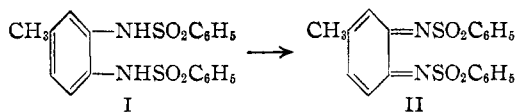


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. VIII. Synthesis and Reactions of *o*-Quinone DiimidesBY ROGER ADAMS AND C. N. WINNICK¹

o-Phenylenedibenzene-sulfonamide was oxidized by means of lead tetraacetate in glacial acetic acid to an ill-defined amorphous product probably formed by dimerization or polymerization of the initial reaction product, *o*-quinonedibenzene-sulfonimide. When substituents in the phenylenediamine ring were present, oxidation proceeded with the same reagent mixture or with acetic anhydride as solvent and *o*-quinonedibenzene-sulfonimides could be isolated in good yields. The 3-methyl-, 4-methyl-, 3,5-dimethyl-, 4,5-dimethyl-, 4-chloro-, 4,5-dichloro- and 3,4,5-trichloro-*o*-quinonedibenzene-sulfonimides were prepared. The products are orange-yellow to red and resemble *o*-quinones in their reactions. Upon treatment of the quinone diimides with hydrochloric acid, one mole of hydrogen chloride added to give chlorinated diimides. The position of the chlorine atom was determined where isomeric products were possible: 4-chloro to 4,5-dichloro; 4,5-dichloro to 3,4,5-trichloro; 3,4,5-trichloro to 3,4,5,6-tetrachloro; 4-methyl to 4-methyl-5-chloro; 3,5-dimethyl to 3,5-dimethyl-4-chloro; 4,5-dimethyl to 3-chloro-4,5-dimethyl.

The procedure for oxidation of *p*-phenylenedibenzene-sulfonamides to *p*-quinonedibenzene-sulfonimides² has now been applied to the oxidation of *o*-phenylenedibenzene-sulfonamides. Although Willstätter was able with silver oxide to obtain the unstable *p*-quinonediimine and its *N*-alkyl derivatives from the corresponding diamines, his attempted isolation of *o*-quinonediimine by the same method failed and only a product dimeric or polymeric in character was obtained.³ *o*-Phenylenedibenzene-sulfonamide is rapidly oxidized by lead tetraacetate in glacial acetic acid at room temperature. By diluting the reaction mixture with water, a brown amorphous product resulted which resisted all attempts to obtain it crystalline. The product was presumably dimeric or polymeric since the common reducing agents did not convert it to *o*-phenylenedibenzene-sulfonamide. The reduced product was red to alkali and green to acids. The structure of this compound has not been clarified. It was assumed that the *o*-quinonedibenzene-sulfonimide was probably the initial product of reaction but subsequent self-condensation occurred, possibly by one molecule reacting as a diene with another as a dienophile. This postulation is supported by oxidations performed on ring-substituted *o*-phenylenedibenzene-sulfonamides in which the diene function of the corresponding diimides is unquestionably less active. Under these structural conditions, the synthesis of monomeric *o*-phenylenedibenzene-sulfonimides was readily realized. Thus, the 3-methyl-, 4-methyl-, 4-chloro- and 4,5-dichloro-*o*-phenylenedibenzene-sulfonamides were converted to the diimides with lead tetraacetate in glacial acetic acid at room temperature. The oxidation of 4-methyl-*o*-phenylenedibenzene-sulfonamide (I) to the corresponding diimide (II) serves as an illustration. The diimides separated in essentially a

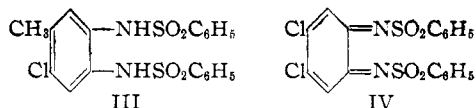


pure state directly from the reaction mixture. The oxidation of the 3,5- and 4,5-dimethyl-*o*-phenylene-

dibenzene-sulfonamides was found to proceed more satisfactorily in acetic anhydride at 60°. The products from these reactions are contaminated with lead acetate, which, however, after removing the acetic anhydride, is readily eliminated by treatment with water. The 3,4,5-trichloro diimide derivative was synthesized in ether as a solvent.

With exception of the 3-methyl derivative, the yields of diimides were 60–90%. Satisfactory solvents for recrystallization were difficult to find for the mono-substituted diimides and relatively large losses occurred in recrystallization. The di-substituted derivatives, on the other hand, were readily recrystallized. The diimides are stable substances and range in color from orange-yellow to carmine red. They melt with decomposition unsharply. They give yellow to red-violet colors with concentrated sulfuric acid. The diimides are readily reduced with zinc and acetic acid to the corresponding diamides. The 4-methyl derivative was also reduced to diamide with sulfur dioxide in water.

The orientation of the chlorine when hydrogen chloride was added to the various *o*-quinone diimides has been explored. Addition of hydrogen chloride takes place rapidly, merely by slurring the diimides in glacial acetic acid with gradual addition of concentrated hydrochloric acid. The reaction of 4-methyl-*p*-quinonedibenzene-sulfonimide and hydrogen chloride resulted in a mixture of monochloro derivatives of the corresponding amide which, after several crystallizations from glacial acetic acid, melted at a constant point, 200–201°. That a mixture was in hand was established by hydrolysis of the benzenesulfonamido groups to 4-methyl-5-chloro-*o*-phenylenediamine which was purified and identified as such by an unequivocal synthesis. When this pure diamine was benzenesulfonylated, the 4-methyl-5-chloro-*o*-phenylenedibenzene-sulfonamide (III) melted at 208–209°. Successful purification of the hydrogen chloride adduct to the quinone diimide was finally achieved through crystallization of the potassium salt from ethanol, followed by acidification. The chief product of the reaction is thus the 5-chloro derivative (III).



If concentrated hydrochloric acid in dioxane was used as a reagent, the products of reaction varied

(1) An abstract of a thesis submitted by C. N. Winnick to the Graduate College of the University of Illinois, 1951, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Standard Oil Company of Indiana Fellow, 1949–1950; Eastman Kodak Company Fellow, 1950–1951.

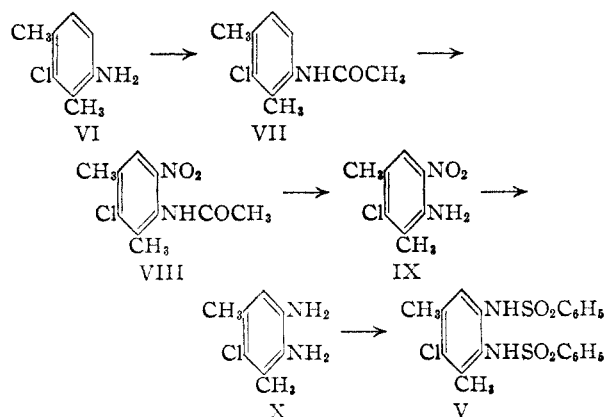
(2) R. Adams, *et al.*, *THIS JOURNAL*, **72**, 4601, 5154 (1950); **73**, 131, 1145, 1149, 1152, 2219 (1951).

(3) R. Willstätter and A. Pfannenstiel, *Ber.*, **38**, 2348 (1905).

with conditions and in different experiments two constant melting mixtures after recrystallization resulted, m.p. 172–173° or 190–191°. These mixtures gave proper analyses for a monochloro derivative but were not separated. They are assumed to contain more of the lower-melting isomers than the mixture obtained with glacial acetic acid as solvent.

A similar mixture attended the addition of hydrogen chloride to 4-chloro-*o*-quinonedibenzenesulfonimide. The principal product, purified through the potassium salt, proved to be 4,5-dichloro-*o*-phenylenedibenzenesulfonamide (IV). Its constitution was proved through its synthesis by the benzenesulfonylation of 4,5-dichloro-*o*-phenylenediamine which was made by reduction of the known 2-nitro-4,5-dichloroaniline. If concentrated hydrochloric acid in dioxane was used as reagent, a lower-melting mixture was isolated which analyzed for a product to which one mole of hydrogen chloride had been added.

Addition of hydrogen chloride by means of hydrochloric acid in acetic acid or less satisfactorily in dioxane to 3,5-dimethyl-*o*-quinonedibenzenesulfonimide resulted in a single product, the 3,5-dimethyl-4-chloro-*o*-phenylenedibenzenesulfonamide (V). Since the 3,5-dimethyl-4-chloro-*o*-phenylenediamine has not been described, it was synthesized by the following series of reactions (VI–X) from the



known 2-chloro-4-amino-*m*-xylene (VI). The structure of X as an *o*-diamine was established by treatment with benzil to form a quinoxaline, identified by the characteristic red color with concentrated sulfuric acid.

In the addition of hydrogen chloride to 4,5-dimethyl-, 4,5-dichloro- and 3,4,5-trichloro-*o*-quinonedibenzenesulfonimides, no isomeric products are possible and the 3-chloro-4,5-dimethyl-, the 3,4,5-trichloro and the 3,4,5,6-tetrachloro diamines were obtained, respectively.

4-Nitro-*o*-phenylenedibenzenesulfonamide was not oxidized to a diimide under the conditions which proved successful with the other derivatives.

The authors are indebted to Miss Elizabeth Petersen for determining, plotting and interpreting the infrared spectra and to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine D. Pih for micro-analytical work.

Experimental

Oxidation of *o*-Phenylenedibenzenesulfonamide.—Oxidation of *o*-phenylenedibenzenesulfonamide with lead tetra-

acetate was carried out in glacial acetic acid, in a mixture of glacial acetic acid and acetic anhydride, in benzene and in ether. The desired monomeric *o*-quinonedibenzenesulfonimide could not be isolated from any of the oxidations.

A solution of 1 g. of the diamide and 1.5 g. of lead tetraacetate in 40 ml. of glacial acetic acid was stirred for 45 minutes at room temperature. The solution turned deep red. By evaporation of the solvent, dilution with water, or addition of concentrated hydrochloric acid, only amorphous products resulted.

Oxidation of the diamide in a mixture of acetic acid and acetic anhydride at room temperature for 30 hours gave a deep red solution. Dilution of this with water gave a precipitate which was redissolved in acetic acid containing a little glycerol and poured into water. The reddish-brown precipitate weighed 6.5 g. It gave a dark green color with concentrated sulfuric acid. Hydrogenation of this product in dioxane over platinum oxide gave a green solution which on exposure to air returned to its initial red color. If the green solution was immediately diluted with a solution of sodium hydrosulfite a greenish precipitate was formed. This precipitate was an acid-base indicator, turning red when treated with base and green with acid.

Oxidation in presence of a larger amount of solvent, in benzene followed by dilution with petroleum ether and in dry ether resulted only in ill-defined products.

4-Methyl-*o*-quinonedibenzenesulfonimide.—A mixture of 9 g. of 4-methyl-*o*-phenylenedibenzenesulfonamide,⁴ m.p. 178–179° (cor.), and 10 g. of lead tetraacetate was stirred in 75 ml. of glacial acetic acid for 30 minutes at room temperature. After addition of a few drops of glycerol to the thick orange slurry, it was stirred for 5 minutes longer, cooled slightly, and the orange-yellow diimide collected on a filter. The yield was 6 g. (67%). This product is entirely satisfactory for subsequent reactions. It was recrystallized from 50 ml. of a mixture of equal parts of glacial acetic acid and freshly distilled nitromethane. Brief cooling in a Dry Ice-acetone bath was necessary to induce crystallization; orange plates, m.p. 155–160° (cor.) (dec.). It gives a red-violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{16}N_2O_4S_2$: C, 57.00; H, 4.00. Found: C, 56.92; H, 4.16.

The compound was reduced to the diamide by treating it with zinc in acetic acid or by shaking it for several days with a saturated aqueous solution of sulfur dioxide.

4-Methyl-5-chloro-*o*-phenylenedibenzenesulfonamide (A).—To a slurry of 2 g. of 4-methyl-*o*-quinonedibenzenesulfonimide in 30 ml. of glacial acetic acid was added 2 ml. of concentrated hydrochloric acid. After stirring for a few minutes, the solution was diluted with water and the adduct filtered off. The yield was 2 g. (91%). It was recrystallized repeatedly from acetic acid until a constant m.p. of 200–201° (cor.) was reached. The product was shown to be impure by hydrolysis⁵ to the 4-methyl-5-chloro-*o*-phenylenediamine dihydrochloride, purification and rebenzenesulfonylation described in (B). The diamine dihydrochloride was treated with alkali to give the free diamine which was purified by crystallization from benzene, m.p. 140–141° (cor.) (lit. m.p. 143°).⁶

The addition of hydrogen chloride by dissolving the diimide in dioxane and adding concentrated hydrochloric acid gave in separate experiments two mixtures of isomers, m.p. 172–173° and 190–191°.

A solution of 1 g. of the adduct of hydrogen chloride to 4-methyl-*o*-quinonedibenzenesulfonimide, m.p. 200–201° (cor.), in 25 ml. of hot 10% ethanolic potassium hydroxide was filtered and cooled. The salt (0.9 g.) which separated out was purified by three crystallizations from ethanol. Upon stirring the salt into dilute hydrochloric acid, the free diamine separated and was recrystallized from glacial acetic acid. It melted at 208–209° (cor.), gave no depression in melting point when mixed with an authentic sample of 4-methyl-5-chloro-*o*-phenylenedibenzenesulfonamide, m.p. 208–209° (cor.). The infrared spectra of both were identical.

Anal. Calcd. for $C_{19}H_{17}ClN_2O_4S_2$: C, 52.23; H, 3.90. Found: C, 52.52; H, 4.23.

(4) O. Hinsberg, *Ann.*, **265**, 190 (1891).

(5) R. E. Heckert, Ph.D. Thesis, University of Illinois, 1949.

(6) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **117**, 784 (1920).

(B).—4-Methyl-5-chloro-*o*-phenylenediamine was also prepared by stannous chloride reduction of 2-nitro-5-chloro-*p*-toluidine.⁷ A solution of 0.4 g. of this diamine in 5 ml. of pyridine was treated with 1 g. of benzenesulfonyl chloride. After standing a short time at room temperature, the solution was added to dilute hydrochloric acid. The precipitate weighed 1 g. (91%), and was purified by crystallization from glacial acetic acid, m.p. 208–209° (cor.).

4-Chloro-*o*-phenylenedibenzenesulfonamide.—To a solution of 25 g. of 4-chloro-*o*-phenylenediamine in 200 ml. of pyridine was added 75 g. of benzenesulfonyl chloride. The addition was carried out slowly with stirring. Most of the pyridine was then distilled off at atmospheric pressure and the residue taken up in 400 ml. of hot ethanol. To this solution was added 100 ml. of concentrated hydrochloric acid. The solution was treated with Darco and filtered hot. Upon cooling the product crystallized out. Additional product was obtained by dilution of the filtrate with water. The total yield was 60 g. (81%). It was purified by crystallization from ethanol, m.p. 154° (cor.).

Anal. Calcd. for $C_{12}H_9ClN_2O_2S_2$: C, 51.12; H, 3.55. Found: C, 51.42; H, 3.85.

4-Chloro-*o*-quinonedibenzenesulfonimide.—Using the same procedure as described for the 4-methyl derivative, 10 g. of 4-chloro-*o*-phenylenedibenzenesulfonamide and 10 g. of lead tetraacetate in 100 ml. of glacial acetic acid yielded 8 g. (80%) of diimide. Recrystallization of 0.4 g. of the diimide was accomplished from 8 ml. of a 9:1 mixture of redistilled nitrobenzene and glacial acetic acid by warming gently until dissolved, filtering and cooling for a period of time. It formed orange-yellow needles, m.p. 176–178° (cor.) (dec.). It gives a red-violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{12}H_7ClN_2O_4S_2$: C, 51.37; H, 3.11. Found: C, 51.30; H, 3.23.

This diimide is reduced to the diamide by zinc and acetic acid.

4,5-Dichloro-*o*-phenylenedibenzenesulfonamide (A).—A slurry of 1 g. of 4-chloro-*o*-quinonedibenzenesulfonimide in 30 ml. of glacial acetic acid was treated with 2 ml. of concentrated hydrochloric acid. After stirring for 5 minutes the nearly colorless solution was diluted with 200 ml. of water. The precipitate weighed 1 g. (93%). After several recrystallizations from ethanol it melted at 174° but it was shown to be impure. Hydrolysis of this product in a manner similar to that used for hydrolysis of 4-methyl-5-chloro-*o*-phenylenedibenzenesulfonamide gave a 20% yield of 4,5-dichloro-*o*-phenylenediamine which was purified from petroleum ether (b.p. 80–110°), m.p. 162–163° (cor.). The addition of hydrogen chloride by dissolving the diimide in dioxane and adding concentrated hydrochloric acid gave a mixture of isomers melting at 161–162°.

The adduct from hydrogen chloride and 4-chloro-*o*-quinonedibenzenesulfonimide, m.p. 174°, was purified through the potassium salt in the same manner previously described for 4-methyl-5-chloro-*o*-phenylenedibenzenesulfonamide. The product after crystallization from glacial acetic acid had an m.p. 186–187° (cor.) and gave no depression in melting point upon mixture with the product made by benzenesulfonylating 4,5-dichloro-*o*-phenylenediamine. The infrared spectra were also identical.

Anal. Calcd. for $C_{12}H_6Cl_2N_2O_4S_2$: C, 47.26; H, 3.06. Found: C, 47.52; H, 2.98.

(B).—4,5-Dichloro-*o*-phenylenediamine was also prepared by reduction of 2-nitro-4,5-dichloroaniline. A mixture of 1 g. of 2-nitro-4,5-dichloroaniline, m.p. 176° (cor.) (lit. 175–176°),⁸ and 3.8 g. of crystalline stannous chloride in 15 ml. of concentrated hydrochloric acid was heated on the steam-bath for one hour. After cooling, the solution was neutralized with sodium hydroxide and the solid diamine filtered off. The yield was 0.8 g. (94%). It was purified by recrystallization from a mixture of equal parts of benzene and petroleum ether (b.p. 80–110°), m.p. 162–163° (cor.).

Anal. Calcd. for $C_6H_3Cl_2N_2$: C, 40.68; H, 3.39. Found: C, 40.86; H, 3.38.

A solution of 0.9 g. of this diamine in 10 ml. of pyridine was treated with 2 g. of benzenesulfonyl chloride. After

15 minutes at room temperature, the solution was poured into dilute hydrochloric acid. The precipitate weighed 2 g. (90%). The crude product was boiled with 40 ml. of ethanol and filtered hot from insoluble by-product. The filtrate was cooled and the product separated. It was crystallized from glacial acetic acid, m.p. 186–187° (cor.).

4,5-Dimethyl-*o*-phenylenedibenzenesulfonamide.—The reduction of 20 g. of 4,5-dimethyl-*o*-nitraniline was carried out according to a previously described procedure⁹ except that twice the proportional amount of ethanol was used and the mixture was refluxed for 2 hours. The yield of diamine was 14 g. (85%). To a solution of 14 g. of 4,5-dimethyl-*o*-phenylenediamine in 70 ml. of pyridine, 36 g. of benzenesulfonyl chloride was added slowly with cooling and the mixture allowed to stand for 30 minutes at room temperature. Upon pouring into 350 ml. of hot 50% aqueous methanol and cooling, the product was obtained. The yield was 35 g. (81%). It was purified by recrystallization from dimethylformamide, m.p. 238° (cor.).

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2$: C, 57.76; H, 4.80. Found: C, 58.10; H, 4.84.

4,5-Dimethyl-*o*-quinonedibenzenesulfonimide.—A mixture of 4 g. of 4,5-dimethyl-*o*-phenylenedibenzenesulfonamide and 4.4 g. of lead tetraacetate in 40 ml. of acetic anhydride was stirred for 15 minutes at 60–70°. After cooling in an ice-bath, the precipitate was filtered off and dried. It weighed 5.7 g. It was washed well with water to remove the lead acetate leaving 2.6 g. (65%) of the orange diimide which was purified by recrystallization from ethyl acetate, m.p. 181–186° (cor.) (dec.). It gives a yellow color with concentrated sulfuric acid.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2$: C, 57.97; H, 4.35. Found: C, 57.90; H, 4.44.

This diimide was reduced to the diamide with zinc and acetic acid.

3-Chloro-4,5-dimethyl-*o*-phenylenedibenzenesulfonamide.—A slurry of 1 g. of 4,5-dimethyl-*o*-quinonedibenzenesulfonimide in 30 ml. of acetic acid was treated with 1 ml. of concentrated hydrochloric acid. After stirring for a few minutes the mixture was heated to boiling, cooled and diluted with water. The nearly white precipitate weighed 1 g. (92%). It was purified by recrystallization from a mixture of 3:2 pyridine and water, m.p. 206–207° (cor.).

Anal. Calcd. for $C_{20}H_{19}ClN_2O_4S_2$: C, 53.27; H, 4.22. Found: C, 53.57; H, 4.42.

3,5-Dimethyl-*o*-phenylenedibenzenesulfonamide.—The reduction of 16.6 g. of 4,6-dimethyl-*o*-nitraniline was carried out according to the directions for the 4,5-dimethyl compound.⁹ A mixture of 20 g. of zinc, 40 ml. of ethanol and 8 ml. of 20% aqueous sodium hydroxide was refluxed for 3 hours. The yield of diamine was 13 g. (95%). To a solution of 13 g. of 3,5-dimethyl-*o*-phenylenediamine in 75 ml. of pyridine was added in small portions 35 g. of benzenesulfonyl chloride. After standing for 1 hour at room temperature the solution was poured into 400 ml. of hot 50% aqueous methanol and cooled. The precipitate weighed 22 g. An additional 9 g. was obtained by dilution of the filtrate with water. The product was purified by recrystallization from ethanol, m.p. 175° (cor.).

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2$: C, 57.76; H, 4.80. Found: C, 57.73; H, 4.91.

3,5-Dimethyl-*o*-quinonedibenzenesulfonimide.—A mixture of 10 g. of 3,5-dimethyl-*o*-phenylenedibenzenesulfonamide and 11 g. of lead tetraacetate in 80 ml. of acetic anhydride was stirred for 40 minutes at 60–65°. After cooling in an ice-salt-bath, the red product was collected by filtration and dried. It was then washed well with water leaving 8 g. (80%) of the carmine-colored diimide. It was purified by recrystallization from glacial acetic acid, m.p. 177–183° (cor.) (dec.). It gives a yellow color on treatment with concentrated sulfuric acid.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2$: C, 57.97; H, 4.35. Found: C, 57.83; H, 4.27.

This diimide was reduced to the diamide with zinc and acetic acid.

3,5-Dimethyl-4-chloro-*o*-phenylenedibenzenesulfonamide.—A slurry of 2 g. of 3,5-dimethyl-*o*-quinonedibenzenesulfonimide in 25 ml. of glacial acetic acid was treated with

(7) J. J. Blanksma, *Rec. trav. chim.*, **29**, 414 (1910).

(8) J. J. Blanksma, *ibid.*, **21**, 420 (1902).

(9) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 501.

2 ml. of concentrated hydrochloric acid. The mixture was stirred for 10 minutes, warmed until the color was discharged, cooled and diluted with water. The precipitate weighed 2 g. (92%). It was purified by recrystallization from glacial acetic acid, m.p. 199° (cor.).

Anal. Calcd. for $C_{20}H_{15}ClO_4N_2S_2$: C, 53.26; H, 4.22. Found: C, 53.33; H, 4.46.

3,5-Dimethyl-4-chloro-*o*-phenylenedibenzene sulfonamide. 2-Chloro-4-nitro-*m*-xylene.—A solution of 11 g. of 2-amino-4-nitro-*m*-xylene,¹⁰ m.p. 80–81°, in 200 ml. of concentrated hydrochloric acid was cooled in an ice-salt-bath. A solution of 4.6 g. of sodium nitrite in 20 ml. of water was added slowly, keeping the temperature at –10 to 0°. The resulting solution was poured into a cold solution of 7.3 g. of cuprous chloride in 200 ml. of concentrated hydrochloric acid. The mixture was allowed to warm to room temperature and then heated to 50°. After cooling it was diluted with an equal volume of water and the precipitate collected. The yield was 8.5 g. (69%) of waxy material. Recrystallized to constant melting point from ethanol, it melted at 48–49° (cor.) (lit., m.p. 46–47°).¹¹

2-Chloro-4-amido-*m*-xylene.—A mixture of 5 g. of 2-chloro-4-nitro-*m*-xylene and 21 g. of crystalline stannous chloride in a mixture of 30 ml. of ethanol and 30 ml. of concentrated hydrochloric acid was stirred until the exothermic reaction had subsided. It was then stirred for 10 minutes longer on a steam-bath. After cooling, it was diluted with 60 ml. of water and neutralized with sodium hydroxide, keeping the mixture cold. The precipitate was filtered off and dried. It was then boiled with 50 ml. of benzene and filtered. The filtrate was evaporated to dryness leaving 3.5 g. (83%) of the amine. A portion was purified by recrystallization from petroleum ether (b.p. 80–110°), m.p. 48–49° (cor.) (lit., m.p. 48–49°).¹¹

2-Chloro-4-acetamido-*m*-xylene.—A solution of 3 g. of 2-chloro-4-amino-*m*-xylene in 50 ml. of water and 1.7 ml. of concentrated hydrochloric acid was heated to boiling (Darco) and filtered. The filtrate was warmed to 50° and 2.4 ml. of acetic anhydride stirred in, followed immediately by a solution of 3 g. of crystalline sodium acetate in 10 ml. of water. The mixture was stirred vigorously for a few minutes, cooled, and the precipitate collected by filtration. The yield was 3.5 g. (92%). It was purified by recrystallization from ethanol, m.p. 156–157° (cor.).

Anal. Calcd. for $C_{10}H_{12}ClNO$: C, 60.76; H, 6.07. Found: C, 60.81; H, 6.09.

2-Chloro-4-acetamido-5-nitro-*m*-xylene.—To a mixture of 6 g. of fuming nitric acid (sp. gr. 1.50) and 2 g. of acetic acid at room temperature, 3 g. of 2-chloro-4-acetamido-*m*-xylene was added in small portions. The addition was complete in 15 minutes and the mixture was allowed to stand for 30 minutes longer. It was then poured into ice and water. The precipitate weighed 3.5 g. (94%). It was purified by recrystallization from ethanol, m.p. 188–189° (cor.).

Anal. Calcd. for $C_{10}H_{11}ClN_2O_5$: C, 49.48; H, 4.53. Found: C, 50.11; H, 4.70.

2-Chloro-4-amino-5-nitro-*m*-xylene.—A mixture of 3 g. of 2-chloro-4-acetamido-5-nitro-*m*-xylene and 50 ml. of 20% hydrochloric acid was refluxed for 1 hour and the solution filtered hot through glass wool. The solid residue was taken up in 50 ml. more of hot 20% hydrochloric acid and filtered. The combined filtrates were diluted with several volumes of water and the orange-yellow precipitate collected on a filter. The yield of nitro amine was 1.8 g. (72%). It was purified by recrystallization from 50% aqueous ethanol; orange crystals, m.p. 137° (cor.).

Anal. Calcd. for $C_8H_7ClN_2O_2$: C, 47.88; H, 4.49. Found: C, 47.88; H, 4.52.

2-Chloro-4,5-diamino-*m*-xylene.—A mixture of 1.3 g. of 2-chloro-4-amino-5-nitro-*m*-xylene and 5 g. of crystalline stannous chloride in 30 ml. of concentrated hydrochloric acid was stirred for 15 minutes at room temperature and then for 30 minutes on a steam-bath. The solution was cooled, diluted with an equal volume of water and neutralized with sodium hydroxide keeping the mixture cool. The solid diamine, contaminated with inorganic material, was filtered off and recrystallized from petroleum ether (b.p. 30–60°), m.p. 82–83° (cor.).

(10) E. Noetting and L. Stocklin, *Ber.*, **24**, 568 (1891).

(11) E. Hoffa and E. Thoma, German Patent 510,438; C. A., **25**, 973 (1931).

Anal. Calcd. for $C_8H_{11}ClN_2$: C, 56.30; H, 6.45. Found: C, 56.23; H, 6.40.

The diamine was warmed in glacial acetic acid with an equivalent weight of benzil. The acetic acid was evaporated and the solid residue tested with a drop of concentrated sulfuric acid. An intense red color developed typical of a quinoxaline.

A solution of 1 g. of 3,5-dimethyl-4-chloro-*o*-phenylenediamine in 10 ml. of pyridine was treated with 2 g. of benzenesulfonyl chloride. After standing for 15 minutes at room temperature, the solution was poured into dilute hydrochloric acid. The precipitate was filtered off. The yield was 1.5 g. (56%). After one recrystallization from toluene followed by recrystallization from glacial acetic acid it melted at 198–199° (cor.). The infrared spectrum is identical with that of the compound obtained by addition of hydrogen chloride to the 3,5-dimethyl diimide. A melting point of a mixture of these compounds showed no depression.

4,5-Dichloro-*o*-quinonedibenzene sulfonimide.—A mixture of 2 g. of 4,5-dichloro-*o*-phenylenedibenzene sulfonamide, m.p. 186–187° (cor.), and 2 g. of lead tetraacetate in 30 ml. of glacial acetic acid was stirred for 20 minutes at room temperature. A few drops of ethylene glycol were added and stirring continued for 5 minutes. The thick orange-yellow slurry of the diimide was filtered. The yield of orange-yellow diimide was 1.8 g. (90%). It was recrystallized from ethyl acetate, giving wooly orange needles, m.p. 185–186° (cor.) (dec.). It gives a red-violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{12}H_8Cl_2N_2O_4S_2$: C, 47.47; H, 2.64. Found: C, 47.73; H, 2.77.

3,4,5-Trichloro-*o*-phenylenedibenzene sulfonamide.—To a slurry of 1 g. of 4,5-dichloro-*o*-quinonedibenzene sulfonimide in 25 ml. of glacial acetic acid was added 1 ml. of concentrated hydrochloric acid. The mixture was stirred until colorless, diluted with several volumes of water and the precipitate collected on a filter. The yield was 1 g. (93%). It was purified by recrystallization from ethanol, 207–208° (cor.).

Anal. Calcd. for $C_{12}H_5Cl_3N_2O_4S_2$: C, 43.95; H, 2.64. Found: C, 44.21; H, 2.78.

3,4,5-Trichloro-*o*-quinonedibenzene sulfonimide.—A mixture of 4.2 g. of 3,4,5-trichloro-*o*-phenylenedibenzene sulfonamide and 5 g. of dry lead tetraacetate in 500 ml. of anhydrous ether was stirred for 30 minutes at room temperature. The mixture was filtered and the precipitate dried and washed with water. The red product, weighing 4 g., was crude diimide. The ether filtrate was evaporated to dryness leaving 0.8 g. of the red diimide. One gram of the crude diimide from the precipitate was recrystallized from a mixture of equal parts of ether and petroleum ether (b.p. 30–60°) by cooling in a Dry Ice-acetone-bath. The red diimide melted at 155–157° (cor.) (dec.). It gives a red-violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{12}H_3Cl_3N_2O_4S_2$: C, 44.13; H, 2.25. Found: C, 44.43; H, 2.37.

Tetrachloro-*o*-phenylenedibenzene sulfonamide.—A solution of 0.8 g. of 3,4,5-trichloro-*o*-quinonedibenzene sulfonimide (which had been obtained from the ether filtrate in the previous experiment) in 25 ml. of acetic acid was treated with 0.5 ml. of concentrated hydrochloric acid. After stirring for 15 minutes, the solution was colorless. It was diluted with water. The precipitate weighed 0.6 g. (70%). It was purified by recrystallization from glacial acetic acid, m.p. 230–231° (cor.).

Anal. Calcd. for $C_{12}HCl_4N_2O_4S_2$: C, 41.06; H, 2.28. Found: C, 41.23; H, 2.55.

3-Methyl-*o*-phenylenedibenzene sulfonamide.—A mixture of 10 g. of 2-amino-3-nitrotoluene, m.p. 96–97° (cor.), and 58 g. of crystalline stannous chloride was stirred until the initial exothermic reaction had subsided. It was then heated on a steam-bath for 15 minutes, cooled and neutralized with sodium hydroxide. The mixture was allowed to stand in the refrigerator for several hours until the diamine solidified.¹² The yield was 7.5 g. (94%). To a solution of 7.5 g. of 3-methyl-*o*-phenylenediamine in 100 ml. of pyridine, 22 g. of benzenesulfonyl chloride was added in one portion. After the reaction mixture had cooled, it was

(12) S. Gabriel and A. Thieme, *Ber.*, **52**, 1081 (1919).

heated to boiling and then allowed to stand for 15 minutes. It was poured into cold dilute hydrochloric acid. The precipitate weighed 18 g. (72%). After several recrystallizations from glacial acetic acid it melted at 188–189° (cor.).

Anal. Calcd. for $C_{10}H_{18}N_2O_4S_2$: C, 56.71; H, 4.48. Found: C, 56.75; H, 4.68.

3-Methyl-*o*-quinonedibenzenesulfonimide.—A mixture of 1 g. of 3-methyl-*o*-phenylenedibenzenesulfonamide and 1.1 g. of lead tetraacetate in 10 ml. of glacial acetic acid was stirred for 30 minutes at 85–90°. The red solution was cooled and the red diimide was filtered off. The yield was 0.3 g. (30%). It was recrystallized from a mixture of equal parts of anhydrous ether and petroleum ether (b.p. 30–60°) by cooling in a Dry Ice-acetone-bath; m.p. 133–135° (cor.) (dec.). It gives a light red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{16}N_2O_4S_2$: C, 57.00; H, 4.00. Found: C, 57.29; H, 4.25.

4-Nitro-*o*-phenylenedibenzenesulfonamide.—To a solution of 10 g. of 4-nitro-*o*-phenylenediamine in 75 ml. of py-

ridine was added 24 g. of benzenesulfonyl chloride. The mixture was allowed to stand for 24 hours at room temperature. It was then poured into 200 ml. of concentrated hydrochloric acid and diluted with an equal volume of water. The brown precipitate was filtered off and stirred into 200 ml. of boiling ethanol and filtered. The residue was extracted with another 100 ml. of hot ethanol leaving 8.2 g. (23%) of product. It was purified by recrystallization from glacial acetic acid; white crystals, m.p. 199° (cor.).

Anal. Calcd. for $C_{18}H_{16}N_2O_6S_2$: C, 49.89; H, 3.46. Found: C, 49.98; H, 3.54.

The filtrates from the ethanol extractions were cooled and the precipitate collected. The yield was 14.5 g. of brown product which is probably the monobenzenesulfonyl derivative.

Attempts to oxidize the 4-nitro-*o*-phenylenedibenzene-sulfonamide in acetic acid with lead tetraacetate were unsuccessful. Only starting material was recovered.

URBANA, ILLINOIS

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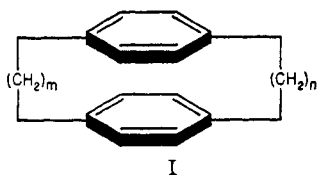
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. I. Preparation and Spectra of the Paracyclophanes

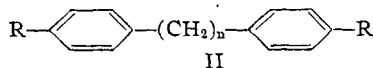
BY DONALD J. CRAM AND H. STEINBERG¹

A macrocyclic system has been prepared by the use of high dilution techniques in which two benzene rings are joined in the para positions by two and two, two and three, two and four, and three and six carbon bridges. The name, "paracyclophane," is suggested for this class of compound. The ultraviolet and infrared absorption spectra of the cycles are compared to the open chain analogs, and the abnormalities of the cycles are attributed to interstitial resonance effects and to the effects of distortion of the benzene rings from planarity.

Of particular interest in the field of molecular structure is the system (I) in which two benzene rings are rigidly held in a face to face position by methylene bridges in the para positions. The name, "paracyclophane," is suggested for this class

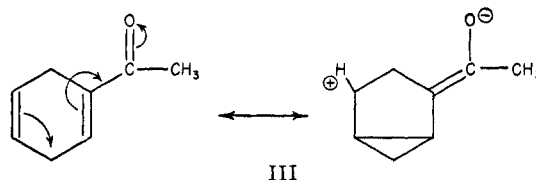


of compound. Such a system offers the unusual opportunity to study the effect of electronic interactions of unsaturated centers in a molecule whose geometry is known and capable of only small variations. When m and n are small, the proximity of the faces of the benzene rings may result in π -orbital overlap which would be expected to produce a marked change in the ultraviolet absorption spectrum of I as compared to the open chain analogs (II). Such a direct spatial electronic interaction is a probable explanation of the ob-



served shift to longer wave lengths and decrease in intensity of the ultraviolet absorption maximum of 2,5-dihydroacetophenone (III) as compared to 1-acetylcyclohexene.^{2,3} Bartlett, *et al.*,⁴ have applied an analogous explanation to account for the

abnormalities in the ultraviolet absorption spectrum of triptycene.



Should there exist interstitial resonance effects of some sort between the two benzene rings in I,⁵ the aromatic properties of this type of compound should be considerably modified. Thus the rates of aromatic substitution of the paracyclophanes as compared to their open chain analogs should be different. With the introduction of groups into one ring the question of the directive and activating (or deactivating) effect on the introduction of groups into the other ring becomes pertinent. A further point of interest in this class of compound lies in the types of molecular asymmetry (due to restricted rotation) that become possible with the successive introduction of functional groups into the benzene rings. Finally, it is hoped that the construction of intramolecular "molecular complexes" (e.g., intramolecular picrate-like salts) will be possible in this system. Thus substitution of electron releasing groups in one ring and electron withdrawing groups in the other should set up strong attractive forces between the aromatic

(1) Atomic Energy Commission Predoctoral Fellow, 1949–1951.

(2) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 52 (1948).

(3) E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *ibid.*, 607 (1949); see also J. C. Lunt and F. Sondheimer, *ibid.*, 3361 (1950).

(4) P. D. Bartlett and E. S. Lewis, *THIS JOURNAL*, **72**, 1005 (1950).

(5) M. J. S. Dewar, *Nature*, **156**, 784 (1945), and *J. Chem. Soc.*, 406 (1946), has discussed the possible existence of π -complexes as intermediate species in intramolecular rearrangements involving aromatic nuclei (such as the benzidine rearrangement). In each case, however, the complex was composed of a cationic and an anionic part rather than two electronically equivalent components. See G. S. Hammond and H. J. Shine, *THIS JOURNAL*, **72**, 220 (1950).