

[CONTRIBUTION FROM THE ORGANIC LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE CONSTITUTION OF THE SECONDARY PRODUCT IN THE SULFONATION OF CINNAMIC ACID.

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Cinnamic acid, when treated with fuming sulfuric acid, yields 2 sulfonic acids, the more abundant being the *para* derivative. Rudnew,¹ who first carried out this reaction, believed the other product to be a *meta* compound because, on fusion with potash, it yielded *m*-hydroxybenzoic acid. Beilstein,² however, questions this conclusion, and points out (1) the frequent rearrangements which take place in a potash fusion, (2) the uniformity with which *ortho* and *para* compounds are simultaneously formed, and (3) the fact that Kafka³ had already prepared a *meta* acid from *m*-sulfo-benzaldehyde by the Perkin synthesis, which leaves hardly a doubt as to the constitution of the product. Doubtless for these reasons Richter's "Lexikon" describes the acid of Kafka as *meta* and the secondary product of Rudnew as *ortho*, in spite of the fact that Kafka's description contains no criteria by which his acid could be distinguished from the other, and that Palmer,⁴ who had oxidized the amide of the latter in the expectation of obtaining "saccharine," was not successful—an argument against the *ortho* position.

The present work shows that the secondary product of sulfonation is a *meta* compound because permanganate transforms it smoothly to *m*-sulfo-benzoic acid. It is also identical with the acid of Kafka which has been prepared for comparison.

Experimental.

In a study of the *para* acid made by one of us⁵ some years ago, several grams of the acid barium salt of the *meta* acid had accumulated, and this material furnished the starting point for the present investigation. The salt is a good deal more soluble in water than is the *para* compound and crystallizes in warty aggregates, very different from the long beautiful needles which characterize the *para* salt.

m-Sulfo-benzoic Acid.—Five g. of this salt was converted into the potassium salt by boiling it with a concentrated solution of 2.5 g. of potassium carbonate. Then 7.2 g. of potassium permanganate was stirred into the warm filtered solution. Oxidation was immediate. After the addition of a little alcohol the solution was filtered from manganese dioxide and evaporated to dryness. The *m*-sulfo-benzoic acid which it contained was not isolated as such, but was identified by the following derivatives.

¹ Rudnew, *Ann.*, **173**, 8 (1874).

² Beilstein, "Handbuch d. org. Chem.," 3rd ed., vol. II, p. 1422.

³ Kafka, *Ber.*, **24**, 796 (1891).

⁴ Palmer, *Am. Chem. J.*, **4**, 161 (1882).

⁵ Moore, *THIS JOURNAL*, **25**, 622 (1903).

***m*-Sulfobenzamide.**—Seven-tenths g. of the residue (containing much potassium carbonate) was heated with 2 g. of phosphorus pentachloride in a small distilling flask, at first on the water-bath and then to about 150°, to remove phosphorus oxychloride. The product, when treated with ice-water, yielded about 1 cc. of a heavy oil. This was added drop by drop to ammonium hydroxide (sp. gr., 0.90). After the product cooled, it was washed with water, dried on a porous tile, and recrystallized from absolute alcohol. It melted at 171–172°, and a mixture of it with *m*-sulfobenzamide prepared from another source melted at the same temperature.

***m*-Hydroxybenzoic Acid.**—To obtain this acid, 1.72 g. of the same residue was fused with 15 g. of potassium hydroxide and a little water at 220–240° for 45 minutes. The melt was dissolved in water, just acidified with hydrochloric acid and extracted thrice with ether. The combined extracts yielded 0.55 g. of a crusty residue. Four crystallizations from water yielded a product melting at 200–201°, and a mixture of this product with *m*-sulfobenzamide from another source melted at the same temperature. Both gave an unmistakable (dirty) brown coloration with ferric chloride which confirms the experience of Velden,⁶ although most books state that this acid gives no color with ferric chloride.

Acetyl Derivative.—For further identification, the acid was transformed into its acetyl derivative according to the directions of Heinz⁷ and a product with the melting point recorded by him (127°) was obtained.

***m*-Sulfobenzaldehyde.**—This substance, which is the necessary starting point in the synthesis of Kafka, had been prepared by Wallach and Wüsten.⁸ They do not state the strength of their sulfuric acid, but we found that any acid containing less than 40% of anhydride was inefficient, and even with this strength it was necessary to warm the mixture for several hours on the water-bath before all the benzaldehyde was sulfonated. From the reaction mixture the barium salt was obtained in the customary way and a barium determination (calc., 27.16%; found, 26.35%) showed that sulfonation had not passed beyond the introduction of one sulfo group.

***m*-Sulfocinnamic Acid.**—Kafka heated the barium salt of *m*-sulfobenzaldehyde with sodium acetate and acetic anhydride. The product was acidified with sulfuric acid and distilled with steam to remove acetic acid. It was then evaporated to dryness and the residue extracted with alcohol. We found it impracticable to remove the large quantities of acetic acid with steam satisfactorily, and obtained only poor yields of impure material in this way. Better results (still far from good) were obtained as follows.

Ten g. of the barium salt of *m*-sulfobenzaldehyde was intimately ground with 5 g. of freshly fused sodium acetate and the mixture treated with 22 cc. of acetic anhydride. The whole was then boiled for 13 hours. After cooling the mixture, it was treated directly with ether to remove as much acetic anhydride as possible at this point. The portion insoluble in ether was dissolved in water and precipitated by sodium carbonate. The filtrate from barium carbonate was then evaporated to dryness. The residue should contain the sodium salt of sulfocinnamic acid along with considerable acetate and carbonate. It was proposed to transform the acetate and sulfonate to the acid chlorides and separate them by the greater sensitiveness of acetyl chloride to water. The original residue had weighed 31 g. Fifteen g. of it was treated with 30 g. of phosphorus pentachloride in the cold and after half an hour the mixture was poured upon ice. When the material soluble in water had been removed, the waxy residue was boiled with water to transform the acid chloride into the free sulfonic acid. The product was a greasy solid unsuitable for analysis (Kafka did not analyze it).

⁶ Velden, *J. prakt. Chem.*, [2] 15, 165 (1877).

⁷ Heinz, *Ann.*, 153, 338 (1870).

⁸ Wallach and Wüsten, *Ber.*, 16, 150 (1883).

but was identified by transformation into the acid barium salt which crystallized in the warty aggregates already described, and by the preparation and analysis of the acid aniline salt.

ANILINE SALT.—Like Palmer, we found it difficult to prepare a homogeneous amide of *m*-sulfocinnamic acid, but one of us^b had already pointed out that it is frequently more convenient to characterize sulfonic acids by their salts with organic bases. This proved to be the case here. A solution of the crude acid in 5 times its weight of water was mixed with its own weight of aniline sulfate in suspension. The mixture solidified at once. It was warmed until solution was complete and then cooled. The product obtained was dried and crystallized 4 times from a mixture of alcohol and ether, from which it separated in lustrous needles melting at 238° with evolution of gas.

Analyses: Subs., 0.4123: 15.2 cc. N, (20°, 744 mm.). Subs., 0.1603, 0.1574: BaSO₄, 0.1174, 0.1153. Calc. for C₁₅H₁₅O₅NS: N, 4.36; S, 9.97. Found: N, 4.28; S, 10.00, 10.06.

The identity of this compound with the acid aniline salt of the acid formed by sulfonating cinnamic acid was established by preparing the salt from that source for comparison. It was found to contain 4.26% of nitrogen and melted at 238°. A mixture of the 2 samples melted at the same temperature.

A *p*-toluidine salt of the acid made by sulfonation was also prepared. It was more difficult to purify and was not analyzed. It melted at 229–230° with gas evolution.

Summary.

1. The secondary product formed in the sulfonation of cinnamic acid is *m*-sulfocinnamic acid. It is identical with that already obtained from *m*-sulfobenzaldehyde by the Perkin synthesis.
2. The *ortho* acid is therefore still unknown. Attempts are in progress to prepare it, and to make a comparative study of the three.
3. Another case has been found which illustrates the convenience of characterizing sulfonic acids by their salts with organic bases.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW YORK STATE HOSPITALS.]
**IDENTIFICATION OF ALKALOIDS UNDER THE MICROSCOPE
FROM THE FORM OF THEIR PICRATE CRYSTALS.**

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No satisfactory systematic scheme for the qualitative identification of all the common vegetable alkaloids is known, and while certain partial schemes serve fairly well for particular groups, they frequently do so only in the known absence of others. Moreover, many of these schemes and in fact the classical methods for identifying organic compounds generally, are quite frequently inapplicable because of the small amount of material available, particularly in the analyses of certain medicines and in forensic cases. The well-known color reactions, often interpreted largely by a