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

Quinone Imides. XXV. Addition of Mercaptans to *p*-Quinonedibenzenesulfonimide

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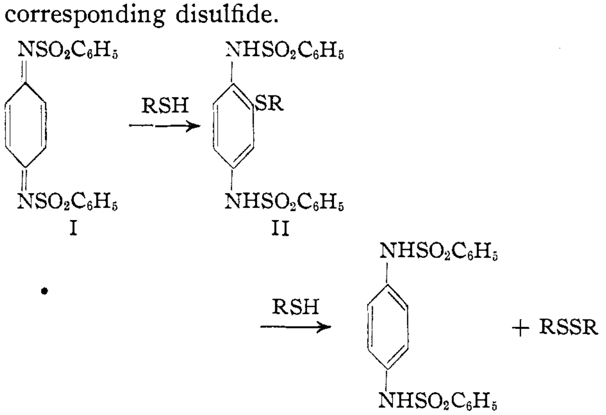
Mercaptans and *p*-quinonedibenzenesulfonimides react in one of two ways; the thiol undergoes conjugate addition to the quinone dimide to yield a monosubstituted *p*-phenylenedibenzenesulfonamide or the quinone diimide is reduced to the corresponding *p*-phenylenedibenzenesulfonamide while the thiol is oxidized to the disulfide. The control of conditions is discussed which permit the former reaction to predominate. Of acidic and basic catalysts studied, triethylamine was found in all cases to be superior for accelerating the addition reaction.

The addition of thiophenol to certain quinone diimides and monoimides has already been reported.[2] The yields were excellent and the oxidation of the thiophenol to diphenyl disulfide with concomitant reduction of the quinone diimide to the diamide was insignificant.

The reactions of thiols with *p*-benzoquinone are affected by the reaction conditions and the oxidation–reduction potentials of the adducts.[3] The addition of the mercaptan may yield the monoaddition product; the quinone may be reduced to the corresponding hydroquinone accompanied by oxidation of the mercaptan to the disulfide; successive addition–oxidation processes may result in polysubstituted quinones and hydroquinones. Thus, when thiophenol reacts with *p*-benzoquinone, 2-phenylmercapto-, 2,5-bis-(phenylmercapto)-, 2,6-bis-(phenylmercapto)- and 2,3,5-tris-(phenylmercapto)-*p*-benzoquinone may be obtained by varying the reaction temperature, solvent and ratio of the reactants.[3,4]

In this investigation, a systematic study has been completed of the reactions of a variety of mercapto compounds with *p*-quinonedibenzenesulfonimide. Initial experiments revealed that these reactions followed one of two courses; the thiol underwent conjugate addition to the quinone diimide (I) yielding a monosubstituted *p*-phenylenedibenzenesulfonamide (II) or the quinone diimide was reduced to *p*-phenylenedibenzenesulfonamide (III) while the thiol was oxidized to the corresponding disulfide. In most instances, these alternative possibilities occurred simultaneously, the predominance of one or the other varying with the purity of the reactants and the trace-presence of acidic or basic additives. No consecutive addition–oxidation reactions similar to those with *p*-benzoquinone were observed; only one mole of mercaptan reacted.



I II III

In the absence of any catalyst and using reactants of ordinary purity, the thiophenols behaved erratically, sometimes undergoing addition, sometimes preponderantly reducing the quinone diimide. When dry, pure redistilled chloroform, carefully purified thiophenols and very pure *p*-quinonedibenzenesulfonimide (m.p. 188–189°) were used, the addition reaction was more often the primary one. With aliphatic mercaptans in the absence of a catalyst, oxidation–reduction was the sole reaction regardless of the purity of the reagents. Thioacetic acid in chloroform and potassium xanthate in acetic acid were exceptions, however, in that they readily gave excellent yields of addition products.

In order to induce addition of the aliphatic mercaptans and to obtain consistently reproducible additions of the thiophenols some additives were sought which might control the course of the reactions.

The use of basic catalysts for the conjugate addition of thiols to a large variety of α,β-unsaturated compounds has been mentioned frequently in the literature[5]; piperidine, sodium alkoxides, Triton B and even potassium carbonate have been quite effective. Acidic reagents, though less common, have also been employed for this purpose.[6]

In the reaction of thiophenol with *p*-quinonedibenzenesulfonimide, a trace of sulfuric acid was adequate to keep the addition reaction in predominance; the presence of dioxane–sulfuric acid complex[7] proved satisfactory for preparing adducts from butyl mercaptan, benzyl mercaptan and 2-mercaptobenzothiazole. In all of these cases, the reaction mixtures initially acquired a deep red to maroon coloration. The time required for decolorization of the solutions varied from 10 minutes to 22 hours suggesting inhibition of the oxidation–reduction reaction rather than catalysis of the addition. Though some reduction of the diimide was always indicated, the yields of adducts were excellent.

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[1] From portions of theses submitted by Edward F. Elslager (Feb., 1951) and by T. E. Young (Oct., 1952) to the Graduate College of the University of Illinois, in partial fulfillment of the requirements for the degrees of Doctor of Philosophy.

[2] (a) R. Adams and J. Looker, THIS JOURNAL, **73**, 1145 (1951); (b) R. Adams and R. Wankel, *ibid.*, **73**, 131 (1951); (c) R. Adams and D. S. Acker, *ibid.*, **74**, 5872 (1952).

[3] J. M. Snell and A. Weissberger, *ibid.*, **61**, 450 (1939).

[4] O. Dimroth, L. Kraft and K. Aichinger, *Ann.*, **545**, 124 (1940).

[5] M. F. Gribbins (to E. I. du Pont de Nemours and Co.) U. S. Patent 2,416,052 (Feb. 18, 1947); C. D. Hurd and L. L. Gershbein, THIS JOURNAL, **69**, 2328 (1947); J. L. Szabo and E. T. Stiller, *ibid.*, **70**, 3667 (1948).

[6] R. B. Thompson (to Universal Oil Products Co.) U. S. Patent 2,492,334 (Dec. 27, 1949).

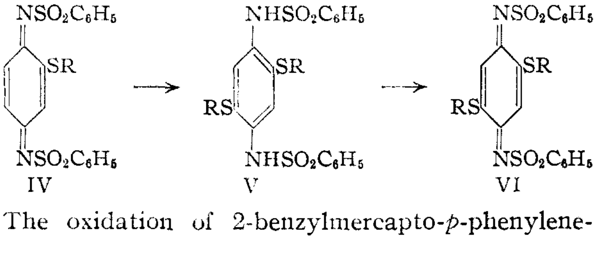
[7] E. Paterno and R. Spallino, *Atti. Accad. Lincei*, **16**, 87 (1907).

The use of secondary amine catalysts such as piperidine and morpholine made possible the rapid addition of the aliphatic thiols, butyl mercaptan, benzyl mercaptan, thioglycolic acid and β-mercaptoethanol. In several instances after the initial deep red color of the reaction mixture had faded, a green color remained indicating some addition of the amine catalyst to the quinone diimide. This color likewise faded but in some cases the mercaptan adducts proved difficult to purify.

While the thiophenols failed to respond to secondary amine catalysis and only selected aliphatic mercaptans could be employed in acidic media, catalysis by a tertiary amine, specifically triethylamine, proved generally excellent for both types of thiols. With the triethylamine catalyst, only a fleeting orange coloration was observed on mixing the reactants in chloroform solution at room temperature. The solutions were completely decolorized within three seconds to five minutes in all cases tried and oxidation of the thiol to disulfide was slight, never exceeding 7%. Moreover, while relatively high purity reagents were required for addition reactions in the presence of acids or secondary amines, this factor did not appear to be critical when triethylamine was used. In an experiment using a very crude sample of *p*-quinonedibenzenesulfonimide (m.p. 150–173°), thiophenol which had been distilled two months previously and commercial triethylamine, an 82% yield of adduct was obtained which was pure after one recrystallization.

High quality crude adducts were the general case when triethylamine or an acidic additive was used. The only exception appeared to be thio-β-naphthol which gave a product which was impossible to purify. The adduct was obtained fortuitously in one experiment with piperidine as catalyst and pure reagents, but the experiment could not be duplicated.

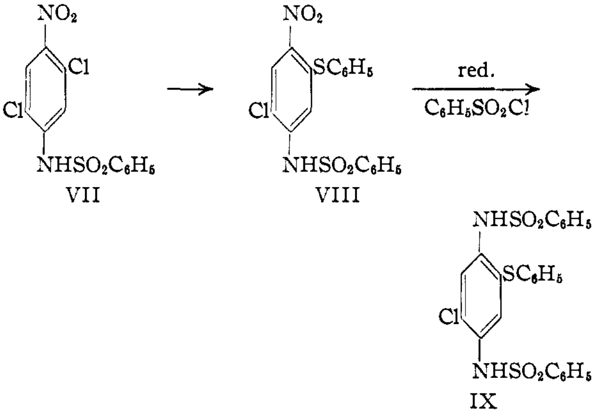
The phenylmercapto-*p*-phenylenedibenzenesulfonamide was readily oxidized with lead tetraacetate in glacial acetic acid to the corresponding diimide (IV). Thiophenol added to this product to give a single isomeric bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide (V), the structure of which was not determined but which is probably 2,5. Oxidation of the bisphenylmercapto derivative gave the corresponding diimide (VI), a purplish crystalline product. Attempts to add thiophenol to this diimide failed whether with or without a catalyst; only reduction occurred with formation of diphenyl disulfide. This reaction resembles the unsuccessful attempt to add thiophenol to 2-phenylmercapto-1,4-naphthalenedibenzenesulfonimide or to 2-chloro-1,4-naphthalenedibenzenesulfonimide.[2c]



IV V VI

The oxidation of 2-benzylmercapto-*p*-phenylenedibenzenesulfonamide was unsuccessful in glacial acetic acid as solvent, but suspended in dry thiophene-free benzene with dry lead tetraacetate the yield of the corresponding diimide was excellent.

2-Chloro-*p*-quinonedibenzenesulfonimide added thiophenol to give a mixture of isomeric phenylmercapto-2-chloro-*p*-phenylenedibenzenesulfonamides from which the least soluble was obtained pure. This was identical with the least soluble of the isomers resulting from the addition of hydrogen chloride to 2-phenylmercapto-*p*-quinonedibenzenesulfonimide. The product was identified as the 2,5-derivative by synthesis through an unequivocal route. 2,5-Dichloroacetanilide was nitrated and hydrolyzed to 2,5-dichloro-4-nitroaniline; this was benzenesulfonated to N-benzenesulfonyl-2,5-dichloro-4-nitroaniline (VII); by treatment of this product with the sodium salt of thiophenol in aqueous dioxane, N-benzenesulfonyl-2-chloro-4-nitro-5-phenylmercaptoaniline (VIII) resulted; subsequent reduction and benzenesulfonation gave 2-chloro-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide (IX) identical with the product isolated in the previous addition reactions.



VII VIII IX

Acknowledgment.—The authors are indebted to Mr. J. Nemeth, Mrs. Katherine Pih and Mrs. Esther Fett for the microanalyses and to Miss Helen Miklas for the infrared determinations and interpretations.

Experimental

All melting points are corrected.

Purification of Materials.—In those reactions where very pure materials were required the *p*-quinonedibenzenesulfonamide was crystallized from glacial acetic acid four to six times until its melting point was the maximum (188–189°); the chloroform was freed from ethanol, dried and distilled; the mercaptans were carefully fractionated or crystallized to maximum melting point.

For the experiments where triethylamine was used as catalyst, reagent grade chloroform (Merck and Co.) was dried over calcium chloride for 12 hours, then either distilled or simply filtered immediately before use. The thiols were used as obtained commercially (Eastman Kodak Co.) with the exception of 2-mercaptobenzothiazole ("Mertax," Monsanto Chemical Co.) which was recrystallized five times from 95% ethanol. The *p*-quinonedibenzenesulfonimide used most frequently was of the quality (m.p. 184–187°) obtained by one or two recrystallizations from glacial acetic acid, though in some experiments a very crude grade of this material (m.p. 150–173°) was employed with only slight lowering of the yield of adduct.

Addition of Mercaptans to *p*-Quinonedibenzenesulfonimide. Method A.—To a solution of 1.93 g. (1 mole equiv.) of *p*-quinonedibenzenesulfonimide in 25 ml. of chloroform was added 1 ml. of a saturated chloroform solution of the dioxane–sulfuric acid complex (or 1 drop of concentrated sulfuric acid). To this mixture was introduced, in one portion, a solution or suspension of a slight excess over one mole equivalent of the mercaptan in 25 ml. of chloroform. The resulting yellow mixture, gradually darkening to a deep orange or red color over a period of 5 to 10 minutes, was then allowed to stand at room temperature for 2 to 24 hours. At the end of this time there resulted a pale yellow or colorless solution, which contained some *p*-phenylenedibenzenesulfonamide in suspension. The mixture was filtered and the filtrate concentrated to dryness *in vacuo* leaving either a crystalline residue or an oil. After washing this residue with ether or petroleum ether (b.p. 35–45°), the product was recrystallized from 95% ethanol or glacial acetic acid.

Method B.—A solution of one mole equivalent or slight excess of the mercaptan and 1 drop of triethylamine in 25 ml. of chloroform was added in one portion to a solution of 1.93 g. (1 mole equiv.) of *p*-quinonedibenzenesulfonimide in 25 ml. of chloroform. The resulting mixture became warm while a transient orange coloration appeared, then turned colorless within 3 seconds to 5 minutes. After seeding the solution with a crystal of *p*-phenylenedibenzenesulfonamide, it was allowed to stand for 2 hours then filtered free of any suspended material. The filtrate was evacuated to dryness and the residue washed with petroleum ether (b.p. 35–45°) then recrystallized from 95% ethanol or glacial acetic acid.

When morpholine or piperidine were used as catalysts, the procedure was essentially the same as with triethylamine as catalyst.

No change was made in the procedure when pure starting materials and no catalyst were employed.

The results of the addition of thiols to *p*-quinonedibenzenesulfonimide are shown in Table I.

2-Phenylmercapto-*p*-quinonedibenzenesulfonimide.—To a stirred slurry of 4.0 g. of 2-phenylmercapto-*p*-phenylenedibenzenesulfonamide and 10 ml. of glacial acetic acid was added at room temperature over a period of 15 minutes 3.5 g. of crystalline lead tetraacetate. The mixture immediately turned blood-red in color. After stirring for one hour, the red quinone diimide separated. The precipitate was collected by filtration and weighed 3.7 g. (93%). After two crystallizations from glacial acetic acid (Darco), glittering red needles were obtained, m.p. 151–152° (dec.).

Anal. Calcd. for $C_{24}H_{18}N_2O_4S_3$: C, 58.27; H, 3.68; N, 5.66. Found: C, 58.13; H, 3.70; N, 5.58.

2,*x*-Bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide.—To a solution of 2.47 g. of 2-phenylmercapto-*p*-quinonedibenzenesulfonimide in 30 ml. of pure dry chloroform was added 0.55 g. of redistilled thiophenol in 5 ml. of chloroform. After standing for 5 hours the mixture was light yellow. Evaporation of the chloroform left 2.75 g. (92% yield) of crude adduct which was crystallized from glacial acetic acid (difficultly soluble) to give pure white product, m.p. 226–227°.

Anal. Calcd. for $C_{30}H_{24}N_2O_4S_4$: C, 59.57; H, 4.01; N, 4.63. Found: C, 59.58; H, 4.24; N, 4.65.

2,*x*-Bis-(phenylmercapto)-*p*-quinonedibenzenesulfonimide.—A suspension of 0.80 g. of 2,*x*-bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide in 50 ml. of glacial acetic acid was heated to 60°. With mechanical stirring, 0.58 g. of lead tetraacetate was added over a period of 15 minutes. Upon initial addition, the solution turned red in color. Stirring at 60° was continued for 4 hours, two drops of ethylene glycol was added and the mixture was cooled. The reddish-purple precipitate which separated weighed 0.75 g. (93%). After two recrystallizations from glacial acetic acid (Darco), shimmering reddish-purple needles were obtained, m.p. 254–255°.

Anal. Calcd. for $C_{30}H_{22}N_2O_4S_4$: C, 59.77; H, 3.69; N, 4.65. Found: C, 59.96; H, 3.86; N, 4.80.

Action of Thiophenol on 2,*x*-Bis-(phenylmercapto)-*p*-quinonedibenzenesulfonimide.—To a solution of 0.3 g. of 2,*x*-bis-(phenylmercapto)-*p*-quinonedibenzenesulfonimide in 10 ml. of pure dry chloroform was added in one portion a mixture of 0.06 g. of thiophenol and 2 ml. of dry chloroform. The solution decolorized in 2 hours and the chloroform was evaporated *in vacuo*. The crystalline residue thus obtained was recrystallized from glacial acetic acid (Darco) and yielded 0.21 g. (70%) of colorless crystals, m.p. 224–226°.

TABLE I: ADDUCTS OF THIOLS TO *p*-QUINONEDIBENZENESULFONIMIDE

Thiol	"Catalyst"	Time for decolorization of reaction mix.	Yield of reduction product, %	Yield of crude adduct, %	M.p. of pure adduct, °C.	Recrystallizations for purity[b]	Formula of adduct	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
n-C_4H_9SH	Piperidine	5 sec. to 2 hr.	17	53	136.5–138.5	Difficult to purify	$C_{22}H_{24}N_2O_4S_3$	55.44	55.46	5.08	5.18	5.88	6.09
	Dioxane-H_2SO_4	22 hr.	8	75		1							
	Triethylamine	3 min.	3	80		1							
$C_6H_5CH_2SH$	Morpholine	1 min.	0	94	148–150.5	7	$C_{25}H_{22}N_2O_4S_3$	58.80	58.93	4.34	4.23	5.49	5.46
	Dioxane-H_2SO_4	18 hr.	8	59		5[c]							
	Triethylamine	5 sec.	0	88		3							
C_6H_5SH	H_2SO_4	12–16 hr.	0–12[a]	96–64[a]	167–168.5	3	$C_{24}H_{20}N_2O_4S_3$	58.04	58.19	4.07	4.16	5.65	5.60
	Triethylamine	5 sec.	Trace	90		1[c]							
p-$CH_3C_6H_4SH$	Triethylamine	3 sec.	0	91	156–157	5	$C_{25}H_{22}N_2O_4S_3$	58.80	58.72	4.34	4.60	5.49	5.67
Mercaptobenzothiazole	Dioxane-H_2SO_4	10 min.	7	52	169.5–172	2	$C_{25}H_{19}N_3O_4S_4$	54.23	54.49	3.46	3.66	7.59	7.64
	Triethylamine	5 min.	7	65		3							
$HSCH_2COOH$	Morpholine	20 min.	11	66	159–161	5[c]	$C_{20}H_{18}N_2O_6S_3$	50.19	50.27	3.79	3.92	5.85	5.88
$HSCH_2CH_2OH$	Piperidine	20 min.	0	92	133–139	5	$C_{20}H_{20}N_2O_5S_3$	51.70	51.34	4.34	4.37	6.03	5.94
	Triethylamine	1 min.	0	93		5							
CH_3COSH	None	1 hr.	0	93	160–162	7	$C_{20}H_{18}N_2O_5S_3$	51.92	52.16	3.92	4.01	6.06	6.26
β-Thionaphthol	Piperidine	6 hr.	13	55	182–182.5		$C_{28}H_{22}N_2O_4S_3$	61.51	61.46	4.06	4.14	5.12	5.32

[a] Yield limits for several runs; when the yield of adduct was at the higher limit, the amount of reduction was negligible. The other limits likewise correspond. [b] Recrystallized from glacial acetic acid except where otherwise indicated. [c] Recrystallized from 95% ethanol.

This melting point was identical with that of the 2,*x*-bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide obtained by the addition of thiophenol to 2-phenylmercapto-*p*-quinonedibenzenesulfonimide and the melting point of the mixture showed no depression. The presence of acidic or basic additives did not change the course of the reaction.

Anal. Calcd. for $C_{30}H_{24}N_2O_4S_4$: C, 59.57; H, 4.01. Found: C, 59.84; H, 4.30.

2-Benzylmercapto-*p*-quinonedibenzenesulfonimide.—To a suspension of 2 g. of 2-benzylmercapto-*p*-phenylenedibenzenesulfonamide in 20 ml. of dry thiophene-free benzene was added 1.8 g. of dry crystalline lead tetraacetate, previously dried *in vacuo* over potassium hydroxide. The mixture was refluxed for 3 hours with mechanical stirring, and the solution turned deep-red as the oxidation progressed. Upon cooling, the suspended material was removed by filtration, and the red filtrate was concentrated *in vacuo* to a volume of 5 ml. Petroleum ether (b.p. 30–60°) was added slowly, and the sticky red gum which separated was scratched until crystallization occurred. The orange-red crystalline material was collected by filtration, and purified by recrystallization from 95% ethanol (Darco) or glacial acetic acid. It weighed 1.75 g. (88%). The product formed glittering deep orange needles, m.p. 135–136°. The reaction was unsuccessful when glacial acetic acid was used as solvent.

Anal. Calcd. for $C_{25}H_{20}N_2O_4S_3$: C, 59.01; H, 3.97; N, 5.51. Found: C, 59.07; H, 4.01; N, 5.49.

N-Benzenesulfonyl-2,5-dichloro-4-nitroaniline.—A solution of 15.0 g. of 2,5-dichloro-4-nitroaniline[8] and 9.5 ml. of benzenesulfonyl chloride in 100 ml. of pyridine was refluxed for 11 hours. The dark reaction mixture was poured into a solution of 100 ml. of concentrated hydrochloric acid in 400 ml. of water, and the resulting mixture stirred until the oily layer had coagulated. The crude brown product dissolved in 250 ml. of glacial acetic acid was treated with Darco, filtered, concentrated to 100 ml. and then cooled. The product which crystallized weighed 5.36 g. (35.8%). After two recrystallizations from glacial acetic acid, pale yellow crystals resulted, m.p. 180.5–181.5°.

Anal. Calcd. for $C_{12}H_8Cl_2N_2O_4S$: C, 41.51; H, 2.32; N, 8.07. Found: C, 41.44; H, 2.35; N, 8.06.

N-Benzenesulfonyl-2-chloro-4-nitro-5-phenylmercaptoaniline.—A solution of 1.20 g. of sodium hydroxide in 8 ml. of water was added to a mixture of 3.00 g. of N-benzenesulfonyl-2,5-dichloro-4-nitroaniline, 3.00 g. of thiophenol and 50 ml. of dioxane. This mixture was refluxed for 5 hours. The resulting yellow solution was poured into 300 ml. of water and warmed while stirring to coagulate the oil which had separated. The supernatant liquors were decanted off and the semi-solid residue dissolved in 75 ml. of boiling 95% ethanol. Concentration of this ethanol solution to 40 ml. and cooling produced 2.54 g. (70%) of N-benzenesulfonyl-2-chloro-4-nitro-5-phenylmercaptoaniline. It was purified from 95% ethanol and formed large yellow plates, m.p. 157–159°.

Anal. Calcd. for $C_{18}H_{13}ClN_2O_4S_2$: C, 51.36; H, 3.11; N, 6.66. Found: C, 51.41; H, 3.12; N, 6.86.

1-N-Benzenesulfonyl-2-chloro-5-phenylmercapto-*p*-phenylenediamine.—To a boiling solution of 1.50 g. of N-benzenesulfonyl-2-chloro-4-nitro-5-phenylmercaptoaniline in 50 ml. of 95% ethanol was added dropwise, over a 3-minute period, a solution of 2.05 g. of sodium hydrosulfite in 19 ml. of water. The resulting colorless mixture contained some suspended white solid, which was brought into solution by the addition of 50 ml. of water. The solution was then concentrated to 50 ml. and cooled yielding 1.00 g. (71.5%) of white product. Purification of this material from 95% ethanol gave white needles, m.p. 157–159°.

Anal. Calcd. for $C_{18}H_{15}ClN_2O_2S_2$: C, 55.30; H, 3.87; N, 7.17. Found: C, 55.51; H, 4.07; N, 7.07.

2-Chloro-5-phenylmercapto-*p*-phenylenedibenzenesulfonamide. Method A.—A solution of 0.72 g. of 1-N-benzenesulfonyl-2-chloro-5-phenylmercapto-*p*-phenylenediamine and 0.35 g. of benzenesulfonyl chloride in 15 ml. of pyridine was refluxed for 15 hours, then poured into 75 ml. of water and acidified. The mixture was stirred for several minutes, then the supernatant liquors poured off. The residual brown oil was dissolved in 25 ml. of glacial acetic acid, and the resulting solution treated with Darco, concentrated to 10 ml. and cooled. There deposited 0.25 g. (26%) of product. Recrystallization from glacial acetic acid gave tiny white needles, m.p. 206–207.5°.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_4S_3$: C, 54.27; H, 3.61; N, 5.28. Found: C, 54.10; H, 3.72; N, 5.22.

Method B.—Hydrogen chloride was bubbled into a solution of 2.0 g. of 2-phenylmercapto-*p*-quinonedibenzenesulfonimide in 30 ml. of dry chloroform. The deep-red color disappeared in one hour, leaving an orange-tinted solution. Concentration of the chloroform solution to a volume of 10 ml. yielded colorless crystals which were collected by filtration. They weighed 0.8 g. Repeated crystallization from glacial acetic acid (Darco) yielded the least soluble isomer, m.p. 206–207.5°. This material did not depress the melting point of the compound prepared by method A and the infrared absorption spectrum was identical with that of the authentic 2,5-isomer.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_4S_3$: C, 54.27; H, 3.61; N, 5.28. Found: C, 54.40; H, 3.85; N, 5.39.

Evaporation of the combined filtrates yielded an additional 1.1 g., m.p. 179–191°. Recrystallization from glacial acetic acid (Darco) gave colorless crystals, m.p. 181–194°, which by analysis was obviously a mixture of more soluble isomers.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_4S_3$: C, 54.27; H, 3.61; N, 5.28. Found: C, 54.37; H, 3.64; N, 5.23.

The total over-all yield of product isolated was 1.9 g. (89%). Both fractions turned yellow when allowed to stand in air in the presence of light.

Method C.—To a solution of 4.21 g. of 2-chloro-*p*-quinonedibenzenesulfonimide in 50 ml. of pure dry chloroform was added in one portion 1.2 g. of redistilled thiophenol in 10 ml. of pure dry chloroform. The red solution turned light orange upon standing for 4 hours. The solution was evaporated to a volume of 2 ml. and the colorless crystals which separated were collected by filtration. They weighed 4.31 g. (81%). Repeated crystallization from glacial acetic acid (Darco) yielded the least soluble isomer as colorless crystals, m.p. 206–207.5° identical with the product synthesized in (A). This reaction was performed before triethylamine was discovered to be a superior catalyst for addition of thiophenols.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_4S_3$: C, 54.27; H, 3.61; N, 5.28. Found: C, 54.48; H, 3.51; N, 5.52.

The acetic acid filtrates were combined and concentrated to a volume of 2 ml. The solid product thus obtained was recrystallized from glacial acetic acid (Darco), washed with petroleum ether (b.p. 30–60°), m.p. 179–188°. From the analysis, it proved to be a mixture of isomers.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_4S_3$: C, 54.27; H, 3.61; N, 5.28. Found: C, 54.49; H, 3.42; N, 5.54.

2-Xanthyl-*p*-phenylenedibenzenesulfonamide.—To a suspension of 1.93 g. (1 molee quiv.) of *p*-quinonedibenzenesulfonimide in 25 ml. of glacial acetic acid was added 0.98 g. (1 mole equiv.) of potassium xanthate. The mixture was shaken for 2 minutes whereupon a colorless solution was obtained. On warming this solution gently on the hot-plate the white product crystallized; it was filtered, washed with glacial acetic acid, then with petroleum ether (b.p. 35–45°) and dried. The yield was 2.06 g. (83%). Recrystallization from glacial acetic acid gave white crystals of pure 2-xanthyl-*p*-phenylenedibenzenesulfonamide, m.p. 182–183°.

Anal. Calcd. for $C_{21}H_{20}N_2O_5S_4$: C, 49.58; H, 3.96; N, 5.51. Found: C, 49.76; H, 4.19; N, 5.65.

Action of Hydrogen Sulfide on *p*-Quinonedibenzenesulfonimide.—Hydrogen sulfide was bubbled into chloroform containing a drop of morpholine and the resulting solution added to a chloroform solution of *p*-quinonedibenzenesulfonimide. From the reaction mixture a yield of 90% of *p*-phenylenedibenzenesulfonamide was isolated.

In a second experiment using triethylamine as catalyst only 25% reduction occurred. The remaining product was a mixture from which no identifiable compound was isolated.

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[8] J. R. H. Whistou, *J. Soc. Chem. Ind.*, **43**, 370T (1924).