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AMINATION OF ALKYL HALIDES

BY

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

IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE
IN CHEMICAL ENGINEERING

NEWARK, NEW JERSEY

1964

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

JUNE, 1964

ABSTRACT

The possibility of aminating alkyl halides with urea was the prime interest of the research undertaken in this thesis. Alkyl halides and urea react only to a slight degree. However the reaction is rapid when dimethylformamide is used as a solvent.

In working with compounds containing halogen on the aromatic ring we always found the halogen to be replaced by the amino group. With alkyl halides, however, this was not so. In the case of the reaction between an alkyl halide and urea in a solvent, a compound of composition close to that of a di-alkylurea was isolated and the halide ion produced. The reaction yield was calculated from the results obtained by the analysis for the halide ion.

There were a number of conditions which had an effect on increasing the final yield of the alkylurea:

- a. by varying temperature; b. changing the solvent;
- c. length of time that the reaction was run; d. an increase of the urea concentration in the experiment; and e. also,

by an increase in the alkyl halide concentration.

The rate of reaction between the halogens varied as normally expected: iodide > bromide > chloride.

PREFACE

The work described in this thesis was suggested by the observation of Professor James A. Bradley that aminating alkyl halides with urea in a suitable solvent was possible.

Alkyl ureas have usually been made from alkyl halides by ammonolysis to the amine, which is in turn reacted with an isocyanate.^{8,14} They have also been made by the action of alkyl halides on cyanates followed by hydrolysis and by other processes discussed in the body of this thesis.

Since urea is a solid the reaction had to be performed in a solvent. After choosing a suitable solvent the author determined and established the suitable reaction conditions.

The work discussed in this thesis deals with reaction conditions and on yields based on the amounts of a halide ion found. The alkyl ureas themselves were not isolated.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Professor James A. Bradley for his suggestions and guidance on the work described in this thesis and also to the Chemical Engineering Department of Newark College of Engineering whose facilities and equipment made work on this thesis possible.

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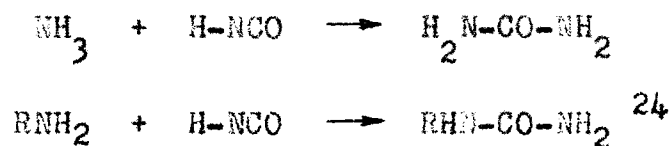
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INTRODUCTION

A literature search was made to determine the various methods of producing N-alkylureas. The resulting products consist of primary, secondary, and tertiary alkyl derivatives of urea. The following are the different ways which have been uncovered in the search.

Alkyl derivatives of urea are compounds in which one or more hydrogen atoms of the urea molecule are replaced by an alkyl group. Compounds of this type can be made by reactions similar to those used by Wohler^{18,21,23} in the preparation of urea except that an amine is substituted for ammonia as pointed out by Bordwell,¹ Sidgwick,²¹ and Wertheim.²⁴



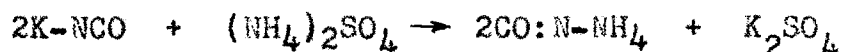
Another means of arriving at the same results shown above is pointed out by Davis and Blanchard⁵ and Dixon⁶ and involves the evaporation of the solution in water or alcohol of an amine and nitrourea. The nitrourea breaks down into cyanic acid and nitroamide; the latter de-

composing into nitrous oxide and water.

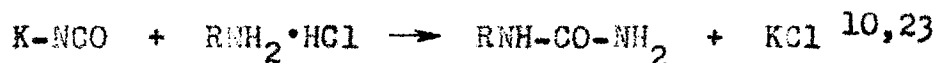


The cyanic acid then combines with the amine to form the substituted urea as previously shown by Bordwell,¹ Sidgwick,²¹ and Wertheim.²⁴

The reaction of potassium cyanate and ammonium sulfate followed by isomerization was pointed out by Rodd:



which in turn produces urea.¹⁹ This will compare with the combination of potassium cyanate and a hydrochloride salt of the amine accounted for by Hickinbottom and Szmant:



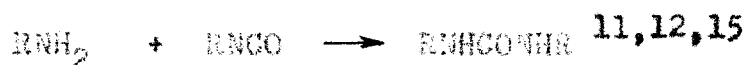
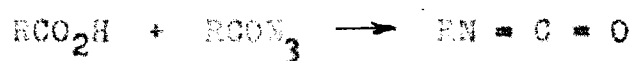
Highly substituted ureas are stable to heat, and may be distilled unchanged. However, the lower substituted N-alkylureas decompose on heating resulting in polymers of cyanic acid and a primary amine.¹⁹

N-alkylureas are uniformly monoacidic bases. They form crystalline salts and are hydrolysed by alkali to carbon dioxide and amines.¹⁹

The decomposition of acid azides to isocyanates and nitrogen is known as the Curtius rearrangement. The reaction is a preparative method.



for isocyanates and for compounds which derive from isocyanates such as amines, ureas, and others. When coupled with a hydrolytic step the Curtius rearrangement becomes a practical procedure for replacing a carboxyl group by an amino group. The overall process of converting an acid through its azide to an amine is commonly referred to as the Curtius reaction, which is then converted to the urea.



Substituted thio-ureas are similarly obtained from the salts of primary and secondary amines and sodium,

potassium, or ammonium thiocyanate.¹⁸



The addition of primary and secondary amines to isothiocyanate takes place readily with the formation of N,N'-substituted thioureas.



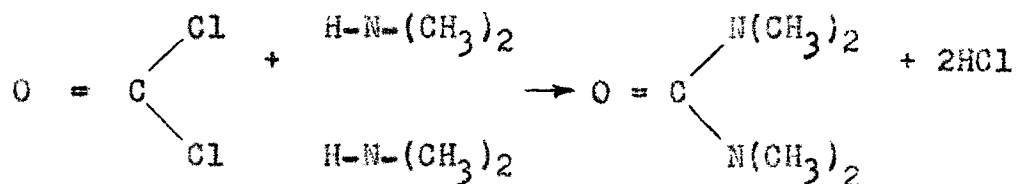
N-alkylureas can then be prepared by removing the sulphur from the alkylthioureas with silver salts.⁶



An additional method of producing a substituted urea is the reaction between an amine and chloroformamide as pointed out by Williams²⁵ and also noted by Caldwell,³

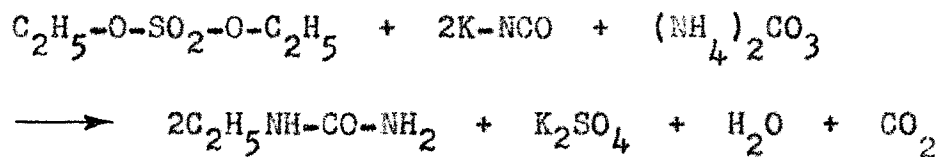


As stated by Wertheim, phosgene (carbonyl chloride), COCl_2 , reacts with secondary amines to form alkyl derivatives of urea.^{21,24}



Slotta and Lorenz reported that an N-alkylurea could

be prepared by heating an alkyl sulphate with potassium cyanate and ammonium carbonate.²²



The following section gives a complete account of the author's laboratory work and experimentation.

As the work progressed it was important to note the effect that the quantity of the halide had on the quantity of alkyl urea produced. This was investigated by observing the reaction of small and large amounts of reactants.

Particular attention was given to the effect of the structure of the alkyl halide on its activity in the reaction.

EXPERIMENTAL

A. Materials

1. Preparation of n-alkyl bromides. The method used to make the primary alkyl bromides was that of reaction with HBr, made from primary alcohol, potassium bromide, and sulfuric acid. The alcohol was weighed into the flask, which was equipped with a stirrer, reflux, and draw-off condenser. The sulfuric acid (98.8 percent) and potassium bromide in a mole ratio of less than one (acid/KBr) were then added.

The reactants were heated to the boiling point of the alkyl bromide. The reactants were refluxed and the n-alkyl bromide was distilled off to a close temperature range. When the temperature of the mixture rose slightly above the desired distilling temperature the reaction was stopped so as not to contaminate the collected alkyl bromide. Initially the stirring was kept slow until the reaction was started. From this point the agitation was made moderately brisk. One gram mole of alcohol was used to one gram mole of potassium bromide.⁷

2. Preparation of secondary alkyl bromides. Practi-

cally the same method was used to produce the secondary alkyl bromides; from secondary alcohol, sulfuric acid, and potassium bromide. This reaction called for an acid to potassium bromide ratio of less than one. The reaction called for acid of less than 70 percent. The quantity of acid used was 1 mole H_2SO_4 , which was put into a flask. One mole of the secondary alcohol was then added and 1.05 mole of fine grain potassium bromide in portions, with swirling. The mixture was warmed and allowed to reflux a short while until the secondary alkyl bromide was formed. The pure bromide was collected over the boiling range.⁷

3. Preparation of iso-butyl chloride. Alcohol and hydrochloric acid in the proportions of 0.5 moles of alcohol and 1.5 moles of acid were added to the reaction vessel. To this mixture was added 0.8 moles of anhydrous zinc chloride with agitation. The mixture was heated to reflux. The isobutyl chloride was purified by distillation.⁷

4. Preparation of tertiary butyl chloride. Tertiary butyl alcohol (0.5 moles) was shaken with 1.5 moles of hydrochloric acid (specific gravity 1.19). The products

separated into an organic phase and an inorganic phase. The organic phase, being on the bottom, was separated by means of the separatory funnel. The organic phase was then washed with ice cold water three different times in order to remove any impurities. It was then neutralized with a cold 5 percent solution of sodium bicarbonate until neutral to litmus paper. The tertiary butyl chloride was cloudy due to the presence of water. The product was then shaken with anhydrous potassium carbonate to remove the water.⁷

B. Procedure

1. Determination of solubility of urea and butyl bromide in solvent. Five grams of urea and six grams of dimethylformamide (approximately 1:1 mole ratio) were placed in a large test tube and stirred until the urea was partially dissolved. The urea would not completely dissolve by stirring. Upon warming the mixture to 80° C. the urea dissolved. Upon cooling to room temperature the urea then separated from the solution.²

By a similar procedure, with 80° C. as the temperature, a solution of urea and dimethylformamide was made. Five

equal samples of five cubic centimeters of each were placed in ten centimeter graduated cylinders. To the five samples was added one, two, three, four and five cubic centimeters of n-butyl bromide respectively. The mixtures were stirred and the separate layers observed. The mixtures were heated slightly in a warm water bath with stirring. Again the separation into layers was observed and a comparison of the results are shown in the Appendix.

2. Amount of halide present in reaction. Two separate experiments were run to determine the effect of varying the number of moles of the alkyl halide on the reaction. In the first was placed one ml. of n-butyl bromide, five grams of urea, and ten grams of dimethylformamide in a test tube. In the second test tube was placed two ml. of n-butyl bromide, five grams of urea, and ten grams of dimethylformamide. Both were heated for one hour at 100° C. The solution was then diluted with distilled water. The percent amination was determined by analyzing the mixture.

3. Amination of alkyl halides. The basic reaction of amination may be assumed as taking place between the halide and urea (NH_2CONH_2),

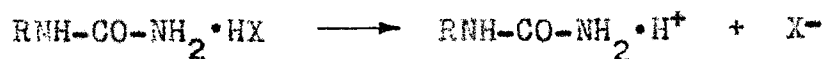


giving an n-alkylurea hydrohalide. The mechanism of the reaction is being studied, but it is not yet completely understood. A considerable amount of ammonium halide has been found as a byproduct. This cannot be explained by assuming thermal decomposition of urea, since it can take place at temperatures below the decomposition point of this compound.

The method of synthesis is as follows: first, the alkyl halide was weighed, 0.015 mole of it, to the nearest milligram, and placed in a glass test tube. Into the test tube were then weighed the solvent, N,N'-dimethylformamide (10.0 grams to the nearest tenth of a gram), and the urea (5.0 grams to the nearest tenth of a gram). An air condenser was attached to the tube to prevent loss of reactants upon heating. Heating of the mixture was accomplished in a constant temperature bath (56° C., 80° C., 100° C., 132° C., and/or 155° C.). The mixtures were heated for various time periods.

If necessary, the reactants were mixed by shaking the test tube slightly to ensure proper mixing, since a

uniform solution was not obtained in every case. They were then replaced in the constant temperature bath and heating was continued. After the heating period the product was transferred to a beaker with distilled water or directly into a volumetric flask containing approximately 100 cc. of distilled water and the flask was filled to the mark (500.0 ml.). In case a beaker was used, a quantitative transfer by distilled water was ensured. In a water solution the alkylurea hydrohalide ionized as follows:



For the analysis a 50.00 ml. sample was transferred to a clean beaker, to which was added a small amount of water to decrease the volume. This solution was titrated with a standard silver nitrate solution.

The halide ion was determined using, at various times, two techniques: (a) the Fajan's adsorption method with Eosin⁹ and (b) the Volhard method.⁹

The Fajan's method of determination of the halide worked very well with the lower carbon chain compounds, C₂, C₃, C₄, etc. However, with the high carbon chain compounds, such as lauryl bromide, there was some inter-

ference when titrating. When dissolving the reaction mixture of the lauryl bromide, a small amount of precipitation formed. A false end point was observed on the precipitate. The usual sharp end point was hard to distinguish in this case.

The Volhard method of analysis gave good results in all cases and was therefore used throughout the remaining study.

The percentage of reaction was obtained from the equations:

$$\text{Percent Reaction} = N_{\text{Ag}} V_{\text{Ag}} 10^{-3} \times \frac{500}{V_s} \times \frac{100}{n_{\text{Br}}} \quad \text{Eosin Method}$$

$$\text{or} \quad (N_{\text{Ag}} V_{\text{Ag}} - N_{\text{CNS}} V_{\text{CNS}}) 10^{-3} \times \frac{500}{V_s} \times \frac{100}{n_{\text{Br}}} \quad \text{Volhard Method}$$

$$\frac{500}{V_s} \times \frac{100}{n_{\text{Br}}}$$

V_s = volume of sample titrated in ml.

n_{Br} = molar amount of RBr put through reaction.

DISCUSSION

It has been shown by Craver and Bradley in work done at Newark College of Engineering that the use of urea in the amination of aryl halides resulted in the formation of aryl amines.⁴ With alkyl halides this was not so. In the case of the reaction between butyl bromide and urea in the solvent N,N-dimethylformamide, the product isolated was N,N-dibutyl urea.

As previously mentioned, the study did not involve the isolation of the products. However, the investigation did involve determination of reaction rates and yield (shown in Figures III to VI in the Appendix), also the effects of the variation of the type and amount of solvent present in the reaction, the temperature, the quantity of reactants present, and the time of the reaction. Along with the various primary alkyl groups, a number of different carbon radicals (benzyl, allyl, and secondary, tertiary, and iso-alkyl were combined with urea in the research project.

Alkyl bromides and urea will not react by themselves. Therefore the task undertaken in this research project would have been impossible without the use of a solvent in which the components could react.

At the very beginning the solvent used in the reaction was acetamide. Later the selection of a new solvent was initiated. At this point the solvent was changed to N,N-dimethylformamide since the reaction had to be run at a higher temperature than the melting point of urea (132° C.) This high temperature was used to ensure a proper reaction mixture. However, the higher temperature resulted in complicating the reaction by decomposing the urea into ammonia, biuret, cyanic acid, cyanuric acid and others when acetamide was used as the solvent.¹³ In addition it was also necessary to have a solvent which would ensure a homogeneous mixture at the new reaction temperature of 100° C. and since the N,N-dimethylformamide was a liquid compound at room temperature¹⁷ and could dissolve all the urea at the reaction temperature it was a suitable solvent to use throughout the rest of the work.

Once the solvent was chosen the conditions needed to obtain the greatest yield of alkylurea were determined. In order to increase further the percent yield of the alkylurea it was considered advantageous to increase the ratio of the solvent in proportion to the urea. As the project advanced the amount of solvent was increased

to 10.0 grams of the N,N-dimethylformamide to 5.0 grams of the urea. The increase in the solvent brought about a rise in the yield of the alkylurea in the reaction.

The rate of the chemical reaction increased rapidly with the rising temperature. As is well known the reaction rate increases when the temperature is increased.¹⁷

At the start of the research, upon using a high temperature, the reaction rate was extremely rapid. By the time a high yield was reached, the reaction rate naturally tapered off until only a small increase in yield was detectable with additional time. The reaction rate became slower due to the low concentration of the remaining alkyl halide and consequently a reduction in the rate.

Figures I and II illustrate the Yield versus Time for reactions at high temperatures when the indicated alkyl halides were used:

Figure I - High Temperature Reactions of Alkyl Bromides
(Constant Temperature - 155° C.)

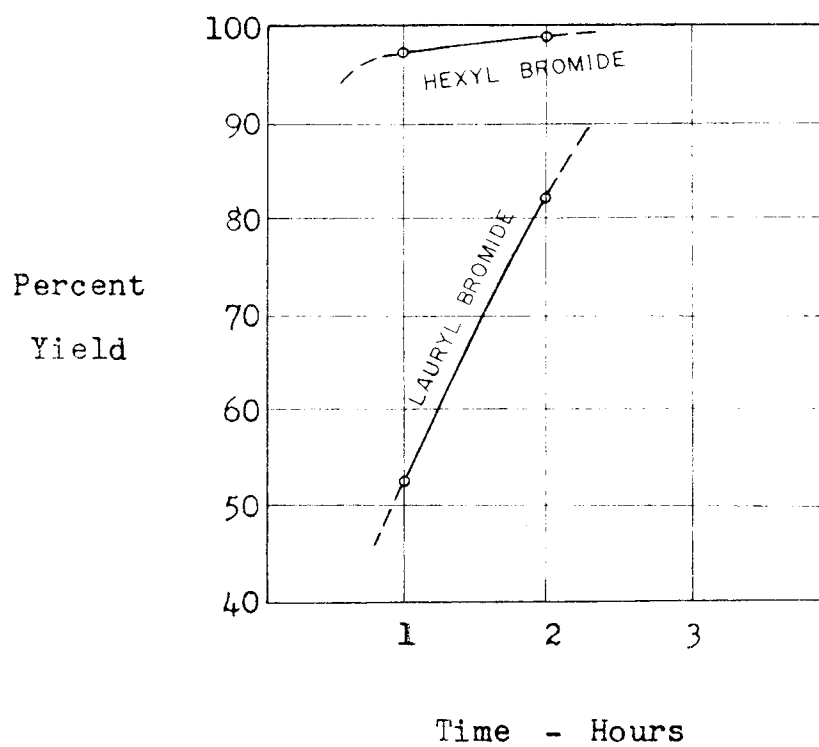
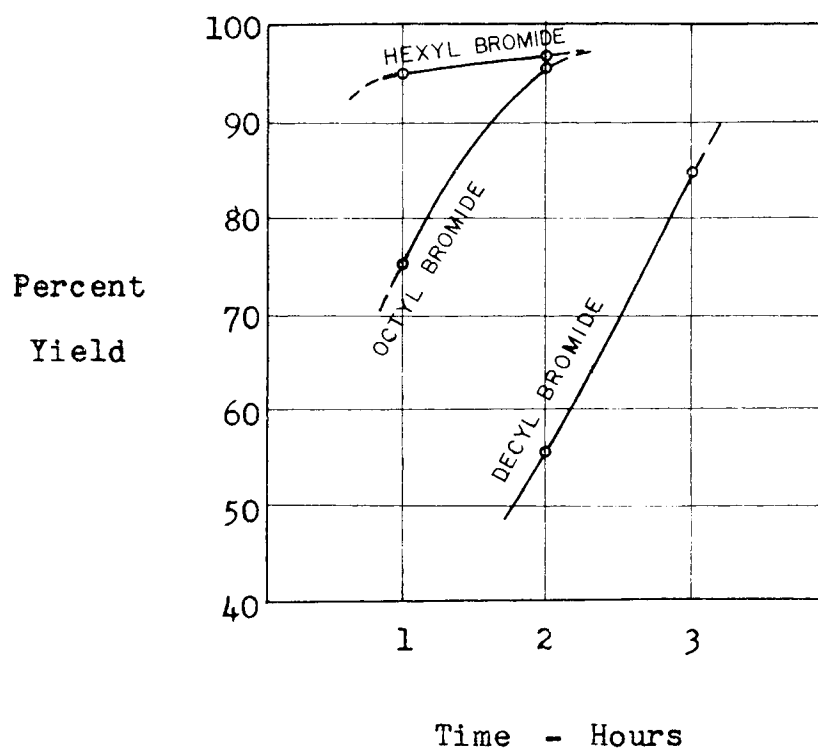


Figure II - High Temperature Reactions of Alkyl Bromides
(Constant Temperature - 132° C.)



A decrease in the temperature reduced the reaction rate of the alkyl iodides, bromides, and chlorides proportionately the same in relation to the yield. The iodides reacted readily, the bromides next in the degree of completion, and the chlorides reacted least readily of the three.

Usually a constant amount of reactants were used throughout the study. The amount of alkyl halides used was .015 mole and the urea ten times as great in quantity. The great difference in quantity would seem to push the reaction to completion in a shorter time period. This was not the case. The reaction progressed at a definite rate showing differentiation only with time and temperature (as indicated in the Appendix).

In one phase of the research the quantity of alkyl halide was varied. It was considered important to determine the effect that the quantity of the halide has on the amount of the alkylurea produced. This was investigated by observing the reaction rate of both large and small amounts of components.

Studies were made of the influence on the reaction rate of factors relating to the size and structure of the alkyl group: such as, the presence of a normal or branched chain; primary, secondary, or tertiary structure; and the presence of a ring of unsaturated linkage. The results of the study are shown in Figure VII of the Appendix.

In the foregoing section the two methods of analysis used in the determination of the halide were (a) Fajan's adsorption method and (b) the Volhard method.

Starting off with the alkyl bromides and chlorides no problem occurred with the use of Fajan's method of analysis. However, with lauryl bromide, alkyl iodides, and secondary, tertiary, benzyl and allyl compounds, the Volhard method was used to overcome complications and false end points obtained when using the eosin indicator.

The complications arose when a slight precipitate in the form of a cloudy or oily substance collected when the reaction mixture was dissolved in water. This precipi-

tate interferred with the titration. As a result approximately half of the reactions were analyzed using the eosin as the indicator and the remainder were analyzed following the Volhard method.

CONCLUSION

This research project was begun to prove that the reaction between normal, secondary, or tertiary alkyl halides and urea could take place and would produce results when analyzed for the product. Analysis was run on the free radical of the halide present, after the reaction had taken place.

The final choice of solvent was necessary to produce the best results. When N,N-dimethylformamide was used, the reaction mixture not only was made uniform but the urea also dissolved completely and the reaction occurred at a temperature of 100° C. without any resulting complications.

An increase in the solvent increased the yield of alkylurea, while the increase in temperature increased the rate of the chemical reaction. On the contrary, the higher temperatures merely complicated the decomposition of the urea and made it impossible to continue successfully with the experiment.

The amount of halide present increased the yield twofold by doubling it. The more urea used, the greater

the yield. This follows the theory of equilibrium in which the unbalanced condition drives the reaction to the other side to achieve a balanced state.

Holding a strict molecular quantity or relative quantity between the halide and the urea along with the solvent decreased the reaction rate with time.

When the number of carbon atoms in the molecule decreased, the percent yield rose as shown in Figure III.

APPENDIX

Table I

Data for Amination of Alkyl Bromides

Urea - 5.0 grams - 0.0833 moles
N,N-dimethylformamide - 10.0 grams - 0.137 moles
Normality of AgNO_3 - 0.1002

A. n-Ethyl bromide

<u>Wt.</u> <u>(Grms.)</u>	<u>Moles</u>	<u>Time</u> <u>(Hr.)</u>	<u>Temp.</u> <u>° C.</u>	<u>ML.</u> <u>(AgNO₃)</u>	<u>%</u> <u>Amin.</u>
1.6350	.01500	2	100	11.90	79.6
1.8180	.01664	4	100	14.75	88.5
1.6460	.01510	6	100	14.60	96.9

B. n-Propyl bromide

1.8600	.01515	2	100	9.90	65.7
1.8530	.01507	4	100	11.85	78.8
1.8550	.01510	6	100	13.57	90.2

C. n-Butyl bromide

2.0855	.01520	2	100	9.90	59.3
2.0980	.01530	3	100	10.25	67.4
2.0313	.01495	4	100	10.70	72.4
2.0641	.01506	6	100	12.65	84.5
2.0556	.01500	8	100	13.65	91.5

D. n-Amyl bromide

2.4090	.01540	2	100	8.28	53.7
2.3485	.01500	4	100	10.23	68.1
2.3174	.01485	6	100	11.49	77.5
2.3610	.01510	8	100	13.83	91.6

E. n-Hexyl bromide

2.4464	.01481	2	100	7.44	50.4
2.5560	.01548	4	100	10.14	65.7
2.6350	.01590	6	100	12.15	76.3
2.4365	.01475	8	100	12.90	87.7

Table I (Cont.)

<u>Wt.</u> <u>(Grms.)</u>	<u>Moles</u>	<u>Time</u> <u>(Hr.)</u>	<u>Temp.</u> <u>° C.</u>	<u>ml.</u> <u>(AgNO₃)</u>	<u>%</u> <u>Amin.</u>
<u>F. n-Heptyl bromide</u>					
2.6640	.01490	2	100	6.30	43.2
2.5900	.01450	4	100	8.23	57.0
2.5850	.01445	6	100	10.85	75.2
2.4880	.01390	8	100	11.90	86.0
<u>G. n-Octyl bromide</u>					
2.8729	.01490	2	100	5.00	33.7
3.0130	.01560	4	100	7.75	49.6
2.8480	.01475	6	100	9.10	61.7
2.8880	.01497	8	100	12.10	81.2
<u>H. n-Decyl bromide</u>					
3.3395	.01510	2	100	3.15	21.25
3.4010	.01535	4	100	4.67	31.2
3.4510	.01557	6	100	7.16	46.0
3.3450	.01512	8	100	9.52	63.0
<u>I. n-Lauryl bromide</u>					
3.7230	.01495	2	100	1.95	13.3
3.5320	.01417	4	100	2.60	18.7
3.7254	.01496	6	100	3.40	23.2
3.7060	.01485	8	100	4.60	31.5

Table IIData for Amination of Alkyl Iodides

Urea - 5.0 grams - 0.0833 moles

N,N-dimethylformamide - 10.0 grams - 0.137 moles

Normality of AgNO_3 - 0.1002A. n-Butyl iodide

<u>Wt.</u> <u>(Grms.)</u>	<u>Moles</u>	<u>Time</u> <u>(Hr.)</u>	<u>Temp.</u> <u>° C.</u>	<u>El.</u> <u>(AgNO_3)</u>	<u>Amin.</u>
2.7560	.01495	2	56	1.95	13.1
2.8300	.01535	4	56	3.70	24.1
2.7610	.01499	6	56	5.40	36.1
2.7690	.01510	8	56	6.76	44.7
2.8030	.01519	2	80	8.60	56.6
2.7730	.01503	4	80	11.00	73.2
2.7510	.01490	6	80	12.24	82.1
2.7690	.01501	8	80	13.43	89.5
2.8150	.01525	2	100	13.25	87.0
2.7720	.01502	4	100	14.70	97.8

B. n-Hexyl iodide

3.1890	.01500	2	80	6.19	41.2
3.5760	.01685	4	80	10.80	64.3
3.1250	.01475	6	80	10.60	72.0
3.1580	.01489	8	80	11.30	76.0

C. n-Octyl iodide

3.6290	.01505	2	100	9.05	60.0
3.6010	.01497	4	100	11.95	79.9
3.6030	.01468	6	100	12.9	86.3
3.6810	.01531	8	100	14.20	93.0

Table IIIData for Amination of Alkyl Chlorides

Urea - 5.0 grams - 0.0833 moles

N,N-dimethylformamide - 10.0 grams - 0.137 moles

Normality of AgNO_3 - 0.1002A. n-Butyl chloride

<u>Wt.</u> <u>(Grms.)</u>	<u>Moles</u>	<u>Time</u> <u>(Hr.)</u>	<u>Temp.</u> <u>° C.</u>	<u>Al.</u> <u>(AgNO_3)</u>	<u>Amin.</u>
1.2800	.01383	2	100	0.83	6.01
1.3913	.01503	4	100	1.04	6.95
1.3680	.01485	6	100	1.31	8.88
1.4340	.01549	10	100	1.70	11.00

B. n-Hexyl chloride

1.7280	.01495	2	100	0.53	3.56
1.8380	.01525	4	100	0.75	4.93
1.7305	.01436	6	100	1.00	6.98
1.8080	.01501	10	100	1.22	8.15

C. n-Octyl chloride

2.2370	.015100	2	100	0.11	0.735
2.3125	.015555	4	100	0.17	1.096
2.2455	.015150	6	100	0.28	1.86
2.3610	.015900	10	100	0.65	4.10

D. n-Lauryl chloride

3.0276	.01380	2	100	0.20	1.45
3.0800	.01405	4	100	0.10	0.712
3.0085	.01370	6	100	0.10	0.73
3.0130	.01375	10	100	0.32	2.33

Table IV

Data for Amination of Chlorides

Urea - 5.0 grams - 0.0833 moles

N,N-dimethylformamide - 10.0 grams - 0.137 moles

Normality of AgNO_3 - 0.1002A. iso-Butyl chloride

<u>Wt.</u> <u>(Grms.)</u>	<u>Moles</u>	<u>Time</u> <u>(Hrs.)</u>	<u>Temp.</u> <u>° C.</u>	<u>ml.</u> <u>(AgNO_3)</u>	<u>%</u> <u>Amination</u>
1.3560	.01465	2	100	6.40	43.7
1.3980	.01517	4	100	6.60	43.7

B. sec-Butyl chloride

1.3490	.01463	2	100	0.16	1.10
1.3828	.01497	4	100	0.50	3.35
1.3790	.01495	6	100	1.30	8.90

C. tert-Butyl chloride

1.3770	.01490	2	100	11.48	77.5
1.3835	.01499	4	100	12.80	86.0
1.3820	.01497	6	100	13.75	92.3

D. Allyl chloride

1.1340	.01483	2	100	4.40	29.8
1.2660	.01575	4	100	7.72	46.8
1.1340	.01483	6	100	9.43	63.8
1.1350	.01485	8	100	11.49	77.8

E. Benzyl chloride

1.9060	.01505	2	100	7.40	49.25
1.8540	.01465	4	100	10.34	70.7
1.8360	.01450	6	100	11.85	81.9
1.8410	.01455	8	100	13.20	91.0

Table VData for Amination of n-Alkyl Bromides

Urea - 5.0 grams - 0.0833 moles
 Normality of AgNO_3 - 0.1002

Key to Solvents:

A - Acetamide

D - N,N-dimethylformamide

<u>Alkyl Bromide</u> <u>Wt.(gm.)-moles</u>	<u>Solvent</u> <u>grms.-moles</u>	<u>Time</u> <u>(Hr.)</u>	<u>Temp.</u> <u>° C.</u>	<u>ml.</u> <u>(AgNO_3)</u>	<u>%</u> <u>Amin.</u>
C_4 -2.0744-.01512	(D)5.0-.068	8	155	13.80	91.4
C_6 -2.476 -.01499	(A)5.0-.085	8	155	11.37	76.2
C_6 -2.4786-.0150	(D)5.0-.068	8	155	14.70	93.0
C_8 -2.897 -.0150	(A)5.0-.085	8	155	14.30	95.6
C_8 -2.9033-.01505	(D)5.0-.068	8	155	14.39	96.1
C_{10} -3.3180-.01505	(D)5.0-.068	8	155	14.96	99.9
C_6 -2.2245-.0136	(D)6.1-.084	1	155	13.10	97.3
C_6 -2.6300-.01595	(D)6.1-.084	2	155	15.70	98.8
C_{12} -3.8290-.01535	(D)6.1-.084	1	155	8.07	52.6
C_{12} -3.7110-.01490	(D)6.1-.084	2	155	12.18	82.0
C_6 -2.4510-.01485	(D)6.1-.084	2	132	14.41	97.3
C_6 -2.5036-.01515	(D)6.1-.084	1	132	14.365	95.0
C_8 -2.8310-.0147	(D)6.1-.084	1	132	11.052	75.4
C_8 -2.8240-.01465	(D)6.1-.084	2	132	14.00	95.7

Table V (Cont.)

<u>Alkyl Bromide</u> <u>Wt.(gm.)-moles</u>	<u>Solvent</u> <u>grms.-moles</u>	<u>Time</u> <u>(Hr.)</u>	<u>Temp.</u> <u>° C.</u>	<u>Yl.</u> <u>(AgNO₃)</u>	<u>%</u> <u>Amin.</u>
C ₁₀ -3.263--.01505	(D)7.05--.097	1	132	5.065	33.8
C ₁₀ -3.2950--.01490	(D)7.05--.097	2	132	8.205	55.6
C ₁₀ -3.2027--.01446	(D)7.05--.097	3	132	12.23	84.5
C ₁₀ -3.7820--.01515	(D)9.00--.123	4	132	9.40	62.1

Figure III
Amination of Alkyl Bromides
Temperature 100° C

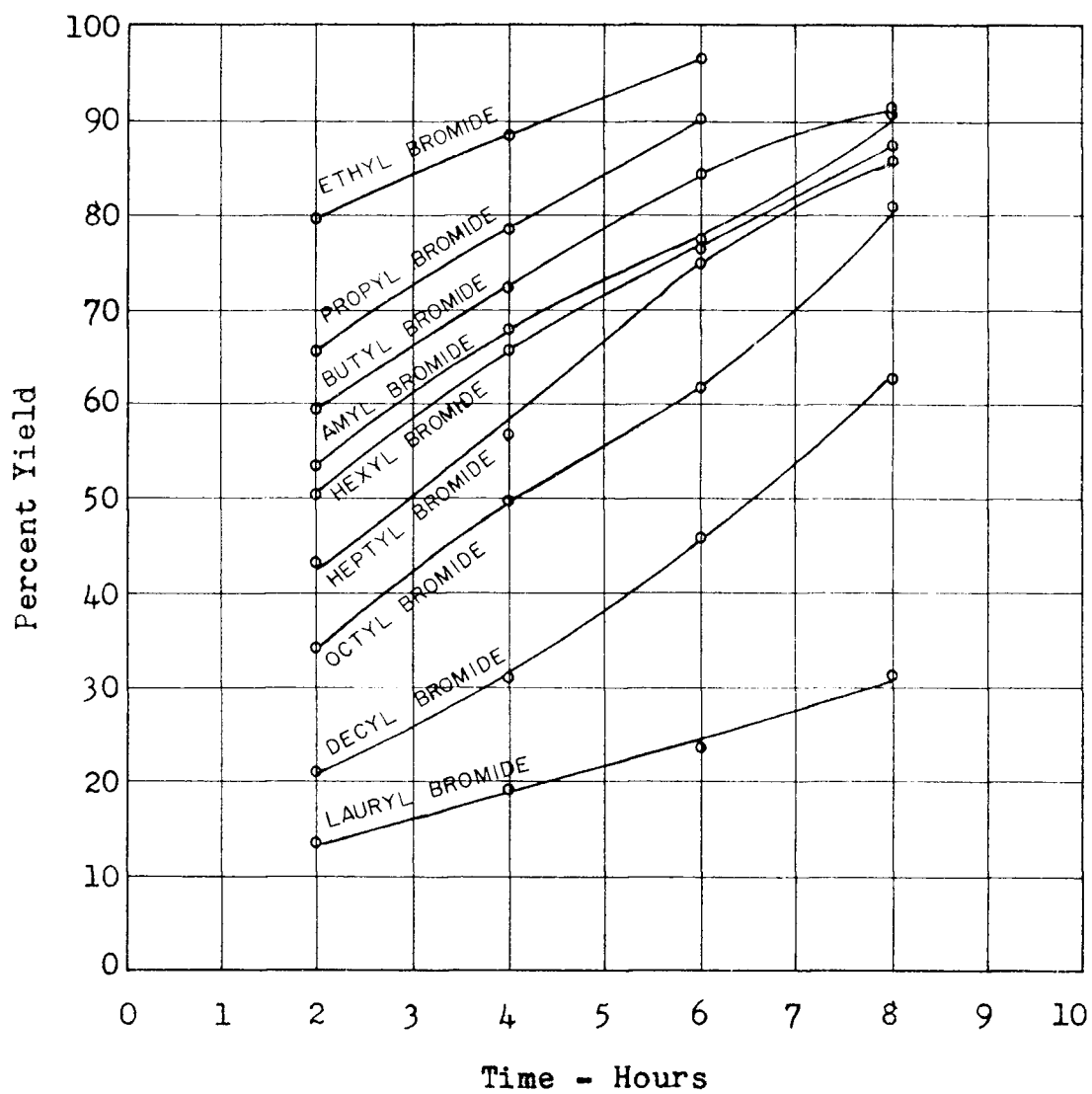


Figure IV
Amination of Alkyl Iodides

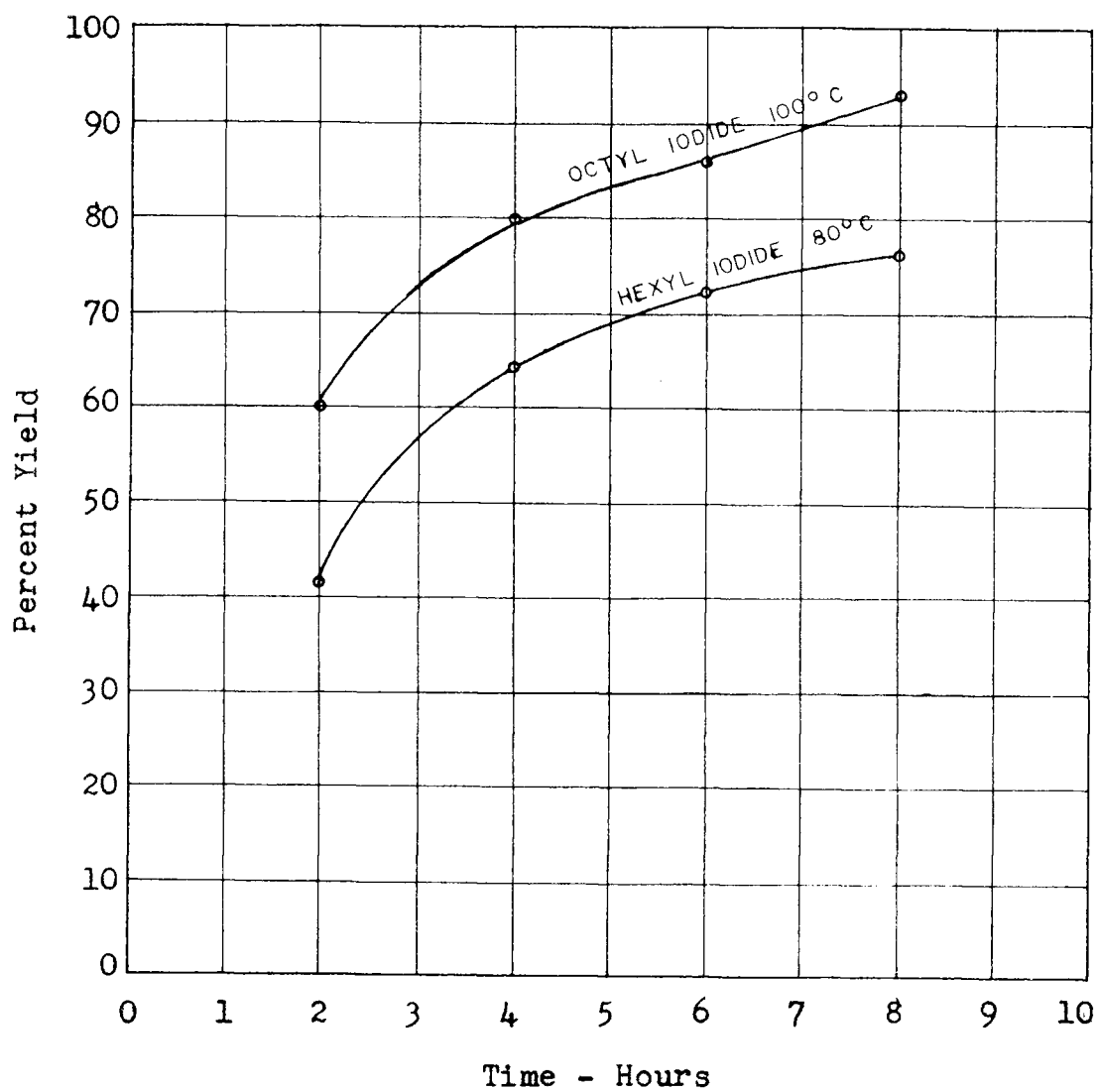


Figure V
Amination of Alkyl Chlorides
Temperature 100° C

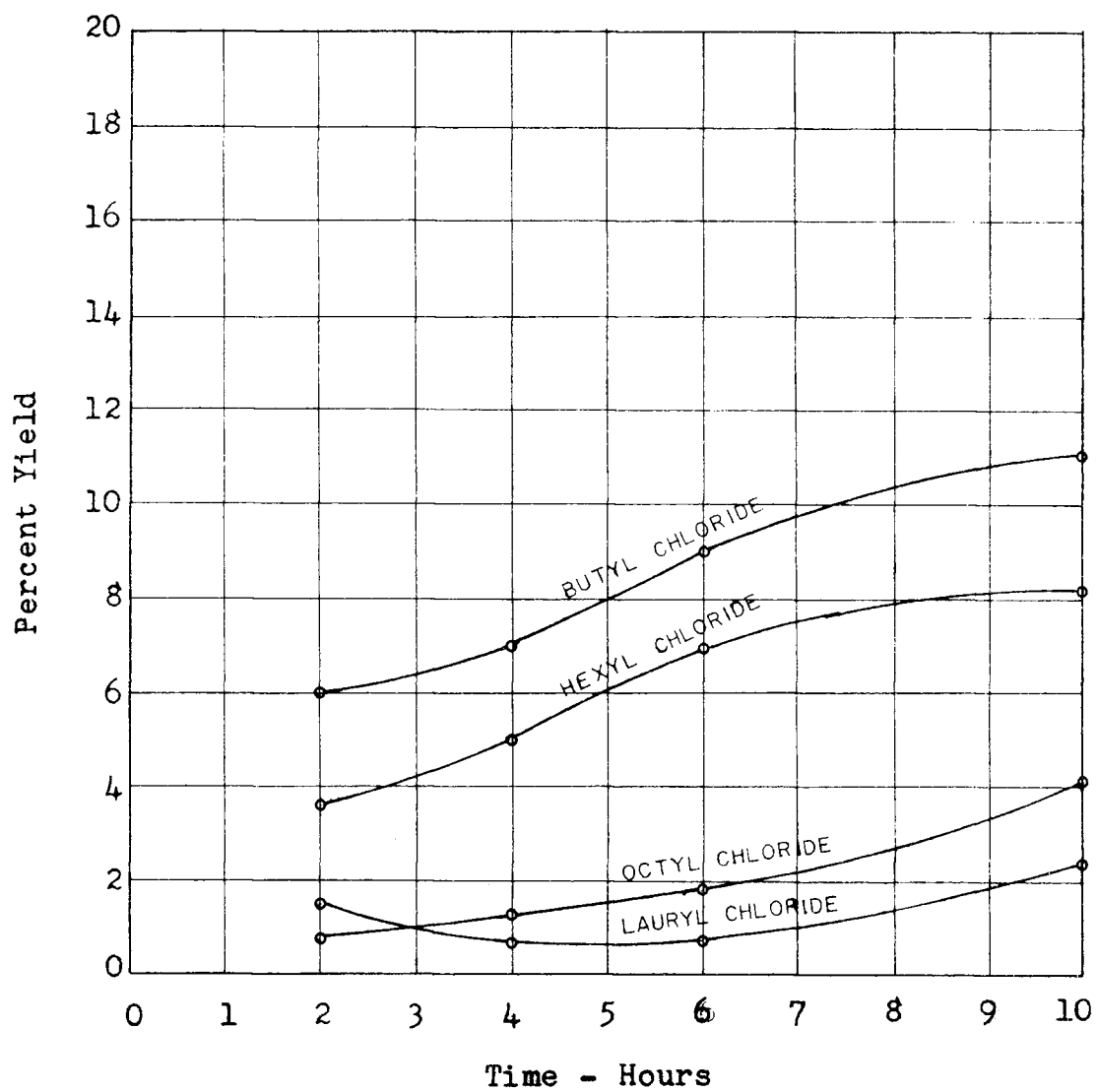


Figure VI
Amination of Chlorides
Temperature 100° C

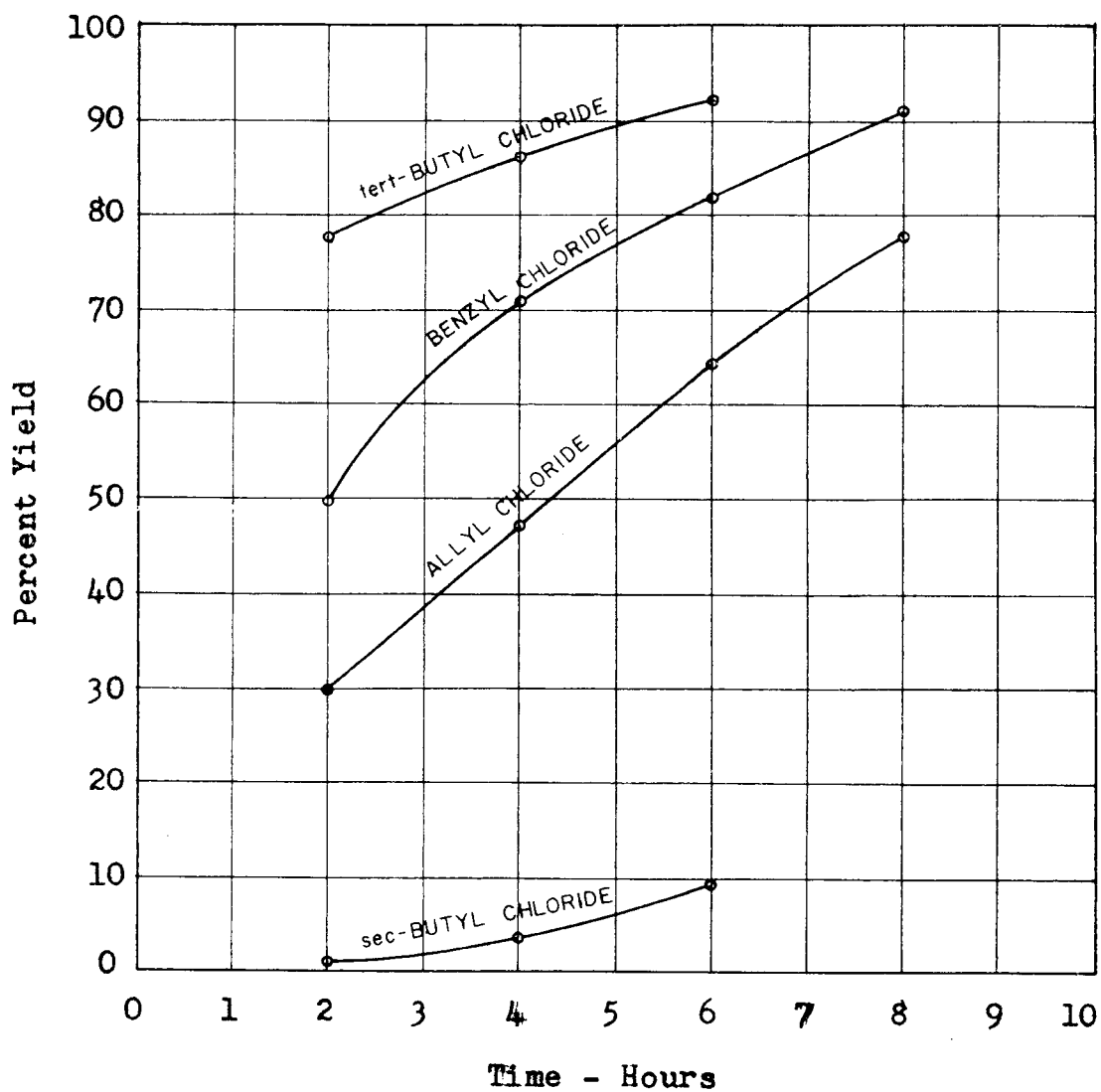
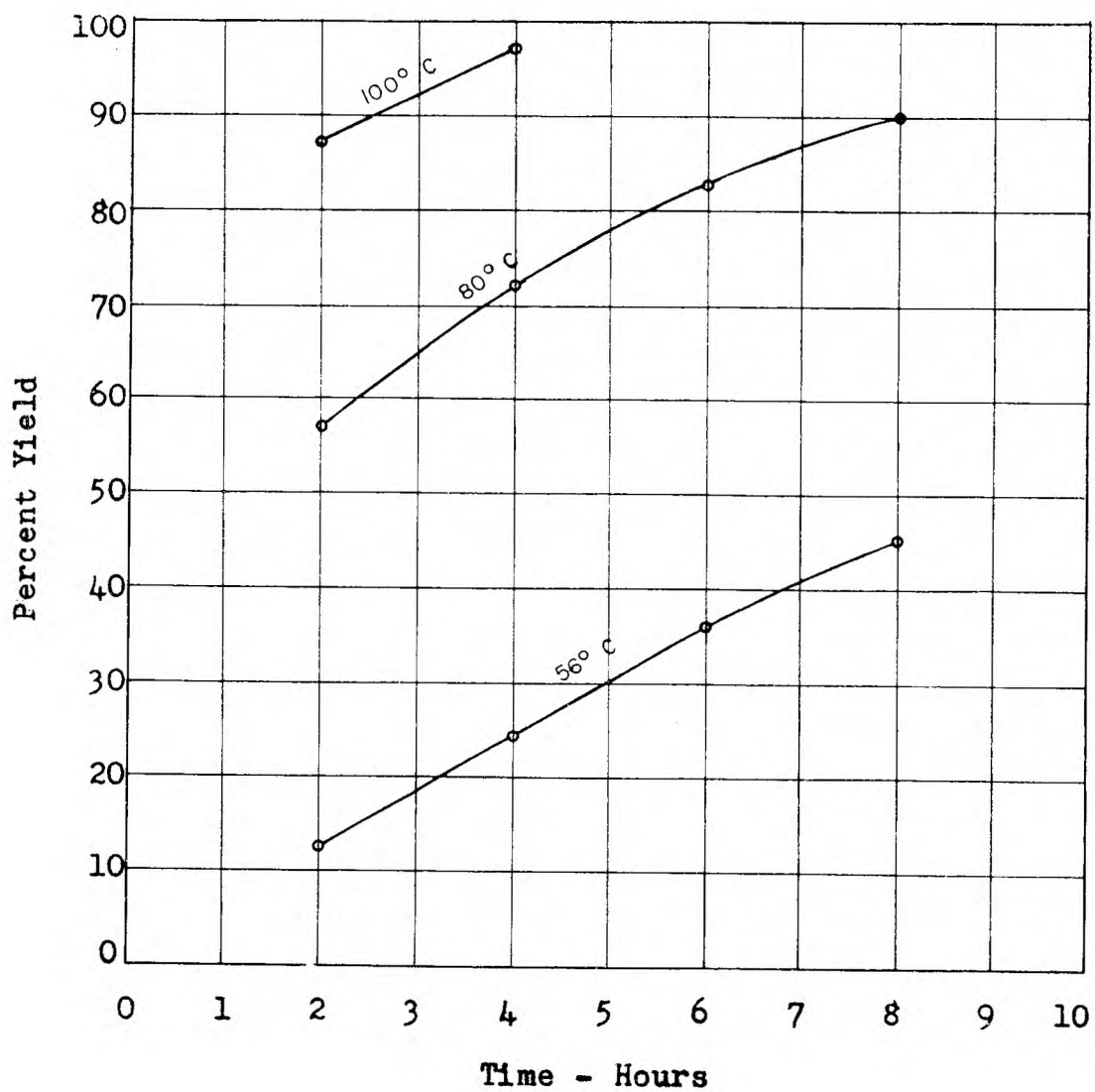


Figure VII
Amination of n-Butyl Iodide
At Various Temperatures



SAMPLE CALCULATIONS

Percent Amination - n-Butyl bromide (MW - 137.03)

Weight - (n-Butyl bromide) used - 2.0641 grams

Total Volume of Solution - 500.0 ml.

Sample used - 50.0 ml.

Eosin -

$$\begin{aligned}\text{Percent Reaction} &= (N_{\text{Ag}} V_{\text{Ag}}) 10^{-3} \times \frac{500}{V_{\text{s}}} \times \frac{100}{n_{\text{Br}}} \\ &= (0.1002)(12.65) 10^{-3} \times \frac{500}{50} \times \frac{100 \times 137.03}{2.0641} \\ &= 84.5\%\end{aligned}$$

Volhard -

$$\begin{aligned}\text{Percent Reaction} &= (N_{\text{Ag}} V_{\text{Ag}} - N_{\text{CNS}} V_{\text{CNS}}) 10^{-3} \times \\ &\quad \frac{500}{50} \times \frac{100 \times 137.03}{2.0641} \\ &= \frac{(0.1002)(15.00) - (.1048)(2.20)}{1000} \times \\ &\quad \frac{500}{50} \times \frac{100 \times 137.03}{2.0641} \\ &= 84.5\%\end{aligned}$$

V_{s} = Volume of sample titrated in ml.

n_{Br} = Molar amount of RBr put through reaction.

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