

A STUDY OF THE OXIDATION
OF
NAPHTHOSULPHONIC ACID
TO THE QUINONE

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fillment of the requirements for the degree
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(Under the direction of Prof. John R. Taylor)

PURPOSE OF RESEARCH

The purpose of this experiment was to determine, to a certain extent, whether the method of preparation of the 8-sulfonic acid of 2-methyl-1,4-naphthoquinone as carried out by Aaron Bendich and Erwin Chargaff¹ is of very limited or of more general applicability by the use of naphthalene rather than 2-methylnaphthalene as the initial compound. The successful method employed by Bendich and Chargaff was the oxidation of the sulfonamide by means of chromic acid in glacial acetic acid.

The series of reactions which they carried out was as follows:

(1) The preparation of 2-methylnaphthalene-8-sulfonic acid by the sulfonation of 2-methylnaphthalene with chlorosulfonic acid.

(2) The preparation of 2-methylnaphthalene-8-sulfonyl chloride from the sulfonic acid by chlorination with phosphorus pentachloride.

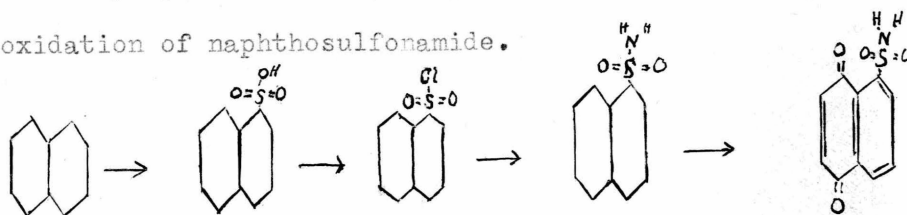
(3) The treatment of the sulfonyl chloride with aqueous ammonia to form the 2-methylnaphthalene-8-sulfonamide.

(4) The oxidation of the sulfonamide to 2-methyl-1,4-naphthoquinone-8-sulfonamide by the addition of chromic acid in 50% acetic acid to the pure sulfonamide in glacial acetic acid.

Since the procedure of Bendich and Chargaff was not followed in detail and the experiment was not carried beyond this point, their further procedure and the details of their work through the oxidation process have been omitted.

They had previously unsuccessfully attempted "to prepare the desired substance by direct sulfonation of 2-methyl-1,4-naphthoquinone with chlorosulfonic acid" and also "by the oxidation of 2-methylnaphthalene-8-sulfonic acid in acetic acid with hydrogen peroxide or chromic acid." In the attempt to perform the direct oxidation, partial hydrolysis of the sulfonic acid occurred, as indicated by the formation of small amounts of 2-methyl-1,4-naphthoquinone. "The oxidation of 2-methyl-naphthalene-8-sulfonyl chloride likewise failed to yield products of sufficient purity."

This thesis was likewise to include an attempt to oxidize naphthosulfonic acid directly; however, the work did not proceed beyond the preparation of 1,4-naphthoquinone-8-sulfonamide by the oxidation of naphthosulfonamide.



A SUMMARY OF THE METHODS SUGGESTED
FOR COMPLETION OF THE FOUR REACTIONS

Sulfonation of naphthalene

The procedure for the preparation of a-naphthosulfonic acid as recommended in Beilstein² is as follows:

a-naphthosulfonic acid is formed with b-naphthosulfonic acid by the action of concentrated sulfuric acid on naphthalene. The naphthalene is warmed to 80° with about an equi-molar amount of concentrated sulfuric acid. The separation of a- & b-naphthosulfonic acids is accomplished by conversion into the lead or calcium salts. The salts of the a-naphthosulfonic acid are the more soluble; therefore the mixture of salts is boiled with an insufficient amount of water for solution. This was the method used.

Also suggested in Beilstein is the mixing of finely divided naphthalene with oleum at 70°, the use of chlorosulfonic acid in carbon disulfide as the sulfonating agent, and in addition the use of $\text{NaH}_3(\text{SO}_4)_2$ as the sulfonating agent.

The material in Beilstein is derived from:

(1) The procedure of Merz and Weith³, which is as follows:

Naphthalene and sulfuric acid in a ratio of 10:9 are heated together for three hours at 100°. The unchanged naphtha-

lene is separated by pouring the reaction mixture into hot water, and the acids are separated as the lead salts.

(2) The procedure of Henry E. Armstrong⁴, which is as follows:

Naphthalene dissolved in carbon disulfide was reacted with an equivalent amount of chlorosulfonic acid. The reaction was terminated after distilling off the carbon disulfide by heating for some time at 100°. The residue remaining after treatment with water was naphthalene.

(3) The procedure of Ernst Lamberts⁵, which is as follows:

The polysulfate formed by the heating together of a bisulfate and sulfuric acid may be used for sulfonation of naphthalene in equivalent amounts. The acid thus formed is remarkably pure as compared to the acid from concentrated sulfuric acid.

The Chlorination of Naphthosulfonic Acid

Beilstein recommends that the sulfonyl chloride be prepared by the action of phosphorus pentachloride on naphthalene. The mixture is heated for 4 hours at 125°, cooled with ice and water, separated, and recrystallized from ether. This is very similar to the methods of Suvern Erdmann⁶ and of Vesely and Pac⁷.

F. Krafft and A. Roos⁸ suggest that the crystals of naphthosulfonyl chloride be purified by vaporization and condensation

under reduced pressure.

The Preparation of Naphthosulfonamide

Beilstein recommends the preparation of the sulfonamide by the treatment of the sulfonyl chloride with concentrated ammonia. This is the method of Kimberly⁹, who recrystallized the final product from alcohol.

The procedure recommended by Shriner and Fuson¹⁰ for the preparation of the sulfonamide from salts of sulfonic acids is carried out without isolation of the sulfonyl chloride. This method was followed closely in the experiment.

The salt is mixed with $2\frac{1}{2}$ times its weight of phosphorus pentachloride in a dry flask. The mixture is heated under reflux to a temperature of 150° for 30 minutes. It is then cooled and dry benzene is added. This suspension is warmed on a steam cone and filtered. The benzene filtrate, after washing with water, is added to concentrated ammonia with stirring. The sulfonamide is removed from the benzene phase by evaporation.

Preparation of the Quinone

According to O. Miller¹¹, who repeated the work of C. E. Grove¹², naphthoquinone may be obtained by the action of chromic

acid in glacial acetic acid on naphthalene. (Four parts chromic acid per part of naphthalene). Oxidation is complete at temperatures between 15-20°. At 100° a resinous product is obtained. In any case, there is some oxidation to phthalic acid. This is one of the procedures recommended in Beilstein. Since this was the method to be used, the investigation of other ways to prepare naphthoquinone was omitted.

EXPERIMENTAL PROCEDURE

Sulfonation of Naphthalene

Preparation of the lead salt

To prepare a-naphthosulfonic acid 200 gm. of concentrated sulfuric acid were added to 125 gm. of naphthalene. The temperature of the mixture was raised to 95° to fuse the naphthalene and thus to initiate a more vigorous reaction. The temperature of the mixture was maintained at 95° for one hour, during which time the mixture became pink in color. The temperature was then lowered to 90° and kept at this point for 2½ hours. The mixture was then poured into 200 cc of warm water. 75 gm. of the naphthalene separated from the solution and was removed by means of a suction filter. Therefore only 50 gm. could possibly have been sulfonated, with a possible theoretical yield of 115 gm. of naphthosulfonic acid.

The sulfate from the sulfuric acid and the naphthosulfonates were precipitated by the addition of 320 gm. of lead nitrate in aqueous solution. The sludge was concentrated to 800 cc and filtered.

To the precipitate was added 150 cc of concentrated ammonia water, which was intended to form the soluble ammonium salt of the naphthosulfonic acids, leaving lead hydroxide and lead sulfate

as residues which could be filtered off. The sludge was removed by means of a suction filter, washed, and discarded. Lead nitrate was again added to the filtrate until no further precipitation occurred. (160 gm. of lead nitrate were added--far in excess of the amount theoretically necessary for the complete precipitation of the naphthosulfonic acid present, denoting a high degree of impurity.) The precipitate was removed by filtration and leached four times with 500 cc of hot water. Only three grams of the lead salt of naphthosulfonic acid were obtained in the concentration of this solution by evaporation under reduced pressure.

Since the apparent yield of the lead salt of naphthosulfonic acid from the original precipitate of lead sulfate and lead naphthosulfonate was extremely low, the filtrate from this first precipitation (see paragraph #2) was concentrated by evaporation until most of the solute was removed. (345 gm.) This precipitate was largely inorganic (ammonium nitrate etc.) as was proven by subsequent attempts to form the naphthosulfonamide. Since this product was obviously extremely impure and could contain only a small amount of the lead naphthosulfonate (32 gm. as calculated from the solubility of lead naphthosulfonate in water) another sulfonation was attempted.

Preparation of the calcium salt*

In this second attempt to prepare naphthosulfonic acid 70 gm.

*Procedure suggested by Dr. Taylor

of fused naphthalene were poured into 110 gm. of concentrated sulfuric acid which was at a temperature of 80°. This temperature was maintained by means of an oil bath for 9 hours. At this point a drop removed and diluted with a little water showed only a slight turbidity. The odor of naphthalene was, however, still present. The mixture was then poured into 250 cc of water, but no naphthalene precipitated. A suspension of calcium hydroxide (5-1) was added until the acid was just neutralized (until a drop of the mixture turned phenolphthalein paper red). This required about 80 grams of calcium oxide. The neutral mixture was boiled and the precipitate filtered off. The hot filtrate, which presumably contained calcium naphthosulfonate, was evaporated to 20 cc in five stages, the precipitate being removed after each stage. 80 gm. of the impure calcium naphthosulfonate were obtained.

Preparation of the Naphthosulfonamide

The sulfonyl chloride was prepared first by the action of phosphorus pentachloride on calcium naphthosulfonate. 20 gm. calcium naphthosulfonate, which had been dried over night at 105°, was mixed with 50 gm. phosphorus pentachloride and the mixture was heated under reflux for thirty minutes at 150°. The mixture was cooled and 200 cc of dry benzene were added. The entire contents of the flask were then warmed on a steam cone, stirred

thoroughly, and finally filtered through a dry gravity filter. The residue was discarded.

The filtrate was washed in a separatory funnel with 50 cc of water five times, and then added with stirring to 200 cc of concentrated ammonia. The reaction was vigorous and was accompanied by the evolution of much heat and the formation of a dense white cloud of ammonium chloride. The benzene solution was added too rapidly and a large proportion of the reaction mixture was lost. Upon evaporation of the benzene phase, a thick oily liquid containing a few crystals was obtained. The melting point of these crystals was 140° (M. P. of a-naphthosulfonamide is given as 150°). The precipitate obtained by retreating the oily liquid with concentrated ammonia had a melting point above 230° (MP of b-naphthosulfonamide is 215°).

Because of the loss of a large proportion of the reaction mixture, the entire process was repeated with the following variations and results:

The solution of naphthosulfonyl chloride in benzene was added to the 200 cc of concentrated ammonia over a period of 25 minutes. The mixture was stirred mechanically. The benzene layer was concentrated, yielding approximately one gram of naphthosulfonamide. The ammonia phase which was yellow in color was neutralized with hydrochloric acid and evaporated almost to dryness. To the residue

thus obtained was added the oil from the benzene phase, and the mixture was subjected to continuous extraction with benzene, and thereafter with ether. The solutions obtained in this way were concentrated to an oil and combined. This oil was extracted repeatedly with concentrated ammonia, which was allowed to stand over the oily phase for an average of five hours before it was filtered off. A total of 500 cc of concentrated ammonia was used in this manner. The ammoniacal solutions were boiled to drive off a large proportion of the ammonia, and the light brown precipitate which formed upon cooling and standing was filtered off. These crystals were large, thin plates, a few of them 2-3 millimeters in diameter. The yield was 7 gm. after recrystallization from 85% alcohol.

The attempt to prepare the α -naphthosulfonyl chloride from the highly impure lead naphthosulfonic acid was unsuccessful. 30 gm. of the lead salt dried at 105° for four hours was mixed with 50 gm. of phosphorus pentachloride. Hydrogen chloride and some chlorine was evolved until the pentachloride was exhausted.

A further attempt to dry another 30 gm. sample of this lead salt was unsuccessful. The salt first dissolved in its own water of crystallization and, after being in the oven at 120° for 48 hours, was a hard mass which showed signs of considerable loss through sublimation. Chlorination was not attempted on this sample.

Oxidation to the Quinone

To 3.49 gm. of naphthosulfonamide suspended in 34 cc of glacial acetic acid at a temperature of 80° was added a solution of 7 gm. of chromic acid in 14 cc of 50% acetic acid, this addition requiring a period of 5 minutes. The mixture turned dark green and heated itself strongly, accompanied by the evolution of a gas. Immediately after the completion of the addition of chromic to the suspension, the reacting mixture was cooled to 15°, at which temperature it was maintained for 15 minutes. It was then left at room temperature for 30 minutes.

150 cc of water were added and the resulting precipitate was filtered off. This precipitate was dark yellow in color, and weighed 1.41 gm. (36% yield).

An attempt was made to recrystallize the quinone from 85% ethyl alcohol. At first the staining impurities dissolved in the alcohol, leaving a bright yellow residue. When the temperature of the alcohol was raised to boiling by heating on a water bath, the substance suddenly went into solution and the alcohol rapidly became black. Upon rapid cooling a dark greenish-yellow precipitate settled out immediately. This was filtered off. A bright yellow precipitate settled out after the alcohol solution was allowed to stand over night.

In both of these precipitates the presence of sulfur and nitrogen was indicated in a sodium fusion test. The presence

of an oxidizing agent was indicated in that a sample of the precipitate discolored freshly distilled aniline almost immediately.

It appeared that the 1,4-naphthoquinone-8-sulfonamide had been prepared, but no quantitative determination of composition has been made.

SUMMARY

Calcium naphthosulfonate was prepared by the action of concentrated sulfuric acid on naphthalene; the naphthosulfonic acid was then neutralized with calcium hydroxide.

α -Naphthosulfonamide was prepared by the action of phosphorus pentachloride on calcium naphthosulfonate followed by reaction with ammonia.

1,4-naphthoquinone-8-sulfonamide was prepared by the action of chromic acid in acetic acid on α -naphthosulfonamide.

C O N C L U S I O N S

The method of preparation of the 8-sulfonic acid of 2-methyl-1,4-naphthoquinone as carried out by Aaron Bendich and Erwin Chargaff is of a wider range of applicability than had been shown before this experiment. The extent to which this reaction may be applied to substituted naphthalenes will have to be determined by future investigation.

It would also be of interest to investigate the reaction between 1,4-naphthoquinone-8-sulfonamide and 85% ethyl alcohol which occurred during the attempted recrystallization of this substance in 85% alcohol.

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