THE STRUCTURE
of
DI-SUBSTITUTED DERIVATIVES
of
PHENYL SULFONE.

Thesis

by

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THE STRUCTURE OF DI-SUBSTITUTED PHENYL SULFONE DERIVATIVES.

INTRODUCTION.

Phenyl sulfone may be considered a diphenyl derivative of sulfuric acid, in which two of the OH groups of the acid are replaced by phenyl groups. It is also called diphenyl sulfone, and in German "sulfobenzid", but in this paper it will always be referred to as phenyl sulfone. It is formed in appreciable quantities as a by-product in the sulfonation of benzene, especially when very concentrated acid is used. Perhaps the best method of preparing it for laboratory use is by the Friedel-Crafts synthesis, in which the chloride of benzene sulfonic acid and benzene condense in the presence of aluminum chloride.

Substituted phenyl sulfones are produced either by the direct substitution of the hydrogen atoms in the benzene rings, or through the action of sulfuric anhydride on substituted benzenes. Thus phenol and sulfur trioxide yield dihydroxy phenyl sulfone; brombenzene and sulfur trioxide yield dibrom phenyl sulfone, etc. Chlorine may be directly substituted under certain conditions, and the nitro and sulfonic acid derivatives may be directly produced by the action of a mixture of fuming nitric and fuming sulfuric acids, and of chlorsulfonic acid, respectively.

After the war considerable quantities of phenyl sulfone were left over from the various industrial processes, and the problem of its use became of importance. This need for a use to which the excess product could be put led M. E.Grandmougin *) to prepare a great many derivatives of the substance with the hope of being able to apply some of them in the dye industry. He based his structures on an assumption, which although it may be correct, cannot be said to absolutely justified. Several other investigators had worked with the directly substituted derivatives of phenyl sulfone, but in no case had the structure of the disubstituted products been unquestionably determined by actually splitting apart the two rings and determining the structure of the resulting products.

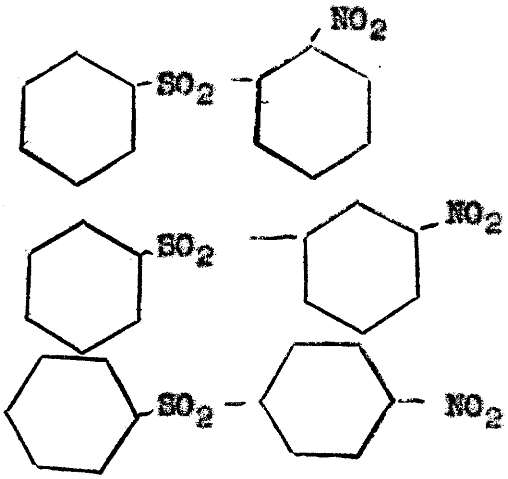
It has always been assumed that these products have a symmetrical constitution. This assumption seems to be justified in that both of the phenyl groups are equivalent, and should be subject to the same directing influence of the SO_2 group. It has also been assumed that all of the products formed with the aid of substituted benzenes conform to that constitution which the directing influence of the substituted benzene group would call for.

*) "Comptes Rendus de L'Academie des Sciences" -- 1922 - CLXXIV, 168-170.

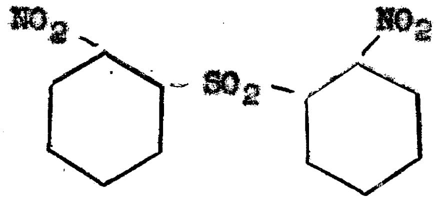
THEORETICAL CONSIDERATIONS.

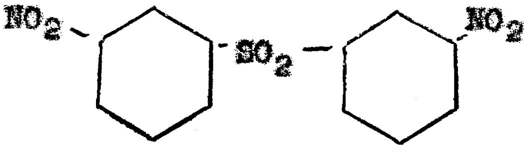
In the reaction of various reagents on phenyl sulfone, the following substituted derivatives are possible:

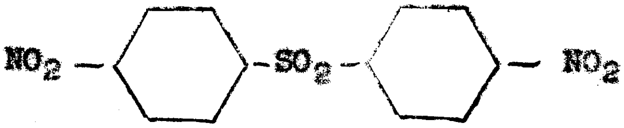
Mono- (Nitro, for example.)

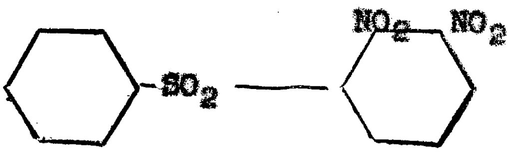


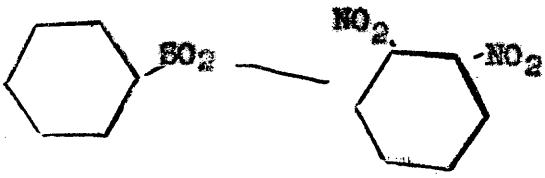
Di-

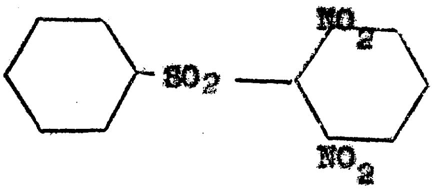


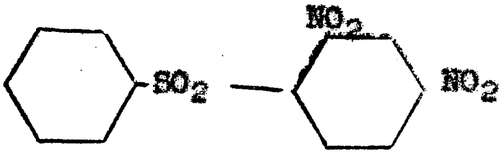












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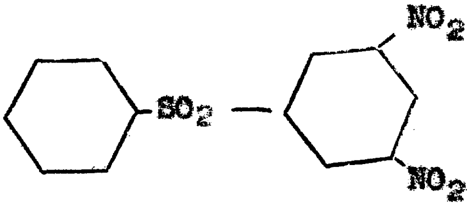
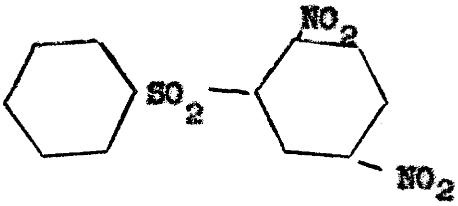
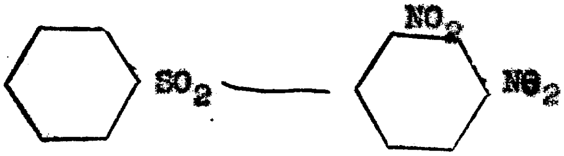
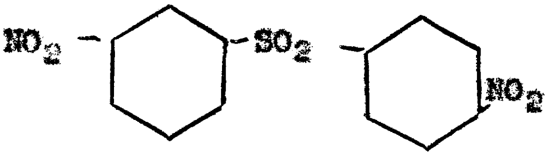
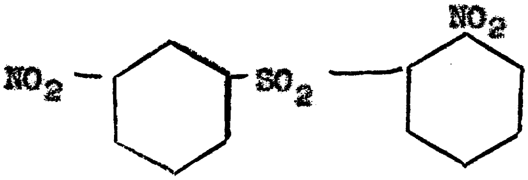
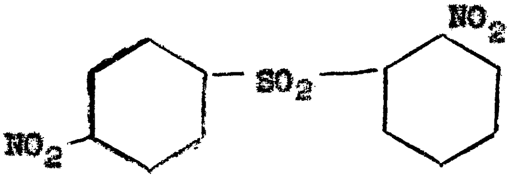












But as has already been mentioned, there is not much reason to expect compounds of the last three structures due to the apparent equivalence of the two phenyl groups. For the same reason it is unnecessary to comment upon the six preceding structures in which the substituents are both on the saem phenyl group, as it would not be expected that one of them would take on a substituent group without the other one doing so also.

In phenyl sulfone the group to which the directing influence is due may be considered $-SO_2C_6H_5$, an $-SO_2OH$ group in which the OH is replaced by C_6H_5. As both the hydroxy and the phenyl groups are negative, the former being much more so than the latter, the character of the sulfonic acid group is not materially changed by the replacement of the hydroxy by the phenyl radical.

The sulfonic acid group is practically universally conceded to be meta directing, and the theories devised to account for the directing influences of the atom groups in the benzene ring are in accord with this experimental fact. Hubner *) stated that an acidic substituent enters the position ortho or para to the least acidic group already present, taking up the meta position in case the group already present is acidic. Noelting **) expressed essentailly the same rule. Several other theories all account for the fact that the $-SO_2OH$ group directs meta. For this reason it would be expected that the products obtained by the direct substitution of the hydrogen atoms of phenyl sulfone would have structures in which the substituents are meta to the SO_2 group.

*) "Berichte" -- 1875 - VIII, 873.
**) "Berichte" -- 1876 - IX, 1797.

SURVEY OF PREVIOUS WORK.

Probably the first work done on the substitution products of phenyl sulfone was that carried out by Mitscherlich in 1834 *). He noted that the phenyl sulfone was not changed by chlorine at ordinary temperatures, and that at a temperature near its melting point chlorinated benzene was formed among other products.

Gericke **) was the next man to do considerable work on the subject. He studied both the action of chlorine and of nitric acid on phenyl sulfone. His dinitro compound he found to melt at 164°. In the chlorination reaction, he claimed to have obtained two compounds, one of which he called bichlorous phenyl sulfone, to which he allotted the formula

$$\left.\begin{matrix} Cl_2C_6H_5SO_2 \\ Cl_2C_6H_5 \end{matrix}\right\}$$

This was formed according to him when phenyl sulfone is treated with chlorine at ordinary temperatures in dispersed light, and more rapidly if the reaction is allowed to take place in the direct sunlight, or the phenyl sulfone is brought to its melting point. This compound, Gericke said, was decomposed by rapid heating or by the action of KOH, into HCl or KCl and bichlor phenyl sulfone, according to the following reactions:

$$\left.\begin{array}{r}Cl_2C_6H_5SO_2\\ Cl_2C_6H_5\end{array}\right\}\xrightarrow{\underline{\text{heat}}}\left.\begin{array}{r}ClC_6H_4SO_2\\ ClC_6H_4\end{array}\right\}+\ 2\ HCl.$$

$$\left.\begin{array}{r}Cl_2C_6H_5SO_2\\ Cl_2C_6H_5\end{array}\right\}+\ 2KOH\rightarrow\left.\begin{array}{r}ClC_6H_4SO_2\\ ClC_6H_4\end{array}\right\}\begin{array}{l}+\ 2\ KCl\\ +\ 2\ H_2O.\end{array}$$

By repeating Gericke's experiments, Otto and Gruber ***) somewhat later were unable to obtain this so-called bichlorous compound. By treating phenyl sulfone heated to its melting point, with chlorine, it decomposed according to the following reaction, in a manner similar to its decomposition with phosphorous pemtachloride:

$$\left.\begin{array}{r}C_6H_5SO_2\\ C_6H_5\end{array}\right\}+\ 2\ Cl\rightarrow\left.\begin{array}{r}C_6H_5\\ Cl\end{array}\right\}+\left.\begin{array}{r}C_6H_5SO_2\\ Cl\end{array}\right\}.$$

$$\left.\begin{array}{r}C_6H_5SO_2\\ C_6H_5\end{array}\right\}+\ PCl_5\rightarrow\left.\begin{array}{r}C_6H_5\\ Cl\end{array}\right\}+\left.\begin{array}{r}C_6H_5SO_2\\ Cl\end{array}\right\}+PCl_3.$$

They found that in the direct sunlight still further decomposition took place. Even at ordinary temperatures the atom-group SO_2 was found to leave the radical $C_6H_5SO_2$ combined with chlorine as sulfuryl chloride.

In his "Lehrbuche der Organischen Chemie" (Vol. III, page 193 et seq.), published at about the same time that Otto was doing his work, Kekulé made the following comments upon the action of chlorine on phenyl sulfone, "The latest experiments on the action of chlorine on phenyl sulfone have led to apparently contradictory results whose difference may be explained by difference in experiment conditions"; and later on "The reason that Otto and Ostrop could not obtain the compound described by Gericke easily finds its explanation in that Gericke heated the phenyl sulfone so that the chlorine therefore acted on the latter essentially in the vapor form, conditions which were also quite especially adapted to the formation of addition products of benzene".

Otto and Ostrop had done their work the prvioms year. This statement by Kekulé led Otto and Gruber to carefully study the reaction, and to accurately test the behavior of phenyl sulfone "toeards chlorine under different conditions, and to finally establish whether or not the compounds described by Gericke can be prepared by one or another means."

They followed Gericke's directions as nearly to the letter as possible, and found that the "yellow oily drops which distil over" were a mixture of equal parts od chlorbenzene and chloride of benzene sulfonic acid. Change in temperature seemed to make no difference in the results for they obtained the same products in every case. In the sunlight the decomposition took place more further, as has been previously stated. They finally concluded that if a compound of the formula ascribed to it was formed at all, it decomposed at once into the products obtained by these two men.

They did not stop at merely disproving Gericke's conclusions, but they attempted to prepare a substitution product in a still different manner. They first tried to form a chlor-substituted phenyl sulfone by dissolving the substance in carbon bisulfide and treating it with chlorine, but nothing happened. When they found that phenyl sulfone took up a small amount of chlorine if it is treated with the gas when it is suspended in heated iodine-containing water, they conceived the idea that iodine might act as a catalyst. By mixing phenyl sulfone with iodine in the dry state, and introducing chlorine under dispersed light at 100°, they found that the phenyl sulfone went over into a no longer congealing thick liquid to which they attributed the formula $C_{10}H_8Cl_2SO_2$, and the equation of its formation they believed to be

$$C_{12}H_{10}SO_2 + 4\ Cl \longrightarrow C_{10}H_8Cl_2SO_2 + 2\ HCl.$$

They studied the properties of theis liquid, and upon analysis found it to conform to their formula for it. As at this time the three isomeric di-substitution products of benzene had not been explained on the basis of their being in different positions with respect to each other in the benzene nucleus, these men did not attempt to finally determine the structure of their compound.

When they treated chlobenzene with sulfur trioxide, they obtained compound which upon analysis was shown to have a formula whose empirical subscripts were the same as the compound described above.1) Otto may be quoted as saying, "Even a superficial glance at the properties of the above~~x~~ dichlor phenyl sulfone obtained by the action of chlorine on phenyl sulfone containing iodine, shows that it is not identical with that preparation obtained by us by the action of sulfur trioxide on chlorbenzene, consisting of brilliently glittering odorless crystals melting at 140-141°."

He accounted for this isomerism in the following manner, "Apparently the basis for this isomerism lies in the fact that in the bichloride arising from the sulfur trioxide and chlorbenzene, the chlorine is partly combined with the SO_2-containing phenyl and partly with the other phenyl; while in the compound coming from the chlorination of phenyl sulfone containing iodine, the chlorine is either exclusively in the one or the other atom-group. If we give to phenyl sulfone the formula

$$\left.\begin{array}{r} C_6H_5SO_2 \\ C_6H_5 \end{array}\right\} \text{ or } C_6H_5{-}S{-}O{-}O{-}C_6H_5,$$

then we can assign to the two chlorine compounds the following formulas:

(a) Dichlor diphenyl sulfone from SO_3 and C_6H_5Cl:

$$\left.\begin{array}{r} C_6H_4ClSO_2 \\ ClC_6H_4 \end{array}\right\} \text{ or } C_6H_4Cl{-}S{-}O{-}O{-}C_6H_4Cl.$$

(b) Dichlor diphenyl sulfone from Ph_2SO_2 and Cl_2:

$$\left.\begin{array}{r} C_6H_3Cl_2SO_2 \\ C_6H_5 \end{array}\right\} = \quad C_6H_3Cl_2\text{-}S\text{-}O\text{-}O\text{-}C_6H_5$$

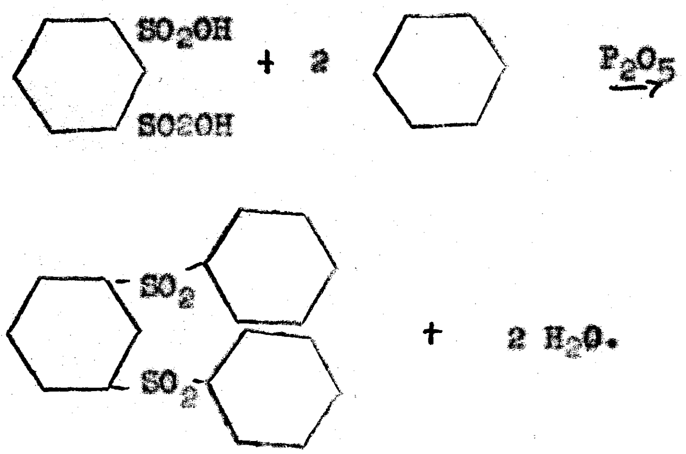
$$\text{or}\quad \left.\begin{array}{l} C_6H_5SO_2 \\ C_6C_3Cl_2 \end{array}\right\} = \quad C_6H_5\text{-}S\text{-}O\text{-}O\text{-}C_6H_3Cl_2.$$

"As Kekulé emphasizes", he continues, "the joining of one of the phenyl groups in the phenyl sulfone seems to take place through the sulfur of the SO_2-group and not through the oxygen. Phenyl sulfone must then have the formula

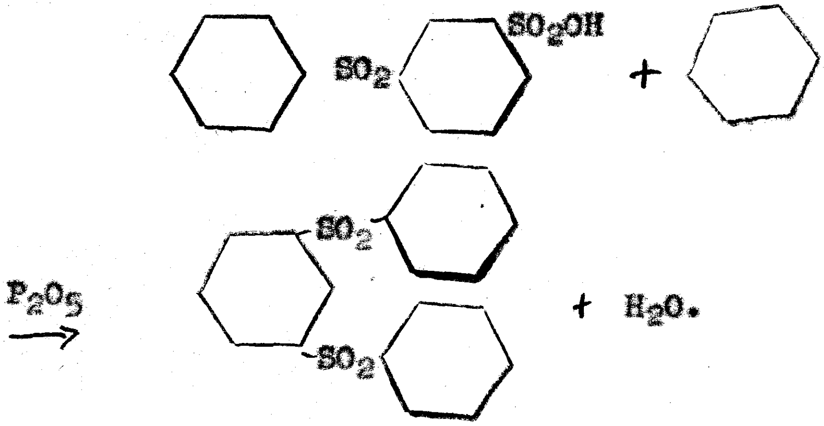
$$C_6H_5\text{-}S\text{-}O\text{-}O\text{-}C_6H_5 \quad \text{and not}$$
$$C_6H_5\text{-}O\text{-}S\text{-}O\text{-}C_6H_5.$$

The favor for the unsymmetrical constitution lies in the fact that the action of chlorine on the phenyl compound does not break it up into twosimilar benzene derivatives and SO_2Cl_2, but that the SO_2 remains attached to one of the phenyls as benzene sulfonic acid chloride, while the other phenyl is transformed into chlorbenzene."

The first successful analysis of a substitution product of phenyl sulfone was made by Robert Otto and Adalbert Rössing in 1886. They reported their work in a paper on "The Question of the Structure of Phenyl Sulfone Disulfonic Acid". 11) They established the fact that the mono-sulfonic-acid is the meta compound, in the following manner: A phenyl sulfone was prepared from meta benzene disulfonic acid and benzene in the presence of phosphoric anhydride according to the following equation:

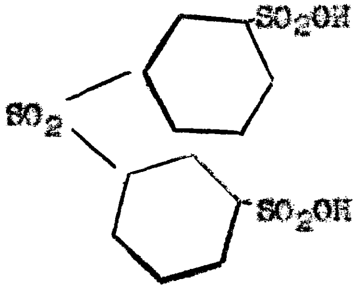


This proved to be identical with the derivative formed by treating the monosulfonic acid of phenyl sulfone (formed bybtreating phenyl sulfone with a molecular quantity of chlorsulfonic acid (11)) with benzene in the following manner:



This establishes the fact that the mono-substituted products are meta.

Otto and Rösseing concluded their paper by saying: "By the ease with which this compound (the monosulfonic acid of phenyl sulfone) allows itself to go over into the disulfonic acid, and the ~~xxxx~~ equivalence of the two phenyl groups in phenyl sulfone, it might now be assumed, that in the formation of the disulfonic acid from the monosulfonic acid, the group SO_2OH enters into the intact C_6H_5 group in the same position to the SO_2 group as the SO_2OH group already present in this manner:



If one wishes however to assume that in the formation of the disulfonic acid, the second SO_2OH group enters the C_6H_4 radical, then due to the undoubted equivalence of the two phenyl groups, the phenyl sulfone should allow a tri- or a tetra-sulfonic acid to be formed by the action of three or of four molecules of chlorsulfonic acid, which however, as has been shown, is not the case."

Schnid and Noelting 1) sought to produce a dinitro phenyl sulfone from nitrobenzene and sulfuric anhydride. They obtained a silver-bright, flakey, crystalline product, and compared it with the dinitro phenyl sulfone which Gericke obtained by direct nitration. The crystal form, solubility (insoluble in water, difficultly soluble in alcohol, and easily soluble in hot acetic acid) were the same for both products. But the melting point determinations by the different investigators gave different results, for Gericke found his compound to melt at

164°, while Schmid and Noelting reported that for their compound as 197°.

In the "Journal of the Chemical Society" (London), there is a reference in the index to an article on "p-dichlorodiphenyl sulfone". II) Quoting this, "One mol of chlorsulfonic acid and one mol of monochlorbenzene. The chief product was a chlor-benzene sulfonic acid, which, from the m.p. pf its chloride (55°) and of the corresponding amide (142°), proved identical with that discovered by Hutchings. (Jahresberichte, 1857, 450) In addition there was formed a dichloro-sulfobenzid (C_6H_4Cl)$_2SO_2$, apparently identical with that obtained by Otto (Annalen, CXLV, 28) by the action of SO_3 upon C_6H_5Cl."

But there was no analysis made that would warrant calling either of these compounds the para one.

Not much work was done on the substitution products of phenyl sulgone until after the war, when as has been previously mentioed, considerable quantities of the product were left over as a by-product from the sulfonation of benzene. M. Grandmougin did considerwork along the line of revising a table of the constants of these substituted derivatives. In his report III) he gave the following account of his attempted derivation of the structure of the dinitro compound.

"If phenyl sulfone is nitrated, a dinitro derivative (m.p. 201°) is obtained, which, from reduction with Na_2S for example, furnishes the corresponding diamido derivative (m.p. 168°). Its constitution has been established by transformation into the diphenol of the same position (m.p. 187°). This is found to be identical with the product obtained by M. Tassinari by oxidizing a dioxythiobenzene formed by the debromination of the condensation product resulting from the action of sulfuryl chloride on p-bromphenol in a solution of carbon bisulfide. As the dioxy derivatives in the 2-2' and 4-4' positions are known with certainty, and melt at 165° and 239° respectively, the dioxy derivative melting at 187° can only be the di-meta derivative (3-3'). This constitution was moreover very probable from the fact that the dinitro derivative, obtained by the direct nitration of phenylsulfide, can be synthesized by the action of the fuming acid on nitrobenzene."

The question which the about remarks give rise to is, how can a change in position from para to meta be accomplished so easily, as would have to be the case if the dimeta compound is formed by combining two para substitued rings?

Grandmougin also believes that the oily derivative which Otto obtained by chlorination of the phenyl sulfone, and which is classified by Beilstein as the m-m' derivative, is without doubt a mistake.

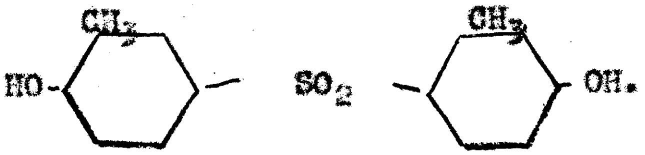
In looking over the work of Tassinari to which

Grandmougin referred '), it was found that he really gave no conclusive evidence that the dioxy derivative which he obtained were the di-meta ones.

Tassinari believed that the di-substitution products would have a symmetrical constitution, because by a priori reasoning, it would be assumed that the SO_2 group would exert the same directing influence towards both of the phenyl groups, and there are, according to him, no substances known which form unsymmetrical substitution products in the manner in which they would have to be produced in case they were formed by the direct substitution of the nuclear hydrogen atoms in phenyl sulfone.

On account of the tendency of several monosubstituted derivatives of benzene (he cited the well-known examples) to rearrange into the para-disubstituted ones, he thought that the para position would be the ones in which the entering groups would be located.

He obtained the dioxy (or dihydroxy) derivativex of phenyl sulfone by the use of bromphenol (he does not say which one) and sulfur dichloride, forming the acetyl derivative of the product resulting from this and oxidizing it. As he had a very small amount of this intermediate compound he did not analyze it but converted it all into the dioxy form, whose composition he found to agree with the formula $HOC_6H_4SO_2C_6H_4OH$. He believed that the dimethyl substitution product of the dioxy derivative which he obtained had the structure:



When he obtained picric acid in an attempted nitration of the dioxy phenyl sulfone, he did not make any further attepts. The fact that he did obtain picric acid would seem to indicate that the OH radicals were in the para positions. And from the above formula for the si-methyl derivative of the dioxy diphenyl sulfone, the same conclusion is to be inferred. For these reasons, it is difficult to see how M. Grandmougin may consider his dinitro compound to be the di-meta from this evidence.

The fact remains that the direct substitution procucts of diphenyl salfone have never been analyzed so that it may be said that their structure has been absolutely determined. There is also the question of the dichlor substituted compound. It is possible that in Otto's work, some of the product underwent further reaction, and decomposed into low-melting compounds, which lowered the melting point of the dichlor compound to such an extent that it appeared as a liquid. It may also be said that it would be very difficult to detect an error in the analysis of the final product due to this source, as the only difference in the composition of equal molal portions of chlorbenzene and the chloride of benzene sulfonic acid, and of dichlor phenyl sulfone is in the content of hydrogen, something which would be difficult to determine.

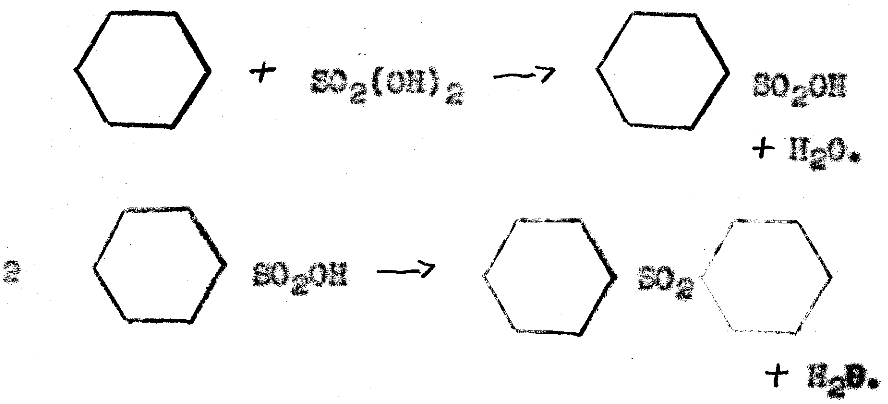
Thus there are two distinct problems left to be solved. 1) What is the structure of the di-substituted derivatives of phenyl sulfone, and 2) what is the true nature of the dichlo substituted phenyl sulfone?

*) "Annalen der Chemie und Pharmacie" -- 1835 - XII, 308.
**) "Annalen .... " -- 1856 - C, 207.
***) "Annalen .... " -- 1869 - CXLIX, 174.
§§) "Berichte der Chemische Gesellschaft" -- 1886, XIX, 3125.
§) "Annalen .... " -- 1868 - CXLV, 28.
§§§) "Berichte ... " -- 1886 -XIX, 2421.
!) "Berichte ... " -- 1876 - IX, 79.
!!) "Journal of the Chemical Society" -- 1879 - Abstracts, 229.
!!!) "Comptes Rendus de L'Acudemie des Sciences" -- 1922 - CLXXIV, 168-170.
°) "Gazzetta Chimica Italiona" -- 1889 - XIX, 345.

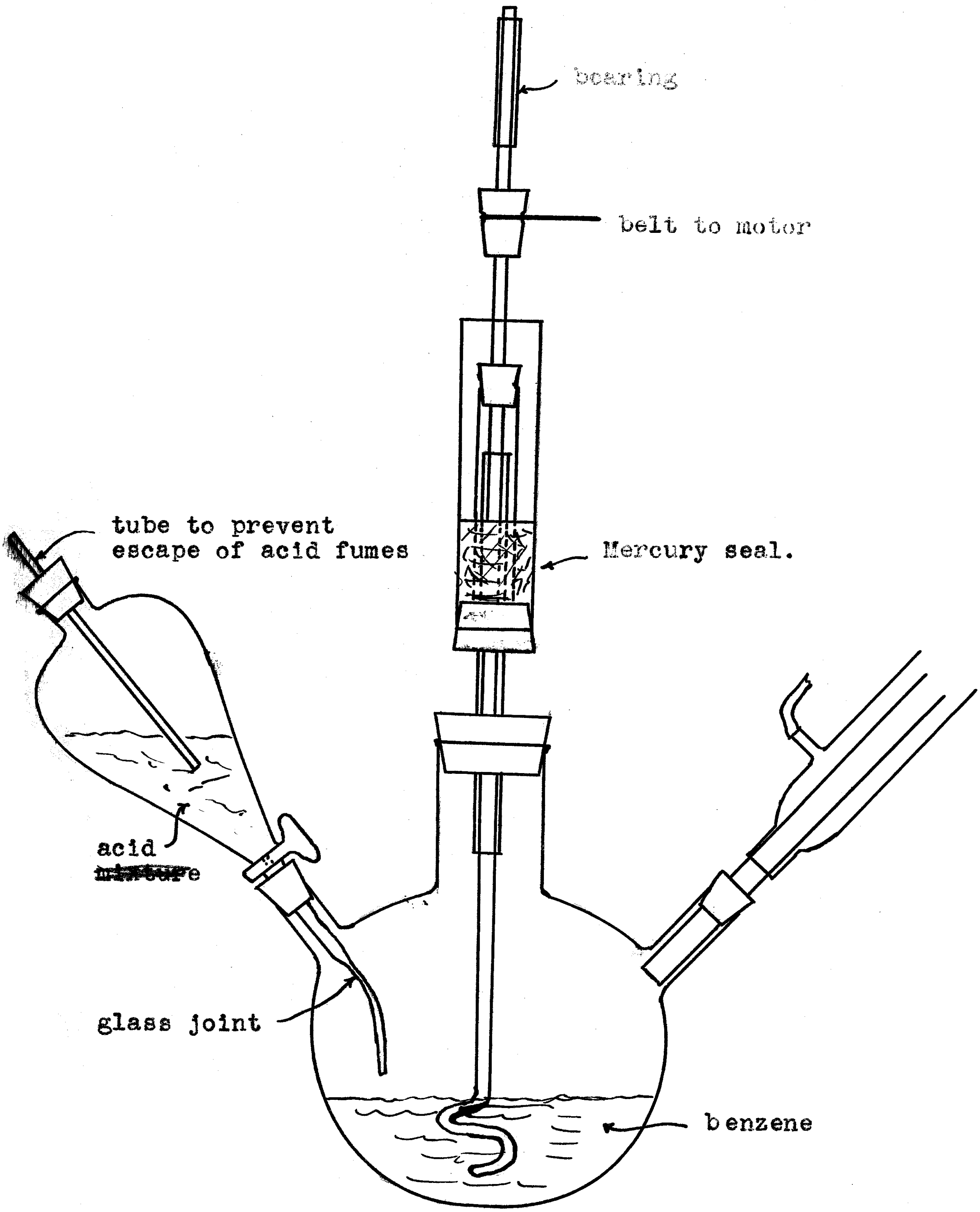
EXPERIMENTAL WORK.

The first step in the work was the preparation of phenyl sulfone. As the nitro compound was believed to be most easily prepared, it was decided to make the first determinations on it, and to work on the chlor compound afterwards.

The simplest way to prepare phenyl sulfone is by the action of fuming sulfuric acid on an excess of benzene. Berthelot *) studied the reaction in detail, and found that by using a large excess of benzene, and refluxing for some time, varying quantities of phenyl sulfone up to one-third the theoretical yield may be obtained. The reaction takes place in the following manner:



500 gm. of benzene were put in a flask as shown on the following page, and 175 gm. of sulfuric acid containing 50% excess SO_3 were gradually added from a separatory funnel, with continual stirring. After all the acid had been added the mixture was refluxed over a water bath at 100° for about



APPARATUS FOR THE PRODUCTION
of
PHENYL SULFONE FROM BENZENE.

six hours. This was treated with cold water, two layers eparating. The benzene layer was washed with water to free it of benzene sulfonic acid, and then allowed to evaporate to dryness. The solid was then recrystallized from hot alcohol, the last portions of the mother liquor being discarded to eliminate the impurities as much as possible. The melting point of the final product was 123-124°. 41 gms. were obtained.

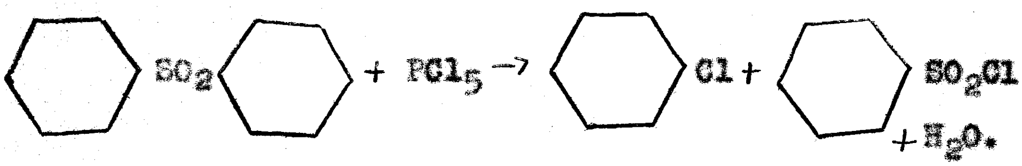
As this was not enough to work with, it was decided to make more of it by a more efficient method. Following the instructions of H.Beckurts and R.Otto **), the Friedel and Crafts synthesis was applied. Phenyl sulfonic acid, made from fuming sulfuric acid and benzene, was passed into a concentrated solution of sodium chloride, and allowed to crystallize out. The sodium benzene sulfonate thus obtained was washed with concentrated sodium chloride solution and dried. It was then treated with phosphorous pentachloride to obtain~~m~~ the benzene sulfonic acid chloride, the ~~acid chloride~~ Na salt being added gradually to the theoretical amount of the pentachloride in a flask. After the reaction was ended the mixture was put into cold water gradually, whereupon the acid chloride separated out. This was freed from water by distilling under reduced pressure at 140-150°. This was then treated with equal quantities of aluminum chloride and benzene. The reaction proceeded smoothly at about 60°, no outside heat being necessary. The phenyl sulfone obtained in this reaction was crystallized from alcohol as before. Its melting point was 124-126°.

For a trial nitration, 5 gm. of phenyl sulfone were treated gradually with a mixture of 6 gm. 1.5 nitric acid and 9 gm. 1.84 sulfuric acid, in a flask. Considerable heat was evolved and there were two layers formed. This was allowed to stand over night, when the whole thing turned solid. This was washed with water to free it of the acids, and with ether to take out the mono-nitro derivative that might have formed. After drying, the product was crystallized from hot acetic acid, 3 gm. of product melting at 196-198° being obtained. The filtrate was treated with water, more solid separating. As its melting poiny was 150-160°, it was not used.

The next batch was treated in a similar manner, 25 gm. of phenyl sulfone being taken. To save time, the mixture was heated on a water bath at a constant temperature of 55° for about three hours. It turned solid in that time and was treated in a manner similar to the preceding. The melting point of the product obtained after the first washing with ether was 170-179°, showing that it still was impure. After the first crystallization from acetic acid this had risen to 180-186°. When recrystallized, 17.5 gm. of product melting at 195 1/2-197° were obtained.

(The melting points of the dinitro compound as given by other investigators are: Gericke - 164°; Schmid & Noelting - 197°; Grandmougin - 201°).

A method for the absolute determination of the structure of the dinitro derivative of phenyl sulfone was suggested by the work of Otto ***) on the reaction between phenyl sulfone and phosphorous pentachloride. He found that the reaction took place according to the following equation when the substances were heated together for several hours on an oil bath at 160-170°. He considered his reaction completed when the mixture no longer congealed when it cooled, but as the melting point of the dinitro compound is so high, and the expected products are all solids, it would not be expected that this would be the case in the reaction between dinitro phenyl sulfone and phosphorous pentachloride.



As the reaction products were all solids, and liable to char or decompose at a high temperature, it was decided to add a little PCl_3 (which is one of the final products) to effect a more intimate mixture of the substances. 10 gm. of the dinitro compound were mixed with 14 gm. of pulverized PCl_5 in a flask, and about 4 gms. of PCl_3 added. This was refluxed on an oil bath at 160° for two hours. Then 6 gm. of PCl_5 were added as some of the other had sublimed and deposited on the walls of the flask where it could not take part in the reaction. As the amount of PCl_3 seemed to increase only very slowly, it was thought that the temperature of the contents of the flask were kept down by its presence. For this reason a small condenser made up of a short piece of glass tubing and a drying tube, was used. This permitted part of the PCl_3 to escape without letting any dampness into the reaction flask. After a short time the whole mass turned liquid, and PCl_3 seemed to be evolved more rapidly than before. Heating was continued for three hours more, and the reaction stopped.

Two ways of separating the products of the reaction presented themselves. One was to put them into cold water to separate out the inorganic materials, then treat the organic portion with dilute sodium hydroxide to form the sodium salt ~~of~~ from the acid chloride. There would now be another separation into two layers, and the organic one could be treated with alcohol to separate the nitrochlorbenzene from the unreacted phenyl sulfone derivative. Another was to dissolve the products in water as much as possible. The residue would then be treated with concentrated ammonium hydroxide to form the amide ~~of~~ from the acid chloride. The residue from this treatment would be treated with alcohol as before. The amide could be recovered by treating the solution in which it was dissolved with concentrated HCl. The disadvantage of the first method was that there would be difficulty in doing much with the sodium salt, whereas in the second method a product would be obtained which could be classified as to structure from its melting point.

The reaction products were treated according to this second method, but such small quantities of materials were obtained that they could not be satisfacorily worked with. And it seemed that the majority of the organic material was in the form of unreacted dinitro phenyl sulfone.

24 gm. of dinitro phenyl sulfone were treated in a manner similar to that in which the trial batch was treated. Heating was continued for almost thirty hours, in the hope of getting the reaction more nearly to completion. But the products had charred so much that it was practically impossible to do anything with them. It was hoped that there would be time to carry out another treatment, but there was not.

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*) "Berichte" -- 1876 - IX, 349.
**) "Berichte" -- 1878 - XI, 2066.
***) "Annalen" -- 1865 - CXXXV.

SUMMARY.

The main part of the work consisted in preparing the derivative which was worked with, and in trying to get the reaction whereby this derivative could be decomposed into components whose structures could be ascertained, to take place in a satisfactory manner. The method for obtaining the dinitro phenyl sulfone in considerable quantities was found, but there was not time enough to make the determinations of the structures of the products.

CONCLUSION.

One conclusion which can be made from the work on the problem of the structure of the directly substituted derivatives of phenyl sulfone is that the literature on the subject is rather conflicting. As most of the structures are based on a priori reasoning, and as there has been no work done to absolutely fix the structures of any of the derivatives of phenyl sulfone formed in this manner, it is hard to see how this could be otherwise.

It is believed that the method outlined and followed as far as possible in the above work, would satisfactorily solve the problem. The evidence favors the meta structure for the di-substituted products, and it is quite probable that the results obtained from an absolute determination would agree with this.