bonate, and the solution was filtered and acidified. The yield of product after one recrystallization from ethyl acetate–cyclohexane was 0.26 g. (43%). Further recrystallization gave the pure product, m.p. 217–217.5°, with evolution of bubbles.

Anal. Calcd. for $C_{20}H_{18}N_2O_6S_2$: C, 53.80; H, 4.06; N, 6.28. Found: C, 54.01; H, 3.92; N, 6.28.

B.—Hydrolysis of ethyl α-(2,5-dibenzenesulfonamidophenyl)-benzoylacetate in the same manner gave a crude yield of 84% of 2,5-dibenzenesulfonamido-α-toluic acid. The product was recrystallized from acetic acid and from ethyl acetate–cyclohexane, m.p. 215.5–217.5°, with evolution of bubbles. It was identical with the product prepared in A.

Attempted Oxidations of Active Methylene Adducts.—The adducts from *p*-quinonedibenzenesulfonimide and acetylacetone, ethyl benzoylacetate and ethyl cyclopentanone-2-carboxylate were treated with lead tetraacetate in glacial acetic acid. Yellow colors developed readily, but the products obtained by pouring the solutions into water were low-melting amorphous yellow solids which were too soluble in organic solvents to recrystallize. Addition of hydrochloric acid to solutions of the materials produced other uncrystallizable amorphous substances which did not resemble monomeric substituted *p*-phenylenedibenzenesulfonamides.

3-Acetyl-5-benzenesulfonamido-1-benzenesulfonyl-x-methyloxindole.—A test-tube containing 0.39 g. of ethyl α-(2,5-dibenzenesulfonamido-x-methylphenyl)-acetoacetate was heated in an oil-bath at 195° for 10 minutes. The compound melted with evolution of bubbles, then resolidified. Recrystallization of the product from ethyl acetate and from ethanol gave 0.27 g. (76%) of a white solid. The pure compound melted at 238–239°. It gave a blue color with ferric chloride.

Anal. Calcd. for $C_{23}H_{20}N_2O_6S_2$: C, 57.01; H, 4.16; N, 5.78. Found: C, 57.03; H, 4.18; N, 5.70.

The infrared spectrum indicated that the compound existed in the 2-hydroxyindole form. The bands at 1688 and 1625 cm.$^{-1}$ were assigned to a conjugated ketone carbonyl and a conjugated carbon–carbon double bond.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. XXIX. Addition of Hydrazoic Acid and Phenols to *p*-Quinonedibenzenesulfonimide and its Derivatives

BY ROGER ADAMS AND DALE C. BLOMSTROM[1]

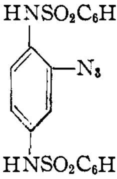
RECEIVED APRIL 13, 1953

By alternate addition of hydrazoic acid and oxidation with lead tetraacetate, the following sequence of reactions results: *p*-quinonedibenzenesulfonimide → 2-azido diamide → 2-azido diimide → 2,x-diazido diamide → 2,x-diazido diimide. 2-Chloro-*p*-quinonedibenzenesulfonimide gives two products: 2,x-diazido diamide and an azidochloro diamide, isomeric with the azidochloro diamide obtained by the addition of hydrogen chloride to the 2-azido diimide. 2-Methyl-*p*-quinonedibenzenesulfonimide yields merely the x-azido-2-methyl diamide. Triethylamine catalyzes the addition of phenol, *o*-cresol and *m*-cresol to give substituted biphenyls. The use of *p*-cresol results in reduction of diimide to diamide.

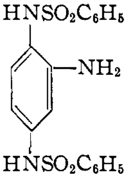
The addition of hydrazoic acid to *p*-benzoquinone was first reported by Oliveri-Mandala and Calderaro,[2] who isolated 2-azidohydroquinone as the product. Fully halogenated quinones were found to react with hydrazoic acid by displacement of halogen by azide groups rather than by addition. Thus, treatment of chloranil with an appropriate amount of sodium azide in ethanol or acetic acid yielded the azidotrichloro-, 2,5-diazido-3,6-dichloro- and tetraazido-*p*-quinones.[3,4] Reaction of hydrazoic acid with 2,3-dichloro-1,4-naphthoquinone gave 2,3-diazido-1,4-naphthoquinone.[4]

When hydrazoic acid was added to 1,4-naphthoquinonedibenzenesulfonimide, 2-azido-1,4-naphthalenedibenzenesulfonamide resulted.[5] Oxidation of this compound with lead tetraacetate yielded the 2-azido diimide, to which another molecule of hydrazoic acid added to form the 2,3-diazido diamide.

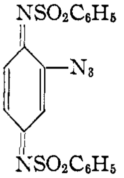
The reactions of *p*-quinonedibenzenesulfonimides with hydrazoic acid have now been studied. The addition of sodium azide to a suspension of *p*-quinonedibenzenesulfonimide in glacial acetic acid afforded 2-azido-*p*-phenylenedibenzenesulfonamide (I) in good yield. Reduction of I with sodium hydrosulfite or with hydrogen over platinum oxide catalyst yielded 2-amino-*p*-phenylenedibenzenesulfonamide (II), which was identical with the amine obtained by hydrosulfite reduction of the known 2-nitro-*p*-phenylenedibenzenesulfonamide. Oxidation of I with lead tetraacetate gave the 2-azido diimide (III) to which a second molecule of hydrazoic acid added readily to form 2,x-diazido-*p*-phenylenedibenzenesulfonamide (IV). Upon reduction of IV with sodium hydrosulfite the corresponding diamine (V) was formed. The diazide (IV) was oxidized with lead tetraacetate to the blood-red crystalline 2,x-diazido diimide (VI).



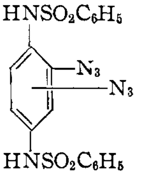
I



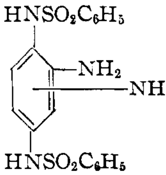
II



III



IV



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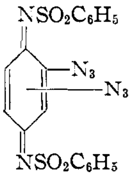

VI

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[1] An abstract of a thesis submitted by Dale C. Blomstrom to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Cincinnati Chemical Company Fellow, 1950–1951; Standard Oil Company of Indiana Fellow, 1951–1952.

[2] E. Oliveri-Mandala and E. Calderaro, *Gazz. chim. ital.*, **45I**, 307 (1915); **45II**, 120 (1915).

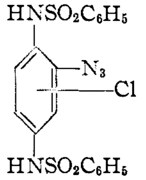
[3] A. Korczynski, *Bull. soc. chim.*, [4] **35**, 1186 (1924).

[4] K. Fries and P. Ochwat, *Ber.*, **56**, 1291 (1923).

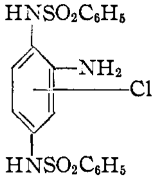
[5] R. Adams and W. Moje, THIS JOURNAL, **74**, 5560 (1952).

Treatment of VI with hydrazoic acid yielded only an amorphous brown solid which did not have the properties of an azide.

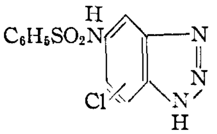
Addition of hydrogen chloride to III gave 2-azido - x - chloro - *p* - phenylenedibenzenesulfonamide (VII), which was reduced to the corresponding amine (VIII). Attempts were made to determine the orientation of the chloro and azido groups in VIII by conversion of the molecule to one of the known dichloro diamides through the Sandmeyer reaction. The product from the Sandmeyer reaction was not one of the desired dichloro diamides, but instead the analytical and infrared data indicated a benzotriazole (IX). Its formation can be explained by the reaction of the diazonium salt with the adjacent benzenesulfonamide group, followed by acid hydrolysis of the N^1-benzenesulfonyl group. Methylation and reduction of VII gave the N,^{1}N^4-dimethyl diamide (X). Application of the Sandmeyer reaction to X produced a mixture from which no pure compound could be isolated.



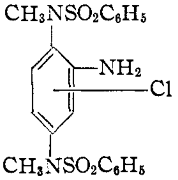
VII



VIII

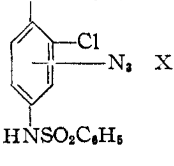


IX



X

Hydrazoic acid added to 2-methyl-*p*-quinonedibenzenesulfonimide to give x-azido-2-methyl-*p*-phenylenedibenzenesulfonamide. The addition of one mole of sodium azide failed to decolorize a suspension of 2-chloro-*p*-quinonedibenzenesulfonimide in acetic acid; an orange color persisted until about 1.4 moles of the reagent had been added. The product was a mixture of two compounds, neither of which was obtained analytically pure. The infrared spectrum of one was identical with that of the 2,x-diazido diamide (IV), and reduction of a somewhat impure sample gave a pure diamine identical in melting point and infrared spectrum with V. The diazide was undoubtedly formed by displacement of the chlorine from the 2-chloro diimide by an azide ion, followed by addition of hydrazoic acid to the resulting 2-azido diimide. The analysis and infrared spectrum of the second reaction product showed it to be *y*-azido-2-chloro-*p*-phenylenedibenzenesulfonamide (XI). The spectra of the two azidochloro diamides (VII and XI) and of the corresponding aminochloro diamides indicated that they were position isomers.

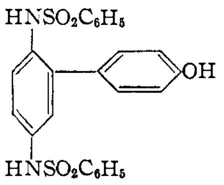


XI

p-Quinones add diazomethane to yield substituted pyrazoles,[6-9] and 1,4-naphthoquinonedibenzenesulfonimide was found to react in an analogous manner.[5] No pyrazole was obtained from diazomethane and *p*-quinonedibenzenesulfonimide however. Reduction to *p*-phenylenedibenzenesulfonamide occurred in both chloroform and dioxane, and in dioxane in the presence of sulfuric acid. Attempted catalysis of the addition with boron trifluoride in chloroform resulted in cleavage of benzenesulfonamide from the diimide. The product resulting from the reaction of diazomethane with 2-methyl-*p*-quinonedibenzenesulfonimide was an uncrystallizable amorphous yellow solid.

The reaction of *p*-benzoquinone with hydrogen cyanide yields 2,3-dicyanohydroquinone.[10] By contrast 1,4-naphthoquinonedibenzenesulfonimide in the presence of hydrogen cyanide and triethylamine is cleaved into benzenesulfonamide and 3,4 - dicyano - 1 - naphthalenebenzenesulfonamide.[11] *p*-Quinonedibenzenesulfonimide was found to react in still another fashion. In the presence of triethylamine or boron trifluoride two moles of benzenesulfonamide was cleaved from the diimide, indicating the probability of 1,2-addition exclusively. No other products could be isolated.

The reaction of *p*-benzoquinone with phenols in the presence of sulfuric acid yields substituted biphenyls formed by coupling at the para position of the phenols.[12-14] The aluminum chloride-catalyzed reaction yields the analogous 2,5-diadducts.[15,16] *p*-Quinonedibenzenesulfonimide and 1,4-naphthoquinonedibenzenesulfonimide undergo the Friedel–Crafts reaction with phenols and aluminum chloride or boron trifluoride to form the para coupling products exemplified by formula XII.[5,17] *p*-Quinonedibenzimide also gives the biphenyl derivative with phenol and boron trifluoride.[18]



XII

It has now been found that phenols add to *p*-quinonedibenzenesulfonimide in the presence of a catalytic amount of triethylamine to give products identical with those formed in the Friedel–Crafts reaction. The reactions were rapid, the products were relatively pure, and the yields were high. Phenol and *o*- and *m*-cresol were successfully added. The addition of *p*-cresol caused almost quantitative reduction to the diimide to *p*-phenyl-

(6) H. von Pechmann and E. Seel, *Ber.*, **32**, 2292 (1899).

(7) L. F. Fieser and M. A. Peters, THIS JOURNAL, **53**, 4080 (1931).

(8) L. F. Fieser and J. L. Hartwell, *ibid.*, **57**, 1479 (1935).

(9) E. Bergmann and F. Bergmann, *J. Org. Chem.*, **3**, 125 (1938).

(10) J. Thiele and J. Meisenheimer, *Ber.*, **33**, 675 (1900).

(11) R. Adams and W. Moje, THIS JOURNAL, **74**, 5562 (1952).

(12) S. Blumenfeld and P. Friedlander, *Ber.*, **30**, 1464, 2563 (1897).

(13) R. Pummerer and G. Huppmann, *ibid.*, **60B**, 1442 (1927).

(14) H. E. Ungnade and H. Hein, *J. Org. Chem.*, **14**, 911 (1949).

(15) R. Pummerer and E. Prell, *Ber.*, **55**, 3107 (1922).

(16) R. Pummerer, M. Dally and S. Reissinger, *ibid.*, **66**, 792 (1933).

(17) R. Adams and K. P. Eilar, THIS JOURNAL, **73**, 1149 (1951).

(18) R. Adams and D. S. Acker, *ibid.*, **74**, 5872 (1952).

enedibenzenesulfonamide. Anisole failed to react with the diimide, with or without the basic catalyst. The reaction is apparently a nucleophilic attack on the 1,4-conjugated system by a resonance form of the phenoxide ion.

Acknowledgment.—The authors are indebted to Mr. J. Nemeth, Mrs. Esther Fett and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas for the infrared determinations and interpretations.

Experimental

All melting points are corrected.

The 2-Azido-*p*-phenylenedibenzenesulfonamide.—To a stirred suspension of 14.65 g. of *p*-quinonedibenzenesulfonimide in 300 ml. of glacial acetic acid was added over a period of 5 minutes 3.8 g. of sodium azide in 10 ml. of water. The yellow color faded in a few minutes and part of the product crystallized from the solution. After one hour the mixture was poured into 500 ml. of water. The white product was filtered and washed with water. After one recrystallization from chloroform-petroleum ether (b.p. 80–100°) the yield was 15.33 g. (94%). The pure product melted at 165–166° (dec. with foaming, darkening from 155°).

Anal. Calcd. for $C_{18}H_{15}N_5O_4S_2$: C, 50.33; H, 3.52; N, 16.31. Found: C, 50.46; H, 3.79; N, 16.07.

All of the compounds containing the azide group are unstable to daylight; exposed samples become colored. Azido diamides were dried at 60° *in vacuo*, azido diimides were dried at room temperature *in vacuo*.

2-Amino-*p*-phenylenedibenzenesulfonamide. A.—To a boiling solution of 0.5 g. of 2-azido-*p*-phenylenedibenzenesulfonamide in 100 ml. of 3% aqueous sodium hydroxide was added portionwise 4 g. of sodium hydrosulfite. Heating was continued 30 minutes. Neutralization of the cold solution with acetic acid produced 0.43 g. (92%) of white solid. It crystallized from ethanol as slightly yellowish prisms, m.p. 232.5–233.5° (dec., with darkening from 227°).

Anal. Calcd. for $C_{18}H_{17}N_3O_4S_2$: C, 53.58; H, 4.25; N, 10.42. Found: C, 53.83; H, 4.18; N, 10.42.

Low-pressure hydrogenation of the 2-azido diamide over platinum oxide catalyst gave a 53% yield of the amine.

B.—To a boiling solution of 0.5 g. of 2-nitro-*p*-phenylenedibenzenesulfonamide[19] in 50 ml. of 2% aqueous sodium hydroxide was added 1 g. of sodium hydrosulfite. Acidification of the cold solution with acetic acid gave 0.35 g. (75%) of a gray product which was recrystallized from ethanol, m.p. 232.5–233.5° (dec., with previous darkening). It was identical with the product formed in A.

2-Azido-*p*-quinonedibenzenesulfonimide.—A suspension of 8 g. of 2-azido-*p*-phenylenedibenzenesulfonamide in 350 ml. of glacial acetic acid was stirred with 8.5 g. of lead tetraacetate. A clear red solution resulted. After 30 minutes 1 ml. of ethylene glycol was added and the solution was poured slowly into 1 l. of water. The gummy mass soon solidified. It was broken up into orange particles and filtered. The yield was 6.73 g. (85%). The compound crystallized from ethyl acetate–petroleum ether (b.p. 80–100°) as red-orange prisms, m.p. 129° (dec. with foaming).

Anal. Calcd. for $C_{18}H_{13}N_5O_4S_2$: C, 50.58; H, 3.06; N, 16.39. Found: C, 50.61; H, 3.12; N, 16.39.

2-Azido-x-chloro-*p*-phenylenedibenzenesulfonamide.—A solution of 2 g. of 2-azido-*p*-quinonedibenzenesulfonimide in 30 ml. of chloroform was shaken with 2 ml. of concentrated hydrochloric acid for one hour, then placed in the ice-box overnight. Into the pale orange solution was stirred 60 ml. of petroleum ether (b.p. 40–60°). The solution was returned to the ice-box for 2 hours. The yield of creamy needles was 2 g. (92%). The compound was recrystallized from ethyl acetate–petroleum ether (b.p. 80–100°), m.p. 178–179° (dec. with foaming, darkening from 150°).

Anal. Calcd. for $C_{18}H_{14}ClN_5O_4S_2$: C, 46.60; H, 3.04; N, 15.10. Found: C, 46.69; H, 3.00; N, 15.07.

2-Amino-x-chloro-*p*-phenylenedibenzenesulfonamide.—A solution of 3.5 g. of 2-azido-x-chloro-*p*-phenylenedibenzenesulfonamide and 6.5 g. of sodium hydrosulfite in 300 ml. of 3% aqueous sodium hydroxide was heated at 100° for 15 minutes. The solution was cooled and acidified with acetic acid. The yield of white solid was 3.17 g. (96%). Recrystallization from ethyl acetate and from ethanol yielded prisms melting at 224–225° (dec.).

Anal. Calcd. for $C_{18}H_{16}ClN_3O_4S_2$: C, 49.37; H, 3.68; N, 9.60. Found: C, 49.61; H, 3.67; N, 9.52.

5-Benzenesulfonamido-x-chlorobenzotriazole.—A solution of 0.37 g. of 2-amino-x-chloro-*p*-phenylenedibenzenesulfonamide in 3 ml. of concentrated sulfuric acid at 0–5° was treated with 0.09 g. of sodium nitrite. The mixture was diluted carefully with 10 g. of ice, the temperature being kept below 5° by external cooling. A buff-colored precipitate formed but was not isolated. The mixture was added to 0.3 g. of cuprous chloride in 5 ml. of concentrated hydrochloric acid. The temperature was raised slowly to 25°, then rapidly to 60–70°, where it was maintained for 10 minutes. No evolution of nitrogen was observed. The gray solid which separated (0.27 g.) was recrystallized from 50% ethanol. It melted at 210–211°, with softening at 208°.

Anal. Calcd. for $C_{12}H_9ClN_4O_2S$: C, 46.68; H, 2.94; N, 18.15. Found: C, 46.91; H, 3.20; N, 18.03.

The infrared spectrum was consistent with the postulated benzotriazole structure.

N^1,N^4-Dimethyl-2-amino-x-chloro-*p*-phenylenedibenzenesulfonamide.—A solution of 1.25 g. of 2-azido-x-chloro-*p*-phenylenedibenzenesulfonamide, 0.3 g. of potassium hydroxide and 4 g. of methyl iodide in 60 ml. of methanol was refluxed for 1.5 hours. One gram of methyl iodide was added and the refluxing was continued for an additional hour. The cooled solution was poured into 150 ml. of 3% aqueous sodium hydroxide. Filtration gave 1.05 g. (79%) of light tan crystals, m.p. 190.5–195.5° (dec. with foaming). The azide was not purified but was reduced directly to the amine.

A boiling solution of 1.05 g. of the crude azide in 150 ml. of ethanol and 80 ml. of acetone was diluted with 50 ml. of water, and 4 g. of sodium hydrosulfite was added in portions. The solution was boiled to a volume of 150 ml. and an equal volume of water was added. The yield of white solid which separated on cooling was 0.96 g. (96%). The compound crystallized from ethanol as fine white needles, m.p. 201–202°.

Anal. Calcd. for $C_{20}H_{20}ClN_3O_4S_2$: C, 51.55; H, 4.33; N, 9.02. Found: C, 51.75; H, 4.23; N, 9.11.

Attempts to convert this amine to a dichloro diamide *via* the Sandmeyer reaction were unsuccessful. A mixture of products was obtained from which no identifiable compound could be separated in a pure state.

2,x-Diazido-*p*-phenylenedibenzenesulfonamide.—To a stirred suspension of 4.73 g. of 2-azido-*p*-quinonedibenzenesulfonimide in 250 ml. of glacial acetic acid was added 0.80 g. of sodium azide. Stirring was continued for 2 hours. Filtration gave 4.8 g. (92%) of pale orange crystals. The compound was purified by dissolving it in the minimum amount of dimethylformamide at 70–80°, stirring in rapidly 2 volumes of hot methanol, and cooling the solution under running tap water. The pure compound was obtained as cream colored prisms, m.p. 198° (vigorous dec., darkening from 150°).

Anal. Calcd. for $C_{18}H_{14}N_8O_4S_2$: C, 45.95; H, 3.00; N, 23.82. Found: C, 46.07; H, 3.21; N, 23.85.

2,x-Diamino-*p*-phenylenedibenzenesulfonamide.—To a boiling solution of 120 ml. of 5% aqueous sodium hydroxide and 110 ml. of ethanol was added 1.5 g. of 2,x-diazido-*p*-phenylenedibenzenesulfonamide. A yellow solid precipitated at once. Four grams of sodium hydrosulfite was added portionwise while the solid was broken up with a stirring rod. The mixture was boiled for one hour, then the slight unreacted residue was removed and the solution was acidified. The gray-white product weighed 1.16 g. (87%). It was purified by dissolving it in dimethylformamide at 70–80°, stirring in one volume each of hot methanol and hot water, and cooling rapidly under the tap. The presence of about 5 mg. of sodium hydrosulfite decreased the formation of colored by-products during the purification. The compound crystallized as creamy leaflets, m.p. 257° (dec., darkening from 210°).

Anal. Calcd. for $C_{18}H_{18}N_4O_4S_2$: C, 51.66; H, 4.34; N, 13.39. Found: C, 51.60; H, 4.53; N, 13.29.

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[19] Kindly furnished by T. E. Young of this Laboratory.

Treatment of the diamine with biacetyl in ethanol and in acetic acid failed to yield an isolable quinoxaline.

2-x-Diazido-*p*-quinonedibenzenesulfonimide.—A suspension of 2.7 g. of 2,x-diazido-*p*-phenylenedibenzenesulfonamide in 250 ml. of glacial acetic acid was stirred for 20 hours with 2.65 g. of lead tetraacetate. After addition of 1 ml. of ethylene glycol the product was filtered and washed with petroleum ether. The yield of blood-red needles was 1.65 g. (61%). Pouring the filtrate into water gave 0.57 g. of a second crop of the diimide. Both crops detonated when heated to 109°. The compound was recrystallized from ethyl acetate–cyclohexane. A pure sample did not detonate, but charred in the range 110–180°.

Anal. Calcd. for $C_{18}H_{12}N_8O_4S_2$: C, 46.15; H, 2.58; N, 23.92. Found: C, 46.34; H, 2.65; N, 23.72.

The reaction of the diazido diimide with sodium azide in acetic acid produced a highly soluble brown amorphous solid which could not be purified.

x-Azido-2-methyl-*p*-phenylenedibenzenesulfonamide.—To a stirred suspension of 1.5 g. of 2-methyl-*p*-quinonedibenzenesulfonimide in 80 ml. of glacial acetic acid was added 0.5 g. of sodium azide in 3 ml. of water. After 30 minutes of stirring the mixture was colorless. The reaction mixture was poured into 200 ml. of water and the product was filtered and washed with water. The yield was 1.53 g. (92%). Recrystallization from ethyl acetate–petroleum ether (b.p. 80–100°) gave the pure product, m.p. 199.5° (dec. with foaming, darkening from 175°).

Anal. Calcd. for $C_{19}H_{17}N_5O_4S_2$: C, 51.45; H, 3.87; N, 15.79. Found: C, 51.66; H, 3.98; N, 15.88.

Reaction of 2-Chloro-*p*-quinonedibenzenesulfonimide with Hydrazoic Acid. A. 2,x-Diazido-*p*-phenylenedibenzenesulfonamide.—To a stirred suspension of 2 g. of 2-chloro-*p*-quinonedibenzenesulfonimide in 100 ml. of glacial acetic acid was added dropwise over a period of one hour a solution of 0.43 g. (1.4 moles) of sodium azide in 14 ml. of water. This was the quantity required to decolorize the suspension completely. The mixture was stirred for an additional hour, then 0.98 g. of pale yellow crystals was removed by filtration. The melting point of the purest sample obtainable by recrystallization from aqueous dioxane and aqueous dimethylformamide was 194° (with vigorous dec.).

Anal. Calcd. for $C_{18}H_{14}N_8O_4S_2$: C, 45.95; H, 3.00; N, 23.82; S, 13.63; Cl, 0.00. Found: C, 46.45; H, 3.16; N, 21.66; S, 13.66; Cl, 2.05.

The infrared spectrum of the compound was essentially identical to that of authentic 2,x-diazido-*p*-phenylenedibenzenesulfonamide. The chlorine-containing impurity was probably x-azido-2-chloro-*p*-phenylenedibenzenesulfonamide described below.

The product from a second run was reduced by the method described for the 2,x-diazido diamide. The crude reduction product was extracted with hot ethanol. The insoluble residue was purified to a melting point of 257° (dec.) by recrystallization from aqueous dimethylformamide. It was shown to be 2,x-diamino-*p*-phenylenedibenzenesulfonamide by the melting point of a mixture with an authentic sample and infrared spectra.

Anal. Calcd. for $C_{18}H_{18}N_4O_4S_2$: C, 51.66; H, 4.34; N, 13.39. Found: C, 51.61; H, 4.43; N, 13.32.

B. x-Azido-2-chloro-*p*-phenylenedibenzenesulfonamide.—The acetic acid filtrate from the original reaction mixture was poured into water and 1.02 g. of solid was obtained. It was recrystallized from ethyl acetate–cyclohexane and from aqueous methanol, m.p. 187° (dec. with foaming).

Anal. Calcd. for $C_{18}H_{14}ClN_5O_4S_2$: C, 46.60; H, 3.04; N, 15.10. Found: C, 46.68; H, 3.16; N, 16.07.

The infrared spectra of this azidochloro diamide and of the azidochloro diamide obtained from the azido diimide and hydrogen chloride showed that the two were position isomers. The principal differences were 15–20 cm.$^{-1}$ shifts in the frequencies of the –NH– and $-N_3$ bands and a marked difference in strength of an aromatic band at 1496 cm.$^{-1}$.

A portion of the crude product was reduced in the usual manner with sodium hydrosulfite. The solid obtained was extracted with hot ethanol. The solution was filtered through Filtercel and an equal volume of water was added. The white needles which separated were recrystallized from aqueous ethanol and from ethyl acetate, m.p. 213–215° (dec.).

Anal. Calcd. for $C_{18}H_{16}ClN_3O_4S_2$: C, 49.37; H, 3.68; N, 9.60. Found: C, 49.33; H, 3.58; N, 9.67.

The infrared spectra of this compound and the 2-amino-x-chloro diamide showed them to be position isomers.

Reaction of *p*-Quinonedibenzenesulfonimide with Diazomethane.—Solutions of 0.5 g. of *p*-quinonedibenzenesulfonimide in 30 ml. of dioxane and in 30 ml. of chloroform were each allowed to stand 2 days with 2.1 ml. (1.1 moles) of an ethereal solution of diazomethane. Only *p*-phenylenedibenzenesulfonamide could be isolated from the reaction mixtures. Addition of one drop of sulfuric acid to a second dioxane solution gave the same result. The presence of 2 drops of boron trifluoride etherate in another chloroform solution caused the cleavage of two moles of benzenesulfonamide from the diimide. A similar reaction of diazomethane and 2-methyl-*p*-quinonedibenzenesulfonimide in chloroform with no catalyst gave only an amorphous product.

Reaction of *p*-Quinonedibenzenesulfonimide with Hydrogen Cyanide.—A solution of 3 g. of *p*-quinonedibenzenesulfonimide and 2 drops of triethylamine in 50 ml. of chloroform and 30 ml. of liquid hydrogen cyanide (97% pure) was allowed to stand for 13 days at 10–15°. The solution was evaporated to 25 ml. with an air jet and 75 ml. of petroleum ether (b.p. 40–60°) was added. The solid product was removed and extracted with 300 ml. of ether. After removal of a slight residue the ether was evaporated. The yield of tan solid was 2.15 g. After recrystallization from water it melted at 151.5–152.5°, and was identified as benzenesulfonamide. The use of 3 drops of boron trifluoride etherate in place of the triethylamine catalyst gave virtually the same result. Potassium cyanide in glacial acetic acid caused reduction of the diimide to diamide.

2-(*p*-Hydroxyphenyl)-*p*-phenylenedibenzenesulfonamide.—To a solution of 0.5 g. of *p*-quinonedibenzenesulfonimide and 0.3 g. of phenol in 20 ml. of chloroform was added one drop of triethylamine. The color faded in 10–15 minutes and the product crystallized from the solution. The yield of the first crop was 0.52 g. (84%); dilution of the filtrate with petroleum ether precipitated 0.07 g. of a less pure product. Recrystallization from ethyl acetate–cyclohexane gave a product melting at 228.5–229.5° (dec.). It was shown to be identical with an authentic sample.

2-(4-Hydroxy-3-methylphenyl)-*p*-phenylenedibenzenesulfonamide.—The red-brown color which formed when *o*-cresol was used in place of phenol faded within 5 minutes and the product crystallized. The yield was 96%. The compound was recrystallized from ethyl acetate-cyclohexane, m.p. 219–220.5° (dec., darkening from 215°). Mixture with an authentic sample did not depress the melting point.

2-(4-Hydroxy-2-methylphenyl)-*p*-phenylenedibenzenesulfonamide.—When *m*-cresol was used the red-brown color faded in 10 seconds. The solution was evaporated and the residual oil was dissolved in ethanol. The addition of water caused the separation of an oil which crystallized on standing. Recrystallization from toluene containing a little ethanol gave the ethanol solvate, which melted at 100° with evolution of bubbles, resolidified and remelted at 175.5–178.5° (dec.). Drying at 120° for 10 hours *in vacuo* produced the unsolvated compound, m.p. 177–179° (dec.), identical with an authentic sample.

Reaction with *p*-Cresol and Anisole.—The addition of *p*-cresol to *p*-quinonedibenzenesulfonimide in chloroform or chloroform–ethanol resulted in quantitative reduction to *p*-phenylenedibenzenesulfonamide.

The diimide was quantitatively recovered from the attempted addition of anisole without catalyst. The presence of triethylamine caused reduction to *p*-phenylenedibenzenesulfonamide.

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