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

Quinone Imides. XXXVIII. Adducts of *p*-Quinonedimethanesulfonimide and their Hydrolysis Products

BY ROGER ADAMS AND WILLIAM P. SAMUELS, JR.[1]

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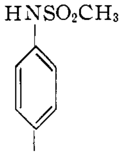
The addition reactions of *p*-quinonedimethanesulfonimides have been studied. Several of the adducts could be hydrolyzed to the corresponding diamines with 1:1 aqueous sulfuric acid under reflux. The acetylacetone adduct of *p*-quinonedimethanesulfonimide gave 3-acetyl-5-methanesulfonamido-1-methanesulfonyl-2-methylindole upon treatment either with 22% hydrochloric acid under reflux or with cold concentrated sulfuric acid.

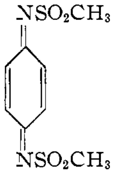
p-Phenylenebis-(dimethylsulfamamide) is hydrolyzed readily to *p*-phenylenediamine by means of hot dilute hydrochloric acid.[2] The corresponding diimide from this compound therefore has been used for formation of various adducts where subsequent removal of the sulfonyl groups from the resulting diamides was to be effected.[3] Although in this respect the dimethylsulfamoyl has a decided advantage over the benzenesulfonyl group, which can be hydrolyzed only with great difficulty, it has the serious disadvantage of not being introduced readily into certain aromatic diamines. For example, 2-methoxy-*p*-phenylenediamine and 1,4-naphthalenediamine could not be bis-(dimethylsulfamidated) by the procedure usually used for benzenesulfonation. In fact, conditions for direct sulfamidation of these compounds were never found.

It has been reported that methanesulfonyl derivatives of primary and secondary aromatic amines may be hydrolyzed with hot 60% aqueous sulfuric acid.[4] Since the methanesulfonyl derivatives of aromatic mono- and diamines are prepared readily a study of *p*-phenylenedimethanesulfonamides and the corresponding imides has been undertaken. The diamides were synthesized most satisfactorily by the use of methanesulfonyl chloride in pyridine.

p-Phenylenedimethanesulfonamide (I), has been prepared previously in this Laboratory[5] and converted to its diimide II.



I



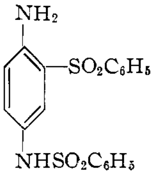
II

Several new addition reactions to II have been achieved and the hydrolysis of the products to diamines has been realized. By the successive additions of hydrogen chloride and oxidations, II was converted to the mono-, isomeric di-, tri- and tetrachloro - *p* - phenylenedimethanesulfonamides. Benzenesulfinic acid, thiophenol and benzyl mercaptan also were added to II. The addition of α-acetoxybutadiene followed by aromatization of the intermediate adduct with 48% hydrobromic acid gave 1,4-naphthylenedimethanesulfonamide.

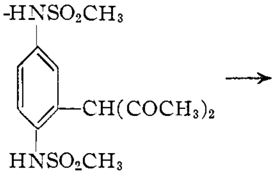
The dimethanesulfonamides of *p*-phenylenediamine and 2-chloro-*p*-phenylenediamine were hydrolyzed to the corresponding diamines in 51 and 63% yields, respectively, by means of hot 1:1 aqueous sulfuric acid. The diamides were unaffected by boiling 22% hydrochloric acid and were hydrolyzed by concentrated hydrobromic acid with the concomitant introduction of a bromine atom into the molecule.[6,7]

2-Benzenesulfonyl-*p*-phenylenedimethanesulfonamide also was hydrolyzed readily by sulfuric acid to 2 - benzenesulfonyl - *p* - phenylenediamine. Attempts to dibenzenesulfonate this diamine with excess benzenesulfonyl chloride in pyridine solution resulted in the introduction of only one benzenesulfonyl group probably in the 4-position (III).

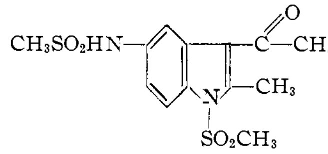
The addition of acetylacetone to II led to the formation of IV. When IV was treated with 22% hydrochloric acid under reflux or with cold concentrated sulfuric acid 3-acetyl-5-methanesulfonamido-1-methanesulfonyl-2-methylindole (V) was formed in 90 and 48% yield, respectively. Hot sulfuric acid gave unsatisfactory results. The acetylacetone adduct of *p*-quinonedibenzenesulfonimide was stable to hot hydrochloric acid.



III



IV



V

2 - Methoxy - *p* - phenylenedimethanesulfonimide added acetylacetone to give a mixture of isomers.

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[1] An abstract of a thesis submitted by William P. Samuels, Jr., to the Graduate College of the University of Illinois, 1955, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Standard Oil of California Fellow, 1952–1954.

[2] R. Adams and P. R. Shafer, THIS JOURNAL, **75**, 667 (1953).

[3] R. Adams and W. P. Samuels, Jr., *ibid.*, **77**, 5375 (1955).

[4] C. S. Marvel, M. D. Helfinch and J. P. Belsley, *ibid.*, **51**, 1272 (1929).

[5] R. Adams and A. S. Nagarkatti, *ibid.*, **72**, 4601 (1950).

[6] H. Ohle and G. Haeseler, *Ber.*, **69B**, 2324 (1936).

[7] H. R. Snyder and R. E. Heckert, THIS JOURNAL, **74**, 2006 (1952).

Meerman for determination of the ultraviolet absorption spectra.

Experimental

All melting points are corrected.

The infrared spectra were run in Nujol mulls using a Perkin–Elmer model 21 double beam spectrophotometer.

***p*-Phenenyledimethanesulfonamide** (I).—To a solution of 10.8 g. of *p*-phenylenediamine in 100 ml. of pyridine cooled to 0°, 22.9 g. of methanesulfonyl chloride was added in one portion and the reaction mixture was allowed to stand at room temperature for 48 hours. At the end of this time the red reaction mixture was poured with stirring into ice-water containing sufficient hydrochloric acid to completely neutralize the pyridine. The crude diamide was filtered, washed with water and then dissolved in 15% aqueous sodium hydroxide (Darco). The diamide was recovered by the addition of 1:1 aqueous hydrochloric acid until an acid reaction to litmus was obtained. There was obtained 23.6 g. (89.5%) of white powder which was recrystallized from glacial acetic acid as white crystals, m.p. 263–265°. A melting point of a mixture with authentic *p*-phenylenedimethanesulfonamide[5] was not depressed.

Sulfuric Acid Hydrolysis of *p*-Phenylenedimethanesulfonamide. *p*-Phenylenediamine.—A suspension of 1.0 g. of *p*-phenylenedimethanesulfonamide in 15 ml. of 1:1 aqueous sulfuric acid was heated under reflux for 80 minutes and then allowed to cool. The resulting brown solution was cooled in an ice-bath, made alkaline with 15% aqueous sodium hydroxide, and extracted with two 75-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and evaporated to dryness. There was obtained 0.21 g. (51.5%) of light tan crystals, m.p. 138–140°, which proved to be *p*-phenylenediamine.

1,4-Naphthylenedimethanesulfonamide.—A solution of 1.0 g. of *p*-quinonedimethanesulfonimide and 1.0 ml. of α-acetoxybutadiene in 80 ml. of reagent grade chloroform was allowed to stand for 7 days. At the end of this time the yellow solution was filtered through a sintered glass funnel to remove a trace of chloroform-insoluble material and the filtrate was evaporated to dryness. The residual orange oil was dissolved in glacial acetic acid and 0.5 ml. of 48% hydrobromic acid added. Upon scratching, a heavy precipitate formed. The product was collected by filtration and dried. There was obtained 0.91 g. (76%) of pale purple solid which was recrystallized from glacial acetic acid as white crystals, m.p. 260–261.5°. A melting point of a mixture with authentic 1,4-naphthylenedimethanesulfonamide[8] was not depressed.

2-Chloro-*p*-phenylenedimethanesulfonamide.—Into a solution of 1 g. of *p*-quinonedimethanesulfonimide in the minimum quantity of reagent grade chloroform, dry hydrogen chloride was passed. The yellow color was discharged in several minutes with the concomitant precipitation of the chloro derivative. Filtration yielded 1.16 g. (100%) of product which was recrystallized from glacial acetic acid as white crystals, m.p. 194.5–196.5°.

Anal. Calcd. for $C_8H_{11}ClN_2O_4S_2$: C, 32.16; H, 3.71; N, 9.38. Found: C, 32.45, H, 3.62; N, 9.09.

Sulfuric Acid Hydrolysis of 2-Chloro-*p*-phenylenedimethanesulfonamide. 2-Chloro-*p*-phenylenediamine.—A suspension of 1.0 g. of 2-chloro-*p*-phenylenedimethanesulfonamide in 10 ml. of 1:1 aqueous sulfuric acid was heated under reflux for 45 minutes during which period the solution became yellow and finally orange. After cooling in an ice-bath the solution was made alkaline with 15% aqueous sodium hydroxide and extracted with two 100-ml. portions of ether. From the combined ether extracts there was obtained 0.3 g. (63%) of pale tan powder, m.p. 62–64°. A melting point of a mixture with authentic 2-chloro-*p*-phenylenediamine was not depressed.

Attempts to hydrolyze this product with hydrochloric acid gave only unchanged starting material and a small amount of brown oil.

Hydrolysis with constant boiling hydrobromic acid resulted in an impure product which contained bromine.

2-Chloro-*p*-quinonedimethanesulfonimide.—To a suspension of 4.89 g. of 2-chloro-*p*-phenylenedimethanesulfonamide in 50 ml. of glacial acetic acid, 7.3 g. of lead tetraacetate was added. The mixture was heated on the steam-bath for 20 minutes, 2 ml. of ethylene glycol was added, and the resulting red solution allowed to cool. Cooling in an ice-bath followed by the addition of 20 ml. of water precipitated the diimide which was collected by filtration, washed with ice-cold 60% aqueous acetic acid, and dried. There was obtained 4.1 g. (85%) of yellow crystals which were recrystallized from chloroform–carbon tetrachloride; m.p. 174–175° dec.

Anal. Calcd. for $C_8H_9ClN_2O_4S_2$: C, 32.38; H, 3.06; N, 9.44. Found: C, 32.62; H, 3.15; N, 9.14.

2,x-Dichloro-*p*-phenylenedimethanesulfonamide.—A suspension of 9.7 g. of 2-chloro-*p*-phenylenedimethanesulfonamide in 100 ml. of glacial acetic acid was oxidized with 14.6 g. of lead tetraacetate. The crude diimide obtained was dissolved in the minimum quantity of reagent grade chloroform and filtered to remove a trace of lead dioxide. Treatment of the filtrate with an excess of hydrogen chloride discharged the color with the concomitant precipitation of the dichloro derivative. After filtering and drying there was obtained 8.7 g. of white solid. Concentration of the filtrate to a volume of 40 ml. afforded another 1.5 g. (total crude yield of 94.5%). The crude product on recrystallization from glacial acetic acid gave white crystals, m.p. 225–266°. The product is a mixture of isomeric dichlorodiamides.

Anal. Calcd. for $C_8H_{10}Cl_2N_2O_4S_2$: C, 28.83; H, 3.03; N, 8.41. Found: C, 29.01; H, 3.29; N, 8.52.

2,x-Dichloro-*p*-quinonedimethanesulfonimide.—To a suspension of 4.7 g. of a mixture of isomeric 2,x-dichloro-*p*-quinonedimethanesulfonamides in 60 ml. of glacial acetic acid was added 6.4 g. of lead tetraacetate. The solution immediately became yellow. The mixture was heated on the steam-bath for 30 minutes, cooled to room temperature and 2 ml. of ethylene glycol was added. After standing for 10 minutes the reaction mixture was cooled in an ice-bath, diluted with 25 ml. of water and filtered. The product was washed with 20 ml. of ice-cold 60% aqueous acetic acid and dried. There was obtained 4.52 g. (97%) of product which was recrystallized from glacial acetic acid as glistening yellow crystals, m.p. 218–235° dec. with darkening from 220°. The product is a mixture of isomeric dichlorodiimides.

Anal. Calcd. for $C_8H_8Cl_2N_2O_4S_2$: C, 29.69; H, 2.49; N, 8.66. Found: C, 29.79; H, 2.53; N, 8.64.

2,3,5-Trichloro-*p*-phenylenedimethanesulfonamide.—A suspension of 1.87 g. of a mixture of isomeric 2,x-dichloro-*p*-quinonedimethanesulfonimides in 400 ml. of reagent grade chloroform was treated with hydrogen chloride for 30 minutes. The color was discharged only after standing at room temperature for several hours and a white solid had separated. The solution was concentrated to 100 ml., cooled and filtered. There was obtained 1.89 g. (91%) of white solid, which was recrystallized for analysis from glacial acetic acid; m.p. 218–219°.

Anal. Calcd. for $C_8H_9Cl_3N_2O_4S_2$: C, 26.13; H, 2.47; N, 7.62. Found: C, 25.95; H, 2.26; N, 7.54.

2,3,5-Trichloro-*p*-quinonedimethanesulfonimide.—To a suspension of 1.4 g. of 2,3,5-trichloro-*p*-phenylenedimethanesulfonamide in 15 ml. of glacial acetic acid, 1.8 g. of lead tetraacetate was added and the mixture was heated on the steam-bath for 30 minutes. After cooling to room temperature 2 ml. of ethylene glycol was added and the reaction mixture was allowed to stand for 15 minutes. It then was cooled in an ice-bath, diluted with 10 ml. of water and the product collected by filtration and dried. There was obtained 1.25 g. (90%) of orange crystals, which were recrystallized from glacial acetic acid; m.p. 213.5–216.5°.

Anal. Calcd. for $C_8H_7Cl_3N_2O_4S_2$: C, 26.28; H, 1.93; N, 7.66. Found: C, 26.57; H, 2.10; N, 7.64.

2,3,5,6-Tetrachloro-*p*-phenylenedimethanesulfonamide.—Hydrogen chloride was passed into a solution of 0.52 g. of 2,3,5-trichloro-*p*-quinonedimethanesulfonimide in 100 ml. of reagent grade chloroform for 20 minutes. The yellow color became very pale after the solution had stood for an hour. The chloroform was removed in a stream of dry air and the residue dissolved in boiling glacial acetic acid. The acetic acid solution was concentrated and then allowed to cool. The product which weighed 0.52 g. (90%) was purified from glacial acetic acid as white needles, m.p. 256–258.5°.

Anal. Calcd. for $C_8H_6Cl_4N_2O_4S_2$: C, 23.89; H, 2.01; N, 6.97. Found: C, 24.18; H, 2.31; N, 6.97.

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[8] R. Adams and H. A. Wankel, This Journal, 73, 131 (1951).

2-Phenylmercapto-*p*-phenylenedimethanesulfonamide.—A solution of 0.42 g. of thiophenol and one drop of triethylamine in 20 ml. of reagent grade chloroform was added in one portion to a solution of 1.0 g. of *p*-quinonedimethanesulfonimide in 25 ml. of reagent grade chloroform. The color was discharged immediately. After standing overnight the volume was reduced to 20 ml. in a stream of dry air and the crude adduct filtered. There was obtained 1.31 g. (90%) of the product which was purified by recrystallization from glacial acetic acid and 95% ethanol as white plates, m.p. 167–169°.

Anal. Calcd. for $C_{14}H_{16}N_2O_4S_3$: C, 45.14; H, 4.33; N, 7.52. Found: C, 45.23; H, 4.22; N, 7.53.

2-Benzylmercapto-*p*-phenylenedimethanesulfonamide.—Prepared in a manner similar to that used for the phenylmercapto derivative, the product separated from the solution in 93% yield. Purification by recrystallization from glacial acetic acid and 95% ethanol gave white crystals, m.p. 157–159°.

Anal. Calcd. for $C_{15}H_{18}N_2O_4S_3$: C, 46.61; H, 4.69; N, 7.25. Found: C, 46.34; H, 4.50; N, 7.30.

2-Benzenesulfonyl-*p*-phenylenedimethanesulfonamide.—To a suspension of 0.3 g. of *p*-quinonedimethanesulfonimide (II) in 15 ml. of glacial acetic acid, 0.25 g. of sodium benzenesulfinate was added. After heating on the steam-bath for 15 minutes the solution was colorless. The reaction mixture was concentrated to 5 ml., allowed to cool, and filtered. The product weighed 0.38 g. (82%) and was recrystallized from glacial acetic acid as white crystals, m.p. 203.5–205.5°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6S_2$: C, 41.57; H, 3.99; N, 6.93. Found: C, 41.84; H, 3.83; N, 6.79.

2-Benzenesulfonyl-*p*-phenylenediamine.—A suspension of 1.0 g. of 2-benzenesulfonyl-*p*-phenylenedimethanesulfonamide in 10 ml. of 1:1 aqueous sulfuric acid was heated under reflux for 30 minutes. The resulting red solution was cooled in an ice-bath, made basic with 15% aqueous sodium hydroxide, and extracted with two 75-ml. portions of ether. From the ether extracts there was obtained 0.46 g. (75%) of yellow needles. The product was recrystallized from benzene as yellow needles, m.p. 119.5–121.5°.

Anal. Calcd. for $C_{12}H_{12}N_2O_2S$: C, 58.04; H, 4.87; N, 11.28. Found: C, 58.22; H, 4.58; N, 11.32.

The infrared spectrum indicated a primary aromatic amine at 3450, 3365 and 1635 cm.$^{-1}$; sulfone, SO_2 at 1323 and 1147 cm.$^{-1}$.

3-Benzenesulfonyl-4-aminobenzenesulfonanilide (III).—To a solution of 0.12 g. of 2-benzenesulfonyl-*p*-phenylenediamine in 15 ml. of dry pyridine, 0.17 g. of benzenesulfonyl chloride was added. The mixture was allowed to stand at room temperature for 45 minutes and then poured into ice-water containing sufficient hydrochloric acid to completely neutralize the pyridine. There was obtained 0.16 g. (86%) which was purified for analysis from 95% ethanol (Darco) as white crystals, m.p. 175–177°.

Anal. Calcd. for $C_{18}H_{16}N_2S_2O_4$: C, 55.65; H, 4.15; N, 7.21. Found: C, 55.76; H, 3.86; N, 7.47.

The infrared spectrum indicated a sulfone, SO_2 at 1308 and 1152 cm.$^{-1}$; sulfonamide, NH at 3260 cm.$^{-1}$; SO_2 at 1344 and 1164 cm.$^{-1}$; primary aromatic amine at 3495, 3390 and 1635 cm.$^{-1}$.

3-(2,5-Dimethanesulfonamidophenyl)-2,4-pentanedione (IV).—To a solution of 0.5 g. of the diimide II and 0.2 g. of redistilled acetylacetone in 80 ml. of anhydrous dioxane, 40 mg. of sodium methoxide was added. The yellow color was discharged in one minute. The volume of the solution was reduced to 10 ml. with a stream of dry air and 100 ml. of petroleum ether (b.p. 30–60°) added. The white solid that separated weighed 0.69 g. (100%). The product was recrystallized from ethyl acetate as white crystals, m.p. 184.5–186.5°.

Anal. Calcd. for $C_{13}H_{18}N_2O_6S_2$: C, 43.08; H, 5.01; N, 7.73. Found: C, 43.35; H, 5.06; N, 7.51.

3-Acetyl-5-methanesulfonamido-1-methanesulfonyl-2-methylindole (V). Method A.—To 0.75 g. of IV, 15 ml. of sulfuric acid (sp. gr. 1.84) was added. The amide dissolved in several minutes. After standing at room temperature for 24 hours the red solution was poured with stirring into 200 ml. of ice-water. The solid that separated weighed 0.34 g. (48%). Several recrystallizations from ethanol gave white crystals, m.p. 232.5–234.5°.

Anal. Calcd. for $C_{13}H_{16}N_2O_5S_2$: C, 45.33; H, 4.68; N, 8.14. Found: C, 45.59; H, 4.63; N, 8.22.

Infrared analysis indicated a C═O at 1633 cm.$^{-1}$. Ultraviolet absorption showed maxima at 205–206 mμ (ϵ 76,800) and 282–283 mμ (ϵ 8,180) and a minimum at 257–258 mμ (ϵ 6,110).

Method B.—A suspension of 0.43 g. of IV in 40 ml. of 22% hydrochloric acid was refluxed for 12 hours. At the end of this time the colorless suspension was cooled and filtered. There was obtained 0.37 g. (90%) of pale tan powder which was recrystallized from ethanol–acetone; white crystals, m.p. 233–234.5°. A melting point of a mixture with a sample of product from method A was not depressed.

3-(2,5-Dibenzenesulfonamidophenyl)-2,4-pentanedione was unaffected by similar treatment with hydrochloric acid.

2-Methoxy-*p*-phenylenedimethanesulfonamide.—A solution of 22.1 g. of 2-amino-5-nitroanisole in 150 ml. of anhydrous dioxane was hydrogenated over 0.3 g. of platinum oxide at 3.5 atmospheres and room temperature. After the theoretical amount of hydrogen had been absorbed, the solution was filtered from the catalyst and the dioxane removed under reduced pressure. The residual solid was dissolved in 300 ml. of dry pyridine, and 28.6 g. of methanesulfonyl chloride was added. The resulting red mixture was cooled until the initial heat of reaction had subsided and then allowed to stand for 72 hours. At the end of this time the reaction mixture was poured with stirring into ice-water containing sufficient hydrochloric acid to completely neutralize the pyridine. The crude diamide weighed 29.3 g. (75%). It was recrystallized from glacial acetic acid; white needles, m.p. 205.5–207.5°.

Anal. Calcd. for $C_9H_{14}N_2O_5S_2$: C, 36.72; H, 4.79; N, 9.52. Found: C, 36.81; H, 5.03; N, 9.22.

2-Methoxy-*p*-quinonedimethanesulfonimide.—To a suspension of 3.0 g. of 2-methoxy-*p*-phenylenedimethanesulfonamide in 30 ml. of glacial acetic acid, 5.7 g. of lead tetraacetate was added. The mixture was heated on the steam-bath for 30 minutes and then allowed to cool. After thorough cooling in an ice-bath the product separated. It weighed 2.85 g. (95%). The product was recrystallized from chloroform–carbon tetrachloride; orange crystals, m.p. 209.5–211.5° dec.

Anal. Calcd. for $C_9H_{12}N_2O_5S_2$: C, 36.98; H, 4.14; N, 9.59. Found: C, 36.84; H, 4.14; N, 9.54.

3-(2,5-Dimethanesulfonamido-x-methoxyphenyl)-2,4-pentanedione.—To a solution of 0.5 g. of 2-methoxy-*p*-quinonedimethanesulfonimide and 0.18 g. of redistilled acetylacetone in 70 ml. of anhydrous dioxane was added 40 mg. of sodium methoxide. The color was discharged in 1 to 2 minutes. Six drops of glacial acetic acid was added and the volume of the solution reduced to 10 ml. in a stream of dry air. The addition of 100 ml. of petroleum ether (b.p. 30–60°) caused the separation of a white solid weighing 0.67 g. (100%). It was recrystallized from ethyl acetate–cyclohexane; m.p. 164–210°. The product is obviously a mixture of isomers.

Anal. Calcd. for $C_{14}H_{20}N_2O_7S_2$: C, 42.84; H, 5.14; N, 7.14. Found: C, 43.11; H, 5.30; N, 6.90.

Urbana, Illinois