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

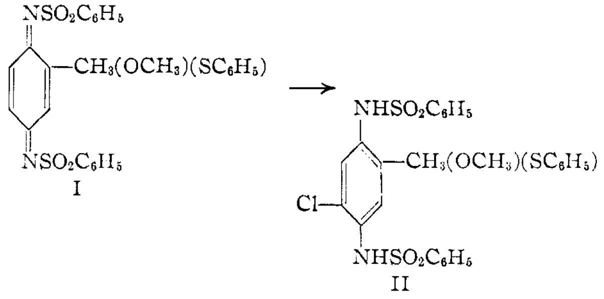
Quinone Imides. XXXIII. Orientation of Adducts from 2-Benzenesulfonyl-*p*-quinonedibenzenesulfonimide

BY ROGER ADAMS, T. E. YOUNG[1] AND R. W. P. SHORT[1]

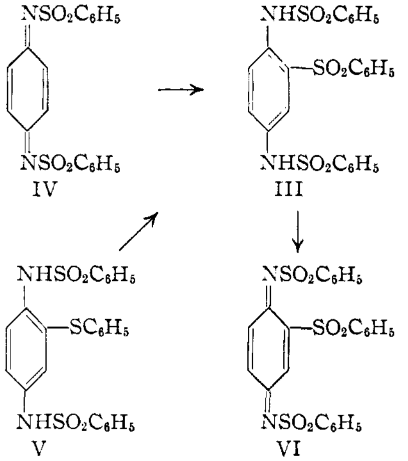
RECEIVED OCTOBER 21, 1953

It has been demonstrated that when hydrogen chloride is added to 2-benzenesulfonyl-p-quinonedibenzenesulfonimide, the only product isolated is 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzenesulfonamide. This structure has been established by oxidizing the product to the corresponding diimide, adding hydrogen chloride and comparing the resulting dichloro-2-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide with the three isomeric dichloro-2-benzenesulfonyl-*p*-phenylenedibenzenesulfonamides of unequivocal structure, produced by adding benzenesulfinic acid to the three structurally-identified isomeric dichloro-*p*-quinonedibenzenesulfonimides. When benzenesulfinic acid is added to 2-chloro-*p*-quinonedibenzenesulfonamide, 2-chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide is the principal product as proved by unequivocal synthesis, and 2-chloro-6-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide, the third isomer, is a by-product.

The addition of hydrogen chloride and certain other reagents to 2-methyl-, 2-methoxy- or 2-phenylmercapto-*p*-quinonedibenzenesulfonimide (I) give almost quantitatively the 5-substituted diamides II.[2-4] When hydrogen chloride is added, the 2,5-dichloro diamide is accompanied by a substantial amount of the 2,3-dichloro isomer and perhaps some of the 2,6-dichloro isomer.[2] The fact that chlorine is an electron-attracting group may account for the formation of isomers.

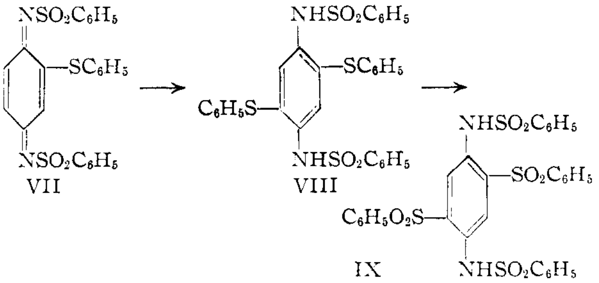


A study of the orientation of adducts when strongly electron-attracting groups are in the 2-position of *p*-quinonedibenzenesulfonimide has been undertaken. The appropriate diamides from which such diimides might be formed are usually difficult to prepare and upon oxidation the diimides are not readily isolated. 2-Benzenesulfonyl-*p*-phenylenedibenzenesulfonamide (III) is an exception, however. It may be synthesized readily either by addition of benzenesulfinic acid to *p*-quinonedibenzenesulfonimide (IV) or by the oxidation of 2-phenylmercapto-*p*-phenylenedibenzenesulfonamide (V) with hydrogen peroxide.



The diamide III was oxidized by lead tetraacetate to 2-benzenesulfonyl-*p*-quinonedibenzenesulfonimide (VI) which was subjected to the addition of several reagents. It added hydrogen chloride in chloroform to give 2-benzenesulfonyl-*x*-chloro-*p*-phenylenedibenzenesulfonamide; it added acetic acid to give 2-benzenesulfonyl-*x*-acetoxy-*p*-phenylenedibenzenesulfonamide; it added benzenesulfinic acid to give in excellent yield 2,*x*-bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide. The probability is that the entering group has the same position in all three adducts.

The addition of benzenesulfinic acid probably does not result in 2,5-orientation. This is strongly indicated by the fact that 2-phenylmercapto-*p*-quinonedibenzenesulfonimide (VII) reacts with thiophenol to give a bis-(phenylmercapto)-*p*-phenylenedibenzenesulfonamide (VIII).[4] By addition of hydrogen chloride to VII it was demonstrated unequivocally that the chlorine entered the 5-position[4] and by analogy the second phenylmercapto group probably entered the same position. The oxidation with peroxide of this bis-(phenylmercapto) diamide derivative (VIII), which has presumably the 2,5-orientation, results in a bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide (IX) different from that obtained by adding benzenesulfinic acid to VI.



Thus it is very probable that in this adduct the entering group is in either the 3- or 6-position.

---

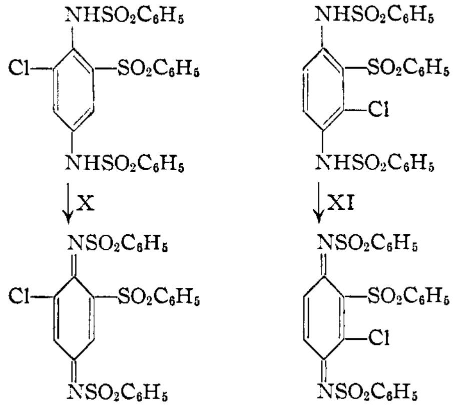
[1] From portions of theses submitted by Thomas E. Young (1952), Standard Oil of California Research Fellow, 1950-1952; and R. W. P. Short (1953) to the Graduate College of the University of Illinois, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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

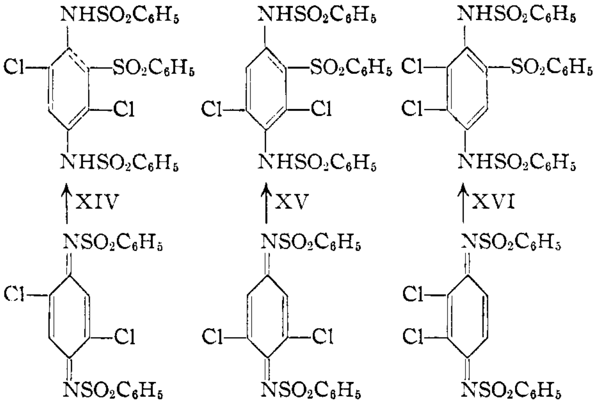
[3] R. Adams and T. E. Young, *ibid.*, **75**, 3235 (1953).

[4] R. Adams, E. F. Elslager and T. E. Young, *ibid.*, **75**, 663 (1953).

The constitution of the hydrogen chloride adduct of VI has been subjected to careful study. It does not have the chlorine in the 5-position since it is different from the substance known to have that structure.[3] The product must be either X or XI. It was oxidized to the corresponding diimide which consequently has either structure XII or XIII. The diimide (XII or XIII) added hydrogen chloride to give a dichloro-2-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide. This last product must have one of the three possible isomeric dichloro structures, XIV, XV and XVI.



XII XIII



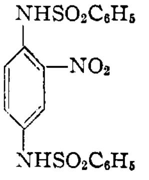
XVII XVIII XIX

A compound of structure XII can by addition of hydrogen chloride give only structures XIV or XVI. A compound of structure XIII, on the other hand, can give only structures XIV or XV. The three compounds XIV, XV and XVI were synthesized by addition of benzenesulfinic acid to the 2,5-(XVII), 2,6- (XVIII) and 2,3-dichloro-*p*-quinonedibenzenesulfonimides (XIX) which left no doubt regarding the structures of the dichlorobenzenesulfonyl diamides. Of the dichlorodiimides the 2,5-(XVII) and 2,3-(XIX) isomers have been described previously[2] but the 2,6-(XVIII) was synthesized for the first time in this investigation. The product XV from the addition of benzenesulfinic acid to the 2,6-dichloro-*p*-quinonedibenzenesulfonimide (XVIII) proved to be identical with the hydrogen chloride adduct of 2-benzenesulfonyl-*x*-chloro-*p*-quinonedibenzenesulfonimide (XII or XIII). Since only structure XIII could on addition of hydrogen chloride provide structure XV, it follows that the monochloro-2-benzenesulfonyl-*p*-quinonedibenzenesulfonimide must have structure XIII and the diamide from which it is formed structure XI, namely, 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzenesulfonamide. It is a fair assumption that the analogous acetoxy and benzenesulfonyl derivatives have similar structures. This orientation coincides with that expected from analogy with the limited number of cases in which the orientation of groups in adducts from *p*-benzoquinone having strongly electron-attracting groups in the 2-position has been established, *e.g.*, the addition of hydrogen cyanide to *p*-benzoquinone to give 2,3-dicyanohydroquinone.

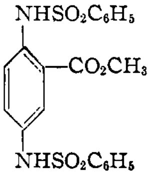
The 2,6-dichloro-*p*-quinonedibenzenesulfonimide (XVIII) proved to be a substance very susceptible to hydrolysis and could not be isolated under the conditions used for isolation of the isomeric dichloro diimides. The product obtained was 2,6-dichloro-*p*-quinone-4-benzenesulfonimide. However, if the oxidation reaction mixture containing the 2,6-dichloro-*p*-quinonedibenzenesulfonimide was treated directly with sodium benzenesulfinate in glacial acetic acid, the adduct was readily obtained in good yield.

When reagents are added to 2-chloro-*p*-quinonedibenzenesulfonimide,[2-4] a mixture of isomers usually results. Upon addition of benzenesulfinic acid the chief product is 2-chloro-5-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide,[3] the structure of which was determined unequivocally. A by-product isomer also was isolated. Since this isomer is not identical with the 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzenesulfonamide (XI) obtained in this investigation it follows that it must be 2-chloro-6-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide (X).

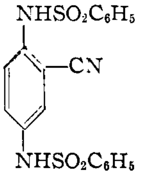
The preparation of several other *p*-quinonedibenzenesulfonimides with electron-attracting groups in the 2-position was studied. There is no difficulty in obtaining 2-nitro-*p*-phenylenedibenzenesulfonamide (XX) by benzenesulfonation of 2-nitro-*p*-phenylenediamine. It appears to oxidize under a variety of conditions, but no diimide could be isolated.



XX

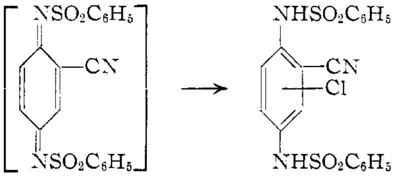


XXI



XXII

The 2-carbomethoxy-*p*-phenylenedibenzenesulfonamide was synthesized by the following series of reactions: 2-carbomethoxyacetanilide, 2-carbomethoxy-4-nitroacetanilide, 2-carbomethoxy-4-nitroaniline, 2-carbomethoxy-*p*-phenylenediamine, 2-carbomethoxy-*p*-phenylenedibenzenesulfonamide (XXI). Oxidation of XXI gave a diimide, but it was never obtained in an absolutely pure state. The 2-cyano-*p*-phenylenedibenzenesulfonamide (XXII) was synthesized by the following series of reactions: 2-cyano-4-nitrochlorobenzene and sodium benzenesulfonamide gave N-benzenesulfonyl-2-cyano-4-nitroaniline; 3-cyano-4-benzenesulfonamidoaniline; 2-cyano-*p*-phenylenedibenzenesulfonamide (XXII). This product was oxidized by lead tetraacetate, but the diimide XXIII could not be isolated. However, treatment of a solution of the diimide with hydrogen chloride resulted in a pure monochloro diamide XXIV, the structure of which was not established. It is assumed to be 2-cyano-3-chloro-*p*-phenylenedibenzenesulfonamide.



XXIII XXIV

Acknowledgment.—The authors wish to thank Mr. J. Nemeth, Mrs. Lucy Chang and Mrs. Esther Fett for the microanalyses and Miss Helen Miklas for the determination of the infrared absorption spectra.

Experimental

All melting points are corrected.

2-Benzenesulfonyl-*p*-phenylenedibenzenesulfonamide. Method A.—To a slurry of 22.0 g. of *p*-quinonedibenzenesulfonimide[5] in 100 ml. of glacial acetic acid was added 14.8 g. of sodium benzenesulfinate and the mixture shaken with occasional cooling (exothermic reaction) for 10 minutes after which it was colorless. The mixture was then heated to boiling giving a pale-yellow tinted solution which was filtered, cooled and scratched for several minutes until crystals appeared, then allowed to stand for 1.5 hours while a slow crystallization occurred. The white crystalline product thus obtained weighed 20.0 g. Dilution of the liquors with water afforded an additional quantity of crude product which was dissolved with difficulty in 150 ml. of 95% ethanol. This solution was filtered, concentrated to 80 ml. then cooled, yielding 4.9 g. of product, bringing the total crude yield to 82.7%.

While small quantities of this compound were best purified from 95% ethanol, large quantities were more conveniently crystallized from a 1:1 glacial acetic acid and 95% ethanol mixture. The pure product forms white crystals, m.p. 154.5–156°.

This product may also be made by refluxing in chloroform equimolar quantities of diimide and benzenesulfinic acid, but the yield of product (63%) is lower.

Method B.—A mixture of 2.1 g. of 2-phenylmercapto-*p*-phenylenedibenzenesulfonamide,[4] 5 ml. of 30% hydrogen peroxide and 20 ml. of glacial acetic acid was gradually heated to boiling under reflux and the resulting solution boiled for 1.25 hours. The pale yellow solution was cooled to yield 1.7 g. (80%) of crude product. Two recrystallizations from glacial acetic acid gave pure product, m.p. 154.5–156°. This material was identical with samples prepared by method A.

Anal. Calcd. for $C_{24}H_{20}N_2O_6S_3$: C, 54.53; H, 3.81; N, 5.30. Found: C, 54.45; H, 3.59; N, 5.25.

2-Benzenesulfonyl-*p*-quinonedibenzenesulfonimide.—A suspension of 8.68 g. of 2-benzenesulfonyl-*p*-phenylenedibenzenesulfonamide and 7.28 g. of dry lead tetraacetate in 50 ml. of glacial acetic acid was stirred at room temperature for 2 hours. The yellow crystalline product which formed was filtered, washed with cold glacial acetic acid, then with absolute ether and dried. It weighed 8.07 g. (93.3%). Recrystallization from dry thiophene-free benzene gave a yellow micro-crystalline powder, m.p. 226–227.5° dec.

Anal. Calcd. for $C_{24}H_{18}N_2O_6S_3$: C, 54.74; H, 3.45; N, 5.32. Found: C, 54.99; H, 3.53; N, 5.20.

The compound is difficultly soluble in benzene (*ca.* 1 g./100 ml. of boiling benzene); it is more easily soluble in anhydrous dioxane from which it slowly crystallizes as a yellow powder. The melting point is found to vary somewhat depending upon the mode of crystallization. The compound is decomposed by hydroxylic solvents including glacial acetic acid.

After filtering off the quinone diimide, the cherry-red acetic acid liquors were allowed to stand for 15 hours. A trace of white needles, m.p. 186.5–187°, deposited which showed no depression of the melting point when mixed with 2-benzenesulfonyl-*x*-acetoxy-*p*-phenylenedibenzenesulfonamide described below.

2-Benzenesulfonyl-*x*-acetoxy-*p*-phenylenedibenzenesulfonamide.—A solution of 1.00 g. of 2-benzenesulfonyl-*p*-quinonedibenzenesulfonimide in 25 ml. of glacial acetic acid and 4 ml. of water was refluxed for 5 hours; at the beginning of the reflux period the solution assumed a cherry-red color, which changed to a reddish-brown as the reaction progressed. The reaction mixture on dilution with 100 ml. of water gave a semi-colloidal suspension. Addition of a few ml. of acetone and rapid stirring coagulated the product which was filtered and dried. The tan crystals obtained weighed 0.72 g. (64%). Recrystallization from glacial acetic acid gave white needles, m.p. 186–187°.

Anal. Calcd. for $C_{26}H_{22}N_2O_8S_3$: C, 53.23; H, 3.78; N, 4.78. Found: C, 53.52; H, 4.03; N, 4.75.

2,*x*-Bis-(benzenesulfonyl)-*p*-phenylenedibenzenesulfonamide.—To a suspension of 1.00 g. of 2-benzenesulfonyl-*p*-quinonedibenzenesulfonimide in 25 ml. of glacial acetic acid was added 0.50 g. of sodium benzenesulfinate and the slurry shaken at room temperature for 10 minutes. A colorless solution was obtained containing a trace of suspended white needles and exhibiting a bluish surface fluorescence. The solution on standing for 3.5 hours deposited 1.01 g. of white crystals. Concentration of the mother liquors to 5 ml. and cooling gave an additional 0.13 g. of product. The total crude yield was 1.14 g. (90%). The combined crudes were boiled with 100 ml. of 95% ethanol and the extract discarded. The ethanol insoluble product was then recrystallized 5 times from glacial acetic acid giving white needles, m.p. 201.5–202.5°.

Anal. Calcd. for $C_{30}H_{24}N_2O_8S_4$: C, 53.87; H, 3.62; N, 4.19. Found: C, 54.06; H, 3.89; N, 3.93.

2-Benzenesulfonyl-3-chloro-*p*-phenylenedibenzenesulfonamide.—Dry hydrogen chloride was bubbled into a suspension of 2.68 g. of 2-benzenesulfonyl-*p*-quinonedibenzenesulfonimide in 100 ml. of dry chloroform for 1.25 hours. The resulting yellow tinted solution was evaporated to dryness *in vacuo* giving an orange-white residue. Trituration of this material with three 10-ml. portions of dry ether removed most of the color and left a white crystalline solid weighing 0.85 g. (30%). Recrystallization from 95% ethanol gave white needles, m.p. 180.5–182°.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_6S_3$: C, 51.19; H, 3.40; N, 4.98. Found: C, 51.09; H, 3.67; N, 5.15.

The infrared spectrum of this compound was quite different from the spectra of the 2,5-isomer and the 2,6-isomer obtained as a by-product with the 2,5-derivative.[3]

2-Benzenesulfonyl-3-chloro-*p*-quinonedibenzenesulfonimide.—A suspension of 1.00 g. of 2-benzenesulfonyl-3-chloro-*p*-phenylenedibenzenesulfonamide and 0.82 g. of lead tetraacetate in 14 ml. of glacial acetic acid was stirred at room temperature. After 2 hours, 1 ml. of ethylene glycol was added and the suspension stirred an additional 10 minutes. The yellow precipitate which formed was filtered, washed with glacial acetic acid, then with petroleum ether (b.p. 30–60°) and dried; it weighed 0.73 g. (72%). Recrystallization from dry thiophene-free benzene gave very small yellow crystals, m.p. 203.5–204.5° dec.

Anal. Calcd. for $C_{24}H_{17}ClN_2O_6S_3$: C, 51.38; H, 3.05; N, 4.99. Found: C, 51.68; H, 2.96; N, 4.86.

2-Benzenesulfonyl-3,5-dichloro-*p*-phenylenedibenzenesulfonamide. Method A.—Dry hydrogen chloride was bubbled into a suspension of 0.35 g. of 2-benzenesulfonyl-3-chloro-*p*-quinonedibenzenesulfonimide in 20 ml. of dry chloroform for 15 minutes. The resulting yellow tinted solution was evaporated to dryness giving a pale yellow gummy residue. This was dissolved in 10 ml. of glacial acetic acid and poured into 125 ml. of water. The white solid which precipitated was filtered off, washed well with water and dried; weight 0.32 g. (87%). Recrystallization from 95% ethanol gave white prisms, which after drying *in vacuo* at 80° had a melting point of 176–177°.

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_6S_3$: C, 48.24; H, 3.04; N, 4.69. Found: C, 48.32; H, 2.82; N, 4.80.

---

[5] R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); R. Adams and K. R. Eilar, *ibid.*, **73**, 1149 (1951).

2-Benzenesulfonyl-5,6-dichloro-*p*-phenylenedibenzenesulfonamide.—To a suspension of 2.0 g. of 2,3-dichloro-*p*-quinonedibenzenesulfonimide[2] in 16 ml. of glacial acetic acid was added 2.0 g. of sodium benzenesulfinate. After standing overnight, the pale yellow solid was filtered off, washed with glacial acetic acid and petroleum ether (b.p. 30–60°) and dried. It weighed 2.09 g. (80%). Recrystallization from glacial acetic acid gave white needles, m.p. 221–222° dec.

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_6S_3$: C, 48.24; H, 3.04; N, 4.69. Found: C, 48.28; H, 3.16; N, 4.59.

2-Benzenesulfonyl-3,6-dichloro-*p*-phenylenedibenzenesulfonamide.—In a similar manner to that just described 2,5-dichloro-*p*-quinonedibenzenesulfonimide[2] and sodium benzenesulfinate in glacial acetic acid were allowed to react. The product was obtained in 65% yield. Recrystallization from glacial acetic acid gave white plates, m.p. 210.5–212°.

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_6S_3$: C, 48.24; H, 3.04; N, 4.69. Found: C, 48.46; H, 3.17; N, 4.76.

2,6-Dichloro-*p*-phenylenedibenzenesulfonamide.—A solution of 5.0 g. of 2,6-dichloro-*p*-phenylenediamine[6] and 11.0 g. of benzenesulfonyl chloride in 50 ml. of dry pyridine was refluxed for 4 hours. After cooling to room temperature, the dark solution was poured into a mixture of ice and concentrated hydrochloric acid. The precipitated crude 2,6-dichloro-*p*-phenylenedibenzenesulfonamide was treated with dilute aqueous sodium hydroxide, heated with Darco, filtered and reprecipitated with concentrated hydrochloric acid to give 6.40 g. (55%) of product. Recrystallization from 95% ethanol gave white needles, m.p. 187–188.5°.

Anal. Calcd. for $C_{18}H_{14}Cl_2N_2O_4S_2$: C, 47.26; H, 3.09; N, 6.12. Found: C, 47.32; H, 3.22; N, 6.10.

The N,N-Dibenzenesulfonyl-2,6-dichloro-*p*-phenylenediamine.—The aqueous alkali-insoluble material collected with the Darco in the preceding experiment was extracted from the Darco with 60 ml. of boiling 95% ethanol and filtered. The brown filtrate was concentrated to 12 ml. and cooled to give 0.14 g. of product. Recrystallization from 95% ethanol (*ca.* 1 g./80 ml.) gave white needles, m.p. 216–217°. The product was insoluble in dilute acid and dilute base.

The position of the two benzenesulfonyl groups was not determined. Since the compound differs from 2,6-dichloro-*p*-phenylenedibenzenesulfonamide, the two benzenesulfonyl groups are obviously on the same nitrogen atom. Since the infrared spectrum was very similar to that of 4-N,N-dibenzenesulfonamido-3-chloroaniline, the benzenesulfonyl groups may be on the amino group situated between the two chlorines.[7]

Anal. Calcd. for $C_{18}H_{14}Cl_2N_2O_4S_2$: C, 47.26; H, 3.09; N, 6.12. Found: C, 47.12; H, 3.01; N, 6.07.

2,6-Dichloro-*p*-quinone-4-benzenesulfonimide. Method A.—A solution of 2.00 g. of 2,6-dichloro-*p*-phenylenedibenzenesulfonamide and 2.00 g. of lead tetraacetate in 60 ml. of glacial acetic acid was stirred at 60° in an oil-bath for 4 hours. By the time the temperature had reached 60°, the suspended solid had dissolved. The resulting solution was orange but turned red in the course of 3.5 hours. The solution was stirred an additional 5 minutes after addition of 5 drops of ethylene glycol and then added dropwise to 300 ml. of water. The yellow solid, which precipitated in quantitative yield, was purified by 3 recrystallizations from ethyl acetate (1 g./2 ml.); yellow plates, m.p. 163–164° (lit.[8] 162–163°). The product was identical with an authentic sample of the monoimide.

Anal. Calcd. for $C_{12}H_7Cl_2NO_3S$: C, 45.59; H, 2.23; N, 4.43. Found: C, 45.80; H, 2.47; N, 4.53.

Infrared analysis showed a carbonyl band at 1691 cm.$^{-1}$, a C=N band at 1624 and/or 1583 cm.$^{-1}$ and $-SO_2-$ bands.

Method B.—A suspension of 1.00 g. of 2,6-dichloro-*p*-phenylenedibenzenesulfonamide and 0.97 g. of dry lead tetraacetate in 50 ml. of dry benzene was heated under reflux for 2.5 hours. The insoluble lead diacetate was removed by filtration and washed with dry benzene. The filtrate was concentrated to 5 ml. on the hot-plate. To the hot solution was added 6 ml. of a 10% solution of acetic anhydride in glacial acetic acid. The resulting 11 ml. of solution was concentrated on a hot-plate to 5 ml. and cooled to room temperature. The yellow crystals which resulted were recrystallized twice from the acetic anhydride–glacial acetic acid mixture; m.p. 161.5–163°.

2-Benzenesulfonyl-3,5-dichloro-*p*-phenylenedibenzenesulfonamide. Method B.—A suspension of 0.47 g. of 2,6-dichloro-*p*-phenylenedibenzenesulfonamide and 0.45 g. of dry lead tetraacetate in 25 ml. of anhydrous benzene was heated under reflux for 2.5 hours. The insoluble lead diacetate was removed by filtration. To the filtrate was added 6 ml. of glacial acetic acid and 0.25 g. of sodium benzenesulfinate. Within 5 minutes, the dark orange solution became pale orange. The mixture was allowed to stand overnight, boiled for 5 minutes and a stream of dry air was used to remove the benzene. To the resulting mixture was added 4 ml. of glacial acetic acid and the resulting solution poured into 100 ml. of water. The precipitate thus formed was collected on a filter, washed with water and dried. It weighed 0.56 g. (90%). The crude product was dissolved in 15 ml. of boiling 95% ethanol (3 treatments with Darco) filtered and concentrated to 12 ml. After 2 subsequent recrystallizations from 95% ethanol the product was pure, m.p. 176–177.5°.

Anal. Calcd. for $C_{24}H_{18}Cl_2N_2O_6S_3$: C, 48.24; H, 3.04; N, 4.69. Found: C, 48.34; H, 3.24; N, 4.68.

The melting point of a mixture of this product with 2-benzenesulfonyl-3,5-dichloro-*p*-phenylenedibenzenesulfonamide obtained by method A showed no depression.

N-Benzenesulfonyl-3,5-dichloro-4-nitroaniline.—A solution of 0.51 g. of 3,5-dichloro-4-nitroaniline[9] and 0.45 g. of benzenesulfonyl chloride in 15 ml. of reagent grade pyridine was refluxed for 14 hours then poured into 50 ml. of water and acidified with hydrochloric acid. The brownish-yellow precipitate which formed was collected and dried; it weighed 0.72 g. (85%). The crude product was dissolved in 20 ml. of glacial acetic acid, treated with Darco and the hot solution filtered then concentrated to 10 ml. Water was then added until crystallization began; on cooling the solution pale yellow needles were obtained. Recrystallization from 75% acetic acid gave cream colored needles, m.p. 212–213.5°.

Anal. Calcd. for $C_{12}H_8Cl_2N_2O_4S$: C, 41.51; H, 2.32; N, 8.07. Found: C, 41.72; H, 2.46; N, 8.06.

2-Nitro-*p*-phenylenedibenzenesulfonamide.—A solution of 15.3 g. of 2-nitro-*p*-phenylenediamine and 25.6 ml. of benzenesulfonyl chloride in 200 ml. of pyridine was refluxed for 20 hours, then 143 ml. of pyridine was removed by distillation. The residual oil was stirred for several minutes with a solution of 40 ml. of concd. hydrochloric acid in 220 ml. of 30% ethanol and the solidified material was decanted off with the liquors. The remaining oil was taken up in 40 ml. of 95% ethanol containing 5 ml. of concd. hydrochloric acid, then diluted with 100 ml. of water, and the solidified material again decanted with the liquid. This latter process was repeated until all of the oil had solidified. All aqueous liquors were combined and allowed to stand for 2 hours yielding 36.4 g. (82%) of crude product. Repeated recrystallization from 95% ethanol, using generous portions of Darco, gave light yellow crystals, m.p. 152–153.5°.

Anal. Calcd. for $C_{18}H_{15}N_3O_6S$: C, 49.87; H, 3.49; N, 9.69. Found: C, 50.04; H, 3.31; N, 9.56.

2-Carbomethoxy-4-nitroacetanilide.—While maintaining the temperature below 0°, 91.3 g. of 2-carbomethoxyacetanilide[10] was added in small portions with stirring to 400 ml. of fuming nitric acid (d. 1.5). The addition required 1.5 hours, and after stirring an additional 2.5 hours the solution was poured over 500 g. of cracked ice. The precipitated product weighed 80 g. (71%). Recrystallization from acetone gave a pure product, m.p. 174–176°.

Anal. Calcd. for $C_{10}H_{10}N_2O_5$: C, 50.42; H, 4.23; N, 11.76. Found: C, 50.35; H, 4.17; N, 11.92.

2-Carbomethoxy-4-nitroaniline.—A suspension of 43.0 g. of 2-carbomethoxy-4-nitroacetanilide in 500 ml. of methanol containing 30 ml. of concentrated hydrochloric acid was refluxed for 0.75 hours. The resulting slurry of fine yellow needles was cooled to 10°, filtered, washed with aqueous sodium carbonate and water and dried. It weighed 32.7 g. (90.1%), m.p. 167–169° (lit.[11] 168°).

---

[6] R. Adams and D. S. Acker, THIS JOURNAL, **74**, 3029 (1952).

[7] R. Adams and R. S. Colgrove, unpublished results.

[8] R. Adams and J. H. Looker, THIS JOURNAL, **73**, 1145 (1951).

[9] F. Beilstein and A. Kurbatow, *Ann.*, **196**, 219 (1879).

[10] H. Mehner, *J. prakt. Chem.*, [2] **64**, 83 (1901).

[11] M. T. Bogert and G. Scatchard, THIS JOURNAL, **41**, 2066 (1919).

2-Carbomethoxy-*p*-phenylenediamine.—A solution of 8.8 g. of 2-carbomethoxy-4-nitroaniline in 175 ml. of pure, dry dioxane was hydrogenated over 0.1 g. of platinum oxide at 3 atm. and room temperature for one hour. After filtering off the catalyst, 125 ml. of dioxane was distilled off at reduced pressure. The cherry-red, oily residue was stirred with 400 ml. of petroleum ether (b.p. 30–60°) until it solidified. It weighed 5.5 g., m.p. 71–74°. Upon evaporating the mother liquors an additional 0.7 g. was obtained; total yield 6.2 g. (83%). This material rapidly deteriorated on standing, and was immediately benzenesulfonated.

2-Carbomethoxy-*p*-phenylenedibenzenesulfonamide.—A solution of 10.0 g. of 2-carbomethoxy-*p*-phenylenediamine in 100 ml. of dry pyridine was stirred while 15.5 ml. of benzenesulfonyl chloride was added dropwise keeping the temperature of the mixture around 25°. After completion of the addition, which required 20 minutes, the dark solution was stirred at room temperature for 20 hours. The solution was distilled *in vacuo* at 35° to remove 80 ml. of pyridine, and the residual oil allowed to stand under water for 2 days to effect solidification. The brown solid was washed with water, dried, and dissolved in 200 ml. of methanol. The solution was treated with Darco, heated on steam-bath and stirred for one hour and filtered. It was concentrated until crystals appeared, and cooled. It weighed 15.0 g. (56%). Recrystallization from 95% ethanol gave white needles, m.p. 155–156.5°.

Anal. Calcd. for $C_{20}H_{18}N_2O_6S_2$: C, 53.80; H, 4.06; N, 6.27. Found: C, 54.10; H, 4.24; N, 6.32.

2-Carbomethoxy-*p*-quinonedibenzenesulfonimide.—A mixture of 0.77 g. of 2-carbomethoxy-*p*-phenylenedibenzenesulfonamide, 0.77 g. of lead tetraacetate and 13 ml. of anhydrous benzene was stirred at room temperature for 2 hours. The precipitated lead diacetate was filtered off, and the yellow filtrate shaken with 1 g. of anhydrous sodium carbonate. The solution was filtered, then evaporated nearly to dryness *in vacuo*. Petroleum ether (b.p. 90–95°) was added causing crystallization of 0.42 g. (55%) of yellow product. Recrystallization from 3:2 petroleum ether (b.p. 90–95°)-benzene mixture gave a bright yellow microcrystalline powder, m.p. 167.5–171° dec.

Anal. Calcd. for $C_{20}H_{16}N_2O_6S_2$: C, 54.04; H, 4.82; N, 6.30. Found: C, 54.60; H, 4.17; N, 6.41.

This compound was very elusive, and frequently turned to a red gum, particularly when moist with solvent. Activated carbon likewise caused immediate decomposition. As a result of this sensitivity, it was not obtained in a state of acceptable analytical purity.

N-Benzenesulfonyl-2-cyano-4-nitroaniline.—A solution of 10.0 g. of 2-cyano-4-nitrochlorobenzene[12] and 10.2 g. of sodium benzenesulfonamide in 100 ml. of dimethylformamide was refluxed for 5 hours. The yellow solution was poured into 300 ml. of water and acidified with hydrochloric acid. The residual oil was washed with hot water causing partial solidification. The semi-solid was stirred with 100 ml. of boiling 95% ethanol and filtered, leaving 0.50 g. of insoluble residue. The ethanol solution was concentrated to 50 ml. and cooled to give 5.85 g. (35%) of crude product. Recrystallization from 95% ethanol gave pale yellow prisms, m.p. 159–160.5°.

Anal. Calcd. for $C_{13}H_9N_3O_4S$: C, 51.48; H, 2.99; N, 13.86. Found: C, 51.71; H, 2.78; N, 13.88.

The 0.50 g. of material insoluble in ethanol was recrystallized from glacial acetic acid to give pale yellow crystals, m.p. 240.5–241.5°. Elementary analysis and the infrared spectrum indicate that it is di-(2-cyano-4-nitrophenyl) ether.

Anal. Calcd. for $C_{14}H_6N_4O_5$: C, 54.20; H, 1.95; N, 18.06. Found: C, 54.16; H, 1.96; N, 18.20.

3-Cyano-4-benzenesulfonamidoaniline.—To a boiling solution of 0.52 g. of N-benzenesulfonyl-2-cyano-4-nitroaniline in 80 ml. of 95% ethanol was slowly added a saturated solution of sodium hydrosulfite until a colorless mixture was obtained. An equal volume of water was added and the resulting colorless solution was concentrated to 70 ml. and cooled to give 0.30 g. (64%) of product. Recrystallization from 95% ethanol gave white needles, m.p. 200.5–203°.

Anal. Calcd. for $C_{13}H_{11}N_3O_2S$: C, 57.13; H, 4.06; N, 15.38. Found: C, 57.31; H, 4.20; N, 15.14.

2-Cyano-*p*-phenylenedibenzenesulfonamide.—A solution of 0.76 g. of 3-cyano-4-benzenesulfonamidoaniline and 0.50 g. of benzenesulfonyl chloride in 20 ml. of pyridine was refluxed for 5 hours, then poured into 100 ml. of water. This mixture was acidified with hydrochloric acid and allowed to stand for 1 hour to permit the partially colloidal suspension to coagulate. It weighed 0.94 g. (82%). Recrystallization from 75% ethanol gave white crystals, m.p. 165.5–168°.

Anal. Calcd. for $C_{19}H_{15}N_3O_4S_2$: C, 55.19; H, 3.66; N, 10.16. Found: C, 55.34; H, 3.66; N, 10.07.

2-Cyano-*x*-chloro-*p*-phenylenedibenzenesulfonamide.—A mixture of 1.00 g. of 2-cyano-*p*-phenylenedibenzenesulfonamide, 1.08 g. of lead tetraacetate and 15 ml. of anhydrous benzene was stirred at room temperature for 1.25 hours. The resulting orange mixture was filtered and dry hydrogen chloride passed into the filtrate for 0.25 hour. After filtering off a small amount of lead chloride, the pale yellow filtrate was evaporated to dryness *in vacuo*. The semi-solid residue, once crystallized from 50% ethanol, gave 0.51 g. (47%) of product. Recrystallization from 70% ethanol gave white needles, m.p. 184–186.5°.

Anal. Calcd. for $C_{19}H_{14}ClN_3O_4S_2$: C, 50.95; H, 3.15; N, 9.38. Found: C, 51.18; H, 3.28; N, 9.37.

URBANA, ILLINOIS

---

[12] H. Ph. Boudet, *Rec. trav. chim.*, **43**, 710 (1924).