HOFMANN REACTION
AND
POLYAMIDES

STUDY OF

THE HOFMANN REACTION BETWEEN SODIUM HYPOCHLORITE

AND SUCCINAMIDE.

PREPARATION OF ISOPROPYLIDENE BIS-PHENYLEN OXYDIACETIC

ACID.

PREPARATION OF POLYAMIDES.

A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the
requirements for the degree of Bachelor of Science in
Chemistry.

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INTRODUCTION TO HOFMANN REACTION

In the Hofmann reaction between succinamide and potassium hypobromite, small yields of dihydrouracil have been obtained. From the reaction of succinamide and sodium hypochlorite it was hoped that larger yields of the dihydrouracil could be obtained and through spectrophotometry identify the compound further.
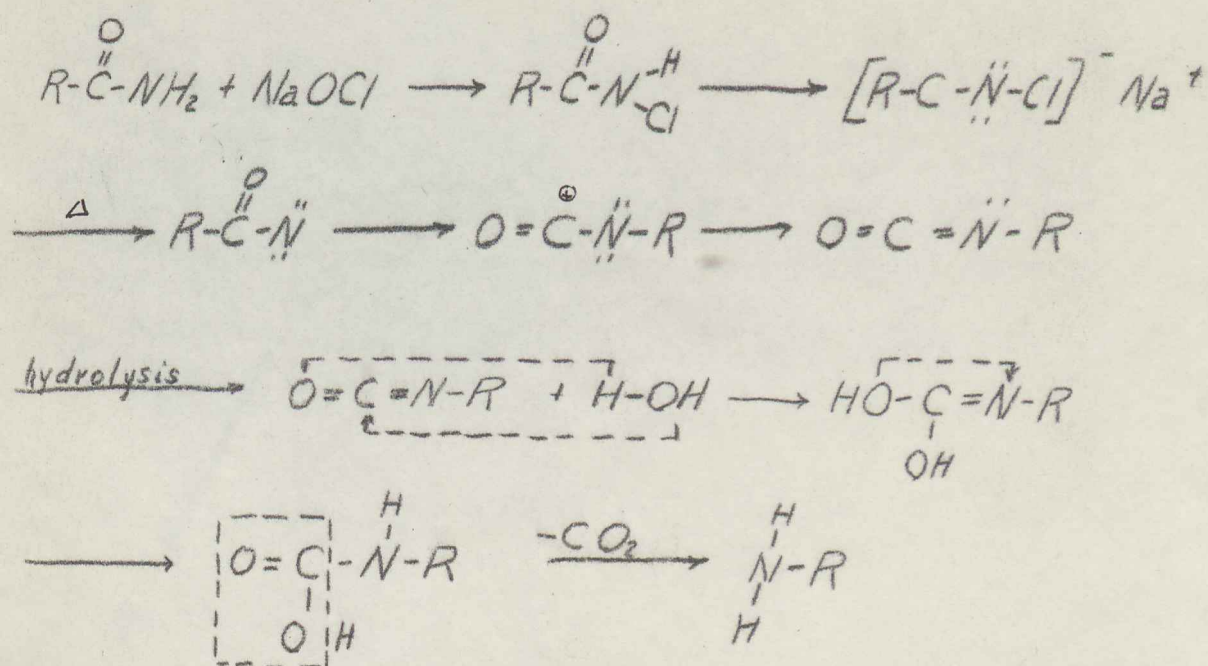
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HISTORY

In 1881 Hofmann prepared primary amines from amides and a hypohalite. This synthesis is now known as the Hofmann reaction. Since then much work has been done on the reaction.

In the investigation of a possible means of the production of ethylene diamine from succinamide and potassium hypobromite, L. R. Rosekrans rediscovered the fact that ethylenediamine did not form but the reaction product was dihydrouracil. This reaction was first reported by Weidel and Roithner.

In his investigation of the reaction of potassium hypobromite and sodium hypochlorite on adipamide W. F. Marzluff found that greater yields of tetramethylene-diamine (putrescine) were obtained when sodium hypo-chlorite was used than that obtained when potassium hypochlorite was used.
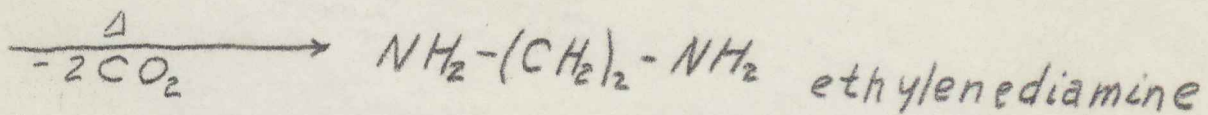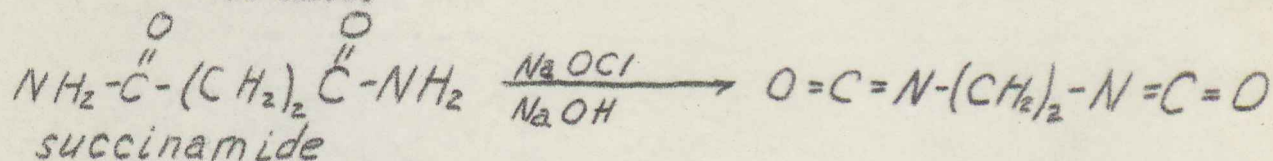
It was hoped that by using this information that greater yields of dihydrouracil could be obtained.

In the Hofmann reaction the hypohalite reacts with the amide to form an unstable salt in the presence of alkali which upon heating decomposes into an amine and carbon dioxide. The net result is an amine with one less carbon than the initial amide.
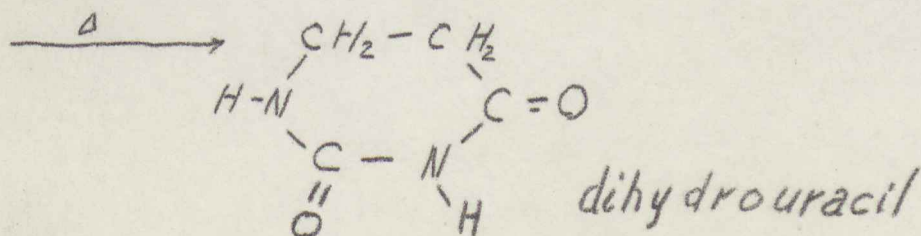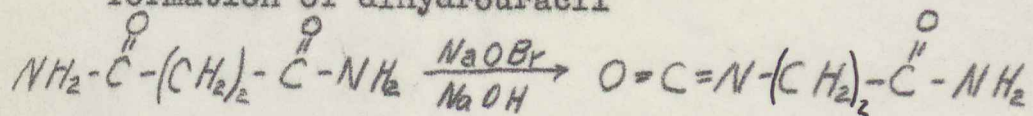
$$R-\overset{O}{\overset{\|}{C}}-NH_2 + NaOCl \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{Cl}{N}} \longrightarrow [R-C-\overset{..}{N}-Cl]^- \ Na^+$$

$$\overset{\Delta}{\longrightarrow} R-\overset{O}{\overset{\|}{C}}-\overset{..}{N} \longrightarrow O=\overset{\oplus}{\overset{\|}{C}}-\overset{\|}{N}-R \longrightarrow O=C=\overset{..}{N}-R$$

$$\xrightarrow{hydrolysis} \quad O=C=N-R \ + \ H-OH \longrightarrow HO-\underset{OH}{\overset{|}{C}}=\overset{..}{N}-R$$

$$\longrightarrow \ O=\underset{O\,H}{\overset{|}{C}}-\overset{H}{\overset{|}{N}}-R \ \xrightarrow{-CO_2} \ \overset{H}{\underset{H}{\overset{|}{\underset{|}{N}}}}-R$$

Applying this general reaction to succinamide,

we have:

$$NH_2-\overset{O}{\overset{\|}{C}}-(CH_2)_2\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[Na\,OH]{Na\,OCl} O=C=N-(CH_2)_2-N=C=O$$

succinamide

$$\xrightarrow[-2CO_2]{\Delta} \quad NH_2-(CH_2)_2-NH_2 \quad ethylenediamine$$
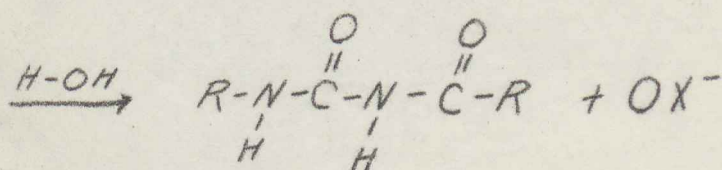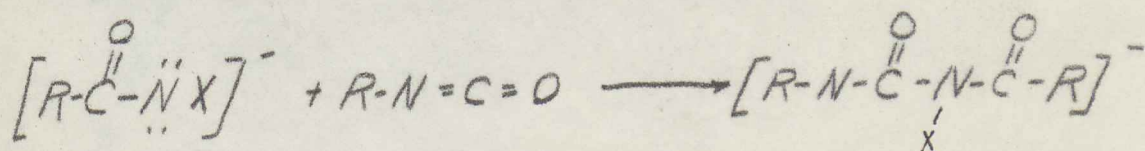
But there is also the possibility of a cyclic

formation taking place, that is what happens in the

formation of dihydrouracil

$$NH_2-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[Na\,OH]{Na\,OBr} O=C=N-(CH_2)_2-\overset{O}{\overset{\|}{C}}-NH_2$$

$$\xrightarrow{\Delta}$$

dihydrouracil

An excess of sodium hydroxide is used to prevent
the formation of alkyl acyl ureas and to insure the
formation of the isocyanates. That is, in the absence
of excess alkali the isocycanates react with the
sodium salt of the haloamide to give salts of the alkyl
acyl ureas from which the ureas themselves result on
hydrolysis.

$$\left[R-\overset{\overset{O}{\|}}{C}-\overset{..}{\underset{..}{N}}X \right]^{-} + R-N=C=O \longrightarrow \left[R-N-\overset{\overset{O}{\|}}{C}-\underset{X}{N}-\overset{\overset{O}{\|}}{C}-R \right]^{-}$$

$$\xrightarrow{H-OH} \quad R-\underset{H}{N}-\overset{\overset{O}{\|}}{C}-\underset{H}{N}-\overset{\overset{O}{\|}}{C}-R \;+\; OX^{-}$$

Where x is either chlorine or bromine group.

EXPERIMENTAL

Hofmann Reaction - Succinamide

Reagent	Weight Added (gms)	Molecular Weight	Moles	Mole Ratio
Part I				
NaOCl	6.7*	74	0.090	2.1
NaOH	7.7	40	0.194	4.5
H_2O	121.	18	6.7	155
Succinamide	5.0	116	0.043	1
Part II				
NaOH	6.1	40	0.154	3.5
H_2O	23.4	18	1.30	3.0

* Note: 128 ml of "Clorox", containing 5.25% NaOCl by
        weight, was added.

The sodium hypochlorite (Clorox), sodium hydroxide,
and water were put in a 500 ml three-neck flask and
cooled to 0° to 5°C. The mixture was stirred with a
mechanical stirrer. The succinamide was added to the
above solution and was allowed to react for 35 minutes.
The temperature of the reaction was held within 0° to 5°C.

through this period. The color of the solution was a milky white during Part 1.

The reagents for Part II were then added to the reaction. The additional sodium hydroxide is added to prevent the formation of the salts of alkyl acyl ureas. The reaction mixture was then allowed to come to room temperature. Then it was heated slowly. The color of the solution changed from a milky white to a clear pale green at 35° C. At temperatures between $75^{\circ} - 80^{\circ}$ C, the reaction began to bubble. This was believed to be the carbon dioxide given off during the decarboxylation.

The reaction mixture was distilled and the distillate was collected in 250 ml of hydrochloric acid (36.9 millimoles of HCl.). This back titrated with 68.9 ml of 0.217 N sodium hydroxide to a phenolphthalein end point. From this information it was calculated that 1.31 gms of ethylenediamine distilled over, giving a yield of 5.16 gms (25.5% of the theoretical amount).

During this distillation a white precipitate was formed, this residue was extracted with ice cold hydrochloric acid. The salts, probably sodium chloride, were dissolved and the remaining precipitate was collected. this white solid was insoluble in hot water. It did not melt nor decompose when heated on a red hot glass rod. The conclusion drawn from this is that probably the compound was some inorganic impurity of the "Clorox".

All the filtrates and distillates were collected and made basic for the preparation of the benzoyl chloride derivative of ethylenediamine. To the above solution 11.0 gms of benzoyl chloride was added. From this 1.231 gms of derivative was collected out of a maximum possible yield of 11.5 gm (12% yield obtained.)

Derivative	Weight Obtained	Melting Pt. Range	Nitrogen Analysis Theoretical	Actual	Yield
Bis-benzamino-ethane	1.231 gms	248°-250°C*	10.4	10.1	12%

*Note: Melting point given in the literature for this compound is 249°C (Hickenbottom) and 252°C (Hulliken.)

Hofmann Reaction - Sebacamide

Reagents	Weight Added (gms)	Molecular Weight	Moles	Mole Ratio
Part I				
NaOCl	10.5*	74	0.704	28.2
NaOH	4.4	40	0.11	4.4
H₂O	4000	18	222	12,000
Sebacamide	5.0	200	0.025	1
Part II				
NaOH	3.5	40	0.087	3.5

* Note: 200 ml of "Clorox" contained 10.5 gms of NaOCl.

The procedure followed was the same as that in the previous reaction involving succinamide. The large volume of water was necessary to dissolve the sebacamide.

To the reacted solution 7 ml of benzoyl chloride and 5 gms of sodium hydroxide were added to form the benzoyl derivative of octylmethylene diamine but no precipitate was formed.

The same reaction was repeated except the reaction mixture was concentrated by distilling off water under acid conditions before the addition of the benzoyl chloride. No precipitate was formed again.

SUMMARY

I. In the Hofmann reaction of succinamide and sodium
    hypochlorite, the product is ethylenediamine.

2. Sebacamide dissolved in water with sodium hypochlorite
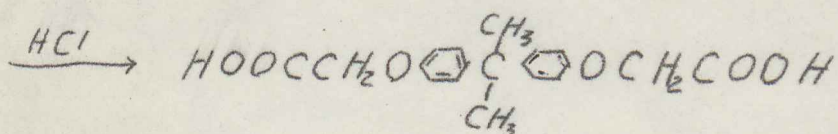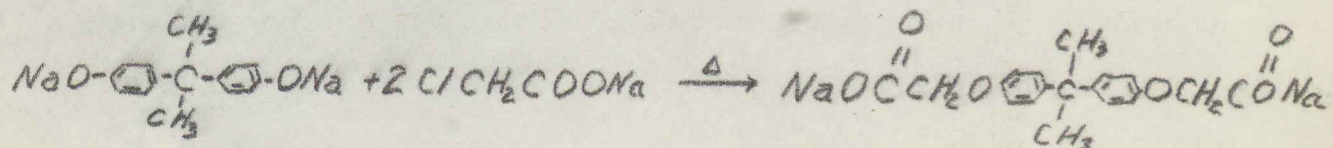   did not yield the benzoyl derivative of octylmethylene-
    diamine.

INTRODUCTION TO THE PREPARATION OF ISOPROPYLIDENE BIS-PHENYLENOXYDIACETIC ACID

The reaction of β,β- Bis (4-oxy-phenyl) propan (Bisphenol) and monochloracetic acid in alkali should yield a dibasic acid called isopropylidene bis-phenylen-oxydiacetic acid which will be referred to as the "dibasic acid". It was the purpose of this research project to prepare this dibasic acid and use it as an intermediate in the study of polyamide (See preparation of polyamides.).

Isolation, purification, and identification of the product was first attempted.

HISTORY

The method used is essentially the same as was
described by Koelsch in the preparation of aryloxacetic
acids. That is:

$$NaO-\langle\rangle-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\langle\rangle-ONa +2\,ClCH_2COONa \xrightarrow{\Delta} NaO\overset{O}{\overset{||}{C}}CH_2O\langle\rangle\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\langle\rangle OCH_2\overset{O}{\overset{||}{C}}Na$$

$$\xrightarrow{HCl} HOOCCH_2O\langle\rangle\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\langle\rangle OCH_2COOH$$

dibasic acid

Although the dibasic acid has been made before by
DuPont not much concerning it could be found in the
literature.

EXPERIMENTAL

Aryloxacetic Acid Reaction

Reagent	Molecular Weight	Weight Added	Moles
$C_{15}H_{16}O_2$ (Bisphenol)	228	228	1
Monochloracetic acid	95	209	2.2
NaOH	40	180	4.5
H_2O	18	1000	55.6

The above reagents were added to a five liter flask and refluxed for about five to ten hours.

In the purification of the reaction products the method discribed by Koelsch was tried and was found to be unsuccessful for large amounts.

The methods of purification tried were as follows:

1. Koelsch method using either as solvent.

2. Koelsch method using ethyl acetate as solvent.

3. Recrystallization of sodium salt of the dibasic acid.

4. Amine salt.

5. Anion exchange.

PURIFICATION METHOD #1 AND #2

If the refluxed solution is cooled and acidified
with hydrochloric acid, a sticky taffy-like mixture results.
This may be prevented by adding two liters of water, more
hydrochloric acid, warming the solution, and stirring. The
brownish precipitate is collected and dried. The purity of
the dibasic acid obtained in this manner is usually about
75% and having a melting point range of $160^{\circ} - 170^{\circ}$ C.

METHOD#1:

Purification can be accomplished by dissolving one gram
of the above sample in 250 ml of ether, and then extracting
this with a dilute 5% sodium carbonate solution. The
carbonate layer is then acidified with hydrochloric acid and
a precipitate is formed. This precipitate was
recrystallized from water. The product was found to be
98.0% pure dibasic acid by dissolving 0.1 gms of the
product in 50 ml of 95% ethyl alcohol and titrated this
with sodium hydroxide to a phenolphthalin end point. The
melting point of the above product ranged from $168^{\circ} - 173^{\circ}$ C.

Because of the large volume of ether needed to dissolve
the impure acid, the method was not considered pratical in
the making of 500 gm of pure di-basic acid.

METHOD #2:

The same procedure was used as in Method #1 except ethyl acetate was used in place of ether. One gram of the impure acid will dissolve in 50 ml of ethyl acetate. The purity of the product was 98.0% having a melting point range from 171° - 174° C.

This method was used to prepare large amounts of pure acid in which 170 gms of crude acid was dissolved in three liters of ethyl acetate. This was extracted with two liters of 5% sodium carbonate. The carbonate layer was acidified and the precipitate formed was collected and recrystallized from eight liters of water. The purity of this product was 96.8% and had a melting point range of 170° - 174° C. Of the 170 gms of crude acid used 120 gms of purified acid was recovered.

One undesirable feature of this method is that the solubility of the ethyl acetate in water is considerable and thus carries some bisphenol into the carbonate layer which in turn lowers the efficiency of this method.

METHOD #3:

If the refluxed solution cooled to 1° C, the sodium salt of the dibasic acid will precipitate. This precipitate is collected and dried. The product obtained is about 90% dibasic acid with a melting point range of 167° - 170° C.

Upon successive recrystallization of the sodium salt of the dibasic acid from water a product with purity as high as 93% can be obtained. This method proved to be the best considering the time involved and the amount of chemicals needed. Since the sodium salt of the acid is highly hydrophilic, it tends to form a gel during the filtering which makes the filtering very difficult. A higher purity could be gotten by finding a method of obtaining courser crystals of the sodium salt of the acid, thereby making the filtering easier which in turn makes the separation of the sodium salt of bisphenol from the sodium salt of the dibasic acid more complete.

By using the Koelsch Method #2 (ethyl acetate) of purification on samples of the dibasic acid which has been purified from the above Method #3 (sodium salt of the acid), small samples of dibasic acid of purity of 100% and a melting point range of $174^{\circ} - 175^{\circ}$ C were obtained.

METHOD #4:

Since the yield and purity from the Koelsch purifications were not too good, the separation of the pure dibasic acid was by-passed by the formation of the amine salt of the acid and an amine. This was done by taking the refluxed mixture (see page 13) and acidifying to obtain the crude acid. Then dissolving the crude acid in alcohol and add to this an equivalent amount of diamine.

(Since not all the crude acid is the dibasic acid, some bisphenol being present, an approximation to the amount of dibasic acid present can be determined by titrating with sodium hydroxide).

The amine salt should be washed in alcohol to remove any bisphenol absorbed on the crystals of the amine salt. Recrystallization of the amine salt from alcohol proved unsuccessful because its solubility in hot alcohol was not much different than in cold alcohol. The above method was tried using both hexamethylenediamine and ethylenediamine. With hexamethylenediamine, yields of 57% of the theoretical amounts of salt were obtained which decomposed at 262° C. (10 gms of 97% pure dibasic acid was dissolved in alcohol and 5 gms of hexamethylenediamine was added, the salt obtained from this was a snow-white and decomposed at 290° C).

Using ethylenediamine in the above method, yields of 78.9% were obtained and the amine salts obtained decomposed at 214° C.

This method is not only quick and good yields are obtained, but the amine salt upon heating will dehydrate, yielding a polyamide, the desired product (see polyamides for further information).

METHOD #5:

An anion exchange column of 80 grams of Amberlite IR-4B was prepared and washed with dilute hydrochloric acid. This was followed by a thorough washing with distilled water to remove any excess hydrochloric acid. Then 0.60 gms of 92.7% dibasic acid was dissolved in water and titrated to a phenolphthalein end point with sodium hydroxide. This solution was then poured in the exchange column and the excess liquid was removed. The column was washed with 200 ml of distilled water. This was followed by a solution of dilute hydrochloric acid. The dibasic acid which was absorbed on the resin was removed by the hydrochloric acid, but due to its insolubility in water the dibasic acid formed a precipitate. This precipitate was not effectively removed from the column when it was washed with distilled water, thus making this approach impractical.

IDENTIFICATION OF THE PRODUCT

Identification of the dibasic acid was accomplished
in two ways:

    1. Titration with sodium hydroxide

    2. From the saponification equivalent of the ethyl

       ester of the dibasic acid.

By titrating a known weight of the unknown with a
standardized sodium hydroxide solution, the amount of
dibasic acid can be determined. If the amount determined
is the same as that weighted out then the purity of the
unknown is 100%.

$$\frac{X = \text{(weight of dibasic acid to be determined)}}{\text{Molecular weight equivalence}} = \text{Volume of sodium hydroxide times the normality of the sodium hydroxide}$$

EXAMPLE:

    0.5890 gms of an unknown purity of acid is dissolved
in 50 ml of 95% ethyl alcohol and titrated to a phenol-
phthalein end point by 13.80 ml of 0.240 N sodium hydroxide.

$$\frac{X}{\frac{344}{2}} = (13.80)(0.240) \quad X = 0.5700 \text{ grams}$$

Then $\frac{0.570}{0.589}$ X 100 = 96.8% of dibasic acid.

SAPONIFICATION EQUIVALENT

In order to determine the saponification equivalent, it was necessary to prepare the diethyl ester of the unknown acid. This was made by refluxing for six hours the following mixture:

Reagents	Molecular Weight	Weight Added (gms)	Moles
Ethyl alcohol	46	400	8.7
Sulfuric acid	98	25.6	0.26
Crude acid	--	100.	--

After refluxing, most of the excess alcohol was distilled off at $79° - 90°$ C. The distillation was stopped when the residue began to turn black. Then 200 ml of diethyl ether and 300 ml of water were added to the residue to remove the sulfuric acid and alcohol. The ether layer then was separated from the water layer. The color of the water layer was light brown and the ether layer contained a light-green oilish compound which was flourescent. The ether layer was collected and the ether was distilled off. The residue was then distilled under vacuum as follows:

Boiling Point Range, °C.	mm. of Mercury	Fraction and Description
103-109	17	#1 Yellow liquid
120-250	17	#2 Yellow soft liquid
280-305	16	#3 Yellow solid
241	16	Boiling point of pure bis-phenol under vacuum

Fration #3 was recrystallized from a solution of 65% alcohol and 35% water. The white crystals obtained were dried and had a melting point range of 70.5° - 71.5°C.

Of this product 0.5149 gms was dissolved in 10 ml of a standardized solution of 0.905 N potassium hydroxide and dipropylene glycol in an open 250 ml round bottom flask. The above mixture was heated to 120° - 130°C for ten minutes. This was allowed to cool. The contents were dissolved with 15 ml of water and back titrated with 25.80 ml of 0.2493 N hydrochloric acid to a phenolphthalein end point. From this the molecular weight of the ester was determined.

Compound	Melting Point, °C	Molecular Weight Experimental	Calculated	Error
$C_2H_5O\overset{O}{\overset{\|}{C}}CH_2O\overset{CH_3}{\underset{CH_3}{C}}CH_2O\overset{O}{\overset{\|}{C}}CH_2CO_2H_5$	70.5-71.5	394	400	1.5%

SUMMARY

I   The dibasic acid was obtained in varing purities

in the following methods.

Method	Purity	Melting Point
1. Koelsch using ether as solvent	98%	168-173° C
2. Koelsch using ethyl acetate as solvent	98%	171-174° C
3. Recrystallization of the sodium salt	93%	167-170° C
4. Method #3 followed by Method #2	100%	174-175° C

II   Preparation of the diamine salt
                    was achieved.

Starting Reagents	Yield	Decomposition Point
Crude acid and hexamethylenediamine	57%	262° C
Pure acid and hexamethylenediamine	--	290° C
Crude acid and ethylenediamine	78%	214° C

III The diethyl ester of the dibasic acid was prepared

having a melting point of 70.5°-71.5°C.

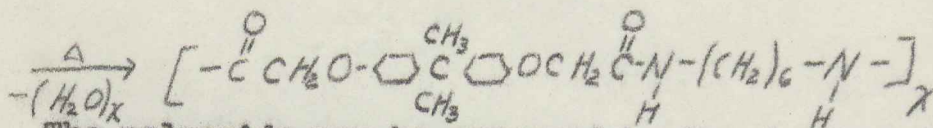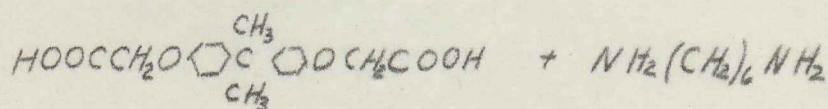## INTRODUCTION TO THE PREPARATION OF THE POLYAMIDE

By the condensation reaction between the dibasic acid and hexamethylenediamine or ethylenediamine, the preparation of the polyamide is desired. The polyamide is to be dissolved in a suitable solvent so that the resulting solution can be used as a wire enamel.

Testing the polyamide obtained by the various industrial tests to see whether it would be a suitable wire enamel, is to be determined.

HISTORY

In 1928 Wallace H. Carothers started on a research project which in 1930 led to the discovery of nylons. It was found that by drawing out a molten superpolyamide into a long fiber that after cooling, the fiber could be drawn further to several times its original length. While the original fiber was not strong nor elastic the new fiber had better properties. After considerable experimenting with hundreds of different polyamides, the polyamide made the condensation of adipic acid and hexamethylenediamine proved to be the best combination for a commercial fiber. Since then nylons have been used as fibers, plastics, wire enamels and etc.

The polyamide is obtained by the condensation of a dibasic acid and a diamine as follows:

$$HOOCCH_2O \bigcirc \overset{CH_3}{\underset{CH_3}{C}} \bigcirc OCH_2COOH \quad + \quad NH_2(CH_2)_6NH_2$$

$$\xrightarrow[-(H_2O)_x]{\Delta} \left[-\overset{O}{\overset{\|}{C}}CH_2O-\bigcirc\overset{CH_3}{\underset{CH_3}{C}}\bigcirc OCH_2\overset{O}{\overset{\|}{C}}-N-(CH_2)_6-N-\right]_x$$

The polyamide may be prepared by the following ways:

1. In a solvent

2. Dry (no solvent present during condensation)

The methods which can be used in either of the above
ways are:

    a. Reacting pure acid and pure diamine together.

    b. Heating a diamine salt of the acid.

No matter what combination of the above ways and
methods of preparation the polyamide is used, the
condensation reaction must be done in an atmosphere of
nitrogen. If oxygen is present the diamine will be
oxidized and a black product of low molecular weight will
be obtained. If a colorless polyamide is desired, it is
necessary to remove the small amounts of oxygen that is
present in the commercial nitrogen tank.

EXPERIMENTAL

The method used in preparing the polyamide was the combination 1. and b. (solvent and the diamine salt of the dibasic acid).

Reagents	Weight added
Hexamethylenediamine salt of the dibasic acid	500 gms
Imported cresylic acid	500 gms

The above reagents were put into a two liter four-neck flask which was fitted with a mechanical stirrer, a Fahrenheit thermometer, a condenser, and a nitrogen intake. The mixture was heated with a heating mantel, at $380°$ F some water, alcohol, and lower boiling cresylic acids started to distill and at $425°$ F the amine salt dissolved. The temperature of the reaction was held within $450° - 470°$ F for four hours.

It is necessary to take the viscosity of the reaction mixture near the end every half hour, because the reaction is complete when the viscosity reaches a maximum.

The viscosity is determined by dissolving one part of the reaction mixture in two parts of cresylic acid by weight, pouring some of this solution in a Gardner-Holt

viscosity tube and comparing it with a standard viscosity tube. The viscosity of the final reaction mixture should be Z-4.

The above reaction was diluted with R-7 cresylic acid until its viscosity was Z-4. This solution was then coated on copper wire and tested by the Schenectady Varnish Company. The results of their tests were as follows:

Test	Results
1. Scrape	3
2. Smoothness	good
3. Snap	failed
4. One-time-Mandrel	failed
5. Solvent (alcohol - toluene)	passed

A brief description of the above tests are:

1. The Scrape is the number of passes that a wire enamel will stand the abrasive action of a weighted needle edge before electrical contact is made.

2. Smoothness is the ability of the wire enamel to adhere to the wire in a continous uniform coat.

3. The Snap determines the ability of the enamel to adhere to the wire and its elasticity. This is done by stretching the wire until it breaks. If the enamel is cracked near the area wherethe break occurred, then the enamel fails the test. However if it stretches with the wire, it passes the test.

4. <u>One-time-Mandrel</u> is a further testing of the enamels ability to adhere to the wire and its elasticity. This is done by taking the end of the wire where the break occurred in the snap test and twisting it around itself. If the enamel cracks, it fails the test.

5. <u>Solvent</u> This determines the enamels ability to resist the solvent action of alcohol-toluene solvent.

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