

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
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**A RENEWED STUDY OF THE SULFONATION OF CINNAMIC
ACID: A NEW PROOF THAT THE SECONDARY PRODUCT
IS META-SULFOCINNAMIC ACID; SYNTHESIS OF THE
TRUE ORTHO-SULFOCINNAMIC ACID, AND THE
ACTION OF SODIUM BISULFITE UPON CINNAMIC
ACID DERIVATIVES**

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When cinnamic acid is sulfonated the principal product of the reaction is *p*-sulfo­cinnamic acid. Whether the isomer formed at the same time is an *ortho* or *meta* compound has, however, been the subject of inconclusive controversy since 1874. In 1922 Moore and Thomas¹ reviewed the discussion and presented convincing evidence for the *meta* structure. They oxidized the product to *m*-sulfo­benzoic acid which they characterized by its diamide and by transforming it to *m*-hydroxybenzoic acid² and the acetyl derivative of the latter. They also identified the product of sulfonation with the substance which Kafka³ had prepared from *m*-sulfo­benzaldehyde by the Perkin reaction (but which he had utterly failed to characterize), establishing identity by a mixed melting point of the acid aniline salts.

A little later in the same year, Van Duin⁴ published a paper in which he supported the *ortho* structure. He, too, oxidized the acid of sulfonation with permanganate, but stated that the product of this reaction, when treated with phosphorus pentachloride, yields the so-called "stable chloride" of *o*-sulfo­benzoic acid; whereas we, like Moore and Thomas, find that the chloride so formed yields with ammonia the diamide of *m*-sulfo­benzoic acid. Van Duin also treated the acid derived from sulfonation with phosphorus pentachloride and the product of that reaction with ammonia and assumed without analysis or characterizing data that the product was the diamide of the sulfo­cinnamic acid, a compound whose preparation has been described by Palmer⁵ but which has been satisfactorily characterized by no one. This substance he treats with alkali to hydrolyze the CONH₂ group and, without isolating the supposed intermediate, oxidizes with permanganate and obtains a product which he considers to be *o*-sulfo­amino­benzoic acid because it does not lower the melting point of that substance. We offer no conjecture concerning the nature of his final product, but our

¹ Moore and Thomas, *THIS JOURNAL*, **44**, 367 (1922).

² As we have determined experimentally, no rearrangement takes place when the sulfo­benzoic acids are fused with alkali under the conditions employed.

³ Kafka, *Ber.*, **24**, 796 (1894).

⁴ Van Duin, *Rec. trav. chim.*, **41**, 402 (1922).

⁵ Palmer, *Am. Chem. J.*, **4**, 161 (1882).

attempts to prepare a homogeneous diamide from the acid of sulfonation lead us to doubt whether that compound has ever been prepared in a pure state. Finally, Van Duin observed that the melting point of the acid aniline salt of the sulfonation acid is lowered only 1° by admixture with a similar salt obtained through the Kafka synthesis, but he does not accept this as evidence of the identity of the salts.

The publication of the foregoing results made it desirable not only that we repeat and verify the work of Moore and Thomas, but that we also prepare synthetically both *o*- and *m*-sulfocinnamic acids and compare them with the products of sulfonation. This work has now been completed. Both acids have been synthesized, each being characterized by its monochloride and by four organic salts, and the comparison verifies once more the identity of the acid of sulfonation with the *meta* compound and its difference from the *ortho*. The latter, also, is easily transformed to salicylic acid, while the product of sulfonation is not.

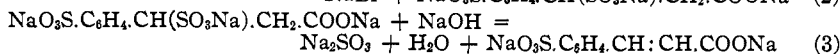
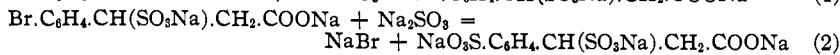
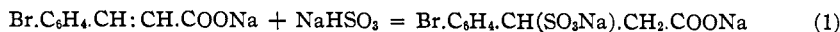
To meet the objection that both *ortho* and *meta* acids may be formed in sulfonation, and that the difference in the products isolated might be due to details of manipulation, we have closely followed the excellent procedure of Van Duin in the separation of the isomers, and we have measured the maximum quantity of possible *ortho* sulfonation by transforming the sulfonic acids to hydroxy acids and measuring the salicylic acid formed colorimetrically. The results show that, if *ortho* sulfonation takes place, it is to a far less extent than 1%. Finally, we have sulfonated at a higher temperature and obtained evidence for the formation of a disulfonic acid, but not for that of an *ortho* compound.

For the synthesis of the sulfocinnamic acids we did not again resort to the method of Kafka. Previous experience with it had revealed the difficulty of separating the desired sulfonate from the large quantities of sodium acetate employed, and had raised some doubt whether other organic acids are not formed. It was also obviously unsuited to the preparation of the *ortho* compound because *ortho* sulfobenzaldehyde is so difficultly accessible. We finally made successful use of the reaction discovered by Rosenmund,⁶ who observed that aromatic bromides exchange halogen for the sulfo group when heated in a sealed tube with aqueous sodium sulfite in the presence of copper sulfate. Our first attempts to apply the reaction to the bromocinnamic acids, however, led to temporary disappointment. No sulfocinnamic acid could be found in the reaction mixture. After a series of interesting preliminary experiments,⁷ however, we were able to isolate from the mixture two salts, one of which was an addition product of sodium bisulfite to bromocinnamic acid and the other a similar compound of the bisulfite with the sulfocinnamate. The first could be readily trans-

⁶ Rosenmund, *Ber.*, **54**, 436 (1921).

⁷ G. R. Tucker, Unpublished *Thesis*, Massachusetts Institute of Technology, 1926.

formed into the second under the conditions of the Rosenmund reaction. It was now clear that our synthesis was to be realized through the steps typified by the following reactions, of which only the second requires the use of sealed vessels.



After carrying out these reactions separately, we succeeded in combining them in a single operation which does not involve the isolation of the intermediates. With slight modifications, it is applicable to the preparation of both the *ortho* and *meta* acids.

One of the most interesting results of the present investigation has been to show that the addition of sodium bisulfite to a double bond is a more general reaction than has been commonly supposed. Several isolated cases are indeed recorded in the literature⁸ but the reaction has been almost utterly ignored by even the largest textbooks. Since the sodium bisulfite is easily added and as easily split off, the possible applicability of the reaction to the separation of unsaturated compounds from saturated ones of similar properties should be as welcome as it is obvious.

Experimental Part

The Sulfonation of Cinnamic Acid and the Separation of the Isomeric Products.—

Fifty g. of finely ground cinnamic acid is added to 150 g. of fuming sulfuric acid (18% anhydride) during constant shaking so that the temperature does not exceed 35°. This requires about two hours. The mixture is heated for one-half hour on the boiling water-bath until sulfonation is complete. After cooling, 200 cc. of water is added and a few crystals of *p*-sulfocinnamic acid, and the whole allowed to stand for ten hours. Most of the *para* acid separates in long needles.⁹ These are washed with 25% sulfuric acid and, after drying at 100°, weigh 43–45 g.

The filtrate is diluted to 1 liter and 275 g. of barium carbonate is added during stirring. This precipitates essentially only barium sulfate. It is washed, and the washings are added to the filtrate, which is heated to boiling and treated hot with 75 g. more of barium carbonate until effervescence ceases, when the solution is again filtered. The filtrate contains the neutral barium salt of the *m*-sulfonic acid and a little of the *para*. The former is quite soluble in water, the latter less so. Accordingly, following Van Duin, this filtrate is evaporated to 100 cc. and the salt of the *para* acid filtered off. Experiments with the pure salts have shown that the *para* is a little more soluble in hot water than in cold, but that its solubility is increased by the addition of hydrochloric acid. With the *meta* compound the reverse is the case. Hence, to the filtrate from the *para* salt is added 10 cc. of 6 *N* hydrochloric acid. This precipitates the acid barium salt of the *meta* acid, which is filtered off and, when washed essentially free from chloride,

⁸ See, for example, Valet [*Ann.*, **154**, 62 (1870)] for cinnamic acid; Credner (*Z. Chem.*, **77**, 1870), and Messel (*ibid.*, 459, 1870) for fumaric and maleic acids; Müller [*Ber.*, **6**, 1441 (1873)] for allyl alcohol and acrolein; and Heusler [*Ber.*, **24**, 1806 (1891)] for cinnamic aldehyde.

⁹ Moore, *THIS JOURNAL*, **25**, 622 (1903).

weighs about 17 g. It is pure after two crystallizations from water. The ratio of sulfur to barium in the product is 1.94:1. This does not prove the absence of the *para* isomer, but that is assured by the solubility relations described above.

Organic Salts of *m*-Sulfocinnamic Acid.—All organic salts described in this paper were prepared by the following method.

Two g. of acid barium sulfocinnamate (0.0068 mole) was dissolved in 25 cc. of water and to the solution was added 0.0034 mole of the neutral sulfate of the organic base (for example, aniline sulfate) dissolved in 10 cc. of hot water. After being filtered, the solution was concentrated to 10 cc. The crystals were then filtered off and recrystallized to maximum melting point. Since the melting points are high and the melting is frequently accompanied by decomposition, it was necessary to avoid long heating, preferably by a preheated bath. Short thermometers were used which had themselves been compared with instruments calibrated by the Bureau of Standards. To ascertain whether we had to do with neutral or acid salts, the molecular weight was determined by titration, for all the salts titrate smoothly with phenolphthalein as dibasic acids.

ACID ANILINE SALT.—This formed needles melting at 237–238°. It was prepared and analyzed by Moore and Thomas and its identity with a similar product from the Kafka synthesis established by mixed melting point. We have verified this result and also proved its identity with the product from *m*-bromocinnamic acid.

ACID *p*-TOLUIDINE SALT.—Crystals of this substance were obtained from alcohol; m. p., 227–230°. We have prepared this salt by sulfonation, by synthesis from *m*-bromocinnamic acid, and by double decomposition from a sample of the acid barium salt prepared by Miss Thomas through the Kafka synthesis, and we have established the identity of the three by mixed melting points.

Mol. wt. Subs., 0.2097, 0.2555: cc. of 0.04694 *N* NaOH, 26.62, 32.37. Calcd. for $C_9H_9O_5S.C_7H_9N$: mol. wt., 335.28. Found: 335.6, 336.4.

ACID (?) *o*-TOLUIDINE SALT.—Although especially purified *o*-toluidine was used in preparing this salt, it always separated as a paste. This was soluble in alcohol and acetone but insoluble in benzene, toluene and petroleum ether. We could not obtain crystals. This is in marked contrast with the behavior of the corresponding salt of *o*-sulfocinnamic acid.

ACID *p*-ANISIDINE SALT.—This was obtained as colorless plates from water; m. p., 238–239°. A mixed melting point identifies it with the salt prepared from *m*-bromocinnamic acid.

Anal. Subs., 0.2634, 0.2832: $BaSO_4$, 0.1712, 0.1853. Calcd. for $C_9H_9O_5S.C_7H_9ON$: S, 9.11. Found: 8.91, 8.98.

Mol. wt. Subs., 0.2024, 0.2775: cc. of 0.04694 *N* NaOH, 24.55, 33.80. Calcd. for $C_9H_9O_5S.C_7H_9ON$: mol. wt., 351.28. Found: 351.2, 349.8.

***p*-ANISIDINE SULFATE.**—We could find no record whether the compound formed when *p*-anisidine is treated with the half molecular quantity of sulfuric acid is the acid or neutral salt. We found it to be the neutral salt by titration.

Mol. wt. Subs., 0.2240: cc. of 0.04694 *N* NaOH, 28.22. Calcd. for $H_2SO_4.2C_7H_9ON$: mol. wt., 344.98. Found: 338.0.

Measurement of Possible *ortho* Sulfonation.—Standard solutions of *o*-, *m*- and *p*-hydroxybenzoic acids, each containing 0.002 g. of reagent per cc., were made up and it was found that 0.1, 0.2 and 0.3 cc. of the salicylic acid solution diluted to 10 cc. gave colors suitable for comparison when treated with 1 drop of ferric chloride solution. Other preliminary tests showed that the water in such mixtures could be largely substituted

by the solutions of *m*- and *p*-hydroxybenzoic acids without appreciably affecting the color produced, save that the addition of *m*-hydroxybenzoic acid made the color more permanent.

Measurements were then carried out as follows.

Five g. of the crude barium acid *m*-sulfocinnamate was oxidized by permanganate and the product fused with alkali, essentially in accordance with the directions given later in this paper for the preparation of salicylic acid from *o*-sulfocinnamic acid. The crude *m*-hydroxybenzoic acid thus obtained weighed 1.5275 g. It was dissolved in 40 cc. of water; hence, 1 cc. of the resulting solution contained 0.038919 g. of material. One cc. of this solution, plus 10 cc. of water, plus 1 drop of ferric chloride solution, gave a color which was darker than a mixture of 1 cc. of standard salicylic acid solution, plus 10 cc. of standard *m*-hydroxybenzoic acid solution, plus 1 cc. of standard *p*-hydroxybenzoic acid solution plus 1 drop of ferric chloride solution. This was, however, lighter than the color produced in a mixture in all respects similar, except that it contained 2 cc. of the standard salicylic acid solution. Hence, if the color were due to salicylic acid, its quantity was $(0.0003/0.03819) \times 100 = 0.8\%$ of the total hydroxy acid present. In other words, 0.8% of the crude barium acid sulfocinnamate was the *ortho* compound. Now the total yield of crude barium acid *m*-sulfocinnamate is only about 15% of the total theoretical sulfonation, and no other portions of the original reaction mixture yield a product giving an appreciable color with ferric chloride. This limits the total possible *ortho* sulfonation to about 0.2% of the whole. The color with ferric chloride may not be due to salicylic acid, but it is almost certainly not due to phenol, for when *m*- and *p*-sulfobenzoic acids are fused with alkali for four hours at 240°, nothing is formed which gives a color with ferric chloride, though phenol is formed at a higher temperature.

Sulfonation at High Temperature.—Fifty g. of cinnamic acid was added to 150 g. of fuming sulfuric acid (20% anhydride) at 90°. Solution required one hour and the liquid grew very dark in color. After cooling, seeding with *p*-sulfocinnamic acid gave no precipitate, so the solution was diluted to 1 liter and treated with barium carbonate, the filtrate from the precipitate formed being concentrated to 100 cc. and 100 cc. of 6 *N* hydrochloric acid added, but no barium salt of the *meta* acid separated. More hydrochloric acid, however, gave a precipitate consisting mostly of barium chloride. When this was removed and the filtrate further concentrated, there resulted a tarry material, acidic in nature, which was soluble in water and in alcohol. It was dissolved in dry alcohol and the solution treated with ammonia gas. The precipitate was washed with alcohol, dried and analyzed for nitrogen and sulfur. Their atomic ratio proved to be 3:1.92, corresponding to the neutral ammonium salt of a disulfocinnamic acid. Evaporation of the ammoniacal filtrate yielded a hard, resinous, neutral substance not further investigated. Two g. of the crude *para* salt was next subjected to oxidation and fusion with potassium hydroxide, but nothing was formed which gave a color with ferric chloride. Apparently, when cinnamic acid is sulfonated at high temperature, no *ortho* acid is formed, and the *meta* compound undergoes further sulfonation.

Preparation of Barium Acid *m*-Sulfocinnamate from *m*-Bromocinnamic Acid in a Single Operation.—Ten g. of *m*-bromocinnamic acid is dissolved in a boiling solution of 3.7 g. of sodium bicarbonate in 25 cc. of water; 5.8 g. of 92% sodium bisulfite is added and the mixture refluxed until a sample gives no precipitate when acidified (about four hours). Seven g. of 95% sodium sulfite and 0.5 g. of copper sulfate are next added, and the whole is heated in a sealed tube at 175° for 45 hours. After removing the red precipitate containing copper,¹⁰ the colorless filtrate is treated with 5 g. of barium hy-

¹⁰ Such a precipitate always forms in the Rosenmund reaction. It is probably the "cupro-cupri salt" described in Gmelin-Kraut's "Handbuch," 7th ed., 1909, vol. 5, p. 825.

droxide which removes all sulfate ion and the excess of sulfite. To the filtrate 15 g. more of barium hydroxide is added, the solution is concentrated to 20 cc. and refluxed until no more barium sulfite precipitates (about two hours). In order to prevent serious bumping it is necessary to filter off the barium sulfite from time to time as it forms. The filtrate is then cooled in a freezing mixture, when most of the unchanged barium hydroxide crystallizes. The filtrate from this is saturated with carbon dioxide and again filtered. The filtrate, now free from barium, is then acidified with 6 *N* hydrochloric acid and a 10cc. excess added. This precipitates about 0.05 g. of unchanged *m*-bromocinnamic acid which is removed by ether. The aqueous layer (about 100 cc.) is heated to boiling and treated with 6 g. of barium chloride in 25 cc. of water. On cooling, a precipitate of barium acid *m*-sulfocinnamate forms which is recrystallized from water. It weighs 5-7 g.

Anal. Subs., 0.2614, 0.2783: BaSO₄ (formed in Carius tube), 0.0976, 0.1049; BaSO₃ (precipitated outside), 0.1015, 0.1075. Calcd. for (C₉H₇O₅S)₂Ba·3H₂O: Ba, 22.20; S, 10.34. Found: Ba, 22.20, 22.15; S, 10.42, 10.43.

The Chlorides and Amides.—When a salt of *m*-sulfocinnamic acid is treated with an excess of phosphorus pentachloride in the usual way, the crude product obtained is a mixture of mono- and dichloride, the latter compound obviously having one chlorine atom extremely sensitive to water. From this crude product, benzene extracts a crystalline compound melting sharply at 168-169°, which is probably the monochloride; but it has not yet been analyzed. The sulfonation acid yields a chloride of the same melting point.

Palmer⁵ describes the preparation of considerable quantities of the diamide by treating what he presumed to be the dichloride with ammonium hydroxide, but since he neither analyzed nor characterized either compound, it is unlikely that he had a homogeneous material in hand. Moore and Thomas¹¹ also attempted the preparation of the amide in the same way, but obtained in small yield a material which they could not bring to constant melting point. Hence we believe that all structural arguments based upon the behavior of the supposed diamide are untrustworthy.

Organic Salts.—The aniline, *o*-toluidine, *p*-toluidine and *p*-anisidine acid salts of the synthetic *m*-sulfocinnamic acid were prepared as already described for those of the acid of sulfonation and found to be identical.

Synthesis of the True *o*-Sulfocinnamic Acid.—The starting point was the purest *o*-bromotoluene.¹² This was transformed to *o*-bromobenzaldehyde by the Etard reaction¹³ (caution against unexpected explosions!!) and the latter to *o*-bromocinnamic acid by the Perkin synthesis. This method of preparation seems to have been nowhere described, but it proceeds smoothly. The aldehyde is, however, very sensitive to oxygen, so that it is advisable to work in a current of carbon dioxide. The crude product can be conveniently freed from tarry matter by solution in sodium

¹¹ Unpublished notes.

¹² Louguinine, *Ber.*, **4**, 514 (1871).

¹³ Stuart and Elliott, *J. Chem. Soc.*, **53**, 140, 804 (1888).

bicarbonate, extraction of the tar by ether and reprecipitation by acid. The product so obtained is sufficiently pure for use in the next step of the synthesis.

Preparation of Barium Acid *o*-Sulfocinnamate from *o*-Bromocinnamic Acid.—The reactions proceed as in the case of the *meta* compounds, but it is more difficult to separate the product from sodium bromide. We isolate the former as the sodium-barium double salt.

Ten g. of *o*-bromocinnamic acid and 6.22 g. of sodium bisulfite are dissolved in a solution of 3.7 g. of sodium bicarbonate in 40 cc. of water, refluxed for two hours until a clear solution results, and only a slight precipitate forms when a sample is acidified. Then 7.3 g. of anhydrous sodium sulfite and 0.8 g. of copper sulfate are added, and the whole is heated in a sealed tube at 170° for 40 hours. The filtered solution is diluted to 100 cc., 40 g. of barium hydroxide octahydrate is added, the precipitated barium sulfate and sulfite are filtered off, and the filtrate is refluxed for ten hours or until no further precipitate forms. The final filtrate (which should still contain barium hydroxide) is concentrated to about 25 cc. and allowed to cool, when the crude sodium-barium double salt of *o*-sulfocinnamic acid crystallizes. This weighs about 6 g. and is too soluble in water for economical purification. Its chemical composition is apparent from the following analysis of a sample now known to have contained barium carbonate.

Anal. Calcd. for $(C_9H_7O_6SNa)_2Ba$: Ba, 21.60; S, 10.05; Na, 7.23. Found: Ba, 28.90; S, 9.16; Na, 7.62; Br, 0.67.

When this material is dissolved in water and the calculated quantity of hydrochloric acid added, long prisms of barium acid *o*-sulfocinnamate separate upon slow evaporation. These contain water which is lost at 120°, but its quantity has not yet been determined. The salt is more soluble than its *meta* or *para* isomers and can only be crystallized with loss, but it was selected as the most appropriate member of the group for complete analysis. The requisite purification involved, however, a curious difficulty. In spite of the far greater solubility of the free acid, the latter is carried down by the salt and obstinately retained. The amount of acid so held could be determined by titration, and when the appropriate quantity of barium hydroxide was added and the whole crystallized, a definite chemical individual was obtained.

Anal. Subs. (dried at 120°), 0.1696, 0.1640: CO₂, 0.2273, 0.2192; H₂O, 0.0395, 0.0381. Subs., 0.3526, 0.2362: BaSO₄ (formed in tube), 0.1368, 0.0924; BaSO₄ (precipitated outside), 0.1382, 0.0934. Calcd. for $(C_9H_7O_6S)_2Ba$: C, 36.51; H, 2.37; S, 10.83; Ba, 23.21. Found: C, 36.55, 36.45; H, 2.61, 2.59;¹⁴ S, 10.71, 10.81; Ba, 22.83, 23.02.

Mol. wt. Subs., 0.1927: cc. of 0.04694 *N* NaOH, 13.88. Calcd. for $(C_9H_7O_6S)_2Ba$: mol. wt., 591.68. Found: 591.4.

Organic Salts

ACID ANILINE SALT.—This formed colorless plates from water; m. p., 208–209°. A mixture with the aniline salt of *m*-sulfocinnamic acid melted at 199–202°.

Mol. wt. Subs., 0.1041: cc. of 0.04694 *N* NaOH, 15.95. Calcd. for $C_9H_8O_6S \cdot C_6H_7N$: mol. wt., 321.2. Found: 318.

ACID *p*-TOLUIDINE SALT.—This gave fine, colorless needles from water, melting at 225–227° with evolution of water vapor.

¹⁴ The hydrogen values in the above analysis contain a correction for the hydrogen content of the (electrolytic) oxygen employed, specially determined in a known volume. The uncorrected values are 2.95 and 2.94.

Mol. wt. Subs., 0.2077: cc. of 0.04694 *N* NaOH, 24.90. Calcd. for $C_9H_8O_6S$.- $C_7H_7N.H_2O$: mol. wt., 353.28. Found: 355.8.

ACID *o*-TOLUIDINE SALT.—This formed colorless plates from water, melting at 234–235° with evolution of gas. The *o*-toluidine salt of the *meta* acid is a paste.

Mol. wt. Subs., 0.2284, 0.1202: cc. of 0.04694 *N* NaOH, 28.85, 15.28. Calcd. for $C_9H_8O_6S.C_7H_7N$: mol. wt., 335.28. Found: 337.4, 335.2.

ACID *p*-ANISIDINE SALT.—These fine, colorless needles from water melted at 226–228° and turned pink in the air. A mixture with the corresponding salt of *m*-sulfocinnamic acid melted at 205–207°.

Mol. wt. Subs., 0.2202, 0.1554: cc. of 0.04694 *N* NaOH, 26.74, 18.86. Calcd. for $C_9H_8O_6S.C_7H_7ON$: mol. wt., 351.28. Found: 350.6, 351.

The Free Acid.—This may be readily obtained from the acid barium salt by the action of sulfuric acid or by the hydrolysis of the chloride. On slow evaporation of its aqueous solution it separates in long needles very soluble in water. These retain their water of crystallization even after long heating at 120°. If even the purest samples of the acid be moistened with aqueous hydrochloric acid and warmed, blackening occurs at or below 100°.

Mol. wt. Subs. (air dried), 0.2700, 0.3351; (dried at 120°), 0.3561: cc. of 0.04694 *N* NaOH, 44.63, 55.22, 58.03. Calcd. for $C_9H_8O_6S.2H_2O$: mol. wt., 264.19. Found: 258.0, 258.4, 261.4.

THE MONOCHLORIDE.—Two g. of the sodium-barium double salt was transformed to the sodium salt by the action of sodium carbonate, the latter was thoroughly dried and ground up with 2 g. of phosphorus pentachloride, and the whole heated at 120° for one-half hour. After cooling, the mixture was stirred into ice water when a colorless, crumbly mass separated which was filtered off and dried. The yield and the quality of product obtained in this way have proved extremely uneven, depending apparently upon the purity of the sodium-barium salt employed. The pure substance is insoluble in carbon tetrachloride, petroleum ether or benzene, but dissolves in ether, acetone, chloroform and ethyl acetate. It is best crystallized from hot bromobenzene, from which it separates in shining plates melting at 179–182°. The compound is stable toward cold water.

Anal. Subs., 0.2081: AgCl, 0.1274; BaSO₄, 0.1934. Calcd. for $C_9H_7O_6S.Cl$: Cl, 14.42; S, 13.00; for $C_9H_8O_6S.Cl_2$: Cl, 26.80; S, 12.08. Found: Cl, 15.05; S, 12.77.

Transformation to Salicylic Acid.—Four g. of barium acid *o*-sulfocinnamate was dissolved in 50 cc. of water and treated with 4 g. of potassium carbonate. After filtering from barium carbonate, 7 g. of potassium permanganate was added and the mixture kept for one hour upon a boiling water-bath. After adding alcohol to reduce the excess of permanganate, the manganese dioxide was filtered off and the filtrate evaporated. The dried residue was then stirred into 25 g. of molten potassium hydroxide in a nickel crucible and held at 190–210° for one-half hour. The cold melt was extracted with water, the solution acidified with sulfuric acid, boiled to expel sulfur dioxide and extracted with ether. On slow evaporation, needles separated from the ether extract. These sublimed without decomposition, gave an intense color with ferric chloride and melted at 158°. When mixed with pure salicylic acid from another source, the melting point was not depressed.

We desire to express our hearty thanks for valuable preliminary studies made in this Laboratory by Dr. H. A. Bruson, Mr. J. H. Fielding and Miss Dorothy M. Stevens.

Summary

1. The secondary product in the sulfonation of cinnamic acid has again been shown to be *m*-sulfo-cinnamic acid by its preparation from *m*-bromo-cinnamic acid, the identity of the products being established by the identity of numerous derivatives.
2. The true *o*-sulfo-cinnamic acid has been prepared (for the first time) and its difference from the foregoing compound completely demonstrated.
3. The addition of sodium bisulfite to the double bond has been shown to be a general reaction of cinnamic acid derivatives.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE STRUCTURE OF HYDROXY-UREAS AND OF CARBAMAZIDES

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It is recognized that most azides of carboxylic acids eliminate nitrogen and rearrange to isocyanates or related compounds under the influence of heat. Carbamazide, $\text{NH}_2\text{—CO—N}_3$, is an outstanding exception. This compound decomposes, to be sure, with the elimination of nitrogen when it is heated alone or when it is heated in such solvents as toluene, xylene or ethyl malonate, but hydrazine or its derivatives have never been found as products of such decompositions. Since the mechanism of the rearrangement of azides (RCON_3) to isocyanates is considered to proceed through an intermediate, hypothetical univalent nitrogen derivative, $[\text{R—CO—N=}]$, Curtius¹ calls $[\text{NH}_2\text{—CO—N=}]$ a "rigid residue." Such an expression is purely descriptive; it would be much more interesting to learn why the residue is rigid. The azide of phenyl-carbamic acid, $\text{C}_6\text{H}_5\text{NH—CO—N}_3$, behaves similarly.² It is peculiarly inert towards boiling water or boiling alcohol. Heating under pressure with these solvents induces hydrolysis and alcoholysis, but never rearrangement.

These non-rearrangements are mysterious, inasmuch as diphenyl carbamazide does rearrange³ with the production of carbonyl diphenylhydrazine, or of compounds which are related to it. Thus, $(\text{C}_6\text{H}_5)_2\text{N—CON}_3 \longrightarrow (\text{C}_6\text{H}_5)_2\text{N—NCO} + \text{N}_2$. There is nothing implied in the formula of the residue, $[(\text{C}_6\text{H}_5)_2\text{N—CO—N=}]$, to explain why it also should not be a "rigid residue."

The cases of hydroxy-urea and of phenylhydroxy-urea, $\text{C}_6\text{H}_5\text{NH—CO—}$

¹ Curtius and Schmidt, *J. prakt. Chem.*, **105**, 177 (1923). Curtius, *Ber.*, **56**, 1577 (1923).

² Curtius and Hofmann, *J. prakt. Chem.*, [2] **53**, 530 (1896). Curtius and Burkhardt, *ibid.*, **58**, 205 (1898).

³ Stolle, *Ber.*, **57**, 1063 (1924).