UNIVERSITY OF CINCINNATI

May 15 1931

I hereby recommend that the thesis prepared under my supervision by Hooper Linford *entitled* "The Reducing Action of Sodium on Benzyl Chloride in Liquid Ammonia Solution

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy.

Approved by:

W. M. Burgess.

W. M. Burgess, Chairman

Form 668—G. S. and Ed.—500—3-30.

THE REDUCING ACTION OF SODIUM ON BENZYL CHLORIDE IN LIQUID AMMONIA SOLUTION.

A dissertation submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1931

by

Hooper Linford

B. S. Utah State Agricultural College 1926.
M. S. State College of Washington 1928.

TABLE OF CONTENTS

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. W. M. Burgess and to Dr. W. E. Bradt for their many valuable suggestions and for their criticisms during this investigation.

THE REDUCING ACTION OF SODIUM ON BENZYL CHLORIDE IN LIQUID AMMONIA SOLUTION

INTRODUCTION

The reducing action of metallic sodium has been used in various non-aqueous solutions. The Wurtz and Fittig reactions are both dependent upon this property. Since sodium is practically insoluble in organic solvents, the reaction here is an interfacial one between the metal and the solution of the reducible organic compound, making such reactions slow and possibly incomplete. Due to the fact that sodium dissolves readily in liquid ammonia these difficulties are overcome by using it as the solvent for this type of reaction.

Kraus (1) has shown that alkali and alkaline earth metals in solution in liquid ammonia ionize to form a positive metallic ion and a negative electron according to equation (1).

$$(1) \qquad Me \rightleftarrows M^{+} + e^{-}$$

It is this negative electron which is the active reducing agent and explains the powerful reducing action of these metal solutions.

Liquid ammonia, in addition to its ability to dissolve metallic sodium, has been shown to be a good solvent for most organic compounds. Franklin and Kraus (2) determined qualitatively the solubility of a large number of organic compounds. They found the lower aliphatic alcohols, ethers, aldehydes, acids and their derivatives, nitrils, cyanates, sulphocyanates, amines, amido-acids, and halogen derivatives to be soluble or miscible in liquid ammonia. The aliphatic hydrocarbons were shown to be practically insoluble while benzene and its homologues are somewhat soluble, the solubility decreasing as the length or number of side chains increased. The derivatives of benzene and naphthalene were all found to be soluble or miscible with the exception of dibasic acids. This unusual solvent power makes liquid ammonia an ideal medium in which to reduce organic compounds with sodium.

Some of the more important literature on reduction by means of sodium in liquid ammonia will be briefly discussed.

Lebeau (3) in 1905 reported some work on the reduction of various aliphatic chlorides. He assumed, as did most of the early workers in this field, that sodium formed sodammonium (NH_3Na or $N_2H_6Na_2$) in liquid ammonia. Propane and propylamine were the products obtained from propyl iodide and he represented the reactions as follows:

$$C_3H_7I + N_2H_6Na_2 \rightarrow C_3H_8 + NH_2Na + NH_3 \qquad (2)$$

$$C_3H_7I + NH_2Na \rightarrow C_3H_7NH_2 + NaI \qquad (3)$$

This conception of sodammonium, or in general metalammoniums, was maintained by the European chemists long after Kraus proved conclusively that the electropositive metals gave true solutions in liquid ammonia (4).

Chabley (5) in 1906 converted cinnamyl alcohol into phenyl propyl alcohol by means of sodium:

$$(4) \quad C_6H_5CH{=}CHCH_2OH + 2NH_3Na \rightarrow C_6H_5CH{=}CHCH_2ONa + C_6H_5CH_2CH_2CH_2ONa + 2NH_3$$

Later the same investigator (6) reduced acid amides and ether salts and reported the following results:

$$(5) \quad 3R\cdot CO\cdot NH_2 + 3NH_3Na \rightarrow 3R\cdot CO\cdot NHNa + 3H + 3NH_3$$

$$(6) \quad RCONH_2 + 3H + NH_3Na \rightarrow RCH_2ONa + 2NH_3$$

and

$$(7) \quad RCOOR' + 2NH_3Na \rightarrow RCONHNa + R'ONa + 2H + NH_3$$

$$(8) \quad RCOOR' + 2H + 2NH_3Na \rightarrow RCH_2ONa + R'ONa + 2NH_3$$

To account for the formation of the acid amides which were among the reaction products of the latter compounds, the following equation was given:

$$(9) \quad RCOOR' + NH_3Na \rightarrow RCONH_2 + R'ONa + H$$

Considerable data on the reducing action of sodium in liquid ammonia solution have been contributed by Lebeau and Picon. They reduced acetylenic hydrocarbons to ethylenic hydrocarbons (7).

$$(10) \quad 3C_2H_2 + 2NH_3Na \rightarrow 2C_2HNa + 2NH_3 + C_2H_4$$

Phenyl acetylene however, was reduced completely to the saturated compound (8).

(11) $3C_6H_5C{\equiv}CH + 4NH_3Na \rightarrow 2C_6H_5C{\equiv}CNa$
$+ C_6H_5CH_2CH_3 + 2NH_2Na + 2NH_3$

Phenyl ethylene yielded the saturated hydrocarbon, phenyl ethane, as might be expected.(9)

An interesting type of reduction obtained with sodium in liquid ammonia is the hydrogenation of ring compounds. Lebeau and Picon obtained pure tetra hydronaphthalene from naphthalene in this manner (10), and later extended their work with equal success to other polycylic compounds (11). These reductions were found to proceed with ease and the extent of hydrogenation could be regulated by the addition of definite amounts of sodium. The number of hydrogen atoms added to the compound corresponded to the number of sodium atoms used.

Nitrobenzene and nitrosobenzene were reduced successfully by White and Knight (12). The reaction in the case of nitrobenzene was reported as proceeding in two stages:

Twice (12) $Na + C_6H_5NO_2 \rightarrow C_6H_5N(Na)ONa$
twice. (13) $C_6H_5N(Na)ONa \rightarrow C_6H_5NNa_2$

This sodium derivative, while stable in liquid ammonia, was decomposed by water and ammonium chloride to give aniline.

Chabley (13) added methyl chloride to a solution of sodium in liquid ammonia and obtained methane, methyl amine, and sodium chloride. He represented the reaction as follows:

(14) $2NH_3Na + 2CH_3Cl \rightarrow 2NaCl + CH_4 + CH_3NH_2 + NH_3$

The same investigator reduced chloroform, iodoform, and carbon tetrachloride with sodium in liquid ammonia but failed in each case to obtain constant results. The presence of more than one halogen atom in the molecule complicated the reaction and increased the number of reactions, and consequently the number of reaction products. Methane, ethylene, and acetylene were obtained from chloroform and also iodoform. Other products, if they were formed, were not identified. No mechanism was postulated for this reaction.

Kraus and White (14) in a preliminary investigation tried the action of sodium in liquid ammonia on a large variety of organic compounds, among them various halogen derivatives of both aliphatic and aromatic residues. Benzyl chloride was one of the compounds used. They reported that the reacting ratio of sodium to benzyl chloride was 1:1, however, they made no attempt to investigate the products of the reaction.

Their conclusions were that organic compounds containing strongly electro-negative groups were in general reduced, the groups or various elements of the groups forming salts with the reducing metal while the organic radical thus freed underwent various reactions depending upon the nature of the radical in question, and upon the nature of various other substances present. In most cases ammonia entered into the reaction.

In a later article White (15) extended this work with more complete data on the phenyl chlorides. He presented three principle reactions accounting for the formation of the products obtained from mono chlor benzene.

(15) $6C_6H_5Cl + 6Na + NH_3 \rightarrow 3C_6H_6 + (C_6H_5)_3N + 6NaCl$

(16) $4C_6H_5Cl + 4Na + NH_3 \rightarrow 2C_6H_6 + (C_6H_5)_2NH + 4NaCl$

(17) $2C_6H_5Cl + 2Na + NH_3 \rightarrow C_6H_6 + C_6H_5NH_2 + 2NaCl$

With an excess of sodium the diphenyl amine and aniline were found to be partially converted into their sodium derivatives.

(18) $(C_6H_5)_2NH + Na \rightleftarrows (C_6H_5)_2NNa$

(19) $C_6H_5NH_2 + Na \rightleftarrows C_6H_5NHNa$

Water, ammonia, or alcohol reversed these reactions, reforming the amines and sodium hydroxide, sodium amide and sodium ethylate respectively.

(20) $(C_6H_5)_2NNa + H_2O \rightarrow (C_6H_5)_2NH + NaOH$

In addition to repeating his original work on methyl chloride, Chabley (16) carried his researches to methylene dichloride, ethylene monochloride, ethylene dichloride, dichloro-ethane, and propylene dichloride. His work shows plainly that where two chlorine atoms are attached to the same carbon atom, a mixture of saturated and unsaturated hydrocarbons is obtained. However, where two chlorine atoms are attached to adjacent carbon atoms they are removed and an unsaturated hydrocarbon results. Ethylene dichloride and dichlor-ethane illustrate this very well. Ethylene dichloride was found to yield ethylene; ethane was not detected.

(21) $CH_2ClCH_2Cl + N_2H_6Na_2 \rightarrow C_2H_4 + 2NaCl + 2NH_3$

Dichlor-ethane, on the other hand, gave rise to ethylene and ethane. Chabley assumed the mechanism to be as follows:

(22) $CH_3CHCl_2 + N_2H_6Na_2 \rightarrow C_2H_6 + 2NaCl + NH_2Na + NH_3$

(23) $CH_3CHCl_2 + NH_2Na \rightarrow NaCl + NH_3 + CH_2{=}CHCl$

(24) $CH_2{=}CHCl + N_2H_6Na_2 \rightarrow C_2H_4 + NaCl + NH_2Na + NH_3$

Chabley (16) also devised a procedure for using the solution of sodium in liquid ammonia to remove halogens quantitavely from organic halides. His results from the determinations on several halogen substituted aromatic hydrocarbons checked very well with the calculated theoretical values.

That this solution of sodium would remove halogens from organic compounds was also noted by Cady (17). Later this procedure was standardized and checked for accuracy by Dains, Vaughan and Janney (18), Clifford (19), and Dains and Brewster (20). The standardized method is very successful.

In connection with their work on triphenyl methane and its derivatives, Kraus and Kawamura (21) obtained a new and interesting type of reaction. Two atoms of sodium were found to react with triphenyl methyl chloride to give a sodium derivative of triphenyl methane, sodium triphenyl methide.

(25) $(C_6H_5)_3CCl + 2Na \rightarrow (C_6H_5)_3CNa + NaCl$

This sodium compound gave a characteristic red solution in liquid ammonia. It was found to be very reactive even at liquid ammonia temperatures. With water its reaction gave triphenyl methane.

(26) $(C_6H_5)_3CNa + H_2O \rightarrow (C_6H_5)_3CH + NaOH$

With ammonium chloride it gave an ammonium derivative which was unstable and broke down into triphenyl methane and ammonia.

(27) $(C_6H_5)_3CNa + NH_4Cl \rightarrow (C_6H_5)_3CNH_4 + NaCl$

(28) $(C_6H_5)_3CNH_4 \rightarrow (C_6H_5)_3CH + NH_3$

Tetraphenyl methane was prepared by treating the sodium derivative of triphenyl methane with phenyl bromide.

(29) $(C_6H_5)_3CNa + C_6H_5Br \rightarrow (C_6H_5)_4C- + NaBr$

An attempt to couple two triphenyl methyl radicals failed but the free radical, triphenyl methyl, was obtained.

(30) $(C_6H_5)_3CNa + (C_6H_5)_3CCl \rightarrow 2(C_6H_5)_3C- + NaCl$

As this reaction took place the red color of the sodium compound disappeared and a yellow color, characteristic of triphenyl methyl, appeared.

It should be noted that all of the work on the reduction of organic halides by sodium in solution in liquid ammonia has been of a qualitative nature.

In many instances only the main reaction products were determined, and in others only the reacting ratio between the sodium and halide was given. And so it was with the idea of determining quantitavely the reaction products of sodium and a typical organic halide and the mechanism of the reaction that this investigation was undertaken.

Benzyl chloride was chosen because it is a monohalogen derivative and less likely to give a complicated reaction. It has a relatively high molecular weight and should give solid or liquid products easily identified. It has been pointed out by Kraus and White (14) that it reacts with sodium in the ratio of one atom of sodium to one molecule of benzyl chloride, indicating a clear cut reaction.

The discussion of this reaction will be divided into five parts and treated in the following sequence: a theoretical discussion of the reactions which may occur, the experimental methods employed, the results obtained, including reaction products, mechanism of the reaction, and finally a brief summary.

THEORETICAL

Sodium has been shown to remove halogens quantitatively from organic halides (18), (19), (20), leaving the free organic radical.

(31) $RX + Na \rightarrow R- + NaX$

The free radical may remain as such in this solution or undergo further reaction. The three most probable reactions are with the solvent ammonia, with sodium, or with another similar free radical. These three reactions will be discussed separately.

The reaction between <u>ammonia</u> and the free radical would lead to amine formation as with methyl chloride (13) and also with phenyl chloride (15).

(32) $2R- + NH_3 \rightarrow RNH_2 + RH$

With benzyl chloride the products would be the primary, secondary, or tertiary benzyl amines and toluene.

(33) $2C_6H_5CH_2- + NH_3 \rightarrow C_6H_5CH_2NH_2 + C_6H_5CH_3$

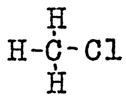
(34) $4C_6H_5CH_2- + NH_3 \rightarrow (C_6H_5CH_2)_2NH + 2C_6H_5CH_3$

(35) $6C_6H_5CH_2- + NH_3 \rightarrow (C_6H_5CH_2)_3N + 3C_6H_5CH_3$

With <u>sodium</u> the free radical would react to form a sodium derivative.

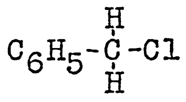
(36) $R- + Na \rightarrow RNa$

Benzyl chloride (B) might be considered to be a compound intermediate in structure between methyl chloride (A) and triphenyl methyl chloride (C).



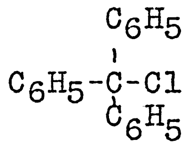
H_3C-Cl

(A)



$C_6H_5-CH_2-Cl$

(B)



$(C_6H_5)_3C-Cl$

(C)

It was shown by Kraus and Kawamura (21) that sodium triphenyl methide, $(C_6H_5)_3CNa$, was formed in the reaction between the corresponding chloride and sodium. This sodium derivative was found to be fairly stable and did not react with triphenyl methyl chloride as long as free sodium, as shown by its characteristic color, was present. In the case of methyl chloride, however, there is no evidence of the formation of a sodium derivative. Benzyl chloride, being intermediate in structure between methyl and triphenyl methyl chlorides, might be expected to form a sodium derivative, but it should not be as stable as the sodium triphenyl methide.

The reaction between two free radicals would lead to the formation of hydrocarbons.

(37) $R- + R- \rightarrow RR$

With Benzyl chloride this reaction should lead to the formation of dibenzyl.

(38) $C_6H_5CH_2- + C_6H_5CH_2- \rightarrow C_6H_5CH_2CH_2C_6H_5$

This work must be carried out in such a manner as to show the presence or the absence of these possible products in order to determine the type and mechanism for the reaction under investigation.

EXPERIMENTAL METHODS

Materials

The benzyl chloride used in this investigation was obtained from two different sources. That used during the first part of the work was an Eimer and Amend product. To insure a pure starting material it was fractionated twice with a twenty inch obstructed fractionating column, and in each fractionation the boiling point limits used were 176° and 177.5° C. The benzyl chloride used during the last part of the investigation was obtained from the Eastman Kodak Company. It was used without further purification.

Kahlbaum's stick sodium was also used in this investigation. Just before weighing, the outer coating of oxide and hydroxide was removed by trimming with a safety razor blade. This was done under anhydrous ligroin to prevent oxidation. The sodium thus prepared was transferred to a weighing bottle, and the ligroin evaporated from its surface by a stream of nitrogen. After weighing, the sodium was transferred to a reaction tube. The metal retained its luster throughout this treatment.

The liquid ammonia was obtained from the Mathieson Alkali Works, Niagara Falls, in one hundred pound cylinders.

It was transferred as a liquid into a laboratory tank of approximately four and one-half pounds capacity, in which had been previously placed two to three grams of metallic sodium. The ammonia used as a solvent in a reaction was vaporized from this small tank and condensed in the reaction tubes, thus assuring an anhydrous solvent.

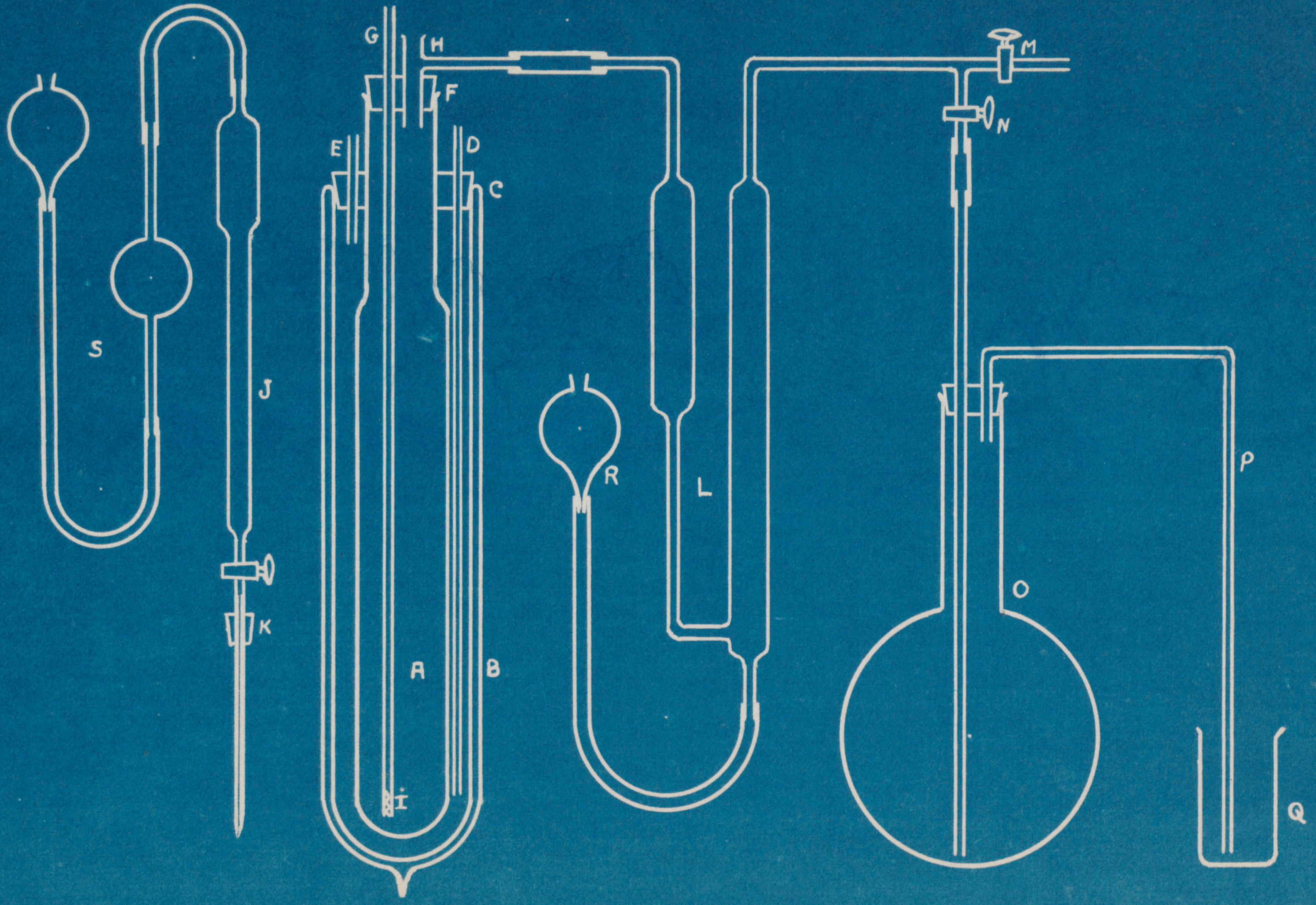


FIGURE I
Apparatus for the Reduction of Organic Compounds in Liquid Ammonia.

Apparatus

The apparatus as shown in Figure I was found to be very satisfactory for the carrying out of this type of organic reaction. The reaction tube A, having a capacity of about six hundred cubic centimeters, was placed in a dewar tube B, and supported by a rubber stopper C. The stopper also carried one long tube D, through which dry air was passed to cool the liquid ammonia in the dewar, and a short tube, E, through which the air and volatilized ammonia passed out of the dewar. A rubber stopper F, in the reaction tube, carried a long tube G, which reached to the bottom of the reaction tube and served as the inlet for the dry gaseous ammonia, and a short tube, H, with a side arm serving as the outlet for the gases in the reaction tube. A glass wool plug, I, placed in the end of the tube G, served two purposes: it prevented the sodium solution from being forced up this tube due to momentary pressure in the reaction tube; and also served as a filter, allowing the removal of the solution without any of the solid matter, at any time during the course of the reaction. A calibrated burette, J, graduated in tenths of a cubic centimeter, fitted with a stopper, K, was inserted through the tube H, and held in place by the stopper.

The gases from tube H, passed through a mercury trap L and thence through tube M to the ammonia collection system, or through tube N into a two liter round bottom flask, O, which contained mercury and concentrated hydrochloric acid. To prevent the escape of HCl from the flask an outlet tube, P, was run into a beaker, Q, containing mercury and water. This latter system was used for the collection of substances volatile with ammonia.

A leveling pear, R, was used for regulating the depth of mercury in the trap L and thus the pressure within the reaction tube.

The pressure required to force the benzyl chloride from the burette J into the reaction tube was supplied by S, which consisted of a leveling pear containing mercury and a bulb for an air reservoir.

The apparatus illustrated and described was the final form used in this investigation and the one which was found to be the most satisfactory. When this work was first undertaken a smaller reaction tube was employed and in place of a calibrated burette, a picnometer pipet was used for the addition of the benzyl chloride. It was necessary to weigh the pipet at the beginning and at the end of the reaction, whereas with the burette, volume readings were recorded, and the weight of benzyl chloride calculated. The latter was found to be advantageous because of the ease of regulating the addition of benzyl chloride, as well as the amount of time saved in this procedure.

Procedure

The method used in carrying out reactions in this apparatus will be described.

The Completed Reaction.

The reaction tube was cleaned with chromic acid cleaning solution, rinsed in turn with water, alcohol, and ether, then dried by a current of dry air. After weighing the reaction tube to one decigram, it was placed in the dewar tube and as ammonia gas was being run through, liquid ammonia was placed in the dewar around the reaction tube. These precautions were taken to prevent any moisture being present in the reaction tube, or from entering when the tube was cooled by the liquid ammonia bath.

With air bubbling through the liquid ammonia in the dewar tube and approximately ten centimeters of mercury in the trap L, ammonia was condensed in the reaction tube. When fifty to one hundred cubic centimeters of ammonia had been condensed, the sodium was introduced through tube H, and the burette containing benzyl chloride inserted through the same tube. The amount of liquid ammonia used for each run was dependent upon the amount of sodium. When ten grams of sodium were used, a volume of about two hundred cubic centimeters was found to be very satisfactory.

The benzyl chloride was added drop by drop, until over half of the theoretical quantity had been added, at which time it was found that the rate of addition could be increased somewhat without excessive boiling or spattering of the reaction mixture. Sufficient stirring was obtained by the entrance of a slow stream of ammonia through the inlet tube G.

Burette readings were taken when the color of the reaction mixture changed from blue to red, and also at the disappearance of the last trace of red color. From these readings were obtained calculations for the ratio of sodium to benzyl chloride at the blue-red change, and also at the end point of the reaction. When the end point was reached, the burette was removed and a solid rubber stopper inserted in its place. Then the solvent ammonia was allowed to evaporate.

In the runs in which an attempt was made to locate material volatile with ammonia, the exhaust gases were run through the stop cock N into the flask, O, contain-mercury, as a safety trap, and concentrated hydrochloric acid. Enough acid was used to insure the solution remaining acid after the solvent ammonia had completely evaporated and been absorbed. After displacing the ammonia from the reaction tube by dry air, it was weighed to determine the weight of volatile products leaving the reaction mixture during the course of the reaction.

The Partial Reaction.

In the runs which had as their purpose the isolation of intermediate reaction products, the addition of benzyl chloride was stopped when the color of the reaction mixture changed from blue to red. This red solution was transferred to a second reaction tube, without coming into contact with the air, and allowed to evaporate.

To facilitate the explanation of the procedure for making this transfer, the second reaction tube and its fittings will be indicated by primed letters corresponding to the reaction tube in Figure I.

Reaction tube A' was prepared in a manner similar to the first reaction tube, then placed in a dewar tube and a little liquid ammonia condensed in it. By means of a short piece of rubber tubing, tubes G and G' were connected, the ammonia supply tube from G was transferred to H, and H' was connected to the mercury trap L. By opening the valve on the ammonia supply tank and forcing ammonia into the first reaction tube, the red solution was forced up through tube G and into the second reaction tube. The glass wool plug I, prevented any of the precipitated solids from passing with the solution.

Separation of the Reaction Products.

The Completed Reaction.

The reaction products remaining in the reaction tube, after the ammonia had completely evaporated, were extracted simultaneously with ether and water. Separation was made by means of a separatory funnel. The aqueous solution was extracted with three or four portions of ether, in order to insure a complete separation. Each of these solutions was then evaporated at a temperature below the boiling points of the respective solvents, to limit volatilization of any of the reaction products.

The water soluble product was analyzed without further treatment.

The ether soluble portion was then redissolved in less than half the amount of ether used in the extraction, leaving a small quantity of fine white crystals undissolved. These crystals were washed with several small quantities of ether, and set aside for analysis.

The ether solution was again allowed to evaporate and the material dissolved in the smallest possible amount of hot absolute alcohol. On cooling a large quantity of a white crystalline compound separated. These crystals were filtered in a Buchner funnel and washed free of mother liquor with several portions of cold alsolute alcohol.

The combined mother liquor and washings were distilled at ordinary pressure until the alcohol had been removed, then under reduced pressure, separated into three fractions. The first fraction distilled between 150°-160°C. at 8 m.m. and crystallized on cooling; the second distilled between 210°-245°C. at 8 m.m. and the third, distilled between 245°-295°C. at 8 m.m. Not more than a few drops of material distilled between 160° and 210°C. and this crystallized on cooling so it was included in fraction one. The second and third fractions were both liquids.

The first crystalline fraction from the distillation was dissolved in ether and a slight amount of solid remained. It was washed several times with ether and saved for analysis. The ether was allowed to evaporate from the solution of fraction one and it was set aside for analysis.

On standing, small white crystals formed in the viscous liquid of fraction three. The addition of ether dissolved the liquid and left the crystalline compound. It was washed several times with small quantities of ether, and the ether then allowed to evaporate.

This completes the separation of the products remaining in the reaction tube. The volatile products which were collected in flask O, were distilled directly from this flask. No separation or purification was made.

The products of the completed reaction have been separated into: one water soluble product; five ether soluble products, of which two are liquids, and three are crystalline solids; and one volatile product.

<u>The Partial Reaction</u>

After the ammonia had completely evaporated from the separated red solution, in the second or auxiliary reaction tube, it was extracted with anhydrous ether. There remained a solid which was deep red when moistened with the solvent, and pink on complete evaporation of the solvent. It was washed five or six times with ether by decantation, and then set aside for analysis.

The ether solution was colorless and as it did not contain any of the red substance it was not further analyzed.

The identification of the products of both the completed reaction and the partial reaction and data concerning their yields will be given under the heading "Reaction Products".

Supplementary Methods and Apparatus.

The method for determining molecular weights and the melting point apparatus used during this investigation are worthy of description since they are both modifications of previously described forms.

Rast's micro <u>molecular weight</u> determination (22), using camphor as the solvent, was found to give very satisfactory results when carried out in the following manner.

Six to ten milligrams of substance was weighed in a tared micro flask, which was made by blowing a one centimeter bulb in the end of a piece of six millimeter pyrex tubing. The neck of the flask was about two centimeters long and flanged at the open end. Into this tube was then weighed from sixty to two hundred milligrams of camphor, depending upon the approximate molecular weight of the substance. The tube was closed with a cork stopper and gently heated over a low flame until fusion occured. Vigorous shaking, while the material was heated just enough to keep it liquified gave sufficient mixing. The tube was then cooled by dipping in a beaker of water and the stopper removed just long enough to scrape down the material from the neck of the flask with a micro spatula. This spatula was prepared by flattening the end of a piece of maleable iron wire, and filing the blade to the correct shape. After replacing the stopper the mixture was refused and then allowed to cool.

An ordinary organic melting point tube was charged with this mixture by pushing it carefully with a twisting motion into the flask, then, by means of a clean piece of iron wire, the material was packed tightly in the bottom of the tube. A depth of one to one and one half millimeters in the melting point tube was found to give best results. The melting point of this mixture was taken by using a thermometer graduated in five tenths of a degree, however, an ordinary laboratory thermometer will suffice. In order to determine accurately the depression of melting point, it was found advantageous to place a melting point tube containing the mixture and one containing pure camphor in the same bath, and to record the melting point of each.

The formula for calculating the molecular weight is as follows:

$$M = \frac{40 \cdot a \cdot 1000}{b \cdot \Delta t}$$

a = gms. solute
b = gms. solvent
Δt = melting point lowering

The melting point apparatus shown in Figure II was found to be a very convenient form to use in connection with the molecular weight determination described above. It is similar in design to that of Friedrichs(23), but of simpler construction, and is easily made in the laboratory.

The outer jacket, A, is a fifty cubic centimeter pyrex distilling flask with the side arm sealed off at its base. The guide tubes, for holding the melting point tubes, B and B', were made from this side arm. The neck ofthe flask is enlarged at the bottom to give more air space above the sulphuric acid. A twelve millimeter pyrex tube, C, with a bulb on the lower end in which are blown two small holes, D and D', to allow the entrance of the melting point tubes, is sealed to the flask at E. A side arm F, allows for expansion of the air in the outer jacket.

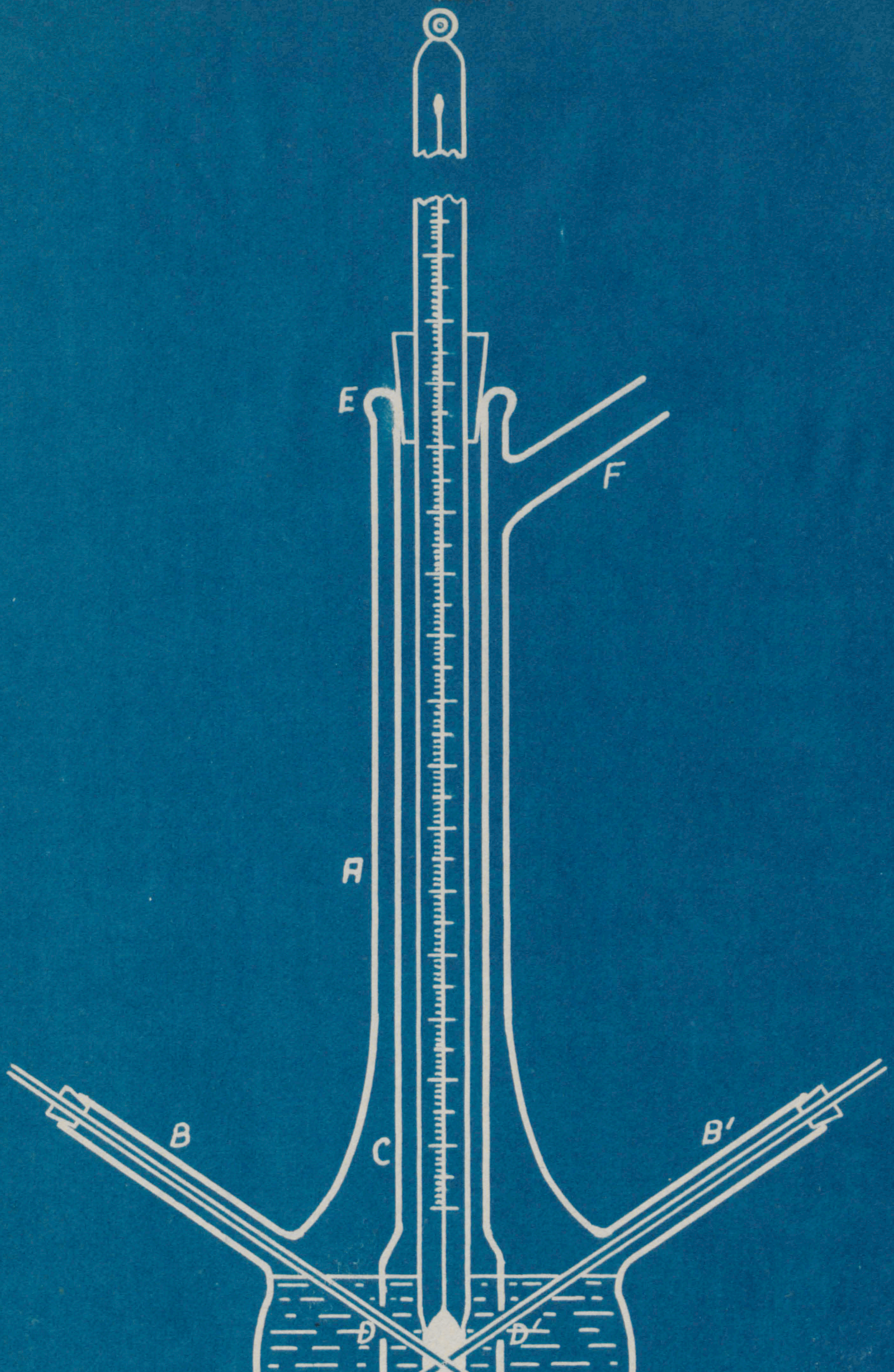


FIGURE II

Melting Point Apparatus

The advantages of this apparatus are that the volume of the bath is small and therefore may be heated and cooled quickly to any desired temperature; convection currents do not affect the thermometer; the thermometer remains in exactly the same position each time with reference to the heating bath and also two melting points may be taken simultaneously without any difficulty; and finally the melting point tubes may be easily inserted and removed while the bath remains near the desired temperature.

EXPERIMENTAL RESULTS

The results of this investigation will be presented under three headings: reaction ratios, reaction products, and partial reaction products. A discussion will follow the experimental data in each division.

Reaction Ratios

When benzyl chloride is added to a solution of sodium in liquid ammonia two distinct color changes occur. The blue color of the sodium disappears and the solution becomes a deep red. This color change from blue to red will be termed the red end point. On further addition of benzyl chloride to this solution the color becomes less intense, and finally, one drop of the chloride completely discharges it, leaving a colorless solution. Further addition does not produce any visible change in the reaction mixture. The point at which the solution becomes colorless will be termed the colorless end point, or simply the end point.

In Table I are shown the ratios of benzyl chloride to sodium at these two end points in eight typical runs.

Table I.

Reaction Ratios between Benzyl Chloride and Sodium

1. Run No.	2. Sodium g.	3. BzCl g. Red End Point	4. Ratio BzCl to Na. Red End Point	5. BzCl g. End Point	6. Ratio BzCl to Na. End Point
104	1.271	6.631	.948	7.028	1.005
151	2.091	10.762	.936	11.578	1.007
152	1.501	7.776	.942	8.144	.987
156	1.795	9.175	.930	------	-----
187	3.889	------	----	21.321	.997
192	8.552	------	----	47.151	1.002
253	3.271	16.875	.938	------	-----
254	0.461	2.383	.941	2.545	1.005

In this table column 1 shows the number of the run; 2, the weight of sodium in grams; 3, the weight of benzyl chloride, at the red end point, in grams; 4, the ratio of mols of benzyl chloride, to atoms of sodium at the red end point; 5, the weight of benzyl chloride at the end point, in grams; and 6, the ratio of mols of benzyl chloride to atoms of sodium at the end point of the reaction.

These data show, that the red end point is obtained when approximately ninety four percent of the theoretical quantity of benzyl chloride has been added, and that the reaction is complete when the reactants are in the proportion of one mole of the chloride to one atom of sodium. The average of all the end point ratios obtained in runs which proceeded without mishap are for the red end point: .938, which includes twenty runs, and for the colorless end point: .999+, which is based on thirty six runs. The extreme variations are in the first case: .916-.955, and in the second: .980-1.026.

The significance of these results is twofold. The disappearance of the blue color, marks the disappearance of free sodium from the solution. It has evidently entered into combination with the organic material. The compound which is formed is reactive, since addition of more benzyl chloride causes the reaction to proceed until the theoretical quantity has been added.

In order to explain these color changes, it is necessary to determine the products of the reaction, both when it is complete and also when it has proceeded only as far as the red end point.

Reaction Products

The reaction products will be presented together with their identification and yields, under these headings: water soluble, ether soluble, and volatile, after which a brief summary will be given.

Water Soluble

The water soluble products were analyzed for sodium chloride by titration with standard silver nitrate solution, according to the method of Volhard (24), without further purification. The results of the analysis, of the products of three separate runs and a mixture of the products of four runs are shown in Table II.

Table II.

Percent Sodium Chloride in the Water Soluble Product

1. Run No.	2. Wt. of Sample g.	3. $AgNO_3$ c.c.	4. Wt. of NaCl g.	5. % NaCl
86	.2360	38.75	.2348	99.50
87	.2774	45.70	.2769	99.84
91	.2435	39.84	.2414	99.15
74, 79, 94, 97	.2612	43.00	.2606	99.77

Column 1 shows the number of the run from which the sample was obtained; 2, the weight of sample taken for analysis, in grams; 3, the volume of silver nitrate solution (1 c.c. = .00606 g. NaCl) in cubic centimeters; 4, the weight of sodium chloride calculated, in grams; and 5, the percent of sodium chloride in the sample.

The water soluble product analyzed over ninety nine and one half percent sodium chloride as this table shows. The impurity is organic in nature for this sodium chloride darkened slightly when it was heated with a bunsen flame. Tests for organic nitrogen(25) and for cyanides were both negative, indicating that the impurity is due to incomplete extraction of the aqueous solution with ether.

In Table III are shown the yields of sodium chloride from a series of runs in which the water soluble material was recovered.

Table III.

Yields of Sodium Chloride

1. Run No.	2. Sodium in grams	3. Benzyl Chloride in grams	4. Sodium Chloride in grams	5. Sodium Chloride Percent
79	1.330	7.075	3.386	100.2
87	1.249	7.136	3.103	98.0
94	1.531	8.450	3.860	99.2
95	1.148	6.177	2.834	98.8
97	1.075	5.769	2.733	100.0
100	1.028	5.465	2.599	99.5
101	1.250	6.739	3.151	99.1
104	1.271	7.028	3.225	99.9
105	1.155	6.375	2.876	98.0
151	2.091	10.762	5.318	100.1
152	1.501	8.144	3.812	99.9
169	4.367	23.270	11.045	99.5
173	3.460	18.823	8.842	100.5
181	3.829	21.168	9.750	100.2
182	4.469	24.562	11.380	100.2
			Mean	99.54

In this table column 1 gives the number of the run; 2, the weight of sodium used, in grams; 3, the weight of benzyl chloride used, in grams; 4, the weight of sodium chloride recovered, in grams; and 5, the percent of sodium chloride recovered based on the weight of sodium used.

The theoretical quantity of sodium chloride is recovered; the mean value for the percentage recovery being 99.54 for fifteen runs. This indicates that when the reaction is allowed to proceed to completion the metallic sodium and the chloride from the benzyl chloride are removed quantitavely from the reaction mixture as sodium chloride.

Ether Soluble Products

Since much of the quantitative data, at the beginning of this investigation, was based on the yield of the total ether soluble material, without further separation, it will be presented before the individual products are considered.

The ether soluble portion consists of the organic reaction products which remain in the reaction tube after evaporation of the solvent ammonia.

This material was tested for organic nitrogen by the usual method of fusion with sodium (24) with negative results. Tests for chlorides, both inorganic and organic (25), were also negative. The ether soluble material is entirely hydrocarbon in nature, and probably results from the coupling of the free benzyl radical. It is on this basis that the yields of ether soluble material have been calculated, as shown in Table IV.

Table IV.

Yields of Total Ether Soluble Products

1. Run No.	2. Sodium Grams	3. Benzyl Chloride	4. Ether Soluble Product		
			(a) Grams	(b) % based on Na	(c) % based on BzCl
87	1.249	7.136	4.502	91.1	87.7
91	1.041	5.736	3.522	85.4	85.3
93	1.055	5.778	3.565	85.4	85.7
94	1.531	8.450	5.402	89.1	88.8
96	1.611	9.094	5.468	85.8	83.5
97	1.075	5.769	3.736	87.8	90.0
100	1.028	5.465	3.311	81.4	84.2
101	1.250	6.739	4.274	86.1	88.1
104	1.271	7.028	4.350	86.5	86.0
105	1.155	6.375	4.012	87.8	84.0
127	.799	4.216	2.613	87.7	86.1
151	2.091	11.578	7.337	87.7	87.1
152	1.501	8.144	5.220	86.9	88.1
169	4.367	23.270	14.795	85.6	88.4
172	3.357	18.164	11.075	83.3	84.7
173	3.460	18.823	11.550	84.3	85.3
181	3.829	21.168	13.495	89.0	88.6
182	4.469	24.562	15.409	87.1	87.2
202,4-7	50.957	276.47	167.76	83.2	84.3
208-213 215,216	93.413	513.49	338.56	91.6	91.6
			Mean	87.3	87.5

In Table IV, column 1 gives the number of the run; 2, the weight of sodium used, in grams; 3, the weight of benzyl chloride used, in grams; 4 (a), the weight of ether soluble material recovered, in grams; 4 (b), the percent of ether soluble material recovered based on the weight of sodium used; and 4 (c), the percent of ether soluble material recovered based on the weight of benzyl chloride used.

The mean value of the percent recovery for thirty one runs, based on sodium is 87.3, the limits of variation being 81.4-91.6; based on benzyl chloride is 87.5, the limits of variation being 83.5-91.6. There is an apparent loss of approximately 12.5% of the organic products of the reaction. This however, may be accounted for by the volatile materials, and the inherent losses of material during the extraction of the reaction products with ether.

The last two rows of data in Table IV are based on combinations of five and eight runs respectively. It is from these two lots of material that the quantitative data concerning the individual ether soluble products were obtained. These results will now be presented.

Dibenzyl. The compound which was crystallized from the alcoholic solution of the ether soluble products was found to be identical with that which was distilled from the alcoholic mother liquor and washings between 150°-160° C at 8 m.m. After two crystallizations from absolute alcohol the compound melted at 53.5° C. (corr.).

Analyses for carbon and hydrogen, molecular weight determinations, and melting point, establish the identity of this compound as dibenzyl. Beilstein (27) gives the melting point as 51.5°-52.5° C.

Molecular Weight, Calculated for $C_{14}H_{14}$: 1821. Found: 185.3, 188.9.

Analysis, Calculated for $C_{14}H_{14}$: C, 92.25; H, 7.75. Found: C, 92.29, 92.61, 92.26; H, 7.12, 7.25, 7.61.

Other Hydrocarbons. The white crystalline compound, which failed to dissolve in the ether when the "ether soluble" products were dissolved in smaller quantities of ether, and the one which crystallized from the very viscous oil, (Fraction three, boiling between 245°-295°C at 8 m.m.), were found to be identical. After several crystallizations from absolute alcohol, in which this compound is but slightly soluble, it melted at 177.5°-178°C. (corr.).

Molecular Weight, Found: 357.9, 363.4, 370.7, 374.9. Mean: 366.7.

Analysis, Found: C, 92.84, 92.71; H, 7.16, 7.11.

The analysis, and molecular weight, give this compound the empirical formula $C_{28}H_{26}$. The first, calculated for $C_{28}H_{26}$: C, 92.77; H, 7.23; calculated molecular weight: 362.3. Further identification of this compound was not made.

The first liquid fraction from the vacuum distillation, collected between 210°-245°C. at 8 m.m., was refractionated twice and the portion boiling between 235°-240° at 8 m.m. was used for molecular weight determinations. It is a viscous oil having a slight yellowish color. Tests for nitrogen were negative, thus it is evidently a hydrocarbon.

Molecular Weight, Found: 272.1, 280.1.

The molecular weight corresponds to that of three benzyl radicals, indicating the formula $C_{21}H_{20}$.

Molecular Weight, Calculated for $C_{21}H_{20}$: 272.
No further analyses were made, so this formula has not been definitely established. For convenience, this oil will be termed Liquid A.

The second liquid fraction from the vacuum distillation, collected between 245°-295°C. at 8 m.m., was not obtained in quantities allowing purification and analysis. It is a very viscous yellow oil, evidently a hydrocarbon. It will be termed Liquid B.

The residue left in the distilling flask after the vacuum distillation, was a dark, very viscous oil. No attempt was made to analyze it.

Amine. The white crystalline compound which distilled with the dibenzyl and was separated by dissolving the dibenzyl in ether, after washing with several small portions of ether, melted at 202°-204°C. (corr.). It is insoluble in ether, alcohol, benzene, and ligroin. However, it dissolves in hot concentrated hydrochloric acid forming an hydrochloride, which crystallizes as the solution cools in fine white needles, melting at 265.5°C. (corr.). A test for organic nitrogen in the original compound, as well as in the hydrochloride, shows that nitrogen is present. It is probably an amine. The slight amounts obtained prohibited further analysis.

Table V.

Yields of Ether Soluble Products

(a) Five Runs Combined

	1. Total Ether Soluble	2. Dibenzyl	3. $C_{28}H_{26}$	4. Liquid A	5. Liquid B	6. Amine	7. Residue
Grams	167.76	134.63	1.464	17.631	6.457	0.302	2.011
% Based on BzCl	81.67	67.66	0.74	8.86	3.25	0.15	1.01
% Based on Total Ether Soluble	100.00	82.85	0.90	10.85	3.97	0.19	1.24

(b) Eight Runs Combined

	1. Total Ether Soluble	2. Dibenzyl	3. $C_{28}H_{26}$	4. Liquid A	5. Liquid B	6. Amine	7. Residue
Grams	338.56	261.01	3.290	40.375	12.382	0.993	2.477
% Based on BzCl	86.73	70.62	0.89	10.93	3.35	0.27	0.67
% Based on Total Ether Soluble	100.00	81.43	1.03	12.60	3.86	0.31	0.77

The yields of each of the constituents of the ether soluble materials are given in Table V.

Table V is divided into two sections; (a) giving the analysis of the ether soluble material obtained by combining the products of five runs, (b), the same for eight runs. The results of the analyses are recorded similarly in both sections. Column 1 shows the yield of total ether soluble in grams, percent based on benzyl chloride, and percent based on total ether soluble. Columns 2-7 show respectively the same data for dibenzyl, $C_{28}H_{26}$, Liquid A, Liquid B, amine, and residue.

Dibenzyl forms by far the largest fraction, being 82% of the total ether soluble. The two liquid fractions, Liquid A 12% and Liquid B about 4%, together with the dibenzyl, constitute almost 98% of the ether soluble material. The compound $C_{28}H_{26}$ is present to the extent of 1% and there is but a trace of the amine. Whether the amine is a product of the reaction between benzyl chloride and sodium, or whether it is due to traces of an impurity, can be determined only by procuring enough of the amine for analysis.

<u>Volatile</u>.

It was observed, shortly after this investigation was undertaken, that the weight of the reaction tube and reaction products was in all cases less than the weight of the empty reaction tube plus the weight of the sodium and benzyl chloride added. After many unsuccessful attempts to isolate a volatile product, from the ammonia leaving the reaction tube, it was found that by absorbing the exhaust ammonia in a sufficient quantity of concentrated hydrochloric acid so that the solution remained after the ammonia had entirely evaporated from the reaction tube, an oil separated out and floated on the acid solution. This oil was distilled directly from the acid solution and was found to be toluene.

After drying over calcium chloride the boiling point was 108.5°-109°C. A sample of pure toluene in the same apparatus boiled 108°-109°C. The oil was further identified by preparing the nitro-derivative,(28), and comparing it with the 2,4 dinitro-derivative of toluene prepared in like manner. Both nitro products, and an intimate mixture of the two products, melted at the same temperature, 170°-170.5°C.

The method which was used for isolating the toluene would not allow of quantitative determinations. However, since the oil which was obtained was shown by test to contain no nitrogen, and therefore no amines, it is logical to assume that the loss in weight which occurs during the reaction is due only to toluene.

Table VI shows a series of runs in which this loss in weight was determined.

Table VI

Loss in Weight During Reaction

1. Run No.	2. Benzyl Chloride Grams	3. Organic Material Grams	4. Loss in Weight Grams	5. Percent Loss in Weight
87	7.136	5.136	.454	8.84
91	5.735	4.128	.467	8.99
94	8.450	6.082	.52	8.55
95	6.177	4.446	.415	9.12
97	5.769	4.152	.343	8.26
101	6.739	4.850	.360	7.42
104	7.028	5.058	.489	9.67
105	6.375	4.588	.371	8.09
151	11.578	8.333	.779	9.35
152	8.144	5.862	.594	10.13
169	23.270	16.749	1.624	9.70
173	18.823	13.547	1.228	9.06
181	21.168	15.236	1.402	9.20
182	24.562	17.679	1.361	7.70
192	47.151	33.937	2.593	7.64
			Mean	8.78

In column 1 is given the number of the run; 2, the weight of benzyl chloride added, in grams; 3, the weight of organic material, or benzyl chloride less chlorine, which was added, in grams; 4, the loss in weight, in grams; and 5, the percent loss in weight based on the organic material. The mean loss in weight for the fifteen runs shown in this table is 8.78% with extreme variations of 7.42% and 10.13%.

The yields of toluene based on benzyl chloride are numerically equal to the values given in Table VI and the mean percent yield for the fifteen runs is 8.78%.

Summary.

The reaction between sodium and benzyl chloride in liquid ammonia is one in which the solvent plays no active part; hydrocarbons and sodium chloride constitute over 99% of the reaction products.

The products with their yields based on benzyl chloride are as follows:

Dibenzyl	70.62%
Toluene	8.78%
Liquid A	10.93%
Liquid B	3.35%
$C_{28}H_{26}$	.89%
Amine	.27%
Residue	.77%
	95.61%
Lost	4.39%

Over 99.5% of the theoretical sodium chloride was recovered.

Partial Reaction Products

The results presented in this section, are based upon a study of the ether insoluble red solid, obtained by allowing the solvent to evaporate from the reaction mixture at the red end point, and also upon its red solution in liquid ammonia.

The red solid, which was left after the ether extraction, consists mainly of sodium chloride. It remains red indefinitely even though no precautions are taken to keep it away from the air. Several unstoppered tubes, containing this substance, have been kept in this laboratory over two years without any apparent change in the color of the solid. After the red solid has been exposed to the air, however, it is not possible to redissolve it in liquid ammonia to obtain the red solution. It decolorizes as it dissolves. This is probably due to the moisture which is adsorbed.

Water dissolves the red solid and decolorizes it immediately. Traces of organic material float on the top of the aqueous solution but have not been obtained in such quantities that analysis was possible.

Since water decolorizes the red compound so readily, yet it is stable in moist air, it is possible that the red compound is occluded in the sodium chloride crystals. When the process of solution in water was observed under the microscope, some of the crystals appeared colorless, while others appeared

red for a time and then became colorless. Still others retained their red color until they were entirely dissolved. No pockets containing the red compound were visible in any of the crystals.

The red compound was analyzed for chlorides and for basicity. The chlorides were calculated to sodium chloride and the basicity, which is due to sodium hydroxide formed on the hydrolysis of the red sodium compound, was calculated to sodium. The difference in the total weights of sodium and sodium chloride, and the sample weight, was assumed to be the weight of organic material in combination with the sodium in the red compound. From this data the molecular weight of the red sodium compound was calculated.

The sample of red material was dissolved in water and titrated with chloride free sulphuric acid, (1 c.c. equivalent to .00116 g. Na), using phenolphthalein as indicator; then with silver nitrate, (1 c.c. equivalent to 0.02895 g. NaCl), using potassium chromate as the indicator. The sulphuric acid was standardized against Kahlbaum's sodium carbonate and the silver nitrate against Kahlbaum's sodium chloride.

In Table VII are shown the results of five analyses.

Table VII

Analyses of the Red Compound

1. Sample Grams	2. H_2SO_4 c.c.	3. Na Found Grams	4. $AgNO_3$ c.c.	5. NaCl Found Grams	6. Organic Found	7. Molecular Weight
0.7269	22.67	0.0263	20.59	0.5960	0.1046	114.1
0.6358	14.95	0.0173	19.08	0.5525	0.0660	110.8
0.5957	13.85	0.0161	17.93	0.5191	0.0605	109.4
0.8261	9.45	0.0110	26.65	0.7715	0.0436	113.9
0.6210	7.09	0.0082	20.02	0.5796	0.0332	116.1
					Mean	112.9

Column 1 gives the weight of sample taken for analysis; 2, the cubic centimeters of sulphuric acid (1 c.c. = 0.00116 g. Na), required for its titration; 3, the grams of sodium present as sodium hydroxide; 4, the cubic centimeters of silver nitrate(1 c.c. = 0.02895 g. NaCl) required for titration; 5, the weight of sodium chloride found; 6, the weight of organic material present in the sample calculated by difference, that is the weight of sample minus the weights of sodium and sodium chloride; and 7, the molecular weight of the red compound calculated from the ratio of sodium to the organic material.

In order to calculate the molecular weight of the red compound from these data it was necessary to assume one atom of sodium per molecule.

The mean value of the molecular weight from five analyses was 112.9, the extreme variations were, 109.4

and 116.1. These values agree very closely with the calculated value, for sodium benzylide, of 114.1.

The evidence supporting the view that the red intermediate compound is sodium benzylide may be briefly summarized as follows:

1. The red color develops in the reaction mixture before the ratio of benzyl chloride to sodium is 1:1 and this red compound which must contain sodium, since the blue color, characteristic of sodium in liquid ammonia, has entirely disappeared, reacts with additional benzyl chloride until the ratio is 1:1. Thus sodium must be combined with an organic radical and the radical which is present is the benzyl radical, $C_6H_5CH_2$-. The product would be sodium benzylide, $C_6H_5CH_2Na$.

2. The red solution is characteristic of sodium organic compounds as was pointed out by Kraus and Kawamura (22). Sodium benzylide would correspond with the red sodium triphenyl methide which they obtained using triphenyl methyl chloride.

3. The value of the molecular weight of the red compound, is within two percent of the calculated value for sodium benzylide, which is well within experimental error.

That the red compound is sodium benzylide was not established however by derivative formation. Attempts to form derivatives of the red compound, using its red solution in liquid ammonia with organic chlorides other than benzyl chloride, were unsuccessful. Monochloro- and monobromo-benzene, and alpha and beta chloro-naphthalene, were added to the red solution in quantities greater than theoretically necessary to decolorize it, however, even on long standing, no appreciable change in color was noted.

With the aim of determining the stability of the red compound its red solution was allowed to stand over night, during which time the solvent ammonia was not entirely volatilized. More ammonia was condensed, then allowed to evaporate completely and stand five days. At the end of this time more ammonia was condensed giving a solution noticeably lighter in color. This solution was again allowed to evaporate and a fourth portion of ammonia condensed. It still gave a red solution and on evaporation a red solid. The red compound must be assumed to be stable in anhydrous liquid ammonia solution.

MECHANISM FOR THE REACTION

In order to determine the mechanism for the reaction, between sodium and benzyl chloride in liquid ammonia, all of the products must be identified. However, the main reaction which leads to the formation of dibenzyl with the intermediate formation of sodium benzylide may be represented by equations (39) and (40).

(39) $C_6H_5CH_2Cl + 2Na \rightarrow C_6H_5CH_2Na + NaCl$

(40) $C_6H_5CH_2Cl + C_6H_5CH_2Na \rightarrow C_6H_5CH_2CH_2C_6H_5 + NaCl$

These two reactions proceed simultaneously but at different rates. The former is complete when the ratio of benzyl chloride to sodium is .94, for it is at this time that the blue color of metallic sodium disappears, and the red color of sodium benzylide appears. If these two reactions proceeded at the same rate the red solution would not be formed. If, on the other hand, benzyl chloride reacted with sodium, and not at all with sodium benzylide, until all the sodium was used up, the red solution would appear when the ratio of benzyl chloride to sodium was .5.

The formation of toluene may be explained by the formation of hydrocarbons of greater molecular weight than dibenzyl. In order to attach additional benzyl radicals, hydrogen must be eliminated since the benzyl radical is saturated. Such reactions may be represented by equations (41) and (42) which show the formation of toluene and $C_{28}H_{26}$ and toluene and $C_{21}H_{20}$.

(41) $6C_6H_5CH_2Cl + 6Na \rightarrow 2C_6H_5CH_3 + C_{28}H_{26} + 6NaCl$

(42) $4C_6H_5CH_2Cl + 4Na \rightarrow C_6H_5CH_3 + C_{21}H_{20} + 4NaCl$

SUMMARY

1. There are two distinct color changes which occur when benzyl chloride is added to a solution of sodium in liquid ammonia. The first, a change from blue to a deep red when the ratio of moles of benzyl chloride to atoms of sodium is .94; the second, a change from red to colorless, which is the end point of the reaction, when the ratio is 1.
2. Evidence is presented to show that sodium benzylide is an intermediate reaction product. Data concerning its stability are given.
3. The products of the reaction are hydrocarbon in nature; the solvent does not enter appreciably into the reaction with amine formation.
4. The coupling reaction, of the Wurtz-Fittig type with the formation of dibenzyl, has been shown to be the predominant reaction.
5. An apparatus has been designed for carrying out this type of organic reaction of such capacity that ten to twelve grams of sodium may be conveniently used. Also a method for collecting volatile hydrocarbons has been devised.

BIBLIOGRAPHY

1. Kraus, J.A.C.S., 30, 1323 (1908).
2. Franklin and Kraus, Am. Chem. Jour., 20, 820 (1898).
3. Lebeau, Compt. Rend., 140, 1264 (1905).
4. Kraus, Loc. cit., Kraus and Johnson, J.A.C.S., 47, 725 (1925).
5. Chabley, Compt. Rend., 143, 829 (1906).
6. Chabley, Compt. Rend., 154, 364 (1912).
7. Lebeau and Picon, Compt. Rend., 157, 137 (1913).
8. Lebeau and Picon, ibid., 157, 223 (1913).
9. Lebeau and Picon, ibid., 175, 223 (1922).
10. Lebeau and Picon, ibid., 158, 1514 (1914).
11. Lebeau and Picon, ibid., 159, 70 (1914).
12. White and Knight, J.A.C.S., 45, 1780 (1923).
13. Chabley, Compt. Rend., 140, 1262 (1905).
14. Kraus and White, J.A.C.S., 45, 768 (1923).
15. White, J.A.C.S., 45, 779 (1923).
16. Chabley, Ann. Chim. Phys., (9), 469 (1914).
17. Cady, See Reference 18.
18. Dains, Vaughan and Janney, J.A.C.S., 40, 936 (1918).
19. Clifford, J.A.C.S., 41, 1051 (1919).
20. Dains and Brewster, J.A.C.S., 42, 1573 (1920).
21. Kraus and Kawamura, J.A.C.S., 45, 2756 (1923).
22. Rast, Ber., 55, 1051 (1922).
23. Friedrichs, Z.f.angew.Ch., 34, 61 (1921).
24. Mahin, "Qualitative Organic Analysis", Third Edition, P. 250, McGraw-Hill Book Co., N. Y.

25. Kamm, "Qualitative Organic Analysis", P. 122,
John Wiley and Sons, 1923.

26. Kamm, Loc. cit.

27. Beilstein, "Handbuch der Organischen Chemie",
Third Edition, II, 232.