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Nitration of derivatives of 2,5-dichlorobenzenesulfonic acid

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NITRATION OF DERIVATIVES
OF 2,5-DICHLOROBENZENESULFONIC ACID

BY

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in Chemical Engineering

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ABSTRACT

The proof that a nitro group enters meta to the sulfonic acid group of 2,5-dichlorobenzenesulfonamide and 2,5-dichlorobenzenesulfonanilide is presented.

The preparation of several new compounds is described.

An unsuccessful attempt to prepare 2,5-dichloro-3-nitrobenzenesulfonyl chloride from 2,5-dichloronitrobenzene is also described.

STATEMENT OF PROBLEM

The object of this project was to study the effect of various groups substituted for the hydroxyl group of 2,5-dichlorobenzenesulfonic acid on an entering nitro group. The compounds reported herein are 2,5-dichlorobenzenesulfonamide and 2,5-dichlorobenzenesulfonanilide.

INTRODUCTION

A thorough search of the literature showed that very little work has been done on the nitration of 2,5-dichlorobenzene-sulfonic acid and its derivatives. Crowell and Raiford (1) nitrated 2,5-dichlorobenzene-sulfonic acid and they came to the conclusion that the nitro group entered in the 4-position or para to the sulfonic acid group. They fail to mention the formation of isomers and it is deduced from their report that no isomers are formed.

Since a sulfonic acid group is usually meta-directing and a halogen is usually ortho-para directing, it would seem likely that the combined influence of these two groups would direct an entering group into the 3-position, that is, meta to the sulfonic acid group.

Others workers (2) assume that the nitro group enters meta to the sulfonic acid group, but no yields are given. Another report (3) states that the nitro group enters chiefly para and to a lesser extent meta to the sulfonic acid group.

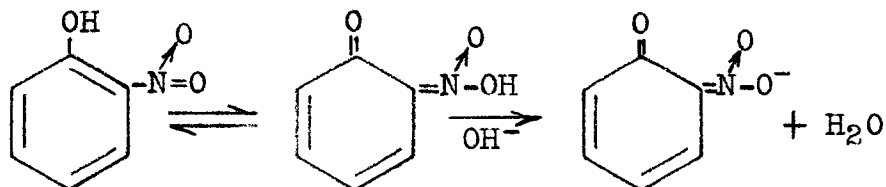
The nitration of 2,5-dichlorobenzene-sulfonyl chloride was reported by Gebauer-Fuhlneig and Figdor (4) to yield 2,5-dichloro-3-nitrobenzene-sulfonyl chloride with a melting point of 65°C.

They fail to report a yield or the presence of isomers. Many attempts to duplicate their results resulted in an oil which was impossible to crystallize and from which no starting material could even be recovered. It was, therefore, assumed that all of the 2,5-dichlorobenzenesulfonyl chloride had reacted.

An unsuccessful attempt was made to prepare 2,5-dichloro-3-nitrobenzenesulfonyl chloride by reacting 2,5-dichloronitrobenzene with chlorosulfonic acid under various conditions.

DISCUSSION

Figure 1 shows the proof of the structure of 2,5-dichloro-3-nitrobenzenesulfonamide. An indication that the nitro group is ortho to the hydroxyl group in Compound VII was given by the fact that upon prolonged heating with sodium hydroxide solution the color of the compound became a dark orange brown differing from the original light orange color. This shows that there is a quinoid structure present



which could not be possible if the nitro and hydroxyl groups were meta to each other. Furthermore, on reducing Compound VII to Compound VIII another colored solid was formed which would not melt and which reduced Tollen's reagent showing that either a para or an ortho aminophenol was present. The sulfonamide was ultimately degraded to Compound X, 4-chloro-2-nitrophenol, which was proven by a mixed melting point with an authentic sample.

The structure of 2,5-dichloro-3-nitrobenzenesulfonamide was proven as shown in Figure 2. The presence of a nitro group ortho to a hydroxyl group was indicated by the use of sodium hydroxide solution as mentioned above. Compound XIV also had the same appearance

as Compound VII. Compound XV also reduced Tollen's reagent as in the case of Compound VIII indicating the presence of a para or an ortho aminophenol. The occurrence of nitration in the anilide ring was also noted as evidenced by the isolation of p-nitroaniline. No explanation can be given for the absence of isomers, but no other nitroaniline could be isolated. The sulfonanilide was finally converted to the known 4-chloro-2-nitrophenol, and a mixed melting point gave no depression thereby proving its identity.

Fig.1. PROOF OF THE STRUCTURE OF
2,5-DICHLORO-3-NITROBENZENESULFONAMIDE

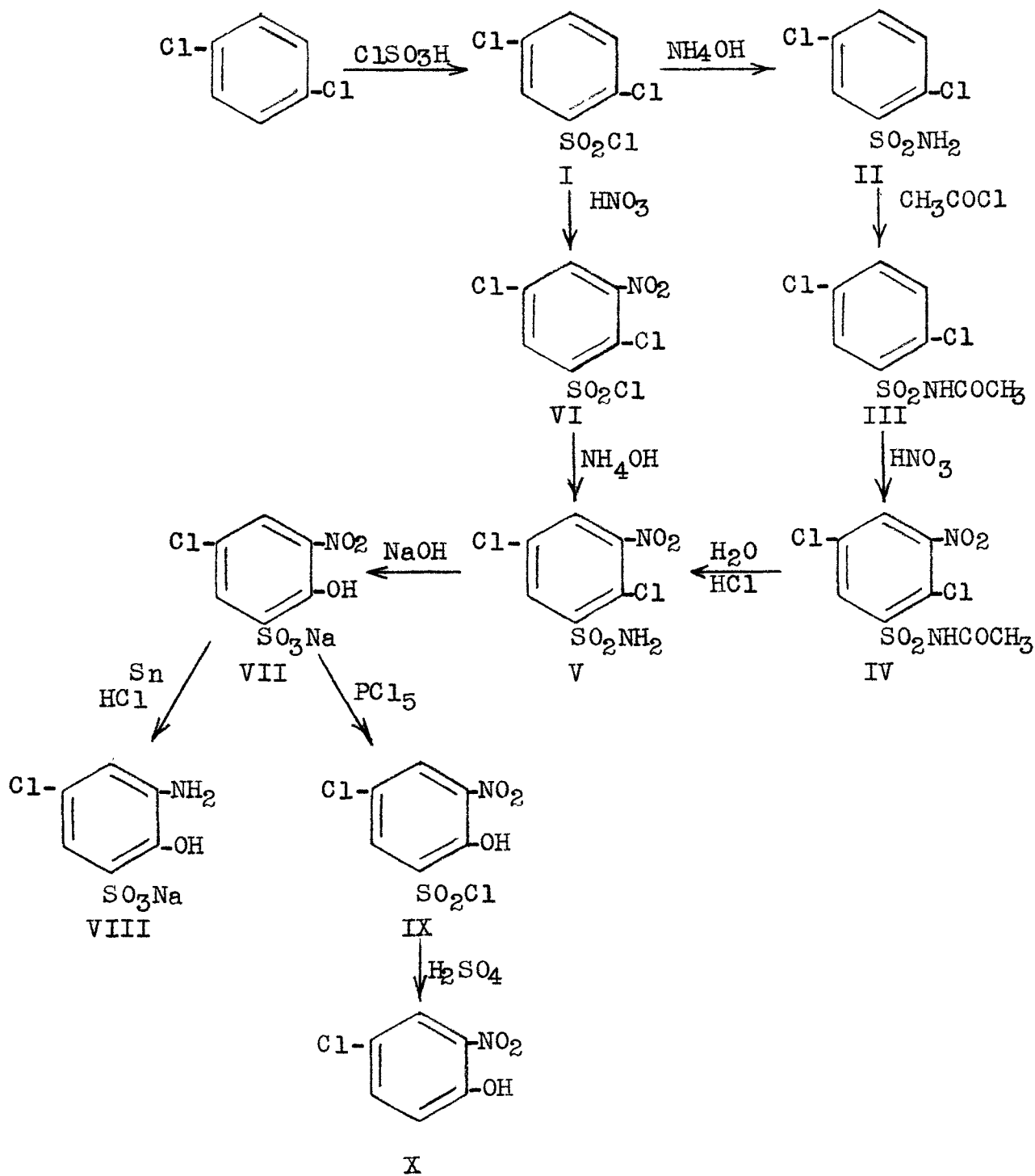
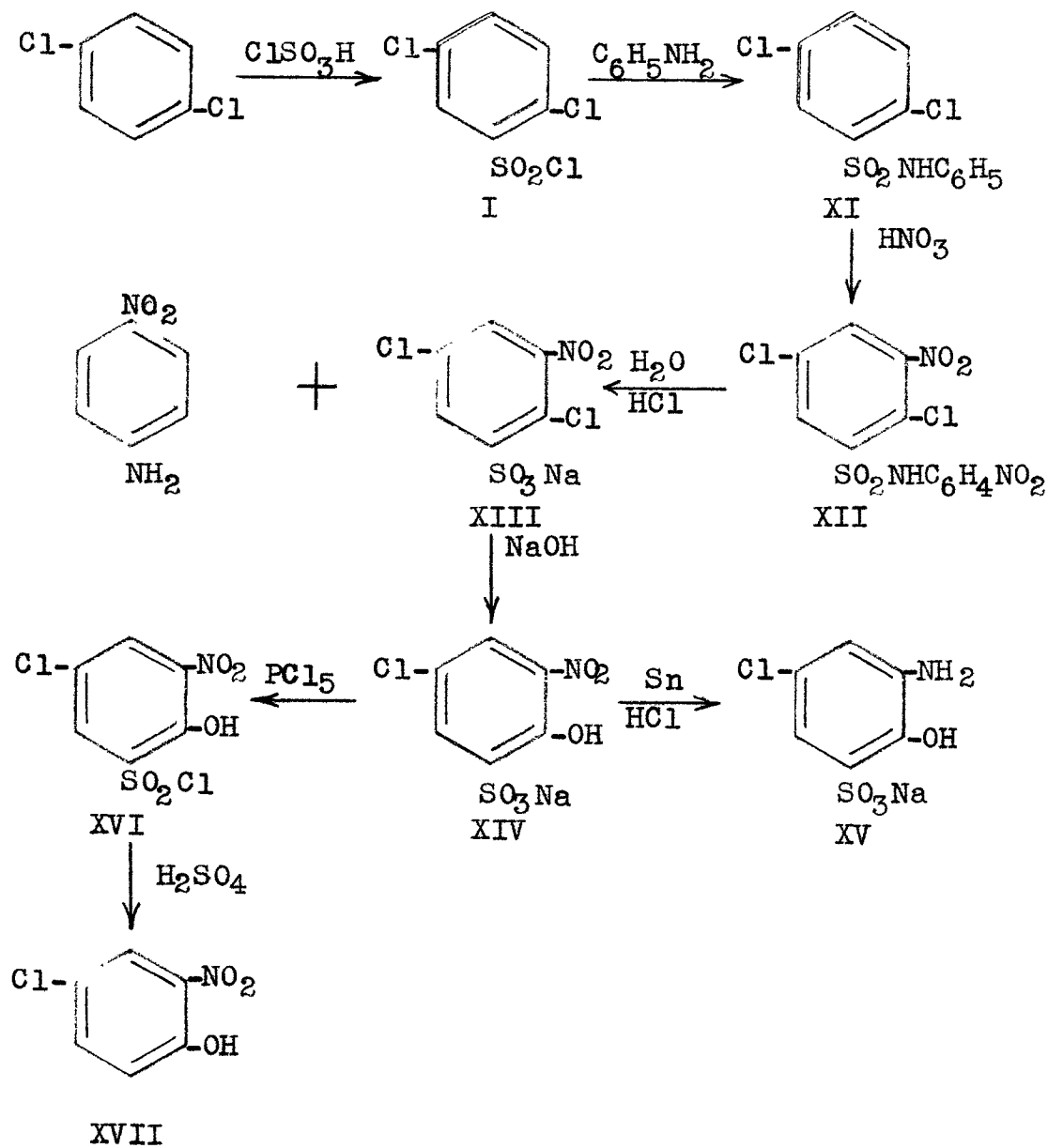


Fig.2. PROOF OF THE STRUCTURE OF
2,5-DICHLORO-3-NITROBENZENESULFONANILIDE



EXPERIMENTAL PROCEDURE (5)

2,5-Dichlorobenzene sulfonyl chloride. I. (6)

One mole of p-dichlorobenzene and 5 moles of chlorosulfonic acid were heated at 120°C. with stirring for one hour. The brown colored oil was cooled to room temperature and poured cautiously on crushed ice while stirring. The solid which formed was filtered off, washed thoroughly with cold water and dried in a desiccator. The yield of crude material was 227 gms. (93%). Upon recrystallization from low boiling (30-75°C.) petroleum ether, white needles were obtained melting at 37-39°C. (lit. 39°C.)

2,5-Dichlorobenzene sulfonamide. II. (7)

Fifty gms. of 2,5-dichlorobenzene sulfonyl chloride and 500 cc. of ammonium hydroxide (sp. g. 0.90) were boiled for 20 mins. The mixture was cooled in an ice-water bath and 500 cc. of cold water was added. The solid was filtered off, washed thoroughly with cold water and dried. A yield of 45 gms. (97%) of crude material was obtained which melted at 179-180°C. (lit. 181°C.) upon recrystallization from aqueous alcohol.

2,5-Dichlorobenzene sulfonanilide. XI. (4)

Twenty-five gms. of 2,5-dichlorobenzene sulfonyl chloride were dissolved in 50 cc. of ether. 23.7 gms. (23.5 cc.) of redistilled aniline were added and the mixture was heated on the water bath for one hour. The ether was distilled off and the resulting light brown

solid was slurried with approximately 50 cc. of N HCl. The solid was filtered off, washed thoroughly with water, and dried in a desiccator. A yield of 88% (27 gms.) of crude material was obtained which, upon recrystallizing from alcohol, formed white crystals melting at 159-160°C. (lit. 160°C.)

2,5-Dichlorobenzenesulfonacetamide. III. (8)

Twenty-one gms. of 2,5-dichlorobenzenesulfonamide and 52.5 gms. (48 cc.) of acetyl chloride were refluxed for 5 mins. Since no solution formed, 45 cc. of gl. acetic acid were added and the mixture was refluxed 30 mins. A cloudy solution resulted. The excess acetyl chloride was driven off and the cold reaction mixture was poured into 25 cc. of water. The solid was filtered and washed with water. Without drying, the solid was taken up in warm 10% Na HCO₃ and filtered while still warm. The filtrate was acidified with gl. acetic acid and, after being cooled to about 15°C., was filtered. The white crystals were washed with water and dried. A yield of 10.5 gms. (42%) of crude material was obtained which, upon recrystallizing from aqueous alcohol, was in the form of short white needles melting at 213-214°C. (lit. 214°C.)

2,5-Dichloro-3-nitrobenzene sulfonyl chloride. VI.

This compound was prepared by a modification of the method of Gebauer-Fühlneg and Figdor (4).

Twenty-five gms. of 2,5-dichlorobenze sulfonyl chloride, 10 cc. of conc. H₂SO₄ (sp. g. 1.84), and 25 cc. of HNO₃ (sp. g. 1.5) were heated

on the steam bath for 5 hours. The mixture was cooled to room temperature and the oil was separated. The oil was washed with water, a 1% solution of Na_2CO_3 , and again with water to remove any occluded oxides of nitrogen. The light yellow oil was dissolved in ether (25 cc.) and dried over Na_2SO_4 . Upon distilling off the ether, 4 gas. (13%) of a light yellow oil were obtained. This oil could not be crystallized and no starting material could be extracted from it.

Amide -- Four gas. of the oil were slowly added to 40 cc. of conc. ammonium hydroxide. Heat was evolved and a yellow solid formed immediately. The mixture was diluted with 40 cc. of cold water and the yellow solid (1 gm.) was filtered off. The solid melted at $203-5^\circ\text{C}$. upon recrystallizing from aqueous alcohol. A mixed melting point with Compound V gave no depression showing that the two compounds were the same.

2,5-Dichloro-3-nitrobenzenesulfonacetamide. IV.

Ten gas. of 2,5-dichlorobenzenesulfonacetamide and 50 cc. of conc. H_2SO_4 (sp. g. 1.84) were cooled to 5°C . Four cc. of HNO_3 (sp. g. 1.5) were added at $5-10^\circ\text{C}$. while stirring over a period of 20 mins. The milky mixture was stirred at room temperature (25°C .) for one hour. The mixture was slowly poured on ice with stirring and a greenish-yellow solution resulted. The solution was concentrated in vacuo until crystals formed. After cooling to about 10°C ., the slightly yellow crystals were filtered on a sintered glass funnel and pressed dry. A yield of 5.1 gas. (43%) of crude material melting at $149-151^\circ\text{C}$. after recrystallization from alcohol was obtained.

Calculated for $C_8H_6Cl_2N_2O_5S$. Cl, 22.6; N, 8.95.

Found: Cl, 23.0; N, 9.22.

2,5-Dichloro-3-nitrobenzenesulfonamide. V.

Four gms. of IV and 25 cc. of 10% HCl were refluxed for one hour. A light yellow solution resulted which deposited short needles on cooling. This solid proved to be unreacted IV. An additional 25 cc. of 10% HCl was added and refluxing was continued for an additional 7 hours. Total time of reflux was 8 hours. On cooling the solution 2.2 gms. (63%) of long, pale yellow needles formed which melted at 205-206°C. after recrystallizing from aqueous alcohol.

Calculated for $C_6H_4Cl_2N_2O_5S$. C, 26.2; N, 10.3.

Found: C, 26.55; N, 9.85.

Sodium salt of 4-chloro-2-nitrophenol-6-sulfonic acid. VII

Three gms. of V and 20 cc. of 8% NaOH were refluxed 8 hours. The original pale yellow color became bright orange. The solid was filtered, washed with water and dried. The yield was 1.8 gms. (59%). This solid was assumed to be the sodium salt since it did not melt.

On prolonged heating with NaOH solution the color became orange brown indicating that a quinoid structure existed and that the nitro group was ortho to the hydroxy group.

Sodium salt of 4-chloro-2-aminophenol-6-sulfonic acid. VIII.

Two gms. of VII and 4 gms. of mossy tin were added to 10 cc. of alcohol. Forty cc. of 10% HCl was added in portions through the reflux condenser. The bright orange color of VII changed to yellow.

The mixture was heated on the steam bath for 20 mins. whereupon all the solid went into solution. The solution was decanted while still hot into 20 cc. of water and 40% NaOH was added to dissolve the tin hydroxide. The yellow oil which formed was separated and upon cooling solidified to a yellow amorphous solid. The yield was 1.3 gms. (73%). The solid did not melt and reduced Tollen's reagent indicating that it was an o-aminophenol.

4-Chloro-2-nitrophenol-6-sulfonyl chloride. IX.

Four gms. of VII was mixed with 10 gms. of phosphorus pentachloride. The mixture was heated in an oil bath at 150°C. for 30 mins. Twenty cc. of dry benzene was added to the oil which resulted on cooling. The benzene solution was washed thoroughly with water and dried over Na_2SO_4 . A light brown oil weighing 3.7 gms. (85%) resulted on distilling off the benzene. Various attempts to crystallize this oil failed.

4-Chloro-2-nitrophenol. X.

Four gms. of IX and 25 cc. of 65% H_2SO_4 were refluxed for 10 hours. The resulting oily mixture was cooled to room temperature and extracted with ether. The ether extract was washed with water, 10% NaHCO_3 , and again with water. The ether was distilled off after drying over Na_2SO_4 leaving 1.4 gms. (55%) of a yellow solid. The solid was recrystallized from alcohol. M. p. 83-84°C. A qualitative test showed sulfur to be absent. A mixed melting point with 4-chloro-2-

nitrophenol prepared by the method of Mottier (9) gave no depression indicating that the two products were identical.

4-Chloro-2-nitrophenol. Prepared by Mottier's method (9)

Five gms. of p-chlorophenol was added slowly to a mixture of 50 cc. of HNO_3 (sp. g. 1.5) and 75 cc. of water at room temperature. The mixture was stirred 48 hours at room temperature. The crystals were filtered on a sintered glass funnel and washed with cold water. Upon recrystallizing from alcohol, yellow needles formed melting at $85-87^\circ\text{C}$.

2,5-Dichloro-3-nitrophenylsulfonamido-4'-nitrobenzene (XII).

Fifteen gms. of 2,5-dichlorobenzenesulfonanilide and 50 cc. of conc. H_2SO_4 (sp. g. 1.84) were cooled to 5°C . in an ice-water bath. Six cc. of HNO_3 (sp. g. 1.5) was added with stirring at $5-10^\circ\text{C}$. over a period of 15 mins. After the first few drops of acid were added an orange-brown solid began to form. The mixture was stirred at room temperature (28°C .) for 30 mins. The dark brown oil which had now formed was poured on crushed ice while stirring. A light yellow solid formed. The solid was filtered, washed with water and dried. The yield was 6.2 gms. (36%). The melting point after recrystallizing from alcohol was $124-125^\circ\text{C}$.

Calculated for $\text{C}_{12}\text{H}_7\text{Cl}_2\text{N}_2\text{O}_6\text{S}$. Cl, 18.1; N, 10.7

Found: Cl, 18.52; N, 10.97.

2,5-Dichloro-3-nitrobenzenesulfonic acid. XIII.

Five gms. of XII and 50 cc. of 10% HCl were refluxed 8 hours. Upon cooling the reaction mixture a brown solid separated. The solid was filtered off, washed with cold water, and dried. It weighed 0.8 gms. after drying and had a melting point of 136-140°C. This solid was recrystallized from alcohol giving yellow needles melting at 144-145°C. An analysis showed it contained no chlorine. A mixed melting point with a commercial sample of p-nitroaniline was not depressed. The compound was proven to be p-nitroaniline by acetylation which gave p-nitroacetanilide, M. p. 213-215°.

No isomeric nitroanilines could be found.

The original filtrate was extracted with benzene and after washing the extract with water it was dried over Na_2SO_4 . Upon distilling off the benzene, 2.9 gms. of a dark brown oil were obtained which would not crystallize. The yield was 74% assuming that the sulfonic acid had been formed.

Sodium salt of 4-Chloro-2-nitrophenol-6-sulfonic acid. XIV.

This compound was prepared in the same manner as VII. The brown oil, XIII, became a dark orange solid after heating 8 hours with 8% NaOH and on prolonged heating the color changed to brown. A yield of 48% of solid which did not melt was obtained.

Sodium salt of 4-Chloro-2-aminophenol-6-sulfonic acid. XV.

Compound XIV was reduced in the same manner as VII. The results were the same except that the yield was only 62%. The yellow solid did not melt and reduced Tollen's reagent indicating the amino group is ortho to the hydroxyl.

4-Chloro-2-nitrophenol-6-sulfonyl chloride. XVI.

Compound XIV was reacted with phosphorus pentachloride in the same manner as VII. 3.2 gms. (73%) of a light brown oil which would not crystallize was obtained.

4-Chloro-2-nitrophenol. XVII.

Six gms. of XVI and 50 cc. of 65% H_2SO_4 were refluxed for 10 hours. The reaction mixture was steam distilled. The yellow solid was filtered from the distillate, washed with water, and dried. Yield 2.3 gms. (60%). The yellow needles melted at $84-85^{\circ}C$. after recrystallizing from alcohol and a mixed melting point with an authentic sample of 4-chloro-2-nitrophenol was not depressed.

Attempted Preparation of 2,5-Dichloro-3-nitrobenzenesulfonyl Chloride from 2,5-Dichloronitrobenzene.

1. Aromatic halogen compounds have been successfully chlorosulfonylated (7).

2,5-Dichloronitrobenzene, 1 gm., was dissolved in 5 cc. of chloroform. The solution was cooled to $0^{\circ}C$. in an ice bath and 5 gms. of chlorosulfenic acid were added dropwise, maintaining the temperature between 0° and $5^{\circ}C$. After the addition of the acid was complete, the mixture was allowed to stand at room temperature for 20 mins. and was then poured into a 50 ml. beaker of crushed ice. The solvent layer was separated and washed with cold water. After drying over anhyd. sodium sulfate, the solvent was distilled off leaving an orange yellow solid which melted at $53-54^{\circ}C$. after recrystallization from low-boiling petroleum ether. A mixed melting point with the

starting material gave no depression showing that no reaction had taken place.

2. A general procedure for the chlorosulfonation of a nitro compound (10) was followed in this experiment.

2,5-Dichloronitrobenzene, 19.2 gms., was added to 58 gms. (33 cc.) of chlorosulfonic acid with stirring. A reddish brown solution resulted and the temperature dropped from 27° to 18°C. The temperature was raised slowly to 100°C. and stirred at 100°C. for 2 hours. The mixture was then stirred at 110-120°C. for 6 hours., and finally at 130-140°C. for 2 hours, giving a total heating time of 10 hours. The mixture was then cooled to room temperature and cautiously poured, with stirring, on crushed ice. The brown solid which formed was filtered off, washed with water, and air dried. The crude material was dissolved in 50 cc. of glacial acetic acid, decolorized with Norit A and filtered while hot. The filtrate was cooled below 15°C. and 20 cc. of cold water was added cautiously. A light orange colored solid precipitated. The solid was filtered, washed with 50% acetic acid, and air dried. Upon recrystallizing from low-boiling petroleum ether the melting point was found to be 52-53°C. A mixed melting point with 2,5-dichloronitrobenzene was not depressed indicating that no reaction had taken place.

CONCLUSIONS

From the results obtained as described above, it is shown that both 2,5-dichlorobenzenesulfonamide and 2,5-dichlorobenzenesulfonamide nitrate in the 3-position, that is, meta to the sulfonic acid group. This fact agrees with the rules of orientation. That is, that a sulfonic acid group is meta directing, a halogen is ortho-para directing, and the combined influence of the two groups would direct an entering group into the 3-position. Other authors (3) have assumed abnormal orientation.

The following new compounds have been prepared:

2,5-Dichloro-3-nitrobenzenesulfonacetamide (IV)

2,5-Dichloro-3-nitrobenzenesulfonamide (V)

4-Chloro-2-nitrophenol-6-sulfonyl Chloride (IX)

2,5-Dichloro-3-nitrophenylsulfonamide-4'-nitrobenzene (XII)

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