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Arylsulfimide Polymers. III. The Syntheses of Some Monomeric Aryl-1,2-disulfonic Acids and Derivatives

G. F. D'alelio[a]; Y. Giza[a]; D. M. Feigl[a]
[a] Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

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Arylsulfimide Polymers. III. The Syntheses of Some Monomeric Aryl-1,2-disulfonic Acids and Derivatives

G. F. D'ALELIO, Y. GIZA, and D. M. FEIGL

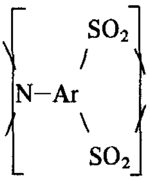
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana

SUMMARY

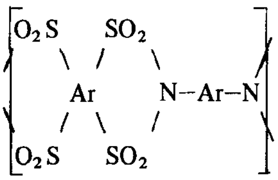
The preparation of derivatives of 4-nitro- and 4-amino-1,2-benzenedisulfonic acid and 3,3′,4,4′-biphenyltetrasulfonic acid are described. Evidence is also presented for the facile elimination of sulfonyl groups from these compounds, particularly in reactions directed toward the formation of acid chlorides.

INTRODUCTION

In the course of our investigations of thermally stable polymers we became interested in polymers incorporating the 1,2-disulfonimide group, including those possessing the following repeating units [(I) and (II)]. Monomers which would be suitable for generating these units by polycondensations such as by

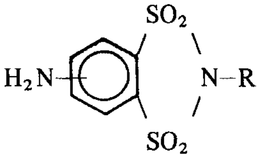


(I)

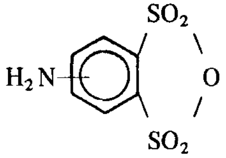


(II)

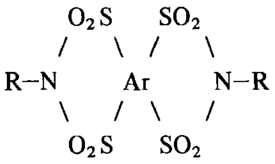
direct reactions or transamidations include the aminobenzenesulfonimides (**III**) or the corresponding anhydride (**IV**), the aryl-bis-sulfonimides (**V**) or the corresponding anhydride (**VI**), or appropriate derivatives of these compounds.



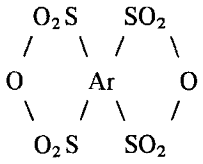
(**III**)



(**IV**)



(**V**)



(**VI**)

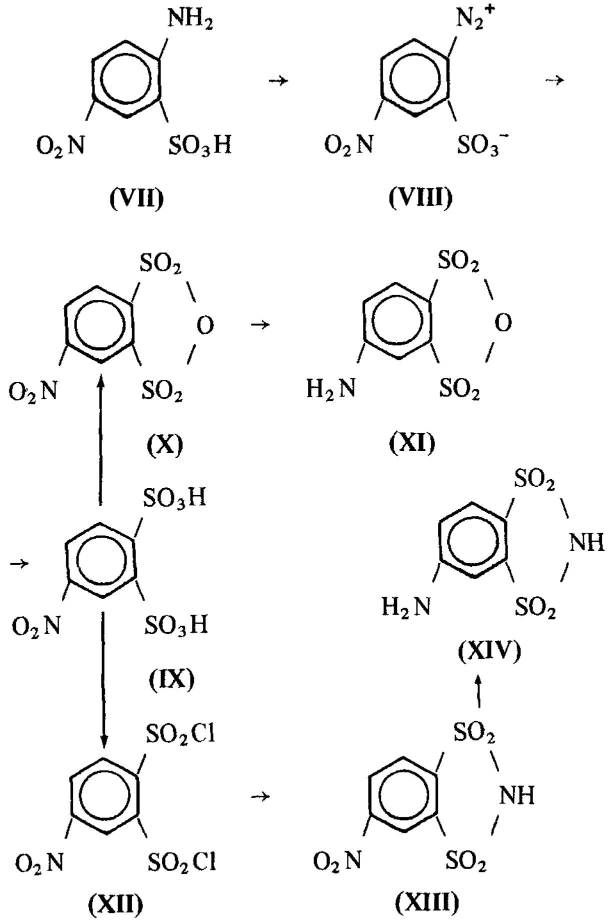
This study was undertaken to develop useful synthetic routes to these new compounds with a view to their subsequent use in polymerization reactions.

Because of their importance to the dye industry, there are numerous references to aminobenzenedisulfonic acids in the literature. However, we found no references to 4-amino-1,2-benzenedisulfonic acid, or the corresponding imide or anhydride. The corresponding nitro compounds are also unreported. This specific arrangement of substituents was desirable in view of the intended use of these compounds. o-Disulfonyl groups were necessary to permit the incorporation of a disulfonimide linkage in the polymer (**I**), and the location of the amine group at C—4 was expected to minimize steric interactions which might interfere with polymerization reactions.

We could locate no report of the synthesis of bis-(phenyldisulfonic acid) or the corresponding imide or anhydride derivative. The synthesis of these compounds, which are suitable for use in the preparation of polymer (**II**), was also undertaken.

DISCUSSION

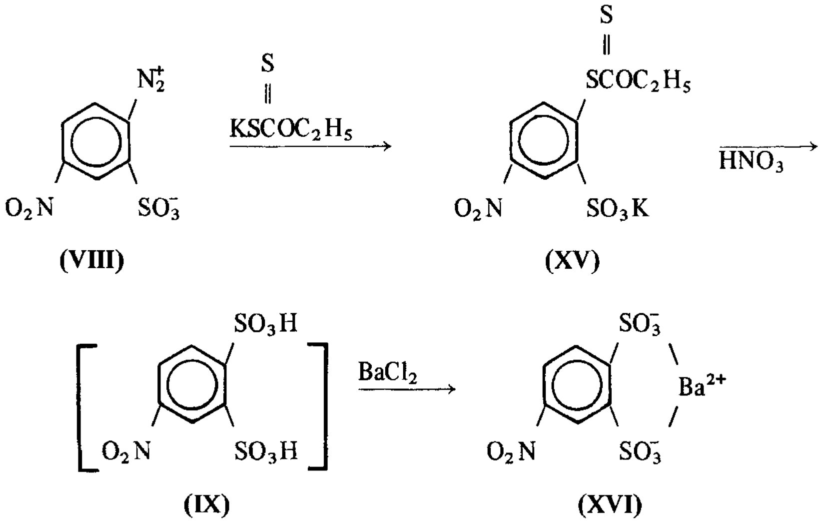
Direct sulfonation of benzene [1] or benzenesulfonic acid [2-4] gives mixtures of the m- and p-benzenedisulfonic acid and not the o-isomer. o-Benzenedisulfonic acid has been prepared via the diazonium salt from o-aminobenzenesulfonic acid [5]. In view of these results, we proposed to prepare the desired aminodisulfonic acid derivatives starting with 5-nitro-2-aminobenzenesulfonic acid **(VII)** and proceeding through the steps outlined in Scheme I.



Scheme I

The preparation of the diazonium compound **(VIII)** has been reported [6]. For the present study the compound was prepared under a variety of conditions with maximum yields of 66%. Addition of a sodium nitrite solution to an acidic solution of the amine, or to an alkaline solution of the amine followed by addition of hydrochloric acid, or addition of the amine to a solution of sodium nitrite in sulfuric acid, gave good yields of the diazonium compound. Only the "paste" method [7], in which a viscous mixture of the amine, sodium nitrite, and water was added to hydrochloric acid, gave very low yields of compound **(VIII)**. The diazonium compound explodes in a flame, but decomposes on a melting point block at 142-145°C. It was further characterized by conversion to the known compound [8], p-toluidinium m-nitrobenzenesulfonate.

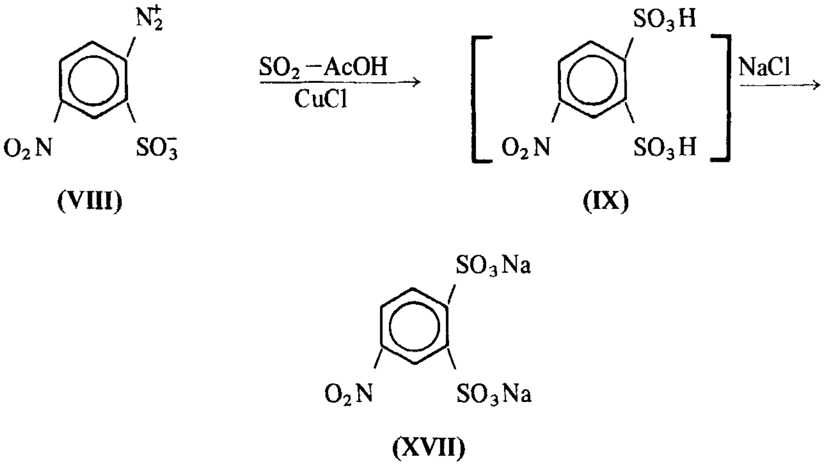
Conversion of the diazonium compound to the disulfonic acid **(IX)** was accomplished in two ways. Compound **(VIII)**, on treatment with potassium ethyl xanthate, followed by the addition of nitric acid, gave the desired disulfonic acid, which was isolated as the barium salt (Scheme II). The



Scheme II

yield of the xanthate derivative **(XV)** was 51%, and the overall yield of the barium salt **(XVI)** was 21% based on the amount of sodium 5-nitro-2-aminobenzenesulfonate [**(VII)**, sodium salt] originally used.

A better yield of the disulfonic acid was obtained when the diazonium compound was treated with a solution of sulfur dioxide in acetic acid, with cuprous chloride as catalyst. The product was isolated as the sodium salt **(XVII)** in 68% yield (Scheme III).

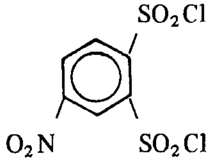


Scheme III

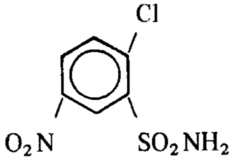
This represents an overall yield from compound **(VII)** of 44%, or about twice the yield obtained via the xanthate.

Acidification of a solution of the barium salt **(XVI)** produced the free acid as an orange-brown semisolid. The sodium salt of the acid **(XVII)** was passed through an ion-exchange column containing Dowex 50 (H^+form) using water as eluent. Concentration of the effluent also gave the apparently hydrated acid as an orange-brown liquid. Vacuum distillation of the crude acid gave a colorless liquid. The acid was never obtained in crystalline form.

All attempts to prepare the acid chloride from the salts of the disulfonic acid were unsuccessful. Krishna [9] tentatively assigned structure **(XVIII)** to a compound obtained from 3-nitro-6-methylthianthrentetroxide, after the latter material was heated in a sealed tube at 250-280°C with phosphorus pentachloride. However, we found that treatment of the sodium or potassium salt of 4-nitro-1,2-benzenedisulfonic acid with phosphorus pentachloride or phosphorus oxychloride apparently gave, not the disulfonyl chloride, but a product in which one of the sulfonyl groups had been replaced by chlorine. The products of these reactions were oils and could not be well characterized as obtained. However, when the products of the reaction with phosphorus pentachloride or phosphorus oxychloride were treated with ammonia, 2-chloro-5-nitrobenzenesulfonamide **(XIX)** was isolated.



(XVIII)



(XIX)

The sulfonyl chloride groups of compound **(XVIII)** would be expected to activate one another toward nucleophilic displacement. In addition, the nitro group located para to one of the sulfonyl groups would further activate that sulfonyl group toward displacement. The reaction conditions needed to form the acid chloride appear to cause a concomitant displacement of the sulfonyl chloride group by chloride ion. Similar displacements have been reported [10, 11]. On the basis of our studies, it appears unlikely that the compound obtained by Krishna [9] has the structure **(XVIII)**, since the conditions used in that study were considerably more vigorous than those used by us.

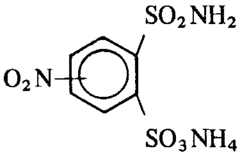
Since the desired acid chloride could not be synthesized, an alternate route to the sulfonimide, via the sulfonic anhydride, was investigated.

Hurtley and Smiles [5] reported that heating the potassium salt of o-benzenedisulfonic acid with chlorosulfonic acid gave benzenedisulfonic anhydride. This reaction was applied to the salts of 4-nitrobenzenedisulfonic acid. The amount of anhydride **(X)** obtained varied, with the best crude yields in the range of 50-70%. Careful drying of the acid salt proved to be essential for better yields. In addition, the product, which was isolated after the reaction mixture was poured onto ice water, had to be separated quickly from the ice water to prevent loss of the anhydride to hydrolysis.

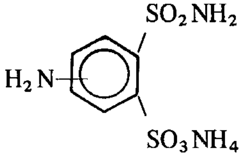
The crude free acid could be converted to anhydride by treatment with phosphorus pentoxide. The yields of anhydride prepared by this method were erratic. The highest value obtained was 52%.

Attempted catalytic reduction of the nitro group of 4-nitro-1,2-benzenedisulfonic anhydride gave a product which could not be well characterized, although the infrared spectrum of the product clearly indicated that the nitro group had been reduced. Like the analogous aminosulfobenzoic anhydride [12], 4-aminobenzenedisulfonic anhydride **(XI)** appears to undergo spontaneous polymerization.

Treatment of 4-nitro-1,2-benzenedisulfonic anhydride with ammonium hydroxide did not give the desired imide **(XIII)**. The product, isolated in 85% yield, was ammonium nitro-o-sulfamidobenzenesulfonate [(XX), mp, 156-158°C]. The position of the nitro group could not be readily determined. This product was hydrogenated over a palladium-on-charcoal catalyst in 84% yield to give ammonium amino-o-sulfamidobenzenesulfonate [(XXI), mp, 223-225°C].

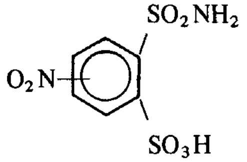


(XX)

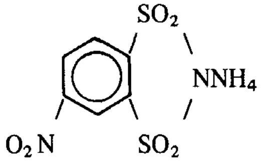


(XXI)

Attempts to obtain the free sulfonic acid (XXII) in crystalline form were unsuccessful. The barium salt of (XXII) could be obtained in crystalline form, but acidification of this compound gave only a viscous, pale-yellow liquid which appears to be the hydrated acid [(XXII) · nH_2O]. Thermal dehydration of the crude acid gave a poor yield of a product tentatively identified as the ammonium salt of 4-nitro-1,2-benzenedisulfonimide (XXIII).



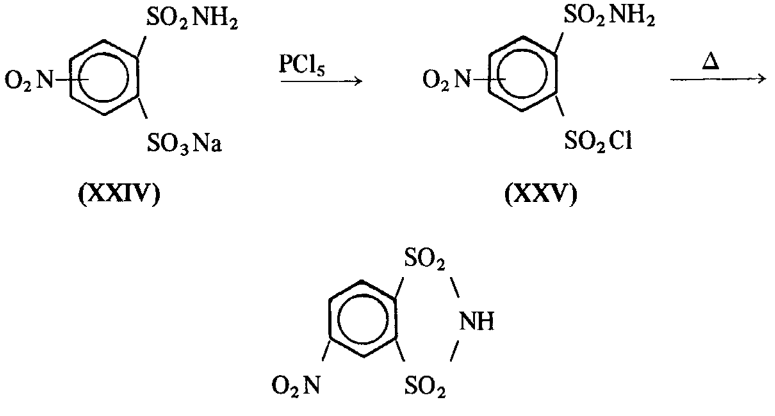
(XXII)



(XXIII)

The attempted chemical dehydration of acid (XXII) with polyphosphoric acid, phosphorus pentoxide, phosphorus oxychloride, or acetic anhydride failed to produce the disulfonimide (XIII). This failure to isolate the imide may be due to the facile formation of the disulfonic anhydride by deamination in preference to sulfonimide formation via dehydration.

Finally, conversion of compound (XX) to the corresponding sodium salt, followed by treatment of this product with phosphorus pentachloride and heat, gave an oily product which, on treatment with ammonia, yielded 2-chloro-5-nitrobenzenesulfonamide (XIX). Instead of proceeding through the desired sequence of reactions (Scheme IV), compound (XXIV) or (XXV) underwent a reaction in which one of the sulfonyl groups was displaced by chlorine. This result again confirms the fact that reactions which proceed readily with unsubstituted benzenedisulfonyl derivatives are seriously hampered by the presence of a nitro substituent which activates the sulfonyl groups toward displacement reactions.



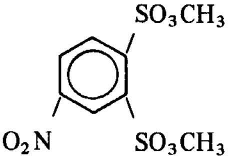
(XXIV) (XXV)

(XIII)

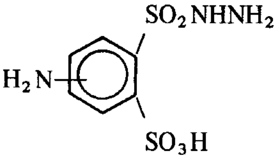
Scheme IV

The dimethyl ester of 4-nitro-1,2-benzenedisulfonic acid [(XXVI), mp, 95-96°C) was prepared by treating the crude disulfonic acid with diazomethane. Yields ranged from 30 to 50%. Only starting material was isolated when dimethylsulfate was used as the alkylating agent. Hydrogenation of the ester gave a compound with a melting point of 210-215°C. The infrared spectrum of the product indicated that the nitro group had been reduced, but the product was insoluble in the common organic solvents and appeared to be an oligomer with an open-chain polysulfonamide structure.

One other derivative of the aminodisulfonic acid was prepared in this study. 4-Nitro-1,2-benzenedisulfonic anhydride was treated with hydrazine hydrate. On the basis of its analysis and infrared spectrum, the product of this reaction was assigned structure (XXVII). It appears that the formation of the hydrazide was accompanied by reduction of the nitro group.

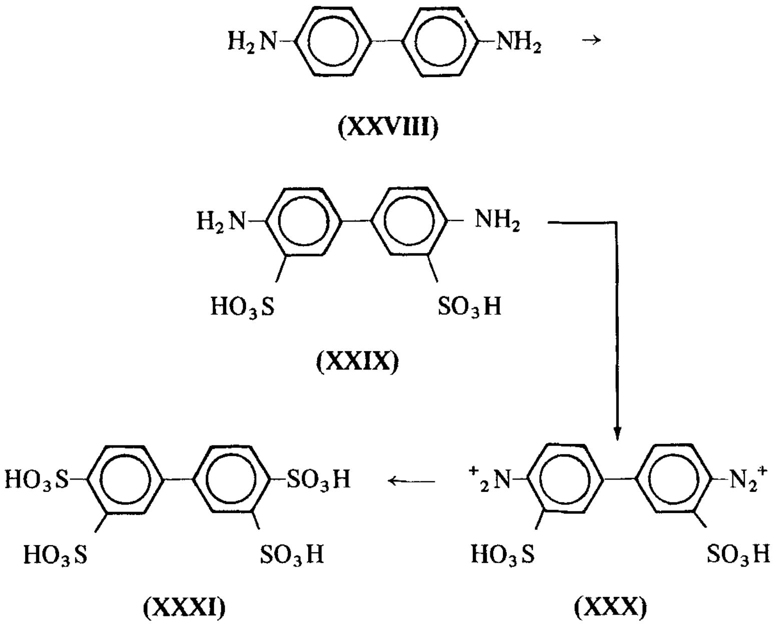


(XXVI)



(XXVII)

With a view to polymerizations involving A-A, B-B-type monomers, we also undertook the synthesis of 3,3′,4,4′-biphenyltetrasulfonic acid [compound (XXXI), Scheme V], and the corresponding diimide and bianhydride.

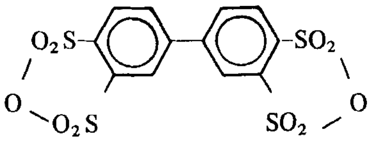


Scheme V

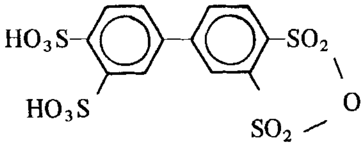
The preparation of 3,3′-benzidinedisulfonic acid (XXIX) has been reported in the literature [13-17]. We found that the yield of compound (XXIX) was significantly improved when the sulfonation of compound (XXVIII) was carried out in the absence of diphenylsulfone. Sulfonation of benzidine in the presence of diphenylsulfone, according to the procedure of Shrowaczewska [17], gave a 58% crude yield of the product, whereas an 80% crude yield was obtained when the sulfone was omitted.

The tetrazonium compound (XXX) was obtained in excellent yield (94%) by standard procedures, and conversion of the tetrazonium compound to the tetrasulfonic acid (XXXI) was accomplished by treatment of the salt with sulfur dioxide-acetic acid in the presence of a catalytic amount of cuprous chloride. The acid was isolated as its sodium or potassium salt. The yield of the sodium salt, based on the amount of 3,3′-benzidinedisulfonic acid used, was 73%; the corresponding yields of potassium salt were in the range of 82-85%.

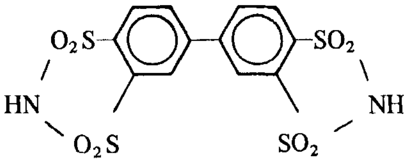
Attempts to convert the acid salts to the bianhydride **(XXXII)** yielded a compound with a melting point of 218-220°C. The neutralization equivalent, molecular weight, and elemental analysis of the product indicated that the compound was a mixture of the bianhydride and the monoanhydride, 3,4-diphenyldisulfonic acid-3′,4′-disulfonic anhydride **(XXXIII)**.



(XXXII)



(XXXIII)



(XXXIV)

Attempts to prepare the bis-(phenylsulfonimide) **(XXXIV)** by treating the corresponding acid salts with phosphorus pentachloride, followed by ammonia, resulted in a product mixture containing compounds in which one or more of the sulfonyl groups had been eliminated from the molecule. Preliminary polymerization studies, using the anhydride as monomer, indicated that polymerization was also accompanied by loss of sulfonyl groups. Since these studies were directed to the ultimate synthesis of polysulfonimides and since elimination of sulfonyl groups prevents the formation of the imide linkage, further attempts to prepare the sulfonimide monomer were not undertaken.

EXPERIMENTAL

Preparation of the Diazonium Derivative of 2-Amino-5-nitrobenzenesulfonic Acid

2-Amino-5-nitrobenzenesulfonic acid (15.0 g, 0.069 mole) was mixed with

31 ml of concentrated hydrochloric acid and 50 g of ice. A solution of 4.7 g (0.069 mole) of sodium nitrite in 15 ml of water was added slowly at 0°C over a period of 1 hr. After standing for 20 min at room temperature, the insoluble, yellow diazonium compound was isolated in 66.1% yield (10.5 g). The diazonium compound was recrystallized from 50% alcohol to give shining, yellow crystals.

The diazonium compound explodes in a flame. However, on a melting point block it decomposes at 142-145°C with color changing from orange to dark brown at 120°C. The diazonium compound is soluble in water and in 3 N hydrochloric acid, but decomposes in 3 N sodium hydroxide. There are two new peaks in its infrared spectrum, at 2300 and 1540 cm^{-1}, which do not appear in the spectrum of the starting material.

Analysis: Calculated for $C_6H_3N_3O_5S$: C, 31.44; S, 13.99. Found: C, 31.24; S, 13.96.

Conversion of 5-Nitro-2-diazobenzenesulfonate to Toluidinium m-Nitrobenzenesulfonate

The diazonium compound (1.12 g, 0.0049 mole) was dissolved in 20 ml of hot 75% alcohol. A small amount of copper powder was added, and the mixture was heated on a steam bath for several minutes. The reddish-brown solution was concentrated, heated with 400 mg of p-toluidine in hydrochloric acid, and decolorized. After three recrystallizations from 50% alcohol, the yellow product melted at 218-218.5°C (Lit. [8], 222°C).

Analysis: Calculated for $C_{13}H_{14}N_2O_5S$: C, 50.32; H, 4.55; N, 9.03; S, 10.33. Found: C, 50.35; H, 4.49; N, 8.92; S, 10.13.

Reaction of the Diazonium Compound with Potassium Ethyl Xanthate

To a yellow solution of 3.50 g (0.022 mole) of potassium ethyl xanthate in 10 ml of water was slowly added the diazonium compound (2 g, 0.0087 mole) at 0-5°C with shaking. The slurry was concentrated almost to dryness. The solid was removed by filtration and dried in air. The reddish-brown xanthate derivative was obtained in 51% yield (1.6 g). A yellow solid was obtained after three recrystallizations from 50% alcohol.

Analysis: Calculated for $C_9H_8NO_6S_3K$: S, 26.60; K, 10.82. Found: S, 27.20; K, 10.46.

Conversion of the Xanthate Derivative to 4-Nitro-1,2-benzenedisulfonates

The crude xanthate (5.0 g, 0.0138 mole) was slowly added to 50 ml of concentrated nitric acid, and the reaction mixture was concentrated to remove excess nitric acid. The brown concentrate was warmed on a steam bath, and a hot, saturated solution of barium chloride (3.58 g in 20 ml of water) was added slowly. The hot reaction mixture was filtered to remove insoluble barium sulfate, and the filtrate was cooled to yield a yellow solid, which was obtained in 20.8% yield based on the amount of 2-amino-5-nitrobenzenesulfonic acid used. The yellow barium salt of 4-nitro-1,2-benzenedisulfonic acid was recrystallized from hot water twice. Elemental analyses (Table 1) were obtained for samples of the product dried in vacuo for 30 min (a) and for 4 hr (b). These analyses indicated that the barium salt was hydrated.

Table 1. Analyses: Calculated and Found for $C_6H_3NO_8S_2Ba \cdot nH_2O$

	Calculated				Found	
n	0	1	2	3	(a)	(b)
C	17.20	16.52	15.85	15.20	16.78	17.97
H	0.72	1.15	1.55	1.92	1.71	1.85
N	3.44	3.22	3.08	2.96	3.32	3.19
S	15.30	14.65	14.10	13.55	–	14.26
Ba	32.80	31.43	30.20	29.04	28.99	29.21

To the barium salt (3 g, 0.0064 mole), dissolved in 50 ml of hot water, was added a hot solution of potassium carbonate (3 g, in 25 ml of water). Insoluble barium carbonate was filtered from the mixture, and the filtrate was concentrated to dryness. The dipotassium salt was isolated as a yellow-orange solid.

Analysis: Calculated for $C_6H_3NO_8S_2K_2$: S, 17.82; K, 21.75. Found: S, 17.15; K, 21.43.

Reaction of the Diazonium Compound with Sulfur Dioxide-Acetic Acid

A solution of the diazonium compound (28.0 g, 0.122 mole) in 125 ml of concentrated hydrochloric acid was introduced slowly into a suspension of 1.6 g of cuprous chloride in 250 ml of 25% sulfur dioxide in acetic acid at room temperature. A vigorous nitrogen evolution occurred and the temperature of the solution increased to 30°C. The dark green-brown solution was heated on a steam bath at 50°C for 3-4 hr. The solution was concentrated almost to dryness. After addition of saturated sodium chloride solution (14.5 g, in 50 ml of water), a yellow solid precipitated.

The solid was removed by filtration and washed with methyl alcohol. The white product weighed 27.0 g (67.6% yield). The molecular weight of the product, determined by vapor phase osmometry, was 334 (calculated for disodium 4-nitro-1,2-benzenedisulfonate, 327).

The infrared spectrum of the product displayed the characteristic peak for the SO_3 group at 1240 cm^{-1} and those for the NO_2 group at 1350 and 1330 cm^{-1}.

Analysis: Calculated for $C_6H_3NO_8S_2Na_2$: S, 19.59. Found: S, 19.38.

Isolation of 4-Nitro-1,2-benzenedisulfonic Acid

The barium salt of 4-nitro-1,2-benzenesulfonic acid was suspended in about 10 ml of water. To this suspension, 25 ml of 10% sulfuric acid were slowly added. The solution was stirred at room temperature for 30 min. Barium sulfate was filtered from the mixture, and the filtrate was concentrated to give an orange-brown liquid (about 7.0 g). On standing at room temperature for 2-3 days, the hydrated disulfonic acid became a semisolid. The waxy solid was subjected to vacuum distillation. A colorless acidic liquid distilled at 130-136°C/0.7 mm Hg (n_D^{20} = 1.4538). The liquid apparently reacted with sodium chloride infrared cells, liberating a gas which had the sharp odor of hydrogen chloride.

Disodium 4-nitrobenzene-1,2-disulfonate (3.0 g) was dissolved in 5 ml of water. The resulting yellow solution was passed over Dowex 50 (H^+ form) in a 1.8-cm × 50-cm column. The column was eluted with about 30 ml of water until the effluent was no longer acidic. The effluent was concentrated almost to dryness to give the disulfonic acid as an orange-brown liquid (2.5 g).

Attempted Preparation of 4-Nitro-1,2-benzenedisulfonyl Chloride

The sodium salt of 4-nitro-1,2-benzenedisulfonic acid (10 g, 0.03 mole) was allowed to react with phosphorus pentachloride (19.1 g, 0.092 mole) at 150-160°C for 90 min. The reaction mixture was poured onto an ice-water mixture, and a yellow oil separated. The aqueous solution was extracted with benzene several times and benzene extracts were mixed with the oil separated previously. The benzene solution was concentrated and treated with about 30 ml of 5 N alcoholic ammonia solution at room temperature. The amide was isolated in 51.8% yield (4 g), mp, 178-180°C. After recrystallization from alcohol, the white amide melted at 189-191°C. The analytical sample melted at 187°C (Lit. [18], val. for 2-chloro-5-nitrobenzenesulfonamide, 186-187°C).

Analysis: Calculated for $C_6H_5N_2O_4SCl$: C, 30.50; H, 2.12; N, 11.88; S, 13.55; Cl, 15.00. Found: C, 31.51; H, 2.46; N, 11.67; S, 13.34; Cl, 14.73.

Preparation of 4-Nitro-1,2-benzenedisulfonic Anhydride Using Chlorosulfonic Acid

Chlorosulfonic acid (15 ml) was placed in a 100-ml round-bottomed flask equipped with a condenser. To this were added 10.0 g (0.03 mole) of dry disodium 4-nitrobenzene-1,2-disulfonate in small portions. The reaction mixture was stirred at 80°C for 3 days. The resulting viscous, brown liquid was then stirred with about 20 ml of ethylene chloride at room temperature. This heterogeneous mixture was poured slowly onto ice water with vigorous agitation. A fluffy, grey-white solid soon separated from the ethylene chloride layer. The solid anhydride was quickly filtered and washed with cold water several times. After drying, the product weighed 5.1 g (64% yield), mp, 130-135°C. After decolorization and recrystallization from ethylene chloride, the anhydride melted at 156-158°C. The yield of crude anhydride varied from 50 to 70%.

The analytical sample, which was recrystallized several times from benzene, had a melting point of 158-160°C.

Analysis: Calculated for $C_6H_3NO_7S_2$: C, 27.17; H, 1.14; N, 5.29; S, 24.13. Found: C, 27.18; H, 1.57; N, 5.53; S, 24.91.

Preparation of 4-Nitro-1,2-benzenedisulfonic Anhydride Using Phosphorus Pentoxide

Crude 4-nitro-1,2-benzenedisulfonic acid (2.0 g) and 0.12 g of Supercel were mixed thoroughly in a 250-ml three-necked flask. To this was added a mixture of 3.5 g of phosphorus pentoxide and 0.24 g of Supercel in small portions. The mixture was stirred at 120°C for 18 hr and then extracted with hot ethylene dichloride three times. After evaporation of the solvent, 1.0 g (52%) of a glistening, white solid, mp, 150-152°C, was obtained. This crude anhydride was recrystallized from ethylene dichloride to give a product with a melting point of 158-160°C.

Preparation of 4-Amino-1,2-benzenedisulfonic Anhydride

The nitroanhydride (0.917 g, 3.46 mmoles) in 100 ml ethylene dichloride was hydrogenated in the presence of palladium-on-charcoal catalyst at 40 psi initial hydrogen pressure for 22 hr. The catalyst was separated by filtration. The filtrate was concentrated under reduced pressure (13 mm Hg), leaving 0.52 g (60%) of slightly pink solid. The pink solid darkened at 130°C, melted partly at 150°C, and blackened with complete melting (without gas formation) at 215-220°C. The infrared spectrum of this solid showed NH absorption at 3350 cm^{-1}, SO_2-O- absorption at 1410 and 805 cm^{-1}, but lacked the two NO_2 absorption peaks. The solid turned brown on standing in air at room temperature, and this new substance had a new characteristic infrared absorption for SO_3 at 1050 cm^{-1}. The absorption peaks for SO_2-O- and NH mentioned previously were broader and less intense. The material (about 0.29 g) adsorbed on the catalyst could be extracted with dimethylformamide.

When the reduction was carried out in acetic acid, the product was isolated from the reaction mixture as a glistening, white solid, mp, 220-225°C, and additional material, a pink, amorphous solid, was extracted from the catalyst. The infrared spectrum of this product also contained the NH absorption band, but was simpler than expected for the aminohydride. This compound appears to undergo polymerization upon formation.

Preparation of Ammonium Nitro-2-sulfamidobenzenesulfonate

Recrystallized nitroanhydride (3.24 g, 0.0122 mole) was added in small portions to 10 ml of concentrated ammonium hydroxide with shaking. The resulting warm, yellow solution was cooled in ice water. The reaction was then concentrated to dryness at 45°C and 15 mm Hg pressure. Glistening needles were obtained in 85% yield (3.1 g), mp, 148-150°C. The product, ammonium nitro-2-sulfamidobenzenesulfonate, was recrystallized from water twice, mp, 156-158°C.

Analysis: Calculated for $C_6H_9N_3O_7S_2$: C, 24.05; H, 3.03; N, 14.05; S, 21.40. Found: C, 23.83; H, 3.35; N, 14.07; S, 21.00.

Preparation of Ammonium Amino-2-sulfamidobenzenesulfonate

The nitro-2-sulfamidobenzenesulfonate (4.4 g, 0.015 mole) in 250 ml of 84% alcohol was hydrogenated in the presence of 0.41 g of palladium-on-charcoal (5%) catalyst for 5 hr at 40 psi initial hydrogen pressure. Approximately 2 psi of hydrogen was taken up by the reaction mixture. The catalyst was filtered from the mixture, and the filtrate was concentrated at 45°C/15 mm Hg to give a yellow, viscous liquid. When the liquid was mixed with absolute alcohol, a white solid separated. Recrystallization from water-alcohol mixture gave a product which melted at 223-225°C. The yield of product was 83% (3.3 g). Its infrared spectrum showed NH absorption at 3200 cm^{-1}, SO_2–N– absorption at 1310 and 1160 cm^{-1}, and SO_3^- absorption at 1220 cm^{-1}, but no NO_2 absorption.

Analysis: Calculated for $C_6H_{11}N_3O_5S_2$: C, 26.75; H, 4.11; N, 15.60; S, 23.70. Found: C, 26.69; H, 4.19; N, 14.89; S, 23.90.

Preparation and Attempted Dehydration of Nitro-2-sulfamidobenzenesulfonic Acid

Ammonium nitro-2-sulfamidobenzenesulfonate (2.7 g, 0.0090 mole) was treated with a saturated barium chloride solution (1.1 g, 5 ml of water) and the reaction mixture was stirred for 30 min. The insoluble barium salt was filtered and dried to give 2.1 g (66%) of product. The barium salt was recrystallized from water and acidified with 1.6 ml of 10% sulfuric acid. Barium sulfate was removed by filtration, and the filtrate was concentrated at room temperature under aspirator pressure (15 mm Hg) to give a yellow liquid. The residue was then concentrated at 70°C/15 mm Hg for 30 min to give a viscous, yellow liquid, probably the hydrated acid.

The crude acid was heated for 24 hr at 95°C. When the resulting viscous, brown liquid was mixed with absolute alcohol, a pale-brown solid (0.8 g) precipitated. The solid was soluble in water and gave an acidic solution (pH 5). The solid decomposed at 247°C. Recrystallization from 50% alcohol gave a white product (0.1 g, 70% loss on recrystallization) which decomposed at 320-325°C. The infrared spectrum of this material is similar to that of the starting material, except for the presence of a shoulder at 1400 cm^{-1}. The elemental analysis is in agreement with that calculated for the dihydrate of the ammonium salt of 4-nitro-1,2-benzenesulfonimide.

Analysis: Calculated for $C_6H_{11}N_3O_8S_2$: C, 22.74; H, 3.47; N, 13.24; S, 20.23. Found: C, 23.11; H, 3.62; N, 12.87; S, 20.71.

Preparation of Dimethyl 4-Nitro-1,2-benzenedisulfonate

Crude 4-nitro-1,2-benzenedisulfonic acid (13.6 g) was suspended in 30 ml of ether, and this mixture was treated with 0.2 mole of freshly made diazomethane in ether. The diacid dissolved as the reaction proceeded with evolution of nitrogen. The ether solution was separated from the reaction mixture and cooled. A pale-yellow solid crystallized in 40.4% yield (5.5 g, mp, 93-95°C). The crude diester was recrystallized twice from methanol to give a white solid, mp, 95-96°C. The infrared spectrum showed SO_3R bands at 1370 and 990 cm^{-1}, SO_2 absorption at 1200 cm^{-1}, a CH_3 rocking band at 825 cm^{-1}, and the NO_2 bands at 1520 and 1350 cm^{-1}.

Analysis: Calculated for $C_8H_9NO_8S_2$: C, 30.87; H, 2.91; N, 4.50; S, 20.60. Found: C, 30.09; H, 3.29; N, 5.19; S. 22.60.

Hydrogenation of Dimethyl 4-Nitro-1,2-benzenedisulfonate

The purified nitro diester (0.51 g, 1.6 mmole) in 150 ml of absolute methanol was hydrogenated in the presence of 0.063 g of palladium-on-charcoal (5%) catalyst at 40 psi hydrogen pressure. The pressure dropped about 0.75 psi during the reaction. The catalyst was filtered from the mixture, and the filtrate was concentrated at room temperature under aspirator pressure. A powdery, grey solid was obtained, mp, 210-215°C. Recrystallization of the product from absolute methanol was not satisfactory since the flocculent, white material could not be isolated by filtration. When the product was heated at 210-215°C for 30 min under a nitrogen stream, a charred, dimethylformamide-soluble material was obtained. The original product was insoluble in the common organic solvents, but somewhat soluble in dimethylformamide and in hot methanol, and very soluble in water. Its infrared spectrum showed no NO_2 absorption bands but did show sharp NH_2 bands at 3320 and 3300 cm^{-1}, SO_3H at 1220 cm^{-1}, SO_3R at 1370 and 990 cm^{-1}, and a band at 1170 cm^{-1} for SO_2N.

Product, isolated from a second reaction, melted at 160-165°C but otherwise exhibited similar properties to those noted for the compound above.

Preparation of Nitrosulfonhydrazidobenzenesulfonic Acid

The nitro anhydride (1.0 g, 0.0034 mole) in a 25-ml round-bottomed flask was treated with 0.80 g (0.016 mole) of hydrazine hydrate to give a reddish-brown solution. Heating at reflux for 30 min produced an opaque, yellow solution. The solution was cooled and a yellow solid precipitated, mp, 190-193°C, 0.9 g (84% yield). After one recrystallization from 50% alcohol, the yellow needles melted at 205-210°C with evolution of a gas and blackening at 290°C. The elemental analysis of this product is in agreement with that expected for the monohydrate of amino-2-sulfonhydrazidobenzenesulfonic acid.

Analysis: Calculated for $C_6H_{11}N_3O_6S_2$: C, 25.33; H, 3.89. Found: C, 25.52; H, 4.23.

Preparation of 3,3'-Benzidine Disulfonic Acid

Benzidine (22.0 g, 0.12 mole) and 10.0 g of diphenylsulfone were placed in a 500-ml, three-necked, round-bottomed flask equipped with a thermometer, a mechanical stirrer, and a condenser with dropping funnel. The mixture was heated to 110°C to give a grey melt. This homogeneous melt was cooled to 80°C, and 25 g of concentrated sulfuric acid were added slowly with stirring. The reddish-brown mass was then heated at 255°C for 5 hr under 17 mm Hg pressure. The resulting black mass was extracted with hot benzene several times to remove diphenylsulfone. The black residue was treated with 700 ml of 3 N ammonium hydroxide, and the insoluble, black material was removed by filtration. The brown filtrate was acidified by the slow addition of about 200 ml of 6 N hydrochloric acid. There were obtained 24.0 g (58%) of a greyish-white solid. The product was found to have an acid number of 1.8 (calculated value, 2.0). Thermogravimetric analysis showed no weight loss up to 140°C, indicating that the disulfonic acid is in the anhydrous form. Differential thermal analysis showed an endotherm at 325°C.

When the above reaction was repeated under essentially the same conditions, except for the presence of the sulfone, an 80% yield of the product (acid number, 2.04) was obtained.

Preparation of 3,3',4,4'-Biphenyltetrasulfonates

3,3'-Benzidinedisulfonic acid (10.0 g, 0.029 mole) was dissolved in a solution of 4.0 g of sodium hydroxide in 50 ml of water to give a brown solution. To the cooled, brown solution was added a saturated sodium nitrite solution (4.7 g in 14 ml of water), and this mixture was allowed to stand in an ice-water bath for 15 min before being poured with occasional shaking onto a mixture of 30 ml of concentrated hydrochloric acid and 50.0 g of ice. Care was taken to keep the temperature of the acidic solution below 5°C during the addition of the reaction mixture. The acidic solution was cooled in an ice-water bath for 30 min, and the insoluble material was removed by filtration. There were obtained 10.0 g (94% yield) of the bright orange-brown tetrazonium compound.

The orange-brown solid was dissolved in 100 ml of concentrated hydrochloric acid. The resulting brown solution was slowly added, over a period of 30 min with occasional shaking, to a suspension of 1.5 g of cuprous chloride in 130 ml of a fresh solution of 20% sulfur dioxide-acetic acid solution. Vigorous foaming occurred immediately, indicating the liberation of nitrogen. The reaction mixture was allowed to stand at room temperature for several hours and was then evaporated to dryness. The titration of a portion of the resulting brown residue with standard sodium hydroxide solution gave an acid number of 3.88 (calculated for 3,3′,4,4′-biphenyltetrasulfonic acid, 4.0).

The remaining brown residue was treated with a saturated sodium chloride solution (8.0 g/30 ml of water). A yellow solid was separated by filtration and washed with methanol. More yellow solid then precipitated from the filtrate. The combined yield of tetrasodium 3,3′,4,4′-biphenyltetrasulfonate was 78% (12.7 g).

Analysis: Calculated for $C_{12}H_6O_{12}S_4Na_4$: S, 22.79. Found: S, 22.06.

The tetrapotassium compound was prepared from 3,3′-benzidinedisulfonic acid according to the synthesis of the corresponding tetrasodium compound, except that potassium chloride was added instead of sodium chloride. The overall yield of the tetrapotassium compound was in the range of 82-85% of theory.

Analysis: Calculated for $C_{12}H_6O_{12}S_4K_4$: S, 20.43. Found: S, 19.28.

Attempted Preparation of Bis-(phenyldisulfonyl Anhydride)

Ten ml of chlorosulfonic acid were placed in a 100-ml, three-necked, round-bottomed flask equipped with a condenser and a thermometer. To this were added with stirring 2.5 g (0.004 mole) of the tetrapotassium compound in small portions. The dark-brown mixture was stirred at 80°C for 17 hr. The reaction mixture was cooled to 25°C and 5 ml of ethylene dichloride was introduced to the cooled mixture. This mixture was poured slowly into ice with stirring, and the resulting insoluble, greyish-white precipitate was removed by filtration and dried in vacuo overnight. It weighed 1.52 g (86% yield), mp, 218-220°C. The neutralization equivalent of the crude product was found to be 111.0 (calculated for 3,3′,4,4′-biphenyltetrasulfonic bianhydride, 110; for 3,4-biphenyldisulfonic anhydride-3′,4′-disulfonic acid, 114).

The molecular weight of the product was found, by vapor pressure osmometry, to be 446 (calculated for bianhydride, 438; calculated for monoanhydride, 456). The solid was very soluble in tetrahydrofuran, N,N-dimethylformamide, and N,N-dimethylacetamide; it dissolved slowly in absolute alcohol and water, and it was soluble in hot dioxane. The solid was insoluble in hexane, ether, chloroform, n-butyl ether, and ethyl acetate, but slightly soluble in hot benzene and hot ethylene dichloride. The infrared spectrum of the solid showed absorption bands characteristic for SO_2-O at 1400 and 800 cm^{-1}, and a SO_3H absorption band at 1230 cm^{-1}. There was a very weak SO_3H absorption band at 1100 cm^{-1}.

Analysis: Calculated for $C_{12}H_6O_{10}S_4$ (bianhydride): S, 29.24. Calculated for $C_{12}H_8O_{11}S_4$ (monoanhydride): S, 28.06. Found: S, 28.76.

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REFERENCES

[1] W. Koerner and G. Monselise, *Gazz. Chim. Ital.*, **6**, 133 (1876).
[2] G. B. Buckton and A. W. Hofmann, *Ann.*, **100**, 155 (1856).
[3] V. Meyer and W. Michler, *Ber.*, **8**, 672 (1875).
[4] L. Barth and C. Senhofer, *Ber.*, **8**, 1477 (1875).
[5] W. R. Hurtley and S. Smiles, *J. Chem. Soc.*, **1926**, 1821.
[6] Kalle and Co., D.R.P. 126671, 133714; *Chem. Zentr.*, **I**, 84 (1902); **II**, 615 (1902).
[7] K. H. Saunders, *The Aromatic Diazo Compounds*, Edward Arnold and Co., London, 1949, pp. 17, 29.
[8] O. C. Dermer and V. H. Dermer, *J. Org. Chem.*, **7**, 581 (1942).
[9] S. Krishna, *J. Chem. Soc.*, **123**, 2786 (1923).
[10] W. M. Blanchard, *Am. Chem. J.*, **30**, 485 (1903).
[11] P. Bertalo and A. Bertalo, *Gazz. Chim. Ital.*, **62**, 487 (1932).
[12] G. F. D'Alelio, W. A. Fessler, and D. M. Feigl, *J. Macromol. Sci.*, **A3**, 941 (1969).
[13] P. Griess, *Ber.*, **14**, 300 (1881).
[14] P. Griess and C. Duisberg, *Ber.*, **22**, 2459 (1889).
[15] L. M. Grubina and V. V. Stender, *J. App. Chem. (USSR)*, **13**, 1028-1039 (1940).
[16] H. Gilman and H. Smith Broadbent, *J. Am. Chem. Soc.*, **74**, 264 (1952).
[17] Z. Shrowaczewska, *Trav. Soc. Sci. Lettres, Wroclaw Ser. B*, **61**, 5-53 (1953); *Chem. Abstr.*, **48**, 7569h (1954).
[18] G. F. H. Allen and G. F. Frame, *J. Org. Chem.*, **7**, 15 (1942).

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