.

of the sulfonic acid mixture with sodium hydroxide and the subsequent separation of these by their different solubilities in water.

On neutralization of the sulfonated mixture with lime much of the calcium salts of mono- β and 2,6 is lost in the calcium sulphate.

2,6-Sodium sulfonate of anthraquinone is very sensitive to sunlight, darkening in color from plum to almost black.

A new substance has been isolated. It has some interesting properties. When suspended in ethyl alcohol and exposed to sunlight an unstable green product results.

"Silver salt" separates best in mildly acid solution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]
**THE NEUTRAL AMMONIUM SALTS OF SOME SUBSTITUTED
BENZOIC ACIDS.**

[FIFTH COMMUNICATION.¹]

BY LEROY McMASTER AND I. H. GODLOVE.

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This work is a continuation of the preparation and investigation of the properties of the neutral ammonium salts of organic acids. This paper deals with the derivatives of benzoic acid. The salts described in the previous papers were prepared by passing dry ammonia into solutions of the organic acids in methyl alcohol, ethyl alcohol, ether, and acetone, or in mixtures of these solvents.

In the following work the neutral ammonium salts of *m*-toluic, *p*-toluic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, *o*-bromobenzoic, *m*-bromobenzoic, *p*-bromobenzoic, *o*-nitrobenzoic, *m*-nitrobenzoic, *p*-nitrobenzoic, 3,5-dinitrobenzoic, *o*-aminobenzoic, *m*-aminobenzoic, and *p*-aminobenzoic acids have been prepared by passing dry ammonia into solutions of the respective acids in the above anhydrous solvents, and some of their properties studied. After the salts were precipitated and tested for neutrality, they were filtered by suction on an alundum crucible and thoroughly washed with anhydrous ether. They were then put into crystallizing dishes and allowed to stand a short time in a vacuum desiccator.

Several of the salts were also prepared in pure benzene. Currie² states that the ammonium salts of weak organic acids can be prepared by passing dry ammonia into a benzene solution of the acids, and in this manner prepared the ammonium salts of caproic, caprylic and capric acids.

¹ For previous papers on this subject see: *Am. Chem. J.*, **49**, 84-7 (1913); *Chem. News*, **108**, 136-7 (1913); *Am. Chem. J.*, **49**, 294-301 (1913); *Chem. News*, **108**, 182-3, 193-4 (1913); *THIS JOURNAL*, **36**, 742-7 (1914); *Chem. News*, **110**, 212-4 (1914); *THIS JOURNAL*, **36**, 1916-25 (1914); *Chem. News*, **110**, 224-8 (1914).

² *J. Agr. Research*, **2**, 8 (1914).