

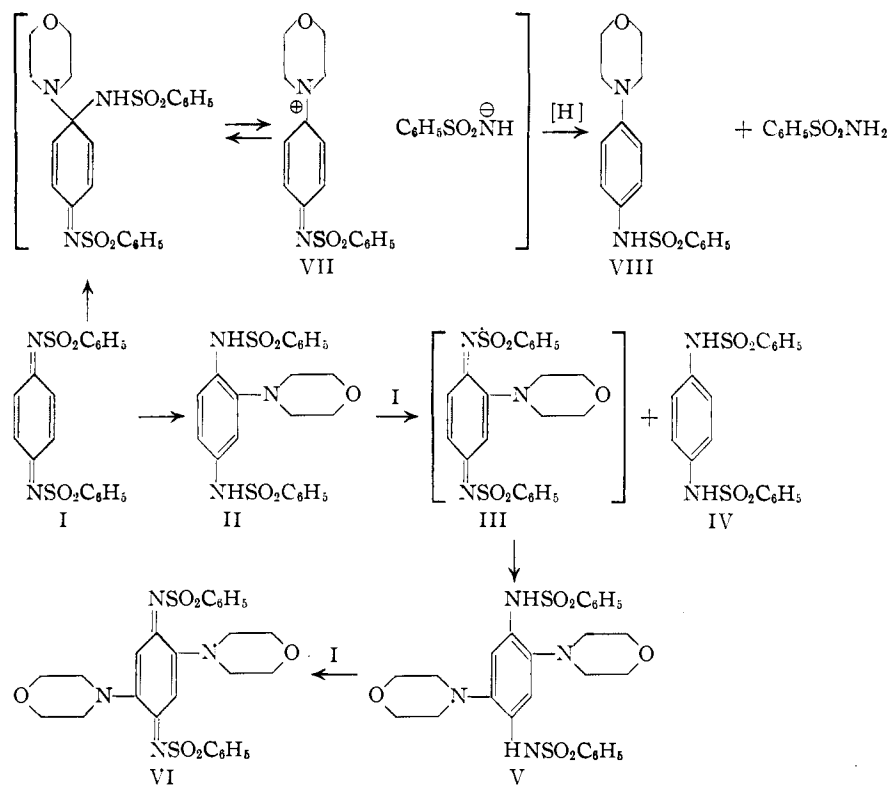
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. X. Addition of Amines to *p*-QuinonedibenzenesulfonimideBY ROGER ADAMS AND K. A. SCHOWALTER¹

Morpholine reacts with *p*-quinonedibenzenesulfonimide to give a variety of products, the amounts of each being dependent on the experimental conditions. In chloroform as solvent, 2,5-dimorpholino-*p*-phenylenedibenzenesulfonamide (A), 2,5-dimorpholino-*p*-quinonedibenzenesulfonimide (B), *p*-benzenesulfonamidophenylmorpholine (C) and *p*-phenylenedibenzene sulfonamide (D) were isolated. In benzene, compound A was the major product; in ether, 2-morpholino-*p*-phenylenedibenzenesulfonamide was present in largest amounts. The structure of B was determined by hydrolysis to 2,5-dimorpholino-*p*-quinone which was synthesized by an independent method. Compound C was also synthesized by an unequivocal method. Piperidine in benzene yields chiefly the compound corresponding to A. Dimethylamine gives mixtures analogous to those from morpholine. Methylaniline reacts to give merely 2-methylanilino-*p*-phenylenedibenzenesulfonamide. Aniline and *p*-quinonedibenzenesulfonimide yield three products, 2,5-dianilino-*p*-quinonedianil, *N,N'*-diphenyl-*p*-phenylenediamine and benzenesulfonamide. *p*-Toluidine reacts similarly. Aliphatic primary amines react to give excellent yields of benzenesulfonamide. No other primary product could be isolated but by reduction of the reaction mixture obtained from *n*-butylamine and *p*-quinonedibenzenesulfonimide, *N,N'*-dibutyl-*p*-phenylenediamine was isolated in excellent yield. It thus appears that *p*-quinonedibutylimine is formed in this reaction. β -Phenylethylamine and ammonia react similarly.

In previous papers, the addition of hydrogen chloride to various *p*- and *o*-quinonedibenzenesulfonimides has been described.² To 1,4-naphthoquinonedibenzenesulfonimide, thiophenol and morpholine were also added and the addition was found to parallel that of hydrogen chloride.³ The study of the addition of various amines to *p*-quinonedibenzenesulfonimide is the subject of this report.

are presumably formed by a series of 1,4-additions and oxidations. The oxidations of II to III and V to VI are effected by the initial *p*-quinone diimide (I) or by the intermediate (VII). Formation of compound VIII is best explained by assuming a 1,2-addition of morpholine followed by reduction of its ionized form (VII) in reacting with II, IV or V.



When chloroform was used as solvent in the addition of morpholine to I, a mixture of compounds resulted from which IV, V, VI and VIII were separated. If, however, a dilute benzene solution of I was introduced slowly with stirring into a benzene solution of an excess of morpholine, the primary product was 2,5-dimorpholino-*p*-phenylenedibenzenesulfonamide (V). This was readily oxidized with lead tetraacetate to VI, and VI was readily reduced to V. When the reaction was run in ether, it was possible to isolate as chief product 2-morpholino-*p*-phenylenedibenzenesulfonamide (II) along with V as by-product.

The structure of compound VI, which was green in color, was established by treatment with hot aqueous alkali. Hydrolysis occurred and the red

The initial experiments which were carried out with morpholine demonstrated that several rapid reactions occur with formation of products, the relative amounts of which are dependent on the conditions used. Products II, III, V and VI

2,5-dimorpholino-*p*-quinone was isolated. This was synthesized by the action of morpholine on *p*-quinone. Compound VIII was synthesized by an unequivocal method and proved to be identical with that isolated from the reaction mixture of morpholine with I; *p*-nitrochlorobenzene \rightarrow *p*-nitrophenylmorpholine \rightarrow *p*-aminophenylmorpholine \rightarrow *p*-benzenesulfonamidophenylmorpholine.

The investigation was extended to the reactions of piperidine and dimethylamine with *p*-quinonedibenzenesulfonimide (I). With piperidine, using

(1) An abstract of a thesis submitted by K. A. Schowalter to the Graduate College of the University of Illinois, 1951, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Cincinnati Chemical Works Fellow, 1949-1950.

(2) R. Adams, *et al.*, THIS JOURNAL, **72**, 460, 5154 (1950); **73**, 1145, 1149, 1152 (1951).

(3) R. Adams and R. A. Wankel, *ibid.*, **73**, 131, 2219 (1951).

Fraction A was heated to boiling with 25 ml. of 95% ethanol. Filtration of the hot suspension yielded 0.117 g. of tan crystals which were combined with Fraction C (0.156 g.) and recrystallized twice from pyridine. When pure, the product melted at 277–280° (cor.) (dec.) and was identified as 2,5-dimorpholino-*p*-phenylenedibenzene-sulfonamide.

Anal. Calcd. for $C_{28}H_{30}N_4O_6S_2$: C, 55.90; H, 5.41; N, 10.03; S, 11.48. Found: C, 56.01; H, 5.52; N, 9.92; S, 11.62.

The ethanolic mother liquor from the boiling of Fraction A with ethanol was evaporated to dryness. The residue consisted of 0.45 g. of tan crystals which were recrystallized once from ethanol and identified as *p*-phenylenedibenzene-sulfonamide, m.p. 245.5–247.5° (cor.).

Fraction B was treated with cold chloroform and the mixture filtered. The crystals, which did not dissolve, were impure 2,5-dimorpholino-*p*-phenylenedibenzene-sulfonamide. The chloroform mother liquor was treated with an equal volume of carbon tetrachloride and cooled in the refrigerator. Greenish-black needles separated which weighed 0.558 g. Treatment of the mother liquor with an equal volume of carbon tetrachloride, followed by cooling and filtration, gave an additional 0.035 g. of product. The two portions of the green compound were combined and purified by dissolving in 15 ml. of chloroform and adding to the solution successive 10-ml. portions of carbon tetrachloride, each followed by cooling and filtration. The third precipitation contained the bulk of the material and was pure. It melted with decomposition at 182.5° (cor.). This compound was identified as 2,5-dimorpholino-*p*-quinonedibenzene-sulfonamide.

Anal. Calcd. for $C_{28}H_{28}N_4O_6S_2$: C, 56.10; H, 5.07; N, 10.07. Found: C, 55.84; H, 4.99; N, 9.92.

A suspension of 0.08 g. of this product in 40 ml. of 50% ethanol was heated with 0.3 g. of sodium hydrosulfite. The gray solid which formed weighed 0.07 g. (87%) and was identified as 2,5-dimorpholino-*p*-phenylenedibenzene-sulfonamide.

Reaction of *p*-Quinonedibenzene-sulfonamide with Morpholine in Benzene Solution.—A solution of 1.0 g. of the quinone diimide in 200 ml. of pure dry benzene was added dropwise with vigorous stirring to a solution of 3.4 g. of redistilled morpholine (b.p. 127°) in 100 ml. of pure dry benzene. The reaction mixture gradually turned brown and was allowed to stand 10 hours after the addition was completed. The tan-colored crystals which separated weighed 0.959 g. From the mother liquor by evaporation to 40 ml., a second crop was obtained weighing 0.128 g. The crystal fractions were combined and heated with 100 ml. of 95% ethanol, then filtered hot. The crude product weighed 0.515 g. (71%). After two recrystallizations from pyridine it was pure 2,5-dimorpholino-*p*-phenylenedibenzene-sulfonamide.

2,5-Dimorpholino-*p*-quinonedibenzene-sulfonamide by Oxidation of the Diamide.—A suspension of 0.463 g. of 2,5-dimorpholino-*p*-phenylenedibenzene-sulfonamide in 10 ml. of glacial acetic acid was treated with 0.404 g. of lead tetraacetate (10% excess). The mixture was stirred vigorously with gentle heating to about 50° until the unreacted lead tetraacetate had disappeared. The mixture was cooled to 15° and filtered to give 0.444 g. of dark green needles containing a few white crystals of unchanged starting material. This was taken up in 25 ml. of chloroform and filtered to remove the white crystals. The chloroform mother liquor was treated with 25 ml. of carbon tetrachloride and the mixture cooled in the refrigerator. Upon filtration, 0.319 g. of greenish-black needles, m.p. 182.5° (cor.) (dec.) was obtained. These were identified as 2,5-dimorpholino-*p*-quinonedibenzene-sulfonamide. The yield was 96.3% based upon the unrecovered starting material.

2,5-Dimorpholino-*p*-quinone (A) From 2,5-Dimorpholino-*p*-quinonedibenzene-sulfonamide.—A suspension of 0.217 g. of the dimorpholinoquinone diimide in 10 ml. of 10% sodium hydroxide solution was boiled for two minutes. The intense green color gradually turned brown and then red with the formation of a red precipitate. The sides of the beaker were washed down with a few milliliters of water and the mixture once more heated to boiling. It was then cooled to room temperature and filtered. The fine red crystalline solid, weighing 0.011 g., was recrystallized from 95% ethanol and identified as 2,5-dimorpholino-*p*-quinone. The mother liquor was acidified to a pH of 3, cooled in the re-

frigerator and filtered. The product, which weighed 0.028 g., was recrystallized from ethanol and identified as *p*-phenylenedibenzene-sulfonamide, an impurity in the starting material which is very difficult to remove.

The mother liquor was then ether extracted. From the extract was obtained 0.106 g. of a compound which, after purification, was identified as benzenesulfonamide. The products of the reaction, therefore, were 2,5-dimorpholino-*p*-quinone in a yield of 11.7% and benzenesulfonamide in 95%.

(B) From *p*-Quinone.—A solution of 1.0 g. of *p*-quinone in 50 ml. of chloroform was treated with 0.9 g. of morpholine, stirred for 5 minutes, and then cooled in the refrigerator. The product which crystallized weighed 1 g. and consisted of a mixture of dark red and tan-colored needles. It was treated with 25 ml. of 95% ethanol, warmed slightly, then cooled and filtered. The product desired is insoluble. The yield was 0.52 g. (39%). It was purified by recrystallization from 95% ethanol, m.p. 236.5–237.5° (cor.) (dec.).

Anal. Calcd. for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.47; H, 6.65; N, 9.95.

***p*-Benzenesulfonamidophenylmorpholine. *p*-Nitrophenylmorpholine.**—A mixture of 15.75 g. of *p*-nitrochlorobenzene and 150 ml. of morpholine was refluxed for 24 hours. It was then steam distilled to remove the morpholine and any unreacted *p*-nitrochlorobenzene. The residue crystallized as orange prisms. They were cooled, collected on a filter and purified by two recrystallizations from methanol, m.p. 150–151° (cor.). The yield was quantitative.

Anal. Calcd. for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.81; N, 13.46. Found: C, 57.62; H, 5.79; N, 13.37.

***p*-Aminophenylmorpholine.**—A solution of 1.0 g. of *p*-nitrophenylmorpholine in 30 ml. of 20% hydrochloric acid solution was treated with small portions of zinc dust with stirring and gentle warming until all of the yellow color of the nitro compound had disappeared. The mixture was filtered to remove the excess zinc and the filtrate made strongly basic with 50% aqueous sodium hydroxide. The crude amine, which separated, weighed 0.80 g. (94%). It was recrystallized once from methanol and twice from a mixture of equal parts of benzene and petroleum ether (b.p. 30–60°). The tan-colored compound melted at 129.5–130.5° (cor.).

Anal. Calcd. for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.18; H, 7.92; N, 15.89.

A suspension of 0.3 g. of *p*-aminophenylmorpholine in 5 ml. of 10% sodium hydroxide solution was treated with 0.33 g. of benzenesulfonyl chloride. The suspension was shaken vigorously for 15 minutes. All of the amine had not reacted; therefore, about 0.5 g. of benzenesulfonyl chloride was added and the mixture shaken further. The amine slowly disappeared and the solution was acidified to pH 3 with concentrated hydrochloric acid. A grey gum formed which would not crystallize. The mother liquor was decanted and the gum (residue) washed with 2 ml. of water. A few ml. of methanol was added and the mixture cooled. The product crystallized and weighed 0.208 g. (38.6%). It was twice recrystallized from 50% ethanol for purification, m.p. 161–162° (cor.).

Anal. Calcd. for $C_{16}H_{18}N_2O_3S$: C, 60.35; H, 5.70; N, 8.80. Found: C, 60.36; H, 5.94; N, 9.09.

Reaction of *p*-Quinonedibenzene-sulfonamide with Morpholine in Ether.—A modified soxhlet extractor was set up so as to provide for the dropwise addition of an ether extract of quinone diimide to a boiling ether solution containing a large excess of morpholine. The entrained morpholine was removed from the ether vapor prior to recycling for extraction by passing the ether vapor through a trap filled with oxalic acid. The quinone diimide (1.0 g.) was placed in the extractor thimble and 20 g. of morpholine in 300 ml. of ether put in the boiling flask. The extraction was run for 48 hours, during which time tan crystals had formed in the ether. The reaction was stopped, the ether solution with the solid removed (portion I) and reaction started again with a fresh 20 g. of morpholine in 300 ml. of ether. The extraction was then allowed to proceed for a second 48-hour period. At the end of the second period, 97% of the quinone diimide had been dissolved. The second reaction mixture was removed (portion II).

Portion I was evaporated to a volume of 50 ml. and filtered. The oily tan crystals were collected by filtration,

washed with a few ml. of ethanol, dried, and washed again with a few milliliters of ether. There was thus obtained 0.574 g. of white crystals (Fraction A). The mother liquor and ethanol wash liquor were combined, treated with 50 ml. of water, and cooled in the refrigerator. The brown crystals which separated were collected on a filter and washed with a few milliliters of ether. Recrystallization of this material from methanol yielded 0.153 g. of brown crystals (Fraction B), m.p. 187–209° (cor.) (dec.).

Portion II was evaporated to a volume of 50 ml. and cooled for 10 hours, then treated with 50 ml. of water and cooled. The crystals (Fraction C) were washed with a few milliliters of ether and weighed 0.237 g., m.p. 198–204° (cor.) (dec.).

Fractions A and B were combined and heated to boiling with 40 ml. of 95% ethanol. Undissolved crystals (Fraction D) were separated by filtering hot. The yield was 0.261 g., m.p. 190–269° (cor.) (dec.). The mother liquor was cooled in the refrigerator for 10 hours. The white crystals (Fraction E) which separated weighed 0.440 g., m.p. 194–207° (cor.) (dec.).

Fraction D was heated to boiling with 15 ml. of 95% ethanol and filtered. This yielded 0.157 g. of white crystals, m.p. 266–279° (cor.) (dec.), which were identified as 2,5-dimorpholino-*p*-phenylenedibenzenesulfonamide.

Fraction E was recrystallized three times from 95% ethanol to yield 0.297 g. of white crystals, m.p. 206–213° (cor.) (dec.). This was identified as 2-morpholino-*p*-phenylenedibenzenesulfonamide.

Anal. Calcd. for $C_{22}H_{23}N_3O_5S_2$: C, 55.80; H, 4.90; N, 8.87. Found: C, 55.92; H, 5.10; N, 8.77.

Fraction B was added to the alcoholic mother liquors from Fractions D and E and the solution concentrated to one-half of its original volume, filtered hot and cooled. The tan crystals weighed 0.206 g., m.p. 190–198° (cor.) (dec.).

The infrared absorption spectrum of this material indicated it to be slightly impure 2-morpholino-*p*-phenylenedibenzenesulfonamide. A total yield of 0.646 g. (54.5%) of monoadduct was thus obtained.

An attempted oxidation of this material with lead tetracetate gave an intensely purple solution from which no crystalline compound could be isolated.

Reaction of *p*-Quinonedibenzenesulfonimide with Piperidine.—A solution of 3.0 g. of the quinone diimide in 600 ml. of pure dry benzene was added dropwise with vigorous stirring to a solution of 10 g. of redistilled piperidine (b.p. 104°) in 200 ml. of pure dry benzene. After the addition was complete, the mixture was allowed to stand for 10 hours at room temperature, concentrated to 95 ml. and cooled. The tan-colored crystals, weighing 3.799 g., were heated to boiling with 75 ml. of 95% ethanol, the solution filtered hot, and the solid washed with 20 ml. of boiling 95% ethanol. The crude 2,5-dipiperidino-*p*-phenylenedibenzenesulfonamide weighed 1.925 g. and was purified by four crystallizations from pyridine, m.p. 255–259° (cor.) (dec.).

Anal. Calcd. for $C_{28}H_{34}N_4O_4S_2$: C, 60.62; H, 6.18; N, 10.10. Found: C, 60.79; H, 6.29; N, 10.24.

The ethanol mother liquor and wash liquor from the crude diamide upon concentration and cooling yielded 0.836 g. of crude *p*-phenylenedibenzenesulfonamide, m.p. 239–244° (cor.).

The benzene mother liquor from the initial reaction mixture was washed with 50 ml. of 10% hydrochloric acid solution to remove the excess piperidine and then evaporated to dryness. The residue was heated to boiling with 25 ml. of 95% ethanol and filtered hot. The crystals thus obtained weighed 0.037 g. and consisted of crude 2,5-dipiperidino-*p*-phenylenedibenzenesulfonamide. The total yield of this product was thus 1.962 g. (90.8%).

2,5-Dipiperidino-*p*-quinonedibenzenesulfonimide by Oxidation of the Diamide.—A suspension of 0.5 g. of the diamide in 50 ml. of pure dry benzene was treated with 0.44 g. of dry recrystallized lead tetraacetate (10% excess). The reaction mixture was stirred for 10 hours and then filtered. The product was a mixture of dark green needles and fine white crystals (Fraction A). The mother liquor was treated with 50 ml. of petroleum ether (b.p. 90–120°), cooled, and filtered. The dark green needles (Fraction B) weighed 0.066 g. The mother liquor was concentrated to a volume of 50 ml., cooled in the refrigerator, and filtered. The green needles (Fraction C) weighed 0.018 g.

Fraction A was washed with 20 ml. of chloroform which dissolved the green crystals and left 0.342 g. of white crys-

tals on the filter, which proved to be a mixture of lead acetate and starting material.

The chloroform solution of the green compound was treated with twice its volume of carbon tetrachloride and cooled in the refrigerator. The product crystallized and weighed 0.237 g. This was combined with Fractions B and C to give a total of 0.321 g. (64.5%) of crude 2,5-dipiperidino-*p*-quinonedibenzenesulfonimide.

The crude product was purified by dissolving in 4 ml. of chloroform and precipitating successive fractions by addition of successive 4-ml. portions of carbon tetrachloride. The third fraction contained the bulk of the material and was pure. The green crystals decompose to a light brown powder at 156.5–166.5° (cor.), and the powder then melts gradually with further decomposition at 166.5–248.5° (cor.).

Anal. Calcd. for $C_{28}H_{32}N_4O_4S_2$: C, 60.84; H, 5.84; N, 10.14. Found: C, 60.85; H, 6.06; N, 10.16.

Reaction of *p*-Quinonedibenzenesulfonimide with Dimethylamine.—A solution of 3.0 g. of the quinone diimide in 600 ml. of pure dry benzene was added dropwise with vigorous stirring to a solution of 7.82 g. of dimethylammonium dimethylcarbamate in 200 ml. of pure dry benzene. The dimethylammonium dimethylcarbamate decomposes readily to yield two molecules of dimethylamine and one of carbon dioxide. The reaction mixture was then permitted to stand at room temperature for 11 hours, concentrated to 95 ml., cooled and filtered. The brown needles (Fraction A) weighed 0.913 g. The mother liquor was concentrated to 30 ml., cooled, and filtered to give dark green crystals (Fraction B). The mother liquor was evaporated to about 5 ml., treated with 10 ml. of hot 95% ethanol, cooled and filtered. The green-brown crystals (Fraction C) weighed 0.301 g. The mother liquor yielded three more crystalline fractions by repeating the process of concentration, cooling and filtration. These were combined (Fraction D) and weighed 0.698 g.

Fraction A was heated to boiling with 20 ml. of ethanol, cooled in the refrigerator for 8 hours and filtered. The tan crystals, which weighed 0.397 g., were combined with crystalline Fraction C. The mother liquor was evaporated to 10 ml. and treated with 10 ml. of water, cooled in the refrigerator and filtered. These white crystals weighed 0.189 g. and were combined with Fraction D.

Fraction B was treated with 15 ml. of chloroform, the mixture stirred well and filtered. The yellow-colored crystals resulting weighed 0.282 g. and were combined with Fraction C. The chloroform solution was then treated with an equal volume of carbon tetrachloride and the mixture cooled and filtered. The dark green needles (Fraction E) weighed 0.323 g. Treatment of the mother liquor with 30 ml. of carbon tetrachloride caused the crystallization of an additional 0.042 g. of green needles which were combined with Fraction E. The crystals obtained by addition of more carbon tetrachloride weighed 0.027 g. and were combined with Fraction E.

Fraction C, totaling 0.980 g., was heated to boiling with 30 ml. of chloroform to dissolve the dimethylamino substituted compound and filtered. The white crystals weighed 0.553 g., m.p. 237.5–243.5° (cor.). The process was repeated with this material with 20 ml. of chloroform to give 0.406 g. of product, m.p. 241.5–245.5° (cor.). This was recrystallized from 95% ethanol, and 0.361 g. of pure *p*-phenylenedibenzenesulfonamide, m.p. 245.5–247.5° (cor.), was obtained.

The chloroform mother liquors were combined and concentrated to 10 ml., cooled, and filtered. The white crystals weighed 0.502 g. They were recrystallized once from chloroform and three times from pyridine, m.p. 241.5–243.5° (cor.) (dec.). The product was identified as the 2,5-bis-(dimethylamino)-*p*-phenylenedibenzenesulfonamide.

Anal. Calcd. for $C_{22}H_{26}N_4O_4S_2$: C, 55.67; H, 5.52. Found: C, 55.73; H, 5.25.

Fraction D was recrystallized four times with 50% ethanol; white crystals, m.p. 133–134° (cor.). The product was identified as *p*-benzenesulfonamidodimethylaniline through synthesis by an unequivocal method described later in this paper.

Fraction E was purified by dissolving in 5 ml. of chloroform and adding successive portions of 5 ml. of carbon tetrachloride followed by cooling and filtration after each addition. The third and fourth fractions contained the bulk of

the material. These were combined and the process repeated. The third fraction was pure; green crystals decomposing to a light brown solid at 158–163° (cor.) which gradually melted with further decomposition at 188–253° (cor.). Analysis of the product indicated it to be 2,5-bis-(dimethylamino)-*p*-quinonedibenzesulfonimide.

Anal. Calcd. for $C_{22}H_{24}N_4O_4S_2$: C, 55.91; H, 5.12; N, 11.86. Found: C, 55.64; H, 5.08; N, 12.15.

***p*-Benzenesulfonamidodimethylaniline.**—A suspension of 12 g. of *p*-aminodimethylaniline in 70 ml. of 10% aqueous sodium hydroxide was treated with 17 g. of benzenesulfonyl chloride and stirred well for 15 minutes. The resulting black solution was treated with Darco, heated to boiling and filtered. The Darco treatment was repeated three times. The brown solution was then acidified to pH 4 with concentrated hydrochloric acid. The dark gray solid which precipitated weighed 11.4 g. (46.7%). It was purified by recrystallization three times from 50% ethanol; white needles, m.p. 132–133° (cor.).

Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.84; H, 5.84; N, 10.14. Found: C, 60.87; H, 6.09; N, 10.09.

2-Methylanilino-*p*-phenylenedibenzesulfonamide.—A solution of 3.0 g. of the *p*-quinonedibenzesulfonimide in 600 ml. of pure dry benzene was added dropwise with vigorous stirring to a solution of 10 g. of redistilled methylaniline (b.p. 193–194°) in 200 ml. of pure dry benzene. When the addition was complete, the reaction mixture was concentrated to a volume of 95 ml., cooled to room temperature and filtered. The purple-gray colored crystals weighed 3.545 g. (92.5%). After three recrystallizations from 95% ethanol, white needles were obtained, m.p. 193.5–195° (cor.) (dec.).

Anal. Calcd. for $C_{26}H_{28}N_2O_4S_2$: C, 60.83; H, 4.70; N, 8.51. Found: C, 60.86; H, 4.57; N, 8.40.

This material was oxidized with lead tetraacetate in glacial acetic acid, benzene and chloroform. In no case could other than amorphous colored products be isolated.

Reaction of *p*-Quinonedibenzesulfonimide with Diphenylamine.—When diphenylamine in chloroform was added dropwise, with stirring, to a solution of the quinone diimide in chloroform, a deep blue developed. Addition of carbon tetrachloride and cooling caused the deposition of a dark blue gum. No crystalline material could be obtained from the solution.

Reaction of *p*-Quinonedibenzesulfonimide with Aniline in Benzene.—A solution of 3.0 g. of the quinone diimide in 600 ml. of pure dry benzene was added dropwise with vigorous stirring to a solution of 10.88 g. of redistilled aniline (b.p. 183°) in 200 ml. of benzene. The mixture which was reddish-brown in color was then allowed to stand at room temperature for 12 hours, concentrated to a volume of 30 ml., cooled and filtered. The product, consisting of brown needles and dark-red crystals (Fraction A), weighed 2.233 g. The mother liquor was evaporated to a viscous oil and cooled in the refrigerator for 10 hours. The crystals (Fraction B) weighed 0.957 g. The mother liquor was treated with 10 ml. of chloroform and then with four 10-ml. portions of carbon tetrachloride, the mixture being cooled and filtered after each addition. The crystalline solids obtained by the first three additions weighed 1.214 g. (Fraction C). The fourth addition precipitated only tar, which was discarded.

Fraction A was heated to boiling with 90 ml. of 95% ethanol and filtered hot. The solid was a mixture of red needles and fine red crystals (Fraction D) which weighed 0.746 g. The mother liquor was evaporated to 30 ml. and treated with 30 ml. of water. Upon cooling, purple-brown needles (Fraction E) separated which weighed 1.267 g.

Fraction B was heated to boiling with 50 ml. of 95% ethanol and filtered hot. The red crystals, which weighed 0.109 g., were combined with Fraction D. The mother liquor was evaporated to 25 ml., treated with 25 ml. of water, cooled in the refrigerator for 10 hours and filtered. The orange platelets (Fraction F) weighed 0.670 g.

Fraction C was heated to boiling with 50 ml. of 95% ethanol and filtered hot. The red crystals, which weighed 0.182 g., were combined with Fraction D. The mother liquor was evaporated to a volume of 25 ml., treated with 25 ml. of water, cooled in the refrigerator for 5 hours and filtered. The brown needles, which weighed 0.204 g., were combined with Fraction E.

Fraction D, totaling 1.037 g., was recrystallized three times from benzene to yield bright red crystalline needles,

m.p. 236.5–237.5° (cor.) (dec.) (lit. 237°).⁶ This was identified as 2,5-dianilino-*p*-quinonedianil.

Anal. Calcd. for $C_{30}H_{24}N_4$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.90; H, 5.79; N, 12.51.

Fraction E, totaling 1.471 g., was heated to boiling with 40 ml. of water and filtered hot. The brown crystals (Fraction G), which weighed 0.274 g., melted at 198–228° (cor.) (dec.). The mother liquor was cooled in the refrigerator for 4 hours and filtered. The light purple-colored needles weighed 0.946 g., m.p. 148–151° (cor.), and were identified as benzenesulfonamide.

Fraction F was recrystallized four times from 95% ethanol for purification; colorless platelets, m.p. 151.5–153.5° (cor.) (lit., m.p. 152°).⁷ This was identified as *N,N'*-di-phenyl-*p*-phenylenediamine.

Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.05; H, 6.20. Found: C, 83.23; H, 6.49.

Fraction G was recrystallized three times from 95% ethanol to give a white crystalline solid, m.p. 206–223° (cor.) (dec.), which was not identified.

Reaction of *p*-Quinonedibenzesulfonimide with *p*-Toluidine in Benzene.—The reaction was carried out in a similar manner to that described for aniline. The mixture was concentrated to a volume of 90 ml., cooled to room temperature and filtered. The mixture of dark red crystals and brown needles (Fraction A) weighed 2.99 g. The mother liquor was washed with three 20-ml. portions of 10% hydrochloric acid and then with one 20-ml. portion of water and evaporated to 25 ml., cooled and filtered. The mixture of light-brown platelets and brown needles (Fraction B) weighed 0.929 g. The mother liquor was further evaporated to 10 ml., cooled and filtered to give 0.244 g. more of crystals which were combined with B.

Fraction A was heated to boiling with 75 ml. of 95% ethanol and filtered hot. The dark red crystals (Fraction C) weighed 1.121 g. The mother liquor was concentrated to a volume of 40 ml., cooled and filtered. The crystals (Fraction D) weighed 0.354 g. The mother liquor was evaporated to 20 ml., treated with 20 ml. of water and cooled in the refrigerator for 10 hours. The tan needles weighed 1.224 g., m.p. 146–149° (cor.), and were identified as benzenesulfonamide.

Fraction B was heated to boiling with 200 ml. of 95% ethanol and filtered hot. The dark red crystals weighing 0.098 g. were combined with Fraction C. The mother liquor was cooled to room temperature and filtered. The orange platelets (Fraction E) weighed 0.769 g. The mother liquor was evaporated to 25 ml., cooled and filtered, and the additional 0.073 g. of orange platelets combined with Fraction E.

Fraction C was recrystallized three times from benzene; bright red needles, m.p. 259° (cor.) (dec.) (lit. m.p. 250°).⁸ This was identified as 2,5-di-*p*-toluidino-*p*-quinonedip-toluidine.

Anal. Calcd. for $C_{24}H_{22}N_4$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.42; H, 6.70; N, 11.46.

Fraction D was recrystallized from 95% ethanol; white crystals, m.p. 243.4–245.5° (cor.). These were identified as *p*-phenylenedibenzesulfonamide.

Fraction E was recrystallized twice from 95% ethanol and once from benzene; white platelets, m.p. 183.5–185.5° (cor.) (lit. m.p. 182°).⁷ These were identified as *N,N'*-ditolyl-*p*-phenylenediamine.

Anal. Calcd. for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99. Found: C, 83.44; H, 7.19.

Reaction of *p*-Quinonedibenzesulfonimide with Butylamine (A).—A solution of 0.2 g. of butylamine in 2 ml. of benzene was added dropwise with stirring to a solution of 1.0 g. of the quinone diimide in 70 ml. of benzene. Crystals separated from the red-brown solution which was cooled in the refrigerator and filtered. They weighed 0.601 g. (74%). Upon two recrystallizations from 50% ethanol and once from water, white crystalline platelets were obtained, m.p. 151–153° (cor.), which were identified as benzenesulfonamide.

The mother liquor from the filtration of the reaction mix-

(6) R. Majima and Y. Aoki, *Ber.*, **44**, 3080 (1911).

(7) A. Calm, *ibid.*, **16**, 2786 (1883). Bandrowski⁴ reports m.p. 132–135°.

(8) C. Kimich, *ibid.*, **8**, 1031 (1875).

ture was treated with petroleum ether (b.p. 90–120°). Only a black tarry product was obtained.

(B).—A solution of 1.26 g. of butylamine in 5 ml. of chloroform was added dropwise with stirring to a solution of 3.0 g. of the quinone diimide in 140 ml. of chloroform. The reaction mixture was stirred at room temperature for 5 minutes and the red-brown solution was filtered. The crystals, which weighed 1.942 g., m.p. 144–147° (cor.), were identified as crude benzenesulfonamide. The mother liquor was treated with 150 ml. of carbon tetrachloride, followed by cooling and filtration. A second crystalline portion weighing 0.218 g. was also benzenesulfonamide. No further crystalline material could be isolated. The total yield was 2.16 g. (88%).

Reaction of *p*-Quinonedibzenzenesulfonimide and Butylamine Followed by Reduction of the Reaction Mixture (A).—A solution of 2.0 g. of quinone diimide in 140 ml. of pure dry benzene was placed in an opaque hydrogenation bottle so as to exclude all light from the reaction mixture. The solution was treated with 0.844 g. of butylamine in 5 ml. of pure benzene and the bottle stoppered and shaken. After 15 minutes the reaction mixture was treated with 0.1 g. of platinum oxide catalyst and hydrogenated at 35 p.s.i. The colorless solution, containing white crystals, immediately began to darken upon exposure to the atmosphere. It was filtered to give 1.341 g. of white crystals which were identified as benzenesulfonamide. The mother liquor was treated with 150 ml. of petroleum ether (b.p. 90–120°) cooled and filtered to yield an additional 0.233 g. of crude benzenesulfonamide. The total yield was, therefore, 1.574 g. (96.4%). The mother liquor, upon further cooling, yielded only a very small amount of dark-blue oil, which collected on the sides and bottom of the beaker. The clear-brown solution was decanted from the oil and extracted with two 20-ml. portions of 10% hydrochloric acid solution. The extracts were combined and made basic. The light brown flocculent precipitate was recrystallized from petroleum ether (b.p. 30–60°); the colorless crystalline platelets weighed 1.01 g. (88.6%). They were recrystallized twice from petroleum ether (b.p. 30–60°); m.p. 53° (cor.) (lit. m.p. 53.2–53.8°).⁹ They were *N,N'*-dibutyl-*p*-phenylenediamine.

Anal. Calcd. for $C_{14}H_{24}N_2$: C, 76.31; H, 10.98; N, 12.71. Found: C, 76.20; H, 11.18; N, 12.98.

(B).—A solution of 1.0 g. of the quinone diimide in 75 ml. of pure benzene was treated with 2.6 g. of butylamine and the mixture shaken vigorously. After just thirty seconds, 30 ml. of water and an excess of sodium hydrosulfite was added and the mixture shaken thoroughly. The red-brown solu-

tion decolorized to a light tan mixture. The mixture was made basic and the two liquid phases separated. The amine was extracted from the benzene portion with dilute hydrochloric acid, the extract made basic, cooled in the refrigerator and filtered. The product was taken up in 25 ml. of petroleum ether (b.p. 30–60°), filtered and the filtrate evaporated to dryness. The product weighed 0.255 g. (44.7%). One recrystallization from petroleum ether (b.p. 30–60°) raised the melting point to 53° (cor.). By allowing the reaction to stand at room temperature for 48 hours before effecting the reduction a yield of 0.427 g. (74.8%) of crude *N,N'*-dibutyl-*p*-phenylenediamine resulted.

Reaction of *p*-Quinonedibzenzenesulfonimide and β -Phenylethyl Amine with Chemical Reduction of the Reaction Mixture.—A solution of 2.0 g. of the quinone diimide in 150 ml. of pure benzene and 9.4 g. of redistilled β -phenylethylamine (b.p. 197–199°) was shaken well and allowed to stand for 48 hours in the dark. The dark brown solution was then treated with 60 ml. of water and an excess of sodium hydrosulfite and shaken vigorously. The color of the solution did not lighten appreciably upon reduction. The mixture was made basic and the two liquid phases separated. The benzene layer was evaporated to a volume of 20 ml., cooled in running tap water and filtered. The crude amine, weighing 1.249 g. (76.3%) was recrystallized three times from 95% ethanol; white platelets, m.p. 127–128.5° (cor.). This compound was identified as *N,N'*-di- β -phenylethyl-*p*-phenylenediamine.

Anal. Calcd. for $C_{22}H_{24}N_2$: C, 83.50; H, 7.65; N, 8.85. Found: C, 83.77; H, 7.80; N, 8.94.

Reaction of *p*-Quinonedibzenzenesulfonimide and Ammonia with Chemical Reduction of the Reaction Mixture.—A solution of 2.0 g. of the quinone diimide in 140 ml. of benzene was saturated with ammonia by bubbling the gas through the solution for 30 seconds. The reaction mixture consisted of a red-brown solution containing tan crystals. About 50 ml. of water and an excess of sodium hydrosulfite was then added and the mixture shaken vigorously. The mixture was then made basic and the two liquid phases separated. The benzene phase was extracted with dilute hydrochloric acid, and the extract made basic with 10% sodium hydroxide solution. The basic solution was then ether extracted in a continuous liquid-liquid extraction apparatus. The ether extract was evaporated to dryness. The light brown platelets weighing 0.461 g. (82.3%) were recrystallized twice from benzene (Darco); white platelets, m.p. 134–136° (cor.). This was identified as *p*-phenylenediamine.

(9) J. V. Capinjoia, *THIS JOURNAL*, **73**, 1849 (1951).