taining a mixture of stereoisomers, crystallized from ether and furnished 111 mg. of prisms melting at 126–127°, λ_{max} 222, 254, 320 mμ; ϵ 37,900, 17,000, 5,680; ν_{max} 1678 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{26}O_5$: C, 73.07; H, 6.64. Found: C, 72.87; H, 6.66.

Reaction of XIa with Acetic Anhydride.—A mixture of 1.0 g. of XIa and 10 ml. of acetic anhydride was treated with 1 ml. of triethylamine. The reaction mixture was heated on the steam-bath until all of the material had dissolved and was then allowed to stand at room temperature. At the end of 6 hours, a considerable amount of crystalline material had separated, and after standing overnight at 0°, 1.07 g. (84%) of product was obtained, which after crystallization from a small volume of methanol, melted at 117–118°. The same compound was obtained by treatment of XIa with acetic anhydride and *p*-toluenesulfonic acid, though in lower yield, and the substance was identified as 2-acetoxymethylene-7-methoxytetralone-1, by direct comparison with a sample obtained by acetylation of I in the presence of acetic anhydride and pyridine.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.20; H, 5.93.

Preparation of XIa from 2-*p*-Toluenesulfonoxymethylene-7-methoxytetralone-1.—A mixture of 107 mg. of 2-*p*-toluenesulfonoxymethylene-7-methoxytetralone-1 (prepared by treatment of I with *p*-toluenesulfonyl chloride and triethylamine)[14] and 67 mg. of 2-hydroxymethylene-7-methoxytetralone-1 (I) was dissolved in 4 ml. of ethanol and treated with 0.1 ml. of triethylamine. After standing at room temperature for 8 hours, the reaction mixture, containing precipitated product, was cooled in ice and filtered. The crude material, m.p. 160–180°, on recrystallization from chloroform–ethanol, afforded 20% of XIa, m.p. 210–211°, identical in all respects with a sample obtained by the β-chlorovinyl methyl ketone synthesis.

Preparation of 2-Isopropoxymethylene-7-methoxytetralone-1.—To a solution of 1.03 g. of 2-hydroxymethylene-7-methoxytetralone-1 (I) and 1.0 ml. of isopropyl iodide in 25 ml. of dry acetone there was added 1.4 g. of freshly ignited potassium carbonate. The mixture was heated under reflux on the steam-bath for 24 hours, at the end of which time the acetone was removed *in vacuo*, and the residue was taken up in water and ether. The ether layer was then washed with potassium carbonate solution, dried and evaporated. The residual oil crystallized on standing, and after several recrystallizations from petroleum ether furnished a pure sample, m.p. 72°, λ_{max} 223, 268, 301, 335 mμ; ϵ 18,000, 7,600, 11,000, 8,000.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.12; H, 7.42.

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[14] The crude tosylate melted at about 76° and was too unstable to be submitted for analysis.

HOUSTON, TEXAS

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

Quinone Imides. XL. Orientation in the Addition of Hydrogen Chloride to 2-Substituted-*p*-quinonedibenzimides

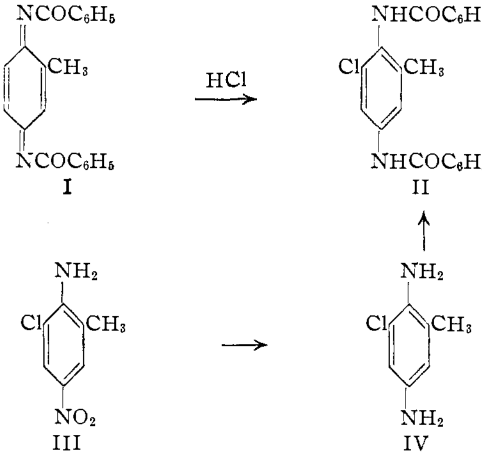
BY ROGER ADAMS AND M. D. NAIR[1]

RECEIVED JULY 30, 1956

2-Methyl-*p*-quinonedibenzimide adds hydrogen chloride to give exclusively 6-chloro-2-methyl-*p*-phenylenedibenzamide. The corresponding 2-phenylmercapto analog gives 3-chloro-2-phenylmercapto-*p*-phenylenedibenzamide. The 2-benzenesulfonyl derivative, on the other hand, gives a mixture composed of the 2-benzenesulfonyl-3-chloro- and 2-benzenesulfonyl-6-chloro-*p*-phenylenedibenzamides. The structures of the various derivatives were determined by unequivocal methods.

The addition of hydrogen chloride to 2-chloro-*p*-quinonedibenzenesulfonimide resulted in a mixture of at least two dichloro diamides, the 2,5-dichloro-*p*-phenylenedibenzenesulfonamide predominating with the 2,3-dichloro isomer in smaller amounts.[2] 2-Methyl-*p*-quinonedibenzenesulfonimide, however, gave only 5-chloro-2-methyl-*p*-phenylenedibenzenesulfonamide. The addition of hydrogen chloride to 2-chloro-*p*-quinonedibenzimide resulted in the exclusive formation of 2,6-dichloro-*p*-phenylenedibenzamide[3] and a similar orientation occurred when hydrogen chloride reacted with 2-chloro-*p*-quinonedipivalimide.[4]

In this communication, results are reported on the addition of hydrogen chloride to *p*-quinonedibenzimides with the 2-position occupied by methyl, phenylmercapto and benzenesulfonyl groups, respectively. From 2-methyl-*p*-quinonedibenzimide (I) only a single adduct was formed, 6-chloro-2-methyl-*p*-phenylenedibenzamide (II). Its constitution was established by synthesis from the known 2-chloro-4-nitro-6-methylaniline (III) by the reduction to the corresponding diamine IV followed by benzoylation.



2-Phenylmercapto-*p*-quinonedibenzimide (V), made by oxidation of the diamide obtained from thiophenol and *p*-quinonedibenzimide, however, added hydrogen chloride to give only one product which proved to be 3-chloro-2-phenylmercapto-*p*-phenylenedibenzamide (VI). Its structure was proved by oxidation to the corresponding benzenesulfonyl analog XI which was identical with a com-

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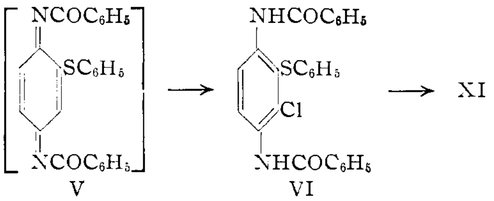
[1] An abstract of a portion of a thesis submitted by M. D. Nair to the Graduate College of the University of Illinois, 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952).

[3] R. Adams and D. S. Acker, *ibid.*, **74**, 3029 (1952).

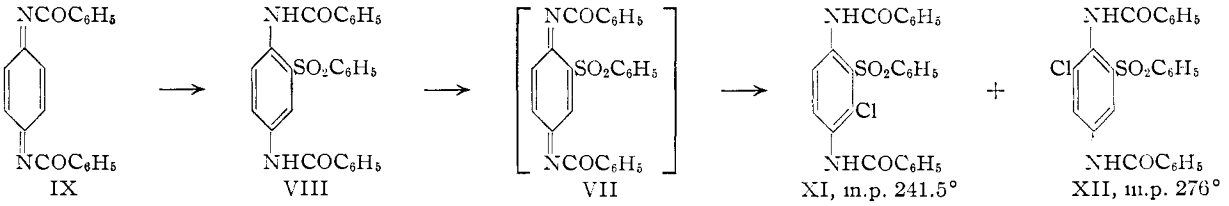
[4] R. Adams and J. M. Stewart, *ibid.*, **74**, 3660 (1952).

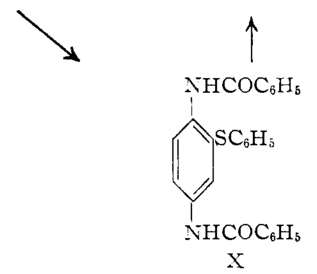
pound of known constitution made by another route and described later in this paper.

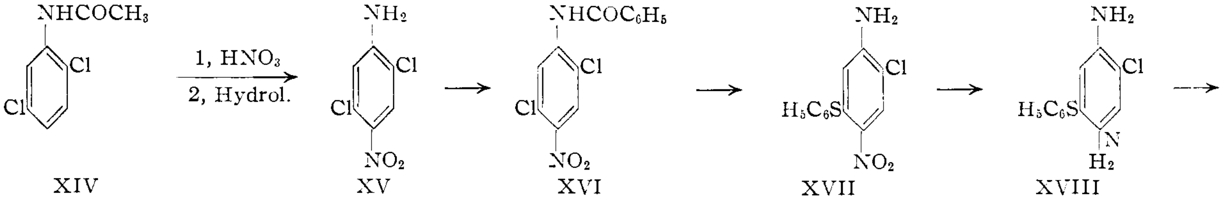


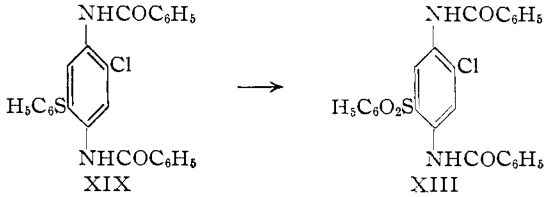
The compound of most interest in this study was the 2-benzenesulfonyl-*p*-quinonedibenzimide (VII) since the 2-benzenesulfonyl group is electron attracting. The quinone diimide VII was made by oxidation of the corresponding diamide VIII which in turn was synthesized by addition of benzenesulfinic acid to *p*-quinonedibenzimide (IX) or by addition of thiophenol to IX followed by peroxide oxidation of the product X.

Addition of hydrogen chloride to the unisolated diimide VII gave a 46% yield of a mixture of isomeric monochloro diamides which were separated by crystallization. The isomer, m.p. 241.5°, was shown to be the 2-benzenesulfonyl-3-chloro diamide (XI) and the other isomer, m.p. 276°, the 2-benzenesulfonyl-6-chloro diamide (XII).







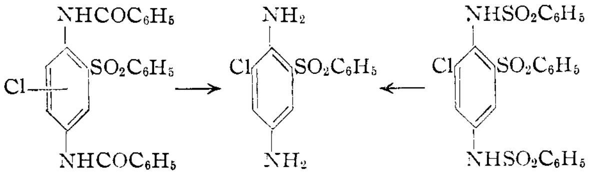


The structures of compounds XI and XII were determined by unequivocal methods. The 2-benzenesulfonyl-5-chloro diamide (XIII) was made by the series of reactions shown in XIV → XIX; the known 2,5-dichloroacetanilide was nitrated, then hydrolyzed and benzoylated. Treatment of this product with the sodium salt of thiophenol caused replacement of one of the chlorine atoms and concomitant hydrolysis of the benzoyl group. The nitro amine was reduced to the diamine and then benzoylated. Finally the phenylmercapto group of the dibenzamide was oxidized with hydrogen peroxide to the benzenesulfonyl group. Compound XIII was not identical with either of the two benzenesulfonyl derivatives isolated from the addition reaction. The latter two were thus identified as the 2,3- and 2,6-isomers.

The benzenesulfonyl chloro diamide, m.p. 276°, was unaffected by boiling hydrochloric acid, lost one benzoyl group presumably from the unhindered benzamide group by treatment with concentrated sulfuric acid at room temperature, and two benzoyl groups by treatment with hot concentrated sulfuric acid for 40 hours to give the diamine XX. An attempt was made to introduce two benzenesulfonyl groups into the amino groups of this product since the three isomeric 2-benzenesulfonylchloro-*p*-phenylenedibenzenesulfonamides were all known. Only one benzenesulfonyl group, however, entered, presumably on the amino group without *ortho* substituents. The problem was solved by debenzenesulfonation of the 2-benzenesulfonyl-6-chloro-*p*-phenylenedibenzenesulfonamide (XXI)[5] by concentrated sulfuric acid at room temperature for 24 hours. The resulting diamine was identical with the diamine from debenzoylation of the diamide, m.p. 276°.

With the structure of the diamide, m.p. 276°, established it follows that the isomer, m.p. 241.5°, is the 2-benzenesulfonyl-3-chloro derivative.

Hot concentrated sulfuric acid converted the 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzamide to 2-benzenesulfonyl-3-chloro-*p*-phenylenediamine, but the 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzenesulfonamide was unaffected by this treatment.



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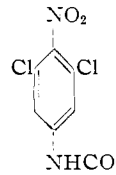
[5] R. Adams and T. E. Young, This Journal, **75**, 3235 (1953).

Another route to the 2-benzenesulfonyl-6-chlorodibenzamide deserves mention even though it failed. Nitration of 3,5-dichlorobenzamide gave mixtures; 3,5-dichloroacetanilide, however, can be nitrated to a pure mononitro compound, presumably XXIII, but replacement of one chlorine in this molecule by a phenylmercapto group was unsuccessful.



XXIII

Of the *p*-quinonedibenzimides described in this research only the 2-methyl derivative was isolated. The addition reactions to the others were carried out in the solutions in which the diimides were formed.

It appears that the electron-donating methyl group and the chlorine atom in the 2-position orient the entering chlorine of the hydrogen chloride to the 6-position. The electron-attracting benzenesulfonyl group also orients the entering chlorine to the 6-position as well as to the 3-position. From the 2-phenylmercapto derivative only the 3-chlorodiamide could be isolated. It may be concluded that regardless of the character of the 2-substituent in *p*-quinonedibenzimides the more favored position of the entering chlorine from hydrogen chloride is the 6-position with the 3-position somewhat less favored. There appears to be a pronounced inhibition to the chlorine entering the 5-position in the molecules in which benzimide groups are present. In this respect, these results coincide with those previously published.

A study of the infrared spectra of the three isomeric benzenesulfonyl chloro dibenzamides and the corresponding diamines revealed that the only difference is found in the 800–900 cm.$^{-1}$ region of the spectra. The characteristic –CH absorption frequency is essentially the same for each pair with identical orientation of groups.

TABLE I

	Compound	Orientation	M.p., °C.	–CH Absorption frequency,[c] cm.$^{-1}$
1	Diamide[a]	1,2,4,6	276	876
2	Diamine[b]	1,2,4,6	137	875
3	Diamide[a]	1,2,4,5	220	833
4	Diamine[b]	1,2,4,5	109	822
5	Diamide[a]	1,2,3,4	241.5	806
6	Diamine[b]	1,2,3,4	118.5	804

[a] Diamides: 2-benzenesulfonyl-x-chloro-*p*-phenylenedibenzamides. [b] Diamines: 2-benzenesulfonyl-x-chloro-*p*-phenylenediamine. [c] The absorption spectra were taken in Nujol mull.

The lowering of the –CH absorption frequency in the case of the 1,2,3,4-isomer in which there are two adjacent hydrogens on the aromatic ring is in keeping with earlier observations in other laboratories.[6] There appears to be some correlation between orientation of groups on the ring and –CH absorption frequency.

Acknowledgment.—The authors are indebted to Mr. J. Nemeth and Mrs. Maria Benassi for microanalyses and to Mr. J. Brader for the infrared spectra and their interpretation.

Experimental

All melting points are corrected.

6-Chloro-2-methyl-*p*-phenylenedibenzamide. A.—To a solution of 2.0 g. of 2-methyl-*p*-quinonedibenzimide[7] was passed a current of hydrogen chloride. The color faded slightly in 10 minutes, but no change occurred thereafter. Hydrogen chloride was passed in for a total of 90 minutes after which the solution was evaporated to dryness under vacuum to give a pale yellow solid. This was recrystallized from ethanol to give 2.0 g. (90%) of white crystals. Two more recrystallizations gave pure white crystals, m.p. 247–248°.

The compound did not depress the melting point of an authentic sample of 2-methyl-6-chloro-*p*-phenylenedibenzamide described under **B**. The infrared spectra are identical.

Anal. Calcd. for $C_{21}H_{17}ClN_2O_2$: C, 69.13; H, 4.69; N, 7.68. Found: C, 69.11; H, 4.79; N, 7.42.

B.—This product was made by benzoylation of the diamine from 6-chloro-2-methyl-4-nitroaniline, synthesized by a modification of the procedure used by Leulier.[8]

To a cooled suspension of 10.0 g. of powdered 2-methyl-4-nitroaniline in 100 ml. of concentrated hydrochloric acid was added with stirring 100 ml. of 30% hydrogen peroxide. The mixture was stirred for 5 minutes and then 50 ml. of water was added. After standing for 30 minutes, during which time a precipitate formed, the solid, weighing 8.9 g. (81.5%), was collected by filtration. Recrystallization from ethanol, with addition of water to turbidity, gave yellow needles, m.p. 172.5° (lit.[8] m.p. 168°).

Anal. Calcd. for $C_7H_7ClN_2O_2$: C, 45.05; H, 3.78; N, 15.01. Found: C, 45.12; H, 3.60; N, 14.97.

A mixture of 5.0 g. of 6-chloro-2-methyl-4-nitroaniline, 30 ml. of concentrated hydrochloric acid, 150 ml. of water and 20 g. of granulated (20 mesh) tin was heated under reflux for 2 hours. At the end of this time the color had practically disappeared. An additional 20 ml. of concentrated hydrochloric acid was added and heating under reflux continued for another half an hour. The mixture was made basic with 10% aqueous sodium hydroxide, then extracted with two 100-ml. lots of ether. The combined ether extracts were dried and the ether distilled. The small amount of yellow oil left behind was triturated with 10 ml. of 50% ethanol. The product solidified *en masse*. More water was added and the precipitate separated by filtration and dried to give 2.65 g. (63%) of grey needles, m.p. 84–86°.

The compound was unstable and hence could not be recrystallized to analytical purity. A dihydrochloride was made by suspending the diamine in water, adding concentrated hydrochloric and slowly evaporating on the water-bath. After repetition of this process the resulting pale pink plates were dried and analyzed. A suitable solvent could not be found for recrystallization. The dihydrochloride decomposed above 290° to a black liquid.

Anal. Calcd. for $C_7H_{11}Cl_3N_2$: C, 36.62; H, 4.83; N, 12.20. Found: C, 37.12; H, 4.73; N, 11.91.

A mixture of 1.0 g. of 6-chloro-2-methyl-*p*-phenylenediamine, 3.00 g. of benzoyl chloride and 35 ml. of α-picoline was heated under reflux for 90 minutes, cooled and poured into cracked ice and water. A white product precipitated along with an oily residue. On cooling in the icebox overnight, the oil solidified. Filtration yielded 2.6 g. (94%) of a crude product. Three recrystallizations from ethanol gave pure white crystals, m.p. 248.5°.

Anal. Calcd. for $C_{21}H_{17}ClN_2O_2$: C, 69.13; H, 4.69; N, 7.68. Found: C, 68.89; H, 4.71; N, 7.51.

2-Benzenesulfonyl-*p*-phenylenedibenzamide.—A mixture of 2.0 g. of 2-phenylmercapto-*p*-phenylenedibenzamide,[9] 6 ml. of 30% hydrogen peroxide and 25 ml. of glacial acetic acid was heated under reflux for 75 minutes and cooled. The reaction mixture, in which a white precipitate had

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(6) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1954, p. 67; P. J. Launer and D. A. McCaulay, *Anal. Chem.*, **23**, 1875 (1951).

(7) R. Adams and D. S. Acker, THIS JOURNAL, **74**, 3657 (1952).

(8) A. Leulier, *Bull. soc. chim. France*, [4] **35**, 1328 (1924).

(9) R. Adams and D. S. Acker, THIS JOURNAL, **74**, 5872 (1952).

formed, was poured into cold water and then filtered. The solid weighed 2.1 g. (97.5%). Two recrystallizations from ethanol gave white crystals, m.p. 193–193.5°.

Anal. Calcd. for $C_{26}H_{20}N_2O_4S$: C, 68.40; H, 4.42. Found: C, 68.26; H, 4.58.

The compound did not depress the melting point of an authentic sample prepared by addition of benzenesulfinic acid to *p*-quinonedibenzimide. The infrared spectrum confirmed the identity.

3-Chloro-2-phenylmercapto-*p*-phenylenedibenzamide.—To a solution of 2.5 g. of 2-phenylmercapto-*p*-phenylenedibenzamide in 125 ml. of reagent chloroform was added in one lot 2.8 g. of lead tetraacetate. The mixture was stirred at room temperature for one hour, after which it was filtered. A stream of hydrogen chloride was passed into the clear chloroform solution for 15 minutes, the solution was then filtered and the filtrate permitted to stand overnight. The chloroform was distilled off under vacuum and the white residue taken up in boiling ethanol (Darco). The filtrate on cooling deposited 1.4 g. (52%) of white needles. Two recrystallizations gave the pure compound, m.p. 254–254.5°.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_2S$: C, 68.04; H, 4.17; N, 6.10. Found: C, 68.02; H, 4.12; N, 6.04.

2-Benzenesulfonyl-3-chloro-*p*-phenylenedibenzamide.—A mixture of 0.5 g. of 3-chloro-2-phenylmercapto-*p*-phenylenedibenzamide in 25 ml. of glacial acetic acid and 2.0 ml. of 30% hydrogen peroxide, was heated under reflux for 3 hours and the cooled solution then poured into cracked ice and water. After standing for two hours the solution was filtered and 0.5 g. (94.5%) of product obtained. Two recrystallizations from ethanol gave pure white needles, m.p. 242.5°.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_4S$: C, 63.60; H, 3.90; N, 5.71. Found: C, 63.49; H, 3.93; N, 5.72.

The compound did not depress the melting point of 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzamide obtained from the addition of hydrogen chloride to 2-benzenesulfonyl-*p*-quinonedibenzimide.

2-Benzenesulfonyl-*p*-phenylenedibenzamide: Method A.—To a solution of 3.0 g. of *p*-quinonedibenzimide in 30 ml. of glacial acetic acid was added 1.9 g. of the sodium salt of benzenesulfinic acid and the mixture was shaken for 7 minutes and then heated to boiling. The hot solution was filtered and cooled. A product deposited which after one recrystallization from ethanol weighed 4.2 g. (95%). Three recrystallizations gave pure white crystals, m.p. 193–194°.

Anal. Calcd. for $C_{26}H_{20}N_2O_4S$: C, 68.40; H, 4.42. Found: C, 68.56; H, 4.42.

Method B.—To a solution of 9.6 g. of *p*-quinonedibenzimide in 100 ml. of thiophene-free benzene was added 4.8 g. of benzenesulfinic acid (prepared from the sodium salt and sulfuric acid). An exothermic reaction occurred and the product separated as a white mass. The slurry was cooled and filtered. The yield of adduct was 14.0 (100%). One recrystallization from ethanol gave white needles, m.p. 194°.

2-Benzenesulfonyl-3-chloro-*p*-phenylenedibenzamide and 2-Benzenesulfonyl-6-chloro-*p*-phenylenedibenzamide.—To a suspension of 3.00 g. of 2-benzenesulfonyl-*p*-phenylenedibenzamide in 150 ml. of reagent chloroform was added 3.6 g. of lead tetraacetate. The mixture was stirred under gentle reflux for 1.5 hours. A dark orange color developed. Five drops of ethylene glycol was added and stirring continued for 10 minutes more. The solution was filtered to remove inorganic salt and a stream of hydrogen chloride passed into the clear solution for 10 minutes. A small amount of inorganic precipitate was removed by filtration and the filtrate was taken to dryness by distillation under vacuum. A pale yellow residue resulted which was triturated with 10 ml. of ethanol and separated by filtration to give 1.5 g. (46.4%) of white product.

The ethanol-soluble material proved to be an oil. This was dissolved in benzene and placed on a column of alumina. Elution was effected with a benzene–ether mixture of increasing ratios. A total of 1.3 g. of product was thus obtained in 5 fractions. All the fractions after recrystallization from ethanol were found to melt at 190–193°. They did not depress the melting point of an authentic sample of 2-benzenesulfonyl-*p*-phenylenedibenzamide.

The ethanol-insoluble material which melted over a wide range, 225–270°, was obviously a mixture. When heated with absolute benzene a small portion remained undissolved. A constant m.p. 276° for this insoluble product was reached after repeated recrystallization from ethanol.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_4S$: C, 63.60; H, 3.90. Found: C, 63.43; H, 3.92.

From the benzene-soluble portion a product was precipitated by the addition of petroleum ether (b.p. 80–110°) and cooling. The crystals that separated were recrystallized from ethanol, m.p. 240–241.5°.

Anal. Calcd. for $C_{26}H_{19}N_2O_4S$: C, 63.60; H, 3.90; N, 5.71. Found: C, 63.89; H, 4.03; N, 5.67.

N-Benzoyl-2,5-dichloro-4-nitroaniline.—A mixture of 6.0 g. of 2,5-dichloro-4-nitroaniline,[10] 100 ml. of triethylamine and 6.0 g. of benzoyl chloride was heated under reflux for a period of 15 hours. At the end of this period the solution was cooled and poured into cracked ice and hydrochloric acid. The precipitated product was filtered, washed with water, dilute aqueous sodium bicarbonate and again with water. After drying and recrystallization from ethanol it weighed 8.9 g. (96%). Two recrystallizations gave very pale tan needles, m.p. 150°.

Anal. Calcd. for $C_{13}H_8Cl_2N_2O_3$: C, 50.18; H, 2.59; N, 9.00. Found: C, 49.97; H, 2.41; N, 8.85.

2-Chloro-5-phenylmercapto-4-nitroaniline.—To a solution of 3.9 g. of N-benzoyl-2,5-dichloro-4-nitroaniline in 150 ml. of dioxane was added 6 ml. of thiophenol and a solution of 10 g. of sodium hydroxide in 60 ml. of water. The mixture was heated gently under reflux for 20 hours, then cooled and poured into cold water. A yellow product weighing 7.2 g. precipitated. This was separated by filtration and recrystallized from ethanol to give yellow plates, m.p. 171°. The yield of the pure compound was 4.1 g. (75.7%). A benzoyl group had been lost, as shown by the analysis and nfrared spectrum.

Anal. Calcd. for $C_{19}H_{13}ClN_2O_3S$: C, 59.34; H, 3.40; N, 7.28. *Anal.* Calcd. for $C_{12}H_9ClN_2O_2S$: C, 51.34; H, 3.20; N, 9.98. Found: C, 51.16; H, 2.85; N, 10.11.

The infrared spectrum of this compound shows the presence of a primary aromatic amine with bands at 3465 and 3330 cm.$^{-1}$, and aromatic nitro at 1550 and 1350 cm.$^{-1}$. No bands corresponding to carbonyl groups were present.

2-Chloro-5-phenylmercapto-*p*-phenylenediamine.—To a hot solution of 3.2 g. of 2-chloro-5-phenylmercapto-4-nitroaniline in 250 ml. of ethanol was added water in drops till a slight precipitate appeared. This precipitate was redissolved by addition of a minimum amount of ethanol. To this solution heated under reflux was added slowly and at intervals solid sodium hydrosulfite until the yellow color disappeared. The mixture was heated under reflux for 15 minutes more, then most of the ethanol was removed by distillation and the aqueous solution cooled. The pale tan crystals which precipitated weighed 1.9 g. (66.5%). Two recrystallizations from ethanol, with addition of water to turbidity, gave pale tan plates, m.p. 102°.

Anal. Calcd. for $C_{12}H_{11}ClN_2S$: C, 57.48; H, 4.42. Found: C, 57.54; H, 4.53.

2-Chloro-5-phenylmercapto-*p*-phenylenedibenzamide.—To a solution of 1.5 g. of 2-chloro-5-phenylmercapto-*p*-phenylenediamine in 50 ml. of reagent pyridine was added 1.7 ml. of benzoyl chloride. The mixture was heated under reflux for 7 hours after which it was poured into cracked ice and water. The precipitated material was separated by filtration and the gummy residue thus obtained taken up in boiling ethanol and cooled in the ice-box. White crystals separated which weighed 1.0 g. (55%). Recrystallization from ethanol gave white needles, m.p. 202.5°.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_2S$: C, 68.03; H, 4.17. Found: C, 67.96; H, 4.16.

5-Benzenesulfonyl-2-chloro-*p*-phenylenedibenzamide.—A solution of 0.25 g. of 2-chloro-5-phenylmercapto-*p*-phenylenedibenzamide and 1.0 ml. of 30% hydrogen peroxide in 20 ml. of glacial acetic acid was heated under reflux for a period of 2 hours. At the end of this period the solution was poured into cold water yielding 0.2 g. (77%) of a white precipitate. It was recrystallized from ethanol to give white needles, m.p. 219.5–220°.

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(10) J. R. H. Whiston, *J. Soc. Chem. Ind.*, **43**, 370T (1924).

Anal. Calcd. for $C_{26}H_{19}ClN_2O_4S$: C, 63.60; H, 3.90; N, 5.71. Found: C, 63.52; H, 4.01; N, 5.92.

The infrared spectrum of this compound is very similar but not identical to the spectrum of either of the isomers obtained by adding hydrogen chloride to 2-benzenesulfonyl-*p*-quinonedibenzimide.

Hydrolysis of 2-Benzenesulfonyl-6-chloro-*p*-phenylenedibenzamide; 2-Benzenesulfonyl-6-chloro-4-N-benzoyl-*p*-phenylenediamine.—A solution of 0.6 g. of 2-benzenesulfonyl-6-chloro-*p*-phenylenedibenzamide in 30 ml. of concentrated sulfuric acid was permitted to stand at room temperature for 24 hours, then poured into cracked ice and water and stirred well. The precipitated material was separated by filtration, washed with water, and recrystallized from ethanol, with addition of water to turbidity, to give 0.23 g. (50%) of crystalline product, m.p. 196°. Analysis indicated that only one benzoyl group had been hydrolyzed.

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2S$: C, 60.97; H, 3.92; N, 9.91. *Anal.* Calcd. for $C_{19}H_{15}ClN_2O_3S$: C, 58.98; H, 3.90; N, 7.24. Found: C, 58.59; H, 3.79; N, 6.93.

The action of concentrated sulfuric acid for 4 days at room temperature resulted in the same product.

2-Benzenesulfonyl-6-chloro-*p*-phenylenediamine.—A solution of 0.9 g. of 2-benzenesulfonyl-6-chloro-*p*-phenylenedibenzamide in 45 ml. of concentrated sulfuric acid was heated on the steam-bath for 40 hours. At the end of this period the mixture was poured into cracked ice and water and the resulting solution made strongly alkaline with 10% aqueous sodium hydroxide. The colloidal suspension was extracted with ether. The material in the ether extracts was dissolved in hot ethanol and water was added to turbidity. On cooling, 0.39 g. (77%) of beautiful yellow crystals deposited. They were recrystallized from ethanol, with addition of water to turbidity, m.p. 137°.

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2S$: C, 50.97; H, 3.92; N, 9.91; Cl, 12.54. Found: C, 50.33; H, 3.64; N, 10.21; Cl, 12.54.

The infrared spectrum of this compound shows absence of carbonyl function. Presence of an aromatic primary amine is indicated by bands at 3440 and 3360 cm.$^{-1}$.

Benzenesulfonation of 2-Benzenesulfonyl-6-chloro-*p*-phenylenediamine; 2-Benzenesulfonyl-4-N-benzenesulfonyl-6-chloro-*p*-phenylenediamine.—To a solution of 0.25 g. of 2-benzenesulfonyl-6-chloro-*p*-phenylenediamine in 15 ml. of reagent pyridine was added 1 ml. of benzenesulfonyl chloride. The mixture was heated under reflux for 18 hours and then cooled. It was poured into cracked ice and water and then acidified with concentrated hydrochloric acid. The precipitated product was separated by filtration and recrystallized from ethanol to give 0.3 g. (81%) of white crystals, m.p. 188°.

Anal. Calcd. for $C_{18}H_{15}ClN_2O_4S_2$: C, 51.12; H, 3.57. Found: C, 51.07; H, 3.67.

The infrared spectrum of this compound shows the presence of a primary aromatic amine (–NH stretching) at 3360 and 3260 cm.$^{-1}$ and is not identical with any of those of the known 2,3-, 2,5-, and 2,6-disulfonamides.

The experiment was repeated using triethylamine as solvent but the same product resulted. On boiling the diamine with benzenesulfonyl chloride it decomposed and no crystalline product could be isolated.

2-Benzenesulfonyl-6-chloro-*p*-phenylenediamine.—A mixture of 0.8 g. of 2-benzenesulfonyl-6-chloro-*p*-phenylenedibenzenesulfonamide and 40 ml. of concentrated sulfuric acid was permitted to stand for 24 hours and then poured into cracked ice and water. The cold solution was made alkaline with 8% aqueous sodium hydroxide and the colloidal solution thus obtained extracted with two 100-ml. lots of ether. The combined ether extracts were evaporated to dryness and the residue taken up in boiling ethanol. The hot solution was made turbid by addition of water and cooled. The precipitate was recrystallized twice from ethanol, with addition of water to turbidity, to give 0.18 g. (45%) of yellow crystals, m.p. 137°.

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2S$: C, 50.97; H, 3.92; N, 9.91. Found: C, 51.05; H, 3.88; N, 9.80.

The compound did not depress the melting point of the hydrolysis product from 2-benzenesulfonyl-6-chloro-1-*p*-phenylenedibenzamide. The infrared spectra of the two compounds are identical.

2-Benzenesulfonyl-5-chloro-*p*-phenylenediamine.—A mixture of 1 g. of 2-benzenesulfonyl-5-chloro-*p*-phenylenedibenzenesulfonamide in 40 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 24 hours and then poured into cracked ice and water. The clear yellow solution thus obtained was neutralized with 10% aqueous sodium hydroxide and extracted with ether. The material from the ether was taken up in boiling ethanol, filtered and cooled to give 0.3 g. (60%) of yellow crystals, m.p. 109°.

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2S$: C, 50.97; H, 3.92; N, 9.91. Found: C, 50.70; H, 3.87; N, 9.80.

The infrared spectrum of this compound is very similar to, but not identical with, that of 2-benzenesulfonyl-6-chloro-*p*-phenylenediamine.

2-Benzenesulfonyl-3-chloro-*p*-phenylenediamine.—A mixture of 0.35 g. of 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzamide and 15 ml. of concentrated sulfuric acid was heated on the water-bath for 24 hours, cooled and poured into cracked ice and water. The solution was made strongly alkaline with 10% aqueous sodium hydroxide and extracted with three 50-ml. portions of ether. The product from the ether was dissolved in 20 ml. of ethanol, filtered, and to the hot filtrate, water was added to the cloud point and cooled. Yellow crystals gradually separated, weighing 0.1 g. (40%). They were purified by recrystallization from ethanol, with addition of water to turbidity, to give yellow plates, m.p. 118.5–119°.

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2S$: C, 50.97; H, 3.92; N, 9.91. Found: C, 50.94; H, 3.66; N, 9.81.

The infrared spectrum of this compound is very similar to those of the 2-benzenesulfonyl-6-chloro and 2-benzenesulfonyl-5-chloro isomers, but not identical with either of them.

N-Benzoyl-3,5-dichloroaniline.—To a solution of 7.0 g. of 3,5-dichloroaniline[11] in 50 ml. of dry pyridine was added 7.0 ml. of benzoyl chloride in 15 ml. of pyridine and the mixture heated under reflux for 30 minutes. At the end of this period the reaction mixture was cooled and 150 ml. of a 5% aqueous sodium bicarbonate added. The oily mass which separated solidified on standing in an ice-box. It was filtered and recrystallized from ethanol to give 9.0 g. (78.5%) of product. One more recrystallization gave the pure compound, m.p. 149°.

Anal. Calcd. for $C_{13}H_9Cl_2NO$: C, 58.67; H, 3.41; N, 5.26. Found: C, 58.74; H, 3.11; N, 5.34.

URBANA, ILLINOIS

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[11] O. N. Witt, *Ber.*, **8**, 145 (1875).