

## **Copyright Warning & Restrictions**

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

**Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation**

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

ESTERS OF SULFANILIC  
AND SUBSTITUTED SULFANILIC ACIDS

BY

STEPHEN J. KOVALSKY

A THESIS  
SUBMITTED TO THE FACULTY OF  
THE DEPARTMENT OF CHEMICAL ENGINEERING  
OF  
NEWARK COLLEGE OF ENGINEERING

IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE WITH A  
MAJOR IN CHEMICAL ENGINEERING

NEWARK, NEW JERSEY

1955

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING  
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

NEWARK, NEW JERSEY

MAY, 1955

TABLE OF CONTENTS

	<u>Page</u>
1. Title Page . . . . .	1
2. Approval . . . . .	2
3. Table of Contents. . . . .	3
4. Abstract . . . . .	4
5. Acknowledgement . . . . .	5
6. Introduction . . . . .	6
7. Experimental Phase . . . . .	12
Part I. Alcoholysis Reactions in an Aqueous Medium Involving Esters of Sulfanilic Acid . . . . .	12
Part II. Alcoholysis of Butyl Sulfanilate in a Non-Aqueous Medium. . . . .	15
Part III. Alcoholysis Reactions Under Press- ure Involving Butyl Sulfanilate. . . . .	18
Part IV. Preparation of p-Acetaminobenzene- sulfonic Acid Esters in an Aqueous Medium	23
Part V. Preparation of Esters of p-Acetamino- benzenesulfonyl Chloride in a Non-Aqueous Medium . . . . .	29
8. Summary . . . . .	34
9. Bibliography . . . . .	35

## ABSTRACT

Attempted esterification of p-acetaminobenzene-sulfonyl chloride with any of the low molecular weight alcohols in aqueous systems always results in the formation of sulfanilic acid. When conducted in a non-aqueous medium, the desired esterification did not occur. A water soluble compound formed, instead, which has not yet been identified.

A study was made of sulfanilic acid esters. Alcoholysis reactions involving the butyl ester and methyl alcohol were successful only when the reaction was conducted under pressure and under anhydrous conditions.

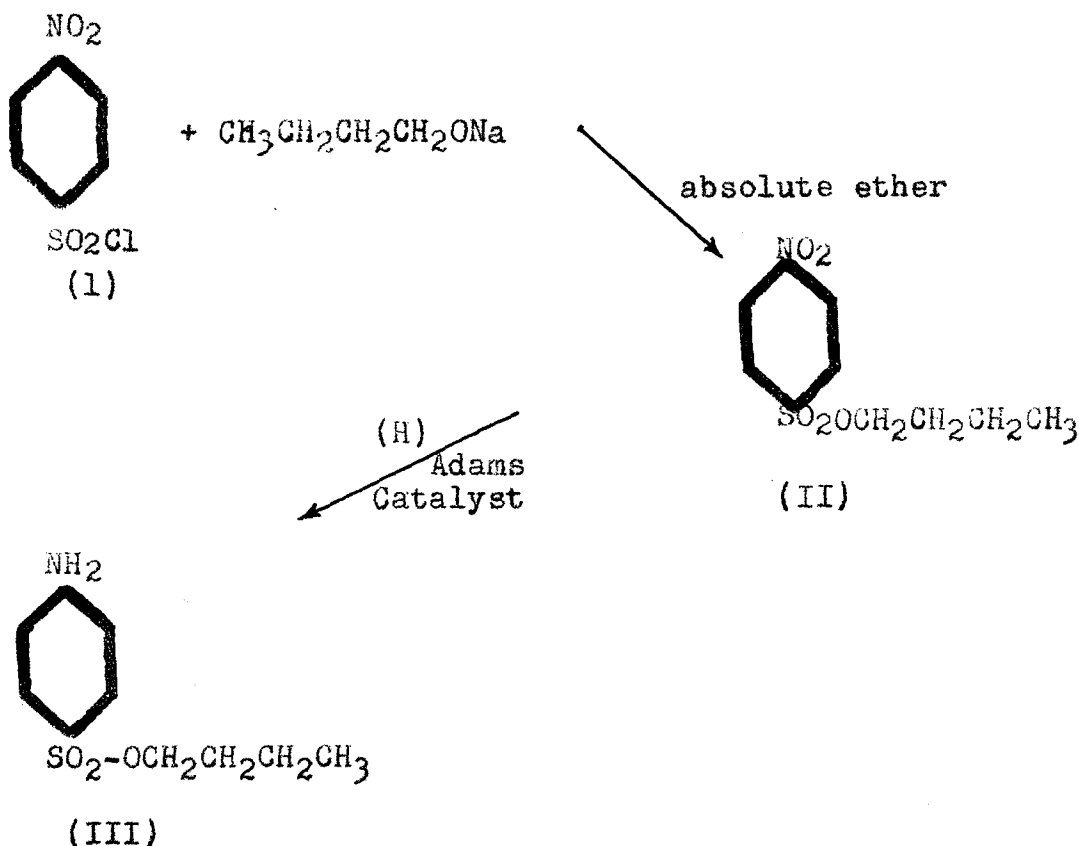
ACKNOWLEDGMENT

Grateful acknowledgment must be made to Dr. Saul I. Kreps of the Chemical Engineering Department, Newark College of Engineering for his timely advise and assistance at critical phases of the program.

## INTRODUCTION

This study was originally intended to develop methods of preparing sulfanilic acid esters. Attention was directed towards an investigation of reactions involving sulfanilic acid and acetylated sulfanilic acid esters. No references were found in Chemical Abstracts or Beilstein on work conducted along the lines selected. For this reason, it was assumed that the information presented here is the result of original research.

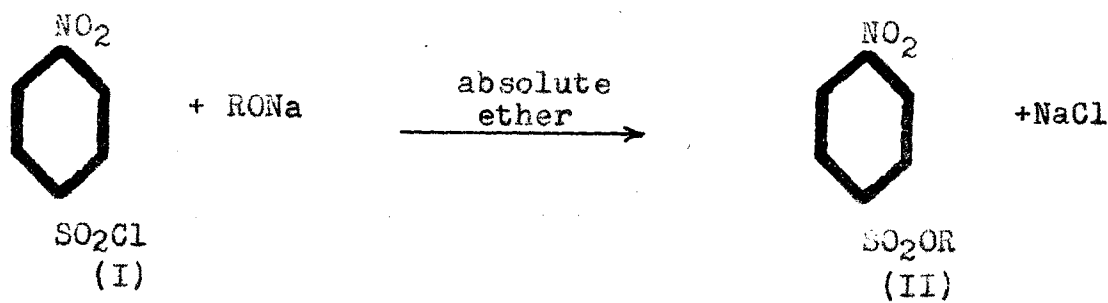
Several methods of preparing esters of sulfanilic acid have been developed in recent years (1, 2, 3). The methods used in preparing these intermediates for study are those advanced by Walters (1) and Kuhn and Ruelius (2).





Walters prepared the ethyl ester of sulfanilic acid by reducing the nitro group of ethyl p-nitrobenzenesulfonate in absolute alcohol. The reduction was accomplished in an autoclave at 35-40 pounds per square inch. The anhydrous reaction was catalyzed by freshly reduced Adams catalyst.

Kuhn and Ruelius have detailed a general method for preparing esters of p-nitrobenzenesulfonyl chloride.



Sodium is added to the absolute alcohol to be esterified. This cooled solution is then added with stirring to a vessel containing the p-nitrobenzenesulfonyl chloride (I) mixed with absolute ether. After refluxing for thirty minutes, the solution is concentrated in vacuo, then cooled and filtered.

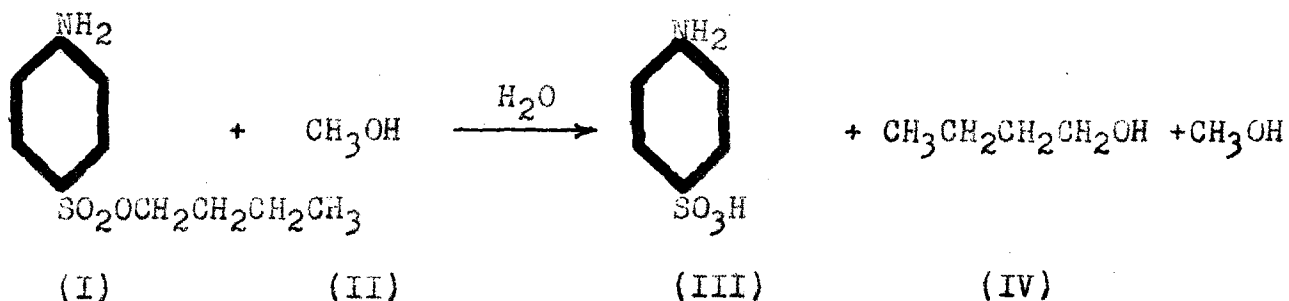
The filtration residue, consisting mainly of the desired ester, is purified by recrystallization from absolute ether.

The intermediate compound, butyl p-nitrobenzenesulfonate (II), was prepared in bulk since it was comparatively stable and could be stored. It was used as needed in producing the unstable compound, butyl sulfanilate (III), which spontaneously decomposes to sulfanilic acid and butyl alcohol when in a dry state.

### Alcoholysis of Sulfanilic Acid Esters:

Various methods were employed in attempting the alcoholysis reactions using the butyl ester of sulfanilic acid and methyl alcohol.

In an aqueous medium, refluxing a mixture of water, methyl alcohol, (II), and the ester, butyl sulfanilate (I), for two hours resulted in the decomposition of the ester to sulfanilic acid and butyl alcohol. This occurred even when the reaction was not refluxed. Reactants left overnight produced the same result.



The same reactants when refluxed for 4 hours with no water present produced some of the methyl ester as indicated by the presence of free butyl alcohol. The amount, however, was too small to be determined quantitatively with the equipment available.

When placed in an autoclave and heated for one hour, however, the reaction proceeded well at 30 - 35 p.s.i. An 82% yield of the methyl ester was achieved, based on the amount of butyl alcohol obtained from a fractional distillation of the liquid phase. The methyl sulfanilate obtained was purified by filtration and recrystallization from absolute ether. It was identified by its melting point (92°) and also the melting point of the hydrochloride salt (340°).

#### Acetylated Sulfanilic Acid Esters:

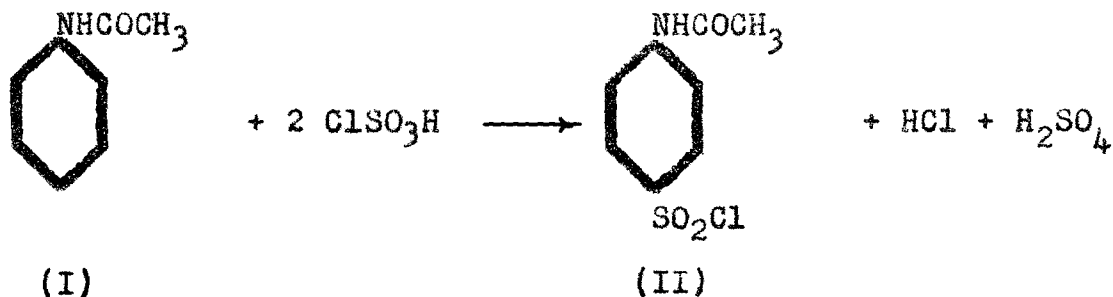
The second part of this study involved the preparation of acetylated sulfanilic acid esters. A method for their preparation has been reported by Keda (4), but the process is laborious and the compound desired must be isolated as an intermediate.

The procedure followed by Keda was used in studying the mechanism of the reaction of 3-(arylsulfonyl)-2-(arylsulfonylimino)-4-thiazolines with alcohols. When compounds with the general form of  $\text{RN}-\text{CH}=\text{CH}-\text{S}-\text{C}=\text{NR}'$ , where  $\text{R} = \text{R}' =$  p-acetaminobenzenesulfonyl, are reacted with primary alcohols in the presence of guanidine carbonate, a mixture of alkyl p-acetaminobenzenesulfonate and 2-arylsulfonyl-imino-4-thiazoline is formed. The second stage of the reaction occurs when the 2-arylsulfonylimino-4-thiazoline is alkylated by the alkyl ester.

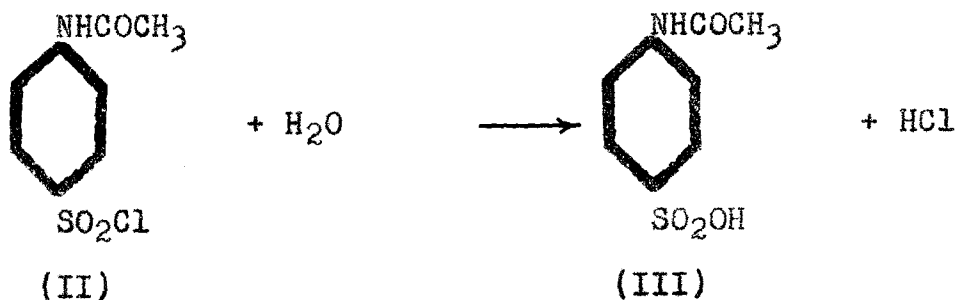
In the first stage of the reaction, the intermediate compound alkyl p-acetaminobenzenesulfonate was isolated. Difficulty in obtaining quantitative yields and problems in purification make direct esterification more realistic.

An attempt was made to develop a method suitable for the preparation of esters using any of the low molecular weight alcohols.

The starting compound used in these experiments was p-acetaminobenzenesulfonyl chloride (II). A convenient method for its preparation from acetanilide (I) is described in several texts (5,6).



The final crude product was purified and made anhydrous by recrystallization from hot chloroform. With water, it slowly hydrolyzes to the acid (7).



One series of experiments where the esterification was attempted in an aqueous medium resulted in the complete hydrolysis of the p-acetaminobenzenesulfonyl chloride to sulfanilic acid.

The same reaction was attempted in a non-aqueous medium. The results obtained in this series of experiments are detailed later. No firm conclusions have been reached concerning this reaction.

## EXPERIMENTAL PHASE

### Part I. Alcoholysis Reactions in an Aqueous Medium Involving Esters of Sulfanilic Acid.

A study of the alcoholysis reaction involving the butyl ester of sulfanilic acid and methyl alcohol was first attempted in an aqueous medium.

Procedure: The butyl sulfanilate was added to a mixture of water and methyl alcohol in a 200 ml. round bottom flask and was refluxed for 2 hours. Two concentrations of water and three of methyl alcohol were tried as shown in Table 1. In all cases, the cooled mixture consisted of a white crystalline precipitate and a slightly yellow solution.

The liquid phase was distilled to dryness leaving a small amount of residue. A qualitative analysis of the distillate showed it consisted of a mixture of water, and butyl and methyl alcohols.

Identification of the white crystalline residue as sulfanilic acid was achieved by physical constants, primarily melting point, solubility in a variety of solvents and the preparation of a derivative, the tri-bromoaniline salt, m.p. 329.8° (8).

TABLE 1

DATA

WEIGHT OF REACTANTS USED

<u>RUN</u>	<u>REFLUX TIME</u>	<u>WATER</u>	<u>BUTYL SULFANILATE ACID</u>	<u>MOLS</u>	<u>METHYL ALCOHOL</u>	<u>MOLS</u>	<u>YIELD SULFANILIC ACID</u>
1	2 hrs.	10 ml.	2 g.	.0087	1.472 g.	.0147	88 %
2	2 hrs.	10 ml.	2 g.	.0087	1.180 g.	.0368	85 %
3	2 hrs.	10 ml.	2 g.	.0087	2.36 g.	.0737	88 %
4	2 hrs.	10 ml.	2 g.	.0087	10.0 g.	.3125	92 %
5	12 hrs.	10 ml.	2 g.	.0087	1.180 g.	.0368	88 %

Identification of White Crystalline Residue as Fulfanilic Acid

1. M.P. decomposed > 280°.
2. Soluble in basic solutions, hot chloroform and benzene.
3. Insoluble in water, acid solutions and methyl alcohol.
4. Melting point of 2,4,6 tribromoaniline (329°) derivative checks with literature.

## DISCUSSION

The efficient hydrolysis of the butyl ester to sulfanilic acid was not unexpected. The literature indicates all of the esters of sulfanilic acid are unstable especially when dry, and they spontaneously decompose into sulfanilic acid and the alcohol.

The large excess of methyl alcohol in run 4 was needed to effect good refluxing. The butyl sulfanilate was miscible in every case. When the hydrolysis reaction commenced, however, its progress was monitored by the increase in bumping during refluxing, caused by the precipitation of the insoluble sulfanilic acid. During the final stages of the hydrolysis (after 50-60 minutes of reflux), the entire apparatus was mechanically agitated to reduce the severity of bumping. No deviation from this description was noted in the four runs except in run 4. There, the hydrolysis reaction extended over a longer period of about 70 minutes. This extended reaction period was apparently caused by the decrease in water concentration effected by the introduction of a large excess of methyl alcohol.



Part II. Alcoholysis of Butyl Sulfanilate in a Non-Aqueous  
Medium

The highly efficient hydrolysis obtained in earlier experiments indicated the desirability of conducting the reaction in a non-aqueous medium. A second series of experiments was attempted in dry methyl alcohol.

Procedure: In each case, precautions were taken to insure the complete removal of moisture. All glassware was heated before use and fitted with drying tubes. Absolute methyl alcohol was obtained by distillation through a calcium metal bed. Traces of moisture in the butyl sulfanilate were removed by heating the ester to 50° in vacuo in a water bath for 1 hour.

The butyl sulfanilate was added to the methyl alcohol in a 200 ml. round bottom flask. The two were refluxed for varying periods of time. In two runs, sodium methylate was added as a possible catalytic agent. The low boiling components were removed by vacuum distillation. This phase was redistilled at one atmosphere using a fractionating column. Two distinct phases were noted. The bulk of the distillate was methyl alcohol. A small amount of butyl alcohol was also isolated. The amount was not enough to determine quantitatively.

TABLE II

RUN	REFLUX TIME	<u>REACTANTS</u>				<u>ANALYSIS AFTER REACTION - (AMOUNT RECOVERED)</u>					
		BUTYL SULFA- NILATE	MOLS	METHYL ALCOHOL	MOLS	MeOH	MOLS	BUTYL ESTER	MOLS	BuOH	MOLS
1*	1 hr.	2.0 g.	.0087	20.0 g.	.625	19.7 g.	.615	1.96 g.	.0085	-	-
2	2 hrs.	2.0 g.	.0087	20.0 g.	.625	19.7 g.	.615	1.94 g.	.0085	Trace	-
3	4 hrs.	2.0 g.	.0087	20.0 g.	.625	19.6 g.	.612	1.90 g.	.0083	Trace	-
4*	4 hrs.	2.0 g.	.0087	20.0 g.	.625	19.6 g.	.612	1.91 g.	.0083	Trace	-

\* Experiments 1 and 4 in this series were catalyzed by 0.5 g. of sodium methylate.

## DISCUSSION

The reactants were separated by vacuum distilling off the volatile alcohols. In runs 1 and 4, where 0.5 g. of sodium methylate was added, the distillate from the first distillation was again sent through a fractionating column. When little or no free butyl alcohol was found, it was assumed that no reaction had occurred. As a result, the total amount of sodium methylate added originally was subtracted from the weight of the residue of the first distillation.

An attempt was made to confirm the data by filtering off the insoluble sodium methylate and weighing the filtrate. The mechanical losses incurred while working with the small amounts used in this series, however, resulted in serious errors as shown in the table.

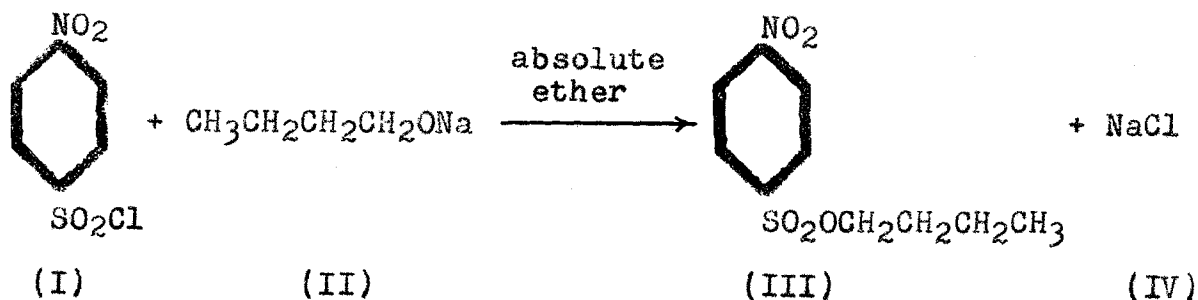
Part III. Alcoholysis Reactions Under Pressure Involving  
Butyl Sulfanilate.

The unsatisfactory results obtained earlier led to attempting the alcoholysis reaction at approximately the same conditions as are required to produce the ester itself.

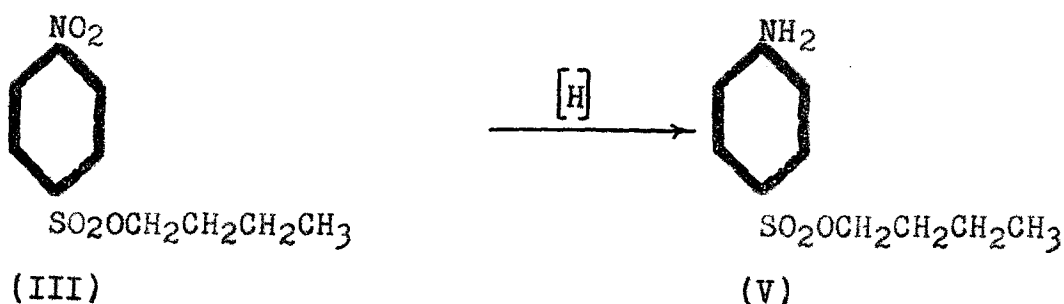
Procedure: The anhydrous butyl sulfanilate and methyl alcohol were added to a heavy walled flask fitted with a pressure indicator. The flask was heated until the pressure within was in the 35-40 p.s.i. range. Heating was then adjusted to maintain this pressure. In the two runs made in this series, the heating continued for 1 hour. The flask was then cooled, and the contents subjected to vacuum distillation. In run I, when it was established that an appreciable amount of butyl alcohol was present, no attempt was made to determine the amount as the methods of analysis used here are not well adapted to working in small quantities.

A second run was made using 10 times the amount of butyl sulfanilate as in run I. Comparable results were achieved. The butyl sulfanilate (V) for this series of experiments was made as follows:

Reaction A



Reaction B



In Reaction A, 34.5 g. of butyl p-nitrobenzenesulfonate (III) were produced by refluxing 20.0 g. of sodium butoxide (II) with 35.0 g. of p-nitrobenzenesulfonyl chloride in 150 ml. of absolute ether for one hour. The reacted solution was then transferred to a separatory funnel and washed with 50 ml. of water. The water layer was drawn off and the ether layer run into a distillation flask. The ether was distilled off in vacuo leaving butyl p-nitrobenzenesulfonate (III). The reaction was 84% efficient.

The butyl p-nitrobenzenesulfonate (III) was reduced in Reaction B to butyl sulfanilate (V). This was done by placing the 34.5 g. of butyl p-nitrobenzenesulfonate (III) obtained from Reaction A in a pressure vessel along with 150 ml. of absolute butyl alcohol and 1 g. of freshly reduced

Adams catalyst ( $\text{PtO}_2$ ). Approximately 1 g. of hydrogen chloride gas was added last. The mixture was heated until the pressure within the vessel was in the range of 35 - 40 pounds per square inch. Heating was adjusted to maintain that pressure for thirty minutes.

The contents were then cooled, and filtered to remove the catalyst. The bulk of the butyl alcohol was removed by distillation in vacuo. When the residue was diluted with 50 ml. of absolute ether, the crystalline hydrochloric acid salt of butyl sulfanilate formed. The crystals were removed by filtration. They melted at  $330^\circ$  which agreed with the literature.

Butyl sulfanilate was made by dissolving the crystals in ice water and adding with stirring an excess of sodium bicarbonate. The oil formed was separated by means of a separatory funnel. Twenty grams of butyl sulfanilate (V) were formed. This represents a reduction efficiency of 66%. The product was made anhydrous by heating at  $50^\circ$  in vacuo for thirty minutes.

TABLE III

	<u>Run 1</u>	<u>Run 2</u>
Heating time	1 hr.	1 hr.
Catalyst used	none	none
Pressure	35-40 p.s.i.	35-40 p.s.i.
Weight methyl alcohol used	20.0 g.	200.0 g.
Mols methyl alcohol used	0.625	6.250
Weight butyl ester used	2.0 g.	20.0 g.
Mols butyl ester used	0.0087	0.087
The product methyl sulfanilate	-	13.8 g. of a heavy oil which slowly crystallized
Moles of product recovered	-	0.0738
Yield of methyl ester	-	82%
Yield of butyl alcohol	-	82%
Weight of methyl alcohol recovered	-	194.10 g.
Mols of methyl alcohol recovered	-	6.07
Weight of butyl alcohol recovered	-	4.48 g.
Mols of butyl alcohol recovered	-	0.060

Identification of methyl sulfanilate:

1. Melting point of 90-92° agrees with literature (9).
2. The melting point of the hydrogen chloride salt also agrees with the literature (340°C.) (9).

## DISCUSSION

The experiments completed to date on this subject all used small amounts of the butyl ester because of the cost and complex preparation involved. It was felt that this amount was sufficient for the exploratory nature of the work.

The increase in the weight of reactants used for run 2 was made to facilitate the determinations for each constituent and also to reduce the effect of mechanical losses.

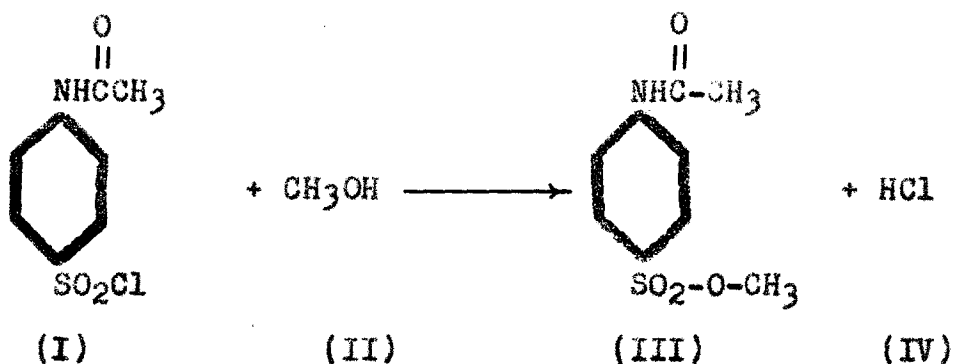
The results of run 1 indicated that an alcoholysis reaction had occurred. Run 2, essentially a large scale re-run of run 1 was then made with the overall operation carefully monitored.

After one hour of heating, the volatile constituents were vacuum distilled out of the reaction vessel. A total of 199.27 grams were extracted in this manner. Fractional distillation of this phase resulted in the isolation of 4.48 g. (0.060 moles) of butyl alcohol.



Part IV. Preparation of p-Acetaminobenzenesulfonic Acid  
Esters in an Aqueous Medium

This series of experiments was conducted to study the following possible reaction:



Procedure: Varied test conditions were applied to the above reaction in an effort to discover the key to the reaction in an aqueous medium.

The procedure followed was to add the p-acetaminobenzenesulfonyl chloride (I) to a mixture of the esterifying alcohol (II) and water. The catalysts listed were added last. The reaction was carried out in a 200 ml. round bottom flask. The latter was fitted with a reflux condenser, and a thermometer in the vapor phase. After refluxing, the solids in the reaction mixture were filtered, washed with water, then identified.

In this series of experiments where in every case the solid was sulfanilic acid, it was felt that physical constants, solubility data, and qualitative analysis of the residue of ignited samples, was sufficient to identify the solid as sulfanilic acid. This information is shown in Table IV following.

The filtrate was in every case distilled through a fractionating column. It was always a mixture of the alcohol involved, water, and acetic acid. The odor of HCl was also evident in those cases where the reaction was conducted in an acid medium. Any distillation residues were treated separately.

TABLE IV

PREPARATION OF P-ACETAMINOBENZENESULFONYL CHLORIDE  
ESTERS IN AN AQUEOUS MEDIUM

RUN	REFLUX TIME	SULFONYL CHLORIDE	MOLS	ALCOHOL (95 %)	MOLS	WATER	CATALYST
1	2 Hrs.	15 g.	0.0643	6 g. EtOH	0.13	50 ml.	-
2	2 Hrs.	10 g.	0.0428	8 g. EtOH	0.174	50 ml.	0.5 ml. H <sub>2</sub> SO <sub>4</sub>
3	2 Hrs.	10 g.	0.0428	8 g. EtOH	0.174	50 ml.	2.0 g. NaOH
4	80 Min.	10 g.	0.0428	10 g. MeOH	0.313	50 ml.	1 g. NaOCH <sub>3</sub>
5	Left overnight at room temp.	10 g.	0.0428	10 g. MeOH	0.313	50 ml.	-
6	" " "	10 g.	0.0428	50 g. MeOH	1.563	50 ml.	1 g. NaOCH <sub>3</sub>
7	" " "	10 g.	0.0428	50 g. EtOH	1.089	-	-
8	30 Min.	10 g.	0.0428	6 g. EtOH	0.13	50 ml.	-
9	15 Min.	10 g.	0.0428	6 g. EtOH	0.13	50 ml.	-

TABLE IV (Continued)

PREPARATION OF P-ACETAMINOBENZENESULFONYL CHLORIDE  
ESTERS IN AN AQUEOUS MEDIUM

<u>RUN</u>	<u>RESULTS</u>	<u>YIELD SULFANILIC ACID</u>	<u>MOLS YIELD</u>
1	Formed sulfanilic acid hydrochloric acid, and acetic acid	83.3 %	.0534
2	Same as 1	80.5 %	.0345
3	Na salts of 1	83.0 %	.0355
4	Na salts of 1	87.7 %	.0376
5	Same as 1	73.0 %	.0312
6	Na salts of 1	63.5 %	.0271
7	Na salts of 1	61.7 %	.0264
8	Same as 1	78 %	.0333
9	Same as 1	71.7 %	.0306

Identification of White Solid as Sulfanilic Acid

M.P. decomposes > 280° C.

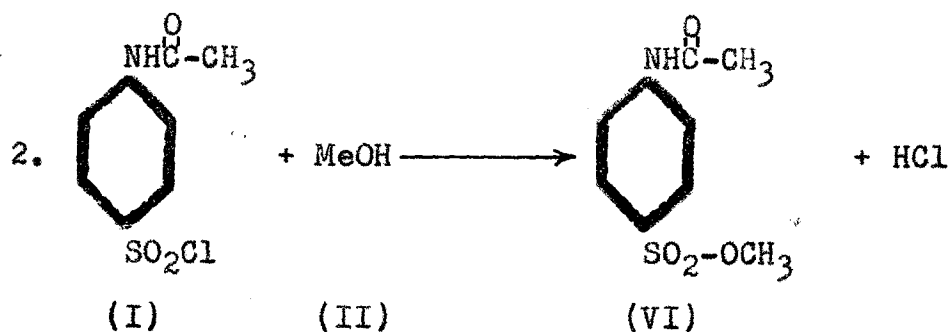
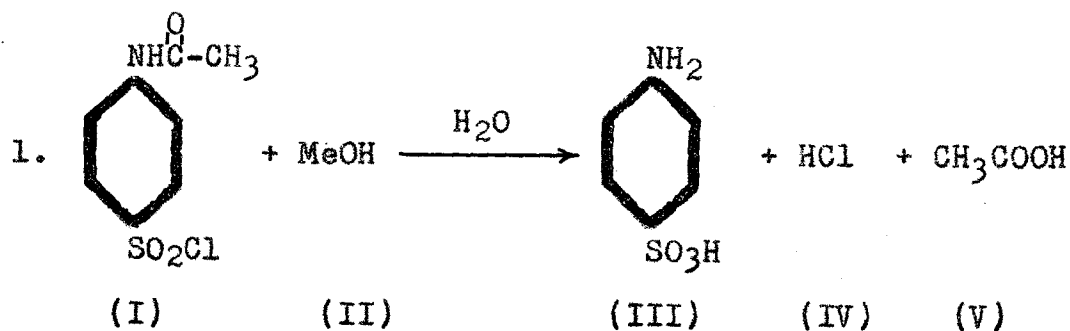
Soluble in basic solutions, hot chloroform and benzene

Insoluble in water, alcohols, acid solutions

Positive test for S in Ignited Sample.

## DISCUSSION

The tests prove fairly conclusively that of the two possible reactions listed below, Reaction 1 occurs.



The data shown at the bottom of Table IV lists identification data for one of the test runs. The other runs produced virtually the same data.

In runs 1 - 4, the reactants were refluxed for about 2 hours. The average yield of sulfanilic acid (III) from the four runs was 83.6%. The same reactants, when refluxed for fifteen and thirty minutes, yielded 71.7% and 78.0% of the theoretical amount of sulfanilic acid. Investigation of this time series was not pursued further. The data available, however, indicates the optimum time of reflux is

probably between 45 minutes and 1 hour for complete hydrolysis.

The interpretation of the data in this way led to the studies in a non-aqueous medium. These are discussed in the next section.

Part V. Preparation of Esters of p-Acetaminobenzene-sulfonyl Chloride in a Non-Aqueous Medium.

Essentially the same reaction shown in Part IV was attempted here. The data obtained there, however, indicated different results, other than the hydrolysis of the sulfonyl chloride to sulfonic acid, might be obtained by conducting the reaction in a non-aqueous medium.

Procedure: The equipment was redesigned to eliminate the introduction of moisture. Prior to use, the reaction flask was heated to insure dryness. The reflux column was also pre-dried by washing its interior with anhydrous methyl alcohol. The equipment was reassembled while still hot and fitted with a drying tube. The dry reactants were introduced into the system through the reflux column. The alcohol was added later.

The reactants were prepared as follows:

1. The p-acetaminobenzenesulfonyl chloride was recrystallized from hot chloroform, after separation of the insoluble water phase.
2. The methyl alcohol used here was distilled through a calcium bed.
3. The sodium methylate used was a chemically pure grade. No analysis of the compound was supplied.

Six runs were made using the procedure first cited.

Some unexplainable results were obtained in run 4 where the sodium methylate in good excess (120%) was entirely consumed.

An attempt was made to determine the stoichiometric amount of sodium methylate required to neutralize the solution. The procedure followed was to titrate a mixture of absolute methyl alcohol and p-acetaminobenzenesulfonyl chloride with an alcoholic solution of sodium methylate. The results were unsatisfactory. It was found that the reactants attacked the phenolphthalein indicator. As a result, the neutralization point was not determined.



TABLE V.

PREPARATION OF ESTERS OF P-ACETAMINOBENZENESULFONYL  
CHLORIDE IN A NON-AQUEOUS MEDIUM

<u>RUN</u>	<u>REFLUX TIME</u>	<u>SULFONYL CHLORIDE</u>	<u>MOLS</u>	<u>ABSOLUTE MeOH</u>	<u>NaOCH</u>	<u>MOLS</u>	<u>OTHER**</u>	<u>RESULTS</u>	<u>% YIELD</u>
1	2 hrs.	4 g.	0.0172	50 ml.	2 g.	0.037	1 g. H <sub>2</sub> O in the salt	Partial hydroly- sis of chloride	Unidentified solid product
2	2 hrs.	4 g.	0.0172	50 ml.	2 g.	0.037	1 g. aniline	Separation impossible	-
3	1 hr.	4 g.	0.0172	50 ml.	2 g.	0.037	1 g. Na <sub>2</sub> CO <sub>3</sub>	Poor separation achieved	-
4	1 hr.	4 g.	0.0172	50 ml.	2 g.	0.037	-	Spontaneous reaction gas emitted	61.4
5	1 hr.	8 g.	0.0344	100 ml.	4 g.	.074	-	Spontaneous reaction gas emitted	78.8
6	1 hr.*	1 g.	0.0043	15 ml.	-	-	-	Fineppt formed	-

\* Attempted titration of the sulfonyl chloride with an alcohol solution of sodium methylate was not successful due to the attack of the reactants on the phenolphthalein indicator.

\*\* In Run 1, the 1 g. H<sub>2</sub>O was found as a contaminant which carried partial hydrolysis of the p-acetaminobenzenesulfonyl chloride to sulfanilic acid.

Aniline and sodium carbonate were used in Runs 2 and 3 respectively, to neutralize the hydrochloric acid, that would have formed, if esterification had occurred.

TABLE VI

Properties of Unknown

Physical Appearance:

Fine, very white powder, which settles and cakes on side of flask during refluxing.

Solubility:

Very soluble in H<sub>2</sub>O, slightly soluble in methyl alcohol. Insoluble in benzene, chloroform, and butyl alcohol.

Melting point:

After 1st reaction (run 5) decomposes 316°C.

After 2nd reaction (run 6) decomposes 285°C.

Combustible properties:

Burns reluctantly, ignition of volatile matter leaves water soluble residue giving positive tests for chlorine and sulfur. Percentage ash found after ignition was 61 %. This was not further identified.

## DISCUSSION

Runs 1,2, and 3 may be discarded as of little importance. The aniline or sodium carbonate was added to react with hydrochloric acid which was thought to form in the flask. No evidence of this was noted in runs 4,5, and 6.

In run 4, when the methyl alcohol was added to the mixture of p-acetaminobenzenesulfonyl chloride and sodium methylate, a spontaneous reaction occurred. Bubbling and a little foam were seen. The temperature also rose, from room temperature of 25°C. to 55°C.

After the reaction had subsided, refluxing for 1 hour was begun. After cooling, the solids were filtered out and studied. The related data are summarized in Table VI, page 28.

The identity of the solid has not been established as yet.

In run 6, the attempt at determining the stoichiometric amount of sodium methylate was unsuccessful due to the decomposition of the phenolphthalein indicator. No neutral point could be firmly established. Further study must be directed along these lines to secure the desired information.

## SUMMARY

It has been found that the butyl ester of sulfanilic acid will react with anhydrous methyl alcohol in an alcohol exchange reaction. Special conditions of temperature and pressure are required to achieve this result.

Esters of p-acetaminobenzenesulfonyl chloride cannot be prepared in an aqueous medium. The hydrolysis reaction of this salt to sulfanilic acid is predominant. Attempts to esterify the salt in a non-aqueous medium have not been successful. The products of this reaction have not been identified.

## BIBLIOGRAPHY

1. Walter, L.A. Journal of the American Chemical Society 65, 739 (1943).
2. Kuhn, Richard and Ruelius, Hans W. Chem.Ber. 83, 420-31 (1950). (Chemical Abstracts 1951, 2408-9).
3. Jenson, K.A., Hanson, O.R., Jorgensen, I.S. and Schmith, K. Davsk, Tids Form. 18, 201-7 (1944). (Chemical Abstracts 40:14667).
4. Keda, Hideo O. (Takaoka Plant, Nippon Soda Co.) Journal of the Pharmaceutical Society (Japan) 70, 734-40 (1950). (Chemical Abstracts, 1951, 7043<sup>g</sup>).
5. Cason, J. and Rapoport, H. Laboratory Text in Organic Chemistry, p.159, Prentice-Hall, Inc. New York, 1950.
6. Fieser, Louis F. Experiments in Organic Chemistry p.262-3, D.C. Heath and Company, New York, 1941.
7. Harding, G. Journal of the Chemical Society, 119, 1261 (1921).
8. Lange, Norbert A. Handbook of Chemistry, p.664-5, Handbook Publishers, Inc., Sandusky, 1949.
9. Bost, R.W. and Deebel, G.F. Journal of the Elisha Mitchell Science Society, 66, 157-62 (1950). (Chemical Abstracts 46: 6094<sup>a</sup>).