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## The Identification of Various Alkyl Halides Through Formation of Quaternary Ammonium Salts

John L. Canning

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## PREFACE

### THE IDENTIFICATION OF VARIOUS ALKYL HALIDES

### THROUGH FORMATION OF QUATERNARY AMMONIUM

### SALTS

By

John L. Canning

A Thesis submitted to the faculty of  
the College of Liberal Arts,  
Marquette University, in partial  
fulfillment of the requirements  
for the Degree of Bachelor  
of Science

MILWAUKEE, WISCONSIN.

June, 1948



## PREFACE

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Within the field of the characterization of organic compounds the preparation of suitable derivatives of the compound to be identified is the final process of the laboratory analysis. When the unknown is of such chemical nature that the preparation of derivatives is difficult or impossible the identification is not too satisfactory. This is often the case when the unknown is an alkyl halide. At present the identification of many of these compounds depends exclusively upon an examination of the physical constants.

It is the purpose of this paper to investigate the possibility of preparing quaternary ammonium compounds by treating the alkyl halides with a tertiary amine. These quaternary salts may then be used as derivatives to identify the alkyl halides.

Acknowledgment for the helpful guidance in the preparation of this paper is given Dr. Clifford R. Haymaker for his patient help in working out this problem.

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## I INTRODUCTION

The general procedure used to identify organic compounds has already been well formulated and consists of the collection of data to show the physical constants, the qualitative analysis of the elements contained, and the functional groups present by specific chemical tests. A literature search is then made to find compounds possessing properties approximating those of the unknown compound. The final decision as to the identification consists of the preparation of a suitable derivative which will have the same melting point or boiling point as that derivative of one of the compounds found in the literature search.

## I INTRODUCTION

The selection and preparation of a suitable derivative is of great importance to the proper identity of an organic compound. The number and type of derivatives that may be prepared depend upon the nature and reactivity of the compound being tested. In some instances, as is the case with the alkyl halides, the selection and preparation of a derivative is not satisfactory.

At present the most common derivatives are prepared by means of the Grignard reaction. The alkyl halide is converted into the corresponding Grignard reagent and the anilide (19,22), toluidide (22), and  $\alpha$ -naphthalide (10,22) prepared from the Grig-

- 
- (19) Schwartz, A. H. and Johnson, J. R., *J. Am. Chem. Soc.*, **53**, 1063 (1931).  
(22) Underwood, R. W. Jr. and Gale, J. C., *J. Am. Chem. Soc.*, **56**, 2117 (1934).  
(10) Gilman, H. and Purry, M., *J. Am. Chem. Soc.*, **47**, 1214 (1925).



## I INTRODUCTION

The general procedure used to identify organic compounds has already been well formulated and consists of the collection of data to show the physical constants, the qualitative analysis of the elements contained, and the functional groups present by specific chemical tests. A literature search is then made to find compounds possessing properties approximating those of the unknown compound. The final decision as to the identification consists of the preparation of a suitable derivative which will have the same melting point or boiling point as that derivative of one of the compounds found in the literature search.

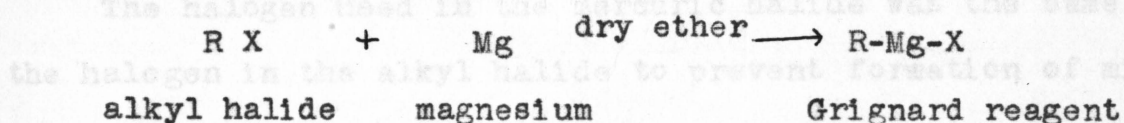
The selection and preparation of a suitable derivative is of great importance to the proper identity of an organic compound. The number and type of derivatives that may be prepared depend upon the nature and reactivity of the compound being tested. In some instances, as is the case with the alkyl halides, the selection and preparation of a derivative is not satisfactory.

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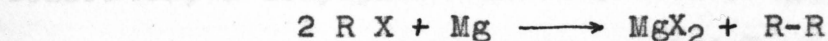
nard reagent by treatment with phenyl, p-tolyl and  $\alpha$ -naphthyl isocyanate respectively.

In the preparation of the Grignard reagent, the alkyl halide was dissolved in perfectly dry ether and added to a calculated amount of magnesium turnings which were covered with dry ether and contained in a flask fitted with an efficient reflux condenser and stirrer. The reaction was exothermic and required cooling in an ice bath to prevent violent boiling of the ether.

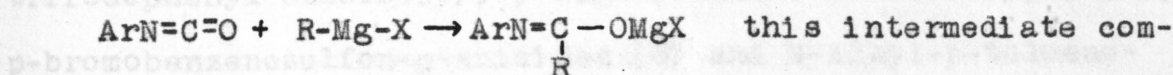


The reagent was not separated for further use but the ether solution was used directly after separation from a few magnesium scraps.

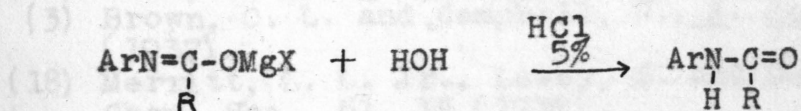
Moisture was eliminated by all possible methods to prevent the side formation:



The Grignard reagent was then treated with the proper aromatic isocyanate:



was decomposed with a five per cent hydrochloric acid solution:



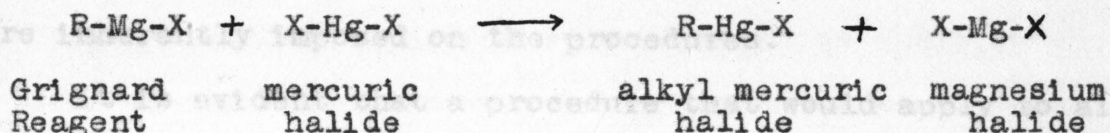
Marvel, Gauerke and Hill (17) have developed a procedure

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(17) Marvel, C. S., Gauerke, C. G. and Hill, E. L., J. Am. Chem. Soc., 47, 3009 (1925).

for identifying the primary alkyl bromides and iodides by converting them into Grignard reagents and allowing the reagent to react with the corresponding mercuric halide. This procedure yielded the best results with the alkyl bromides.

The Grignard reagent was prepared as above and then treated with the corresponding mercuric halide:



The halogen used in the mercuric halide was the same as the halogen in the alkyl halide to prevent formation of mixtures of alkylmercuric halides.

Hill (11) reviewed and extended this work.

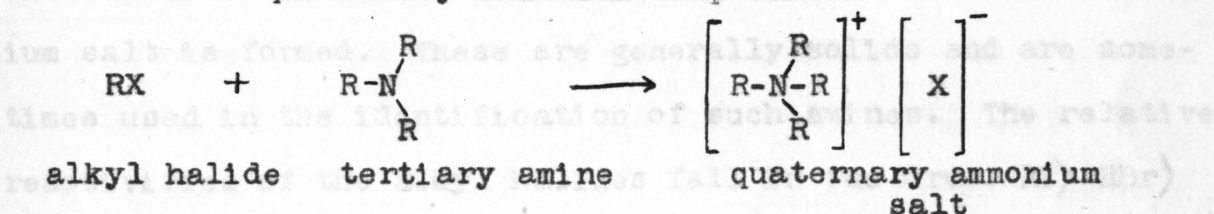
The above procedures are not the only methods that have been used to identify the alkyl halides. Other derivatives of importance that have been prepared include: 3,5 dinitrobenzoates, N-alkylphthalimides, N-alkyl-3-nitrophthalimides, N-alkyltetrachlorophthalimides, alkyl/3-naphthyl ethers, S-alkylthiourea picrates (3), N-alkylsaccharins (18), alkyl triiodophenyl ethers (6), p-alkoxybenzoic acids (15), N-alkyl-p-bromobenzenesulfon-p-anisides (8) and N-alkyl-p-toluenesulfonoluides (25).

- 
- (11) Hill, E. L., J. Am. Chem. Soc., 50, 167 (1927).  
 (3) Brown, O. L. and Campbell, N., J. Chem. Soc., 357, 1699 (1937).  
 (18) Merritt, L. L. Jr., Levey, S. and Cutter, H. B., J. Am. Chem. Soc., 61, 15 (1939).  
 (6) Drew, R. D. and Sturtevant, J. M., J. Am. Chem. Soc., 61, 2666 (1939).  
 (15) Lauer, W. M., Sanders, P. A., Leekley, R. M. and Ungnade, H. E., J. Am. Chem. Soc., 61, 3050 (1939).  
 (8) Gillespie, H. B., J. Am. Chem. Soc., 56, 2740 (1934).  
 (25) Young, G. H., J. Am. Chem. Soc., 56, 2167 (1934).



None of the methods mentioned is applicable to all alkyl halides. The conversion to a mercuric halide is of value only if the halide is primary. Tertiary halides do not yield derivatives by any of the above methods. All of the methods are subject to rearrangements. These limitations in the range of application of the present methods of identification are inherently imposed on the procedures.

It is evident that a procedure that would apply to all alkyl halides and one that can be used under ordinary laboratory conditions using standard apparatus and reagents is most desirable. Such a procedure might be possible through the formation of quaternary ammonium compounds.



In order to demonstrate the suitability of this reaction for analytical purposes the following questions must be answered:

1. Can the quaternary salts be successfully prepared under ordinary laboratory conditions?
2. Are these salts so prepared suitable for identification purposes?
  - (a) Do they crystallize properly with good formation?
  - (b) Are they readily purified?
  - (c) Do they possess sharp melting points or decomposition points?

If the above questions can be answered then a table of melting (or decomposition) points is to be prepared.

The quaternary ammonium compounds were reported by Hofmann in 1850 as the final product of the action of the alkyl halides on alcoholic ammonia. Although practically all organic chemistry textbooks or reference books make mention of the work of Hofmann and of the reaction of an alkyl halide on a tertiary amine to form the quaternary ammonium compounds they do not summarize the various aspects of the latter reaction.

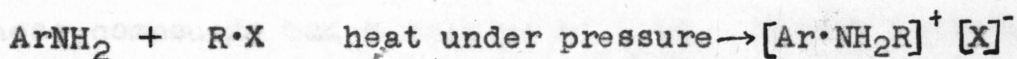
Fuson and Snyder (7) report that when a tertiary amine is allowed to react with an alkyl halide a quaternary ammonium salt is formed. These are generally solids and are sometimes used in the identification of such amines. The relative reactivities of the alkyl halides fall in the order  $RI > RBr > RCl$  and primary < secondary < tertiary.

Sidgwick (21) similarly states that quaternary ammonium compounds may be made by the reaction of the alkyl halides with tertiary amines. He adds that the reaction proceeds with varying success in different cases. Thus trimethylamine combines with methyl chloride at ordinary temperatures with the evolution of heat but it will not combine with ethyl chloride at ordinary temperatures at all. The velocity of reaction of triethylamine with ethyl iodide to form tetra-

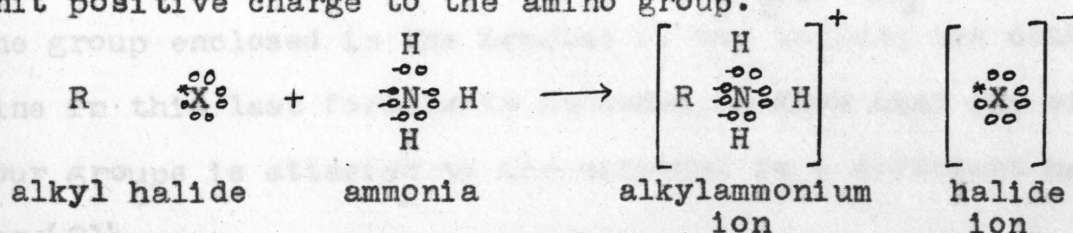
- 
- (7) Fuson, R. C. and Snyder, H. R., Organic Chemistry, New York, John Wiley and Sons, Inc., (1942) 250.  
 (21) Sidgwick, N. V., The Organic Chemistry of Nitrogen, Oxford, The Clarendon Press, (1910) 22.

ethyl ammonium iodide is enormously affected by the solvent. It is 720 times as great in acetophenone as in hexane. The haloid salts all break up on heating into a tertiary amine and an alkyl halide. If one of the alkyl groups is a methyl group, it is always the methyl halide that is split off.

Degering (5) includes the reaction of an alkyl halide with the primary aromatic monoamines with the listing of the addition reactions of those amines. The primary aromatic amines are sufficiently basic to enter into these reactions readily. Substitution of negative groups reduces this basicity and shows a direct effect on the reaction with an alkyl halide to the extent that diphenylamine is so weakly basic that it forms unstable salts, and triphenylamine does not form salts at all. He represents the reaction with alkyl halides as follows:



Each of these reactions is assumed to involve direct addition of the proton or the alkyl residue to the spare pair of electrons carried by the nitrogen atom, thus imparting a unit positive charge to the amino group.



- \* represents an electron supplied by an alkyl group  
 o represents an electron supplied by a halide or a hydrogen  
 -o represents an electron supplied by nitrogen

(5) Degering, E. F., An Outline of Organic Nitrogen Compounds, Ypsilanti, University Lithoprinters, (1945) 304.



This is perfectly analogous to the reaction between ammonia and the mineral acids to give the ammonium salts. The nitrogen with its exposed pair of electrons acts in the capacity of a proton acceptor with the consequent formation of a positively charged ion (5).

A question which may be conveniently discussed in connection with the quaternary ammonium compounds is that of the structure of ammonium compounds and of pentavalent nitrogen derivatives. The early supporters of the theory of constant valency held that nitrogen was triad, and explained the existence of the quaternary derivatives by calling them molecular compounds. This view was generally abandoned when in 1876 Victor Meyer and Lecco showed that the same body was obtained from trimethylamine and ethyl iodide as from ethyl-dimethylamine and methyl iodide. It was then recognized that the nitrogen in these compounds had a valence of five. Werner introduced a view not unlike that of molecular compounds when he proposed that in ammonium chloride, for example, the whole hydrochloric acid molecule is attached to the ammonia by a new kind of bond. He wrote it  $\text{NH}_3 \dots \text{HCl}$  and gave a diagram  $\left[ \begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \right] \text{Cl}$ ; the group enclosed in the bracket is the cation; the dotted line in this last formula is intended to show that one of the four groups is attached to the nitrogen in a different manner (21).

- 
- (5) Degering, E. F., An Outline of Organic Nitrogen Compounds, Ypsilanti, University Lithoprinters, (1945) 46.  
 (21) Sidgwick, N. V., The Organic Chemistry of Nitrogen, Oxford, The Clarendon Press, (1910) 23.

Werner's theory of the addition of the positive charge to the unshared electron pair of the nitrogen is the basis for the representation of the reaction of a tertiary amine and an alkyl halide today.

The readiness with which a given quaternary salt is formed depends to a large extent upon (a) the order in which the radicals are introduced, (b) the nature of the alkyl halide used; chloride, bromide, or iodide, (the last reacting most readily), (c) the solvent and (d) the temperature. It has been found that in the preparation of phenyldimethylethyl ammonium iodide a 100 per cent yield is obtained when methylethyl aniline is combined with methyl iodide, but only a 15 per cent yield when dimethyl aniline is combined with ethyl iodide under similar conditions (2).

The rates of reaction of the different alkyl halides with different tertiary amines will give additional information on the practicality of the procedure to be investigated.

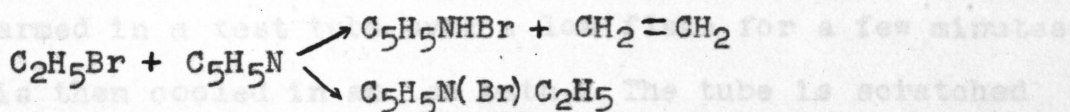
The rates of reaction of fourteen alkyl bromides with piperidine have been investigated (9). Under the conditions of the investigation there was no appreciable amount of side reactions with the primary and a negligible amount with the secondary alkyl bromides. The rates of reaction of the tertiary bromides in alkylation could not be compared with the

- 
- (2) Bernthsen, A. and Sudborough, J., A Textbook of Organic Chemistry, Blackie and Son Limited, (1927) 403.  
 (9) Gilman, H., Organic Chemistry, Volume I, New York, John Wiley and Sons, Inc., (1938) 835.

primary and secondary bromides because the main reaction of the former was the loss of hydrogen bromide. The rates of the reaction in petroleum ether were determined from the amounts of piperidine hydrobromide which had precipitated from the reaction mixture after a given time interval.

Among the straight chain primary alkyl bromides only ethyl showed a marked divergence from the average of the six bromides of this type investigated. Branching of the chain (isobutyl and isoamyl) greatly lowered the rate of the reaction. The phenyl group when attached to the carbon atom holding the halogen (benzyl) enormously increased reactivity. The effectiveness of the phenyl group was also manifest in phenylpropyl and to a less extent in phenylethyl. The secondary bromides, especially cyclohexyl, were very much less reactive than the other compounds investigated.

When several alkyl bromides were treated with pyridine the two main reactions were the formation of pyridine hydrobromide and alkene, and the formation of the alkylpyridinium bromides:



The investigation showed the greater tendency of secondary and especially tertiary bromides to lose hydrogen bromide and the slowness of the addition of these latter halides to nitrogen. The reactivity of the four primary bromides tested appeared to be of the same order of magnitude, the variation in relative reactivity between the extremes of normal butyl



and ethyl bromide was 1 to 2 (9).

This investigation corroborates the theory that the yield of amine (other than primary) decreases as the molecular weight of the alkyl halides used increases (24).

Quaternary ammonium compounds are currently used to identify tertiary amines by treating the unknown tertiary amine with methyl iodide. Various procedures, very similar to each other, may be found for the laboratory preparation of quaternary ammonium compounds.

A mixture of 0.5 gram of the tertiary amine and 0.5 milliliter of methyl iodide is allowed to stand for five minutes. The mixture is heated in a water bath for a further five minutes whether a reaction has occurred or not and then is cooled in an ice bath. The mixture should solidify when the container is scratched with a glass rod. The product, which may be colorless or yellow, is recrystallized from a suitable solvent such as absolute alcohol, acetone, acetic acid or ethyl acetate (12).

A mixture of equal parts of the amine and methyl iodide is warmed in a test tube over a low flame for a few minutes and is then cooled in an ice bath. The tube is scratched with a glass rod to hasten crystallization. The product is purified by recrystallization from absolute alcohol (ethyl

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- (9) Gilman, H., Organic Chemistry, Volume I, New York, John Wiley and Sons, Inc., (1938) 842.
  - (24) Wertheim, E., Textbook of Organic Chemistry, 2nd Ed., The Blakiston Company, (1945) 305.
  - (12) Hopkins and Williams Research Laboratory Staff, Organic Reagents for Organic Analysis, Brooklyn, Chemical Publishing Company, Inc., (1946) 61.

or methyl) or ethyl acetate (20) .

A generalization of the procedure is that quaternary ammonium compounds may be prepared by mixing one part of the halogen compound with approximately the theoretical proportion of a tertiary amine, such as dimethylamine, pyridine, quinoline, trimethylamine, and others. The particular tertiary amine chosen should be one yielding a derivative with a convenient melting point (13) .

## II. EXPERIMENTAL WORK

- 
- (20) Shriner, R. L. and Fuson, R. C., The Systematic Identification of Organic Compounds, 2nd Ed., New York, John Wiley and Sons, Inc., (1946) 149.
- (13) Kamm, O., Qualitative Organic Analysis, 2nd Ed., New York, John Wiley and Sons, Inc., (1932) 194.

## II EXPERIMENTAL WORK

It was desired to conduct this investigation using only standard laboratory apparatus and reagents. These limitations on the scope of variables were imposed by the nature of the investigation. This was to be a primary investigation, that is, it was to determine the practicality of this method of identification. If the investigation was successful even to a moderate degree, later investigations could determine more specific operating conditions.

The apparatus used consisted of test tubes with corks to fit, glass tubing in three foot lengths to serve as air condensers, water baths, ice baths, three five milliliter pipettes graduated in tenths of a milliliter, and the necessary clamps, Bunsen burners, and other miscellaneous items.

## II EXPERIMENTAL WORK

The reagents used were the alkyl halides, pyridine and dimethylaniline. Ether, ethyl acetate, methyl alcohol, ethyl alcohol and acetone were used at various times as washes or as recrystallization media.

Two milliliters of the alkyl halide and two milliliters of the tertiary amine were placed in the test tube which was closed by a cork and a cork containing a length of glass tubing (air condenser) was placed on the test tube. The test tube was gently warmed over a low flame for about one minute or until the reaction mixture appeared to be ready to boil. The test tube was then placed in a clamp and allowed to cool to the point where it could safely be placed in boiling water.



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It was then placed in a water bath for five minutes. When cool enough, the test tube was cooled in an ice bath and scratched to aid crystallization. The solid matter was filtered, washed with absolute ether and recrystallized from the minimum possible quantity of a fifty per cent ether-ethyl alcohol solution.

The melting point of the purified product was determined immediately after drying to reduce the possibility of decomposition. The melting point determination was made by the conventional open capillary tube method using Dow-Corning Silicon oil as the heating bath.

### III. EXPERIMENTAL DATA AND RESULTS

### III EXPERIMENTAL DATA AND RESULTS

| <u>Alkyl Halide</u>               | <u>Amine Used</u> | <u>Rate of Formation</u> | <u>Recrystallization Medium</u>                  | <u>Melting Point °C</u> |
|-----------------------------------|-------------------|--------------------------|--------------------------------------------------|-------------------------|
| Methyl iodide                     | Pyridine          | Excellent                | Ethyl acetate<br>Ethyl alcohol<br>50% ether-alc. | 118<br>117<br>117       |
| Ethyl iodide                      | Pyridine          | Very good                | 50% ether-alc.                                   | 156                     |
| Ethyl bromide                     | Pyridine          | Very good                | 50% ether-alc.                                   | Unobtainable            |
| Methyl iodide                     | Dimethyl aniline  | Excellent                | Ethyl acetate<br>Ethyl alcohol<br>50% ether-alc. | 229<br>228<br>228       |
| Ethyl iodide                      | Dimethyl aniline  | Very good                | 50% ether-alc.                                   | 134                     |
| Ethyl bromide                     | Dimethyl aniline  | Very good                | 50% ether-alc.                                   | 195                     |
| III EXPERIMENTAL DATA AND RESULTS |                   |                          |                                                  |                         |
| n-Propyl iodide                   | Dimethyl aniline  | Very poor                | -                                                | Unobtainable            |
| n-Propyl bromide                  | Dimethyl aniline  | None                     | -                                                | Unobtainable            |
| n-Propyl chloride                 | Dimethyl aniline  | None                     | -                                                | Unobtainable            |
| iso-Propyl iodide                 | Dimethyl aniline  | Fair                     | 50% ether-alc.                                   | 162                     |
| iso-Propyl bromide                | Dimethyl aniline  | None                     | -                                                | Unobtainable            |
| n-Butyl iodide                    | Dimethyl aniline  | Good                     | 50% ether-alc.                                   | 147                     |
| n-Butyl chloride                  | Dimethyl aniline  | None                     | -                                                | Unobtainable            |
| sec-Butyl iodide                  | Dimethyl aniline  | Very poor                | -                                                | Unobtainable            |
| sec-Butyl bromide                 | Dimethyl aniline  | None                     | -                                                | Unobtainable            |



## III EXPERIMENTAL DATA AND RESULTS

| <u>Alkyl Halide</u> | <u>Amine Used</u> | <u>Rate of Formation</u> | <u>Recrystallization Medium</u> | <u>Melting Point °C.</u> |
|---------------------|-------------------|--------------------------|---------------------------------|--------------------------|
| Methyl iodide       | Pyridine          | Excellent                | Ethyl acetate                   | 118                      |
|                     |                   |                          | Ethyl alcohol                   | 117                      |
|                     |                   |                          | 50% ether-alc.                  | 117                      |
| Ethyl iodide        | Pyridine          | Very good                | 50% ether-alc.                  | 156                      |
| Ethyl bromide       | Pyridine          | Very good                | 50% ether-alc.                  | Unobtainable             |
| Methyl iodide       | Dimethyl aniline  | Excellent                | Ethyl acetate                   | 229                      |
|                     |                   |                          | Ethyl alcohol                   | 228                      |
|                     |                   |                          | 50% ether-alc.                  | 228                      |
| Ethyl iodide        | Dimethyl aniline  | Very good                | 50% ether-alc.                  | 134                      |
| Ethyl bromide       | Dimethyl aniline  | Very good                | 50% ether-alc.                  | 195                      |
| n-Propyl iodide     | Dimethyl aniline  | Very poor                | -                               | Unobtainable             |
| n-Propyl bromide    | Dimethyl aniline  | None                     | -                               | Unobtainable             |
| n-Propyl chloride   | Dimethyl aniline  | None                     | -                               | Unobtainable             |
| iso-Propyl iodide   | Dimethyl aniline  | Fair                     | 50% ether-alc.                  | 162                      |
| iso-Propyl bromide  | Dimethyl aniline  | None                     | -                               | Unobtainable             |
| n-Butyl iodide      | Dimethyl aniline  | Good                     | 50% ether-alc.                  | 147                      |
| n-Butyl chloride    | Dimethyl aniline  | None                     | -                               | Unobtainable             |
| sec-Butyl iodide    | Dimethyl aniline  | Very poor                | -                               | Unobtainable             |
| sec-Butyl bromide   | Dimethyl aniline  | None                     | -                               | Unobtainable             |

| <u>Alkyl Halide</u>                                     | <u>Amine<br/>Used</u> | <u>Rate of<br/>Formation</u> | <u>Recrystalliza-<br/>tion Medium</u> | <u>Melting<br/>Point °C.</u> |
|---------------------------------------------------------|-----------------------|------------------------------|---------------------------------------|------------------------------|
| sec-Butyl chloride                                      | Dimethyl<br>aniline   | None                         | -                                     | Unobtain-<br>able            |
| iso-Butyl iodide                                        | Dimethyl<br>aniline   | Good                         | 50% ether-alc.                        | 94-96                        |
| iso-Butyl bromide                                       | Dimethyl<br>aniline   | None                         | -                                     | Unobtain-<br>able            |
| t-Butyl iodide                                          | Dimethyl<br>aniline   | Excellent                    | 50% ether-alc.                        | 114                          |
| t-Butyl bromide                                         | Dimethyl<br>aniline   | None                         | -                                     | Unobtain-<br>able            |
| 1 Bromo 2 methyl<br>butane<br>(pri act amyl<br>bromide) | Dimethyl<br>aniline   | None                         | -                                     | Unobtain-<br>able            |

#### IV DISCUSSION

Methyl iodide was selected as the alkyl halide to be used for the preliminary work as the melting point of the addition compound was available in the reference literature. The preliminary work consisted of: the introductory familiarization with the reaction; the determination of the best laboratory procedure to produce the desired results; the determination of the best washing and recrystallizing media; the determination of the proper drying and handling technique.

The first experiments were performed using pyridine as the tertiary amine. The results secured from the reaction of pyridine and methyl iodide were satisfactory. The quaternary salt formed rapidly and responded well to purification. The procedure to be used with the pyridine-methyl iodide reaction. The next work was to determine the best recrystallization conditions. Ethyl acetate was used as the solvent and was rejected because the quantity of solvent was too large for efficient work. Absolute ethyl alcohol was then used as the solvent and the result was good with the only difficulty being that the salt was too readily soluble. A solution of 50 per cent ether and 50 per cent absolute alcohol was tried as the solvent and gave excellent results. The salt dissolved readily in the hot solvent and precipitated when the solution was cooled.

The purified salt was dried by three different methods.

1. The salt was pressed dry with filter papers and the melting point of the dried salt determined.



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The purified salt was dried by three different methods.

1. The salt was pressed dry with filter papers and the melting point of the dried salt determined.

2. It was dried by rubbing gently on a porous plate and the melting point determined.

3. It was dried overnight in a dessicator.

The first two methods of drying are equally satisfactory but the third, while satisfactory for some of the quaternary salts, resulted in decomposition in other cases. The salts formed were pressed dry.

It was expected that the quaternary salts would be difficult to handle. The preliminary work revealed that this was not the case. Apparently the decomposition of the quaternary salt into a tertiary amine and an alkyl halide does not take place rapidly at room temperature. The quaternary salt obtained from the pyridine-methyl iodide reaction was permitted to stand in the reaction solution at room temperature for three months after which time only partial decomposition had taken place. Samples were withdrawn and purified weekly and the melting points determined. No change in the melting points occurred for the first seven weeks. The sample tested at the end of the eighth week failed to melt sharply. In order to insure accuracy and to eliminate decomposition of the salts which may not be as stable as the salt tested, the melting points of the salts obtained in the investigation were determined as quickly as possible after drying.

The investigation was started with pyridine as the tertiary amine. The reaction between pyridine and methyl iodide, as noted previously, was very successful and the reaction with ethyl iodide was also successful. The reaction with ethyl



bromide, however, was not successful. A well formed salt precipitated but it defied purification and drying efforts. The salt apparently was hygroscopic. Even after purification it remained moist in appearance and could not be placed in a capillary tube. (This may have been due to decomposition.) Ether, ethyl alcohol, methyl alcohol, acetone, ethyl acetate, and acetic acid were used as washes and as recrystallizing media without success. In order to avoid this condition dimethylaniline was then used as the tertiary amine and the investigation was conducted with this compound.

The investigation indicated that the procedure as performed was very limited. The salts that were obtained consisted of well formed crystals. When crushed in drying they had a luster similar to mica.

The melting points of the salts were sharp but careful observation was required as some of the salts decomposed upon melting. The melting points listed were determined by a minimum of five trials to make certain that the melting point reported was accurate.

The reaction with methyl iodide was excellent. The salt formed quickly and was readily purified and dried. It was a lustrous white solid.

The reaction with ethyl bromide was very good. The salt formed after a few minutes cooling and was readily purified and dried. It was a lustrous white solid.

The reaction with ethyl iodide was very good. The salt formed upon cooling and was readily purified and dried. It



was a light yellow-white solid but not as lustrous as the two previous solids.

The reaction with normal butyl iodide was good. The first crystals of the salt formed rapidly and after three minutes cooling in the ice bath a quantity suitable for purification and a melting point determination was formed. It was readily purified and dried. The salt was light brown and had no luster.

The reaction with iso-butyl iodide was good. The salt formed after about five minutes cooling in the ice bath and was readily purified and dried. It was a light yellow-white lustrous solid.

The reaction with tertiary butyl iodide was very vigorous. This reaction must be handled carefully as the salt formation takes place immediately after removal from the free flame with the evolution of dense red-brown fumes (iodine) and a marked increase in volume. It was a yellow-brown solid that was readily purified and dried.

The reaction with iso-propyl iodide was fair. The salt required four days to form in sufficient quantity for a melting point determination. Once formed the salt was excellent. It was purified and dried readily and possessed a sharp melting point. It was a white, very lustrous solid.

The reactions listed above were the only successful ones. The tests with normal propyl iodide and secondary butyl iodide yielded only partial results. The former gave a small amount of a red jelly like precipitate which did not change with

washing and could not be purified. The latter gave good crystals but of insufficient quantity for a determination. All other reactions failed to produce crystals even after two weeks standing.

#### V SUMMARY AND CONCLUSIONS

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1. The investigation was not as successful as had been desired but it did answer some of the questions posed by the problem.

2. The preparation of quaternary ammonium salts not listed in literature was possible under ordinary laboratory conditions and these salts so prepared were suitable for identification purposes.

3. The procedure used in the investigation was not suitable for general application to all alkyl halides.

4. The halogen of the alkyl halide was of prime importance to the success of the reaction. The iodides yielded the best results and the chlorides did not yield any result.

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5. The results obtained indicated that the nature of the carbon structure was also of importance. This procedure seemed to apply only to the primary compounds.



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## VI SUGGESTIONS FOR FURTHER STUDY

1. The investigation was conducted without the use of a solvent for the reagents although the reference texts indicated that the solvent effect on the rate of reaction was great. An investigation to determine the best solvent for the reaction may permit the preparation of those salts which could not be obtained by the procedure used in this investigation. It was noticed that when the filtrate (reactant liquor) from the original separation of the precipitated salt was treated with ether, a cloudiness, similar to that which preceded precipitation, was produced. It is suggested that ether be one of the solvents investigated. The use of ether as a solvent should

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formation of the quaternary salt as the reagents are very soluble in the non polar solvent, ether, while their addition compound, being polar, is not soluble.

2. The effect of temperature on the reaction should yield important information. A sealed tube reaction procedure should be investigated.

3. The reaction may be extended to include aromatic halides. At present the time required for the reaction was excessive but if the above procedures are successful, the inclusion of aromatic halides may be possible. Cumming (4) reports that the time required for the reaction of diethyl-aniline and benzyl chloride was two to three months.

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(4) Cumming, William M., Hopper, I. Vance and Wheeler, I. Sherlock, Systematic Organic Chemistry, New York, D. Van Nostrand Company, Inc., (1937) 295.

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4. It is suggested that other tertiary amines be used with the alkyl halides that yielded good results in this investigation.

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The reference contains information pertaining to the factors which influence the formation of a quaternary ammonium salt.

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This work contains a discussion of the reactions of amines.

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