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Quinone Diimides. XV. Diphenoquinonediimides

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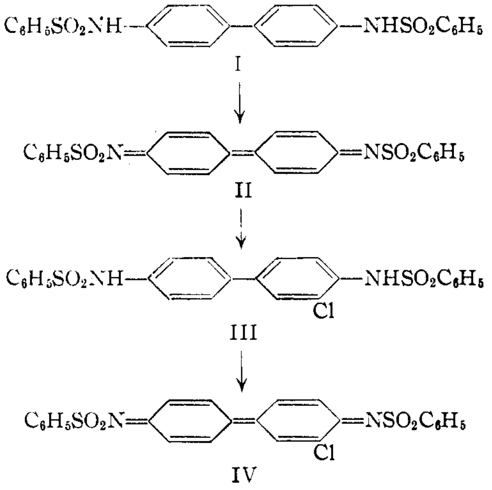
The dibenzenesulfonamide of benzidine is oxidized with lead tetraacetate in acetic acid to diphenoquinonedibenzenesulfonimide. Action of dry hydrogen chloride on this substance gives a single adduct, the dibenzenesulfonamide of 3-chlorobenzidine. This is oxidized in a similar way to 3-chlorodiphenoquinonedibenzenesulfonimide. Action of hydrogen chloride on this substance leads to a mixture of two adducts: the dibenzenesulfonamide of 3,3′-dichlorobenzidine and an isomeric diamide, assigned the 3,5-dichloro structure. The dibenzenesulfonamide of 3,3′-dichlorobenzidine is oxidized to the corresponding diimide which adds hydrogen chloride to form a single product, the dibenzenesulfonamide of 3,3′,5-trichlorobenzidine. Oxidation of this last product proceeds with difficulty with formation of 3,3′,5-trichlorodiphenoquinonedibenzenesulfonimide which adds dry hydrogen chloride to give the dibenzenesulfonamide of 3,3′,5,5′-tetrachlorobenzidine. The proof of structure of the dibenzenesulfonyl derivatives of 3,3′-dichlorobenzidine and of 3,3′,5,5′-tetrachlorobenzidine by unequivocal methods is described. The addition of hydrogen chloride to the diimides appears to proceed exclusively by a 1,8-process, with the formation of chlorinated benzidinedibenzenesulfonamides in which the chlorines are ortho to sulfonamido groups in the products. The diphenoquinonedibenzenesulfonamides are dark red or black crystalline solids which give deep wine-red solutions. They are easily reduced to the corresponding diamides. They do not add thiophenol or hydrogen bromide but are reduced by these reagents. Aqueous ethanolic alkali destroys them rapidly.

Previous papers in this series[1] have described the preparation of stable derivatives of quinone diimines by oxidation of the N,N′-disulfonyl and diacyl derivatives of appropriate diaminobenzenes and naphthalenes. A study of the synthesis and of certain reactions of the diphenoquinonedibenzenesulfonimides has now been completed.

Diphenoquinone[2] and a number of substituted diphenoquinones[3] have been prepared but the chemistry of this group of substances has been largely neglected. Fieser[4] measured the oxidation potential of diphenoquinone. Liebermann and Cybulski[5] added hydrogen chloride to 3,3′,5,5′-tetramethoxydiphenoquinone and obtained a monochlorotetramethoxydiphenohydroquinone. Auwers and Markovitz[6] added the same reagent to 3,3′,-5,5′-tetramethyldiphenoquinone and obtained a monochlorotetramethyl diphenohydroquinone. No addition reactions of diphenoquinone itself have been reported. Liebermann and Flatau[7] discovered that an anilino group replaced one of the methoxyls when aniline was allowed to react with 3,3′,5,5′-tetramethoxydiphenoquinone.

The few unstable derivatives[8] of diphenoquinonediimine have not been investigated other than their reduction to the corresponding benzidines. Willstätter and Kalb[9] were unable to isolate diphenoquinonediimine itself because of its instability.

When the dibenzenesulfonamide of benzidine (I) was stirred at room temperature with a solution of lead tetraacetate in glacial acetic acid a deep orange-red solution was formed, from which shimmering black platelets of the diimide (II) separated in excellent yield. The reaction was more rapid when warmed but if the temperature went above about 70°, the product decomposed as fast as it was formed. It could be recrystallized only with difficulty in small amounts and with considerable loss. The product is only slightly soluble in organic solvents, forming wine-red solutions, and is destroyed by prolonged boiling with any of them. Cold aqueous ethanolic alkali decomposed it rapidly.



The infrared spectrum of II revealed the absence of bands in the region characteristic of the –NH– group. Stannous chloride in acetic acid reconverted II to the diamide (I). Dry hydrogen chloride in chloroform decolorized II almost instantly and a white, crystalline monochloro compound (III) was produced in high yield. Hydrogen bromide or thiophenol did not add to II, but caused its reduction to I.

Although addition of hydrogen chloride may occur in more than one way, only one product was isolated. Fractional crystallization and chromatography of the crude product failed to reveal the presence of any by-product or isomer.

The monochlorobenzidinedibenzenesulfonamide (III) was oxidized to the corresponding diimide (IV) by action of lead tetraacetate in glacial acetic acid. This substance was obtained as red-black platelets on crystallization from ethylene dichloride, but its solutions, like those of II, were a deep wine-red in color. The diimide (IV) was

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(1) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950); R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951).

(2) R. Willstätter and L. Kalb, *Ber.*, **38**, 1235 (1905).

(3) (a) G. Magatti, *ibid.*, **13**, 227 (1880); (b) A. W. Hofmann, *ibid.*, **11**, 335 (1878); (c) K. v. Auwers and G. Wittig, *ibid.*, **57**, 1271 (1924); (d) A. A. Levine, THIS JOURNAL, **48**, 2720 (1926).

(4) L. F. Fieser, *ibid.*, **52**, 4915 (1930).

(5) C. Liebermann and G. Cybulski, *Ber.*, **31**, 616 (1898).

(6) K. v. Auwers and Th. v. Markovitz, *ibid.*, **38**, 232 (1905).

(7) C. Liebermann and J. Flatau, *ibid.*, **30**, 235 (1897).

(8) W. Schlenk, *Ann.*, **363**, 317 (1908); F. Kehrman, G. Roy and M. Ramm, *Helv. Chim. Acta*, **5**, 156 (1922).

(9) R. Willstätter and L. Kalb, *Ber.*, **38**, 1235 (1905); **39**, 3477 (1906).

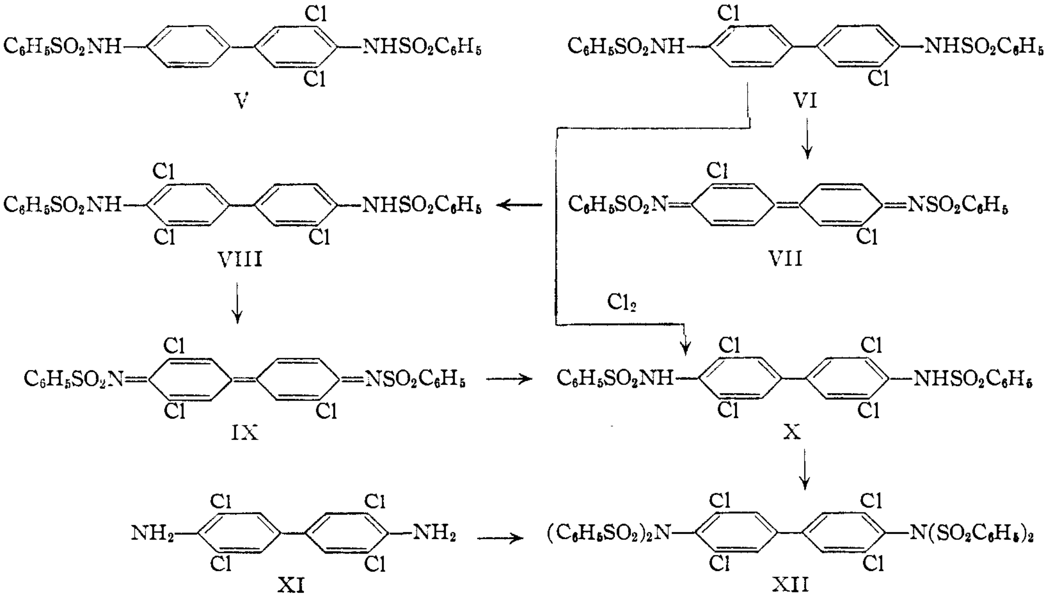
as sensitive to prolonged boiling with most solvents as the unchlorinated diimide (II). Stannous chloride or zinc dust in acetic acid reduced it to the diamide (III). The infrared spectrum of IV showed the absence of bands in the region characteristic of the -NH- group.

Addition of dry hydrogen chloride in chloroform to IV led to a mixture of two dichlorobenzidinedibenzenesulfonamides. By fractional crystallization of the sodium salts, the mixture was separated into a lower-melting isomer (V) (m.p. 177°) and a higher-melting isomer (VI) (m.p. 242°). No other isomers appeared to be present.

The structure of the lower-melting dichlorodiamide (V) was not rigorously proved. It was observed, however, that this product was resistant to oxidation with lead tetraacetate in glacial acetic acid, a property characteristic of those diamides with two chlorines substituted on each side of an amido group. The formation of *o*-chlorobenzidinesulfonamides in all other examples of hydrogen chloride addition to diimides of this series is also presumptive evidence for the 3,5-dichloro structure of V.

The higher-melting dichloro diamide (VI) was shown to be the dibenzenesulfonamide of 3,3'-dichlorobenzidine by direct comparison with an authentic sample prepared by the action of benzenesulfonyl chloride on 3,3'-dichlorobenzidine.

With the structure of VI established it follows that the monochlorobenzidinedibenzenesulfonamide (III) was a derivative of 3-chlorobenzidine and that IV was the corresponding diimide.



Oxidation of VI with lead tetraacetate in glacial acetic acid, either hot or at room temperature, produced 3,3'-dichlorodiphenoquinonedibenzenesulfonimide (VII) as dark red platelets with a metallic luster. The infrared spectrum of VII showed the expected absence of bands in the region characteristic of the -NH- group. This substance was considerably more stable than the parent diimide (II) or the monochloro diimide (IV). It could be boiled for some time with glacial acetic acid, or glacial acetic acid containing sulfuric acid or boron fluoride, without change. Like the other diimides, however, it was rapidly destroyed by aqueous ethanolic alkali. Treatment of VII with stannous chloride in acetic acid regenerated the diamide (VI), as did attempts to add hydrogen bromide or thiophenol. Addition of dry hydrogen chloride to VII produced a single trichlorobenzidinedibenzenesulfonamide (VIII) in high yield.

In contrast to the less highly substituted amides (I, III and VI) the trichlorodiamide (VIII) was resistant to the oxidizing action of lead tetraacetate in glacial acetic acid. Under somewhat vigorous but carefully controlled conditions it was found possible to convert VIII to the trichlorodiimide (IX), though in very low yield. This diimide, like the parent compound II, separated from its deep red solution in ethylene dichloride as black platelets with a metallic luster. Its infrared spectrum showed the absence of the -NH- group.

Dry hydrogen chloride in chloroform converted IX to 3,3',5,5'-tetrachlorobenzidinedibenzenesulfonamide (X) which was found to be identical with an authentic sample made by an unequivocal route.

With the structure of X established it became evident that VIII was 3,3',5-trichlorobenzidinedibenzenesulfonamide and that IX was the corresponding diimide.

The synthesis of 3,3',5,5'-tetrachlorobenzidinedibenzenesulfonamide by another method with the object of establishing its structure unequivocally was successful only after several routes had been explored. 3,3',5,5'-Tetrachlorobenzidine (XI), the structure of which is known,[10] was unaffected by treatment with benzenesulfonyl chloride in boiling pyridine, and was even recovered unchanged when it was boiled with benzenesulfonyl chloride alone for a short time. Under the more drastic conditions of prolonged boiling with a large excess of benzenesulfonyl chloride the tetrabenzenesulfonyl derivative (XII) resulted.

(10) F. L. W. van Roosmalen, *Rec. trav. chim.*, **53**, 359 (1934).

The formation of XII from XI is in line with the observation[11] that tetra-*o*-substituted benzidines tend to form tetraacetyl rather than diacetyl derivatives when they are treated with excess of acetic anhydride. Formation of N,N-dibenzenesulfonyl derivatives of certain aromatic amines by drastic treatment with benzenesulfonyl chloride has also been reported by Adams and Englund.[12]

Chlorination of 3,3′-dichlorobenzidinedibenzenesulfonamide (VI) in ethylene dichloride at 70° led to recovery of essentially all the starting material unchanged. This was a surprising result for 3,3′-dichlorobenzidinedi-*p*-toluenesulfonamide has been prepared in excellent yield by chlorination of the di-*p*-toluenesulfonamide of benzidine in tetrachloroethane at 50°.[13] Apparently VI is resistant to further chlorination beyond the dichloro stage under these conditions. Moreover, long continued action of chlorine on VI in boiling *o*-dichlorobenzene failed to produce more than a trace of the desired tetrachloro compound.

The dichloro compound (VI) in dimethylformamide as solvent was treated with chlorine in the presence of ferric chloride.[14] The product, isolated conveniently and in good yield, was 3,3′,5,5′-tetrachlorobenzidinedibenzenesulfonamide, free from higher or lower chlorination products. This material was identical with X produced by addition of hydrogen chloride to the quinone diimide (IX).

That the chlorine atoms in this compound occupied the 3,3′,5,5′-positions was established by converting the substance to its tetrabenzenesulfonyl derivative which was found to be identical with the tetrabenzenesulfonamide (XII) prepared from 3,3′,5,5′-tetrachlorobenzidine (XI).

The tetrachloroamide (X) was even more resistant to oxidation than the trichloroamide (VIII). Apparently compounds of this type containing a chlorine atom on each side of one or both of the sulfonamido groups are much more difficult to oxidize than compounds which do not have this structural feature.

The addition of hydrogen chloride to quinone diimides of the benzene and naphthalene series, like the addition of hydrogen chloride to quinones[15] has been formulated[16] as occurring 1,4- by a conjugated process. On the assumption that addition to diphenoquinone diimides occurs by a similar mechanism, the observed products must have been formed by a 1,8-addition of hydrogen chloride. Examples of 1,8-addition are rare.[17]

The exclusive formation of *o*-chlorobenzidinedibenzenesulfonamides by these addition reactions will be discussed in a subsequent paper.

Acknowledgment.—The authors are indebted to Miss Elizabeth Petersen for the determination and interpretation of the infrared spectra and Miss Emily Davis, Mrs. Katherine Pih and Mrs. Jean Fortney for the microanalyses.

Experimental

Benzidinedibenzenesulfonamide (I).—A mixture of 50 g. of benzidine with 300 ml. of pyridine and 100 g. of benzenesulfonyl chloride was heated at 100° for 10 hours. Upon addition with stirring of 150 ml. of water, a gray solid separated. The solution was filtered and the solid boiled with 300 ml. of 3 *N* aqueous hydrochloric acid. The product, which weighed 120 g. (95%) was crystallized from 600 ml. of boiling methyl cellosolve (25 g. of Darco). The massive, colorless rods weighed 55 g. By diluting the filtrate with water an additional 43 g. was obtained. Recrystallization from nitromethane and then from glacial acetic acid gave a pure product, m.p. 241–242° (cor.) (lit. m.p. 232° and 234.5°).[18]

Diphenoquinonedibenzenesulfonimide (II).—A stirred suspension of 10 g. of the finely powdered dibenzenesulfonamide of benzidine in 300 ml. of glacial acetic acid was treated with 10 g. of dry lead tetraacetate (previously crystallized from glacial acetic acid) at room temperature, and stirring was continued for 14 hours. Shimmering black platelets of the diimide separated. These were removed and stirred for one hour with 300 ml. of glacial acetic acid and 10 ml. of ethylene glycol. They were then stirred with 300 ml. of water for one hour and finally with 300 ml. of acetone for an hour. The dried crystalline product weighed 8.5 g. (85%) and decomposed gradually starting at 200°.

The product could be recrystallized by suspending 1 g. in 50 ml. of boiling chloroform. After addition of 50 ml. of nitromethane, the boiling mixture was filtered by suction at once. The filtrate after cooling and standing several hours deposited 0.4 g. of blue-black platelets of the pure diimide. The substance could also be recrystallized from boiling ethylene dichloride, although prolonged boiling with this or other solvents caused decomposition.

Anal. Calcd. for $C_{24}H_{18}N_2O_4S_2$: C, 62.32; H, 3.92; N, 6.06. Found: C, 62.40; H, 4.18; N, 6.16.

The infrared spectrum of II showed no band in the region characteristic of the -NH- group. There was a strong band at 1495 cm.$^{-1}$ and possibly a weak one at 1542 cm.$^{-1}$, one of which may have been due to the =C=N— grouping, but it was not possible to make a definite assignment. The band at 1495 cm.$^{-1}$ is about 50 cm.$^{-1}$ lower in frequency than that associated with the =C=N— group in less complex quinone diimides,[1] but in view of the extended conjugation present in II, this is perhaps not unexpected.

Cold aqueous ethanolic alkali decolorized the product rapidly with formation of a pale yellow solution. By acidification a colorless gum precipitated but no crystalline product could be isolated.

Addition of lead tetraacetate to the amide in glacial acetic acid at 95° gave an instantaneous red color which within 40 seconds faded to yellow and no pure product could be isolated. Oxidation at 70° was successful if the lead tetraacetate was added all at once and as soon as the depth of color had reached a maximum, the solution was cooled rapidly. The diimide separated but in only 40% yield.

A mixture of 0.1 g. of diimide with 0.2 g. of stannous chloride dihydrate and 5 ml. of acetic acid, when warmed, lost its color at once and a white solid was formed. This was crystallized from glacial acetic acid. The colorless crystals, m.p. 239–241° (cor.), proved to be the diamide (I), as shown by a mixed melting point determination.

A mixture of 0.2 g. of diimide and a solution of 0.4 g. of thiophenol in 10 ml. of glacial acetic acid was warmed gently. The white solid which separated was crystallized from glacial acetic acid and proved to be the diamide (I), melting point and mixed melting point 239–241°.

An experiment with 2 ml. of 48% hydrobromic acid and 3 ml. of glacial acetic acid gave similar results.

3-Chlorobenzidinedibenzenesulfonamide (III).—Upon bubbling dry hydrogen chloride through a suspension of 7.5

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[11] C. Mills, *J. Chem. Soc.*, **65**, 55 (1894); W. Schlenk, *Ann.*, **363**, 334 (1908).

[12] R. Adams and B. E. Englund, This Journal, **72**, 135 (1950).

[13] R. Schuloff, R. Pollak and E. Riess, *Ber.*, **62**, 1854 (1929).

[14] R. Adams and B. H. Braun, This Journal, **74**, June (1952).

[15] C. F. H. Allen and A. H. Blatt, in Gilman's "Organic Chemistry," Second Edition, John Wiley and Sons, New York, N. Y., 1943, p. 691.

[16] R. Adams and A. S. Nagarkatti, This Journal, **72**, 4601 (1950); R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951); R. Adams and E. F. Elslager, *ibid.*, **74**, 2608 (1952).

[17] C. F. H. Allen and A. H. Blatt, in Gilman's "Organic Chemistry," Second Edition, John Wiley and Sons, New York, N. Y., 1943, p. 694.

[18] O. Hinsberg, *Ann.*, **272**, 231 (1893); R. Willstätter and L. Kalb, *Ber.*, **37**, 3772 (1904).

g. of diphenoquinonedibenzenesulfonimide in 200 ml. of chloroform the color of the solution was discharged rapidly and completely. A minute or two later white needles of the adduct began depositing from the colorless solution. The product, whether crystallized from chloroform, boiling glacial acetic acid, ethyl acetate–cyclohexane, or ethylene dichloride, always gave material melting over a range and with gas evolution indicative of solvent retention. It was found that by drying the crystals obtained from any of these solvents *in vacuo* solvent-free material was obtained which melted with no gas evolution. The yield was 7.6 g. (93%). By crystallization from ethyl acetate, the substance separated solvent-free at once, and when pure had a melting point of 184–185° (cor.).

Anal. Calcd. for $C_{24}H_{19}ClN_2O_4S_2$: C, 57.77; H, 3.84; N, 5.62. Found: C, 57.92; H, 3.56; N, 5.89.

A chromatographic analysis of solvent-free product, using ethyl acetate as solvent and aluminum oxide as adsorbent gave no indication of the presence of any by-product. Fractional crystallization of the crude adduct from ethyl acetate led to the same conclusion.

3-Chlorodiphenoquinonedibenzenesulfonimide (IV).—A mixture of 10 g. of powdered monochlorobenzidinedibenzenesulfonamide and 250 ml. of glacial acetic acid containing 10 g. of dry lead tetraacetate was stirred for 14 hours at room temperature. The oxidation appeared to be done after 4 hours. The product was removed by filtration and freed of lead salts by stirring with 200 ml. of glacial acetic acid containing 5 ml. of ethylene glycol, then with 200 ml. of water and finally with 200 ml. of acetone. The tiny red-black platelets weighed 6.5 g. (65%). They gradually decomposed starting somewhat below 200°.

Purification was effected unsatisfactorily by boiling 2.0 g. with 200 ml. of ethylene dichloride and filtering hot by suction. After several hours the deep wine-red filtrate deposited 0.2 g. of tiny red-black platelets of the pure diimide.

Anal. Calcd. for $C_{24}H_{17}ClN_2O_4S_2$: C, 58.00; H, 3.45; N, 5.64. Found: C, 57.97; H, 3.65; N, 5.60.

The diimide was completely decolorized on prolonged boiling with ethylene dichloride or a variety of other common solvents. Colorless, soluble products resulted.

The infrared spectrum of this material showed no band in the region characteristic of the –NH– group. Although there was some indication of a weak band at 1500–1508 cm.$^{-1}$, no definite assignment of a band as due to the =C=N– grouping could be made.

By warming the diimide with zinc dust and acetic acid or with stannous chloride in acetic acid, reduction occurred and the corresponding diamide resulted.

Two Isomeric Dichlorobenzidinedibenzenesulfonamides (V) and (VI).—Upon bubbling dry hydrogen chloride through a stirred suspension of 22 g. of 3-chlorodiphenoquinonedibenzenesulfonimide in 400 ml. of chloroform, the color was completely discharged within a few minutes and the solution began depositing short white needles. These were removed and boiled with 500 ml. of glacial acetic acid for several hours. The product which weighed 19 g. was a mixture of adducts and melted over the range 167–203°. Addition of water to the filtrate gave a white solid which was crystallized from glacial acetic acid and weighed 1.9 g. Total yield was 20.9 g. (91%).

A solution of 10 g. of this mixture of amides in 300 ml. of 5% aqueous sodium hydroxide was cooled to 15°. After several hours colorless needles of a sodium salt separated. These weighed 3.2 g. and were recrystallized from 300 ml. of hot acetic acid. The free amide, weighing 2.6 g., was crystallized six times from acetic acid giving small white prisms, m.p. 241–243° (cor.). Formula VI was assigned this isomer.

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_4S_2$: C, 54.04; H, 3.40; N, 5.25. Found: C, 54.29; H, 3.53; N, 5.42.

The filtrate from which needles of the sodium salt had separated was chilled to 10°. Within an hour a mixture, weighing 1.9 g., of the same white needles obtained before and some very long, thin hairlike white needles of another sodium salt had separated. These were removed, and the filtrate was again set aside to cool at 10°. After several hours a heavy crop of the long hairlike crystals had separated. These weighed 2.7 g. Another 1.9 g. could be obtained by further concentration. Upon crystallization from hot acetic acid, the free amide was obtained as small white crystals containing solvent. Recrystallization from ethanol gave 2 g. of solvent-free material. After three crystallizations from acetic acid and once more from ethanol they were pure, m.p. 175–177° (cor.). This product was assigned structure V.

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_4S_2$: C, 54.04; H, 3.40; N, 5.25. Found: C, 53.90; H, 3.52; N, 5.40.

3,3′-Dichlorobenzidinedibenzenesulfonamide.—A mixture of 10 g. of 3,3′-dichlorobenzidine[19] and a solution of 18 g. of benzenesulfonyl chloride in 150 ml. of pyridine was heated for 12 hours at 100°. The gray solid obtained by pouring the solution with stirring into 500 ml. of water was separated by filtration and dissolved in a hot mixture of 150 ml. of water and 100 ml. of ethanol containing 3.5 g. of sodium hydroxide. After addition of 4 g. of Darco the mixture was filtered hot. The cooled filtrate deposited white needles of the sodium salt of the amide. They were recrystallized from 2 l. of boiling glacial acetic acid. White prisms of the free sulfonamide weighing 16 g. resulted. After four crystallizations from glacial acetic acid, the product was pure, m.p. 243–245° (cor.).

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_4S_2$: C, 54.04; H, 3.40. Found: C, 54.00; H, 3.35.

The melting point of a mixture of this product and the higher-melting dichlorobenzidinedibenzenesulfonamide (VI) obtained by addition of hydrogen chloride to the 3-chlorodiphenoquinonedibenzenesulfonimide showed no depression.

Oxidation of V and VI: 3,3′-Dichlorodiphenoquinonedibenzenesulfonimide (VII).—A mixture of 4 g. of the powdered dibenzenesulfonamide of 3,3′-dichlorobenzidine and a warm (65°) solution of 4 g. of dry lead tetraacetate in 200 ml. of glacial acetic acid was stirred. The solution rapidly turned a deep wine-red and soon the diimide began crystallizing out as small, shimmering maroon-red platelets. After two hours the material was separated by filtration and freed of lead salts as usual by stirring with acetic acid containing ethylene glycol, then water, and finally acetone. The crystalline diimide weighed 3.9 g. (97%). It was purified by recrystallization from ethylene dichloride. The product could also be obtained by carrying out the oxidation at room temperature for 12 hours.

Anal. Calcd. for $C_{24}H_{16}Cl_2N_2O_4S_2$: C, 54.24; H, 3.04; N, 5.27. Found: C, 54.22; H, 3.17; N, 5.26.

This diimide was considerably more stable to hot glacial acetic acid in the presence of lead acetate than some of the others. It could be prepared on a small scale by boiling the powdered amide with a glacial acetic acid solution of lead tetraacetate. The diimide could be boiled with glacial acetic acid alone, or even acetic acid containing boron fluoride or concentrated sulfuric acid, without change. However, cold aqueous ethanolic alkali destroyed it rapidly with formation of a pale yellow solution. When this solution was acidified a colorless gum precipitated, but attempts to isolate a crystalline solid from it were fruitless.

The infrared spectrum of this product showed no bands in the region characteristic of the –NH– group. It was not possible to make a definite assignment of two strong bands at 1516 and 1535 cm.$^{-1}$. The bands associated with the =C=N– group in simpler quinone diimides[1] usually occur at a frequency about 50 cm.$^{-1}$ higher than this.

Efforts to add hydrogen bromide or thiophenol in acetic acid to this product failed. Reduction to the diamide occurred. Reduction also took place readily by treatment with stannous chloride in glacial acetic acid.

Under conditions that led to oxidation of the higher-melting dichloroamide (VI) to diimide (VII), the lower-melting dichloroamide (V) was unaffected.

3,3′,5-Trichlorobenzidinedibenzenesulfonamide (VIII).—A suspension of 17 g. of 3,3′-dichlorodiphenoquinonedibenzenesulfonimide in 200 ml. of chloroform when treated with hydrogen chloride as described in previous experiments was completely decolorized in a few minutes. Shortly thereafter the colorless solution began depositing white needles which were solvated. By dissolving in the minimum of boiling acetic acid (1 liter) and cooling, 15 g. of white crystals deposited in a few hours. More could be obtained from the mother liquors by dilution with water. It was purified by recrystallization from acetic acid and then twice from ethylene dichloride, m.p. 207–209° (cor.).

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(19) P. Cohn, *Ber.*, **33**, 3552 (1900).

Anal. Calcd. for $C_{24}H_{17}Cl_3N_2O_4S_2$: C, 50.76; H, 3.02; N, 4.93. Found: C, 50.99; H, 2.82; N, 5.22.

3,3',5-Trichlorodiphenoquinonedibenzenesulfonimide (IX).—A mixture of 10 g. of powdered trichloroamide, 200 ml. of redistilled acetic anhydride and 10 g. of dry lead tetraacetate was heated to 110° with shaking. A very deep red solution formed. The source of heat was removed and after a few seconds beautiful gleaming black platelets began to separate. The solid product was removed and freed of lead salts by successive treatments with ethylene glycol in acetic acid, water and acetone, as previously described. It weighed 1.3 g. Recrystallization from 250 ml. of boiling ethylene dichloride gave 0.26 g. of glittering black platelets of the pure diimide (IX).

Anal. Calcd. for $C_{24}H_{15}Cl_3N_2O_4S_2$: C, 50.94; H, 2.67; N, 4.95. Found: C, 51.12; H, 2.72; N, 4.82.

In glacial acetic acid at 65°, the oxidation was slow and the yield of diimide very low (0.07 g. from 10 g.). At room temperature no oxidation occurred.

The infrared spectrum of IX showed the absence of bands in the region characteristic of the –NH– group, but it was not possible to make a definite assignment of a band in the double bond region as due to the =C=N— grouping.

Addition of Hydrogen Chloride to IX: 3,3',5,5'-Tetrachlorobenzidinedibenzenesulfonamide (X).—When the colorless solution obtained by passing dry hydrogen chloride through a suspension of 0.25 g. of the trichlorodiimide in 10 ml. of chloroform was evaporated to a volume of 1–2 ml. and cooled, 0.2 g. of white crystals separated. After four recrystallizations from glacial acetic acid, 0.11 g. of small white prisms of the pure tetrachlorodiamide (X) resulted, m.p. 245–247° (cor.).

Anal. Calcd. for $C_{24}H_{16}Cl_4N_2O_4S_2$: C, 47.85; H, 2.68; N, 4.70. Found: C, 47.98; H, 2.78; N, 4.83.

N,N,N',N'-Tetrabenzenesulfonyl-3,3',5,5'-tetrachlorobenzidine (XII).—A mixture of 6 g. of 3,3',5,5'-tetrachlorobenzidine[20] and 50 ml. of benzenesulfonyl chloride was boiled for 12 hours. Evolution of hydrogen chloride was steady. The cooled solution was poured into 200 ml. of 5% aqueous sodium hydroxide. After 12 hours the gummy solid was removed and boiled with 5% aqueous sodium hydroxide. The insoluble solid was dissolved in 50 ml. of hot ethylene dichloride (Darco) and the solution was filtered. Upon addition of 50 ml. of ether to the filtrate, 3.1 g. of small white needles separated in a few hours. The substance was purified by dissolving in 300 ml. of chloroform and passing through a column (2 × 20 cm.) of alumina (ALCOA F-20). Elution with 400 ml. of chloroform gave, after evaporation of the solvent, a colorless crystalline solid. This was dissolved in 100 ml. of hot chloroform and 100 ml. of hot cyclohexane was added. Brilliant white needles (2.2 g.) of the tetrabenzenesulfonyltetrachlorobenzidine (XII), m.p. 333–335° (cor.), separated.

Anal. Calcd. for $C_{36}H_{24}Cl_4N_2O_8S_4$: C, 48.99; H, 2.74; N, 3.18. Found: C, 48.78; H, 2.77; N, 3.09.

No reaction was obtained when benzenesulfonation was attempted by boiling with benzenesulfonyl chloride in pyridine, or with a small amount of benzenesulfonyl chloride for a short time.

Chlorination of 3,3'-Dichlorobenzidinedibenzenesulfonamide (VI): 3,3',5,5'-Tetrachlorobenzidinedibenzenesulfonamide (X).—Attempts to chlorinate VI in ethylene dichloride at 70° led only to recovery of unchanged starting material. Action of chlorine on a solution of VI in boiling *o*-dichlorobenzene for 18 hours produced a trace of the tetrachloro diamide (X), but most of the starting material was recovered unchanged.

To a solution of 10 g. of (VI) in 200 ml. of dimethylformamide[14] at room temperature 1 g. of ferric chloride was added. A moderate stream of chlorine was passed through the solution for 40 minutes. By this time the temperature had risen to 110° and considerable hydrogen chloride was being evolved. The clear solution was poured into one l. of cold water with stirring and the white solid was dissolved in 300 ml. of boiling 5% aqueous alkali containing 5 g. of sodium hydrosulfite. After addition of 5 g. of Darco the mixture was filtered hot. On allowing the filtrate to cool, white needles of the sodium salt of the amide separated. These were dissolved in 300 ml. of boiling glacial acetic acid. The cooled solution deposited 5.3 g. of small chunky white prisms of the tetrachlorobenzidinedibenzenesulfonamide, m.p. 245–247° (cor.). When mixed with a sample of X, the melting point was not depressed. The infrared spectra of this substance and X were identical.

Under the ordinary procedure for oxidation with lead tetraacetate this compound was unaffected.

N,N,N',N'-Tetrabenzenesulfonyl-3,3',5,5'-tetrachlorobenzidine (XII) by Action of Benzenesulfonyl Chloride on 3,3',5,5'-Tetrachlorobenzidinedibenzenesulfonamide (X).—A mixture of 2 g. of tetrachlorobenzidinedibenzenesulfonamide (X) was boiled with 20 ml. of benzenesulfonyl chloride for 12 hours, and the mixture was poured into 200 ml. of 10% aqueous sodium hydroxide. The mixture was boiled for an hour, and the insoluble material was dissolved in 100 ml. of chloroform. The solution was poured through a column (2 × 10 cm.) of alumina (ALCOA F-20) and the column was eluted with 300 ml. more chloroform. The tan solid obtained was dissolved in chloroform and rechromatographed as before. The white solid resulting was dissolved in 20 ml. of boiling chloroform and 30 ml. of hot cyclohexane was added. A yield of 0.4 g. of small white crystals separated from the hot solution, m.p. 331–334° (cor.). A mixture of this material with the tetrabenzenesulfonyl derivative (XII) prepared from 3,3',5,5'-tetrachlorobenzidine melted at 333–335° (cor.). The infrared spectra of this substance and of XII were also identical.

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[20] W. Schlenk, *Ann.*, **363**, 317 (1908).