University of Louisville

ThinkIR: The University of Louisville's Institutional Repository

Electronic Theses and Dissertations

1936

A study of fuoyl chloride.

Luella Shehan
University of Louisville

Follow this and additional works at: <https://ir.library.louisville.edu/etd>

Part of the [Chemistry Commons](#)

Recommended Citation

Shehan, Luella, "A study of fuoyl chloride." (1936). *Electronic Theses and Dissertations*. Paper 1894.
<https://doi.org/10.18297/etd/1894>

This Master's Thesis is brought to you for free and open access by ThinkIR: The University of Louisville's Institutional Repository. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of ThinkIR: The University of Louisville's Institutional Repository. This title appears here courtesy of the author, who has retained all other copyrights. For more information, please contact thinkir@louisville.edu.

UNIVERSITY OF LOUISVILLE

A STUDY OF FUROYL CHLORIDE

A Dissertation

Submitted to the Faculty of the
Graduate School of the University of Louisville
In Partial Fulfillment of the
Requirements for the Degree
of Master of Science

Department of Chemistry

By

Luella Shehan

1936

TABLE OF CONTENTS

Page No.

I. Introduction	
A. The Furans.....	1
B. Furoyl Chloride.....	3
II. Furoyl Chloride: Preparation	
A. Theoretical.....	4
B. Objective.....	5
C. Experimental.....	6
D. Equations.....	10
E. Conclusions.....	11
III. Furoyl Chloride: Reaction with Tartaric Acid	
A. Theoretical.....	12
B. Objectives.....	13
C. Experimental.....	14
D. Equations.....	20
E. Conclusions.....	21
IV. Furoyl Chloride: Reaction with Ethylene Glycol	
A. Theoretical.....	22
B. Objectives.....	23
C. Experimental.....	24
D. Equations.....	28
E. Conclusions.....	29

V. Furoyl Chloride: Reaction with Glycerol	
A. Theoretical.....	30
B. Objectives.....	31
C. Experimental.....	32
D. Equations.....	36
E. Conclusions.....	37
VI. General Summary.....	38
Bibliography.....	39

I. Introduction

A. The Furans

In the field of chemistry, particularly that of organic chemistry, the last decade has witnessed the rise to recognition and importance of many compounds, heretofore considered only as laboratory curiosities. For over 100 years furfural has been known but little used. It was first prepared by Dobereiner(1) in 1830 while he was preparing formic acid from sugar by the action of manganese dioxide and sulfuric acid. There followed a half century of indifference and lack of interest in the subject, after which rather extensive investigations were undertaken on the preparation and properties of furfural. Eventually it was recognized that pentoses and pentosans were the substances ordinarily yielding furfural. With this fact in mind, numerous methods for the preparation of furfural have been devised, the raw materials including oat hulls, tobacco stems, corn cobs, wood waste, sunflower seed and straw. **Furfural** production has increased from a few barrels per year to millions of pounds per year.

Furfural is a pale yellow or water white liquid which boils at 158° - 168° C. It has a flash point of 55° - 57° C. and its specific gravity is 1.159-1.161 (2). Furfural is an aldehyde the reactions of which are similar to those of formaldehyde and benzaldehyde (3). Yet the furan ring

structure is responsible for many curious properties found in neither of these two typical aldehydes. As can be expected from a study of its structure, furfural serves as the source compound for a group of compounds not hitherto available. Many of these derivatives have been prepared and can now be had as commercial need for them arises. It is to furfural and this series of compounds that we refer as "The Furans". They include furfuryl alcohol, ethyl furoate, furoyl chloride, hydrofuroamide, tetrahydrofurfuryl alcohol and others. The furans as a group have several characteristic properties. They are, in general, high boiling compounds which are fairly stable despite their tendency to darken on standing. They are, however, highly sensitive to acidic reagents due to the effect which these substances seem to have on the furan ring (3). Due to their distinctive properties these furfural derivatives are finding extensive application in widely divergent fields of industry. They are being used as solvents, as accelerators in certain kinds of rubber, as constituents of resins, perfumes, fungicides, and dyestuffs, and in numerous other capacities in industrial production.

B.Furoyl Chloride

The member of this series of furfural derivatives or furans with which this paper is particularly concerned is furoyl chloride, commonly referred to in the earlier literature as pyromucyl chloride. Furoyl chloride was first prepared by the action of phosphorous pentachloride on furoic acid (4). Later methods of preparation include: a modification of the original method by Frankland and Aston (5), who devised a special method of procedure; the treatment of furoic acid with thionyl chloride on a water bath (6); the use of benzene as a solvent in the last mentioned process (7); and a slight modification of this process, which is the one most in use at present (8). The yields in this process are about 89 %.

Furoyl chloride is a colorless, strongly refracting liquid which boils at 170°C . It is more stable than benzoyl chloride, being unaffected by cold water and only slightly attacked by hot water. It is a vigorous lachrymator, the vapor being quite irritable to the eyes. With ammonia, furoyl chloride reacts to give furamide. With hydrogen cyanide, in the presence of pyridine, furoyl chloride forms furoyl cyanide, which on hydrolysis with hydrochloric acid gives furoyl formic acid (3). Due to its stability and multiplicity of reactions furoyl chloride is one of the most useful of the furans from a synthetic point of view (8).

II. Furoyl Chloride: Preparation

A.Theoretical

As was mentioned earlier in this paper, furfural resembles benzaldehyde in some of its reactions (3). This is particularly true where the aldehyde group alone is involved. In 1832 Liebig and Wohler(9) obtained the first acid chloride when they treated benzaldehyde with chlorine to form benzoyl chloride. Therefore, on the basis of the analogy between the reactions of benzaldehyde and furfural, the preparation of furoyl chloride from the chlorination of furfural can be assumed as a possibility. Before such a reaction could be undertaken there was one disturbing factor which had to be taken into consideration. In view of the high sensitivity of the furans to hydrochloric acid and the fact that this acid would be produced in the suggested reaction, some provision had to be made for the removal of this acid as soon as it was formed. In 1908, however, as a result of experiments(10) pyridine bases were suggested as halogen carriers in reactions involving halogen substitution. Later Darzens(11) used pyridine to unite with the hydrochloric acid formed when chlorides are prepared from alcohols. Kirner (12) used the same means of hydrochloric acid removal in the conversion of furfuryl alcohol into furfuryl chloride. Due to the success with which these men used pyridine in dealing with the

furans in the presence of hydrochloric acid, it was thought advisable in this study to use pyridine.

B. Objective

The objective of this study is to show the similarity between the activity of furfural and that of benzaldehyde with chlorine, by the preparation of furoyl chloride.

C.Experimental

Experiment No. #1 Preparation of Pyridine Dichloride

This reaction was carried out in a 250 cc. round bottom flask(three neck).To one opening was a delivery tube leading from a chlorine generator containing 0.5 mol manganese dioxide and 2.0 mols of hydrochloric acid.The center opening of the flask was fitted with a mercury sealed, motor driven stirrer.From the remaining opening was an outlet tube leading through a trap into a bottle containing a dilute solution of sodium hydroxide.0.2 mol of pyridine and 25 cc.of anhydrous ether were placed in the flask and stirred vigorously,the entire flask being immersed in an ice bath.When the temperature had fallen to about 6° the chlorine was slowly bubbled into the pyridine solution, which was stirred constantly.When about one-half of the chlorine had been introduced small white crystals began to form on the sides of the flask.By the time all of the chlorine had been introduced a white crystalline mass remained.The crystals were very unstable,however,and turned yellow and brown as soon as they came into contact with the air.When these crystals were isolated and examined they were found to manifest all of the properties ascribed to pyridine dichloride,

, in the literature(13).

Experiment No. #2-Preparation of Pyridine Hydrochloride

A mixture of 0.2 mol of pyridine and 25 cc. of anhydrous ether was treated in exactly the same fashion as that described in the preceding experiment, with the exception that hydrogen chloride was introduced instead of chlorine. The hydrogen chloride was generated from a flask containing sodium chloride and concentrated sulfuric acid. The product which resulted consisted of white hygroscopic crystals with all of the properties ascribed to pyridine hydrochloride. (14) (15).

Experiment No. #3-Attempted Preparation of Furoyl Chloride

The furfural used in this and subsequent experiments was purified by distillation (3). The technical furfural was distilled under reduced pressure (30 mm.), the fraction containing the last 65 % of the distillate being collected and stored in amber colored bottles. A mixture of 25 cc. of anhydrous ether and 0.2 mol of purified furfural was placed in a 500 cc. round bottom flask, 0.2 mol of pyridine was added and the flask immersed in an ice bath. The openings of the flask were fitted as in the two preceding experiments. The solution was stirred until the temperature reached 6° C. Chlorine was slowly bubbled into the solution over a period of two hours. When about one-half of the chlorine had been introduced, white crystals began to form around the edge of the solution. As the reaction proceeded, however, they turned yellow. At the end of two hours the ether

solution was extracted and distilled under reduced pressure (30 mm.), the major portion of the distillate coming over at 48°C . Treatment of the distillate with concentrated ammonium hydroxide yielded a white precipitate which melted at $117^{\circ}\text{--}121^{\circ}\text{C}$, hydrofuramide. Hydrofuramide is the ammonia derivative of furfural, therefore the distillate consisted of unchanged furfural. An examination of the crystals which remained in the flask revealed all of the properties ascribed to pyridine dichloride (13).

Experiment No. # 4-Attempted Preparation of Furoyl Chloride

A mixture of 0.2 mol of furfural and 25 cc. of ether was treated in exactly the same fashion as that outlined in the preceding experiment, with the exception that the reaction was carried out at room temperature. The white crystals formed as before, but decomposed more readily into a brown waxy mass which eventually turned into a brown liquid. The ethereal solution after distillation again yielded an ammonia derivative which melted at $117^{\circ}\text{--}121^{\circ}\text{C}$, hydrofuramide. As before, this derivative indicated the presence of unchanged furfural.

Experiment No. # 5-Attempted Preparation of Furoyl Chloride

As before, a mixture of 0.2 mol of furfural and 25 cc. of ether was chlorinated, but in the absence of pyridine. A yellow oily liquid was produced which turned reddish brown as the reaction proceeded. Two layers formed in the solution

The ether layer formed an ammonia derivative melting at 117° - 121° C. The other layer which was very acid was cooled to 5° C. No crystals appeared. The properties of furoyl chloride were revealed in none of the products formed. The ammonia derivative was that of furfural. Furthermore, no lachrymatory effect, a characteristic of furoyl chloride, was noticed. The furfural was apparently unchanged. The absence of crystals in this reaction in which pyridine was absent might be taken as further proof of the fact that the crystals in the two preceding reactions were pyridine compounds.

Experiment No. # 6-Reaction of Aldehydes and Acid Chlorides

A mixture of 0.2 mol of furfural and furoyl chloride was placed in a tightly stoppered flask and allowed to stand in contact with one another for eight hours. Apparently no reaction took place for there was no change in the appearance of the mixture. This experiment was performed to determine the properties of a solid addition product formed from the reaction between an aldehyde and acyl halide, as is true in the case of benzaldehyde and benzoyl chloride(17). Apparently furoyl chloride and furfural do not react in this manner.

D. Equations

Predicted reaction:

Actual reaction:

E. Conclusions

1. The precipitate which formed in every reaction in which pyridine was present did not possess the properties ascribed to pyridine-HCl salt (14) (15). Neither can it be attributed to the formation of a solid addition product formed from the reaction between an aldehyde and an acyl halide in the halogenation of an aldehyde (17), for furfural and furoyl chloride apparently do not react in this manner.

2. The properties of the precipitate which formed indicated that it was the dichloride of pyridine. From this it can be inferred that at least a major portion of the chlorine was used by the pyridine rather than by the furfural.

3. The findings of these experiments indicate that the investigator was unable to accomplish the reaction between chlorine and furfural to produce furoyl chloride. Likewise the attempt to use pyridine as a halogen carrier was unsuccessful.

III. Furoyl Chloride: Reaction with Tartaric Acid

A.Theoretical

The general properties of furoyl chloride have been shown to be quite similar to those of benzoyl chloride (3). As a result of experimentation (21) general claim has been made to the preparation of esters of hydroxy acids having more than one carboxyl group in which a hydrogen of the hydroxyl group is replaced by a benzoyl group. Thus mono-benzoyl butyl tartrate has been prepared as a result of of the reaction between dibutyl tartrate and benzoyl chloride. Furthermore, in 1901 Frankland and Ashton (5) demonstrated the action of furoyl chloride on hydroxyl groups by the preparation of diethylpyromucyltartrate,

That furoyl chloride might be assumed to react in a manner analogous to that of benzoyl chloride is demonstrated by the fact that Baumann (22) has shown that furoyl chloride can replace benzoyl chloride in the Scotten-Baumann reaction, in which compounds are formed with the hydroxyl groups.

B.Objectives

The objectives of this study are:

- 1.To give further proof of the similarity between the reactions of benzoyl chloride and those of furoyl chloride;
- 2.To demonstrate the esterification of the hydroxyl groups of tartaric acid by furoyl chloride;
- 3.To isolate and identify the reaction product of the above reaction.

C.Experimental

Experiment No.# 1-Preparation of Furoyl Chloride

The general method of preparation used was that outlined by Hartman and Dickey (8).The reaction was carried out in a three neck,500 cc. round bottom flask,fitted with a thermometer,a separatory funnel and an inverted Liebig condenser arranged in such a way as to remove the hydrogen chloride and sulfur dioxide formed during the reaction.A mixture of 0.2 mol of furoic acid and 35 cc. of dry benzene was placed in the flask and heated to gentle refluxing on a water bath.From the separatory funnel 0.3 mol of thionyl chloride was added gradually, about 3 cc. at a time.The entire mixture was heated, gentle refluxing being continued for about 12 hours. After being cooled the reaction mixture was filtered into a Claissen flask and the benzene and excess thionyl chloride removed by distillation.The furoyl chloride was distilled under reduced pressure (20 mm.),the major portion distilling over at 76° - 80° C.The yield was approximately 85%.

Experiment No.# 2-Preparation and Isolation of the Ester

A mixture consisting of 0.2 mol of furoyl chloride and 0.1 mol of tartaric acid(m.p. 170° C.)was placed in a 250 cc. round bottom flask and heated to gentle re-

fluxing for 5-6 hours. If heated above 120°C , a black tarry mass separated, so the temperature was maintained below 100°C . by heating on a water bath. After the mixture was cooled it was filtered. The filtrate was shaken vigorously with a 10% solution of sodium carbonate. Following some preliminary effervescence, due to the presence of some unchanged furoyl chloride, a light brown emulsion formed and settled to the bottom of the flask. The mixture was immersed in an ice bath and in about ten minutes crystals began to appear. These crystals were filtered off, recrystallized from anhydrous ether, and allowed to dry on a porous plate. The yield was very small, approximately 25%.

Experiment No. # 3-Identification of the Ester

A study of the product of the above reaction revealed the following:

a. Appearance

The product was a white crystalline substance, the crystals being fluffy and needle-shaped. On ignition of the compound no residue remained.

b. Solubility

The reaction product was soluble in ether and alcohol, but insoluble in water.

c. Physical constants

(1) Melting point

The compound melted at $68^{\circ}-70^{\circ}\text{C}$. (uncorrected).

(2) Molecular weight

The molecular weight was determined by Smith's and Young's modification of the Rast method for the determination of molecular weights (23). A capillary tube about 2 mm. in diameter and 10 cm. in length was made by drawing out a piece of heavy walled glass tubing. This was weighed accurately on an analytical balance and a known amount of the compound under examination was placed in the tube. A known weight of camphor, approximately ten times the amount of the sample was tightly packed into the tube. The tube was then carefully sealed in a flame, following which the total weight of the tube, sample, and camphor was determined. The contents of the tube were thoroughly mixed by repeated melting and shaking. When mixing was complete the tube was carefully wired to a thermometer and immersed in an oil bath, as in the determination of a melting point. As the temperature was gradually raised the contents of the tube were observed very closely, preferably with an electric light in the background. The temperature at which the last small crystal disappeared was recorded. The bath was slowly cooled and the temperature at which the first small crystal reappeared was recorded. There was a lag of two or three de-

grees between these readings. The readings were taken three times each for the ascending and descending temperatures. The values obtained were substituted in the following equation which is based on the principle that the compound under examination acts as an impurity in lowering the melting point of camphor:

$$\text{Mol. Wt.} = \frac{39.7 \times 1000 \times \text{wt. sample}}{D t \times \text{wt. camphor}}$$

The following were the values obtained:

Wt. tube-----..2045gm
 Wt. tube+sample-----..2047gm
 Wt. tube+sample+camphor--..2080gm
 Wt. sample-----..0002gm
 Wt. camphor-----..0033gm

Temperatures

171.5°	168.0°
170.0°	167.5°
170.5°	168.0°

Average temp. = 169.25°

$$\text{Mol. Wt.} = \frac{39.7 \times 1000 \times .0002}{(176.4 - 169.25) \cdot 0003}$$

$$\text{Mol. Wt.} = 336.5$$

(Calculated Mol. Wt. = 338
 % error = .44%)

(3) Saponification Equivalent (24)

2.0 gm of finely cut sodium were placed in 50 cc. of absolute alcohol and 10 cc. of water were added. When all of the sodium had dissolved the alkalinity of this solution

was determined by titration with standard acid. An accurately weighed amount of the solid sample and 40 cc. of the alkali were placed in a round bottom flask and the mixture was heated for 30 minutes to gentle refluxing. After the solution had cooled a 10 cc. portion was withdrawn and titrated against standard acid.

$$10 \text{ cc. alkali} = 35.3 \text{ cc. } .1123 \text{ N HCl}$$

$$.3964 \text{ N} = \text{Normality of alkali}$$

$$\begin{array}{rcl} \text{cc. N acid required for 40 cc. alkali} & \rightarrow & \\ & 40 \times .3964 = & 15.856 \\ \text{cc. N acid required for excess alkali} & = & \\ & 57.1 \times .1123 = & 6.4123 \\ \text{cc. N alkali used by sample} & = & 9.4437 \end{array}$$

$$\text{S.E. } \frac{\text{wt. sample} \times 1000}{\text{cc. N alkali used}}$$

$$\text{S.E. } \frac{.2795 \times 1000}{9.4437}$$

$$\text{S.E.} = 295.9$$

$$\begin{array}{l} (\text{Calculated S.E.} = 299.0 \\ \% \text{ error} = 1.04\%) \end{array}$$

d. Derivatives

The remainder of the alkaline saponification product was acidified with dilute sulfuric acid and shaken with 10 cc. of anhydrous ether. The ether layer was evaporated leaving white crystals which when examined could be indentified as furoic acid (m.p. 128°C.) The water soluble

layer was evaporated leaving white crystals which when treated with a b-naphthol- H_2SO_4 solution produced a blue green color changing to an intense green, a color test for tartaric acid (29).

D. Equations

The reactions involved in the above described experiments may be represented by the following equations:

E. Conclusions

The findings of these experiments indicate that:

1. Furoyl chloride reacts with the hydroxyl groups of tartaric acid in a manner analogous to that of benzoyl chloride.
2. When furoyl chloride reacts with the hydroxyl groups of tartaric acid an ester is formed.
3. The behaviour of the compound formed indicates it to be difuroyltartrate, which has not been previously prepared.
4. The physical and chemical properties were determined as far as possible.

IV. Furoyl Chloride: Reaction with Glycol

A.Theoretical

As was stated above (p.12), the activity of furoyl chloride is quite similar to that of benzoyl chloride. In 1888 Baumann (25) demonstrated for the first time that polyhydric alcohols can be isolated in an insoluble form as the benzoyl ester. A dilute solution of the alcohol was shaken with benzoyl chloride and sodium hydroxide for a few minutes and the ester was produced. In the following year Skraup (26) demonstrated that these esters of polyhydric alcohols are always resinous compounds which crystallize only on repeated purification with alcohol. They are difficultly soluble in water, ether, and cold alcohol, but soluble in hot alcohol and benzene. Later Diez (27) devised a simple method for the detection of small amounts of glycerine by the use of the above method, and at present benzoyl esters are among the most commonly prepared derivatives of polyhydric alcohols (28). The benzoyl esters of glycol, glycerine, erythritol, and mannitol have been prepared and their physical constants determined. The glycol ester, ethylene dibenzoate, melts at 70° - 71° C. (28).

B.Objectives

The objectives of this study are:

- 1.To demonstrate the similarity between the activities of benzoyl chloride and furoyl chloride;
- 2.To demonstrate the reaction of furoyl chloride on the hydroxyl groups of a polyhydric alcohol,ethylene glycol;
- 3.To isolate and identify the product formed by the action of furoyl chloride on ethylene glycol.

C. Experimental

Experiment No. # 1-Preparation of Furoyl Chloride

The furoyl chloride used in this experiment was prepared according to the method outlined above(III,C,10).

Experiment No. # 2-Preparation and Isolation of the Ester

A mixture consisting of 4 cc. of glycol(from which all the water had been removed),10 cc. of furoyl chloride, and 50 cc. of 10% sodium hydroxide was placed in an eight inch test tube.The tube was stoppered tightly and shaken vigorously under cold water for several minutes until a white solid separated out.15 cc. of cold water were added and the shaking continued for 2 minutes.The precipitate was filtered and washed with cold water followed by dilute acetic acid.The precipitate was dissolved and recrystallized from hot dilute alcohol.The crystals were dried on a porous plate.The yield was approximately 50%.

Experiment No. # 3-Identification of the Ester

An examination of the ester revealed the following:

a.Appearance

The product was a white crystalline compound,the crystals being very fine and needle-shaped.On ignition no residue remained,showing that the compound consisted essentially of carbon,hydrogen,

or oxygen and contained no metallic elements.

b. Solubility

The compound was soluble in ether and hot alcohol, but insoluble in water and cold alcohol.

c. Physical constants

(1) Melting point

The compound melted at 110°C. (uncorrected).

(2) Molecular weight

The molecular weight was determined by the method previously outlined (this thesis III, C, 16).

The values obtained were:

Wt. tube-----	.2632gm
Wt. tube+sample-----	.2663gm
Wt. tube+sample+camphor---	.3043gm
Wt. sample-----	.0031gm
Wt. camphor-----	.0371gm

Temperatures

164.5°	162.5°
164.0°	162.0°
164.0°	161.5°

Average temp. = 163.0°

$$\text{Mol. Wt} = \frac{39.7 \times 1000 \times .0031}{(176.4 - 163.0) \cdot 0.0371}$$

Mol. Wt. = 248.1

(Calculated Mol. Wt. = 250
% error = .76%)

(3) Saponification Equivalent

The procedure followed was that previously outlined (this thesis III, C, 17).

The following values were obtained:

$$10 \text{ cc. alkali} = 21.3 \text{ cc.} / .08937 \text{ N HCl}$$

$$.19088 \text{ N} = \text{Normality of alkali}$$

$$\begin{aligned} \text{cc. N acid required for 40 cc. alkali} &= \\ &40 \times .19088 = 7.6076 \end{aligned}$$

$$\begin{aligned} \text{cc. N acid required for excess alkali} &= \\ &73.8 \times .08937 = 6.5955 \end{aligned}$$

$$\begin{aligned} \text{cc. N alkali used by sample} &= \\ &= 1.0121 \end{aligned}$$

$$\text{S.E.} = \frac{.2268 \times 1000}{1.0121}$$

$$\text{S.E.} = 224.8$$

(Calculated S.E.=224
% error=.31%)

d. Derivatives

From the saponification mixture 5 cc. were distilled. The distillate was evaporated to dryness and the residue was extracted with a mixture of alcohol and ether. The solvent was evaporated leaving a syrup. One drop of this syrup was mixed with 0.5 gm of potassium acid sulphate and the mixture was placed in a test tube fitted with a delivery tube leading into a flask of distilled water. The sulphate mixture was ignited until frothing ceased and the mass completely liquefied. A 2 cc. portion of this mixture was withdrawn and treated with 5 cc. of fuchsine aldehyde reagent. A lavender-pink coloration resulted showing the presence of an aldehyde,

acetaldehyde, produced by the decomposition of ethylene glycol. By this examination of the saponification products the presence of the glycol grouping in the compound formed was demonstrated. The remainder of the alkaline saponification product was acidified with dilute sulfuric acid and shaken with ether. The ether layer was evaporated leaving white crystals which were furoic acid (m.p. $128^{\circ}\text{C}.$).

D. Equations

The reactions involved in the above described experiments may be represented by the following equations:

E. Conclusions

The findings of these experiments serve as a basis for the following conclusions:

1. Furoyl chloride reacts with both of the hydroxyl groups of ethylene glycol in a manner analogous to that of benzoyl chloride.

2. Furoyl chloride reacts with ethylene glycol to form an ester.

3. The behaviour of the compound formed indicates it to be glycol difuroate or ethylene difuroate.

4. The physical and chemical properties of this compound, which had not previously been prepared, were determined as far as possible.

V. Furoyl Chloride: Reaction with Glycerol

A.Theoretical

For the action of benzoyl chloride, an analogue of furoyl chloride, on polyhydric alcohols see the preceding discussion (this thesis IV, A, 16). Suffice it to say here that glycerine dibenzoate (m.p. 60° C.) and glycerine tribenzoate (m.p. 70° - 76° C.) have been prepared and identified from the reaction of benzoyl chloride on glycerine.

B.Objectives

The objectives of this study are:

- 1.To demonstrate the similarity between the reaction of benzoyl chloride and that of furoyl chloride;
- 2.To demonstrate the action of furoyl chloride on the hydroxyl groups of glycerol;
- 3.To isolate and identify the product formed by the action of furoyl chloride on glycerol.

C.Experimental

Experiment No.# 1-Preparation of Furoyl Chloride

The furoyl chloride used in this experiment was prepared by the same method as that used in the preceding experiments(this thesis II,C,10).

Experiment No.# 2-Preparation and Isolation of the Ester

A mixture consisting of 4 cc. of glycerol(from which all the water had been removed),10 cc. of furoyl chloride and 50 cc. of 10% sodium hydroxide was placed in an eight inch test tube .The tube was stoppered and shaken vigorously until a white resinous precipitate appeared.20 cc. of cold water were then added and the shaking continued for two minutes under cold water. The precipitate was separated by filtration and washed with cold water and dilute acetic acid.The crystals were dissolved and recrystallized from hot dilute alcohol and dried on a porous plate.

Experiment No.# 3-Identification of the Ester

An examination of the product revealed the following:

a.Physical Appearance

The product was a white fluffy,crystalline compound possessing a pleasant odor.On ignition no residue

remained, showing that the compound consisted essentially of carbon, hydrogen or oxygen and contained no metallic elements.

b. Solubility

The compound was soluble in ether, hot water and hot alcohol, but insoluble in cold water, cold alcohol, and dilute acids and alkalies.

c. Physical constants

(1) Melting point

The compound under examination melted at 98.5° C. (uncorrected).

(2) Molecular weight

The molecular weight was determined according to the method outlined above (this thesis, III, C, 11). The values obtained were as follows:

Wt. tube-----	.1950 gm
Wt. tube+sample-----	.1980 gm
Wt. tube+sample+camphor----	.2231 gm
Wt. sample-----	.0030 gm
Wt. camphor-----	.0251 gm

Temperatures

165.0°	162.0°
165.0°	163.0°
165.0°	162.5°

Average temp. = 163.75°

$$\text{Mol. Wt.} = \frac{39.7 \times 1000 \times .003}{(176.4 - 163.75) \cdot 0.0251}$$

$$\text{Mol. Wt.} = 375.1$$

(Calculated Mol.Wt.=374.09
%error=.25%)

(3) Saponification Equivalent

The procedure outlined was like that outlined above (this thesis, III, C, 13). The values obtained were:

$$10 \text{ cc. alkali} = 18.9 \text{ cc. acid} / .08937 \text{ N}$$

$$.16891 \text{ N} = \text{Normality of alkali}$$

$$\begin{aligned} \text{cc.N acid required for 40 cc. alkali} &= \\ &40 \times .16891 = 6.7564 \end{aligned}$$

$$\begin{aligned} \text{cc.N acid required for excess alkali} &= \\ &68.6 \times .08937 = 6.1308 \end{aligned}$$

$$\text{cc.N acid used by sample} (.2707 \text{ gm}) = .6256$$

$$\text{S.E.} = \frac{.2080 \times 1000}{.6256}$$

$$\text{S.E.} = 332.4$$

(Calculated S.E. 336
% error 1.10%)

d. Derivatives

5 cc. of the alkaline saponification mixture were distilled. The distillate was evaporated to dryness over a water bath and the residue extracted with a mixture of alcohol and ether. The solvent was evaporated, leaving a syrup. One drop of this syrup was treated with 0.5 gm of potassium acid sulphate and placed in a test tube fitted with a delivery tube leading to a tube of distilled water. The sulphate mixture was ignited until frothing ceased

and the mixture was completely liquefied. The aqueous solution immediately acquired the odor characteristic of acrolein. Of this solution a 2 cc. portion was treated with 5 cc. of fuchsine aldehyde reagent. An initial vivid violet coloration appeared and then turned to orange and to blue-green after standing overnight followed by treatment with hydrochloric acid. This color change is characteristic of acrolein and serves to identify glycerol as one of the original products of saponification. The remainder of the saponification mixture was acidified with dilute sulfuric acid and shaken with ether. The ether solution was separated and evaporated after being dried with fused magnesium sulphate. A white crystalline solid, furoic acid resulted (m.p. 128°C.).

D. Equations

E. Conclusions

The findings of these experiments serve as the basis for the following conclusions:

1. Furoyl chloride reacts with glycerol in a manner analogous to that of benzoyl chloride;
2. Furoyl chloride reacts with all of the hydroxyl groups of glycerol to form an ester;
3. The product formed by the action of furoyl chloride upon glycerol has the properties which would identify it as glycerine trifur~~ate~~ate, not previously prepared;
4. The physical and chemical properties of the newly prepared compound were determined as far as possible.

VI. General Summary

General Summary

The findings of this series of investigations indicate that:

1. As far as the author was able to determine, furfural does not react with chlorine to form the acid chloride as benzaldehyde does.

2. Furoyl chloride reacts with the hydroxyl groups of hydroxy acids and of polyhydric alcohols to form esters. This is additional proof of the analogy between the activity of benzoyl chloride and that of furoyl chloride.

3. Difuroyltartrate, ethylene difuroate, and glycerine trifuroate have been prepared and their properties determined.

Bibliography

Bibliography

1. Dobereiner-Ann., 3, 141 (1832).
2. The Furans, Quaker Oats Co., Technical Division,
p. 6, (1935).
3. Miner, Trickey and Brownlee-Chem. and Met. Eng., 27,
299, (1922).
4. Lies Bodart-Ann., 100, 325, (1856).
5. Frankland and Ashton-J. Chem. Soc., 79, 511, (1901).
6. Gelissen and Van Roon-Rec. trav. chim., 43, 359, (1924).
7. Gilman and Hewlett-Iowa State College J. Sci., 4,
27, (1929).
8. Hartman and Dickey-Ind. and Eng. Chem., 24, 151, (1932).
9. Richter's Organic Chemistry-D'Albe-I, 269. P. Blakis-
ton's Sons and Co., 1922.
10. Cross and Cohen-Proc. Chem. Soc., 24, 15 (1908).
11. Darzens-Compt. rend., 152, 1314, (1911).
12. Kirner-J. Am. Chem. Soc., 50, 1955, (1928).
13. Williams-J. Chem. Soc., 109, 2783, (1931).
14. Kaufler and Kunz-Ber., 42, 385, (1909).
15. Barthe-Compt. rend., 145, 75, (1854).
16. Miner, Trickey and Brownlee-Chem. and Met. Eng., 27,
362, (1922).
17. Adams and Vollweiler-J. Am. Chem. Soc., 40, 1732, (1918).
18. Gilman and Towne-Rec. trav. chim., 51, 1054, (1932).
19. Gilman and Young-J. Am. Chem. Soc., 56, 464, (1934).

20. Gilman and Calloway-J. Am. Chem. Soc., 55, 4197, (1933*).
21. Davis, U. S. l., 834, 686. Dec. l., C. A., 26, 994, (1933).
22. Baumann-Ber., 37, 2949, 4756 (1904).
23. Smith and Young-J. Biol. Chem., 75, 289, (1927).
24. Baumann-Ber., 21, 2744, (1888).
25. Kamm, Qualitative Organic Analysis, John Wiley and Sons, N. Y., p. 140.
26. Skraup-Ber., 22, R. 668, (1889).
27. Diez-Z. f. Physiol. Chemie, XI, 472.
28. Mullikan-Identification of Pure Organic Compounds, I, 169, John Wiley and Sons.
29. Mullikan-Identification of Pure Organic Compounds, I, 63, John Wiley and Sons.