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Thesis

ATTEMPTS TO PREPARE THE SULPHONIC ACIDS OF TOLUENE

Submitted by

Katharine Marie Hale
(B.S. in Ed., Boston University, 1930)

In partial fulfillment of requirements for the degree of
Master of Education
1932

FIRST READER: Dr. Lyman C. Newell, Professor of Chemistry, Boston
University.

SECOND READER: Dr. J. Philip Mason, Assistant Professor of Chemistry,
Boston University.

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INTRODUCTION

This thesis is a record of the attempts made to prepare the sulphonic acids of toluene. Two methods of preparation were tried out first by using bromobenzene instead of the bromine derivatives of toluene, which are more expensive. A third method of preparation was tried using para-toluidine. The experiments using bromobenzene and para-toluidine are written up in detail.

In the literature, the existence and methods of preparing ortho- and para-toluene-sulphonic acids were mentioned, but no mention of the existence or methods of preparing meta-toluene-sulphonic acid was found, except general methods, which covered the entire group of sulphonic acids. There, was, however, reference made to the preparation of the barium salt of this particular acid. John J. Griffin describes this in his "Dissertation on the Reaction of Ethyl and Methyl Alcohol with Para-diazometatoluenesulphonic Acid in the the Presence of Certain Substances; and on Meta toluene-sulphonic Acid" (pages 36-37). He does not tell how he prepared the pure meta-toluene-sulphonic acid. Victor VonRichter in "Organic Chemistry" gave the properties (page 175) of the derivatives of meta-toluol-sulphonic

acid, which are contradicted by J. Bernard Coleman and Francis Arnall in "The Preparation and Analysis of Organic Compounds" (page 194). Coleman and Arnall claim that the derivatives of para-toluene-sulphonic acid have these properties.



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PREPARATION OF PHENYL SULPHONIC ACID

Phenyl magnesium bromide (C_6H_5MgBr) was prepared by adding a molecular weight (157 grams or 105 cubic centimeters) of bromobenzene (C_6H_5Br) dissolved in 150 cubic centimeters of absolute ether to a molecular weight (24 grams) of pure metallic magnesium turnings in 250 cubic centimeters of absolute ether. The bromobenzene was added slowly and the mixture was stirred constantly by an electric mixer. A three neck flask was used with a separatory funnel in one opening with the solution of bromobenzene in it, with the electric mixer in the middle opening, and with a condenser in the third opening, which was used to take care of the ether vapor. A separatory funnel was used to keep the rate of adding the solution of bromobenzene and absolute ether uniform and very slow. When the addition was complete, the solution, which was black, was filtered through glass wool to remove the excess of magnesium turnings. The black solution was phenyl magnesium bromide. During this reaction heat was generated.¹

To the phenyl magnesium bromide, a molecular

1. For illustration of this method see - Cohen, Julius Breed - "Organic Chemistry - Reactions" - Volume I - Pages 208 - 258.

weight (119 grams or 70 cubic centimeters) of thionyl chloride or sulphurous oxychloride, as it is sometimes called, (SOCl_2) was added. The thionyl chloride was added slowly and evenly from the separatory funnel, while the mixture was stirred constantly by the electric mixer. As the thionyl chloride was added, the temperature of the mixture increased. It was necessary to lower the apparatus, so that the three neck flask was resting in a pan of cold water. Even though the mixture was cooled by the cold water bath, the temperature of the mixture increased until it was finally necessary to set the flask in an ice bath. The mixture was allowed to cool in the ice bath for an hour without adding any thionyl chloride. about three fourths ($3/4$) of the thionyl chloride had been added at this point.

At the end of an hour, the mixture had solidified. It was impossible to add the thionyl chloride and stir the mixture with the electric mixer. The rest of the thionyl chloride was added slowly (in the hood). The mixture was stirred constantly with a large stirring rod. (The stirring rod was about 8 millimeters in diameter. A rod of less

diameter was not strong enough to stir the heavy pasty mixture.) It took about an hour and a half to add the last fourth of thionyl chloride, which was about 17 cubic centimeters.

This mixture was allowed to stand over night. One of the products, which should be present in this mixture, is phenyl sulphinyl chloride (C_6H_5SOCl), which is soluble in benzene.¹ Benzene was added to the mixture, which was now a light brownish yellow color. When most of the solid was dissolved in the benzene, it was filtered through a suction filter. The solution that came through to the flask was a dark amber color (or a light red-brown) color and was very clear. When all the phenyl sulphinyl chloride had dissolved, the apparatus to distill off the benzene was set up. Most of the benzene was to be distilled off and the small portion that would be left was going to be allowed to evaporate off slowly. It was found though that instead of pure benzene distilling off at the boiling point of benzene ($80^{\circ}C$) that there was a mixture of benzene and probably

1. Coleman, J. Bernard and Arnall, Francis - "Preparation and Analysis of Organic Compounds" - Page 193.

phenyl sulphinyl chloride distilling off. The liquid boiled at 60°C. A fractionating column was used to effect a separation, but a mixture of benzene and probably phenyl sulphinyl chloride distilled off again. Phenyl sulphinyl chloride melts at 38°C and fumes in the air.¹

"Phenyl sulphinyl chloride is rapidly decomposed by water or hydrolyzed by water to phenyl sulphinic acid (C_6H_5SOOH)."¹ Water was added to a small portion. No reaction took place, but on heating the solution to boiling and continuing to boil for five minutes, the water layer gave an acid test, when tested with blue litmus paper. Before the reaction took place, there were two layers with the benzene solution as the upper layer. After the reaction had taken place, the benzene layer was the lower one. The two layers were separated with a separatory funnel. The acid solution was evaporated down to a small volume. This was allowed to stand for one week and the water had evaporated at the end of this time leaving small needle-like white crystals.

1. VonRichter, Victor - "Organic Chemistry" - translated by E. E. Fournier from the 11th German edition - Page 180.

"Phenyl sulphinic acid melts at 83°C."¹

There were not enough crystals obtained to take a melting point, so about 100 cubic centimeters of the phenyl sulphinyl chloride and benzene solution were hydrolyzed. (This was done in an open beaker and the benzene vapor caught on fire.) The two layers were separated as before. The small volume of the acid solution was set aside for a week, but no crystals were formed from this portion. The carbon tetrachloride (CCl_4) must have reacted with this portion, because only a gummy brown substance was obtained from this acid solution. The last portion of the phenyl sulphinyl chloride and benzene solution was put in a large round-bottom flask with twice as much water and was set up to reflux. The mixture was refluxed for two days and hydrolysis did not take place. Both layers boiled, but the reaction did not go to completion. The top layer (phenyl sulphinyl chloride and benzene) boiled before the lower layer, although the layer of water finally boiled.

1. VonRichter, Victor - "Organic Chemistry" - translated by E. E. Fournier from the 11th German edition - Page 180.

A three neck flask with the electric mixer and a condenser was set up. A separatory funnel was not used. The third opening was sealed with a cork. Alkaline hydrolysis was tried. Fifteen per cent (15%) sodium hydroxide (NaOH) was used instead of water. A temporary emulsion was formed by using the electric mixer. The emulsion was heated for about three hours. Then the two layers were separated by a separatory funnel. The alkaline layer was made acidic with concentrated hydrochloric acid (HCl) and evaporated to a small volume. The solution became turbid. No crystals appeared, even after the solution stood for several weeks.

The other layer was a light orange brown. The benzene was distilled off from this and a dark reddish-brown liquid was left. An elementary analysis was run on this and a positive test for the presence of sulphur and a positive test for the presence of a halogen were obtained. Negative tests were obtained for bromine and iodine, but a positive test for chlorine.

A small portion of this liquid was treated with hydrogen peroxide (H_2O_2), but no reaction took

place, which showed that phenyl sulphinic acid was not present. "The air and oxidizing agents convert the sulphinic acids into their corresponding sulphonic acids."¹

Phenyl sulphonyl chloride ($C_6H_5SO_2Cl$) "is an oil, but" phenyl sulphonamide ($C_6H_5SO_2NH_2$) "is crystalline, and melts at $150^{\circ}C$."² This oil was treated with concentrated ammonia (NH_3), but no reaction was evident and no heat was evolved. The mixture was warmed and still no reaction took place.

1. VonRichter, Victor - "Organic Chemistry" - translated by E. E. Fournier from the 11th German edition - Page 180.

2. Perkin, W. H. and Kipping, F. Stanley - "Organic Chemistry" - Part II - Pages 395 - 396.

A second portion of phenyl magnesium bromide was prepared. To this, 100 grams (or 68 cubic centimeters) of thionyl chloride was added very slowly. The mixture was kept cool by setting the three neck flask in a pan of cold water. The addition of the thionyl chloride was done very slowly. It took about three hours and a half. When all of the thionyl chloride had been added, the pan of cold water was removed and the three neck flask was placed in a pan of boiling hot water for twenty minutes to be sure that all of the Grignard reagent had reacted. During the addition of the thionyl chloride, an excess of absolute ether (100 cubic centimeters) was added to the mixture in the flask by means of the condenser, in an attempt to keep the mixture in solution.

After this reaction was completed, there were only a few cubic centimeters of liquid and the rest was a dirty yellow solid. Cold water was added slowly to this solid and a great deal of heat was generated. Water was added until there was no further action. There were two layers, a water solution and a dark brown oil. The dark brown oil had a specific gravity less than water.

The two layers were separated with a separatory funnel. The water solution was tested with litmus and found to be acidic. It was also tested with aqueous silver nitrate (AgNO_3) and a white precipitate was obtained, which showed the presence of a halogen.

Ten per cent (10%) sodium hydroxide (NaOH) was added to the water solution and a white precipitate, which looked like magnesium hydroxide ($\text{Mg}(\text{OH})_2$), was obtained. This precipitate was filtered off by a suction filter. The filtrate was tested with blue litmus and found to be still acidic. More ten per cent (10%) sodium hydroxide was added and the solution filtered again. This reaction was continued until an alkaline test was obtained from the filtrate. The filtrate was made acidic with hydrochloric acid (HCl), evaporated down to a small volume and then set aside to evaporate to dryness slowly. Two different kinds of white crystals and an orange solution were obtained from this aqueous solution. The orange solution was filtered off the crystals. The orange solution was then extracted with ether and the aqueous portion from

this extraction was allowed to evaporate to dryness. More white crystals similar to the first ones were obtained. These white crystals were magnesium chloride ($MgCl_2$) and sodium chloride ($NaCl$). The first and second set of crystals were ground up and then extracted with ether. This procedure was repeated several times until the ether layer was colorless.

The ether was distilled off and a dark reddish-brown liquid remained. An elementary analysis was run on this liquid and positive tests were obtained for the presence of sulphur and for the presence of chlorine and negative tests for the presence of bromine and iodine.

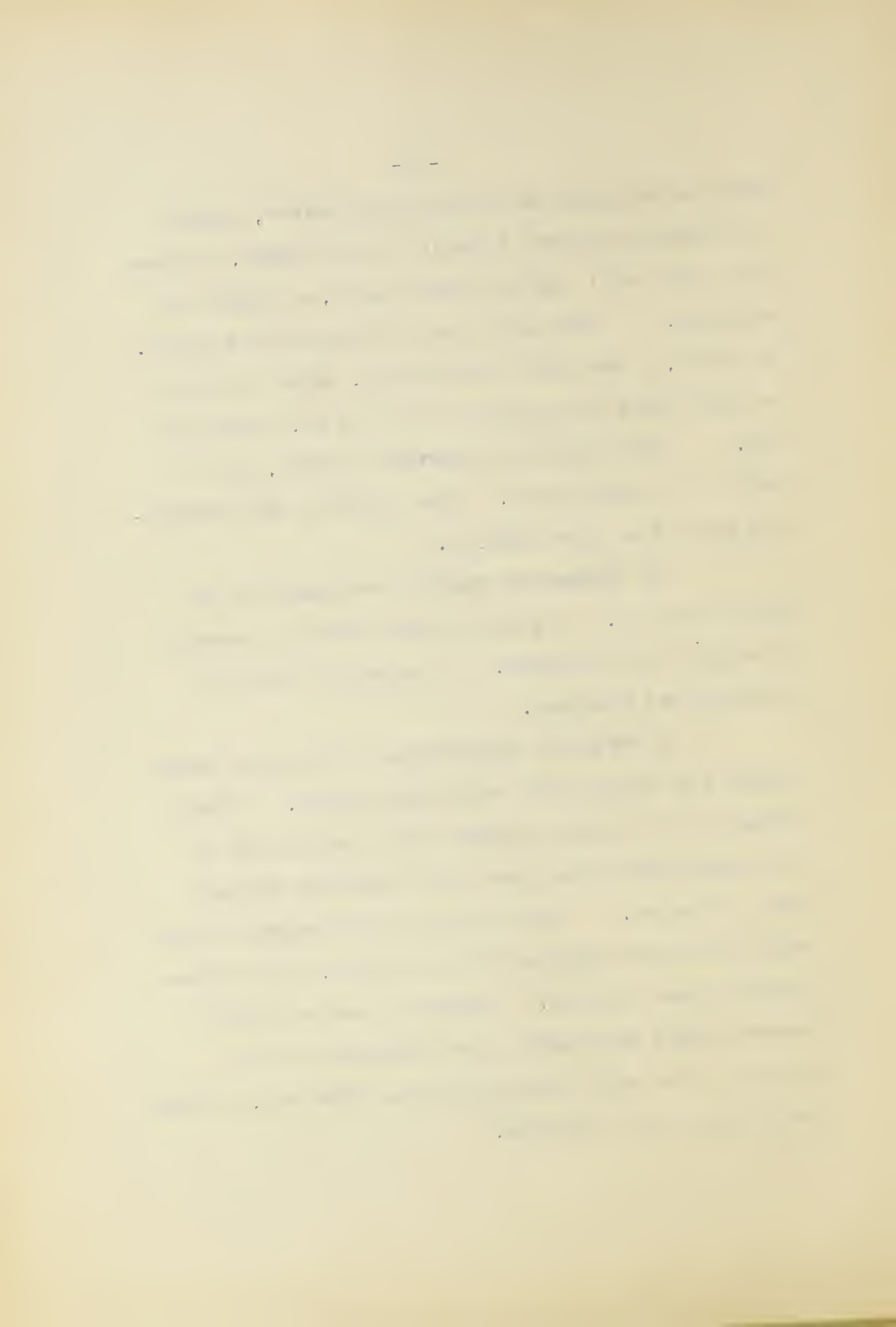
A small portion of this oil was treated with concentrated ammonia, but no reaction took place. The mixture was warmed, but still no reaction took place, which showed that the oil was not phenyl sulphinyl chloride or phenyl sulph^honyl chloride. Another small portion of this oil was treated with hydrogen peroxide, but no reaction took place.

On standing the dark brown oil, which was obtained when the dirty yellow solid from the thionyl

chloride reaction was treated with water, seemed to separate into two layers; the top layer, a clear dark brown oil; and the lower layer, a light tan emulsion. The dark brown oil would not distill. At 125°C, a few cubic centimeters, which seemed to be water with a few drops of oil in it, distilled off. The liquid was heated to 215°C, but it would not distill over. The liquid in the distilling flask was quite charred.

An elementary analysis was made on the dark brown oil. A positive test for the presence of sulphur was obtained. A negative test for nitrogen was obtained.

A few cubic centimeters of the dark brown liquid was washed with water three times. There seemed to be a white crystal which settled out in the separatory funnel when the liquid was washed with the water. One portion of the washed liquid was tested with aqueous silver nitrate, but no precipitate was obtained. Another portion of the washed liquid was tested with alcoholic silver nitrate and a white precipitate was obtained, showing the presence of a halogen.



The dark brown liquid was hydrolyzed in the presence of alkali for three hours. A light brown solid and a few cubic centimeters of dark brown solution (Filtrate I) were obtained. This was filtered by a suction filter and part of the residue was put on an unglazed porcelain plate to dry in the air. On drying in the air, it became dark brown.

This dark brown residue from the alkaline hydrolysis was extracted several times with ether. The ether was then distilled off and a dark brown oil was left. An elementary analysis was run on this oil, and the following results were obtained:-

Sulphur test	+
Nitrogen test	-
Halogen test	+.
Iodine test	-
Bromine test	-
Chlorine test	+

A few drops of the oil were then treated with concentrated ammonia. No reaction was evident and no heat was evolved. The mixture was warmed

but still no reaction took place.

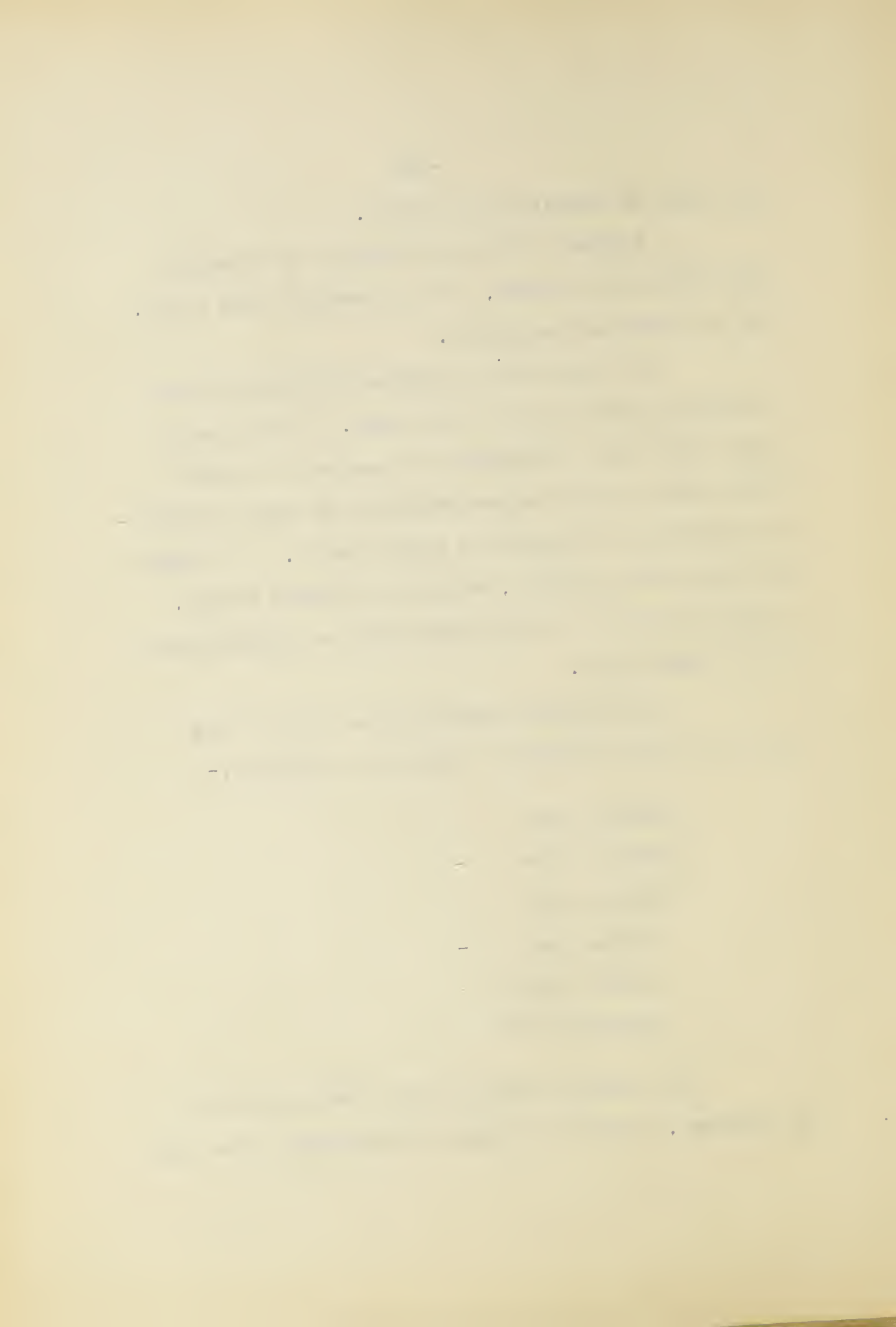
Another portion of the oil was treated with hydrogen peroxide, but no reaction took place. The oil remained unchanged.

The dark brown solution (Filtrate I) was extracted several times with ether. The aqueous layer from this extraction was heated on a water bath until a small volume remained and then evaporated carefully to dryness on a wire gauze. A light tan solid was obtained, which was allowed to dry. A water solution of this solid gave an alkaline test with litmus paper.

An elementary analysis was run on this solid and the following results were obtained:-

Sulphur test	+
Nitrogen test	-
Halogen test	+
Iodine test	-
Bromine test	-
Chlorine test	+

The melting point of this solid could not be obtained, because it seemed to decompose after the



temperature reached 150°C.

The ether was distilled off Filtrate I and a dark brown oil remained. An elementary analysis of this oil gave the following results:-

Sulphur test	+
Nitrogen test	-
Halogen test	+
Iodine test	-
Bromine test	-
Chlorine test	+

A few drops of the oil were treated with concentrated ammonia. No reaction took place and no heat was evolved. The mixture on warming remained unchanged.

Another portion of the liquid was treated with hydrogen peroxide. No reaction was evident and the oil remained unchanged.

No products were obtained which had physical or chemical properties corresponding to phenyl sulphinyl chloride or phenyl sulphinic acid. Phenyl sulphinyl chloride (C_6H_5SOCl) "has colorless plates, melts at 38°C, fumes in the air, and is

rapidly decomposed by water, with the regeneration of phenyl sulphinic acid."¹ Phenyl sulphinic acid (C_6H_5SOOH) "melts at $83^\circ C$ " and is easily converted into phenyl sulphonic acid by the air or a mild oxidizing agent.¹

1. VonRichter, Victor - "Organic Chemistry" - translated by E. E. Fournier D'Albe from the 11th German edition - Page 180.

A third portion of phenyl magnesium bromide was prepared. The separatory funnel was removed and a short glass tube was substituted in its place. Sulphur dioxide (SO_2) was passed into the solution, which had been cooled in an ice bath. The sulphur dioxide was dried by being passed through two sulphuric acid (H_2SO_4) wash bottles and through a dry trap. At first the glass tube was placed, so that it was a half an inch ($1/2$) above the surface of the phenyl magnesium bromide. The sulphur dioxide was passed in for three hours, but no reaction took place. Then the glass tube was placed just below the surface of the solution and the sulphur dioxide continued to be passed through.

On passing in the sulphur dioxide with the glass tube under the surface of the phenyl magnesium bromide, a solid yellow precipitate formed. Sulphur dioxide continued to be passed in until no more heat was liberated. Enough heat was evolved, so that the ether refluxed gently for a time even though the flask was in an ice bath. The solution was stirred continuously. The addition of sulphur dioxide was continued until it was impossible to use the

mechanical stirrer.

This addition took about four hours after the glass tube had been placed under the surface of the liquid. The excess sulphur dioxide was removed by connecting the top of the condenser to an air condenser by means of a double right angle bend. The air condenser had a two-hole stopper. In the second hole there was a right angle bend which connected to the tap water by a long rubber tube. This allowed a steady flow of water down the air condenser, which absorbed the excess sulphur dioxide forming sulphurous acid (H_2SO_3). The air condenser was connected to a bottle, which was filled with water and which had a two-hole stopper. The bottle had an outlet which went to the sink and thus carried the sulphurous acid off.

After the reaction was complete, the solution was neutralized by the addition of 49 grams (1/2 mole) of sulphuric acid (H_2SO_4) in 500 cubic centimeters of water, which served to decompose the addition product. A half mole of magnesium hydroxide ($Mg(OH)_2$) was formed, which made it necessary to neutralize with a half mole of sulphuric acid.

Inasmuch as the product had caked on considerably on standing overnight, some time was required for all to pass into solution. The ether and water layers were separated. A small amount of black dirt-like substance was removed, which contained small particles of unreacted metallic magnesium turnings.

The water and ether layers were both treated with ten per cent (10%) ferric chloride (FeCl_3). No reaction took place. With ten per cent (10%) ferric chloride, sulphinic acids are precipitated as orange precipitates.

The ether layer was dried over anhydrous calcium chloride (CaCl_2) and then the ether was distilled off using a fractionating column to effect a good separation. A dark brown oil remained in the distilling flask. On standing small crystals settled out and the oil had the odor of phenol. The yield was so small that it was impossible to identify the final product.

On treating the water layer with concentrated sulphuric acid, a very fine yellow precipitate was formed. This was extracted with ether. (Treat-

ing with sulphuric acid should have precipitated any of the sulphinic acid as the magnesium salt.)¹ This ether extraction was dried over anhydrous calcium chloride and then the ether was distilled off using a fractionating column. Phenol was obtained again.

1. Rosehein and Singer - "Deutsche Chemische Gesellschaft Berichte" - Volume 37 - Page 2152 - (1904).

Para-toluene diazonium sulphate was prepared by dissolving thirty (30) grams of para-toluidine in ninety (90) grams of concentrated sulphuric acid and three hundred (300) cubic centimeters of water. The solution was cooled to 5°C and a solution of twenty-four (24) grams of sodium nitrite (NaNO_2) in forty (40) cubic centimeters of water was added. After standing for three minutes it gave a positive test with potassium-iodide starch paper. It was also tested with sodium acetate solution and no precipitate was formed, showing that there was an excess of nitrous acid (HONO).

The solution was kept cool with an ice-salt mixture. Sulphur dioxide was passed in for ~~an~~ hour. The solution remained clear. Without interrupting the stream of gas, with continual stirring by an electric mixer, and with careful cooling, finely powdered copper was added little by little. (The copper powder was washed before using with ether to remove any traces of oil.) The sulphur dioxide was passed in for three hours in all. (A stream of sulphur dioxide is passed through the solution during the addition of the copper powder, because the sulphur dioxide tends to come off with the nitrogen.)

The mixture was filtered. The filtrate, which was blue, showing the presence of copper sulphate (CuSO_4), was extracted with ether (Extraction I). The residue was also extracted with ether (Extraction II). Both extractions were then treated with sodium carbonate solution (Na_2CO_3). A slightly green colored solution was obtained from this treatment. This solution was then acidified with dilute sulphuric acid.

After acidifying with dilute sulphuric acid, a very fine white precipitate was obtained, which went through the filter, when filtered by suction. This solution was then extracted with ether and the ether allowed to evaporate off slowly at ordinary temperature. Small needle-like white crystals were formed. These crystals were not pure, because there was an orange precipitate also present.

The crystals were dissolved in hot distilled water and the hot solution filtered by the suction filter. The solution was then cooled in an ice bath. Care was taken at this point to be sure that all the apparatus used was clean, so that the crystals would not be contaminated by the presence of iron. This was the reason that distilled water was used for the recrystallization.

On purification the crystals were white and very flaky. There was a yield of four and three tenths (4.3) grams, which was a ten per cent (10%) yield. When the crystals had dried, the melting point of them was taken. The melting point of para-toluene-sulphinic acid was found to be 87°C.

Three and five tenths (3.5) grams of the acid was dissolved in water and treated with sodium hydroxide (NaOH) to form the sodium salt of the acid. This solution was filtered and the salt was dissolved in hot water (50 cubic centimeters) containing one and six tenths (1.6) grams of potash. Then three and nine tenths (3.9) grams of potassium permanganate ($KMnO_4$) was added and the whole heated on a water-bath for a half an hour. The excess of permanganate was then removed by adding a small quantity of alcohol. (Care should be taken here, because the alcohol causes the solution to spatter.) The precipitated manganese dioxide was removed by filtering the hot liquid. The filtrate was tested with a drop of alcohol to be sure that all the permanganate had been removed.¹

The filtrate was then treated with saturated

1. "Deutsche Chemische Gesellschaft Berichte" - Volume 32 - Page 1156 - (1899).

sodium chloride solution. Enough solution was added to saturate the solution and finally a little sodium chloride crystals were ground up and a pinch added. This did not dissolve, showing that the solution was saturated. No precipitate was obtained.

Another part of the para-toluene-sulphinic acid was dissolved in water and heated to boiling and the solution was neutralized with barium carbonate. The solution was then filtered and evaporated to a small volume. On cooling the barium salt of the sulphinic acid crystallized out.¹

The barium salt was treated the same way that the sodium salt was treated. After adding the alcohol to the potassium permanganate mixture and filtering, the filtrate was made neutral with dilute hydrochloric acid and filtered. The filtrate was treated with saturated barium chloride solution. A slight precipitate was formed. Then a little barium chloride was ground finely and a pinch added to be sure that the solution was saturated. This dissolved and a little more was added, which did not dissolve, which proved that the solution

1. Griffin, John J. - "Dissertation on the Reaction of Ethyl and Methyl Alcohol with Para-diazometatoluene Sulphonic Acid in the Presence of Certain Substances; and on Metatoluene Sulphonic Acid"

was saturated. There was only a slight trace of a precipitate, but not enough precipitate to filter from the solution. This may have been the barium salt of para-toluene-sulphonic acid.

CONCLUSION

The experiments using the Grignard reagent and thionyl chloride were not successful, although theoretically it should be possible to obtain sulphinic acids from this method. It may be that it is necessary to have a catalyst present to have this reaction go through to completion. This may also have been the difficulty with the Grignard reagent and the sulphur dioxide method.

The diazonium salt and sulphur dioxide preparation was successful, although the yield was very small. There was not enough para-toluene-sulphinic acid obtained to oxidize it to para-toluene-sulphonic acid.

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