

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

## Quinone Imides. XXVI. Adducts of *p*-Quinonebis-(dimethylaminosulfonimides) and their Hydrolysis Products

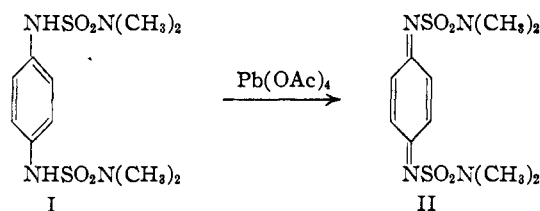
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*p*-Phenylenebis-(dimethylaminosulfonamides) are readily oxidized with lead tetraacetate to *p*-quinonebis-(dimethylaminosulfonimides). These diimides appear to add various molecules in a manner similar to the corresponding dibenzenesulfonimides. The diamides thus obtained, unlike the dibenzenesulfonamides, are readily hydrolyzed to the diamines by aqueous hydrochloric acid or preferably, hydrobromic acid. The products may be isolated readily in good yield and thus a convenient procedure is provided to utilize the versatile addition products of the diimides to synthesize a wide variety of substituted *p*-phenylenediamines.

The numerous addition reactions of *p*- and *o*-quinonedibenzenesulfonimides, *p*-quinonedibenzimides and *p*-quinonemonobenzenesulfonimide have been described in the previous papers in this series.<sup>1</sup> Many hitherto difficultly accessible classes of compounds have thus been made available. Their utility, however, has been limited by the stability to hydrolysis of the benzenesulfonamido or benzamido groups in the adducts. In occasional instances, hydrolysis was effected by vigorous treatment with hydrochloric or sulfuric acid and by other means to be described in a later paper but the isolation in a pure state of the resulting diamines or aminophenols was difficult and the yield of products usually low. Substituents on the nitrogen atoms of the *p*-phenylenediamine or *p*-aminophenol have been sought that would not interfere with oxidation to the corresponding di- or monoimides or with the subsequent addition reactions, and that could be hydrolyzed readily with facile isolation of the diamines and aminophenols. Such a substituent has been found in the dimethylaminosulfonyl group.

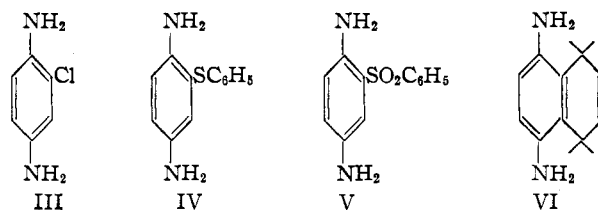
*p*-Phenylenediamine dihydrochloride in ethereal suspension reacts with dimethylaminosulfonyl chloride in presence of sodium acetate to give good yields of *p*-phenylenebis-(dimethylaminosulfonamide) (I). Similar derivatives of ring-substituted diamines would appear to be equally readily synthesized.



When I is oxidized with lead tetraacetate *p*-quinonebis-(dimethylaminosulfonimide) (II) is formed. This diimide undergoes addition reactions in exactly the same way as *p*-quinonedibenzenesulfonimide, exemplified by successive oxidations and additions of hydrogen chloride to form the mono-, isomeric di-, tri- and tetrachloro-*p*-phenylenebis-(dimethylaminosulfonamides). Thiophenol, benzenesulfonic acid and dienes have also been added. It is unnecessary to purify the intermediate quinone di-

imides in these reactions; the oxidation and subsequent addition may be carried out in essentially one operation with an over-all 80% yield or better of substituted diamide.

The hydrolysis of the dimethylaminosulfonamides may be achieved either by boiling with constant boiling hydrochloric acid or hydrobromic acid. Although the former was satisfactory in a few instances, the time required for solution and hydrolysis (one to three hours or more) was much greater than with hydrobromic acid. The latter is therefore to be preferred in most instances. The hydrobromic acid was used in amounts just necessary to dissolve the diamide at the boiling point; the hydrolysis usually occurred in one to two minutes and the dihydrobromide of the diamines began to separate almost immediately from the hot solution. The yields of the hydrobromides were 70–85%, but would probably be greater if the experiments had been performed on a larger scale. Some of the diamines were characterized also as their dibenzenesulfonamides. The hydrobromides of some of the diamines synthesized are shown in III–VI.

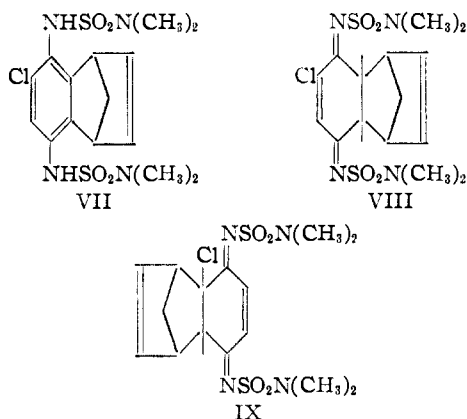


The 2-chloro-*p*-quinonebis-(dimethylaminosulfonimide) was obtained in two crystalline forms, fine yellow needles and heavy red tablets. The former is more soluble than the latter and can be dissolved away by means of a little cold chloroform. The pure red form may be recrystallized in the usual way without contamination of the product with the yellow form but recrystallization of the yellow form always resulted in a mixture. The pure yellow isomer was obtained by mechanical separation. Slow evaporation of the chloroform solutions of the single pure isomers gave mixtures containing approximately the same relative amounts of both isomers. The thermal conversion of the lower melting yellow to the red form was observed in solution or by gradual heating in a melting point tube. Since the chloroform solutions of the isomers show essentially identical spectra and since the two have different melting points and solubilities and separate concomitantly from

(1) R. Adams, *et al.*, *THIS JOURNAL*, **72**, 4601, 5154 (1950); **73**, 131, 1145, 1149, 1152, 2219, 5687 (1951); **74**, 2593, 2597, 2603, 2605, (a) 2608, (b) 3029, 3033, 3038, 3657, 3660, 5557, 5560, 5562, 5889, 5872, 5876 (1952); (c) **75**, 683 (1953).

solution, it would appear that the two are not isomorphs but possibly readily interchangeable *syn-anti* isomers. Two forms were not observed in any of the other diimides synthesized.

The condensation of the 2-chloro-*p*-quinonebis-(dimethylaminosulfonimide) with cyclopentadiene yielded two isomeric products, a yellow and a white solid, which are adducts of one molecule of diimide and one molecule of cyclopentadiene. The white compound obviously is an aromatized molecule (VII). The yellow, on the other hand, is stable to acid which usually catalyzes aromatization and is not, therefore, the intermediate VIII in the formation of the white isomer. Infrared spectra confirm the presence of carbon double bond nitrogen in the yellow but not in the white isomer. It has been assumed, therefore, that the diene has added partly on one side of the ring and partly on the other. The yellow isomer, which probably results from addition on the side with the chlorine atom, should not rearrange under the conditions used and may be represented by IX.



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

### Experimental<sup>2</sup>

**Dimethylaminosulfonyl Chloride.**—This reagent was prepared essentially according to the procedure of Wheeler and Degering.<sup>3</sup> It should be emphasized that it is imperative to maintain the temperature below 60° at all times prior to the final distillation of the product. The initial phase of the reaction is quite endothermic but as the evolution of hydrogen chloride begins to slow up, it is necessary to decrease the temperature of the bath at frequent intervals. The final purification is best effected in two steps, an initial rapid distillation followed by a slower distillation to obtain colorless product boiling over a narrow range; b.p. 74–76° (12 mm.) (lit.<sup>3</sup> 66° (10 mm.)) (60–70%).

***p*-Phenylenebis-(dimethylaminosulfonamide).**—A mixture of 36.2 g. of recrystallized *p*-phenylenediamine dihydrochloride, 70 g. of anhydrous sodium acetate, 35.2 g. of dimethylaminosulfonyl chloride and 500 ml. of anhydrous ether was refluxed with vigorous stirring for 48 hours. The heavy suspension was cooled, filtered and the residue extracted with four 250-ml. portions of cold water. There was obtained 57.0 g. of product as a water-insoluble gray powder. The ethereal mother liquor was evaporated under reduced pressure and the residual oil triturated with water.

(2) All melting points were taken with calibrated total immersion Anschütz thermometers.

(3) K. W. Wheeler and E. P. Degering, *THIS JOURNAL*, **66**, 1242 (1944).

An additional 2.8 g. of product was obtained and the total yield was 93%. The crude product was dissolved in the minimum quantity of cold 15% aqueous sodium hydroxide, treated with Darco and then acidified with cold aqueous 15% hydrochloric acid. The product was obtained as a white powder which was pure enough for most purposes. It can be recrystallized from 95% ethanol or from acetone-carbon tetrachloride, small colorless crystals, m.p. 227–228° (dec.).

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub>S<sub>2</sub>: C, 37.25; H, 5.63; N, 17.38. Found: C, 37.35; H, 5.67; N, 17.41.

Various attempts to prepare this derivative in the customary manner with pyridine as the solvent gave inferior yields of a highly colored product which required as many as three successive treatments with Darco before it was suitably purified for further use.

***p*-Quinonebis-(dimethylaminosulfonimide).**—This procedure illustrates the general method used to prepare all of the diimides described in this paper. To a suspension of 14.2 g. of *p*-phenylenebis-(dimethylaminosulfonamide) in 300 ml. of glacial acetic acid at 45° was added 24 g. (20% excess) of lead tetraacetate in two portions with stirring. The solution immediately became yellow and the color deepened to orange as the oxidation proceeded. After 15 minutes the mixture was warmed briefly on the steam-plate until all of the precipitate had gone into solution and then the reaction mixture was allowed to cool to room temperature and stand for 1 hour. The imide separated as small orange plates. At the end of this time the mixture was cooled in an ice-bath, diluted with 100 ml. of water with stirring, and after 30 minutes an additional 100 ml. of cold water was added (final concentration, 60% by volume acetic acid). The product was isolated by filtration and washed with three 10-ml. portions of ice-cold 60% aqueous acetic acid. The product is essentially insoluble in 60% aqueous acetic acid and in spite of the high concentration of water it was found that the excess lead tetraacetate was not hydrolyzed at a sufficient rate to contaminate the products with lead dioxide. There was obtained 14.2 g. (quantitative) of the diimide which was purified by recrystallization from chloroform-carbon tetrachloride, m.p. 182.5–183° (dec.) with darkening from 178°. The crude yields of this product and of the other diimides were customarily about 95%.

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 37.72; H, 4.43; N, 17.60. Found: C, 37.44; H, 4.68; N, 17.39.

**The Addition of Hydrogen Chloride.**—In each case the appropriate crude diimide was dissolved in a minimum amount of reagent grade chloroform and filtered through a sintered glass funnel to remove any traces of lead dioxide. An excess of hydrogen chloride from a tank was passed into the orange solution which initially deepened in color and then rapidly decolorized within about 1 to 5 minutes with the concomitant precipitation of the chloro derivative. No precautions were taken to exclude moisture. The solvent was removed from the reaction mixture at the water-pump and the essentially colorless product recrystallized from the appropriate solvent. Unless otherwise specified, the yields given are for two steps and based upon the amount of starting diamide.

**2-Chloro-*p*-phenylenebis-(dimethylaminosulfonamide).**—From 8.50 g. of *p*-phenylenebis-(dimethylaminosulfonamide) 9.2 g. (98%) of the crude monochloro derivative was obtained. After recrystallization from chloroform-carbon tetrachloride it melted at 171.5–172.5°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>17</sub>ClN<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 33.66; H, 4.80; N, 15.70. Found: C, 33.63; H, 4.87; N, 15.68.

**2-Chloro-*p*-quinonebis-(dimethylaminosulfonimide).**—From 1.73 g. of the corresponding chloro diamide, 1.62 g. (94%) of the crude chloro diimide was obtained as an orange powder. Upon recrystallization from carbon tetrachloride or carbon tetrachloride-*n*-hexane there always resulted a mixture of fine yellow needles and heavy red tablets. Washing with small amounts of cold chloroform dissolved the much more soluble yellow form. The red form was then crystallized from chloroform-carbon tetrachloride by dissolving hot and cooling, m.p. 144–145° (dec.).

*Anal.* (red isomer) Calcd. for C<sub>10</sub>H<sub>16</sub>ClN<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 33.84; H, 4.26; N, 15.79. Found: C, 34.02; H, 4.07; N, 15.62.

The yellow form was obtained pure by mechanical separation, m.p. 136–137° (dec.). Attempts to recrystallize

the pure yellow form from solvents resulted in a mixture of the red and yellow crystals.

*Anal.* (yellow isomer) Calcd. for  $C_{10}H_{16}ClN_4O_4S_2$ : C, 33.84; H, 4.26; N, 15.79. Found: C, 33.84; H, 4.48; N, 15.62.

Slow evaporation of solutions of the pure red or yellow isomers always gave mixtures containing approximately the same relative amounts of both isomers. The yellow isomer on very slow heating in a melting point tube gradually changed to the red form and melted at 142–143° (dec.). The infrared spectra of the single isomers in chloroform solution were essentially identical; in Nujol mull the major bands from 1400 to 4000  $cm^{-1}$  were very similar but from 600 to 1400  $cm^{-1}$  the curves were quite dissimilar. These differences would be expected to result either from the differences in crystal structure or from geometrical isomerism or possibly from both.

**2,3-Dichloro-*p*-phenylenebis-(dimethylaminosulfonamide).**—From 4.0 g. of 2-chloro-*p*-phenylenebis-(dimethylaminosulfonamide), 4.1 g. (93.5%) of a crude mixture of the 2,3- and 2,5-dichloro isomers resulted. The 2,3-dichloro isomer was extracted from the mixture by refluxing with three 25-ml. portions of carbon tetrachloride. The combined extracts were evaporated to dryness. There was obtained 1.9 g. (46.5%) of the crude 2,3-dichloro isomer; fine needles, which were recrystallized from carbon tetrachloride, m.p. 135.6–136.6°.

*Anal.* Calcd. for  $C_{10}H_{16}Cl_2N_4O_4S_2$ : C, 30.69; H, 4.12; N, 14.32. Found: C, 30.88; H, 3.03; N, 14.43.

Hydrolysis with 48% hydrobromic acid to the diamine dihydrobromide and conversion of the product to the corresponding dibenzenesulfonamide by means of benzenesulfonyl chloride in pyridine established the structure as the 2,3-dichloro isomer. After purification from chloroform-carbon tetrachloride the m.p. was 213.5–214°, not depressed upon admixture with an authentic sample, m.p. 214–215°. <sup>1a</sup>

**2,5-Dichloro-*p*-phenylenebis-(dimethylaminosulfonamide).**—The residue from the carbon tetrachloride extraction of the 2,3-dichloro isomer weighed 2.2 g. (53.5%) and was purified by recrystallization from a large volume of acetone; stout prisms, m.p. 215.5–216° (dec.) with darkening from 200°.

*Anal.* Calcd. for  $C_{10}H_{16}Cl_2N_4O_4S_2$ : C, 30.69; H, 4.12; N, 14.32. Found: C, 30.96; H, 4.39; N, 14.60.

This isomer was identified by the same procedure used for the 2,3-isomer by preparing the 2,5-dichloro-*p*-phenylenebisbenzenesulfonamide which, after purification from acetone-carbon tetrachloride, melted at 248–248.5°, not depressed upon admixture with an authentic sample, m.p. 248–249°. <sup>1a</sup>

**2,3,5-Trichloro-*p*-phenylenebis-(dimethylaminosulfonamide).**—From 1.68 g. of a mixture of 2,3- and 2,5-dichloro-*p*-phenylenebis-(dimethylaminosulfonamide), there was obtained 1.7 g. (95%) of product which was recrystallized from chloroform-carbon tetrachloride; felted needles, m.p. 180–180.5°.

*Anal.* Calcd. for  $C_{10}H_{16}Cl_3N_4O_4S_2$ : C, 28.21; H, 3.55; N, 13.16. Found: C, 28.26; H, 3.45; N, 13.40.

**2,3,5,6-Tetrachloro-*p*-phenylenebis-(dimethylaminosulfonamide).**—From 1.0 g. of 2,3,5,6-trichloro-*p*-phenylenebis-(dimethylaminosulfonamide), 1.0 g. (92.5%) of product resulted, which was purified by recrystallization from acetone; stout needles, m.p. 231–232° (dec.).

*Anal.* Calcd. for  $C_{10}H_{14}Cl_4N_4O_4S_2$ : C, 26.10; H, 3.07; N, 12.18. Found: C, 25.91; H, 2.69; N, 12.11.

**2-Phenylmercapto-*p*-phenylenebis-(dimethylaminosulfonamide).**—Crude *p*-quinonebis-(dimethylaminosulfonamide), prepared by lead tetraacetate oxidation of 2.0 g. of *p*-phenylenebis-(dimethylaminosulfonamide), was dissolved in 30 ml. of reagent grade chloroform and a solution of 0.75 g. (10% excess) of redistilled thiophenol in 5 ml. of chloroform containing one drop of triethylamine<sup>9</sup> was added at once. After a slight deepening of color the reaction mixture became colorless within about one minute with a noticeable evolution of heat. The solvent was removed by warming and the semi-solid residue was dissolved in a minimum amount of hot 95% ethanol. Upon cooling there was obtained 2.5 g. (93%) of product as fine white needles. When crystallizing from 95% ethanol, the hot solution was treated with Darco to remove a trace of color. It became

deep orange but upon standing overnight turned colorless and the product again separated as white needles, m.p. 144.8–145.6°.

*Anal.* Calcd. for  $C_{16}H_{22}O_4N_4S_2$ : C, 44.63; H, 5.15; N, 13.01. Found: C, 44.73; H, 5.24; N, 12.72.

**2-Benzenesulfonyl-*p*-phenylenebis-(dimethylaminosulfonamide).**—The crude diimide prepared from 4.0 g. of *p*-phenylenebis-(dimethylaminosulfonamide) was added in small portions over a 10-minute interval to a solution of 3.0 g. (50% excess) of sodium benzenesulfinate in 60 ml. of glacial acetic acid containing 2 drops of concentrated sulfuric acid. After 20 minutes the colorless reaction mixture was diluted with 300 ml. of water and the white product isolated by filtration; yield 5.3 g. (92%). It was recrystallized from 95% ethanol; fine white crystals, m.p. 181.8–182.6°.

*Anal.* Calcd. for  $C_{16}H_{22}O_6N_4S_3$ : C, 41.54; H, 4.80; N, 12.11. Found: C, 41.76; H, 4.63; N, 11.84.

**5,8-Dihydronaphthalene-1,4-bis-(dimethylaminosulfonamide).**—Ten grams of liquid butadiene was added to a solution of 4.3 g. of crude *p*-quinonebis-(dimethylaminosulfonamide) in 100 ml. of chloroform containing 0.25% ethanol and the thick walled container was capped and set aside at room temperature for 30 days. At the end of this time the solution was still red-orange and contained a small amount of dark, chloroform-insoluble material which was removed by filtration and discarded. The solution was concentrated and diluted with *n*-hexane. The oil which separated slowly solidified upon scratching. The solvents were removed under reduced pressure, the semi-solid product was taken up in glacial acetic acid and 3 drops of 48% hydrobromic acid was added. Upon scratching vigorously a heavy precipitate formed. The suspension was diluted with 3 volumes of water and the solid product collected by filtration. After recrystallization from chloroform-carbon tetrachloride 3.7 g. (74.5%) of short white needles resulted, m.p. 182.8–183.6°.

*Anal.* Calcd. for  $C_{14}H_{20}N_4O_4S_2$ : C, 44.90; H, 5.92; N, 14.96. Found: C, 45.12; H, 6.02; N, 14.75.

**Naphthalene-1,4-bis-(dimethylaminosulfonamide).**—A solution of 3.7 g. of crude *p*-quinonebis-(dimethylaminosulfonamide) and 1.1 ml. (10% excess) of acetoxybutadiene in 60 ml. of reagent grade chloroform was allowed to stand for 6 days. At the end of this time the red-orange reaction mixture contained a small amount of flocculent precipitate. The mixture was diluted with *n*-hexane until no more material separated, the solid was collected and then taken up in boiling glacial acetic acid. After cooling to room temperature about 1 ml. of 48% hydrobromic acid was added. The initial precipitate redissolved and then reprecipitated. The solution was diluted with water and the bulk of the product was obtained as an amorphous tan powder which was dried, dissolved in hot chloroform, treated with Darco and allowed to crystallize. The yield of crude product was 1.0 g. (25%) and was recrystallized for analysis from 95% ethanol; colorless plates, m.p. 167–168° (dec.).

*Anal.* Calcd. for  $C_{14}H_{20}N_4O_4S_2$ : C, 45.14; H, 5.41; N, 15.04. Found: C, 45.34; H, 5.20; N, 14.97.

**7-Chloro-1,4-dihydro-1,4-methanonaphthalene-5,8-bis-(dimethylaminosulfonamide) and 4a-Chloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-bis-(dimethylaminosulfonamide).**—The crude imide prepared from 1.0 g. of 2-chloro-*p*-phenylenebis-(dimethylaminosulfonamide) was dissolved in 10 ml. of anhydrous benzene and 1.0 ml. of freshly distilled cyclopentadiene was added at once. The solution became deep red and after 5 minutes the color slowly began to fade. After standing for 12 hours the light yellow solution was diluted with an equal volume of *n*-hexane and concentrated to 10 ml. on the steam-plate. Upon cooling and scratching the first isomer separated as a fine tan powder and was collected by filtration. The product was taken up in a minimum amount of glacial acetic acid and 1 drop of 48% hydrobromic acid was added. The light tan solution became almost colorless and upon diluting with water 0.4 g. (34%) of the 7-chloro isomer separated as a white powder which was purified by crystallization from 95% ethanol, m.p. 209.6–210.6° (dec.) with previous shrinking from 206°.

*Anal.* Calcd. for  $C_{16}H_{21}ClN_4O_4S_2$ : C, 42.80; H, 5.03; N, 13.31. Found: C, 42.56; H, 4.85; N, 13.29.

TABLE I  
 HYDROLYSIS OF *p*-PHENYLENEBIS-(DIMETHYLAMINOSULFONAMIDES) TO DIAMINES

Ring substituents	Reagent	Time	Isolated yield, %	Formulas	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
...	HCl	1.5 hr.	85	$C_6H_8N_2 \cdot 2HCl$	39.80	39.96	5.70	5.84	15.48	15.42
2-Chloro-	HCl	2 hr.	82.5	$C_6H_7N_2 \cdot 2HCl$	33.44	33.67	4.21	4.31	13.00	12.87
2,3-Dichloro-	HBr	1 min.	85.5	$C_6H_4Cl_2N_2 \cdot 2HBr$	21.26	21.45	2.38	2.31	8.27	8.35
2,5-Dichloro-	HBr	10 min.	86	$C_6H_4Cl_2N_2 \cdot 2HBr$	21.26	21.41	2.38	2.21	8.27	8.14
2,3,5-Trichloro- <sup>a</sup>	HBr	15 min.	85.6	$C_6H_3Cl_3N_2 \cdot 2HBr \cdot H_2O$	18.41	18.21	2.32	1.83	7.16	7.02
2,3,5,6-Tetrachloro <sup>b</sup>	HBr	5 min.	71.3	$C_6H_2Cl_4N_2$	29.30	29.32	1.64	1.53	11.39	10.96
$C_6H_5S$ - <sup>c</sup>	HCl	18 hr.	0	.....	...	...	...	...	...	...
	HBr	1 min.	95.5	$C_{12}H_{12}N_2S \cdot 3HBr$	31.40	32.74	3.29	3.20	6.10	63.4
$C_6H_5SO_2$ - <sup>d</sup>	HCl	6 hr.	77	$C_{12}H_{12}N_2O_2S \cdot 2HCl$	44.87	44.61	4.39	4.23	8.72	8.94
	HBr	1 min.	72	$C_{12}H_{12}N_2O_2S \cdot 2HBr$	35.14	35.18	3.44	3.57	6.85	6.64
	HCl	2 hr.	70	$C_{10}H_{12}N_2 \cdot 2HCl$	51.51	51.69	6.05	5.97	12.02	11.82

<sup>a</sup> The salt isolated after recrystallization from 48% hydrobromic acid gave erratic analytical results. The sample reported was repurified until two consecutive analyses gave concordant results. <sup>b</sup> Isolated as free diamine, m.p. 221–222° (lit. m.p. 223–224°) not depressed on admixture with an authentic specimen, m.p. 223–224°. The low nitrogen value may indicate that a small amount of phenolic material was present which was not removed by recrystallization from benzene-*n*-hexane. <sup>c</sup> This product darkened upon exposure to air and further attempts to purify it by recrystallization from hydrobromic acid gave dark colored material. The sample reported here was taken directly from the reaction mixture and dried at 28° (0.2 mm.) for 24 hours. The analysis indicates the material to be predominantly the trihydrobromide. The third molecule of HBr may be associated with the sulfur atom. <sup>d</sup> Based on 25% recovered starting material.

The yellow mother liquor from which the 7-chloro isomer was isolated was further concentrated and then diluted with *n*-hexane. A yellow powder weighing 0.4 g. (34%) separated and was recrystallized from 95% ethanol containing 4 drops of 48% hydrobromic acid, then a second time from pure 95% ethanol; clumps of yellow blades, m.p. 140–141° (dec.) with previous darkening from 138°. The infrared spectrum of a Nujol mull showed a strong band at 1590  $cm^{-1}$  characteristic of the carbon-nitrogen double bond of the quinone diimides and no -NH band in the region from 3100 to 3500  $cm^{-1}$ . This evidence taken with the failure of the compound to aromatize with hydrobromic acid supports the assigned structure with the 4a-chloro group.

*Anal.* Calcd. for  $C_{15}H_{21}ClN_4O_4S_2$ : C, 42.80; H, 5.03; N, 13.31. Found: C, 43.02; H, 5.17; N, 13.43.

**Diamine Hydrohalides by Hydrolysis of the Dimethylaminosulfonamides. Method A. Hydrochloric Acid.**—A suspension of 1 part of diamide in 75 parts of constant boiling hydrochloric acid containing about 0.1% of zinc chloride was refluxed vigorously; sufficient *n*-octanol was added dropwise to just prevent excessive foaming. The results are given in Table I.

The 2-chloro-*p*-phenylenebis-(dimethylaminosulfonamide) and the 5,8-dihydronaphthalene-1,4-bis-(dimethylaminosulfonamide) were completely dissolved and hydrolyzed within 2 hours whereas the 2-benzenesulfonyl-*p*-phenylenebis-(dimethylaminosulfonamide) was only partially hydrolyzed after 6 hours and 25% of the starting material did not go into solution. The 2-phenylmercapto-

*p*-phenylenebis-(dimethylaminosulfonamide) was largely undissolved after 18 hours and about 60% of unchanged starting material was recovered. No identifiable hydrolysate was isolated.

The hydrochlorides were prepared for analysis by dissolving them in a minimum amount of hot dilute hydrochloric acid, filtering through a sintered glass funnel and then adding an equal volume of concentrated hydrochloric acid.

**Method B. 48% Hydrobromic Acid.**—One part of the diamide and sufficient redistilled colorless 48% hydrobromic acid to give complete solution at the boiling point (between 10 to 15 parts by volume) were heated to boiling and refluxed gently. After 1 to 2 minutes the dihydrobromide of the diamine usually began to separate from the boiling solution and the reaction mixture was allowed to cool to room temperature. The solution usually became a light tan but no bromination of the diamines was observed as when the benzenesulfonamides are hydrolyzed<sup>4</sup> with hydrobromic acid.

The hydrobromides were isolated by filtration and redissolved in the minimum amount of hot dilute hydrobromic acid. The hot solution was filtered through a sintered glass funnel and diluted with an equal volume of 48% hydrobromic acid. The product thus obtained was pure enough for analysis.

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