3,4-dihydronaphthalene and 1-ethylidine-2,3,4-trihydronaphthalene, was filtered from the catalyst and then rapidly distilled through a short column. Fractions with $n^{20}D$ 1.5730 to 1.5711 were combined (b.p. 72 to 76° at 1 mm. pressure). The yield of distillate from two preparations was 1082 g. (6.8 moles, 68% of theory, based on 1-tetralone). Treatment of individual fractions with activated silica gel had no significant effect on the refractive indices. The infrared spectrum of the combined sample indicated the absence of detectible amounts of any unreacted alcohol and of 1-ethylnaphthalene, a possible dehydrogenation product.

1-Ethyl-1,2,3,4-tetrahydronaphthalene.—The hydrogenation of 1082 g. (6.8 moles) of the olefinic product was carried out in a rocking autoclave of approximately 4.5-l. capacity at 200°, at an initial pressure of 3000 p.s.i. of hydrogen using approximately 10% by weight of barium-promoted copper chromite as catalyst. The hydrogenation was completed in about one hour. The product was filtered from the catalyst. Treatment of the catalyst with refluxing ethanol afforded substantial quantities of hydrocarbon that had been adsorbed on the catalyst.

The hydrocarbon was fractionally distilled at approximately 50 mm. of pressure. The fractions of the distillate within the refractive index range of 1.5313 to 1.5322 were combined (785 g.) and refractionated in a six-foot Podbielniak column at 20 mm. pressure with a reflux ratio of approximately 200 to 1.

For combination of fractions from the final distillation, uniformity of composition was determined by constancy of refractive indices and densities of individual fractions.

After passage through columns of activated silica gel, 540 g. (3.4 moles) of high purity 1-ethyl-1,2,3,4-tetrahydronaphthalene was obtained (yield 34% of theory, based on 1-tetralone).

Summary of Preparations of 1-Alkyl-1,2,3,4-tetrahydronaphthalenes.—The details of the syntheses of the other hydrocarbons characterized in this report are essentially analogous to those described for the typical case of the preparation of 1-ethyl-1,2,3,4-tetrahydronaphthalene. In each instance, the Grignard reagent obtained from six moles of the appropriate halide was treated with five moles of 1-tetralone. Because of a general tendency of the resulting carbinols to dehydrate even on simple distillation, these materials were not highly purified prior to the dehydration step. The olefin mixture was hydrogenated in the presence of approximately 10% by weight of a barium-promoted copper chromite catalyst. No solvents were added to the hydrogenation charges, except in the case of the preparation of 1-pentyl-1,2,3,4-tetrahydronaphthalene in which a charge of 1230 ml. of olefins was reduced in the presence of 270 ml. of water-free dioxane. Initial hydrogen pressures were between 1800 and 3000 p.s.i., reaction temperatures between 190 and 210°. The purification procedures were also essentially similar to those employed for 1-ethyl-1,2,3,4-tetrahydronaphthalene. The experimental details are summarized in Table II.

TABLE II

SUMMARY OF EXPERIMENTAL DETAILS FOR THE PREPARATION OF 1-ALKYL-1,2,3,4-TETRAHYDRONAPHTHALENES

Alkyl substituent	B.p. range, °C. at 1 mm.	$n^{20}D$ range	Wt. of olefin, g.	Wt. of product isolated, g.	Yield, g.	Overall yield based on 1-tetralone, %
1-Methyl	65–75	1.5768–1.5752	1102	1028	625	43
1-Ethyl	72–76	1.5730–1.5711	1082	785	540	34
1-Butyl	63–120	1.5740–1.5522	860	725	574	24
1-Pentyl[a]	94–102	1.5548–1.5479	1183	1125	675	33

[a] It is recognized that the 1-bromopentane could have been contaminated with other isomers. The density and refractive index of the 1-bromopentane were d^{20} 1.2206 g./ml. and $n^{20}D$ 1.4450 as compared with d^{20}_4 1.2160[9] and $n^{20}D$ 1.4448[10] in the literature. Data from propyl and butyl derivatives of several homologous series[2,8,11] show that branched chain impurities in the final hydrocarbon would have boiling points sufficiently lower than the boiling point of the desired compound to be removed by distillation.

Repeated efforts to prepare 1-(2-propyl)-1,2,3,4-tetrahydronaphthalene by a similar procedure resulted in exceedingly small yields of the final product in a state of purity that was considered too poor to permit inclusion of the compound in the present report.

Acknowledgment.—The authors wish to thank the members of the analytical and physical constants groups of this Laboratory for their assistance.

(9) W. H. Heston, Jr., E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **72**, 2071 (1950).

(10) L. M. Kushner, R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 1091 (1950).

(11) I. A. Goodman and P. H. Wise, National Advisory Committee for Aeronautics, Technical Note 2419, Cleveland (1951).

CLEVELAND, OHIO

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

Quinone Imides. XXVII. Addition Reactions of Substituted *p*-Quinonedibenzenesulfonimides

BY ROGER ADAMS AND THOMAS E. YOUNG[1]

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Hydrogen chloride, thiophenol and sodium benzenesulfinate add readily to 2-methoxy-*p*-quinonedibenzenesulfonimide to give in excellent yield the 2-methoxy diamides with the chlorine, phenylmercapto and benzenesulfone groups in the 5-position. The products whose structures were proved by unequivocal syntheses were all readily oxidized to the corresponding diimides. 2-Chloro-*p*-quinonedibenzenesulfonimide adds sodium benzenesulfinate to give two isomeric benzenesulfones, one of which was proved unequivocally to be the 2-chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide. 2-Phenylmercapto-*p*-quinonedibenzenesulfonimide adds sodium benzenesulfinate to give a high yield of 2-phenylmercapto-x-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide which upon oxidation with peroxide yields a 2,x-bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide identical with that formed from the addition of thiophenol to 2-phenylmercapto-*p*-quinonedibenzenesulfonimide followed by peroxide oxidation. The orientation was not proved but is probably 2,5. 2-Methyl-*p*-quinonedibenzenesulfonimide adds thiophenol and sodium benzenesulfinate to give presumably the 2-methyl-5-phenylmercapto- and 2-methyl-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamides, respectively. The former was converted to the latter by peroxide oxidation.

p-Benzoquinones bearing a single electron-donating substituent undergo conjugate addition reactions to give predominantly 2,5-disubstituted hydroquinone derivatives. Methoxy-*p*-quinone, for example, undergoes the Thiele–Winter reaction to produce a 98% yield of 2-methoxy-1,4,5-triacetoxybenzene.[2] Toluquinone similarly gives good yields of 2-methyl-1,4,5-triacetoxybenzene,[3] and adds hydrogen chloride to produce chiefly 5-chlorotoluhy-

(1) From portions of a thesis submitted by Thomas E. Young (Sept., 1952) to the Graduate College of the University of Illinois, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Standard Oil Company of California Research Fellow, 1950–1952.

(2) H. G. H. Erdtman, *Proc. Roy. Soc.* (*London*), **A143**, 177 (1934).

(3) J. Thiele and E. Winter, *Ann.*, **311**, 349 (1900).

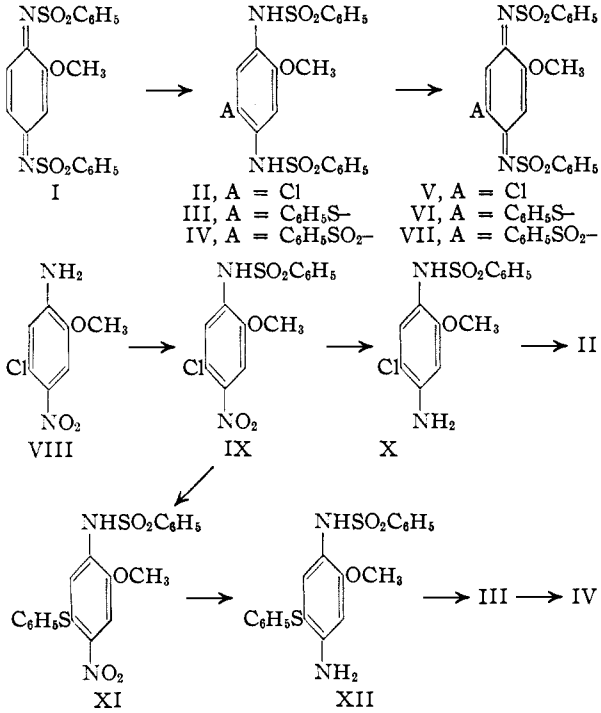
droquinone along with some of the 3-chloro isomer.[4] Some of the theoretical aspects of the orienting influence of this type of functional group on additions to the quinonoid nucleus have been discussed by Erdtman.[2]

Analogous addition reactions in the quinone diimide series have also been studied. The addition of hydrogen chloride to 2-chloro-, 2-methyl- and 2-phenylmercapto-*p*-quinonedibenzenesulfonimides, and the addition of thiophenol to 2-chloro-*p*-quinonedibenzenesulfonimide have already been reported.[5] In each of these cases the product consisted of a fair to major proportion of a 2,5-disubstituted-*p*-phenylenedibenzenesulfonamide. Further reactions of these same mono-substituted quinone diimides have now been studied in addition to the synthesis and reactions of 2-methoxy-*p*-quinonedibenzenesulfonimide.

2-Methoxy-*p*-phenylenediamine,[6] obtained by catalytic hydrogenation of 5-nitro-2-aminoanisole over a platinum catalyst, was benzenesulfonated in pyridine solution to form 2-methoxy-*p*-phenylenedibenzenesulfonamide. Oxidation of this diamide with lead tetraacetate in glacial acetic acid produced excellent yields of 2-methoxy-*p*-quinonedibenzenesulfonimide (I). This quinone diimide added dry hydrogen chloride in chloroform solution to give exclusively 2-methoxy-5-chloro-*p*-phenylenedibenzenesulfonamide (II), which was also synthesized unequivocally by the following sequence of reactions: 2-amino-4-chloro-5-nitroanisole[7] (VIII) on treatment with benzenesulfonyl chloride in pyridine solutions afforded 2-benzenesulfonamido-4-chloro-5-nitroanisole (IX); reduction of the nitro group with sodium hydrosulfite gave the corresponding amine X, which was then benzenesulfonated, giving 2-methoxy-5-chloro-*p*-phenylenedibenzenesulfonamide (II).

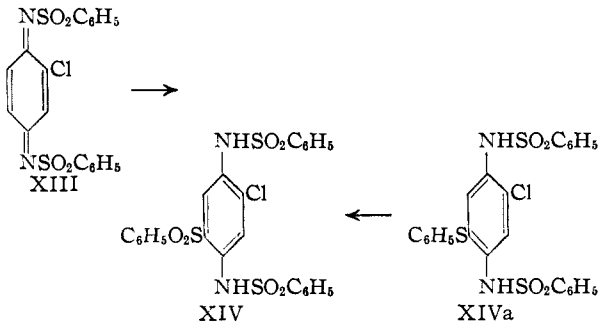
2-Methoxy-*p*-quinonedibenzenesulfonimide also reacted with thiophenol in dry chloroform solution in the presence of a trace of concentrated sulfuric acid. Reduction of the diimide to 2-methoxy-*p*-phenylenedibenzenesulfonamide occurred to the extent of about 10%, while conjugate addition of thiophenol to the quinone diimide produced 62% of 2-methoxy-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide (III). Again the structure of this adduct was proved by unequivocal synthesis; the 2-benzenesulfonamido-4-chloro-5-nitroanisole (IX), mentioned previously, reacted with sodium thiophenate with replacement of the nitro-activated chlorine atom by a phenylmercapto group. This product, 2-benzenesulfonamido-4-phenylmercapto-5-nitroanisole (XI), was then reduced by sodium hydrosulfite to the amine XII, which on benzenesulfonation afforded 2-methoxy-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide (III).

Sodium benzenesulfinate, likewise, reacted rapidly with 2-methoxy-*p*-quinonedibenzenesulfonimide in glacial acetic acid to give a high yield of 2-methoxy-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide (IV), identified by comparison with the same product obtained by hydrogen peroxide oxidation of the corresponding sulfide III.



Lead tetraacetate oxidation of all three of the 2-methoxy-5-substituted-*p*-phenylenedibenzenesulfonamides (II, III and IV) to the corresponding quinone diimides (V, VI and VII) proceeded readily in glacial acetic acid at room temperature.

2-Chloro-*p*-quinonedibenzenesulfonimide (XIII) was prepared by the procedure previously reported[8]; it reacted with sodium benzenesulfinate in glacial acetic acid to produce 44% of essentially pure 2-chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide (XIV) and an indeterminate quantity of 2-chloro-z-benzenesulfonyl isomer, in which the arbitrarily designated z-position was unestablished. The structure of the 2,5-isomer was proved by showing its identity with the sulfone obtained by hydrogen peroxide oxidation of the known[5b] 2-chloro-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide (XIVa).



The reaction of 2-phenylmercapto-*p*-quinonedibenzenesulfonimide (XV) with thiophenol has already been reported.[5b] The product, 2,x-bis-

(4) T. H. Clark, *Am. Chem. J.*, **14**, 573 (1892).

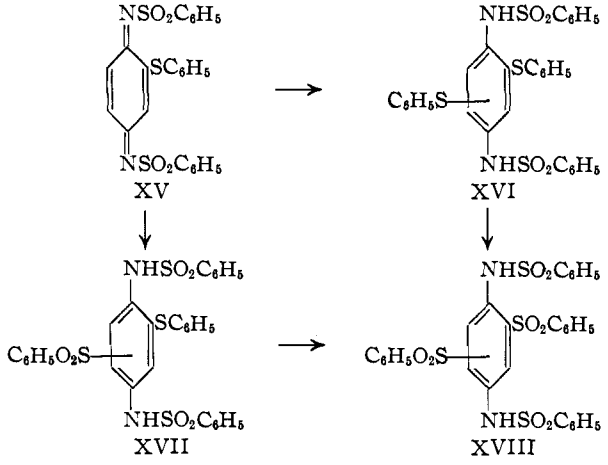
(5) (a) R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952); (b) R. Adams, E. F. Elslager and T. E. Young, *ibid.*, **74**, 663 (1953).

(6) S. I. Burmistrov and N. A. Zuikova, *Zhur. Obschei. Khim.*, **20**, 1852 (1950).

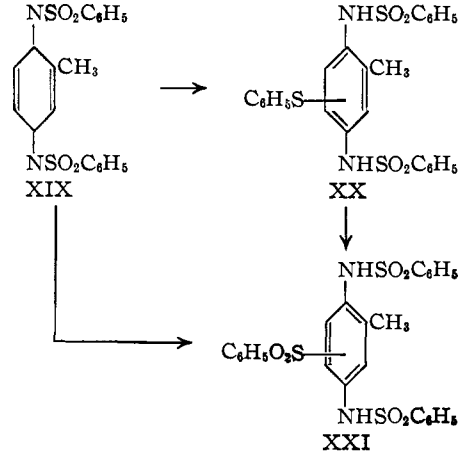
(7) "Aktien-Gesellschaft für Anilin-Fabrikation," German Patent 137,956 (Aug. 25, 1901); *Chem. Zentr.*, **74**, I, 112 (1903).

(8) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950).

(phenylmercapto) - *p* - phenylenedibenzenesulfonamide (XVI) was tentatively presumed, but not proved, to be the 2,5-isomer by analogy with the corresponding compound in the quinone series. In the present investigation it was found that this same quinone diimide also added benzenesulfinic acid to give high yields of 2-phenylmercapto-x-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide (XVII). Oxidation of either of these adducts with hydrogen peroxide led to the same 2,x-bis-(benzenesulfonyl) - *p* - phenylenedibenzenesulfonamide (XVIII), showing that the orientation of substituents in those adducts is the same.



A similar series of reactions was carried out starting with 2-methyl-*p*-quinonedibenzenesulfonimide[8] (XIX), which rapidly added thiophenol in the presence of a catalytic amount of triethylamine in chloroform solution to give a high yield of 2-methyl-y-phenylmercapto-*p*-phenylenedibenzenesulfonamide (XX). Reaction of the methylquinone diimide with sodium benzenesulfinate in glacial acetic acid also proceeded readily to give 2-methyl-y - benzenesulfonyl - *p* - phenylenedibenzenesulfonamide (XXI); this same product was obtained by hydrogen peroxide oxidation of the phenylmercapto derivative (XX). The orientation of substituents in these two adducts is therefore the same, and by analogy with the hydrogen chloride adduct[5a] may be expected to have the 2,5-orientation.



Acknowledgment.—The authors are indebted to Mrs. Elizabeth Leighly and Miss Helen Miklas for the determination and comparison of infrared spectra, and to Miss Emily Davis, Mrs. Jean Fortney, Mrs. Esther Fett, Mrs. Katherine Pih and Mr. Joseph Nemeth for the microanalyses.

Experimental

All melting points are corrected.

2-Methoxy-*p*-phenylenediamine.—A solution of 22.1 g. of 5-nitro-2-aminoanisole in 170 ml. of dry dioxane was hydrogenated over 0.2 g. of platinum oxide at 3 atmospheres pressure and room temperature. After 1.5 hours, the theoretical amount of hydrogen had been absorbed; the solution was then filtered free of catalyst and distilled at 20 mm. pressure to remove 140 ml. of solvent. The residual oil was stirred with 150 ml. of petroleum ether (b.p. 30–60°), precipitating 17.1 g. (95%) of crude product. Recrystallization from benzene, which had previously been boiled in contact with sodium hydrosulfite solution, gave white crystals of 2-methoxy-*p*-phenylenediamine, m.p. 105.5–107.5°. This compound has been previously prepared[6] by sodium sulfide reduction of 5-nitro-2-aminoanisole; the reported melting point was 103.5°.

2-Methoxy-*p*-phenylenedibenzenesulfonamide.—To a solution of 8.50 g. of freshly prepared 2-methoxy-*p*-phenylenediamine in 150 ml. of dry redistilled pyridine was added 15.8 ml. of benzenesulfonyl chloride; a strongly exothermic reaction occurred. After refluxing this mixture for 3 hours, 100 ml. of excess pyridine was distilled off, and the residue poured into a solution of 60 ml. of concentrated hydrochloric acid in 300 ml. of water. The oil which separated was triturated for 10 minutes to effect solidification. The crude gray product was collected, washed several times with water, dried, then dissolved in 140 ml. of boiling glacial acetic acid. This solution was treated with 3 g. of Darco, filtered, concentrated to 100 ml., then cooled, yielding 21.3 g. (82.6%) of white product. Recrystallization from glacial acetic acid gave pure 2-methoxy-*p*-phenylenedibenzenesulfonamide, m.p. 194–195°.

Anal. Calcd. for $C_{19}H_{18}N_2O_5S_2$: C, 54.54; H, 4.33; N, 6.70. Found: C, 54.63; H, 4.28; N, 6.70.

2-Methoxy-*p*-quinonedibenzenesulfonimide.—To a mechanically stirred suspension of 10.0 g. of 2-methoxy-*p*-phenylenedibenzenesulfonamide in 50 ml. of glacial acetic acid was added 10.7 g. of lead tetraacetate in one portion. Within a minute the mixture turned yellow-orange in color. After stirring for 1 hour at room temperature, 2 ml. of ethylene glycol was added, and stirring continued an additional 10 minutes. The light orange product was filtered off, washed with glacial acetic acid, then with petroleum ether (b.p. 30–60°) and dried; it weighed 8.40 g. Dilution of the mother liquors with water afforded another 1.00 g. bringing the total crude yield to 94.5%. Recrystallization from glacial acetic acid gave pure 2-methoxy-*p*-quinonedibenzenesulfonimide, m.p. 160–162°. This product began to decompose after standing for about 2 weeks to a brown substance of unknown constitution.

Anal. Calcd. for $C_{19}H_{16}N_2O_5S_2$: C, 54.79; H, 3.87; N, 6.73. Found: C, 54.63; H, 3.91; N, 6.98.

2-Benzenesulfonamido-4-chloro-5-nitroanisole.—A solution of 4.4 g. of 2-amino-4-chloro-5-nitroanisole[7] and 2.9 ml. of benzenesulfonyl chloride in 40 ml. of pyridine was refluxed for 6 hours, then poured into a solution of 50 ml. of concentrated hydrochloric acid in 100 ml. of water. The precipitated solid was collected, dissolved in 50 ml. of dioxane, and treated with Darco. To the resulting light yellow solution was added 500 ml. of petroleum ether (b.p. 30–60°), precipitating 4.7 g. (63%) of crude product. Recrystallization of this material from glacial acetic acid gave pale yellow needles, m.p. 212–213.5°.

Anal. Calcd. for $C_{13}H_{11}ClN_2O_5S$: C, 45.55; H, 3.23; N, 8.17. Found: C, 45.71; H, 3.44; N, 8.15.

2-Benzenesulfonamido-4-chloro-5-aminoanisole.—A solution of 2.0 g. of 2-benzenesulfonamido-4-chloro-5-nitroanisole in a solution of 0.5 g. of potassium hydroxide in 50 ml. of water was heated to boiling, and 7.0 g. of sodium hydrosulfite added in portions. Within a few minutes the solution was nearly colorless and a white solid separated. This crude amine was filtered off, then recrystallized from 95% ethanol to give 1.0 g. (55%) of pure product; long white needles, m.p. 172.5–174° (dec.).

Anal. Calcd. for $C_{13}H_{13}ClN_2O_3S$: C, 49.91; H, 4.19; N, 8.96. Found: C, 50.10; H, 4.40; N, 9.04.

2-Methoxy-5-chloro-*p*-phenylenedibenzenesulfonamide. Method A.—A solution of 1.73 g. of 2-benzenesulfonamido-4-chloro-5-aminoanisole and 1.00 g. of benzenesulfonyl chloride in 15 ml. of dry pyridine was refluxed for 2 hours. The reaction solution was treated with Darco, filtered, diluted with 50 ml. of water, then acidified with hydrochloric acid. The nearly white product, which precipitated, weighed 2.00 g. (80%). After two recrystallizations from glacial acetic acid, pure 2-methoxy-5-chloro-*p*-phenylenedibenzenesulfonamide was obtained as white crystals, m.p. 235.5–237.5° (dec.).

Method B.—Dry hydrogen chloride was bubbled into a solution of 1.04 g. of 2-methoxy-*p*-quinonedibenzenesulfonimide in 25 ml. of dry chloroform for a period of 15 minutes. At the end of this time the solution was completely decolorized and some white crystals had deposited on the walls of the flask. The chloroform solution was evaporated to dryness with an air jet and heat lamp, yielding 1.08 g. (95%) of 2-methoxy-5-chloro-*p*-phenylenedibenzenesulfonamide. One recrystallization from glacial acetic acid gave the pure product, m.p. 234.5–236.5° (dec.). The melting point was not depressed on admixture with a sample prepared by method A, and material prepared by both methods showed identical infrared absorption spectra.

Anal. Calcd. for $C_{19}H_{17}ClN_2O_5S_2$: C, 50.38; H, 3.78; N, 6.19. Found: C, 50.39; H, 4.01; N, 6.21.

2-Methoxy-5-chloro-*p*-quinonedibenzenesulfonimide.—To a mechanically stirred suspension of 5.00 g. of 2-methoxy-5-chloro-*p*-phenylenedibenzenesulfonamide in 35 ml. of glacial acetic acid was added 5.00 g. of dry lead tetraacetate. Almost immediately the mixture turned to a yellow color. After stirring the slurry for 1 hour at room temperature, the orange product was filtered off, washed with glacial acetic acid, then with petroleum ether (b.p. 30–60°), and dried. The yield of crude product was 4.90 g. (98.5%). Two recrystallizations from 125-ml. portions of glacial acetic acid gave orange needles, m.p. 218.5–220.5° (dec.), with darkening around 200°.

Anal. Calcd. for $C_{19}H_{15}ClN_2O_5S_2$: C, 50.61; H, 3.35; N, 6.21. Found: C, 50.80; H, 3.26; N, 6.18.

2-Benzenesulfonamido-4-phenylmercapto-5-nitroanisole.—To a solution of 0.80 g. of sodium hydroxide in 5 ml. of water was added 1.93 g. of thiophenol. This mixture was added to a suspension of 3.00 g. of 2-benzenesulfonamido-4-chloro-5-nitroanisole in 25 ml. of dioxane. The mixture became warm, turned dark red, and in a few minutes a clear solution resulted, which was then refluxed for 3 hours. At the end of this time a quantity of small crystals had deposited on the walls of the flask. The red mixture was poured into 200 ml. of water and acidified. Decantation of the yellow liquors left a gummy residue which was triturated with 50 ml. of 95% ethanol leaving a nicely powdered, bright yellow product weighing 2.90 g. Concentration of the ethanol wash to 30 ml. afforded another 0.21 g. bringing the total crude yield to 85.2%. The crude product on recrystallization from 95% ethanol gave brilliant yellow needles, m.p. 180–181.5°.

Anal. Calcd. for $C_{19}H_{16}N_2O_5S_2$: C, 54.79; H, 3.87; N, 6.73. Found: C, 54.91; H, 3.94; N, 6.62.

2-Benzenesulfonamido-4-phenylmercapto-5-aminoanisole.—A slurry of 1.30 g. of 2-benzenesulfonamido-4-phenylmercapto-5-nitroanisole in 50 ml. of 1% aqueous sodium hydroxide was heated to boiling, then 1.85 g. of sodium hydrosulfite added gradually. The resulting yellow-tinted white solid was collected, then dissolved in 60 ml. of boiling 95% ethanol. On cooling, this solution deposited 0.63 g. of pretty white plates. The yellow ethanolic liquors were reheated to boiling and solid sodium hydrosulfite added until the mixture was colorless. Concentration of this solution to 30 ml. and cooling produced an additional batch of white product, which after recrystallization from 15 ml. of 95% ethanol, weighed 0.29 g.; the total yield was 76%. The combined crudes were recrystallized once more from 95% ethanol to give pure product, m.p. 169.5–170.5°.

Anal. Calcd. for $C_{19}H_{18}N_2O_3S_2$: C, 59.04; H, 4.69; N, 7.25. Found: C, 59.16; H, 4.91; N, 7.21.

2-Methoxy-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide. Method A.—A solution of 0.40 g. of 2-benzenesulfonamido-4-phenylmercapto-5-aminoanisole and 0.19 g. of benzenesulfonyl chloride in 10 ml. of pyridine was refluxed for 5 hours. Pouring the reaction mixture into a solution of 11 ml. of concentrated hydrochloric acid in 30 ml. of water precipitated 0.52 g. (95%) of crude product. One recrystallization from 8 ml. of glacial acetic acid (Darco) gave 0.38 g. of pure white crystals, m.p. 209–211°.

Method B.—To a solution of 0.28 g. of thiophenol in 10 ml. of dry chloroform was added 1 drop of concentrated sulfuric acid. This mixture was then immediately added to a solution of 1.03 g. of 2-methoxy-*p*-quinonedibenzenesulfonimide in 25 ml. of dry chloroform. The resulting solution slowly assumed a cherry red color which did not disappear after 8 hours. An additional 3 drops of thiophenol, then added to the reaction mixture, caused the color to fade to a pale yellow within 15 minutes. The solution was evaporated to dryness and the residue washed with 25 ml. of methanol, then with 10 ml. of ether. The white insoluble product remaining weighed 0.80 g. (62%); it was twice recrystallized from 15-ml. portions of glacial acetic acid to give 0.69 g. of pure 2-methoxy-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide, m.p. 209.5–210.5°. This product and a sample prepared by method A showed identical infrared absorption spectra and a mixture of the two gave no depression of the melting point.

Anal. Calcd. for $C_{25}H_{22}N_2O_5S_3$: C, 57.02; H, 4.21; N, 5.32. Found: C, 57.08; H, 4.23; N, 5.37.

The combined ethanol–ether wash liquors above were concentrated to half volume and cooled giving 0.17 g. of crystals, m.p. 175–180°. This material appeared to be a mixture of adduct and reduction product and was not examined further. Evaporation of the remaining liquors to dryness left 0.13 g. (10%) of crude 2-methoxy-*p*-phenylenedibenzenesulfonamide, which was pure after two recrystallizations from glacial acetic acid; it melted at 193.5–195.5°, and showed no depression of the melting point when mixed with an authentic sample.

2-Methoxy-5-phenylmercapto-*p*-quinonedibenzenesulfonimide.—To a suspension of 0.78 g. of 2-methoxy-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide in 10 ml. of glacial acetic acid was added 0.66 g. of lead tetraacetate. The mixture, which immediately turned deep red, was stirred at room temperature for 1 hour, then filtered, giving 0.64 g. (82%) of red crystals. Three recrystallizations from glacial acetic acid gave pure 2-methoxy-5-phenylmercapto-*p*-quinonedibenzenesulfonimide as small, deep red transparent prisms, m.p. 216.5–218° (dec.).

Anal. Calcd. for $C_{25}H_{20}N_2O_5S_3$: C, 57.23; H, 3.84; N, 5.34. Found: C, 57.26; H, 3.96; N, 5.42.

2-Methoxy-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide. Method A.—A mixture of 0.40 g. of 2-methoxy-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide, 1 ml. of 30% hydrogen peroxide and 10 ml. of glacial acetic acid was cautiously heated to boiling and the resulting solution refluxed for 1.25 hours. The pale yellow reaction solution was diluted to 40 ml. with water, precipitating a light cream colored solid, which was collected and dried. The crude solid was washed with 10 ml. of dry ether, removing the color and leaving 0.38 g. (89%) of white powder; one recrystallization from glacial acetic acid gave pure 2-methoxy-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide, m.p. 185–187.5°.

Method B.—To a suspension of 2.00 g. of 2-methoxy-*p*-quinonedibenzenesulfonimide in 10 ml. of glacial acetic acid was added 0.90 g. of sodium benzenesulfinate (Eastman Kodak Co., White Label) in 7 ml. of glacial acetic acid. This mixture was warmed gently for 5 minutes after which it was colorless; it was then heated to boiling, giving a clear solution, filtered hot, then cooled yielding a crop of white crystals. The crude product was washed with ether then with water, and dried; the yield was 2.30 g. (86%). Recrystallization from glacial acetic acid gave the pure 2-methoxy-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide, m.p. 185.5–188°. This product and a sample prepared by method A showed identical infrared spectra, and on admixture showed no depression of the melting point.

Anal. Calcd. for $C_{25}H_{22}N_2O_7S_3$: C, 53.74; H, 3.97; N, 5.02. Found: C, 53.91; H, 4.09; N, 4.91.

2-Methoxy-5-benzenesulfonyl-*p*-quinonedibenzenesulfonimide.—A suspension of 1.11 g. of 2-methoxy-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide and 0.88 g. of dry lead tetraacetate in 17.5 ml. of glacial acetic acid was

stirred at room temperature; immediately on mixing the reactants, the mixture became yellow to orange, and the product began to crystallize out after 20 minutes. After 2 hours the nicely crystalline product was collected, washed with absolute ether, then dried. The yield was 1.07 g. (96.4%). Recrystallization from dry, thiophene-free benzene gave 2-methoxy-5-benzenesulfonyl-*p*-quinonedibenzenesulfonimide as an orange micro-crystalline powder, m.p. 225.5–229° (dec.) with gradual prior darkening. A sample placed in the bath at 220° melted at 231–232° (dec.).

Anal. Calcd. for $C_{26}H_{20}N_2O_7S_3$: C, 53.93; H, 3.62; N, 5.03. Found: C, 54.06; H, 3.65; N, 5.29.

2-Chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide. Method A.—A solution of 0.177 g. of 2-chloro-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide[5b] and 0.5 ml. of 30% hydrogen peroxide in 15 ml. of glacial acetic acid was refluxed for 1.5 hours, then poured into 20 ml. of water. The white product which precipitated was filtered off and dried over phosphorus pentoxide. The yield was 0.174 g. (93%). Recrystallization from 95% ethanol gave tiny white needles of 2-chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide, m.p. 201–201.5°.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_6S_3$: C, 51.19; H, 3.40; N, 4.98. Found: C, 51.31; H, 3.49; N, 4.90.

Method B.—To a suspension of 6.53 g. of 2-chloro-*p*-quinonedibenzenesulfonimide[8] in 60 ml. of glacial acetic acid was added 3.74 g. of sodium benzenesulfinate (Eastman Kodak, White Label). The slurry was shaken for 10 minutes during which an exothermic reaction occurred and a white solid precipitated from solution. The resulting nearly colorless mixture was heated to boiling to give a pinkish-yellow tinted solution, which was filtered then cooled and allowed to stand for 6 hours with occasional scratching. There deposited 3.80 g. (43.5%) of white product which after recrystallization from 95% ethanol melted at 201–201.5°, and proved to be 2-chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide; this product exhibited an infrared absorption spectrum identical with that of the 2,5-isomer prepared by method A, and admixture of the two samples produced no depression of the melting point. The solubility of this 2,5-isomer in 95% ethanol was low, and quantities larger than 0.5 g. were best recrystallized from glacial acetic acid.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_6S_3$: C, 51.19; H, 3.40; N, 4.98. Found: C, 51.29; H, 3.45; N, 4.94.

The acetic acid mother liquors from the initial crystallization of the 2,5-isomer were poured into water, precipitating an additional 4.52 g. of white solid. This material was extracted with 100 ml. of ether. The insoluble residue, after recrystallization from 95% ethanol, afforded another 0.17 g. of the 2,5-isomer. The ether extract was evaporated to dryness and the residue recrystallized from 20 ml. of benzene to give 0.68 g. of white prisms. Four recrystallizations of this material from 95% ethanol gave thick, colorless prisms of 2-chloro-z-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide, m.p. 196.5–198.5°.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_6S_3$: C, 51.19; H, 3.40; N, 4.98. Found: C, 51.46; H, 3.34; N, 5.04.

A mixture of this compound with the 2,5-isomer melted 179.5–195.5°, and the infrared absorption spectra of the two compounds were quite different.

2-Phenylmercapto-x-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide.—To a suspension of 1.00 g. of 2-phenylmercapto-*p*-quinonedibenzenesulfonimide in 10 ml. of glacial acetic acid was added 0.50 g. of sodium benzenesulfinate (Eastman Kodak Co., White Label) in 5 ml. of glacial acetic acid. After warming the mixture gently for 5 minutes, it was colorless; it was heated to boiling, filtered hot, then cooled yielding 0.96 g. of white crystals. The mother liquors on dilution with 30 ml. of water precipitated a sticky white solid, which after washing with 5 ml. of ether then 5 ml. of 95% ethanol left an additional 0.10 g. of crystalline crude. The total yield was 82.3%. Recrystallization of the combined crude products from 95% ethanol gave white needles, m.p. 174.5–177°.

Anal. Calcd. for $C_{30}H_{24}N_2O_6S_4$: C, 56.58; H, 3.80; N, 4.40. Found: C, 56.52; H, 3.87; N, 4.31.

2,x-Bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide. Method A.—A mixture of 0.67 g. of 2,x-bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide (m.p. 224–226°),[5b] 2 ml. of 30% hydrogen peroxide and 30 ml. of glacial acetic acid was refluxed for 1.25 hours. The resulting yellow tinted solution, allowed to cool slowly to room temperature, deposited 0.67 g. (91%) of white product. Recrystallization from 30 ml. of glacial acetic acid afforded 0.62 g. of pure 2,x-bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide, m.p. 232.5–234°.

Method B.—A solution of 0.27 g. of 2-phenylmercapto-x-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide (m.p. 174.5–177°), and 1 ml. of 30% hydrogen peroxide in 9.5 ml. of glacial acetic acid was refluxed for 2 hours. On cooling the solution, 0.21 g. (74%) of white crystals deposited. Recrystallization from glacial acetic acid gave white needles of 2,x-bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide, m.p. 233–234°. Materials prepared by both methods A and B showed identical infrared absorption spectra and a mixture of the two showed no depression of the melting point.

Anal. Calcd. for $C_{30}H_{24}N_2O_6S_4$: C, 53.87; H, 3.62; N, 4.19. Found: C, 54.01; H, 3.58; N, 3.88.

2-Methyl-y-phenylmercapto-*p*-phenylenedibenzenesulfonamide.—To a solution of 2.01 g. of 2-methyl-*p*-quinonedibenzenesulfonimide[8] in 25 ml. of reagent grade chloroform (Merck and Co.) was added in one portion a solution of 0.63 g. of thiophenol and 1 drop of triethylamine in 10 ml. of chloroform. The resulting solution exhibited a fleeting orange coloration, then decolorized to water white within 10 seconds, and after standing for 10 minutes, deposited a white solid. This crude product was filtered, washed with chloroform, then with absolute ether, and dried; the yield was 2.04 g. (80%). Recrystallization from glacial acetic acid gave small white needles, m.p. 226–228° (dec.). By repeated recrystallization of this material, the melting point may be raised to 230–231°.

Anal. Calcd. for $C_{25}H_{22}N_2O_4S_3$: C, 58.80; H, 4.34; N, 5.49. Found: C, 58.94; H, 4.48; N, 5.44.

2-Methyl-ẏ-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide. Method A.—A solution of 0.94 g. of 2-methyl-y-phenylmercapto-*p*-phenylenedibenzenesulfonamide (m.p. 226–228°) and 2 ml. of 30% hydrogen peroxide in 20 ml. of glacial acetic acid was refluxed for 3 hours. The resulting pale yellow solution was poured into 75 ml. of water to give a white solid weighing 0.80 g. (80%). Recrystallization from glacial acetic acid gave white crystals, m.p. 212–213°.

Anal. Calcd. for $C_{25}H_{22}N_2O_6S_3$: C, 55.34; H, 4.09; N, 5.16. Found: C, 55.30; H, 3.85; N, 5.07.

Method B.—To a suspension of 2.42 g. of 2-methyl-*p*-quinonedibenzenesulfonimide in 15 ml. of glacial acetic acid was added 1.50 g. of sodium benzenesulfinate (Eastman Kodak Co., White Label). The mixture was shaken for 15 minutes during which a slightly exothermic reaction occurred. As the last trace of quinone diimide dissolved, a white product began to crystallize. This first crop was collected, washed with petroleum ether (b.p. 35–45°), and dried; it weighed 1.22 g. The liquors, on standing for 1 hour, deposited a second crop, 0.63 g., and on dilution with water gave another 1.05 g. bringing the total crude yield to 88%. Several recrystallizations from glacial acetic acid gave pure 2-methyl-y-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide, m.p. 212–213°. This product was identical with that prepared by method A as shown by identity of infrared spectra, melting points, and melting point of a mixture of the two.

Anal. Calcd. for $C_{25}H_{22}N_2O_6S_3$: C, 55.34; H, 4.09; N, 5.16. Found: C, 55.34; H, 4.25; N, 5.18.

URBANA, ILLINOIS