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Quinone Imides. XIII. Orientation of Groups in Adducts of Hydrogen Chloride with Quinone Diimides

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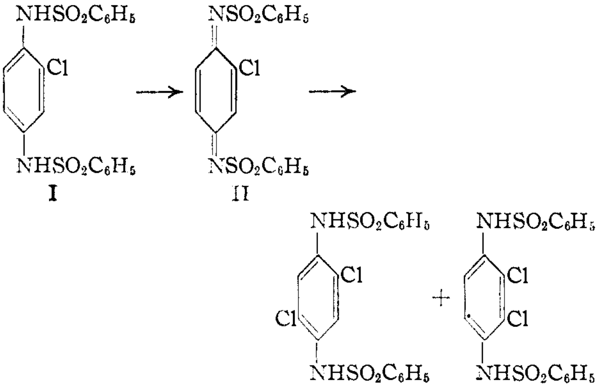
The orientation of the hydrogen and chlorine when hydrogen chloride is added to certain *p*-quinone diimides has been determined. 2-Chloro-*p*-quinonedibenzenesulfonimide is converted to a mixture of 2,3- and 2,5-dichloro-*p*-phenylenedibenzenesulfonamide, the structures of which were proven by unequivocal syntheses. Oxidation of the mixture or of the pure individual compounds, followed by addition of hydrogen chloride, yields the same product, 2,3,5-trichloro-*p*-phenylenedibenzenesulfonamide. By a similar oxidation–addition sequence, the latter is converted to 2,3,5,6-tetrachloro-*p*-phenylenedibenzenesulfonamide, which can be oxidized to 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulfonimide. 2-Methyl-*p*-quinonedibenzenesulfonimide reacts with hydrogen chloride to give chiefly 2-methyl-5-chloro-*p*-phenylenedibenzenesulfonamide. Subsequent oxidation followed by addition of hydrogen chloride yields a dichloro-2-methyl-*p*-phenylenedibenzenesulfonamide, the structure of which was not determined. Oxidation with lead tetraacetate in benzene gives the corresponding quinone diimide, which readily adds hydrogen chloride to give 2-methyl-3,5,6-trichloro-*p*-phenylenedibenzenesulfonamide. However, oxidation of 2-methyl-x,5-dichloro-*p*-phenylenedibenzenesulfonamide with lead tetraacetate in glacial acetic acid yields primarily a dichloromethyl-*p*-quinone monobenzenesulfonimide, the structure of which was not determined. The latter, when treated with concentrated hydrochloric acid in glacial acetic acid, is converted to 2-methyl-3,5,6-trichlorohydroquinone. 2,5-Dimethyl-3-chloro-*p*-phenylenedibenzenesulfonamide is also oxidized by lead tetraacetate in benzene to the corresponding diimide; in glacial acetic acid 2,5-dimethyl-3-chloro-*p*-quinonemonobenzenesulfonimide is obtained.

Recent work[2] has shown that monochloro-*p*-phenylenediamides are formed when hydrogen chloride is added to various *p*-quinone diimides. For example, *p*-quinonedibenzenesulfonimide is converted into 2-chloro-*p*-phenylenedibenzenesulfonamide (I), the structure of which is established since only one monochloro compound can exist.[2a] The orientation of hydrogen and chlorine when hydrogen chloride is added to 2-chloro-*p*-quinonedibenzenesulfonimide has now been studied. 2-Chloro-*p*-phenylenedibenzenesulfonamide (I) was oxidized with lead tetraacetate in glacial acetic acid to 2-chloro-*p*-quinonedibenzenesulfonimide (II). Subsequent addition of hydrogen chloride yielded a mixture of isomeric dichloro-*p*-phenylenedibenzenesulfonamides, which upon fractional crystallization yielded the least soluble isomer, 2,5-dichloro-*p*-phenylenedibenzenesulfonamide (III), and the most soluble isomer, 2,3-dichloro-*p*-phenylenedibenzenesulfonamide (IV) in pure form. Their structures were proved unequivocally by reducing the dioximes of the known 2,5- and 2,3-dichloro-*p*-benzoquinones to the corresponding diamines and benzenesulfonating. Since all three isomeric dichlorohydroquinones have been isolated from the reaction of hydrogen chloride with 2-chloro-*p*-benzoquinone,[3,4] it is likely that the 2,6-dichloro-*p*-phenylenedibenzenesulfonamide was also present in some of the intermediate fractions.

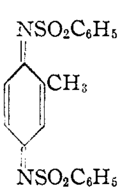


I II

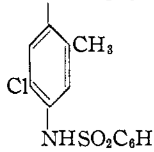
III IV

If the mixture of the dichloro compounds resulting from the addition of hydrogen chloride to 2-chloro-*p*-quinonedibenzenesulfonimide was oxidized to the corresponding mixture of dichloro-*p*-quinonedibenzenesulfonimides and hydrogen chloride then added, 2,3,5-trichloro-*p*-phenylenedibenzenesulfonamide was obtained in excellent over-all yield. The same product resulted when pure 2,3- or 2,5-dichloro-*p*-phenylenedibenzenesulfonamide was oxidized and the resulting oxidation products treated with hydrogen chloride. The trichloro compound in turn was oxidized to 2,3,5-trichloro-*p*-quinonedibenzenesulfonimide which added hydrogen chloride with the formation of 2,3,5,6-tetrachloro-*p*-phenylenedibenzenesulfonamide. Further oxidation gave the 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulfonimide, which is analogous to chloranil.

2-Methyl-*p*-quinonedibenzenesulfonimide (V), in contrast to the 2-chloro analog, added hydrogen chloride to give an excellent yield of essentially a single product, 2-methyl-5-chloro-*p*-phenylenedibenzenesulfonamide (VI) with apparently little or no tendency to form isomers. The structure of VI was proved by showing its identity with the product formed by converting the known 2-methyl-5-chloro-*p*-benzoquinone to the dioxime, reducing the latter to the diamine and benzenesulfonating.



V



VI

When VI was oxidized to the corresponding quinone diimide and hydrogen chloride was added,

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[1] From abstracts of theses submitted by E. F. Elslager and K. F. Heumann to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the Degrees of Doctor of Philosophy.

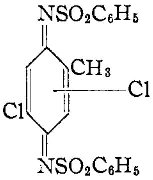
[2] R. Adams, *et al.*, (a) THIS JOURNAL, **72**, 4601 (1950); (b) *ibid.*, **72**, 5154 (1950); (c) *ibid.*, **73**, 131 (1951); (d) *ibid.*, **73**, 1145 (1951); (e) *ibid.*, **73**, 1148 (1951); (f) *ibid.*, **73**, 1152 (1951); (g) *ibid.*, **73**, 2219 (1951); (h) *ibid.*, **73**, 5687 (1951). See also *ibid.*, **74**, 2593, 2597, 2603, 2605 (1952).

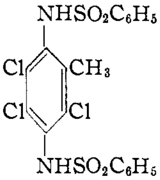
[3] A. Peratoner and A. Genco, *Gazz. chim. ital.*, **24**, II, 375 (1894).

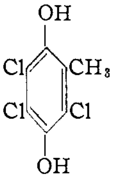
[4] A. J. Den Hollander, *Rec. trav. chim.*, **39**, 481 (1920).

apparently only a single dichloro monomethyl *p*-phenylenedibenzenesulfonamide was produced. Whether the second chlorine was in the 3- or 6-position was not determined. An attempt to prepare for comparison the 2-methyl-5,6-dichloro-*p*-phenylenedibenzenesulfonamide by an unequivocal synthesis failed. 2-Methyl-5,6-dichloro-*p*-benzoquinone[5] was treated with hydroxylamine in order to form the dioxime which was to be reduced and benzenesulfonated. The hydroxylamine, however, caused reductive replacement of one of the chlorine atoms by hydrogen so that the product isolated was the dioxime of 2-methyl-5-chloro-*p*-benzoquinone.

Oxidation of 2-methyl-x,5-dichloro-*p*-phenylenedibenzenesulfonamide with lead tetraacetate in dry benzene yielded the orange 2-methyl-x,5-dichloro-*p*-quinonedibenzenesulfonimide (VII), which readily added hydrogen chloride to give 2-methyl-3,5,6-trichloro-*p*-phenylenedibenzenesulfonamide (VIII). However, when the above oxidation was carried out for 20 hours using lead tetraacetate in glacial acetic acid at 60°, the product was almost exclusively (77%) the yellow 2-methyl-x,5-dichloro-*p*-quinone-(1- or 4)-monobenzenesulfonimide. The hydrolysis of one benzenesulfonamido group occurred during the reaction. The infrared spectrum showed the presence of a carbonyl group, but its position in the molecule was not determined. The course of this reaction is in doubt since the diimide VII, formed by the oxidation of the corresponding diamide in benzene, was not converted to the monobenzenesulfonimide by heating for 20 hours in glacial acetic acid alone or with lead tetraacetate. When the above monobenzenesulfonimide was heated with concentrated hydrochloric acid in glacial acetic acid, the yellow color was discharged, and the product of the reaction was 2-methyl-3,5,6-trichlorohydroquinone (IX).[6] The hydrolysis of the second benzenesulfonamido group probably occurred previous to the addition of hydrogen chloride. This is deduced from the fact that the benzenesulfonamides of *p*-phenylenediamine and *p*-aminophenol are difficult to hydrolyze. The monobenzenesulfonimides, on the other hand, as exemplified by *p*-quinone or 2-methyl-*p*-quinonemonobenzenesulfonimide, are easily hydrolyzed to *p*-benzoquinone or 2-methyl-*p*-benzoquinone and benzenesulfonamide.[2d] The 2-methyl-3,5,6-trichlorohydroquinone was oxidized with lead tetraacetate in glacial acetic acid to 2-methyl-3,5,6-trichloro-*p*-benzoquinone, identical with the product formed by oxidation of *o*-toluidine with sodium dichromate in the presence of hydrochloric acid.[7]


VII


VIII


IX

A restudy of earlier work[2a] on the oxidation of 2,5-dimethyl-3-chloro-*p*-phenylenedibenzenesulfonamide indicated that when benzene was used as a solvent for the oxidation instead of acetic acid, the corresponding diimide was formed in excellent yield. With acetic acid, the primary product was usually 2,5-dimethyl-3-chloro-*p*-quinone-(1- or 4)-monobenzenesulfonimide, although the diimide was sometimes isolated in appreciable amounts when just the right conditions happened to be employed.

In the benzenesulfonation of 2,3-dichloro-*p*-phenylenediamine dihydrochloride it was found that excess of benzenesulfonyl chloride in pyridine resulted in formation of the N,N,N′,N′-tetrabenzenesulfonyl derivative of 2,3-dichloro-*p*-phenylenediamine. This is similar to the polybenzenesulfonation observed with triaminomesitylene.[8]

Acknowledgment.—The authors are indebted to Miss Emily Davis, Mr. Maurice Dare, Miss Rachel Kopel and Mrs. Jean Fortney of the University of Illinois for carrying out microanalyses, and to Miss Elizabeth Petersen for the determination and interpretation of the infrared absorption spectra.

Experimental

All melting points are corrected.

The identification of the chloro-*p*-phenylenedibenzenesulfonamides prepared by addition of hydrogen chloride to the appropriate diimide and by other unequivocal methods was achieved by identity of melting points and undepressed melting points of mixtures and by comparison of the infrared spectra. The spectra of the diamides are recorded in Table I.

General Methods for Preparing Chloro-*p*-phenylenedibenzenesulfonamides from *p*-Quinonedibenzenesulfonimides. Method A.—Dry hydrogen chloride was bubbled into a chloroform solution containing up to 0.06 mole of the *p*-quinonedibenzenesulfonimide. The deep yellow to orange color of the solution was discharged in 5 to 50 minutes, during which time most of the chloro-*p*-phenylenedibenzenesulfonamide separated as colorless crystals. The mixture was concentrated to a small volume, and the crude *p*-phenylenedibenzenesulfonamide was collected by filtration. Two recrystallizations from glacial acetic acid or 95% ethanol (Darco) gave the pure chloro-*p*-phenylenedibenzenesulfonamides (see Table II).

Method B.—A solution of 0.001 mole of the *p*-quinonedibenzenesulfonimide in 25 ml. of glacial acetic acid was treated with 5 ml. of concentrated hydrochloric acid. The mixture was heated at 80° for 15 minutes, during which time the yellow to orange color was discharged and the colorless crystals of the chloro-*p*-phenylenedibenzenesulfonamide separated. Upon cooling, the addition product was collected by filtration, and recrystallized from glacial acetic acid or 95% ethanol (Darco). Additional amounts of crude product can be obtained by pouring the filtrate into a mixture of ice and water (see Table II).

General Methods for Preparing Chloro-*p*-quinonedibenzenesulfonimides from Chloro-*p*-phenylenedibenzenesulfonamides. Method A.—To a suspension of 0.01 mole of the chloro-*p*-phenylenedibenzenesulfonamide in 75 ml. of glacial acetic acid, heated to 60°, was added with mechanical stirring 0.0103 mole of crystalline lead tetraacetate[9] in small portions over a period of 10 minutes. The solution gradually developed a deep yellow to orange color. After addition was complete, the mixture was stirred at 60° for one hour, 2 ml. of ethylene glycol was added, and stirring was continued for 10 minutes. Upon cooling, the bright yellow to orange crystals of the *p*-quinone diimide separated. Additional small amounts of product can be obtained by pouring the filtrate into an ice–water mixture. Two recrystallizations from glacial acetic acid (Darco) gave the pure chloro-*p*-quinonedibenzenesulfonimide (see Table III).

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[5] T. H. Clark, *Am. Chem. J.*, **14**, 571 (1892).

[6] M. S. Southworth, *Ann.*, **168**, 275 (1873).

[7] E. Elbs and E. Brunnschweiler, *J. prakt. Chem.*, [2] **52**, 559 (1895).

[8] R. Adams and B. E. Englund, THIS JOURNAL, **72**, 5080 (1950).

[9] The lead tetraacetate was obtained from Arapahoe Chemicals, Inc.

TABLE I

INFRARED ABSORPTION SPECTRA OF CHLORINATED *p*-PHENYLENEDIBENZENESULFONAMIDES[a]

	2,3-Dichloro-	2,5-Dichloro-	2,3,5-Trichloro-	2,3,5,6-Tetrachloro-	2-Methyl-5-chloro-	2-Methyl-3,5,6-trichloro-	2,5-Dimethyl-3-chloro-	2,5-Dimethyl-3,6-dichloro-
-NH-	3347	3244	3209	3238	3253	3250	3232	3238
-SO_2-	1330	1340	1335	1358	1340	1336	1332	1335
	1169	1330	1166	1173	1329	1331	1161	1160
	1162	1165	1161	1156	1163	1164	1090	1088
	1090		1089	1088	1090	1089		
Other prominent bands	1487	1485	1363	1449	1493	1450	1381	1032
	1449	1374	925	1436	1380	1363	1364	809
	1388	1188	829	1327	1190	906	1290	757
	1244	1091	757	1311	1146	756	1035	722
	962	1085	725	757	1023	743	925	689
	946	981	689	731	1009	724	757	
	826	751	657	704	998	686	742	
	760	723		687	970	656	722	
	735	683		655	912		690	
	715				884			
	712				841			
	685				751			
					722			
					683			

[a] The infrared spectra were determined in a nujol suspension on a Perkin–Elmer Model 12-B Spectrometer.

TABLE II

CHLORO-*p*-PHENYLENEDIBENZENESULFONAMIDES

	Substituent	Method	Yield of crude, %	M.p., °C. pure	Solvent for crystallization	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
1	2-Chloro-[a]	A[b]	99	175–176	Gl. HAc	$C_{18}H_{15}ClN_2O_4S_2$	...	...	..	..	..	..
2	Isomeric dichloro-	A	99	209–241	Gl. HAc	$C_{18}H_{14}Cl_2N_2O_4S_2$	47.26	47.39	3.09	3.19	6.12	6.15
3	2,3-Dichloro-	A[c]	...	214–215	Gl. HAc	$C_{18}H_{14}Cl_2N_2O_4S_2$	47.26	47.53	3.09	3.34	6.12	6.27
4	2,5-Dichloro-	A[c]	...	248–249	Gl. HAc	$C_{18}H_{14}Cl_2N_2O_4S_2$	47.26	47.04	3.09	3.01	6.12	6.12
5	2,3,5-Trichloro-	A[d]	100	217–218	Gl. HAc	$C_{18}H_{13}Cl_3N_2O_4S_2$	43.95	44.12	2.67	2.83	5.69	5.89
6	2,3,5,6-Tetrachloro-	A; B	76; 74	273–274	Gl. HAc	$C_{18}H_{12}Cl_4N_2O_4S_2$	41.08	41.19	2.30	2.44	5.32	5.57
7	2-Methyl-5-chloro-	A	98	271–273	95% Ethanol	$C_{19}H_{17}ClN_2O_4S_2$	52.23	51.99	3.92	3.77	..	..
8	2-Methyl-x,5-dichloro-	A	98	237–240	95% Ethanol	$C_{19}H_{16}Cl_2N_2O_4S_2$	48.41	48.43	3.42	3.33	..	..
9	2-Methyl-3,5,6-trichloro-	A; B	89; 82	270–271	Gl. HAc	$C_{19}H_{15}Cl_3N_2O_4S_2$	45.11	45.19	2.99	3.13	5.55	5.71
10	2,5-Dimethyl-3-chloro-[a]	B	87	275–276[e]	Gl. HAc	$C_{20}H_{19}ClN_2O_4S_2$	...	...	...	..	...	..
11	2,5-Dimethyl-3,6-dichloro-[a]	B	83	291 (dec.)	Gl. HAc	$C_{20}H_{18}Cl_2N_2O_4S_2$	...	...	..	..	..	..

[a] Previously prepared by Adams and Nagarkatti.[2a] [b] Although the best yields of this product are obtained by Method A, it has been found that merely boiling the diimide with 10% hydrochloric acid gives an 87% yield.[2a] Even with zinc and hydrochloric acid, a strong reducing mixture, only the addition product results. [c] This isomer was obtained pure by fractional crystallization of the isomeric dichloro-*p*-phenylenedibenzenesulfonamides. [d] This product was synthesized from the isomeric mixture and from the pure 2,3- and 2,5-dichloro-*p*-quinonedibenzenesulfonimides. [e] A melting point of 261° has been previously reported.[2a]

TABLE III

CHLORO-*p*-QUINONEDIBENZENESULFONIMIDES[a]

	Substituent	Method	Yield of crude, %	Color and crystal form	M.p., °C. pure	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
12	2-Chloro-[b,c]	B	93	Yellow needles	179–180	$C_{18}H_{13}ClN_2O_4S_2$	...	...	..	..	..	..
13	Isomeric dichloro-[d]	B	87	Yellow needles	199–231	$C_{18}H_{12}Cl_2N_3O_4S_2$	47.47	47.59	2.67	2.83	6.16	6.28
14	2,3-Dichloro-[d]	A	80	Yellow needles	208–209	$C_{18}H_{12}Cl_2N_2O_4S_2$	47.47	47.29	2.67	2.82	6.16	6.22
15	2,5-Dichloro-[d]	A	89	Yellow needles	234–235	$C_{18}H_{12}Cl_2N_2O_4S_2$	47.47	47.75	2.67	2.97	6.16	6.09
16	2,3,5-Trichloro-[e]	B; C	77; 89	Orange needles	185–186	$C_{18}H_{11}Cl_3N_2O_4S_2$	44.13	44.17	2.27	2.23	5.72	5.70
17	2,3,5,6-Tetrachloro-[e]	A	83	Orange-red needles	241–242	$C_{18}H_{10}Cl_4N_2O_4S_2$	41.24	41.46	1.93	2.14	5.34	5.35
18	2-Methyl-5-chloro-	A	99	Yellow needles	211–214	$C_{19}H_{15}ClN_2O_4S_2$	52.47	52.53	3.48	3.52	..	..
19	2-Methyl-x,5-dichloro-	C	86	Orange prisms	154–157	$C_{19}H_{14}Cl_2N_2O_4S_2$	48.62	48.81	3.01	3.18	5.97	6.15
20	2,5-Dimethyl-3-chloro-[b]	C	87	Orange prisms	153–154	$C_{29}H_{17}ClN_2O_4S_2$	...	...	..	..	..	..

[a] These were all purified by crystallization from glacial acetic acid. [b] Previously prepared by Adams and Nagarkatti.[2a] [c] Orange-yellow to brown (slow) in concentrated sulfuric acid. [d] Bright yellow in concentrated sulfuric acid. [e] Orange-yellow to orange in concentrated sulfuric acid.

Method B.—When relatively large quantities of the *p*-quinone diimides were required, the procedure using red lead as the oxidizing agent was utilized. To a suspension of 0.05 mole of the chloro-*p*-phenylenedibenzenesulfonamide in 250 ml. of glacial acetic acid was gradually added with mechanical stirring 0.051 mole of red lead (Pb_3O_4, J. T. Baker Analyzed) in small portions over a period of one-half hour while the temperature of the reaction mixture was maintained at 60°. The mixture was stirred at 60° for one hour after addition was complete, 5 ml. of ethylene glycol was added, and stirring was continued for 15 minutes. The slurry was cooled to room temperature, and the reaction product was collected by filtration. Additional amounts of product were isolated by concentration of the filtrate in *vacuo*, or by pouring the filtrate onto a mixture of ice and water. Several recrystallizations from glacial acetic acid (Darco) gave the pure *p*-quinone diimide (Table III). *p*-Quinone diimides prepared by this procedure often required an additional crystallization before pure compounds were obtained.

Method C.—A suspension of 0.01 mole of the chloro-*p*-phenylenedibenzenesulfonamide and 0.0103 mole of crystalline lead tetraacetate[10] in 75 ml. of dry thiophene-free benzene was refluxed for 4 hours with mechanical stirring. The solution turned deep orange in color as the oxidation progressed. Upon cooling, the suspended material, consisting of unchanged sulfonamide and inorganic residues, was removed by filtration, and the deep orange benzene filtrate was concentrated *in vacuo* to a volume of 10 ml. Petroleum ether (b.p. 30–60°) was added, and the orange *p*-quinone diimide thus precipitated was crystallized twice from glacial acetic acid (see Table III).

2,5-Dichloro-*p*-phenylenedibenzenesulfonamide. Method A.—The isomeric dichloro-*p*-phenylenedibenzenesulfonamides were subjected to a systematic fractional crystallization from glacial acetic acid. The least soluble 2,5-dichloro isomer was finally obtained of constant m.p. 248–249°.

Method B.—The dioxime of 2,5-dichloro-*p*-benzoquinone[11] and the corresponding diamine[11] were prepared by a modification of the procedure used by Kehrmann[12] in the synthesis of 2-methyl-5-chloro-*p*-benzoquinone dioxime and the corresponding diamine.

From 17.7 g. of 2,5-dichloro-*p*-benzoquinone and 27.8 g. of hydroxylamine hydrochloride in 600 ml. of absolute ethanol, after refluxing for 24 hours with gradual addition of 42.4 g. of anhydrous sodium carbonate, concentrating to 50 ml. and cooling, was obtained 13.3 g. (64%) of 2,5-dichloro-*p*-benzoquinone dioxime. For purification, the dioxime was dissolved in dilute aqueous alkali, heated with Darco, and reprecipitated with acetic acid; m.p. 278° (dec.) (lit. > 250°).[12]

A mixture of 4.5 g. of the dioxime, 29.6 g. of stannous chloride dihydrate, 250 ml. of concentrated hydrochloric acid and 150 ml. of 95% ethanol was heated until a clear solution resulted, then concentrated *in vacuo* to 25 ml. The tin chloride–diamine complex was filtered, dissolved in water and saturated with hydrogen sulfide. After filtration to remove the tin sulfide, 25 ml. of concentrated hydrochloric acid was added, and the solution was heated to boiling. The mixture was concentrated *in vacuo* with heating to a volume of 5 ml. Several small portions of concentrated hydrochloric acid were added at intervals during the concentration. The diamine dihydrochloride separated and weighed 2.1 g. (39%); m.p. > 320°. Neutralization of the diamine dihydrochloride with dilute sodium carbonate solution and extraction with ether yielded the free diamine, m.p. 171° (lit. reports 170°).[11,13]

To a solution of 2 g. of 2,5-dichloro-*p*-phenylenediamine dihydrochloride in 50 ml. of pyridine was added in several portions 5.6 g. of benzenesulfonyl chloride in 20 ml. of pyridine. An exothermic reaction took place with the formation of a deep red coloration. The mixture was allowed to stand at room temperature for 24 hours; it was subsequently poured onto a mixture of 500 g. of ice and 200 g. of concentrated hydrochloric acid. A light pink flocculent precipitate separated. The yield was 2.2 g. (60%). Two recrystallizations from glacial acetic acid (Darco), followed by two crystallizations from 95% ethanol, yielded colorless crystals, m.p. 248–249°.

The melting point was identical with that of the 2,5-dichloro-*p*-phenylenedibenzenesulfonamide prepared by addition of hydrogen chloride to 2-chloro-*p*-quinonedibenzenesulfonimide. The melting point of the mixture showed no depression, and the infrared spectra were identical.

Anal. Calcd. for $C_{18}H_{14}Cl_2N_2O_4S_2$: C, 47.26; H, 3.09; N, 6.12. Found: C, 47.04; H, 3.01; N, 6.12.

2,3-Dichloro-*p*-benzoquinone Dioxime.—A mixture of a solution of 5 g. of 2,3-dichloro-*p*-benzoquinone in 125 ml. of 95% ethanol and 7.85 g. of hydroxylamine hydrochloride was heated to reflux. To it was added over a period of 12 hours a solution of 11.1 g. of potassium acetate in 125 ml. of 95% ethanol. After refluxing for an additional hour, the mixture was concentrated *in vacuo* to a volume of 10 ml. The crude dioxime was filtered, dissolved in 5% aqueous sodium hydroxide, treated with Darco, filtered and the filtrate neutralized with glacial acetic acid. The dry dioxime weighed 3.3 g. (56%). Additional treatment with Darco in sodium hydroxide solution and recrystallization from absolute ethanol yielded pale yellow crystals, m.p. 271.5° (dec.).

Anal. Calcd. for $C_6H_4Cl_2N_2O_2$: C, 34.80; H, 1.95; N, 13.53. Found: C, 34.85; H, 1.93; N, 13.69.

2,3-Dichloro-*p*-phenylenediamine Dihydrochloride.—A mixture of 4.5 g. of 2,3-dichloro-*p*-benzoquinone dioxime, 29.6 g. of stannous chloride dihydrate, 250 ml. of concentrated hydrochloric acid and 150 ml. of 95% ethanol was refluxed for 18 hours. Concentration *in vacuo* yielded the tin chloride–diamine complex, which was dissolved in distilled water and decomposed with hydrogen sulfide. The tin sulfide was removed by filtration, and 30 ml. of concentrated hydrochloric acid was added to the filtrate. Concentration by heating, accompanied by periodic additions of concentrated hydrochloric acid, yielded 2.4 g. (44%) of the diamine dihydrochloride, lavender crystals, m.p. > 370°. The crude diamine dihydrochloride was dissolved in a hot mixture of 25 ml. of water and 100 ml. of concentrated hydrochloric acid (Darco), filtered, 100 ml. of concentrated hydrochloric acid added and the solution cooled in an ice–salt-bath. Colorless crystals separated, and were dried *in vacuo* at 70° for 12 hours before analysis. The compound readily sublimes.

Anal. Calcd. for $C_6H_6Cl_2N_2 \cdot 2HCl$: C, 28.82; H, 3.22; N, 11.21. Found: C, 28.80; H, 3.18; N, 11.03.

2,3-Dichloro-*p*-phenylenedibenzenesulfonamide. Method A.—From the fractional crystallization of isomeric dichloro-*p*-phenylenedibenzenesulfonamides a small amount of the most soluble isomer, 2,3-dichloro-*p*-phenylenedibenzenesulfonamide was isolated. After several crystallizations from glacial acetic acid (Darco), colorless needles separated, m.p. 214.5–215.5°.

Method B.—To a solution of 0.5 g. of 2,3-dichloro-*p*-phenylenediamine dihydrochloride dissolved in 15 ml. of pyridine was added in one portion 0.71 g. of benzenesulfonyl chloride in 5 ml. of dry pyridine. The mixture turned orange-red in color; it was allowed to stand at room temperature for 24 hours. The solution was poured slowly onto a mixture of 200 g. of ice and 150 ml. of concentrated hydrochloric acid. A white, flocculent precipitate appeared which turned yellow on standing. After filtration and drying, the material was crystallized from glacial acetic acid (Darco). It weighed 0.42 g. (46%); m.p. 214–215°. The sample was dried *in vacuo* over phosphorus pentoxide for 12 hours before analysis.

Anal. Calcd. for $C_{18}H_{14}Cl_2N_2O_4S_2$: C, 47.26; H, 3.09; N, 6.12. Found: C, 47.53; H, 3.34; N, 6.27.

The melting point and infrared spectrum were identical with those of the compound prepared by Method A, and a melting point of the mixture showed no depression.

2-Methyl-5-chloro-*p*-phenylenedibenzenesulfonamide from 2-Methyl-5-chloro-*p*-benzoquinone.—The dioxime of 2-methyl-5-chloro-*p*-benzoquinone was prepared by the method of Kehrmann[12] from 2-methyl-5-chloro-*p*-benzoquinone[7,14] and hydroxylamine hydrochloride, except that the conversion was carried out without the isolation of the monoöxime. The dioxime melted at 280° (dec.), yield 76%. Reduction of the dioxime with stannous chloride[12] gave a 33% yield of 2-methyl-5-chloro-*p*-phenylenediamine dihydrochloride, m.p. 320° (dec.) with darkening at 280°. Using the conventional procedure[2a] this diamine dihydrochloride was converted to 2-methyl-5-chloro-*p*-phenylenedibenzenesulfonamide. After two recrystallizations from 95% ethanol this product had m.p. 270–272°.

Anal. Calcd. for $C_{19}H_{17}ClN_2O_4S_2$: C, 52.23; H, 3.92. Found: C, 51.93; H, 4.21.

The melting point of this compound was not depressed by the addition of 2-methyl-5-chloro-*p*-phenylenedibenzenesulfonamide, m.p. 271–273°, prepared by the addition of hydrogen chloride to 2-methyl-*p*-quinonedibenzenesulfonimide. The infrared absorption spectra of the two preparations were identical.

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[10] Previously dried *in vacuo* over potassium hydroxide.

[11] F. Kehrmann, *Ber.*, **21**, 3320 (1888).

[12] F. Kehrmann, *ibid.*, **48**, 2027 (1915).

[13] E. Noelting and E. Kopp, *ibid.*, **38**, 3515 (1905).

[14] J. Cason, C. F. Allen and S. Goodwin, *J. Org. Chem.*, **13**, 403 (1948).

2-Methyl-x,5-dichloro-*p*-quinone-(1 or 4)-monobenzenesulfonimide.—To a suspension of 3.0 g. of 2-methyl-x,5-dichloro-*p*-phenylenedibenzenesulfonamide in 30 ml. of glacial acetic acid was added 3.30 g. of lead tetraacetate. The mixture was mechanically stirred and maintained at 60° for 20 hours. A few drops of ethylene glycol were added, stirring was continued for 5 minutes, and the solution was cooled and filtered. The filtrate was poured into a mixture of ice and water. The yellow crystals weighed 1.62 g. (77%). After recrystallization from glacial acetic acid, the compound formed yellow needles, m.p. 180–180.5°.

Anal. Calcd. for $C_{13}H_9Cl_2NO_3S$: C, 47.28; H, 2.75; N, 4.24. Found: C, 47.20; H, 2.78; N, 4.43.

The infrared spectrum showed the -CO- function was at 1670 cm.$^{-1}$ while the presence of a —C═N— group was indicated by bands at 1562 or 1547 cm.$^{-1}$. Bands at 1324, 1162 and 1087 cm.$^{-1}$ showed that a -SO_2- group was also present. Other prominent bands were found at 1637, 1312, 1303, 1033, 1024, 1011, 1000, 893.5, 867, 861.5, 759, 746, 726, 688 and 674 cm.$^{-1}$.

2-Methyl-3,5,6-trichlorohydroquinone.—A mixture of a solution of 0.40 g. of 2-methyl-x,5-dichloro-*p*-quinone-(1- or 4)-monobenzenesulfonimide in 25 ml. of glacial acetic acid and 5 ml. of concentrated hydrochloric acid was heated and cooled several times until the color was nearly discharged (4 hours), and then placed in an ice-box for several days. The crystals which separated weighed 0.18 g. By adding the filtrate to water, an additional 0.01 g. resulted; total weight 0.19 g. (85%). After several crystallizations from an ethanol-water mixture, the compound melted at 209–211° (lit. 211–212°).[6]

Anal. Calcd. for $C_7H_5Cl_3O_2$: C, 36.97; H, 2.21; Cl, 47.25. Found: C, 37.27; H, 2.49; Cl, 47.22.

The infrared spectrum showed an -OH- band at 3364 cm.$^{-1}$. Other prominent bands were found at 1424, 1420, 1320, 1225, 1183, 1027 and 869 cm.$^{-1}$.

2-Methyl-3,5,6-trichloro-*p*-benzoquinone (A).—To a suspension of 0.22 g. of 2-methyl-3,5,6-trichlorohydroquinone in 3 ml. of glacial acetic acid was added 0.25 g. of lead tetraacetate. The mixture was stirred and maintained at 65° for 4 hours. Ethylene glycol was added to destroy excess oxidant. The product separated on cooling and 0.13 g. of yellow crystals resulted; precipitation of the filtrate with water gave an additional 0.05 g. The total yield was 0.18 g. (82%). After crystallization from ethanol and water, it melted at 238–239.5°.

Anal. Calcd. for $C_7H_3Cl_3O_2$: C, 37.27; H, 1.34; Cl, 46.73. Found: C, 37.21; H, 1.55; Cl, 47.02.

(B).—The method of Elbs and Brunnschweiler[7] was used which consisted in the oxidation of *o*-toluidine in hydrochloric acid by means of sodium dichromate. The product proved to be identical with that prepared in (A). Reduction of the quinone with aqueous sulfur dioxide yielded a hydroquinone which was identical with the compound obtained by the action of hydrochloric acid in glacial acetic acid on 2-methyl-x,5-dichloro-*p*-quinone-(1- or 4)-monobenzenesulfonimide. The infrared spectrum of 2-methyl-3,5,6-trichloro-*p*-benzoquinone showed the presence of a -CO- group by bands at 1690 and 1669 cm.$^{-1}$. Other prominent bands were found at 1160, 1048, 1030, 894.5, 873, 765 and 710 cm.$^{-1}$

2,5-Dimethyl-*p*-quinonedibenzenesulfonimide.[2a]—To a suspension of 4.17 g. of 2,5-dimethyl-*p*-phenylenedibenzenesulfonamide[2a] in 50 ml. of glacial acetic acid was added at 65° with mechanical stirring 4.33 g. of lead tetraacetate. The mixture gradually turned yellow in color. After 3 hours, 2 ml. of ethylene glycol was added and the slurry was cooled to room temperature. The quinone diimide that separated weighed 3.54 g. (84%). It melted at 200°. This compound had been prepared previously by oxidation with bromine in pyridine.

2,5-Dimethyl-3-chloro-*p*-quinone-(1- or 4)-monobenzenesulfonimide.—To a suspension of 9.44 g. of 2,5-dimethyl-3-chloro-*p*-phenylenedibenzenesulfonamide in 250 ml. of glacial acetic acid heated to 70° was added with stirring 9.28 g. of crystalline lead tetraacetate. The solid material slowly dissolved, yielding a clear orange solution in 70 minutes. After adding 3–4 ml. of ethylene glycol, the solution was permitted to stand 10 minutes, then filtered and the filtrate poured onto ice. The yellowish-orange precipitate weighed 8.4 g. (90%). Recrystallization from 95% ethanol (Darco) gave a small amount of orange 2,5-dimethyl-3-chloro-*p*-quinonedibenzenesulfonimide along with the main product, 7.8 g. of yellow needles, m.p. 216–217°.

Anal. Calcd. for $C_{14}H_{12}ClNO_3S$: C, 54.27; H, 3.92; N, 4.56. Found: C, 54.08; H, 3.60; N, 4.52.

The relative proportion of diimide and monoimide varied with minor changes in conditions. The infrared spectrum showed the presence of a -CO- group by a band at 1667 cm.$^{-1}$ while a monosubstituted phenyl group was observed at 1592 cm.$^{-1}$. The —C═N— function was observed at 1545 cm.$^{-1}$, and an unknown band appeared at 1645 cm.$^{-1}$. No -NH- band could be detected. The -SO_2- function was indicated by bands at 1328, 1187 or 1160, and 1090 cm.$^{-1}$. Other prominent bands were found at 1025, 885, 873, 852, 779, 762, 748, 731, 687, 657 and 653 cm.$^{-}$.^{1}

Action of Hydrochloric Acid on Tetrasubstituted Chloro-*p*-phenylenedibenzenesulfonamides.—A mixture of 1 g. of 2,3,5,6-tetrachloro-*p*-phenylenedibenzenesulfonamide with 8 ml. of glacial acetic acid and 2 ml. of concentrated hydrochloric acid was refluxed for 48 hours. No hydrolysis occurred. 2-Methyl-3,5,6-trichloro-*p*-phenylenedibenzenesulfonamide and 2,5-dimethyl-3,6-dichloro-*p*-phenylenedibenzenesulfonamide were also recovered unchanged by similar treatment.

N,N,N,'N'-Tetrabenzenesulfonyl Derivative of 2,3-Dichloro-*p*-phenylenediamine.—To a solution of 1.0 g. of 2,3-dichloro-*p*-phenylenediamine dihydrochloride in 25 ml. of pyridine was added in several portions 2.8 g. of benzenesulfonyl chloride in 10 ml. of dry pyridine. The mixture was allowed to stand at room temperature for 24 hours with occasional shaking. It was subsequently poured slowly with stirring into a mixture of 100 ml. of concentrated hydrochloric acid and 250 g. of ice. A white flocculent precipitate was deposited which turned yellow on standing. The material weighed 1.8 g. (61%). Crystallization from glacial acetic acid (Darco) yielded colorless plates, m.p. 287–288°. 2,3-Dichloro-*p*-phenylenedibenzenesulfonamide, m.p. 214–215°, was also isolated from the mother liquors.

Anal. Calcd. for $C_{30}H_{22}Cl_2N_2O_8S_4$: C, 48.84; H, 3.02; N, 3.81. Found: C, 48.72; H, 3.26; N, 4.05.

The infrared spectrum showed the presence of an -SO_2- function by strong bands at 1177–1173 cm.$^{-1}$, 1085 cm.$^{-1}$ and either 1386 or 1369 cm.$^{-1}$, while no -NH- band could be detected. Other prominent bands were found at 1318, 1244, 995, 962, 956, 938, 913, 791, 759, 728, 720 and 686 cm.$^{-1}$. The spectrum as a whole was similar to that of the N,N,N'N',N",N"-hexabenzenesulfonyl derivative of triaminomesitylene.

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