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### Arylsulfimide Polymers. I. The Synthesis of *m*-Bisaccharin and Derivatives

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## Arylsulfimide Polymers. I. The Synthesis of *m*-Bisaccharin and Derivatives<sup>†</sup>

G. F. D'ALELIO, D. M. FEIGL, W. A. FESSLER, Y. GIZA, and A. CHANG

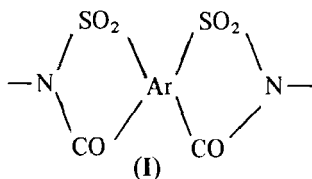
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Notre Dame, Indiana*

### SUMMARY

*m*-Bisaccharin and a number of its derivatives have been synthesized. Structural assignments were based on elemental and infrared analyses and, where appropriate, neutralization equivalents and thermal gravimetric analysis.

### INTRODUCTION

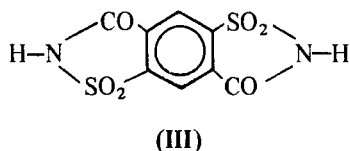
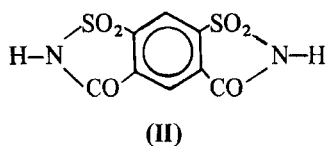
In the course of our investigation of thermally stable polymers, we became interested in the properties of polymers incorporating the benzosulfonimide group, including those possessing the following repeating unit (I).



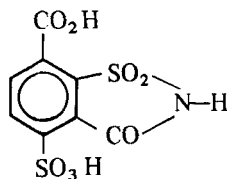
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<sup>†</sup>Taken in part from the Ph.D. dissertation of W. A. Fessler.

Monomers which would be suitable for generating this unit include 2H,6H-benzo[2,1-d, 4,5-d']-diisothiazole-1,1,7,7-tetroxide-3,5-dione (**II**) and the [2,1-d, 5,4-d']-isomer (**III**).



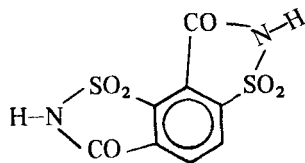
For the sake of simplicity, these two compounds are referred to as *m*-bisaccharin (**II**) and *iso-m*-bisaccharin (**III**). In both of these bisaccharins, a sulfonic and carboxylic acid are paired in ortho dispositions and these pairs are separated by nonfunctionalized positions. This latter requirement assures that by-products of the type shown below (**IV**) will not interfere with the desired polymerization reaction.



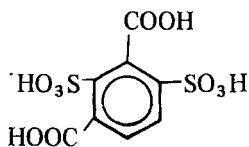
In addition to the bisaccharins, the corresponding tetraacids, acid anhydrides, and ester and amide derivatives were considered to be suitable monomers or intermediates.

There have been a number of reports of the synthesis of bisaccharins. Holleman and Choufoer [2, 3] claimed to have isolated compounds (**II**), and (**III**) from the oxidation of the corresponding xylenedisulfonamides. However, these authors [4] later reported that only one of the methyl groups had been oxidized and the products isolated were actually methyldisulfamidobenzoic acids. Further attempts by the authors to prepare the bisaccharins were unsuccessful.

Wischin [1] reported the preparation of both bisaccharin (**V**) and the tetracid (**VI**).

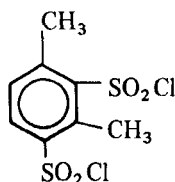


(V)

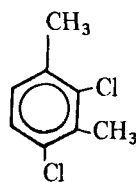


(VI)

His structural assignment was made on the basis of the conversion of a precursor of (V), an *m*-xylenedisulfonyl chloride (assigned structure VII) to the known compound [5], 2,4-dichloro-*m*-xylene (VIII).

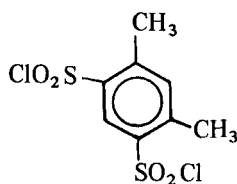


(VII)



(VIII)

However, Holleman and Choufoer [4] found that Wischin's compound (VII) was identical to the compound that these authors identified as *m*-xylene-4,6-disulfonyl chloride (IX), and they concluded that the vigorous conditions employed by Wischin



(IX)

in converting (VII) to (VIII) had caused a rearrangement of the functional groups. It was also suggested by Holleman and Choufoer that the oxidation product, identified as bisaccharin (V) by Wischin, was in fact an unresolved mixture of *m*-xylene-4,6-disulfonamide and 3-methyl-4,6-disulfamidobenzoic acid, which these authors also obtained.

Wischin [1] also prepared the tetraacid, which he identified as 2,4-dicarboxylbenzene-1,3-disulfonic acid (X), by the permanganate oxidation of the sodium salt (XI) of *m*-xylene-2,4-disulfonic acid. However, the evidence of Holleman and Choufoer also suggests that the structural assignment of this acid should be changed to 2,4-dicarboxylbenzene-1,5-disulfonic acid. It is somewhat disconcerting, therefore, that the identical acid salt mentioned above (XI) was prepared by Wischin through an independent route involving the disulfonation and debromination of 4-bromo-*m*-xylene. There is no apparent explanation for this anomaly. The melting point of the Wischin tetraacid (X) is different from that of the acid reported in the present paper.

In summary, it appears that heretofore none of the desired monomers has been synthesized.

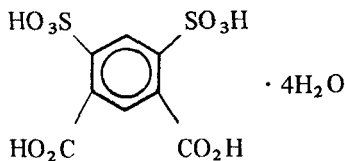
## DISCUSSION

The disulfonation of *p*-xylene gives only low yields of *p*-xylene-2,5-disulfonic acid. Since this acid is the precursor of iso-*m*-bisaccharin (III), we decided to undertake the synthesis of *m*-bisaccharin (II) from the more readily available *m*-xylene-4,6-disulfonic acid.

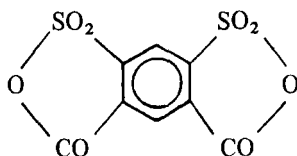
According to the procedure of Holleman and Choufoer [4], *m*-xylene-4,6-disulfonamide was prepared from *m*-xylene via the disulfonyl chloride. Oxidation of the disulfonamide was carried out using potassium dichromate and sulfuric acid in place of the permanganate reagent used by Holleman and Choufoer in their attempts to oxidize the compound. The success of this procedure depended on careful control of reaction temperature. If the reaction was carried out at too low a temperature, oxidation was incomplete. If the reaction was allowed to proceed without cooling, a violent reaction occurred and carbon dioxide was detected as a by-product. Therefore, the reaction flask was immersed in a large, thermostated water bath, through which the heat of reaction could be efficiently dissipated without causing a concomitant incomplete oxidation. An 84% yield of recrystallized product was obtained, mp 405–410°C (with decomposition, by differential thermal analysis). The elemental analysis, infrared spectrum, and neutralization equivalent of the product indicated that both methyl groups had been oxidized and that the accompanying ring closure had given the desired *m*-bisaccharin (II).

*m*-Bisaccharin could be hydrolyzed by heating the compound in a mixture of hydrochloric and nitric acids. On the basis of the elemental

analysis, thermogravimetric analysis, infrared spectrum, and neutralization equivalent, the product of this hydrolysis was identified as the tetrahydrate of 1,3-dicarboxylbenzene-4,6-disulfonic acid (*m*-tetraacid **XII**). Attempts to obtain the anhydrous acid by repeated treatment of the tetrahydrate with acetic anhydride were not successful. The melting point of *m*-tetraacid, 110-112°C, indicates that this product is not the same acid (mp 250°C) obtained by Wischin.



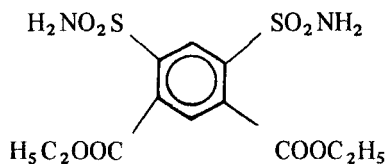
(XII)



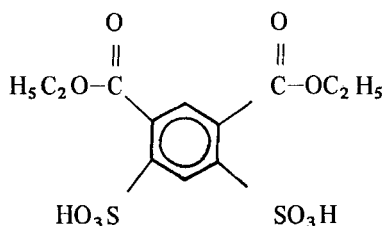
(XIII)

Treatment of *m*-tetraacid with acetyl chloride gave benzo[1,2-*c*, 5,4-*c'*]-1,2,6,7-diisooxathiole-1,1,7,7-tetroxide-3,5-dione (*m*-bianhydride, **XIII**). The compound is extremely hygroscopic and is rapidly converted to *m*-tetraacid on exposure to the atmosphere. However, with suitable protection, *m*-bianhydride could be recrystallized from dry benzene to give white needles melting at 265-267°C. A second method for purifying the bianhydride was more involved but yielded a purer product. In this procedure, the crude bianhydride, dissolved in acetic anhydride, was treated with chlorosulfonic acid and allowed to crystallize from the reaction medium. The material thus obtained melted at 268°C. Carefully protected samples of *m*-bianhydride were subjected to elemental analysis, infrared analysis, and titration with sodium hydroxide. In all instances the assigned bianhydride structure was confirmed.

*m*-Bisaccharin was solvolyzed in ethanol saturated with hydrogen chloride to give diethyl 4,6-disulfamidoisophthalate (**XIV**), mp 230-232°C. The elemental and infrared analysis of the product confirmed the structural assignment.

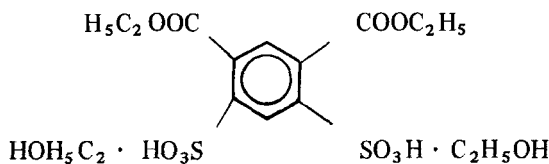


(XIV)



(XV)

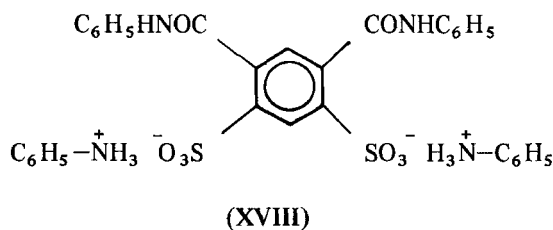
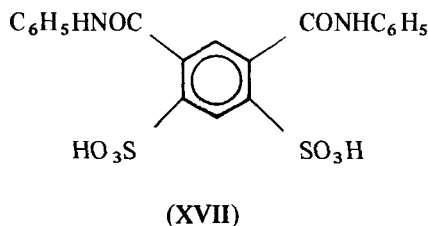
1,3-Dicarboethoxybenzene-4,6-disulfonic acid (XV) was prepared from *m*-bianhydride and absolute ethanol. The product initially isolated from this reaction was identified by its elemental analysis and neutralization equivalent as the solvated ester (XVI). The solvent molecules were removed by drying this intermediate at reduced pressure for a prolonged period. Ester (XV) is extremely hygroscopic and melted over a broad range, 188-202°C, with decomposition even when the sample was protected by a nitrogen atmosphere. The elemental analysis, neutralization equivalent, and infrared spectrum of this product were in agreement with the assigned structure.



(XVI)

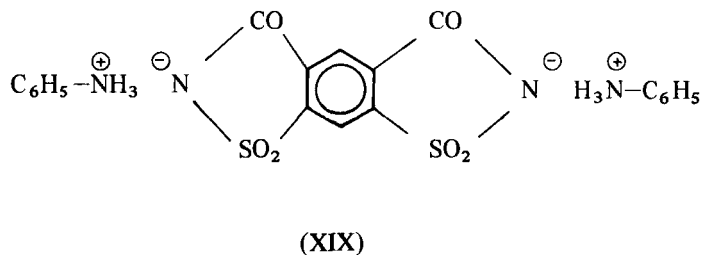
The reactions of *m*-bianhydride with two moles of aniline under a variety of solvent conditions and concentrations failed to yield,

unequivocally, pure 1,3-dicarbanilidobenzene-4,6-disulfonic acid (XVII), but gave instead mixtures of compound (XVII) with anilinium salts. Therefore, *m*-bianhydride was treated with an excess of aniline and from this reaction, dianilinium 1,3-dicarbanilidobenzene-4,6-disulfonate (XVIII) was isolated, mp 298-300°C. The corresponding disodium salt was prepared by treating compound (XVIII) with sodium hydroxide solution.

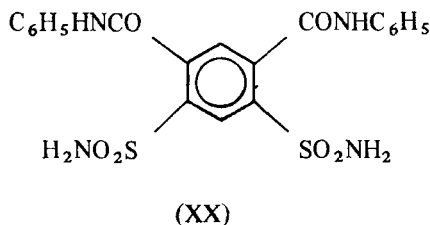


*m*-Bisaccharin, *m*-tetraacid, *m*-bianhydride, and ester (XIV) have all been used in conjunction with polyfunctional amines to prepare arylsulfimide polymers which will be described in future publications.

The dianilinium salt (XIX, mp 215-217°C) precipitated from both water and benzene-ethanol solutions of bisaccharin and aniline. When bisaccharin was treated with aniline under more rigorous conditions, the product isolated was 1,3-dicarbanilidobenzene-4,6-disulfonamide (XX), mp 245-247°C.







## EXPERIMENTAL

### **m-Xylene-4,6-Disulfonamide**

m-Xylene-4,6-disulfonamide was prepared from m-xylene according to the procedure of Holleman and Choufoer [4].

### **m-Xylene-4,6-Disulfonyl Chloride (IX)**

The yield of recrystallized m-xylene-4,6-disulfonyl chloride obtained from 50 g (0.47 moles) of m-xylene and 400 ml of chlorosulfonic acid was 97% of theory. The melting point was 120-122°C (lit. [4] 129°C).

### **m-Xylene-4,6-Disulfonamide**

Treatment of 140.0 g of m-xylene-4,6-disulfonyl chloride in 1 liter of benzene with 600 ml of 5 N alcoholic ammonia solution gave the sulfonamide, which was recrystallized from 10% ethanol-90% water. The yield of recrystallized product was 76% of theory, mp 255-258°C (lit. [4] 249°C). The infrared spectrum of this product showed the absorption characteristics of the  $\text{SO}_2\text{NH}_2$  groups at 7.6  $\mu$  and  $\text{SO}_2\text{-N}$  at 8.6  $\mu$ . About 10 g of an insoluble residue (mp 275-280°C) were isolated during the recrystallization procedure. The by-product is probably a sulfone formed during the reaction.

### **m-Bisaccharin (II)**

Sodium dichromate (25.0 g) was added to a cold mixture of 21.0 g of water and 57.6 g of sulfuric acid (specific gravity 1.84) in a 2-liter, three-necked, round-bottom flask equipped with a mechanical stirrer and a condenser. After the ingredients were mixed, the flask was placed in a thermostatically controlled bath maintained at 54°C, and the contents were stirred for 2-3 min. m-Xylene-4,6-disulfonamide (11.0 g, 0.0415 mole) was added

very slowly while the mixture was stirred vigorously. After 1-2 min, 102.0 g of sulfuric acid (specific gravity 1.84) were added slowly to the mixture from a dropping funnel. The reaction started immediately and proceeded smoothly. Stirring was continued for 30 min and the brown-red color of the solution turned green. The mixture was then poured onto crushed ice. A white product precipitated and was separated by filtration. This material was dissolved in aqueous sodium carbonate solution and precipitated by the addition of sulfuric acid. This procedure was repeated once, and the isolated product was recrystallized from distilled water, then dried and weighed. The yield of the recrystallized product was 84% of theory, mp 405-410°C (with decomposition) by differential thermal analysis.

The infrared spectrum showed the absorption characteristics of N-H at 3.4  $\mu$ , SO<sub>2</sub>-N at 8.4  $\mu$ , and carbonyl groups at 5.9  $\mu$ . m-Bisaccharin was dissolved in water and titrated with standard sodium hydroxide solution using a Beckman pH meter. The acid number was 1.98 (calculated value, 2.0).

Anal: Calculated for C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 33.30; H, 1.40; N, 9.70; S, 22.20. Found: C, 33.16; H, 1.41; N, 9.75; S, 22.14.

### m-Tetraacid (XII)

m-Bisaccharin (6.05 g, 0.021 mole) was mixed with 52.5 ml of 12 N hydrochloric acid in a three-neck, round-bottom flask equipped with a mechanical stirrer, a condenser, and a thermometer. The mixture was heated to 60-65°C and maintained at that temperature for 30 min. Foaming and evolution of gases were observed. From a dropping funnel, 5.6 ml of nitric acid (90%) were slowly added to the mixture. After the addition was completed, the mixture was heated to 90-95°C and maintained at that temperature for 4 hr. After 3 hr of heating, the solution became clear. The solution was filtered, and the clear filtrate was evaporated at reduced pressure until it appeared completely free from fumes. The residue was dried in a vacuum over for 15 hr, and the resulting viscous mass was then cooled to give a white solid. The yield of crude material was 97% of theory (on the basis of tetrahydrate). The crude m-tetraacid was kept over phosphorus pentoxide in a vacuum desiccator for 15 days to remove any free moisture present. The melting point of the dried tetraacid was 110-112°C. The tetraacid was subjected to thermogravimetric analysis (heating rate of 2°C/min), which indicated a loss of four molecules of water per molecule of acid up to 125°C. The tetrahydrate was dissolved in acetic anhydride at 75°C, and the solvent was then removed under reduced pressure. The product isolated after several repetitions of this

procedure was identical to the product identified as the tetrahydrate. The infrared spectrum of the tetraacid (KBr disk) showed distinct absorptions for COOH at  $6.1 \mu$  and for  $\text{SO}_3\text{H}$  at  $8.1 \mu$  and  $9.4 \mu$ . Titration of tetraacid with standard sodium hydroxide using a Beckman pH meter gave a value of 4.08 for the acid number (based on tetrahydrate, calculated value, 4.0).

Anal: Calculated for  $\text{C}_8\text{H}_6\text{O}_{10}\text{S}_2 \cdot 4\text{H}_2\text{O}$ : C, 24.15; H, 3.52; S, 16.10. Found: C, 24.47; H, 3.52; S, 16.31.

### m-Bianhydride (XIII)

m-Tetraacid (5.0 g, 0.0152 mole) was treated with 25 ml (26.5 g, 0.34 mole) of acetyl chloride and heated under reflux for 5 hr in a round-bottom flask equipped with a condenser and a calcium chloride drying tube. Foaming was observed during the initial stages of the reaction. After the reaction was completed, the solids were removed by filtration and recrystallized from benzene (dried over sodium) avoiding exposure to atmosphere as far as possible. Needle-shaped white crystals, melting at  $265\text{-}267^\circ\text{C}$ , were obtained. The filtrate was distilled under reduced pressure, and a dark-brown semisolid residue was obtained. This material was recrystallized in the same manner, and a small additional portion of m-bianhydride was recovered. The yield of m-bianhydride was 80% of theory.

A better method of purifying the crude bianhydride was used for some samples. The crude m-bianhydride (7.3 g) was dissolved in 30 ml of warm ( $60^\circ\text{C}$ ) acetic anhydride and cooled to room temperature. To this cooled solution were added dropwise 1.5 ml of chlorosulfonic acid. Some crystals appeared after the addition of chlorosulfonic acid. The solution was allowed to stand at room temperature for 2 hr and then in a refrigerator overnight, after which the shining white crystals (4.0 g) were removed by filtration. This product melted at  $268^\circ\text{C}$ .

The m-bianhydride is unstable, and, when exposed to air, it readily absorbs moisture and is converted to m-tetraacid. Samples were stored in vacuum desiccators over phosphorus pentoxide. An analytical sample of m-bianhydride was prepared in the following way. A portion of m-bianhydride prepared in the usual way was again treated with excess of fresh acetyl chloride and heated under reflux for 5-6 hr. The solids were filtered and placed immediately in an Abderhalden drying pistol. After drying for 5-6 hr under reduced pressure, a portion of the solid was immediately sealed in an ampoule under high vacuum and sent for analysis.

Another portion was immediately titrated with standard sodium hydroxide solution. The neutralization equivalent thus determined was 73.3 g equivalent (calculated value, 72.5). This corresponds to an acid number of 3.96 compared with the value of 4.0 calculated for the conversion of the bianhydride to the tetrasodium salt of the tetraacid. The infrared spectrum was also immediately recorded and showed a distinct doublet at about  $5.5 \mu$  characteristic of the anhydride carbonyl group and no absorption at  $6.0 \mu$  (carboxyl carbonyl group).

Anal: Calculated for  $C_8 H_2 O_8 S_2$ : C, 33.05; H, 0.69; S, 22.01. Found: C, 33.16; H, 0.95; S, 21.64.

#### Diethyl 4,6-Disulfamidoisophthalate (XIV)

m-Bisaccharin (5.0 g) was suspended in 130 ml of absolute ethanol, and the mixture was saturated with hydrogen chloride at  $5^\circ C$ . The solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was purified by washing with water to remove any m-bisaccharin present and finally by recrystallization from absolute ethanol. The ester is soluble in ethanol and insoluble in water. The melting point of the ester was  $230-232^\circ C$ . The yield was 86% of theory. The infrared spectrum showed the characteristic absorptions for  $SO_2 NH_2$  at  $7.5 \mu$  and  $8.6 \mu$  and for ester carbonyl at  $5.9 \mu$ .

Anal: Calculated for  $C_{12} H_{16} N_2 O_8 S_2$ : C, 37.90; H, 4.21; N, 7.36; S, 16.83. Found: C, 37.27; H, 4.08; N, 7.90; S, 17.23.

#### 1,3-Dicarboethoxybenzene-4,6-Disulfonic Acid (XV)

m-Bianhydride (4.35 g, 0.015 mole) and 126.28 g (160 ml, 2.745 moles) of absolute ethanol were placed in a 250-ml, three-neck, round-bottom flask equipped with a thermometer, heating mantle, reflux condenser, and magnetic stirrer. The mixture was refluxed under a dry nitrogen atmosphere at  $80^\circ$  for 1 hr, after which the excess ethanol was removed by evaporation without heating at 1- to 2-mm pressure, yielding a viscous hygroscopic oil which, when dried further at room temperature for 24 hr at 1- to 2-mm pressure, became a semisolid, hygroscopic glass (A).

The product was then dried further at  $60^\circ C$ , at 1-mm pressure for 6 days, yielding a white solid (B) which was highly hygroscopic and which melted in a dry nitrogen atmosphere over the range of  $188-202^\circ C$  with decomposition. The infrared spectrum of (B) showed the presence of strong ester carbonyl peaks at  $5.78-5.82 \mu$ , sulfonic acid peaks at 7.69, 8.70, and  $9.71 \mu$ , and hydroxyl peaks at  $3.4-3.5 \mu$ . The acid numbers of

(A) and (B) were determined by dissolving the products in standardized sodium hydroxide and back-titrating with standardized hydrochloric acid. The acid number of (B) was 1.98, in accordance with structure (XV). The acid number of (A) was 1.96 on the basis of structure (XVI), as compared with a value of 1.71 for (A) based on structure (XV). The elemental analyses supported the assignment of structure (XV) to compound (B) and structure (XVI) to compound (A).

Anal: Calculated for  $C_{16}H_{26}O_{12}S_2$  (XVI): C, 40.51; H, 5.48; S, 13.50. Found for (A): C, 41.24; H, 5.56; S, 13.73. Calculated for  $C_{12}H_{14}O_{10}S_2$  (XV): C, 37.70; H, 3.66; S, 16.75. Found for (B): C, 38.36; H, 3.71; S, 16.68.

#### Dianilinium 1,3-Dicarbanilidobenzene-4,6-Disulfonate (XVIII)

m-Bianhydride (2.75 g, 0.00945 mole) was added to 150 ml of dry benzene, and the mixture was heated to reflux. Aniline (3.566 g, 0.0382 mole) in 15 ml of benzene was added slowly to the refluxing solution, over a period of 15 min. Heating was continued for 1 hr, the mixture allowed to cool to room temperature, and the white solid isolated by filtration and dried, yielding 6.25 g of crude products, mp 187-190°C; recrystallized from water, mp 298-300°C. The infrared spectrum showed the characteristic absorption for CONH at 6.2 and 3.4  $\mu$ . The neutralization equivalent was determined using standardized sodium hydroxide which was back-titrated with standardized hydrochloric acid. The acid number thus determined was 1.96 (calculated value, 2.0).

Anal: Calculated for  $C_{32}H_{30}N_4O_8S_2$ : C, 58.02; H, 4.54; N, 8.46; S, 9.66. Found: C, 57.62; H, 5.01; N, 8.38; S, 9.65.

#### Disodium 1,3-Dicarbanilidobenzene-4,6-Disulfonate

The sodium salt of the bis-hemiamic acid was prepared by adding the equivalent amount of sodium hydroxide as a 10% aqueous solution to the anilinium salt (XVIII). The resulting clear solution was concentrated at 5-mm pressure at 50°C to remove water and aniline and yield the product, which was very soluble in cold water and insoluble in acetone and alcohol.

#### Dianilinium m-Bisaccharinate (XIX)

**In Water.** m-Bisaccharin (1.44 g, 0.005 mole) was dissolved in 50 ml of water. To this stirred solution was added dropwise, under a nitrogen atmosphere, 0.95 g (0.01 mole) of distilled aniline. The mixture was then stored

in a refrigerator for 3 days. A precipitate formed which was removed by filtration, and there was obtained about 0.6 g of glistening needle-crystals (30% yield). The product could be recrystallized from 100% alcohol and from water, mp 210-213°C. When the reaction mixture was allowed to stand in the refrigerator for 6 days, a 55% yield of the product was obtained. The infrared spectrum showed C=O absorption at 6.1  $\mu$  and  $C_6H_5NH_3^+$  absorption at 3.85  $\mu$ .

When 0.57 g of the dianilinium salt in 15 ml of water was treated with 5 ml of concentrated hydrochloric acid, there was obtained 0.23 g of a shiny white solid. Its infrared spectrum was identical with that of m-bisaccharin.

**In Benzene-Alcohol Mixture.** m-Bisaccharin (2.88 g, 0.01 mole) was dissolved in 120 ml of benzene-ethanol (1:1), and 1.86 g of distilled aniline was added dropwise to the solution with stirring. The stirring was continued for 30 min at room temperature under a nitrogen atmosphere. The reaction mixture became milky and was placed in a refrigerator overnight. A white solid which separated was removed by filtration. There were obtained 3.5 g (74%) of crude product (mp 210-215°C). The product was recrystallized from water (mp 215-217°C). Its infrared spectrum showed  $C_6H_5NH_3^+$  absorption at 3.82, amide carbonyl (amide I band) at 6.06  $\mu$ , amide III band at 7.81  $\mu$ , and  $SO_2N$  absorptions at 7.41 and 8.55  $\mu$ .

Differential thermal analysis of dianilinium m-bisaccharinate showed a sharp endotherm at 222°C, but there was no second sharp endo- or exotherm at higher temperature when the compound was heated to 450°C.

Anal: Calculated for  $C_{20}H_{18}N_4O_6S_2 \cdot H_2O$ : C, 48.77; H, 4.09; N, 11.38; S, 13.02. Found: C, 48.62; H, 4.00; N, 11.47; S, 12.65.

### 1,2-Dicarbaniilidobenzene-4,6-Disulfonamide (XX)

m-Bisaccharin (1.45 g, 0.0050 mole) was placed in a reaction tube equipped with a condenser. To this were added 0.997 g (0.010 mole) of distilled aniline and 1.2 g (0.066 mole) of water. The formation of a light-yellow slurry was accompanied by the evolution of heat. This slurry was heated at 100°C for 1 hr under a slow stream of nitrogen; the resulting yellow solution was heated at 120°C for 2 hr, during which time water distilled slowly from the mixture. Finally, the contents were heated at 150°C for 3 hr. A greenish-yellow residue (2.12 g) was obtained.

A portion of the residue was recrystallized from 50% alcohol. The melting point of the purified material was 245-247°C and its infrared spectrum (Nujol mull) showed a sharp NH absorption band at 3.01  $\mu$ , a sharp open-chain amide carbonyl absorption band at 6.06  $\mu$ , and a sharp SO<sub>2</sub>NH<sub>2</sub> absorption band at 7.52  $\mu$ . When the crude residue was dissolved in 5 N sodium hydroxide and then treated with concentrated hydrochloric acid to pH 8.0 or 6.0, there was no precipitation. However, on further addition of concentrated hydrochloric acid to pH 1.0, there precipitated a greenish-white solid. The infrared spectrum of this solid in Nujol was identical to that of the recrystallized product.

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