

To the Committee on Graduate Study: 33

I submit herewith a thesis by Miss Cora Louise Carson, "Identification of Carboxylic Acids as the Salts of Benzylamine," and recommend that it be accepted for eighteen quarter hours credit in fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

C. Buehler

Major Professor

At the request of the Committee on Graduate Study, I have read this thesis, and recommend its acceptance.

Judson H. Robertson

Wm. T. Smith, Jr.

Accepted by the Committee

J. E. Dues  
Acting Chairman

IDENTIFICATION OF CARBOXYLIC ACIDS  
AS THE SALTS OF BENZYLAMINE

A THESIS

Submitted to the Graduate Committee  
of  
The University of Tennessee  
in  
Partial Fulfillment of the Requirements  
for the degree of  
Master of Science



by

Cora Louise Carson

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## CONTENTS

## Page

## CHAPTER I

|              |   |
|--------------|---|
| Introduction | 1 |
|--------------|---|

## CHAPTER II

|                 |   |
|-----------------|---|
| Historical Part | 3 |
|-----------------|---|

## CHAPTER III

|                                                        |    |
|--------------------------------------------------------|----|
| Experimental Part                                      | 9  |
| A. Procedure                                           | 9  |
| I. Materials                                           | 9  |
| II. Preparation of Derivatives                         | 9  |
| a. Combinations Attempted                              | 9  |
| b. Preparation and Purification of Derivatives         | 10 |
| III. Methods of Checking Purity and Ratio of Compounds | 11 |
| 1. Melting Points                                      | 11 |
| 2. Neutralisation Equivalents                          | 13 |
| 3. Nitrogen Determination                              | 14 |
| B. Results                                             | 15 |
| I. Difficulties Met in Isolation of Compounds          | 15 |
| II. Compounds Isolated                                 | 17 |
| III. Physical Properties - Table I                     | 19 |
| IV. Analytical Data - Table II                         | 22 |

## CHAPTER IV

|                        |    |
|------------------------|----|
| Theoretical Discussion | 24 |
|------------------------|----|

## CHAPTER V

|              |    |
|--------------|----|
| Conclusion   | 28 |
| Bibliography | 30 |

## CHAPTER I

### INTRODUCTION

Molecular compounds have become of increasing interest in organic chemistry since they furnish a valuable group of derivatives for the identification of certain classes of organic compounds, notably, the aromatic hydrocarbons, the amines, and the phenols. In the identification of such compounds it should be pointed out, as Kamm<sup>1</sup> has stated, that the reactions used in the identification of inorganic compounds, namely, color tests, precipitation of an insoluble compound, and decomposition with certain reagents, can be used merely as indications, not as final tests of identification. In identifying any single chemical individual Wise<sup>2</sup> pointed out that it often becomes necessary to prepare a derivative which may be readily isolated and purified. The physical constants of such a derivative will serve as a definite means of identification since the physical properties of a compound are a function of the structure of that compound. Hence it is of interest to prepare molecular compounds and to determine the physical constants of these derivatives.

For some time in the Chemistry Laboratories of the University of Tennessee a series of investigations on organic molecular compounds has been carried on with the hope that data may be obtained which will throw more light on the structure of these interesting additive compounds.

1. Kamm, "Qualitative Organic Analysis." John Wiley and Sons, New York, 1932, p. 163.
2. Reid, "Introduction to Organic Research." Van Nostrand and Co., New York, 1924, pp. 288-9.

This particular investigation was carried on with the idea of adding to the data already collected and with the purpose of determining the suitability of benzylamine as a reagent for the identification of carboxylic acids. A similar problem, using *o*-phenylethylamine, is now being investigated in the same Laboratories.

In this investigation the following aims were kept in view:

- (1) To collect any data in the literature previously obtained pertaining to the molecular compounds of benzylamine;
- (2) To find a simple method for the preparation of as many salts of benzylamine with carboxylic acids as possible;
- (3) To determine the melting points of the compounds prepared;
- (4) To determine the ratio of the two components in the compounds prepared by means of nitrogen analyses and by the determination of neutralization equivalents;
- (5) To determine the suitability of these salts for the identification of carboxylic acids.

## CHAPTER II

### HISTORICAL PART

In a search of the literature no systematic investigation of the molecular compounds of benzylamine was found. Investigations have been made in which a number of common amines were used with some other compound to prepare addition products for identification purposes, but it appears that benzylamine was seldom included in these investigations.

A molecular compound of benzylamine and 3,5-dinitrobenzoic acid was prepared by Buehler, Currier, and Lawrence<sup>1</sup> in 1933. This compound was prepared by dissolving 0.01 mole of the acid in 0.01 mole of the amine, heating the solution to boiling, and allowing the crystals to form on a watch glass. The excess liquid was poured off; the crystals were dried between filter paper and recrystallized from ethanol. The molecular ratio was 2:1; the color, yellow; and the melting point, 143.5° corrected.

Calfee<sup>2</sup> listed a compound prepared from 2,4-dinitrobenzoic acid and benzylamine. The hot benzylamine was added to an equimolecular amount of finely powdered 2,4-dinitrobenzoic acid and the resultant product was purified by pulverizing in ethanol and filtering. The compound thus prepared was yellow in color, had a molar ratio 1:1, and a melting point of 199.1-200.1° corrected.

Among the reactions of benzylamine with acids may be mentioned the one with symmetrical dibromosuccinic acid, investigated

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1. Buehler, Currier, and Lawrence, Ind. Eng. Chem., Anal. Ed., 5, 277 (1933).

2. Calfee, John D., Thesis, University of Tennessee, 1934.

by Frankland.<sup>3</sup> On mixing alcoholic solutions of benzylamine and the dibromosuccinic acid in the ratio of four moles of the amine to one of the acid and heating the mixture on a water bath, two substances were deposited; the monobenzylamine salt of benzylaminobromosuccinic acid, m. p. 156-157°, and the monobenzylamine salt of dibenzylaminosuccinic acid which decomposed at 232°.

The same author<sup>4</sup> also investigated the reaction of benzylamine and racemic dibromosuccinic acid using the same methods as in the investigation with the symmetrical dibromosuccinic acid. With benzylamine, the racemic dibromosuccinic acid yielded an isomeric dibenzylaminosuccinic acid, decomposing at 250°, together with a small quantity of the dibenzylamide of the racemic acid, melting at 208-210°. The melting points were uncorrected.

Kamm<sup>5</sup> has stated that the derivatives which can be used in the identification of carboxylic acids may be grouped as follows:

1. Amides, anilides, and toluidides,
2. Solid esters,
3. Elimination of carbon dioxide,
4. Anhydrides and miscellaneous derivatives.

A brief resume of the methods used in preparing these derivatives and the use of these derivatives in the identification of carboxylic acids follows:

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3. Frankland, J. Chem. Soc., 99, 1775-1783 (1911).
  4. Frankland, J. Chem. Soc., 105, 2879-2887 (1914).
  5. Kamm, "Qualitative Organic Analysis." John Wiley and Sons, New York, 1932, p. 176.

A method for preparing amino derivatives of the acids has been given by Kamm.<sup>6</sup> The acid was converted into the acid chloride with phosphorus pentachloride and the resulting product was treated with ammonia to produce the amide. It was found that this method of identification could not be applied to the hydroxy and to the amino acids.

The para toluidides have been used by Mulliken<sup>7</sup> in the identification of acetic, propionic, butyric, and isobutyric acids. The sodium salt of the acid was treated with para toluidine and concentrated hydrochloric acid and boiled. The product was extracted with alcohol and crystallized from hot water.

Thionyl chloride has been used by McElvain<sup>8</sup> and his associates for preparing the acyl chlorides of the carboxylic acids. No by-products were produced when this method was used. The resulting acyl chloride was then treated with a benzene solution of para toluidine or para bromoaniline. The product obtained was crystallized from methyl alcohol.

A method similar to the one just described had previously been used by Robertson<sup>9</sup> in identifying organic acids as amides, p-toluidides, o-toluidides,  $\beta$ -naphthylamides, and the 2,4,6-tribromoanilides. This author was especially concerned with the melting points of the derivatives prepared.

6. Kamm, Ref. 5, p. 152.

7. Mulliken, "Identification of Pure Organic Compounds." John Wiley and Sons, New York, 1904, Vol. I, pp. 80-81.

8. McElvain and Kuehn, J. Am. Chem. Soc., 53, 1173 (1931).

9. Robertson, J. Chem. Soc., 115, 1210 (1919).

Substituted benzimidazoles have been prepared by the use of ortho phenylenediamine.<sup>10</sup> The melting points of these compounds were satisfactory but purification was difficult.

The methyl esters of a limited number of acids can be prepared. Mulliken<sup>11</sup> has stated that these compounds may be prepared by treating the acid chloride with methyl alcohol. These esters were frequently crystalline solids, suitable for identification purposes, although many of the higher alkyl esters were liquids.

Reid<sup>12</sup> and his co-workers have made a series of investigations in which the para nitrobenzyl esters and the phenacyl esters have been used for the identification of organic acids. An alcoholic solution of the sodium salt of the acid was treated with para nitrobenzyl bromide to produce the para nitrobenzyl ester. The phenacyl ester was produced by substituting  $\alpha$ -bromoacetophenone for the nitrobenzyl bromide. In addition to its use in the identification of individual acids, this method seemed to be of some value in the separation and identification of mixtures of acids.

Blicke and Smith<sup>13</sup> reported that they were unable to obtain satisfactory results by the use of Reid's method which has just been described. Reid's method was modified by Blicke and Smith in their study of the hydroxy acids so as to favor the formation of the dinitrobenzyl products of the hydroxy acids. In this modified method an aqueous solution of the hydroxy acid was treated with sodium hydroxide

10. Seka and Muller, *Monatsh.*, 57, 97-105 (1931).

11. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1904, Vol. IV, p. 15.

12. Reid, et. al., *J. Am. Chem. Soc.*, 39, 124, 304, 791, 1727 (1917); 41, 75 (1919); 42, 1043 (1920); 43, 629 (1921); 52, 818 (1930).

13. Blicke and Smith, *J. Am. Chem. Soc.*, 51, 1947 (1929).

and para-nitrobenzyl bromide. The derivative of the p-hydroxy acid separated out as a crystalline solid, of the ortho and meta acids, as oils which solidified when cool. The advantages of this method were that larger yields could be obtained than when the formation of the mononitrobenzyl products was favored and that a mixture of two isomeric hydroxy acids could be separated.

Para-phenylphenacyl bromide has been proposed as a reagent for identifying organic acids by Drake and Bronitsky.<sup>14</sup> The advantages of this reagent were its cheapness, the ease with which it could be prepared, the ease with which its crystalline derivatives could be purified, and its ability to form solid derivatives with a number of acids. These advantages were contrasted with the disadvantages of Reid's method, mentioned above, in which purification was sometimes difficult and by which it was not always possible to obtain a satisfactory solid derivative. In this method a solution of sodium carbonate, barely acidified with the organic acid, was treated with alcohol and para-phenylphenacyl bromide to produce the derivative which was purified by recrystallization.

Kamm<sup>15</sup> has stated that a dicarboxylic acid can be converted into the monocarboxylic acid by heating to a temperature of 140-160°. The monocarboxylic acids can also be made to lose carbon dioxide when heated with soda lime. This reaction is of value when dealing with carboxyl derivatives of solid hydrocarbons.

Kamm<sup>15</sup> has also given some examples of miscellaneous methods

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14. Drake and Bronitsky, J. Am. Chem. Soc., 52, 3715 (1930).

15. Kamm, Ref. 5, p. 182.

used in the identification of acids. Among these may be mentioned the following:

The readily sublimable phthalic anhydride, m. p.  $132^{\circ}$ , which can be produced by heating o-phthalic acid to its melting point.

The production of the dibromide addition product of cinnamic acid.

Substitution reactions which take place in the aromatic nucleus of phenolic acids.

## CHAPTER III

### EXPERIMENTAL PART

#### A. Procedure.

##### I. Materials.

The benzylamine used was the chemically pure grade of the Eastman Kodak Company.

The acids used were the chemically pure grade of the Eastman Kodak Company and products prepared in the Chemistry Laboratories of the University of Tennessee.

##### II. Preparation of Derivatives.

###### a. Combinations Attempted.

The following acids were used in preparing derivatives with benzylamine:

1. Formic acid
2. Acetic acid
3. Propionic acid
4. n-Butyric acid
5. Caproic acid
6. Chloroacetic acid
7. Trichloroacetic acid
8. Phenylacetic acid
9. o-Toluic acid
10. Cinnamic acid
11. Phthalic acid
12. Benzoic acid
13. o-Aminobenzoic acid

14. m-Aminobenzoic acid
15. p-Aminobenzoic acid
16. m-Bromobenzoic acid
17. o-Chlorobenzoic acid
18. m-Chlorobenzoic acid
19. p-Chlorobenzoic acid
20. o-Hydroxybenzoic acid
21. m-Hydroxybenzoic acid
22. p-Hydroxybenzoic acid
23. o-Methoxybenzoic acid
24. m-Methoxybenzoic acid
25. p-Methoxybenzoic acid
26. o-Nitrobenzoic acid
27. m-Nitrobenzoic acid
28. p-Nitrobenzoic acid
29. 2,4-Dinitrobenzoic acid

b. Preparation and Purification of Derivatives.

The solution method was used in the preparation and purification of the salts. The solvent used was anhydrous ethyl acetate.

In general, to form the salts, 0.01 mole of the acid was dissolved in the smallest possible amount of boiling ethyl acetate and then a slight excess of the hot solvent was added. Into this hot solution 0.01 mole of benzylamine was stirred and the resultant solution was quickly poured on a watch glass to allow crystallization to take place. After the bulk of the crystals had formed, the mother

liquor was poured off and discarded. The crystals thus formed were allowed to dry for a while on the watch glass and then were scraped off onto filter paper where drying was completed.

The crystals thus formed were used in the determination of melting points, neutralization equivalents, and in the nitrogen analyses.

A portion of each of the compounds prepared in the ethyl acetate solution was recrystallized from hot absolute ethyl alcohol and dried on filter paper. The melting points of the crystals formed from the ethanol solution were determined in the regular manner. The results were compared with the melting point data of the crystals prepared with ethyl acetate as a solvent. The comparison is believed to indicate the stability of the derivative in the two solvents.

To prepare the salts with liquid acids, such as acetic, formic, caproic, and propionic, 0.01 mole of the acid in each case was added to 0.01 mole of benzylamine on a watch glass and the two components were mixed by gently tapping the watch glass. As soon as there was evidence of crystal formation, tapping of the watch glass was discontinued, most of the crystals were allowed to form, and the watch glass was tilted so that any excess liquid could drain off.

The compounds formed with acetic and formic acids were dried in a desiccator; the compounds with caproic and propionic acids, on filter paper.

### III. Methods of Checking Purity and Ratio of Derivatives Prepared.

#### 1. Melting Points.

The capillary tube method described by Mulliken<sup>1</sup> was used in determining the melting points of the salts prepared.

A suitable melting point apparatus was made by fitting a short test tube into a short necked 250 cc. round-bottom flask. The flask and the test tube were filled about two thirds full with concentrated sulfuric acid to which a crystal of potassium nitrate had been added to prevent discoloration of the acid. A thermometer, calibrated by the Bureau of Standards, was suspended in the test tube in such a manner that the bulb was immersed in the sulfuric acid, but did not touch the bottom of the test tube. A small thermometer was suspended so that the bulb rested against the standard thermometer about midway between the level of the acid and the top of the thermometer. This small thermometer was used to record the mean temperature of the emergent stem.

A small amount of the compound, the melting point of which was to be determined, was placed in the sealed end of a capillary tube. The capillary tube was made to adhere to the standard thermometer by surface tension in such a position that the closed end of the capillary tube containing the sample rested against the bulb of the thermometer.

The temperature of the bath was raised at the rate of about three degrees per minute until the melting point of the compound was approached when the temperature was raised at the rate of not more than two degrees per minute. The melting point was considered as the

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1. Mulliken, "Identification of Pure Organic Compounds." John Wiley and Sons, New York, 1904, Vol. I, p. 218.

range of temperature from the appearance of the first drop of melted material until the entire sample was melted.

Stem corrections and absolute corrections were made to the readings. The stem corrections were made by the following expression:

$$\text{Stem Correction} = K \times N (T - t)$$

where K is the differential expansion of mercury in the particular kind of glass of which the thermometer is made, N, the number of degrees from the top of the bath to the melting temperature of the compound, T, the temperature of the bath, and t, the mean temperature of the emergent stem. The value of K in this case was 0.00016.

The absolute corrections were determined from a graph made by plotting the temperature against the corrections given by the Bureau of Standards.

## 2. Neutralization Equivalents.

A method suggested by Perkin and Sewell<sup>2</sup> for the determination of neutralization equivalents was used satisfactorily.

A 0.200 gram sample of the molecular compound was dissolved in water and, using phenolphthalein as the indicator, was titrated at boiling temperature against standard sodium hydroxide solution (0.1N), the end point being considered as the first tinge of pink which remained after boiling the solution for five minutes.

The neutralization equivalent was calculated by means of the following formula:

$$\text{Neutralization Equivalent} = \frac{\text{wt. of sample} \times 1000}{\text{cc. of normal alkali}}$$

2. Perkin and Sewell, J. Soc. Chem. Ind., 42, 27T (1923).

### 3. Nitrogen Determination.

The following method, evolved from a modification of the Kjeldahl method,<sup>3</sup> was used in the determination of the nitrogen present:

About 200 milligrams of the compound to be analyzed was placed in a 500 cc. Kjeldahl digestion flask. To this was added 0.5 gram copper sulfate and 10 grams potassium sulfate. A 30 cc. portion of concentrated sulfuric acid in which 1 gram salicylic acid had been dissolved was then poured into the flask, care being taken to wash down any particles adhering to the neck of the flask. A Hengar tube was inserted to prevent the escape of sulfur dioxide fumes. After shaking, the flask was heated gently for a few minutes and then the temperature was gradually increased until the mixture boiled steadily. Heating was continued for a half hour after the contents of the flask had become clear and green in color. The solution was then cooled, diluted with 150 cc. water, shaken vigorously to dissolve any material which had crystallized out, and cooled again. Seventy-five cc. of cold 30% sodium hydroxide solution was introduced into the cold flask in such a manner that the sodium hydroxide and sulfuric acid solutions formed two separate layers, the sodium hydroxide solution forming the lower layer. After 2 grams zinc dust had been added to prevent bumping, the flask was quickly connected to the distilling apparatus, rotated gently to mix the two layers, and heated until about two thirds of the volume of the liquid had distilled over into

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3. Dyer, J. Chem. Soc., 67, 811 (1895).

25 cc. of standard 0.1 N hydrochloric acid solution to which 25 cc. water had been added. The hydrochloric acid solution was titrated against standard 0.1 N sodium hydroxide solution using methyl orange as indicator.

The percentage of nitrogen was calculated by the following formula:

$$\% \text{ Nitrogen} = \frac{\text{cc. acid} \times N \times 0.014 \times 100}{\text{wt. of sample}}$$

where cc. of acid is the number of cc. of standard acid equivalent to the ammonia of the sample, N is the normality of the acid, and 0.014 is the milliequivalent weight of nitrogen.

#### B. Results.

Molecular compounds were prepared with twenty-nine acids and benzylamine, but one of the compounds prepared defied purification.

##### I. Difficulties Met in Isolation of Compounds.

The chief difficulty met in this investigation was in attempting to isolate the derivative formed with n-butyric acid.

When 0.01 molar quantities of the two components were poured together on a watch glass, heat was evolved and white crystals appeared. Cooling with an ice-salt mixture or with dry ice hastened the appearance of these crystals, but attempts to remove the adhering thick sirupy material by pouring or by washing with ether failed.

Another method used to prepare the molecular compound consisted in pouring 0.01 molar quantities of the two components into a small quantity of ligroin on a watch glass. A fair crop of crystals soon separated out, the ligroin was poured off, and ether was used in a futile attempt to wash off the sirup surrounding the crystals.

A third method used in preparing this derivative was to add an excess of one of the components to 0.01 mole of the other component, await crystal formation, and then pour off the excess liquid. Here again attempts to remove all the sirup clinging to the crystals by washing with ether failed.

In no case, using the methods described above, was the derivative of benzylamine with n-butyric acid obtained in a pure form so that the physical constants could be determined. It should be noted that the best crystals formed in ligroin. In each of the methods used, white crystals, presumably the derivative, were obtained, but attempts to remove the adhering sirupy film failed. On standing, this sirup dissolved the crystals and it was not possible to re-crystallize the derivative from ethyl acetate, ethyl alcohol, ether, or benzene, either when the crystals had been freshly prepared or when they had been allowed to dissolve in the sirup.

In a preparation of the derivative when the method using an excess of one of the components (in this case, benzylamine) was employed, a white, finely divided, starchy-appearing precipitate separated out. It was washed with ether several times, filtered off, and dried. This substance was soluble in water, very slightly soluble in ethyl acetate, ethyl alcohol, ether, and benzene, and had a melting point of  $289^{\circ}$  corrected. The substance appeared to be some polymerization product, not the derivative sought, and so was not further investigated. It is interesting to note, however, that this substance was obtained only during one of several attempts.

Another difficulty met was in drying the molecular compounds

prepared with acetic and formic acids. The solution of this difficulty has already been described.

In the case of the acids very soluble in the acetate, some difficulty was experienced in getting the derivative to crystallize out. This difficulty was circumvented by decreasing the amount of solvent used and by tilting the watch glass so that the mother liquor could drain off.

## II. Compounds Isolated.

The following is a list of compounds prepared, the physical constants of which were determined:

1. Benzylammonium formate
2. Benzylammonium acetate
3. Benzylammonium propionate
4. Benzylammonium butyrate\*
5. Benzylammonium caproate
6. Benzylammonium chloroacetate
7. Benzylammonium trichloroacetate
8. Benzylammonium phenylacetate
9. Benzylammonium o-toluate
10. Benzylammonium cinnamate
11. Benzylammonium phthalate
12. Benzylammonium benzoate
13. Benzylammonium o-aminobenzoate
14. Benzylammonium m-aminobenzoate
15. Benzylammonium p-aminobenzoate

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\*Could not be obtained in a form pure enough to determine the physical constants.

16. Benzylammonium m-bromobenzoate
17. Benzylammonium o-chlorobenzoate
18. Benzylammonium m-chlorobenzoate
19. Benzylammonium p-chlorobenzoate
20. Benzylammonium o-hydroxybenzoate
21. Benzylammonium m-hydroxybenzoate
22. Benzylammonium p-hydroxybenzoate
23. Benzylammonium o-methoxybenzoate
24. Benzylammonium m-methoxybenzoate
25. Benzylammonium p-methoxybenzoate
26. Benzylammonium o-nitrobenzoate
27. Benzylammonium m-nitrobenzoate
28. Benzylammonium p-nitrobenzoate
29. Benzylammonium 2,4-dinitrobenzoate

### III. Physical Properties.

The following table gives the molar ratios, the melting points, and the colors of the compounds prepared:

TABLE I

|                             | Ethyl Acetate |             | Ethyl Alcohol |             | Molar Ratio | Color |
|-----------------------------|---------------|-------------|---------------|-------------|-------------|-------|
|                             | Obs. C°       | Corr. C°    | Obs. C°       | Corr. C°    |             |       |
| Formic acid <sup>a</sup>    | 94-96         | 94.9-96.9   | 94-96         | 94.9-96.9   | 1:1         | white |
| Acetic acid <sup>a</sup>    | 95.4-96.2     | 96.3-97.1   | 95.4-96.2     | 96.3-97.1   | 1:1         | white |
| Propionic acid              | 46.5-47.3     | 46.7-47.5   | 46.5-47.3     | 46.7-47.5   | 1:1         | white |
| n-Butyric acid <sup>b</sup> |               |             |               |             |             | white |
| Caproic acid                | 51.6-52.6     | 51.7-52.7   | 51.6-52.6     | 51.7-52.7   | 1:1         | white |
| Chloro-acetic acid          | 118.4-119.4   | 119.9-120.9 | 118.4-119.4   | 119.9-120.9 | 1:1         | white |
| Trichloro-acetic acid       | 118.8-119.8   | 120.3-121.3 | 118.8-119.8   | 120.3-121.3 | 1:1         | white |
| Phenyl-acetic acid          | 120.4-121     | 122-122.6   | 120.4-121     | 122-122.6   | 1:1         | white |
| o-Toluoic acid              | 143.2-144.2   | 145.4-146.4 | 143.2-144.2   | 145.4-146.4 | 1:1         | white |
| Cinnamic acid               | 134-134.6     | 135.9-136.5 | 134-134.6     | 135.9-136.5 | 1:1         | white |
| Phthalic acid               | 84.6-85.6     | 85.3-86.3   | 84.6-85.6     | 85.3-86.3   | 1:1         | white |

<sup>a</sup>Hygroscopic.

<sup>b</sup>The compound, which was obviously present, could not be purified to a point where consistent physical constants could be determined.

## Melting Point

|                                       | Ethyl Acetate   |                 | Ethyl Alcohol   |                 | Molar<br>Ratio | Color          |
|---------------------------------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|
|                                       | Obs. C°         | Corr. C°        | Obs. C°         | Corr. C°        |                |                |
| Benzoic acid                          | 125.4-<br>126.6 | 127.2-<br>128.4 | 125.4-<br>126.6 | 127.2-<br>128.4 | 1:1            | white          |
| o-Aminobenzoic<br>acid                | 110.8-<br>112   | 112-<br>113.2   | 110.8-<br>112   | 112-<br>113.2   | 1:1            | light<br>pink  |
| m-Aminobenzoic<br>acid                | 134-<br>134.6   | 135.9-<br>136.5 | 134-<br>134.6   | 135.9-<br>136.5 | 1:1            | pinkish<br>tan |
| p-Aminobenzoic<br>acid                | 194.6-<br>195.6 | 197.6-<br>198.6 | 194.6-<br>195.6 | 197.6-<br>198.6 | 1:1            | light<br>tan   |
| m-Bromobenzoic<br>acid                | 157.6-<br>158.2 | 160.6-<br>161.2 | 157.6-<br>158.2 | 160.6-<br>161.2 | 1:1            | white          |
| o-Chlorobenzoic<br>acid               | 148.4-<br>149.4 | 150.5-<br>151.5 | 148.4-<br>149.4 | 150.5-<br>151.5 | 1:1            | white          |
| m-Chlorobenzoic<br>acid               | 146.8-<br>147.4 | 149.2-<br>149.8 | 146.8-<br>147.4 | 149.2-<br>149.8 | 1:1            | white          |
| p-Chlorobenzoic<br>acid               | 157.4-<br>158.4 | 160.3-<br>161.3 | 157.4-<br>158.4 | 160.3-<br>161.3 | 1:1            | white          |
| o-Hydroxybenzoic<br>acid              | 93.4-<br>94.6   | 94.3-<br>95.5   | 93.4-<br>94.6   | 94.3-<br>95.5   | 1:1            | white          |
| m-Hydroxybenzoic<br>acid              | 184.6-<br>186   | 188.2-<br>189.6 | 184.6-<br>186   | 188.2-<br>189.6 | 1:1            | white          |
| p-Hydroxybenzoic<br>acid <sup>c</sup> | 211.4-<br>212   | 216.6-<br>217.2 | 211.4-<br>212   | 216.6-<br>217.2 | 1:1            | white          |
| o-Methoxybenzoic<br>acid              | 119.8-<br>120.6 | 121.5-<br>122.3 | 119.8-<br>120.6 | 121.5-<br>122.3 | 1:1            | white          |

<sup>c</sup>Showed tendency to decompose below the melting point.

|                          | Melting Point   |                 |                 |                 |       |                 |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-------|-----------------|
|                          | Ethyl Acetate   |                 | Ethyl Alcohol   |                 | Molar |                 |
|                          | Obs. C°         | Corr. C°        | Obs. C°         | Corr. C°        | Ratio | Color           |
| m-Methoxybenzoic acid    | 111.8-<br>112.8 | 113.1-<br>114.1 | 111.8-<br>112.8 | 113.1-<br>114.1 | 1:1   | white           |
| p-Methoxybenzoic acid    | 142.6-<br>143.4 | 144.8-<br>145.6 | 142.6-<br>143.4 | 144.8-<br>145.6 | 1:1   | white           |
| o-Nitrobenzoic acid      | 141.4-<br>143.2 | 143.9-<br>145.7 | 141.4-<br>143.2 | 143.9-<br>145.7 | 1:1   | light<br>yellow |
| m-Nitrobenzoic acid      | 171.4-<br>172   | 174.9-<br>175.5 | 171.4-<br>172   | 174.9-<br>175.5 | 1:1   | light<br>yellow |
| p-Nitrobenzoic acid      | 193-<br>194.6   | 197.3-<br>198.9 | 193-<br>194.6   | 197.3-<br>198.9 | 1:1   | light<br>yellow |
| 2,4-Dinitrobenzoic acid* |                 |                 | 194.8-<br>195.8 | 199.1-<br>200.1 | 1:1   | yellow          |

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\*Calfee, John D., Thesis, The University of Tennessee, 1934.

## IV. Analytical Data.

The following table gives the neutralization equivalents and the nitrogen analyses of the compounds prepared:

TABLE II

|                             | Neutralization Equivalent |       |       | Nitrogen Analysis |        |        |
|-----------------------------|---------------------------|-------|-------|-------------------|--------|--------|
|                             | Calc.                     | Found | Found | %Calc.            | %Found | %Found |
| Formic acid                 | 153.1                     | 155.5 | 156.2 | 9.15              | 9.09   | 8.99   |
| Acetic acid                 | 167.1                     | 167.6 | 167.5 | 8.38              | 8.45   | 8.48   |
| Propionic acid              | 181.1                     | 185   | 188   | 7.72              | 7.58   | 7.60   |
| n-Butyric acid <sup>a</sup> |                           |       |       |                   |        |        |
| Caproic acid                | 223.2                     | 223.7 | 225.9 | 6.28              | 6.20   | 6.17   |
| Chloro-acetic acid          | 201.6                     | 199.8 | 200.3 | 6.95              | 6.89   | 6.93   |
| Trichloro-acetic acid       | 270.5                     | 274.8 | 275.4 | 5.18              | 5.32   | 5.33   |
| Phenyl-acetic acid          | 243.1                     | 241.4 | 241.7 | 5.76              | 5.92   | 5.88   |
| o-Toluic acid               | 243.1                     | 242.8 | 241.2 | 5.76              | 5.82   | 5.85   |
| Cinnamic acid               | 255.1                     | 255.1 | 253.6 | 5.49              | 5.50   | 5.34   |
| Phthalic acid               | 136.6                     | 141.2 | 137.9 | 5.13              | 5.03   | 5.15   |
| Benzoic acid                | 229.1                     | 230.4 | 229.1 | 6.11              | 5.92   | 5.99   |
| o-Aminobenzoic acid         | 244.1                     | 242.9 | 239.1 | 11.48             | 11.60  | 11.64  |
| m-Aminobenzoic acid         | 244.1                     | 248.7 | 246.8 | 11.48             | 11.47  | 11.67  |
| p-Aminobenzoic acid         | 244.1                     | 247.8 | 247.7 | 11.48             | 11.31  | 11.35  |
| m-Bromobenzoic acid         | 308.0                     | 303.2 | 306.5 | 4.55              | 4.58   | 4.58   |
| o-Chlorobenzoic acid        | 263.6                     | 261.9 | 263.8 | 5.31              | 5.18   | 5.19   |

<sup>a</sup>The compound, which was obviously present, could not be purified to a point where consistent physical constants could be determined.

|                                      | Neutralization Equivalent |       |       | Nitrogen Analysis |        |        |
|--------------------------------------|---------------------------|-------|-------|-------------------|--------|--------|
|                                      | Calc.                     | Found | Found | %Calc.            | %Found | %Found |
| m-Chlorobenzoic acid                 | 263.6                     | 266.3 | 264.4 | 5.31              | 5.21   | 5.45   |
| p-Chlorobenzoic acid                 | 263.6                     | 261.4 | 263.2 | 5.31              | 5.50   | 5.45   |
| o-Hydroxybenzoic acid                | 245.1                     | 246.7 | 244.8 | 5.71              | 5.59   | 5.48   |
| m-Hydroxybenzoic acid                | 245.1                     | 244.5 | 240.9 | 5.71              | 5.85   | 5.88   |
| p-Hydroxybenzoic acid                | 245.1                     | 218.6 | 220.0 | 5.71              | 5.70   | 5.73   |
| o-Methoxybenzoic acid                | 259.1                     | 261.2 | 258.7 | 5.41              | 5.62   | 5.61   |
| m-Methoxybenzoic acid                | 259.1                     | 258.1 | 253.0 | 5.41              | 5.37   | 5.54   |
| p-Methoxybenzoic acid                | 259.1                     | 258.9 | 261.8 | 5.41              | 5.45   | 5.49   |
| o-Nitrobenzoic acid                  | 274.1                     | 276.3 | 277.9 | 10.22             | 10.35  | 10.33  |
| m-Nitrobenzoic acid                  | 274.1                     | 269.1 | 270.0 | 10.22             | 10.12  | 10.20  |
| p-Nitrobenzoic acid                  | 274.1                     | 274.1 | 270.0 | 10.22             | 10.25  | 10.23  |
| 2,4-Dinitrobenzoic acid <sup>b</sup> | 319.1                     | 325   | 315   | 13.17             | 13.16  | 13.11  |

<sup>b</sup>Determined by Calfee, John D., Thesis, University of Tennessee, 1934.

## CHAPTER IV

### THEORETICAL DISCUSSION

Various theories have been advanced in attempts to explain the types of linkage found in organic compounds. This is particularly true in organic molecular compounds, which are formed from two apparently saturated compounds without the loss of atoms. A recent theory which may be used to explain the peculiar type of linkage found in organic molecular compounds has been proposed by Sidgwick<sup>1</sup> in his discussion of the electronic theory of valency.

Sidgwick<sup>2</sup> stated that the chemical evidence points to the existence of three different types of linkage:

(1) Polar or ionizable linkages between the oppositely charged ions of a salt.

(2) Non-polar, non-ionizable linkages especially prevalent in organic compounds.

(3) Coordinate links, capable of uniting apparently saturated molecules; the number of these not being determined, as (1) and (2) are, by the group in the Periodic Table to which the element belongs.

Sidgwick<sup>3</sup>, in view of the chemical evidence, classified valency as follows:

(1) Electrovalency. Polar or ionized linkages which are due to the transference of electrons from one atom to another.

(2) Covalency. Non-polar, non-ionizable type which is due to the sharing of two electrons between two atoms. This sharing of electrons can arise in two ways:

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1. Sidgwick, "The Electronic Theory of Valency." Oxford University Press, London, 1929, p. 61.
  2. Sidgwick, Ref. 1, p. 52.
  3. Sidgwick, Ref. 1, p. 61.

(a) By normal covalency in which one electron is contributed by each atom.

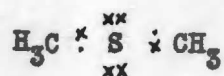
(b) By coordinate covalency in which both electrons are contributed by the same atom.

The formation of hydrogen chloride illustrates the electrovalent type of linkage. In this union the chlorine with seven electrons in the outer layer completes its octet by gaining an electron from the hydrogen. The formation of this compound may be represented as



in which the negative charge ( - ) represents the electron gained by the chlorine atom and the positive charge ( + ) represents the positive charge on the hydrogen atom by reason of the loss of the electron to the chlorine.

A typical example of the covalent type of union is found in dimethyl sulfide:



Here each dot ( . ) represents an electron furnished by a carbon atom of the methyl group, while each cross ( x ) represents an electron provided by the sulfur atom.

In this compound sulfur has formed only two normal covalences which gives it a full valency group of eight electrons. Two pairs of these eight are shared with the two carbon atoms, while the other four form what are known as "lone pairs." This would appear to saturate the sulfur atom in the dimethyl sulfide but two more covalences of the coordinate covalent type may be formed by sharing the lone pairs with an atom which needs two electrons to complete its octet. This

would enable the sulfur atom to increase its covalency from two to four. An example of this coordinate covalence is found in dimethyl sulfone where the sulfur contributes both electrons in each link with the oxygen. The formula of this compound may be represented as



In I the electrons furnished by the sulfur atom are represented by crosses (x) and those supplied by the carbon atoms are represented by dots (.). In II a bond (-) represents a normal covalent link while an arrow ( $\rightarrow$ ), representing a coordinate covalent link, points away from the atom which provides the pair of electrons.

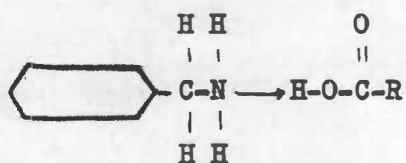
Another example of the coordinate covalent type of linkage is to be found in the formation of ammonium chloride. Here the nitrogen of the ammonia furnishes a lone pair and the hydrogen of the hydrogen chloride acts as the acceptor.



The arrow, pointing toward the acceptor of the electrons, represents the coordinate covalent bond.

In the formation of the molecular compounds obtained in this investigation the union appears to have been of the coordinate covalent type analogous to that shown in the formation of ammonium chloride. A formula proposing the coordinate covalent type of link-

age for these derivatives is given below.



The arrow, representing the coordinate covalent bond, points toward the hydrogen atom of the carboxyl group in the acid. This atom acts as the acceptor of the lone pair of electrons furnished by the nitrogen in the amino group of the benzylamine.

## CHAPTER V

## CONCLUSION

In carrying out the aims of this investigation the following accomplishments may be summarized:

(1) A simple method for preparing derivatives of benzylamine with carboxylic acids was found.

(2) Twenty-nine crystalline derivatives of benzylamine with carboxylic acids were prepared. Twenty-eight of these derivatives were purified.

(3) The melting points of twenty-eight of the twenty-nine derivatives were determined, both when the derivatives had been prepared in ethyl acetate solution and when they had been recrystallized from absolute ethyl alcohol.

(4) The neutralization equivalents of the twenty-eight pure salts were determined.

(5) The percentage of nitrogen present in the twenty-eight pure salts was determined.

In studying the suitability of benzylamine as a reagent for the identification of carboxylic acids, it was noted that the derivatives were satisfactory in the following respects:

(1) The derivatives met the requirements for a good derivative as set down by Kamm<sup>1</sup>, since

a. They were easily prepared by a general reaction;

b. They (except in one case) were easily purified;

1. Kamm, "Qualitative Organic Analysis." John Wiley and Sons, New York, 1932, p. 163.

- c. They were crystalline solids;
- d. They possessed readily determinable physical and chemical properties.

(2) The derivatives possessed characteristic melting points and could be titrated so as to determine the neutralization equivalents. Kamm<sup>2</sup> stated that this double-check feature is desirable in a derivative.

(3) A satisfactory derivative was formed with every acid tried, with one exception.

In contrasting the use of benzylamine as a reagent in the identification of carboxylic acids with the other methods now in use, it should be noted that practically all the desirable features of the other methods used in the identification of acids, which methods and their uses have already been described in the Historical Part of this paper, are found to be present in this one method. Outstanding among these desirable features is the very simple method used in the preparation of the derivatives. Judging from the success obtained with the acids tried, it also appears to be applicable to a great variety of similar types.

From a consideration of the advantages of the method of identification described in this paper, it was concluded that benzylamine is not only a suitable reagent for use in the identification of carboxylic acids, but its use offers certain advantages over any other reagent now in use for the identification of carboxylic acids.

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2. Kamm, Ref. 1, p. 163.

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