heated in a test-tube with 5–6 drops of 0.5 H_2SO_4 for 10–15 minutes in a steam-bath. A strong cresolic odor was noticed. In a larger sample similarly treated *p*-cresol was identified and determined by ultraviolet analysis (absorption band at 279 mμ), which also showed a strong absorption band at 226 mμ in the acidified and ether-extracted alkaline wash. An even stronger band at the same wave length was obtained with the original (although ether-extracted) reaction mixture. The location of the band is consistent with the assumption of structure M.

Hydrogenation of *p*-Menthenetriol II.—1.69 g. of II was dissolved in 40 ml. water and hydrogenated at atmospheric pressure in a closed system which allowed the volumetric measurement of the hydrogen absorbed; 1.2 g. of platinum oxide catalyst was used and the mixture was agitated by a magnetic stirrer; 1.08% hydrogen was absorbed. The product was crystallized from ethyl acetate. Two crops, 0.74 and 0.7 g., were obtained, melting point 139–140°.

Conversion of *p*-Menthanetriol VIII to the Tribromide.—To the second crop of the above hydrogenated crystals 12.7 g. of a 40% hydrogen bromide solution in glacial acetic acid was added in a Pyrex weighing bottle. The solid was dissolved with shaking in about 15–30 minutes, but shortly after the whole mixture solidified to a purplish brown crystalline mass. Small pieces of ice were added, while cooling from the outside in ice water. The whole mixture was then filtered on a fritted glass funnel and the solids were washed with water, 4% sodium bicarbonate and again with water until neutral to litmus. The product was dried at 50° in vacuum. After two recrystallizations from isopropyl alcohol, it melted at 106–108°. Mixed melting point with an authentic (see below) 1,4,8-tribromo-*p*-menthane was 108.5°.

Preparation of 1,4,8-Tribromo-*p*-methane.—Anhydrous hydrogen bromide was passed into 100 g. of steam-distilled dipentene ($n^{20}D$ 1.4728) in an all-glass apparatus which was cooled in a water-bath. After six hours, 113 g. of hydrogen bromide had been absorbed. The reaction mixture was almost completely solidified, white crystals in a purplish-brown liquid. The solid was triturated with cold methanol; weight of vacuum-dried product, 83.7 g. A small sample was recrystallized from ethanol, melting points 63–63.5°. Wallach gives melting point 64° for his "dipentene dihydrobromide."[18] The main product, without recrystallization, was brominated according to Wallach's procedure[10] which was improved by washing the crude tribromide crystals with ethanol, or recrystallizing from this solvent. The yield was low, 21.2 g., and the product melted at 108.5°.

Acknowledgment.—We are indebted to Professor C. C. Price of the University of Notre Dame for stimulating suggestions and to Eleanor I. Lansing for assistance in the experimental work. Dr. Evelyn Cook of this laboratory took the ultraviolet absorption readings.

Summary

1. The structure and the chemical behavior of the water-soluble products, obtained from terpinolene by oxidation with molecular oxygen in aqueous dispersion, were investigated.

2. It was shown that the three crystalline *p*-menthenetriols (m. p. 136, 124 and 121°, respectively) are new compounds and that even their hydrogenation products are different from the known menthanetriols.

3. Oxidation experiments (a) on the high-melting (136°) isomer with peracetic acid, followed by periodic acid titration of the resulting trihydric cineole, and (b) on both the menthenetriol and its hydrogenation product with chromic acid yielding "β-thujaketolactone" and "homoterpenyl methyl ketone," respectively, proved that the substance is a 3-*p*-menthene-1,2,8-triol.

4. The structure of the isomer melting at 124° was determined by two independent methods: (a) periodic acid oxidation followed by acid dehydration to yield acetone and *p*-cresol, and (b) hydrogenation followed by reaction with hydrogen bromide to yield Wallach's 1,4,8-tribromo-*p*-menthane, so that the compound must be a 2-*p*-menthene-1,4,8-triol.

5. A reaction mechanism based on resonance between two free radicals with alternative conjugated-double-bond systems is offered to explain the formation of the two triols.

WILMINGTON, DELAWARE RECEIVED DECEMBER 12, 1949

---

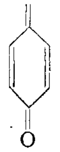
[18] Wallach, *Ann.*, **239**, 3 (1887).

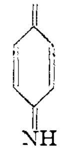
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. I. *p*-Quinone Disulfonimides

BY ROGER ADAMS AND A. S. NAGARKATTI[1]

p-Quinone mono- (I) and di-imines (II) were first prepared by Willstätter[2] by oxidation of *p*-aminophenol or *p*-phenylenediamine to the *p*-quinone monochloroimine or dichloroimine with bleaching powder followed by treatment of the products with hydrogen chloride. A more satisfactory procedure was oxidation of the appropriate aromatic amines in dry ether by means of dry silver oxide.


I


II

The products are colorless. They are very unstable to light, acids or in solution and polymerize with great ease. A characteristic property is the ease of hydrolysis to ammonia or amines and

---

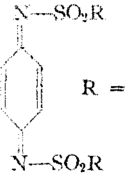
[1] An abstract of a thesis submitted by Mr. A. S. Nagarkatti to the Graduate College of the University of Illinois, 1949, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] Willstätter and Mayer, *Ber.*, **37**, 1494 (1904); Willstätter and Pfannensteil, *ibid.*, **37**, 4605 (1904); **38**, 2244 (1905); Kehrmann and Cordone, *ibid.*, **56**, 2398 (1923); Cordone, *Helv. Chim. Acta*, **7**, 956 (1924).

p-quinone. *p*-Quinone mono- and di-imines with alkyl groups substituted on the nitrogen atom or in the ring have also been prepared and their stability is recorded as only slightly greater than that of the unsubstituted compounds. The N-aryl or N,N′-diaryl analogs are definitely more stable. In the form of their salts, the hydroxy- and amino-phenyl-*p*-quinone imines behave as dyes but are of little importance because of ease of hydrolysis in acid solution to *p*-quinone and an amine or aminophenol. On the other hand, important color formers in photography fall in this class of compounds The phenazine and thiazine dyes are also salts of complex *p*-quinone diimines and exhibit a stability which permits commercial use.

The reactions of *p*-quinone mono- and di-imine and their alkyl derivatives have been virtually unexplored because of the difficulty of preparation and their instability. Only recently has it been demonstrated that *p*-quinone mono- and di-imines condense with cyclopentadiene in a manner similar to *p*-benzoquinone.[3]

The acyl, aroyl, alkylsulfonyl, arylsulfonyl and related derivatives of *p*-phenylenediamine or *p* aminophenol should undergo oxidation and it might be expected that the resulting *p*-quinone diimides would be more stable than the aryl or alkyl analogs. No *p*-quinone diimide of this type has previously been reported, though a mixture of lead dioxide and *p*-phenylenedi-*p*-toluenesulfonamide is described in a patent[4] as a vulcanizer for rubber and the author postulates that the activity is probably due to the corresponding *p*-quinone diimide formed *in situ*. This preliminary paper covers the oxidation of various disulfonamides of *p*-phenylenediamine and certain of its ring-substituted derivatives, the isolation of the *p*-quinone diimides and a description of some of their chemical properties.



R = C_6H_5–, *p*-$CH_3C_6H_4$–, CH_3–

III

The *p*-quinone disulfonimides appear to be a class of stable compounds. The benzenesulfonyl, the *p*-toluenesulfonyl and methanesulfonyl derivatives of *p*-phenylenediamine are all oxidized with equal ease to corresponding diimides. On account of the insolubility of the disulfonamides of *p*-phenylenediamine in dry ether, oxidation by means of silver oxide in this solvent is slow and unsatisfactory. In acetone, oxidation proceeds more rapidly but certain uninvestigated side reactions appear which do not permit a maximum yield of product. Much better results are obtained with chromic acid or sodium dichromate in glacial acetic acid but the most effective oxidation procedure found is the use of lead tetraacetate in acetic acid (or red lead and acetic acid) at room temperature or at somewhat higher temperatures. This latter reaction results in 90–95% yield of product. No oxidation was effected by hydrogen peroxide, mercuric oxide, commercial lead dioxide or ferric chloride under the conditions used. Bromine in pyridine usually caused tar formation but was effective for oxidation in one experiment.

The *p*-quinone disulfonimides are more soluble in organic solvents than the corresponding *p*-phenylenedisulfonamides from which they are derived. They are stable under all ordinary conditions and are unaffected by recrystallizations from the common solvents. It is only after heating for some time at 80° that the *p*-quinone dibenzenesulfonamide decomposes (possibly polymerization).

The presence of ring substituents in the *p*-phenylenediamine does not interfere with the oxidation of the sulfonyl derivatives. The 2-chloro, 2-methyl, 2,5-dimethyl, 3-chloro-2,5-dimethyl derivatives of *p*-phenylenedibenzenesulfonamides have been converted smoothly to the corresponding *p*-quinone diimides by lead tetraacetate. An oxidation temperature above that of the room is advantageous with the polysubstituted derivatives. Bromine in pyridine is a successful oxidizing agent for 2,5-dibenzenesulfonamido-*p*-xylene and presumably may be satisfactory for other polysubstituted *p*-phenylenedibenzenesulfonamides.

There appears no theoretical reason why these neutral *p*-quinone diimides should not in their general reactions resemble those of the quinones. Initial experiments have confirmed this expectation. The reduction, and the action of chlorine, bromine, hydrochloric acid, hydrobromic acid, dilute sulfuric acid and sodium hydroxide on the *p*-quinone diimides are described in this paper.

Sulfur dioxide reacts slowly upon a water suspension of *p*-quinone dibenzenesulfonimide to reduce it gradually to *p*-phenylenedibenzenesulfonamide. Aqueous sodium hydrosulfite reacts similarly. Concentrated aqueous hydriodic acid, zinc and acetic acid or hydrogen in presence of platinum leads to rapid and quantitative reduction.

Chlorine adds to *p*-quinone dibenzenesulfonimide in chloroform solution but the crystalline addition product is not readily purified. The analysis indicated a trichloro derivative which may be due to addition of four chlorine atoms and elimination of one molecule of hydrogen chloride. Bromine similarly gives a crystalline dibromide which does not analyze perfectly for the expected addition of two atoms of bromine. These results resemble those obtained with *p*-quinone. Derivatives of the latter were more readily obtained pure

---

[3] Sunde, Erickson and Raunio, *J. Org. Chem.*, **13**, 742 (1948).

[4] Harry L. Fisher, U. S. Patent 2,170,191, August 22, 1939.

since they were soluble in low boiling solvents and therefore permitted crystallization without simultaneous dehydrohalogenation.[5]

Hydrogen chloride adds very readily when hydrogen chloride is passed into a chloroform solution of the *p*-quinone diimide. Presumably the addition is 1,4 followed by rearrangement since 2-chloro-*p*-phenylenedibenzenesulfonamide is obtained quantitatively. Zinc and hydrochloric acid gives the same product. Merely boiling a suspension of the *p*-quinone diimide with 10% aqueous hydrochloric acid results in the addition of hydrogen chloride. The *p*-quinone diimides are thus more susceptible to certain addition reactions than the corresponding quinones since the latter are unaffected by aqueous hydrochloric acid. 2,5-Dimethyl-*p*-quinone dibenzenesulfonimide is converted by hydrogen chloride to 2,5-dimethyl-3-chloro-*p*-phenylenedibenzenesulfonamide and 2,5-dimethyl-3-chloro-*p*-quinone dibenzenesulfonimide to 2,5-dimethyl-3,6-dichloro-*p*-phenylenedibenzenesulfonamide. These reactions illustrate the ease with which hydrogen chloride may be added even to highly substituted *p*-quinone diimides.

Hydrogen bromide on the other hand is oxidized to bromine by *p*-quinone dibenzenesulfonimide and *p*-phenylenedibenzenesulfonamide is formed. Hydriodic acid reacts similarly with liberation of iodine. The *p*-quinone diimide is clearly a strong oxidizing agent.

In contrast to the susceptibility of alkyl or aryl *p*-quinone diimines to hydrolysis, the *p*-quinone disulfonimides could not be hydrolyzed to *p*-quinone and benzenesulfonamide by the methods attempted. Aqueous sodium hydroxide or dilute sulfuric acid merely caused the reduction of *p*-quinone dibenzenesulfonimide to *p*-phenylenedibenzenesulfonamide, the former reagent in the cold, the latter by boiling. No hydrogen peroxide was detected in the reaction mixtures.

p-Quinone dibenzenesulfonamide forms a yellow-brown solution changing to olive green in concentrated sulfuric acid. Other diimides give somewhat similar color reactions.

A description of other reactions of *p*-quinone dibenzenesulfonimide, the preparation and reactions of *p*-quinone monobenzenesulfonimide, the acyl and aroyl derivatives in both series and the preparation of the corresponding *o*-quinone analogs will appear in future communications.

Experimental

***p*-Quinone Dibenzenesulfonimide. (A).**—A suspension of 28.1 g. of finely powdered *p*-phenylenedibenzenesulfonamide[6] in 300 ml. of glacial acetic acid was treated with stirring with 33 g. of pure lead tetraacetate. The mixture in the flask immediately became yellow and a thick mass formed in one-half hour. One hour and a half later the mixture thinned and shining yellow crystals were formed. The reaction was stirred for two hours more. To this reaction mixture was added 2–3 ml. of ethylene glycol and stirring was continued for five minutes. The yellow product was collected by filtration and washed with two 5-ml. portions of glacial acetic acid. After drying, the product weighed 25 g. After one crystallization from ethyl acetate, it was pure and melted at 178–179° (cor.). On concentration of the filtrate, 2.2 g. more of the same product was obtained making a total yield of 27.2 g. (97%). The product was dried in a desiccator. Heating in an oven at 80° for several hours caused it to change to a brittle black mass. In concentrated sulfuric acid, a yellow-brown solution is formed which changes to olive green.

By repeated recrystallization, the melting point of this product may be raised 8–10° higher than that reported. A discussion of the melting point will appear in a subsequent paper.

Anal. Calcd. for $C_{18}H_{14}N_2O_4S_2$: C, 55.95; H, 3.62; N, 7.25. Found: C, 56.17; H, 3.78; N, 7.22.

(B).—A solution of 0.97 g. of *p*-phenylenedibenzenesulfonamide in 40 ml. of acetone was shaken with 0.575 g. of freshly prepared dry silver oxide. The reaction mixture immediately became colored yellow and turned to orange in two hours. After shaking for ten hours more, the acetone solution was filtered from the silver oxide. By evaporation, yellow crystals weighing 0.25 g. resulted. After two crystallizations from ethyl acetate, the product melted at 178–179° (cor.).

Further concentration of the filtrate yielded 0.22 g. more of the compound. The total yield was 50%.

(C).—To a mixture of 0.74 g. of chromic acid in 20 ml. of glacial acetic acid, 0.97 g. of *p*-phenylenedibenzenesulfonamide was added in small portions. After the addition, the mixture was refluxed for ten minutes. The initial orange color changed to green. After cooling, 0.56 g. of crystals separated which proved to be unchanged material. Upon pouring the filtrate into ice and water, a yellow precipitate resulted, weighing 0.36 g. (40%). After crystallization from ethyl acetate, it melted at 178–179° (cor.), and proved to be *p*-quinone dibenzenesulfonimide.

(D).—To a hot solution of 0.372 g. of sodium dichromate monohydrate in 20 ml. of glacial acetic acid was added 0.97 g. of *p*-phenylenedibenzenesulfonamide in small portions (2–3 minutes). Gentle reflux was maintained by the rate of addition. The reaction mixture was kept warm for fifteen minutes then cooled and poured into ice. The product weighed 0.75 g. (75%) and after recrystallization from ethyl acetate melted at 178–179° (cor.).

Commercial lead dioxide and mercuric oxide did not oxidize *p*-phenylenedibenzenesulfonamide after long shaking in acetone solution at room temperature. Ferric chloride or hydrogen peroxide were equally unsuccessful as oxidizing agents in cold or hot glacial acetic acid as solvent. Bromine in pyridine solution converted *p*-phenylenedibenzenesulfonamide to a tarry product.

Reduction of *p*-Quinone Dibenzenesulfonimide. (A).—A mixture of 20 mg. of platinum oxide and 40 ml. of dioxane was shaken with hydrogen until the oxide was reduced. There was then introduced 0.48 g. of *p*-quinone dibenzenesulfonimide and reduced at 40 lb. p.s.i. In twenty minutes the theoretical amount of hydrogen was absorbed. The colorless filtrate from the catalyst was poured into 250 ml. of water. A fine white crystalline precipitate separated, weighing 0.48 g. It proved to be *p*-phenylenedibenzenesulfonamide, m. p. 247°.

(B).—A suspension of 0.965 g. of *p*-quinone dibenzenesulfonimide in 150 ml. of water was saturated with sulfur dioxide and permitted to stand at room temperature for two to three days. The yellow color was completely discharged. The white solid weighed 0.92 g. (95%) and proved to be pure *p*-phenylenedibenzenesulfonamide, m. p. 247°.

(C).—A suspension of 0.965 g. of *p*-quinone dibenzenesulfonimide in 10 ml. of ethanol was treated with 1.5 g. of sodium hydrosulfite in 5 ml. of water. The mixture was boiled for ten minutes during which time the yellow color was complete discharged. The white product was col-

---

(5) Nef, *Am. Chem. J.*, **13**, 423 (1891); Clark, *ibid.*, **14**, 553 (1892).

(6) Hinsberg, *Ann.*, **265**, 178 (1891).

lected on a filter. It weighed 0.725 g. (82%) and proved to be *p*-phenylenedibenzenesulfonamide, m. p. 247°.

(D).—From a mixture of 0.965 g. of *p*-quinone dibenzenesulfonimide and 7 ml. of hydriodic acid (sp. gr. 1.50), iodine was immediately liberated. After heating a half hour on a steam-bath, it was cooled and filtered. Most of the free iodine was thus evaporated and the remainder stayed in solution. The product weighed 0.95 g. and after one crystallization from glacial acetic acid proved to be pure *p*-phenylenedibenzenesulfonamide, m. p. 247°.

(E).—A solution of 0.48 g. of *p*-quinone dibenzenesulfonimide in 20 ml. of glacial acetic acid was mechanically stirred and 0.2 g. of zinc dust was added in portions. Reaction proceeded rapidly and the yellow color was discharged in five to ten minutes. The solution was filtered and, upon cooling, colorless crystals deposited. They weighed 0.48 g. and proved to be pure *p*-phenylenedibenzenesulfonamide, m. p. 247°.

(F).—A mixture of 5 g. of crystalline stannous chloride in 10 ml. of concentrated hydrochloric acid and 0.48 g. of *p*-quinone dibenzenesulfonimide was warmed for fifteen minutes on a steam-bath. The yellow color was discharged. After cooling, the white solid was collected by filtration. It weighed 0.31 g. By crystallization from glacial acetic acid, *p*-phenylenedibenzenesulfonamide, m. p. 247°, separated and weighed 0.115 g. (24%). From the filtrate by evaporation 0.18 g. (36%) of a product resulted which, after crystallization from glacial acetic acid, melted at 174–175° and proved to be 2-chloro-*p*-phenylenedibenzenesulfonamide as determined by the melting point of a mixture with an authentic sample, prepared as described later in this paper.

Addition of Hydrogen Chloride to *p*-Quinone Dibenzenesulfonimide: 2-Chloro-*p*-phenylenedibenzenesulfonamide. (A).—Into a solution of 0.965 g. of *p*-quinone dibenzenesulfonimide in 75 ml. of chloroform, dry hydrogen chloride was bubbled. The color was discharged within five minutes. No solid was deposited even after cooling the solution in the refrigerator for fifteen hours. The chloroform was then evaporated and 0.975 g. (93%) of solid remained. It was crystallized from glacial acetic acid and then melted at 174–175° (cor.). It proved to be 2-chloro-*p*-phenylenedibenzenesulfonamide.

(B).—A mixture of 0.5 g. of fused zinc chloride in 5 ml. of concentrated hydrochloric acid and 0.48 g. of *p*-quinone dibenzenesulfonamide was warmed on a steam-bath for one and a half hours. The color was discharged in about half an hour. After cooling, the solid was collected by filtration and weighed 0.42 g. (80%). On purification from glacial acetic acid it melted at 174–175° (cor.) and proved to be 2-chloro-*p*-phenylenedibenzenesulfonamide.

(C).—A mixture of 0.965 g. of powdered *p*-quinone dibenzenesulfonimide and 20 ml. of 10% hydrochloric acid was refluxed for one hour and a half until the yellow color was discharged. The resulting solid weighed 0.92 g. (87.5%) and proved to be essentially pure 2-chloro-*p*-phenylenedibenzenesulfonamide, m. p. 175°.

Action of Hydrogen Bromide, Dilute Sulfuric Acid and Aqueous Sodium Hydroxide on *p*-Quinone Dibenzenesulfonimide.—Into a solution of 0.965 g. of *p*-quinone dibenzenesulfonimide in 25 ml. of dry chloroform, dry hydrogen bromide was bubbled. Bromine was liberated and in fifteen minutes a white solid separated. The crude product weighed 0.91 g. and on recrystallization from glacial acetic acid melted at 247°. It proved to be *p*-phenylenedibenzenesulfonamide.

A suspension of 0.48 g. of *p*-quinone dibenzenesulfonamide in 15 ml. of 10% sulfuric acid was refluxed for three hours. The crystalline solid was brown in color and weighed 0.40 g. After one crystallization it melted at 247° and proved to be *p*-phenylenedibenzenesulfonamide.

A mixture of 2 g. of *p*-quinone dibenzenesulfonimide and 15 ml. of 5% aqueous sodium hydroxide was stirred for half an hour at room temperature. A brown color developed. After acidification the solid was removed by filtration and weighed 1.9 g. On purification from glacial acetic acid, it melted at 247° and proved to be *p*-phenylenedibenzenesulfonamide.

Bromination and Chlorination of *p*-Quinone Dibenzenesulfonimide.—A solution of 0.14 ml. (0.4 g.) of bromine in 5 ml. of chloroform was added drop by drop to a solution of 0.965 g. of *p*-quinone dibenzenesulfonimide in 25 ml. of dry chloroform. After complete addition, the deep red colored solution was shaken and allowed to stand overnight. The solution became very light in color and some colorless crystals had deposited. On cooling the mixture and scratching the sides with a glass rod more crystals were deposited. The product weighed 0.455 g. and melted at 194–196°. A further 0.82 g. was obtained by evaporation of the filtrate and melted at 192–194°. These two fractions were combined and recrystallized from glacial acetic acid. The light yellow crystals melted at 199–200° (cor.). These were not entirely pure as shown by analysis. Two atoms of bromine, however, obviously had added.

Anal. Calcd. for $C_{18}H_{14}N_2O_4Br_2S_2$: C, 39.58; H, 2.58; N, 5.13. Found: C, 40.52; H. 2.69; N, 5.38.

Dry chlorine was bubbled into a solution of 0.965 g. of *p*-quinone dibenzenesulfonimide in 25 ml. of dry chloroform until saturated. A white crystalline precipitate deposited in one hour and the solution was light yellow in color. The solid weighed 0.455 g. and melted at 170–175°. On evaporation of the filtrate, 0.675 g. more of a solid melting at 155–170° was obtained. Both these fractions when crystallized several times from glacial acetic acid gave light yellow crystals, m. p. 200–201° (cor.). The product, although nice in appearance, was not pure. It analyzed closer to a trichloro compound than to a di- or tetra-chloro.

Anal. Calcd. for dichloro, $C_{13}H_{14}N_2O_4S_2Cl_2$: C, 47.28; H, 3.09. For trichloro, $C_{18}H_{13}N_2O_4S_2Cl_3$: C, 43.95; H, 2.88. For tetrachloro, $C_{18}H_{14}N_2O_4S_2Cl_4$: C, 40.93; H, 2.67. Found: C, 44.28; H, 2.86.

***p*-Quinone Di-*p*-toluenesulfonimide.**—A suspension of 1.04 g. of powdered *p*-phenylenedi-*p*-toluenesulfonamide[7] in 40 ml. of glacial acetic acid was treated with 1.1 g. of lead tetraacetate. The mixture, which became yellow within five minutes, was stirred at room temperature for six hours. After addition of 0.15 ml. of ethylene glycol, stirring was continued for a few minutes more. The yellow crystals which had separated were collected by filtration and washed with acetic acid. The product weighed 0.94 g. (90%). It was purified by crystallization from glacial acetic acid, m. p. 206.5–207.5° (cor.). In concentrated sulfuric acid, a red-brown solution is formed which changes to olive green.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2$: C, 57.95; H. 4.38; N, 6.76. Found: C, 57.98; H, 4.41; N, 6.76.

***p*-Phenylenedimethenesulfonamide.**—To a solution of 5.4 g. of *p*-phenylenediamine in water was added 20 ml. of a 20% aqueous solution of sodium hydroxide. While the mixture was stirred and the flask was cooled by cold water, 8.4 ml. (12.5 g.) of methanesulfonyl chloride was added drop by drop during fifteen minutes. In order to keep the reaction mixture alkaline, 10 ml. more of the alkali was added. After an hour and a half, the mixture was made slightly acidic and the resulting solid collected by filtration. The wet cake was dissolved in alkali and clear solution was obtained by warming on a steam-bath. After treatment with Darco and filtration, the colorless solution was poured into ice and hydrochloric acid. The product weighed 6.4 g. (50%). It was purified by crystallization from glacial acetic acid and formed colorless crystals, m. p. 264° (cor.).

Anal. Calcd. for $C_8H_{12}N_2O_4S_2$: C, 36.37; H, 4.58; N, 10.60. Found: C, 36.52; H, 4.62; N, 10.80.

***p*-Quinone Dimethanesulfonimide.**—To a suspension of 0.99 g. of *p*-phenylenedimethanesulfonamide in 25 ml. of glacial acetic acid, while stirring, 1.7 g. of lead tetraacetate was added, and the reaction allowed to proceed for six hours. Then 2.2 ml. of ethylene glycol was introduced and stirring was continued for a few minutes.

---

(7) Willstätter and Pfannenstiel, *Ber.*, **38**, 2244 (1905).

The yellow crystals were collected by filtration, washed with glacial acetic acid and dried. They weighed 0.87 g. (87%). After purification by crystallization from glacial acetic acid, the product melted at 200–201° (cor.). On drying in the Abderhalden at 100° and under 3 mm. pressure for four hours a slight brown color developed. In concentrated sulfuric acid, it forms a yellowish-brown solution which changes to deep green.

Anal. Calcd. for $C_8H_{10}N_2O_4S_2$: C, 36.64; H, 3.81; N, 10.68. Found: C, 36.82; H, 3.97; N, 10.88.

2-Methyl-*p*-phenylenedibenzenesulfonamide.—To a solution of 8 g. of 2-methyl-*p*-phenylenediamine in 50 ml. of pyridine was added cautiously a solution of 17 ml. of benzenesulfonyl chloride in 10 ml. of pyridine. The mixture was shaken and kept overnight. Upon pouring into ice and hydrochloric acid, a solid resulted. This was collected by filtration, dissolved in alkali, warmed with Darco and filtered. On acidification of the filtrate, the product precipitated. It weighed 22.5 g. (85%) and after crystallization from ethanol melted at 193–194° (cor.).

Anal. Calcd. for $C_{19}H_{18}N_2O_4S_2$: C, 56.70; H, 4.51; N, 6.96. Found: C, 56.96; H, 4.69; N, 7.21.

2-Methyl-*p*-quinone Dibenzenesulfonimide.—To a suspension of 2 g. of powdered 2-methyl-*p*-phenylenedibenzenesulfonamide in 20 ml. of glacial acetic acid was added 2.2 g. of lead tetraacetate. The mixture was stirred and warmed on a hot water-bath maintained at 60°. After four hours, 0.3–0.4 ml. of ethylene glycol was added and the mixture stirred for five minutes more. After cooling, the orange crystals were collected by filtration. The product weighed 1.55 g. It was purified by crystallization from glacial acetic acid, m. p. 167–168° (cor.). The filtrate was poured into water when 0.15 g. more of the same compound was obtained. The total yield was 85%.

Anal. Calcd. for $C_{19}H_{16}N_2O_4S_2$: C, 56.98; H, 4.03; N, 7.00. Found: C, 57.26; H, 4.14; N, 7.19.

2-Chloro-*p*-phenylenedibenzenesulfonamide.—To a solution of 2.15 g. of 2-chloro-*p*-phenylenediamine dihydrochloride in 200 ml. of water was added 15 ml. of a 20% aqueous solution of sodium hydroxide. While stirring, 2.6 ml. of benzenesulfonyl chloride was added drop by drop. After two hours the mixture was acidified. The resulting solid was then collected by filtration and purified by dissolving in aqueous sodium hydroxide, boiling with Darco, filtering the solution and reacidification. The product, after drying, weighed 2.2 g. (52%). This was crystallized from glacial acetic acid and melted at 174–175° (cor.).

Anal. Calcd. for $C_{16}H_{15}N_2O_4S_2Cl$: C, 51.12; H, 3.58; N, 6.63. Found: C, 51.15; H, 3.63; N, 6.62.

2-Chloro-*p*-quinone Dibenzenesulfonimide.—To a suspension of 1.06 g. of finely powdered 2-chloro-*p*-phenylenedibenzenesulfonamide in 20 ml. of glacial acetic acid was added 1.11 g. of lead tetraacetate. A clear solution was obtained in ten minutes, after which yellow crystals began to separate. The reaction mixture was permitted to stand for four hours. After adding 0.15 ml. of ethylene glycol and stirring for a few minutes, the crystals were collected on a filter, washed with 5 ml. of acetic acid and dried. They weighed 0.89 g. (92%) and were purified by crystallization from glacial acetic acid, m. p. 178–179° (cor.). The filtrate on dilution gave 0.1 g. more of the same product. In concentrated sulfuric acid, an orange-yellow solution is formed which changes slowly to brown.

Anal. Calcd. for $C_{18}H_{13}N_2O_4S_2Cl$: C, 51.37; H, 3.11; N, 6.66. Found: C, 51.15; H, 3.25; N, 6.53.

2,5-Dibenzenesulfonamido-*p*-xylene.—The preparation of 2,5-diamino-*p*-xylene was improved.

2-Acetamido-*p*-xylene.—To a solution of 60.5 g. of 2-amino-*p*-xylene in 1 l. of petroleum ether (b. p., 40–60°) was added 40 ml. of acetic anhydride drop by drop. The solution was stirred vigorously and the temperature was maintained between 25–30° for half an hour after addition of the acetic anhydride. A white flocculent crystalline precipitate was formed which was washed with 150 ml. of petroleum ether and dried. The product weighed 80 g. (quant.). This product has previously been prepared by the direct action of glacial acetic acid[8] or acetic anhydride.[9]

2-Acetamido-5-nitro-*p*-xylene.—Into a solution of 65.2 g. of 2-acetamido-*p*-xylene in cold (below 5°) concentrated sulfuric acid, a mixture of 27.7 ml. of concentrated nitric acid (sp. gr. 1.42) and 40 ml. of concentrated sulfuric acid was introduced drop by drop (approximately one drop every two seconds) while maintaining the temperature at 0° and stirring vigorously. After two and one-half hours, the addition was completed and the stirring was continued for ten minutes more with the temperature still at 0°. The reaction mixture was then poured into crushed ice. The nitro derivative was collected on a filter, washed with water repeatedly until all the acid was removed and then hydrolyzed directly without drying. Previous investigators have obtained substantial by-products of trinitro[9] or isomeric mononitro derivatives.[10] Repetition of the latter process yielded in our hands considerable dinitro derivative.

2-Amino-5-nitro-*p*-xylene.—The wet cake of 2-acetamido-5-nitro-*p*-xylene was stirred with 300 ml. of a 10% aqueous solution of sodium hydroxide. A yellow product was immediately formed. The alkaline mixture was heated on a steam-bath for one hour, cooled to room temperature and the solid separated by filtration. The nitro compound was washed with hot water until free from alkali. After drying, the substance weighed 40 g. (60%). After crystallization from ethanol, the 2-amino-5-nitro-*p*-xylene melted at 145°.

The alkaline filtrate was acidified and the solid that separated was collected by filtration, washed free from acid and dried. This weighed 7.2 g. and, after crystallization from ethanol, melted at 202°. The product is 2-amino-3,5-dinitro-*p*-xylene.

2,5-Diamino-*p*-xylene.—A suspension of 8.3 g. of 2-amino-5-nitro-*p*-xylene in 100 ml. of ethanol was reduced in presence of Raney nickel and hydrogen at 40 lb. p.s.i. The theoretical amount of hydrogen was absorbed in thirty minutes. After filtering the solution from the catalyst and distillation of the solvent under diminished pressure, 6.7 g. (98.5%) of product was obtained. After crystallization from benzene, it formed light yellow needles, m. p. 149–150°.

A solution of 5.3 ml. of benzenesulfonyl chloride in 10 ml. of dry pyridine was cautiously added to a solution of 2.59 g. of 2,5-diamino-*p*-xylene in 25 ml. of dry pyridine. The reaction mixture was allowed to stand at room temperature overnight and then poured into a mixture of ice and hydrochloric acid. The pasty mass that separated from the solution became solid within a short time. This was powdered and washed free from acid. A solution of the wet cake in 10% aqueous sodium hydroxide was heated on a steam-bath for ten minutes with Darco. After filtration, the solution was cooled and poured into ice and hydrochloric acid. The white precipitate was collected by filtration, washed with water and dried. The yield of product was 6 g. (76%). After crystallization from pyridine, it melted at 293° (cor.). It was insoluble in most all the common organic solvents, sparingly soluble in glacial acetic acid.

Anal. Calcd. for $C_{20}H_{20}N_2O_4S_2$: C, 57.68; H, 4.86; N, 6.72. Found: C, 57.55; H, 4.99; N, 6.63.

2,5-Dimethyl-*p*-quinone Dibenzenesulfonimide. (A).—In 20 ml. of pyridine, 1.43 g. of 2,5-dibenzenesulfonamido-*p*-xylene was dissolved by heating and the solution then cooled carefully to avoid the crystallization of the compound. A solution of 0.35 ml. (1.1 g.) of bromine in 7 ml. of pyridine was added cautiously with cooling. Within five minutes after the addition was completed, the mixture was poured into ice and hydrochloric acid. The yellow compound that separated was collected by filtration, washed repeatedly with water and dried. This weighed 1.16 g. (80%). The disulfonimide was crystallized from

---

(8) Schaumann, *Ber.*, **11**, 1537 (1878).

(9) Noelting, Witt and Forel, *ibid.*, **18**, 2664 (1885).

(10) Fisher and Walling, THIS JOURNAL, **57**, 1700 (1935).

glacial acetic acid and formed yellow crystals, m. p. 199° (cor.). In concentrated sulfuric acid, a straw yellow solution is formed which changes slowly to orange.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2$: C, 57.97; H, 4.32; N, 6.76. Found: C, 58.17; H, 4.22; N, 6.92.

(B).—To a suspension of 70 mg. of finely powdered 2,5-dibenzenesulfonamido-*p*-xylene in 40 ml. of dry ether and 5 mg. of anhydrous sodium sulfate was added 39 mg. of freshly prepared dry silver oxide. The mixture was agitated on a mechanical shaker for fifteen hours then filtered from the silver oxide. Upon evaporation of the ether a yellow solid weighing 10 mg. was obtained. It was crystallized from acetone and melted at 199° (cor.). It was identical with the product formed by oxidation with bromine and pyridine.

Addition of Hydrogen Chloride 2,5-Dimethyl-*p*-quinone Dibenzenesulfonimide: 2,5-Dimethyl-3-chloro-*p*-phenylene Dibenzenesulfonamide.—Dry hydrogen chloride was bubbled into a solution of 8 g. of 2,5-dimethyl-*p*-quinone dibenzenesulfonimide in 200 ml. of dry chloroform. A white crystalline precipitate was deposited and the yellow color of the solution was completely discharged in one hour. The solid was collected by filtration and the filtrate was evaporated to obtain the balance of the material. The product weighed 8.5 g. (quant.). It was purified by crystallization from glacial acetic acid and formed colorless crystals, m. p. 261° (cor.) with darkening at 257–258°. *Anal.* Calcd. for $C_{20}H_{19}N_2O_4S_2Cl$: C, 53.26; H, 4.25. Found: C, 53.06; H, 4.52.

2,5-Dimethyl-3-chloro-*p*-quinone Dibenzenesulfonimide.—A suspension of 4.72 g. of finely powdered 2,5-dimethyl-3-chloro-*p*-phenylenedibenzenesulfonamide in 125 ml. of glacial acetic acid and 4.64 g. of lead tetraacetate was warmed on a water-bath maintained at 70–75°. The solid material went slowly (one hour) into solution which was orange in color. After adding 3–4 ml. of ethylene glycol, and allowing to stand for a few minutes, the solution was cooled, filtered to remove traces of unreacted original compound, then poured onto ice. A yellowish-orange precipitate formed which weighed 4.68 g. (99%). By crystallization from glacial acetic acid, orange crystals resulted, m. p. 152–153° (cor.). In concentrated sulfuric acid, a golden yellow solution is formed which remains unchanged on standing.

Anal. Calcd. for $C_{20}H_{17}N_2O_4S_2Cl$: C, 53.51; H, 3.82; N, 6.24. Found: C, 53.54; H, 3.97; N, 6.14.

2,5-Dimethyl-3,6-dichloro-*p*-phenylenedibenzenesulfonamide.—Into a solution of 3.5 g. of 2,5-dimethyl-3-chloro-*p*-quinone diimide in 150 ml. of chloroform, hydrogen chloride was bubbled. In the course of ten to fifteen minutes, a white solid deposited and the yellow-orange solution became colorless. The product weighed 3.72 g. (94%). It was purified by two crystallizations from glacial acetic acid in which it was only sparingly soluble. It turned dark without melting at about 280°.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2Cl_2$: C, 49.49; H, 3.74. Found: C, 49.21; H, 3.90.

Summary

1. *p*-Phenylenedibenzenesulfonamide has been oxidized by a variety of reagents to *p*-quinone dibenzenesulfonimide which is a stable yellow crystalline compound. The di-*p*-toluenesulfonyl and dimethanesulfonyl derivatives of *p*-phenylenediamine, the dibenzenesulfonyl derivatives of 2-methyl-, 2-chloro-, 2,5-dimethyl- and 2,5-dimethyl-3-chloro-*p*-phenylenediamine were equally readily oxidized to stable *p*-quinone diimides. The reactions are essentially quantitative when lead tetraacetate in glacial acetic acid is used as oxidizing agent. The 2,5-dimethyl derivative was oxidized successfully with bromine in pyridine solution.

2. *p*-Quinone dibenzenesulfonimide resembles quinone in being readily reduced by various reagents, such as hydrogen in presence of platinum, hydriodic acid, zinc and acetic acid, tin and hydrochloric acid and sulfurous acid to the *p*-phenylenedibenzenesulfonamide. It is also reduced by heating with dilute sulfuric acid or by cold dilute sodium hydroxide.

3. The diimides add readily hydrogen chloride to yield the 2-chloro-*p*-phenylenedibenzenesulfonamides.

4. The diimides oxidize hydrogen bromide to bromine and hydriodic acid to iodine.

URBANA, ILLINOIS RECEIVED MARCH 10, 1950

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

Restricted Rotation in Aromatic Amines. XIII. The Effect of Monosubstitution in the *Ortho* Position

BY ROGER ADAMS AND A. S. NAGARKATTI

In exploring the effect of ring substituents on the restricted rotation of N,N′-disubstituted aromatic amines,[1] various compounds have been synthesized with merely one methyl group *ortho* to the amino group and with two groups, benzenesulfonyl and methyl or carboxymethyl, substituted on the nitrogen.

Attempts to resolve N-carboxymethyl *o*-benzenesulfonamidotoluene (I) failed, though in one experiment which could not be repeated, the cinchonidine salt exhibited mutarotation. It was obvious that restriction of the carbon–nitrogen bond is so slight, if any, that minor experimental factors might influence the results. The isolation of *cis* and *trans* forms in molecules with two points of restricted rotation appeared from past experience to offer a more reliable means of determining the presence of restricted rotation in molecules where the restriction was very small since resolution may be avoided. The three diamine derivatives II, III and IV were, therefore prepared. In no case could two isomers be isolated. Excellent yields of single compounds resulted in all cases. It is evident then that the combinations of groups on the nitrogen atoms in I, II, III and IV with a methyl group in the *ortho* position in the ring are not adequate to permit measurable restricted rotation.

---

[1] For previous papers see Adams and Tjepkema, THIS JOURNAL, **70**, 4204 (1948); Adams, *et al.*, *ibid.*, **71**, 1620 (1949); **72**, 128, 132, 135 (1950).