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THE REDUCTION OF BENZAL CHLORIDE BY SODIUM IN LIQUID AMMONIA SOLUTION

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By

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I.

INTRODUCTION

The reducing action of the alkali metals in liquid ammonia solution on organic halides has been known for many years. The first investigations in this field were carried out independently by Chablay,[1] and Lebeau,[2],[3] in 1905.

Chablay's[1] work consisted in a study of the reducing action of sodium in liquid ammonia on methyl chloride, chloroform, iodoform, and carbon tetrachloride. In the case of methyl chloride,he obtained sodium chloride, methane and methyl amine as reaction products. The formation of these products was explained by assuming that the sodium reacted with the solvent, ammonia, to form a compound, the so-called "metal ammonium" which in turn reacted with the methyl chloride. This mechanism is explained by the following equations.

$$Na + NH_3 \longrightarrow NaNH_3$$

$$2\ NaNH_3 + 2\ CH_3Cl \longrightarrow 2NaCl + CH_4 + CH_3NH_2 + NH_3$$

The products found in the investigation of chloroform, iodoform and carbon tetrachloride were the sodium halides, saturated and unsaturated hydrocarbons with small amounts of sodium cyanide, hydrogen and nitrogen. Chablay made no attempt to explain the mechanism that would account for these products.

The investigations carried out by Lebeau[2],[3] were for the purpose of preparing paraffin hydrocarbons and primary amines by treating a solution of sodium in liquid ammonia with the mono-halogen derivatives of the lower paraffin hydrocarbons. The mechanism by which he accounted for his reaction products was more complete than that of Chablay, in that he explained the amine formation by a separate reaction. His explanation may be represented by the following equations:

$$Na + NH_3 \rightarrow NaNH_3$$

$$C_3H_7I + 2\ NaNH_3 \rightarrow C_3H_8 + NaNH_2 + NH_3 + NaI$$

$$C_3H_7I + NaNH_2 \rightarrow C_3H_7NH_2 + NaI$$

The sodium first reacts with the solvent ammonia to form sodammonium. The reaction of one molecule of alkyl halide with two molecules of sodammoniun then occurs with the formation of the saturated hydrocarbon, sodium amide, ammonia and sodium halide. The sodium amide formed immediately reacted with additional alkyl halide forming the primary amine and the sodium halide.

Aside from the work mentioned above, very few investigations of importance were carried out in this field prior to 1914. At this time, Chablay, [4] after a series of investigations, established the fact that the halogen in an organic compound was removed quantitatively by alkali metals in liquid ammonia solution. Obviously this principle was one of fundamental importance. Subsequent investigations by Dains, Vaughan and Janney,[5] Clifford, [6] and Dains and Brewster, [7] substantiated the conclusions reached by Chablay and resulted in the development of an analytical method for the determination of halogens in organic compounds. In this method the halogen is removed quantitatively as the alkali metal halide and then determined by the usual methods.

The next work of importance was carried out by Kraus and White, [8] White, [9] and Kraus and Kawamura, [10] and the results published in a series of papers in 1923. Their investigations consisted in the study of the reducing action of sodium in liquid ammonia on a large number of organic compounds which included many halogen compounds. The phenyl halides and triphenyl methyl chloride were most carefully studied and furnished more general information as to type reactions than any work that had been done previously.

Subsequent investigations by Wooster and Mitchell, (11) Dean and Berchet,[12] and Burgess and Linford,[13] added further information and aided in the formulating of type reactions for the action of sodium in liquid ammonia solution on mono-halogen organic compounds.

On the basis of the results obtained by workers in this field, the following equations are given as representative of the type of reactions that occur when mono-halogen organic compounds react with sodium in liquid ammonia.[14] In these equations, R represents an alkyl or aryl radical and X, a halogen.

I. $2\ RX + 2\ Na + NH_3 \rightarrow RH + RNH_2 + 2\ NaX$

II. $2\ RX + 2\ Na \rightarrow R - R + 2\ NaX$

III. $RX + 2\ Na \rightarrow R - Na + NaX$

IV. $RX + Na \rightarrow R + NaX$

Equation I illustrates a very common type of reaction, in which the ratio of organic halide to sodium is one mol to one mol, and in which the solvent ammonia plays a part as one of the reactants. This type may be illustrated specifically by the following examples from the literature.[2], [3], [4]

$$2\ CH_3Cl + 2Na + NH_3 \rightarrow CH_4 + CH_3NH_3 + 2\ NaCl$$

$$2\ C_2H_5Br + 2\ Na + NH_3 \rightarrow C_2H_6 + C_2H_5NH_2 + 2\ NaBr$$

Equation II is representative of another type of reaction in which the ratio of halide to sodium is one mol to one mol, but in which the solvent plays no part as a reactant. This reaction is identical with the Fittig synthesis of aromatic hydrocarbons and may be illustrated thus: (11), (12), (13)

$$2\ C_6H_5CH_2Cl + 2\ Na \rightarrow C_6H_5\text{-}CH_2\text{-}CH_2C_6H_5 + 2\ NaCl$$

Equation III represents a type of reaction in which a sodium organo-compound is formed and the molar ratio of the chloride to the sodium is one to two. Examples of this are rarely found in the literature. The outstanding example is that of the formation of sodium triphenyl methyl by Kraus and Kawamura (10) as follows:

$$(C_6H_5)_3C\text{-}Cl + 2\ Na \rightarrow (C_6H_5)_3C\text{-}Na + NaCl$$

Regardless of the scarcity of examples of this type at present, the appearance of a large number may be anticipated when the mechanism of the reducing action of sodium on the organic halides in liquid ammonia is more thoroughly understood. These organo-sodium compounds are undoubtedly formed as intermediates in many of the reactions, but due to their great instability, are never isolated under the conditions which exist when the reaction takes place and when the products are examined.

In Equation IV, a reaction is shown which represents the formation of a free and independent radical containing a trivalent carbon atom. This type of reaction has only one example in the realm of purely organic compounds. That example is the formation of triphenyl methyl by Kraus and Kawamura (10) as shown by the following equation:

$$(C_6H_5)_3C\text{-}Cl + Na \rightarrow (C_6H_5)_3C + NaCl$$

In this reaction, the ratio of sodium to organic halide is one mol to one mol. However, it is known that this reaction proceeds in steps and passes through a stage in which a sodium organo-compound is formed as represented by Equation III. [10] Thus the reaction may be represented in the following way:

$$(C_6H_5)_3C\text{-}Cl + 2\ Na \rightarrow (C_6H_5)_3C\text{-}Na + NaCl$$

$$(C_6H_5)_3C\text{-}Na + (C_6H_5)_3C\text{-}Cl \rightarrow 2\ (C_6H_5)_3C + NaCl$$

It cannot be assumed that any reaction will proceed quantitatively as represented by any one of the above type equations. Probably many reactions would require a combination of these equations to represent their procedure, although one may be predominant. Moreover, in formulating these type equations, no provision has been made for the formation of cyanides,[6] and for secondary and tertiary amines,[9] which have been found to be formed in some reactions.

Very few attempts have been made to explain the mechanism for the formation of the reduction products in these reactions. The comparatively little work that has been done in this field does not furnish enough knowledge to formulate basic principles upon which to anticipate the results in any particular case.

The first effort to explain the mechanism of these reactions was made by Chablay [1] and Lebeau [2], [3] and has already been mentioned. Since the "metal ammoniums" have been proved to be non-existant by Kraus, [15], [16], [17], [18] the explanation of Chablay and Lebeau is of no value.

Kraus, [15], [16], [17], [18] by a series of brilliant and exhaustive investigations on the physical properties of liquid ammonia solutions of the alkali metals, proved conclusively that true solutions result when these metals are dissolved in liquid ammonia and that there is no compound formed by combination of the metal and solvent.

These investigations also proved that when the alkali metals dissolve in liquid ammonia, they dissociate into positive metallic ions and free electrons, a true ionic equilibrium resulting, in which the positive metallic ion is identical with that formed when any corresponding metallic salt is dissolved and the negative ion is identical with the electron. The free electrons were shown to be associated more or less with the solvent, this association increasing as the concentration of the solution decreased. The following equations will illustrate the conditions existing in a solution of an alkali metal in liquid ammonia, the electron being represented by e^-.

$$Na \rightleftarrows Na^+ + e^-$$

$$e^- + n(NH_3) \rightleftarrows e^-(NH_3)_n$$

$$\overline{Na + n(NH_3) \rightleftarrows Na^+ + e^-(NH_3)_n}$$

The strong reducing action of sodium in liquid ammonia may then be attributed to the presence of the free electrons. Kraus and White [8] have explained this reducing action as follows.

The introduction of an organic halide into a solution of sodium in liquid ammonia results in the combination of the free electron with the strongly electro-negative halogen forming a normal halogen anion in the solution. This stage of the reducing action may be represented thus:

$$RX + e^- \longrightarrow R + Xe^-$$

This leaves the organic radical, R, free, which may remain as an independently free radical (Type Equation IV) or react with:

1. Molecules of the solvent
2. Other organic radicals
3. Electrons

If the radical reacts with the solvent, the formation of primary amines and a hydrocarbon results, and is therefore classified under type Equation I.

When the R-radicals react by direct combination, the formation of a hydrocarbon occurs and is therefore classified under the reactions as represented by type Equation II.

The reaction of the group R with electrons results in the formation of Re^- as follows:

$$R + e^- \longrightarrow Re^-$$

This would then permit the combination of the positive sodium ion with Re^-, forming R-Na as shown in type Equation III.

Until this present investigation was undertaken, no work of quantitative aspect had been attempted to establish the nature of the reducing action of sodium in liquid ammonia on the di-halogen derivatives of aliphatic or aromatic hydrocarbons.

Since the possibility of position isomerism is increased in the di-halides, the complexity of the reactions which they will undergo is likewise increased. It is obvious that a di-halide of the type $RCHX_2$ will not react the same as one of the type $R\underset{X}{C}H-\underset{X}{C}HR$. Also, it would be expected that aromatic hydrocarbons, in which the two halogens were nuclear substituted, would react differently from the di-substituted paraffin hydrocarbons.

All the work that has been accomplished in studying the reactions of dihalides and sodium in liquid ammonia, has been done by Chablay,[4] and Kraus and White [8]. Chablay attempted to obtain quantitative data in his investigations but the endeavor to have his experimental results coincide with his theoretical speculations, has let his results open to deserved criticism. The qualitative data of Kraus and White are reliable but they have not attempted to interpret their investigations quantitatively.

Chablay's work consisted in a study of the reaction of sodium in liquid ammonia on the compounds methylene chloride, ethylidene chloride, 2,2 dichloropropane, ethylene dichloride, propylene dibromide and butylene dibromide. In the reactions of the first three mentioned he gives as products, the saturated hydrocarbon from which the dihalide had been derived, sodium amide and sodium chloride. His results were explained by the following equations:

$$CH_2Cl_2 + 4\ Na + 2\ NH_3 \rightarrow CH_4 + 2\ NaNH_2 + 2\ NaCl \quad (4)$$

$$CH_3CHCl_2 + 4Na + 2\ NH_3 \rightarrow C_2H_6 + 2\ NaNH_2 + 2\ NaCl \quad (4)$$

$$CH_3CCl_2CH_3 + 4\ Na + 2\ NH_3 \rightarrow C_3H_8 + 2\ NaNH_2 + 2\ NaCl \quad (4)$$

It is noticed the Chablay represents the molar ratio of dihalide to sodium as 1 to 4 in his equations, whereas he found this ratio to be 1 to 2.5 in his experimental work. Thus it is obvious that the above equations are not reliable.

In the case of the reactions of the last three compounds mentioned with sodium in liquid ammonia, Chablay used a molar ratio of 1 to 2, and obtained, as products, the olefine hydrocarbons from which the di-halides were derived and sodium halide. The equations offered for these reactions follow:

$CH_2Cl-CH_2Cl + 2\ Na \longrightarrow CH_2=CH_2 + 2\ NaCl$ (4)

$CH_3CHBr-CH_2Br + 2\ Na \longrightarrow CH_3CH=CH_2 + 2\ NaBr$ (4)

$CH_3CH_2CHBr-CH_2Br + 2\ Na \longrightarrow CH_3CH_2CH=CH_2 + 2\ NaBr$ (4)

Kraus and White (8) investigated the reaction of three di-halides, namely ethylene dichloride, dibromo-ethylene and ortho-dichlor benzene, on sodium in liquid ammonia solution. In the case of ethylene dichloride, the results they obtained substantiated those of Chablay, in that they obtained ethylene and sodium chloride as shown in the following equation:

$CH_2Cl-CH_2Cl + 2\ Na \longrightarrow CH_2=CH_2 + 2\ NaCl$ (8)

This equation is identical with the one which Chablay offered.

In the study of the reaction in which di-bromo-ethylene was used, Kraus and White found the products, which were produced, were acetylene, sodium acetylide, hydrogen and sodium bromide. The formation of the acetylene and sodium bromide was accounted for by assuming that the following reactions took place:

$CHBr=CHBr + 2\ Na \longrightarrow CH\equiv CH + 2\ NaBr$ (8)

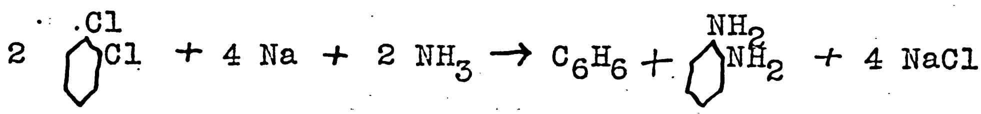
The formation of the hydrogen and the sodium acetylide was accounted for in two ways. First, the reaction of the sodium directly on the di-halide to give hydrogen, sodium acetylide and sodium bromide as illustrated in the following equation:

$CHBr=CHBr + 4\ Na \longrightarrow H_2 + NaC\equiv CNa + 2\ NaBr$ (8)

Second, that the sodium reacted with the acetylene formed in the reaction to give sodium acetylide and hydrogen as shown by the following equation:

$$CH \equiv CH + 2\ Na \rightarrow H_2 + NaC \equiv CNa \quad (8)$$

In the investigation of the reaction in which ortho-dichlorbenzene was used as the di-halide, benzene, orthophenylene diamine and sodium chloride were found to be the major products. This reaction was represented by the following equation:

 (8)

The reported formation of benzylamine and dibenzyl by the reaction of sodium in liquid ammonia on benzal chloride and the formation of tetra-phenyl ethylene by sodium in liquid ammonia on di-phenyl dichloro-methane (12) complete the investigations which have been reported in the literature on the reactions of dihalogen derivatives of the hydrocarbons with sodium in liquid ammonia solution.

Thus it is obvious that even qualitative data on reactions of this type are extremely scarce. Nevertheless, it is possible to speculate on the type of reactions that might occur, basing these speculations on the theory of reduction as proposed by Kraus and White (8) and which has already been applied to the reactions involving monohalogen derivatives.

Since the investigation considered in this thesis is a study of the reaction of benzal chloride and sodium in liquid ammonia, only the reactions involving a di-halide of the type $RCHX_2$ in which both halogens are attached to an alpha carbon atom, will be considered.

There are many types of reaction possible when sodium in liquid ammonia reacts with a di-halide of the class $RCHX_2$ and many of these reactions are quite complex, resulting in the formation of hydrocarbons, amines, and intermediate sodium-organo-compounds. The classification of the many possible type reactions will be presented under three heads.

I. REACTIONS INVOLVING THE GROUP $RCH=$ AS A REACTANT.

II. REACTIONS INVOLVING THE GROUPS $RCH=$ AND $\overset{|}{R}\!CH-\overset{|}{C}HR$ AS REACTANTS.

III. REACTIONS INVOLVING THE GROUPS $RCH=$ AND RCH_2- AS REACTANTS.

I.

REACTIONS INVOLVING THE GROUP $RCH=$ AS A REACTANT.

If the compound $RCHX_2$ is added to a solution of sodium in liquid ammonia, the free electrons present in the solution would combine with the strongly electronegative halogen forming the normal chloride anion. The organic group $RCH=$ is thus set free which immediately reacts in one of the following ways:

A. Direct Reaction Between the $RCH=$ Groups.

B. Reaction of the $RCH=$ Group With the Solvent Ammonia.

C. Simultaneous Reaction of the $RCH=$ Groups With the Solvent Ammonia.

A. Direct Reaction Between the $RCH=$ Groups. The simplest type of reaction possible would be the combination of two of the organic radicals thus set free, to form an unsaturated hydrocarbon, and will be classified as type equation I.

I. $2\ RCHX_2 + 4\ Na \rightarrow RCH{=}CHR + 4\ NaX$

B. Reaction of the RCH< Group With the Solvent Ammonia. Another very simple type of reaction would be the direct union of the group RCH< with the solvent NH_3, resulting in the formation of a primary amine. This reaction will be classified as type equation II.

II. $RCHX_2 + 2\ Na + NH_3 \rightarrow RCH_2NH_2 + 2\ NaX$

C. Simultaneous Reaction of the RCH< Groups With Each Other and With the Solvent Ammonia. If two or more of the RCH< groups combine before the reaction with the solvent takes place, amines of higher molecular weight than in type II are obtained. The simplest case of this type is illustrated by the following type equation.

III. $2\ RCHX_2 + 4\ Na + NH_3 \rightarrow \underset{NH_2}{RCH}{-}CH_2R + 4\ NaX$

There is also a possibility of a diamine being formed, the solvent furnishing the NH_2 groups and the hydrogen thus freed adding to the unsaturated bonds of the RCH< group thus:

IV. $3\ RCHX_2 + 6\ Na + 2\ NH_3 \rightarrow \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + RCH_3 + 6\ NaX$

A reaction similar to type IV, but in which two RCH< groups combine before the addition of hydrogen takes place, is illustrated by type equation V.

V. $4\ RCHX_2 + 8\ Na + 2\ NH_3 \rightarrow \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + RCH_2{-}CH_2{-}R + 8\ NaX$

If more than two RCH< groups joined before the addition of hydrogen, the reaction would be illustrated by the following type equation:

$$\text{VI.}\quad 5\ RCHX_2 + 10\ Na + 2\ NH_3 \rightarrow \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + RCH_2-\underset{R}{CH}-CH_2R + 10\ NaX$$

This principle exhibited by combination of the RCH< groups in type equations V and VI would possibly lead to the formation of long chain compounds of phenyl substituted aliphatic hydrocarbons.

Thus the reactions that might occur when the freed RCH< group reacts directly with a similar group, with the solvent ammonia or by a combination of the two, forming hydrocarbons, amines, and both simultaneously in their respective cases, are illustrated in the type equations I to IV inclusive, as given.

II.

REACTIONS INVOLVING THE GROUPS RCH< AND RCH-CHR AS REACTANTS.

If the free RCH< group reacts with one electron, which is present in the solution, it would form an $RCHe^-$ group as shown by the equation:

$$RCH< + e^- \rightarrow RCHe^-$$

This group, possessing one free bond is then available to react with another similar bond and the presence of the electron would make possible the formation of an independent free radical. However, since the probability of the free radical, RCH-CHR, being formed with two trivalent carbon atoms adjacent, is exceedingly remote, it will not be considered in this discussion.

It is, however, quite probable that the above group would combine with another similar group and add sodium with the formation of a sodium organo-compound as shown by the following equation:

$$2\ RCHe^{-} + 2\ Na \rightarrow \underset{Na}{RCH} - \underset{Na}{CHR}$$

Type equation VII may be used to represent the formation of this sodium organo-compound.

$$\text{VII.}\quad 2\ RCHX_2 + 6\ Na \rightarrow \underset{Na}{RCH} - \underset{Na}{CHR} + 4\ NaX$$

Moreover, it is possible for three or more groups to enter into the reaction with the formation of long chain compounds. This would be represented by type equation VIII.

$$\text{VIII.}\quad 3\ RCHX_2 + 8\ Na \rightarrow \underset{Na}{RCH} - \underset{R}{CH} - \underset{Na}{CHR} + 6\ NaX$$

Since the intermediate sodium organo-compounds will react with further $RCHX_2$, with the formation of NaX, it is obvious that in the case of $\underset{Na}{RCH} - \underset{Na}{CHR}$, the two groups $\underset{|}{RCH}-\underset{|}{CHR}$ and $RCH<$ would be freed for further reaction as is shown by the following equation:

$$\underset{Na}{RCH} - \underset{Na}{CHR} + RCHX_2 \rightarrow \underset{|}{RCH}-\underset{|}{CHR} + RCH< + 2\ NaX$$

The reaction of $\underset{Na}{RCH} - \underset{R}{CH} - \underset{Na}{CHR}$ would be similar to the above and the type equations developed for the former would be applicable also to this compound. Therefore, type equations will be presented for the reactions of the $\underset{|}{RCH}-\underset{|}{CHR}$ and $RCH<$ groups only, and will be classified under the following heads:

A. Reaction Between Identical Groups.

B. Reaction Between the Two Different Groups.

C. Reaction of Each Group Separately with the Solvent Ammonia.

D. Simultaneous Reaction of the Groups with Each Other and with the Solvent Ammonia.

In order to formulate a type equation for the completed reaction in which $\underset{Na}{RCH} - \underset{Na}{CHR}$ is formed as an intermediate, the reaction must be considered as taking place in two steps, first, the formation of the sodium organo-compound, and second, the reaction of this intermediate with additional $RCHX_2$. The summation of these two reactions will then be the type reaction. In the following discussion, as outlined above, the reactions of the freed groups will be shown by equation, followed by the type equation for the completed reaction.

<u>A. Reaction Between Identical Groups</u>. Since the $R\underset{|}{C}H-\underset{|}{C}HR$ and $RCH<$ groups are present in equivalent amounts, the following equations represent simultaneous reactions:

1. $2\ R\underset{|}{C}H - \underset{|}{C}HR \rightarrow \begin{array}{c} RCH - CHR \\ |\qquad\ \ | \\ RCH - CHR \end{array}$

2. $2\ RCH< + RCH{=}CHR$

IX. $6\ RCHX_2 + 12\ Na \rightarrow \begin{array}{c} RCH - CHR \\ |\qquad\ \ | \\ RCH - CHR \end{array} + RCH{=}CHR + 12\ NaX$

<u>B. Reaction Between the Two Different Groups</u>. If the two groups, $RCH<$ and $R\underset{|}{C}H - \underset{|}{C}HR$ react with each other, a cyclic hydrocarbon will be formed as shown in the following equation:

$RCH< + R\underset{|}{C}H - \underset{|}{C}HR \rightarrow \begin{array}{c} RCH-CHR \\ \diagdown\ \diagup \\ CHR \end{array}$

Thus the type equation for the completed reaction would be:

$$\text{X.}\quad 3\ RCHX_2 + 6\ Na \longrightarrow \begin{array}{c} RCH-CHR \\ \diagdown\ \diagup \\ CHR \end{array} + 6\ NaX$$

C. <u>Reaction of Each Group Separately With the Solvent Ammonia</u>. If each group as freed reacts directly with the solvent ammonia, two primary amines would be formed as shown in the following equations:

$$RCH{<} + NH_3 \rightarrow RCH_2NH_2$$

$$\underset{|}{RCH} - \underset{|}{CHR} + NH_3 \longrightarrow RCH_2-\underset{NH_2}{\underset{|}{CHR}}$$

The completed reaction would then be summed up in the following type equation:

$$\text{XI.}\quad 3\ RCHX_2 + 6\ Na + NH_3 \rightarrow RCH_2-\underset{NH_2}{\underset{|}{CHR}} \quad RCH_2NH_2 + 6\ NaX$$

D. <u>Simultaneous Reaction of the Groups With Each Other and With the Solvent Ammonia</u>. In the case where the groups $RCH{<}$ and $\underset{|}{RCH} - \underset{|}{CHR}$ react with each other as well as with the solvent ammonia, various combinations are possible. In the following equations, possible reactions of the freed groups are first given, followed immediately by the type equation for the completed reaction.

$$\underset{|}{RCH} - \underset{|}{CHR} + RCH{<}\ \ 2\ NH_3 \rightarrow \underset{NH_2}{\underset{|}{RCH}} - \underset{NH_2}{\underset{|}{CHR}} + RCH_3$$

$$\text{XII.}\quad 3\ RCHX_2 + 6\ Na + 2\ NH_3 \longrightarrow \underset{NH_2}{\underset{|}{RCH}} - \underset{NH_2}{\underset{|}{CHR}} + RCH_3 + 6\ NaX$$

$$2\ \underset{|}{RCH} - \underset{|}{CHR} + 2\ RCH + 3\ NH_3 \longrightarrow \underset{NH_2}{\underset{|}{RCH}} - \underset{NH_2}{\underset{|}{CHR}} + RCH_2\underset{R}{\underset{|}{C}}H-CH_2R$$

$$+ RCH_2NH_2$$

XIII. $$6\ RCHX_2 + 12\ Na + 3\ NH_3 \rightarrow \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + RCH_2\underset{R}{CH}-CH_2R$$
$$+ RCH_2NH_2 + 12\ NaX$$

$$\underset{|}{RCH} - \underset{|}{CHR} + RCH< + NH_3 \rightarrow RCH_2-\underset{R}{CH}-\underset{NH_2}{CH}-R$$

XIV. $$3\ RCHX_2 + 6\ Na + NH_3 \rightarrow RCH_2-\underset{R}{CH}-\ \underset{NH_2}{CH}-R + 6\ NaX$$

$$2\ \underset{|}{RCH} - \underset{|}{CHR} + 2\ RCH< + 3\ NH_3 \rightarrow RCH_2-CH_2R + \underset{NH_2}{RCH} - \underset{R}{CH} - \underset{NH_2}{CHR} + RCH_2NH_2$$

XV. $$6\ RCHX_2 + 12\ Na + 3\ NH_3 \rightarrow RCH_2-CH_2R + \underset{NH_2}{RCH} - \underset{R}{CH} - \underset{NH_2}{CHR}$$
$$+ RCH_2NH_2 + 12\ NaX$$

The type equations VII and VIII have been presented to show the type of reaction occuring in the formation of sodium organo-intermediate compounds. The reactions, that have been illustrated by type equations IX and through XV inclusive, are those which occur on completing the reaction by the addition of $RCHX_2$ and which are dependent on the formation of the $\underset{|}{RCH}-\underset{|}{CHR}$ and $RCH<$ groups resulting from the reaction of the di-halide on the intermediate compound.

III.

REACTIONS INVOLVING THE GROUPS $RCH<$ AND RCH_2- AS REACTANTS.

If the freed $RCH<$ radical reacts with two electrons, the group $RCH(e^-)_2$ would be formed as shown in the following equation:

$$RCH< + 2\ (e^-) \rightarrow RCH(e^-)_2$$

There would then be the possibility of the $RCH(e^-)_2$ group adding two strongly electropositive groups, or the formation of a free radical. The possibility of the independent existance of the free RCH radical or the formation of the compound $RCHNa_2$ has never been indicated in the realm of organic chemistry and therefore will not be considered in the formulation of type reactions. However, if the $RCH(e^-)_2$ group adds the strongly electropositive sodium ion and the positive hydrogen ion, there would be formed a mono-sodium organo-compound as follows:

$$RCH(e^-)_2 + Na^+ + H^+ \rightarrow RCH_2Na$$

Since this reaction requires hydrogen, the solvent must play a part as reactant and there would be a simultaneous formation of amine. This reaction may then be classified under the following type equation:

$$\text{XVI.} \quad 4\ RCHX_2 + 10\ Na + 3\ NH_3 \rightarrow 2\ RCH_2Na + \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + 8\ NaX$$

If additional $RCHX_2$ is added to the compound RCH_2Na, the groups RCH_2- and $RCH<$ will be formed along with the sodium halide. This reaction would be illustrated by the following equation:

$$2\ RCH_2Na + RCHX_2 \rightarrow 2\ RCH_2- + RCH< + 2\ NaX$$

From this equation, it is evident that the groups, as freed, will be in the ratio of two mols of RCH_2- to one mol of $RCH<$. These groups will then react as follows:

A. Reaction Between Identical Groups.

B. Reaction Between the Two Different Groups.

C. Reaction With the Solvent Ammonia.

D. Simultaneous Reaction of the Groups With Each Other and With the Solvent Ammonia.

The consideration of these topics will be presented as in the previous discussion by first showing the reaction of the freed $RCH<$ and RCH_2- groups, followed by a summation of this reaction and the reaction in which the intermediate was formed. It should be kept in mind that the first step of the reaction produces an amine which will therefore appear in all the type equations.

A. Reaction Between Identical Groups. If a reaction occurs between identical groups, as freed, two hydrocarbons would result as shown in the equation:

$$4\ RCH_2- + 2\ RCH< \rightarrow 2\ RCH_2\text{-}CH_2R + RCH{=}CHR$$

$$\text{XVIII.}\quad 8\ RCHX_2 + 16\ Na + 2\ NH_3 \rightarrow 2\ RCH_2\text{-}CH_2R + RCH{=}CHR + \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + 16\ NaX$$

B. Reaction Between the Two Different Groups. If the two groups react with each other, the following possibilities occur, the formation of hydrocarbons resulting in each case. The type equation for the completed reaction will follow the reaction of the freed groups.

$$2\ RCH_2- + RCH< \rightarrow RCH_2\text{-}\underset{R}{CH}\text{-}CH_2R$$

$$\text{XVIII.}\quad 5\ RCHX_2 + 10\ Na + 2\ NH_3 \rightarrow RCH_2\text{-}\underset{R}{CH}\text{-}CH_2R + \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + 10\ NaX$$

$$8\ RCH_2^- + 4\ RCH\langle \rightarrow RCH{=}CHR + 2\ RCH_2{-}CH_2R + 2\ RCH_2{-}\underset{R}{CH}{-}CH_2R$$

$$\text{XIX.}\quad 14\ RCHX_2 + 28\ Na + 2\ NH_3 \rightarrow RCH{=}CHR + 2\ RCH_2{-}CH_2R + 2\ RCH_2{-}\underset{R}{CH}{-}CH_2R + \underset{NH_2}{RCH}{-}\underset{NH_2}{CHR} + 28\ NaX$$

C. <u>Reaction With the Solvent Ammonia</u>. The reaction of either group with the solvent ammonia results in the formation of RCH_2NH_2 and simultaneous formation of a hydrocarbon by the addition of hydrogen to the other group. This reaction is shown as follows:

$$2\ RCH_2^- + RCH + 2\ NH_3 \rightarrow 2\ RCH_2NH_2 + RCH_3$$

$$\text{XX.}\quad 4\ RCHX_2 + 8\ Na + 4\ NH_3 \rightarrow 2\ RCH_2NH_2 + RCH_3 + \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + 8\ NaX$$

D. <u>Simultaneous Reaction of the Groups With Each Other and With the Solvent Ammonia</u>. The 2 RCH_2^- and $RCH\langle$ groups as freed may react simultaneously with each other and with the solvent. This leads to the formation of mono and di-amines and hydrocarbons of high molecular weight. These reactions of the groups and solvent are shown as follows, the derived type equation for the completed reaction being given after each equation.

$$2\ RCH_2^- + RCH\langle + NH_3 \rightarrow RCH_2{-}CH_2R + RCH_2NH_2$$

$$\text{XXI.}\quad 5\ RCHX_2 + 10\ Na + 3\ NH_3 \rightarrow RCH_2{-}CH_2R + RCH_2NH_2 + \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + 10\ NaX$$

$$4\ RCH_2^- + 2\ RCH\langle + 2\ NH_3 \rightarrow \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + 2\ RCH_3 + RCH_2{-}CH_2R$$

$$\text{XXII.}\quad 8\ RCHX_2 + 16\ Na + 4\ NH_3 \rightarrow 2\ \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + 2\ RCH_3 + RCH_2{-}CH_2R + 16\ NaX$$

$$2\ RCH_2- + RCH< + NH_3 \rightarrow RCH_2-\underset{NH_2}{CHR} + RCH_3$$

XXIII. $$5\ RCHX_2 + 10\ Na + 3\ NH_3 \rightarrow \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + RCH_2-\underset{NH_2}{CHR} + RCH_3 + 10\ NaX$$

Thus the type equation has been presented which accounts for the formation of a sodium organo-compound directly responsible for the production of the RCH_2- group on further addition of $RCHX_2$, and is shown in type equation XVI. The completed reactions, depending on the reactions of the $RCH<$ and RCH_2- groups formed from the above mentioned action of the intermediate compound with $RCHX_2$, are represented in type equations XVII to XXIII inclusive.

The type equations I to XXIII inclusive are offered as representative of reactions that a dihalide of the class $RCHX_2$ might undergo with sodium in liquid ammonia solution. The reactions of these dihalides, as can be seen from the above possibilities are obviously complex, and as stated in the case of the mono-halides, many reactions would take place in more than one way and would be represented by two or more of the formulated types.

The study of the reducing action of sodium on benzal chloride in liquid ammonia solution was chosen for the following reasons:

1. To add to the knowledge of the action of sodium in liquid ammonia as a reducing agent on a typical dihalide of the class represented by the type formula $RCHX_2$.

2. To be the second step in a series of investigations being planned in the Liquid Ammonia Laboratory of the University of Cincinnati, the first step being the reducing action of sodium in liquid ammonia on benzyl chloride and carried out by H. Linford (12).

3. To determine, as far as possible, the mechanism of the reaction by a study of intermediate compound formation, a quantitative estimation of the products formed, and to classify the reaction under the types as outlined in this introduction.

The investigation will be presented in the following manner:

1. Materials
2. Apparatus
3. Procedure and experimental results.
   Separation, identification and estimation of reaction products.
4. Formulation of equations and classification of the reaction.

II.

MATERIALS

The benzal chloride used in this investigation was prepared by the Eastman Company from benzaldehyde and had a boiling point of 95 - 96 degrees C. at 15 m.m. pressure. The benzyl chloride that was used in part of the work was also obtained from the Eastman Company and had a boiling point of 88 - 90 degrees C. at 10 m.m. pressure.

The sodium employed was Kahlbaum's "Sodium zur analyze". Before use, the coating of oxide was shaved off with a safety razor blade under petroleum ether. The sodium was then placed in a small weighing bottle fitted with a ground glass stopper and the petroleum ether evaporated by a stream of anhydrous nitrogen passed into the weighing bottle through a small rubber tube. This provided an atmosphere of nitrogen for the sodium, which prevented oxidation and enabled the sodium to keep its metallic luster while being weighed and until it was used in the reaction.

The liquid ammonia that was used in carrying out the reactions was obtained from the Mathieson Alkali Company in 100 pound cylinders. In order to insure the use of anhydrous ammonia as the solvent in the reactions, smaller laboratory tanks of about 4½ pound capacity containing 2 or 3 grams of metallic sodium were filled from the large cylinder. The sodium served as a dehydrating agent by reacting with any moisture that might be present forming sodium hydroxide and hydrogen which do not interfere in the reaction. The liquid ammonia used as the cooling bath was employed directly as drawn from the large cylinder.

III.

APPARATUS.

In carrying out reactions in liquid ammonia solutions, two methods are available. First, the reaction may be carried out in a sealed tube at room temperature, the pressure being that of the vapor pressure of liquid ammonia at room temperature, namely 8 atmospheres. Second, the reaction may be carried out below -33.5 degrees C. the boiling point of liquid ammonia, and at 1 atmosphere pressure. The latter method is more convenient for the reduction of organic compounds in liquid ammonia for two reasons. First, larger amounts of material can be used in this method thus furnishing greater yields of products per reaction. Second, there is less danger of a serious accident occurring. Many reactions of this type are very vigorous, and the heat of reaction causing great pressure to develop in the tube may result in an explosion. The method chosen in the following investigation, therefore, is that of carrying out the reaction below -33.5 degrees C. and at atmospheric pressure and is a modification of that used by White [9] and Linford [13].

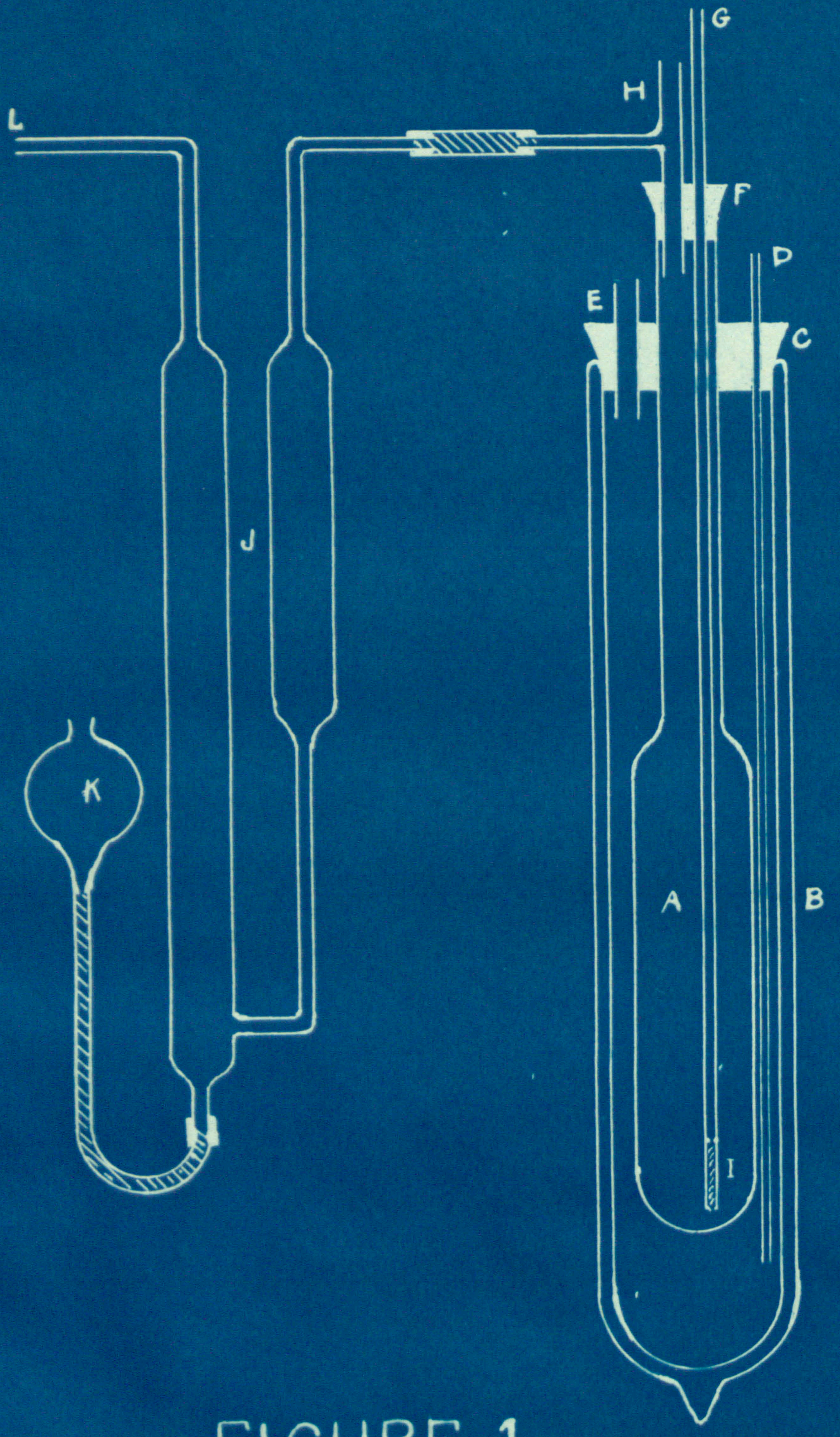


FIGURE 1

Apparatus for the Reduction of Organic Compounds in Liquid Ammonia at Atmospheric Pressure.

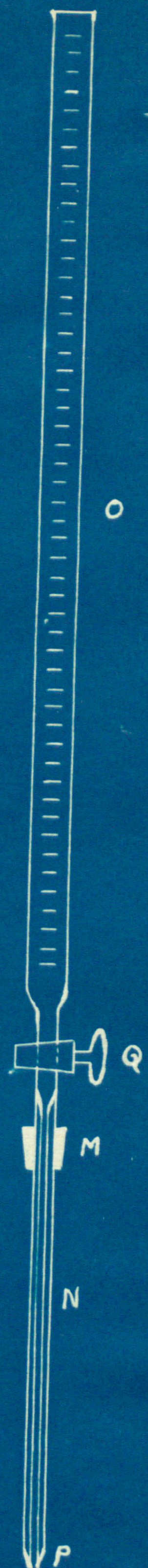


FIGURE 2.

Pipet for the addition of Organic Liquids to Sodium in Liquid Ammonia Solution.

The apparatus used is shown in Figure 1 and Figure 2. A is the tube in which the reaction is carried out, and has a capacity of 400 c.c. This reaction tube is immersed in a cooling bath of liquid ammonia contained in Dewar flask B. The Dewar flask is fitted with a three hole rubber stopper through which passes (1) the reaction tube A, (2) a 4 m.m. glass tube D, and (3) an eight m.m. glass tube E. Through tube D, air, dried by passage through a calcium chloride tower, is run to cause rapid evaporation of the liquid ammonia bath in Dewar flask B. The 8 m.m. glass tube E, is used for the outlet of air and ammonia gas from the cooling bath and leads through a safety bottle to a bottle of water where the ammonia is absorbed.

The reaction tube A is fitted with a two hole rubber stopper, F, through which passes (1) a six m.m. glass tube G, and (2) a T-tube, H, of 12 m.m. glass tubing. The 6 m.m. glass tube ,G, is used to introduce anhydrous ammonia gas into the reaction tube for condensation of the solvent in the reaction. About 2 c.m. of the lower end of tube G, are filled with glass wool as shown at I to prevent precipitated solids from entering. The T-tube H of 12 m.m. glass tubing has a 6 m.m. side arm. During condensation of the solvent, H is closed with a rubber stopper. The sodium, used in the reaction, is introduced through H into the reaction tube A. H is then fitted with a one hole rubber stopper, M, and the buret, illustrated in Figure 2. This consists of a capillary tube, N, of 1 m.m. bore, joined to a 25 c.c. buret, O, used to measure the benzal chloride. The tube N is ground to a point at P to insure the formation of small drops of benzal chloride when the reaction is carried out. The buret, O, is graduated in tenths of a c.c. and may be read in hundredths of a c.c. The buret was calibrated by weighing accurately the delivery of benzal chloride between each one c.c. graduation and between divisions of five c.c. It was found that each one c.c. division delivered 1.23 grams of benzal chloride.

The side arm of H is connected to mercury trap J. K is the mercury reservoir connected to J by means of rubber pressure tubing. The height of mercury in the trap J may be adjusted by raising or lowering K, thus regulating the pressure in the reaction tube A. Vaporized ammonia from the reaction tube is led off through L to the water absorbtion bottle.

IV.

STUDY OF THE COMPLETED REACTION

The completed reaction is assumed to be the reaction that takes place between 1 mol of benzal chloride and 2 mols of sodium, resulting in the formation of 2 mols of sodium chloride. That this assumption is correct is proved by a quantitative determination of the sodium chloride formed in the reaction, and by the presence of benzal chloride in the reaction product if this ratio is exceeded.

The discussion of the completed reaction will be presented under four heads, namely, procedure, separation of reaction products, identification of reaction products, and a quantitative estimation of these products. A brief summary of the results will then complete the discussion.

A.

Procedure.

The completed reaction is carried out in the following manner. The apparatus is set up as shown in Figure 1, the tube H being closed with a rubber stopper. Anhydrous ammonia gas is run in from the laboratory tank through tube G for several minutes to sweep out air and moisture present in the reaction tube. Liquid ammonia is then drawn from the large supply cylinder into a Dewar flask and transfered by a pressure siphon to Dewar flask B, until 8 to 10 c.m. from the top, stopper C being raised for this operation. Stopper C is then firmly replaced and air, previously dried by passage through a calcium chloride tower, is run through tube D, its rate being adjusted by a glass stop cock. The dry air is thus bubbled through the liquid ammonia bath in Dewar flask B causing rapid evaporation with consequent lowering of temperature. In this way, temperatures as low as -40 degrees C. can be obtained without difficulty. The mercury reservoir K is then adjusted to give about a 10 c.m. column of mercury in the trap J. The ammonia gas, entering reaction tube A under 10 cm. of mercury pressure and at a temperature of -40 degrees, readily condenses.

While the ammonia is condensing, about two grams of sodium prepared as described before under materials, are weighed out accurately to one milligram. When about 200 c.c. of ammonia has condensed in the reaction tube, the air and ammonia are turned off and the sodium is introduced into the reaction through tube H.

It was found by experience that a two gram portion of sodium was the most efficient for use in this reaction. If a larger amount was used, the reaction was so vigorous that the material splashed to the top of the reaction tube and could not be washed down by further condensation of ammonia. If a smaller amount was used, the advantage of obtaining the maximum amount of product was lost. The use of two grams of sodium resulted in a smooth reaction, any material splashing on the reaction tube was easily washed down by condensing ammonia on the walls of the tube.

After the addition of sodium to the liquid ammonia in the reaction tube, the buret O is inserted through H and the stopper M fixed tightly in place. Since in the completed reaction the ratio of benzal chloride to sodium is one mol to two mols, the ratio of the weight of benzal chloride to sodium is determined as follows.

$$\frac{C_6H_5CHCl_2}{2\ Na} = \frac{161}{46} = 3.5$$

Therefore, for every gram of sodium used there must be added 3.5 grams of benzal chloride. Calculating this to volume, there must be added $\frac{3.5}{1.23} = 2.84$ c.c. of benzal chloride.

After the buret has been fixed in place the mercury reservoir K is lowered until the mercury column in the trap J is about two cm. in height. The air is again turned on in the cooling bath until the mercury in the right hand column of the trap J rises to a height of 6 or 8 cm. thus showing a reduction of pressure in the reaction flask.

The carrying out of the reaction at this reduced pressure resulted in a smoother action taking place and also eliminated the need of pressure on the benzal chloride in the buret to cause it to flow out.

Ammonia gas is again turned on at the tank, the rate being adjusted to give efficient stirring to the solution in the reaction tube without overcoming the reduced pressure caused by the cooling bath. If necessary, the amount of air entering the cooling bath was increased.

The stop-cock Q of the buret is then adjusted to allow the benzal chloride to enter the reaction flask at the rate of one drop every two or three seconds. The reaction takes place instantaneously and is very vigorous during the addition of the first portion of the benzal chloride. Splashing of the solution often occurs and necissitates an increase in the flow of ammonia into the cooling bath, the resulting condensation washing down the splattered material.

A red coloration in the reaction mixture is noticed soon after the addition of benzal chloride is started. This red coloration increases in intensity as the addition continues, until 80% of the theoretical benzal chloride is added. At this point the last indication of the characteristic blue color of the sodium solution disappears and the solution is a bright red. At this point also the solution becomes transparent and a heavy flocculent precipitate is visible in the solution.

From this point on, the reaction takes place very slowly. The benzal chloride can now be run in rapidly until the theoretical amount has been added. Evidence that the reaction is slow during the latter part of the reaction is shown by the gradual change of color from red to yellowish brown on standing for several hours after the last addition of benzal chloride. No visible end point occurs on addition of the theoretical amount of benzal chloride.

After the theoretical quantity of benzal chloride has been added, the buret is removed and replaced by a rubber stopper in H. The air and ammonia gas are turned off and the liquid ammonia allowed to evaporate from the solution in the reaction tube, under a pressure of 6 to 8 cm. of mercury in trap J. This evaporation requires about 30 hours.

After the liquid ammonia has completely evaporated, the sides and bottom of the reaction tube are coated with the substances that were produced in the reaction and which are light yellow in color.

B.

Separation of Reaction Products.

This method of extraction was employed in separating the various products left in the reaction tube. The first procedure consisted in the separation of these reaction products into ether insoluble products and ether soluble products. Another procedure established the absence of volatile products. Each will now be discussed under its appropriate heading.

1. Separation of the Ether Insoluble Products.

After the liquid ammonia had evaporated from the reaction tube, the product was extracted with small portions of anhydrous ether until no further coloration was noted in the ether solution. This extraction was done by decantation, the fine, white, ether insoluble product settling out quickly, allowing the ether solution to be poured off through a filter. Thus the ether insoluble products were separated from the ether soluble ones.

2. Separation of the Ether Soluble Products.

The separation of the ether soluble products consisted in the successive extraction of an ether solution of the ether soluble products with water, and dilute hydrochloric acid, a residue still remaining in the ether solution. This separation will therefore be discussed as follows:

(a). Separation of water soluble product.

(b). Separation of dilute hydrochloric acid product.

(c). Separation of residue.

(a). Separation of water soluble product. The ether soluble reaction product, dissolved in about 300 c.c. of ether, was extracted 12 to 15 times by 300 c.c. portions of distilled water by vigorously shaking in a separatory funnel. Some difficulty was experienced by emulsion formation in this extraction but was overcome by the addition of 5 to 10 c.c. of ethyl alcohol, which resulted in the breaking of the emulsion and the separation of the ether-water layers.

About 5 c.c. of dilute hydrochloric acid was added to the water solution, and the water evaporated, leaving a white crystalline solid. In this way the water soluble amine was recovered as the hydrochloride salt.

(b). Separation of dilute hydrochloric acid soluble product. The ether solution from which the water soluble amine had been removed was now extracted with two 300 c.c. portions of 0.1 N hydrochloric acid. The ether solution was then washed by extraction with water until the wash water gave no precipitate when added to silver nitrate solution acidified with nitric acid. This test showed complete removal of HCl from the ether layer. The HCl solution was then evaporated leaving as a product the HCl soluble amine hydrochloride.

(c). Separation of residue. The ether layer remaining was dried for about twelve hours over anhydrous sodium sulfate and then evaporated. The remaining product was a viscous yellow oil.

3. Absence of Volatile Products.

The possibility of hydrogen or volatile organic compounds capable of distilling with the liquid ammonia, being formed in the reaction, led to an investigation to establish the presence or absence of these products.

(a). Absence of hydrogen. During several reactions, the gas issuing from the reaction tube through the side arm of H, (Figure 1), was passed through one inch of mercury and enough concentrated hydrochloric acid to completely fill an eight ounce bottle, and thence to a gas buret standing over water. The mercury in the bottle acted as a trap to prevent the hydrochloric acid from entering the reaction tube and the concentrated hydrochloric acid absorbed the gaseous ammonia. Only a few c.c. of gas were collected in this manner and the gas analyzed by the usual method of combustion showed the absence of hydrogen. The small amount of gas collected was undoubtedly air that was present in the system, swept out by the stream of ammonia.

(b). Absence of volatile organic products. The method used for determining the presence or absence of volatile organic products was that devised and used successfully by White (9) and modified by Linford (13). This method consisted in the absorbtion of the evolved ammonia gas during the reaction and the evaporation of the solvent after the completion of the reaction, with the consequent concentration of the volatile component and separation from the absorbant. Concentrated hydrochloric acid contained in a large flask and cooled in ice was used to absorb the ammonia. Application of this method gave negative results, no toluene or other substance separating.

These results were further substantiated by allowing the ammonia gas escaping from the reaction tube to pass upward over a column of ice, thus being absorbed, the water produced by the melting ice flowing back into a large flask. The results by this method were also negative.

Thus the conclusion was reached that the reaction produced no substances which were volatile with evaporating liquid ammonia.

C.

Identification of Reaction Products.

The identification of the reaction products will be discussed under two main headings, first, the identification of the ether insoluble product, and second, the identification of the ether soluble products.

1. Identification of Ether Insoluble Product.

The ether insoluble product was assumed to be NaCl and prepared for analysis by thoroughly washing with ether and drying in the air. Samples were weighed out accurately on a watch glass and transferred to 400 c.c. beakers. About 100 c.c. of distilled water was then added, in which the sample was readily soluble. The solution was acidified with nitric acid and the chloride precipitated as silver chloride with silver nitrate solution. After one hour of digestion of the hot plate, the beakers were allowed to stand over night in the dark. The solutions were then filtered through weighed Gooch crucibles and the weight of silver chloride determined. The results of the analysis of two samples from each of two reactions are given in the following table.

Table 1.

Analysis of Ether Insoluble Product.

I. Sample Number	II. Sample Grams	III. AgCl Grams	IV. NaCl Grams	V. % NaCl
1A	.4613	1.1197	.4566	98.98
1B	.3210	.7801	.3181	99.09
2A	.3641	.8838	.3604	98.99
2B	.2963	.7201	.2937	99.12

Column I indicates the sample number, the figure indicating the reaction and the letter the sample. Thus samples 1A and 1B indicate two samples of the ether insoluble material produced in the same reaction. Column II gives the weight in grams of the sample of the ether insoluble material. The weight in grams of silver chloride produced on treating a solution of the sample with silver nitrate is given in column III. The weight of sodium chloride which is equivalent to the weight of silver chloride recorded in column III is shown in column IV. These figures are obtained by multiplying the weight of AgCl by the factor $\frac{NaCl}{AgCl} = \frac{58.47}{143.35} = .4078$. Column V represents the percentage of NaCl, as computed in column IV, in the sample.

Since the results of the above analysis give 99.05 as the percentage of sodium chloride present in the sample, the conclusion is reached that the ether insoluble product is pure sodium chloride, the deviation from 100% being within the limit experimental error.

2. Identification of Ether Soluble Products.

The ether soluble products were identified and will be discussed as follows:

(a). Water soluble product.

(b). Dilute hydrochloric acid soluble product.

(c). Residue.

(a). Identification of water soluble product. Fifteen c.c. of 2 N hydrochloric acid was added to the water solution, obtained by extracting the ether solution of the reaction product as previously described. This solution was then evaporated to a small volume on the electric hot plate and finally to dryness on a water bath. The crystalline product obtained in this manner was recrystallized several times from ethyl alcohol and thoroughly dried. The purified substance possessed the following properties.

1. Colorless
2. Crystalline
3. Soluble in alcohol and water, insoluble in ether
4. M. P. 246 - 248 degrees C.
5. A concentrated aqueous solution treated with a concentrated NaOH solution gave the free amine, a colorless liquid, insoluble in the concentrated NaOH solution, possessing a strong ammoniacal odor, and having a boiling point of 183 degrees C. at 741 m.m. pressure.

The above properties indicated benzyl amine hydrochloride, whose melting point is 246 - 248 degrees C. Therefore benzylamine with a boiling point of 184 degrees C. is the water soluble component of the ether soluble reaction product.

This conclusion was further substantiated as follows. 1. To a portion of the colorless liquid, obtained by treatment with concentrated NaOH was added dilute hydrochloric acid, the hydrochloride thus formed being obtained by crystallization. 2. To another portion of the colorless liquid in ether solution was added carbon disulfide, resulting in a white crystalline precipitate settling out.

The above derivatives were also prepared from pure benzylamine obtained from the Eastman Company. Melting points of these derivatives were now determined as well as mixtures of the derivatives prepared from the colorless liquid obtained in the reaction with those obtained from the pure benzyl amine. The results follow.

Table 2.

Melting Points of Benzylamine and Reaction Product Derivatives.

I. Derivative	II. Unknown M.P.	III. Benzylamine M.P.	IV. Mixture M.P.
Hydrochloride	246° - 248°	247° - 248°	246° - 248°
Dithio-Carbamic acid	127°	127°	127°

Column I indicates the type of derivative. Columns II and III give the melting points of the derivatives shown in Column I. Column IV records the melting points of the half and half mixture of the derivatives whose separate melting points are given in Columns II and III.

The results in Table 2 show that derivatives prepared from the water soluble compound present in the ether soluble reaction products have identical melting points with those prepared from benzylamine, and that mixing the derivatives does not change this melting point. Therefore the conclusion is reached that the water soluble component of the ether soluble reaction products is benzyl amine.

The formation of the above derivatives is illuatrated in the following equations:

$$C_6H_5CH_2NH_2 + HCl \rightarrow C_6H_5CH_2NH_2 \cdot HCl$$

$$2\ C_6H_5CH_2NH_2 + CS_2 \rightarrow \begin{array}{l} \ \ NHCH_2C_6H_5 \\ / \\ C{=}S \\ \backslash \\ \ \ SNH_3CH_2C_6H_5 \end{array}$$

<u>(b). Identification of dilute hydrochloric acid soluble product.</u> The dilute hydrochloric acid extraction solution was evaporated to a small volume on an electric hot plate and then to dryness on a water bath. The substance resulting from this evaporation consisted of crystals and a small amount of resinous material. By recrystallization from ethyl alcohol, pure white needle-like crystals were obtained. The resinous material could not be crystallized and was not investigated further. It may have been the hydrolytic product of an amine hydrochloride.

The crystals had the following properties:

1. Colorless
2. Needle-like crystals
3. Soluble in hot alcohol and water, insoluble in ether
4. M. P. 244 - 246 degrees C.
5. A concentrated solution of the solid when treated with a solution of sodium hydroxide gave a white crystalline precipitate, which, when purified by recrystallization from acetone had a M. P. of 86 degrees C.

The above properties indicated diphenyl ethylene diamine hydrochloride with a melting point of 246 - 248 degrees C. Therefore diphenyl ethylene diamine whose melting point is 90 - 92 degrees C. is the dilute hydrochloric acid soluble component of the ether soluble reaction products.

As further proof, derivatives were made from the free amine as follows. 1. To an aqueous solution of the amine obtained by reaction of concentrated NaOH, a small amount of HCl was added and the hydrochloride obtained by crystallization. 2. To another portion dissolved in ether, CS_2 was added and a white crystalline precipitate of the dithiocarbamic acid separated. 3. To another portion dissolved in ether, a solution of NaOH and benzoyl chloride was added. On separating the ether layer from the aqueous layer, drying over anhydrous sodium sulfate and evaporating the ether, white crystals of the benzoyl derivative were obtained. These crystals were then purified by recrystallization from chloroform. The melting points of all the above derivatives were determined. The following table gives the comparison of the melting points of these derivatives with those on record in the literature.

Table 3.

Melting Points of Diphenyl Ethylene Diamine and Derivatives.

I. Derivative	II. Diphenyl ethylene Diamine M.P.	III. Unknown M.P.
Dihydro-chloride	$246^\circ - 248^\circ$ C. (19)(20)	$245^\circ - 247^\circ$ C.
Dithio-carboxy	132° C. (21)	130° C.
Dibenzoyl	287° C. (22)	$287^\circ - 288^\circ$ C.

Table 3 gives the melting points of the above amine derivatives as listed in Column I. Column II gives the melting points and references of these derivatives as recorder in the literature, while Column III gives the melting points of the derivatives prepared from the reaction product.

The results recorded in Table 3 show remarkable agreement between the melting points of the derivatives prepared from the dilute hydrochloric acid soluble component of the ether soluble reaction products and the melting points of the derivatives of diphenyl ethylene diamine as recorded in the literature. Therefore, the conclusion is reached that the dilute hydrochloric acid component of the ether soluble reaction product is diphenyl ethylene diamine.

As further evidence confirming the identity of diphenylethylene diamine, a complete analysis was made of the hydrochloride with the results of two determinations shown in the following table.

Table 4.

Analysis of Reaction Product.

Diphenyl ethylene Diamine Hydrochloride	%C	%H	%N	%Cl
Computed	58.93	6.36	9.82	24.88
Found Analysis 1.	62.40	6.90	9.76	24.80
Found Analysis 2.	62.08	6.61	9.71	24.74

The equations for the formation of the derivatives prepared are as follows:

$$C_6H_5-\underset{NH_2}{CH}-\underset{NH_2}{CH}-C_6H_5 + 2\ HCl \rightarrow C_6H_5-\underset{\substack{NH_2\\HCl}}{CH} - \underset{\substack{NH_2\\HCl}}{CH}-C_6H_5$$

$$C_6H_5\underset{NH_2}{CH} - \underset{NH_2}{CH}C_6H_5 + CS_2 \rightarrow C_6H_5\underset{NH_2}{CH} - \underset{\substack{NH\\C=S\\SH}}{CH}C_6H_5$$

$$C_6H_5\underset{NH_2}{CH} - \underset{NH_2}{CH}-C_6H_5 + 2\ C_6H_5COCl + 2\ NaOH \rightarrow$$

$$C_6H_5\underset{\substack{NH\\C=O\\C_6H_5}}{CH} - \underset{\substack{NH\\C=O\\C_6H_5}}{CH}C_6H_5 + 2\ NaCl + 2\ H_2O$$

<u>(c). Identification of residue</u>. The ether solution remaining after the water and dilute hydrochloric acid extractions was dried over anhydrous sodium sulfate for 12 hours and the ether carefully evaporated. The substance remaining was a viscous yellow oil with a mild aromatic odor. Various attempts

to produce crystallization and prepare derivatives failed.

The molecular weight of the yellow oil was then determined by the freezing point method, benzene being employed as the solvent. The values 286.8, 275.7, and 279.4 were obtained from three determinations. The substance was analyzed for nitrogen by Kjeldahl determinations, the values found being 1.74 and 1.51%. Since these values would indicate a compound having a molecular weight above 850, it was concluded that the compound was a hydrocarbon and that the nitrogen present was due to a small amount of amine which had not been extracted.

A carbon and hydrogen determination was carried out on two samples, the percentage of carbon found being 91.66 and 91.17 respectively, and the percentage of hydrogen 7.54 and 7.51 respectively.

A search of the literature for hydrocarbons with a molecular weight around that determined for the substance, having a percentage composition as shown in the above analysis, and with a possibility of formation in the reaction, disclosed the fact that α, β, γ triphenyl propane possesses the same properties as did the yellow oil. These properties are compared in the following table.

Table 5.

Comparison of Properties of Residue and

α, β, γ Triphenyl Propane

I. Residue		II. α, β, γ Triphenyl Propane (23)	
1. Molecular weight	280.6	1. Molecular weight	273
2. % C	91.42	2. % C	92.65
% H	7.53	% H	7.35
3. Viscous yellow oil		3. Viscous yellow oil	
4. Mild aromatic odor		4. "not unpleasant odor"	
5. Boils around 350 C. with decomposition and charing		5. Boils above 340 C with decomposition	
6. Refractive index at 20 C.	1.6015	6. Not given	

In Column I are given various properties of the ether soluble residue obtained from the ether soluble reaction product after extraction with water and dilute hydrochloric acid. Similar properties obtained from the literature, of α, β, γ triphenyl propane are listed in Column II.

From the excellent agreement of the above data, the conclusion was reached that the substance remaining in the ether solution after the extraction with water and dilute hydrochloric acid was α, β, γ triphenyl propane, $C_6H_5CH_2\underset{\displaystyle C_6H_5}{\underset{|}{C}}HCH_2C_6H_5$.

On addition of absolute ethyl alcohol to the reaction product, a very small amount of a light yellow substance remained undissolved. This substance was removed by filtration and dried. It appeared non-crystalline and its molecular weight, determined by the freezing point method was above 1000. This material was not further investigated since the amount produced in one reaction was almost negligible.

D.

Quantitative Estimation of Reaction Products

The quantitative estimation of the reaction products will be discussed under two heads, estimation of the ether insoluble product, and estimation of ether soluble products.

1. Quantitative Estimation of Ether Insoluble Product.

It has been proved that the ether insoluble product is pure sodium chloride. Thus the determination of this component consisted in determining the amount of chloride formed in the reaction. This was accomplished by adding a mixture of ether and distilled water to the reaction tube after the liquid ammonia had evaporated and separating the two layers. The ether layer was again washed with distilled water and this wash water added to the previous aqueous layer. Thus the ether soluble materials were efficiently separated from the ether insoluble sodium chloride which was removed quantitatively in the aqueous layer. This aqueous solution of sodium chloride was then diluted to 2 liters in a volumetric flask and three 50 c.c. aliquot portions removed by a 50 c.c. pipette for titration with standard silver nitrate, potassium chromate being used as the indicator. The following table records the results of the analysis.

Table 6.

Determination of NaCl.

I. Reaction Number	II. $C_6H_5CHCl_2$ Grams	III. NaCl Computed	IV. $AgNO_3$ Solution	V. NaCl Found	VI. % NaCl
1.	4.920	3.575	6.00	3.593	100.50
2.	4.402	3.198	5.38	3.222	100.74
3.	3.598	2.614	4.40	2.635	100.79
Average	4.307	3.129	5.26	3.150	100.68

Column I gives the number of the reaction. In Column II is recorded the weight of benzal chloride used in the reaction. Column III gives the weight of sodium chloride that is equivalent to the benzal chloride used. The average number of c.c. of standard $AgNO_3$ solution (1 c.c. $\approx$ .01497 grams NaCl) used in titrating three 50 c.c. aliquot portions of the aqueous NaCl solution obtained from the reaction products is given in Column IV. The figures in Column V give the number of grams of NaCl present in each reaction product as determined by the analysis. These figures were obtained by multiplying the number of c.c. of standard $AgNO_3$ used by the equivalence of the solution and then by 40, the number of 50 c.c. aliquot portions in 2 liters. In Column VI is given the percentage of sodium chloride found to sodium chloride computed from the weight of benzal chloride used.

The close agreement of the theoretical sodium chloride with the sodium chloride found, as shown in Table 6, indicates within the limit of experimental error, that all sodium and chlorine present in the reacting substances, form sodium chloride and it is thus obtained as a reaction product.

2. Quantitative Estimation of Ether Soluble Products.

The method of quantitative estimation of the ether soluble reaction products as identified in the preceeding section consisted in weighing to centigrams, the products obtained by careful evaporation of the acidified water extraction, the dilute hydrochloric acid extraction and the dried ether solution remaining after extraction.

Thus the weight of benzylamine hydrochloride produced from the benzylamine formed in the reaction was determined. Likewise, the diphenyl ethylene diamine hydrochloride produced from the diphenyl ethylene diamine formed in the reaction was determined. The weight of α, β, γ triphenyl propane formed in the reaction was thus determined directly by weighing.

The results and calculations of five reactions are listed in the following table. A detailed description will follow the table.

Table 7.

Analysis of the Ether Soluble Products.

I.	Reaction Number	1.	2.	3.	4.	5.	Ave.
II.	Sodium Grams	1.90	2.08	2.03	2.02	1.98	2.00
III.	Benzal Radical Grams	3.70	4.07	3.96	3.94	3.86	3.91
IV.	Benzylamine Hydrochloride Found Grams	2.03	2.44	2.28	2.22	2.25	2.24
V.	Diphenyl Ethylene Diamine Hydrochloride Found Grams	1.45	.992	1.36	1.13	1.01	1.17
VI.	α, β, γ Triphenyl Propane Found Grams	.831	1.08	1.12	1.06	1.05	1.03
VII.	Benzal Radical as Benzylamine Hydrochloride Grams	1.27	1.53	1.44	1.39	1.44	1.41
VIII.	Benzal Radical as Diphenyl Ethylene Diamine Hydrochloride Grams	.915	.626	.859	.713	.638	.750
IX.	% Benzal Radical as Benzyl Amine Hydrochloride	34.5	37.8	36.4	35.3	37.3	36.3
X.	% Benzal Radical as Diphenyl Ethylene Diamine Hydrochloride	24.7	15.4	21.7	18.1	16.5	19.3
XI.	% Benzal Radical as α, β, γ Triphenyl Propane	22.5	26.6	28.3	26.9	27.2	26.3
XII.	% Accounted for	81.7	79.8	86.4	80.3	81.0	81.9

A description and interpretation of this table is best done by specific example. Therefore, the results of Reaction Number 1. will be described. The number of the reaction is listed in Column I. The weight in grams of the sodium used in this reaction, namely 1.90 grams, is listed in Column II.

It has already been stated that for every gram of sodium used in the reaction there are required 3.5 grams of benzal chloride. In these 3.5 grams of benzal chloride the weight due to the organic group $C_6H_5CH<$ is $\frac{C_6H_5CH}{C_6H_5CHCl_2} \times 3.5 = \frac{90}{160.92} \times 3.5$ $= 1.95$ grams. Therefore for every gram of sodium used in the reaction, 1.95 grams of the group $C_6H_5CH<$ will be set free to enter into the reaction. In Reaction 1., therefore, 1.95×1.90 $= 3.70$ grams of the residue $C_6H_5CH<$ will enter into the reaction. This value is recorded in Column III.

In Column IV is recorded the weight of benzylamine hydrochloride that was actually obtained by evaporation of the water extract of the ether solution of the ether soluble products, 2.03 grams.

Column V records the diphenyl ethylene diamine hydrochloride that was obtained by evaporating the hydrochloric acid extraction. In the example this was 1.45 grams.

In Column VI is given the weight of the α, β, γ triphenylpropane that was recovered from the dried ether solution, namely, .831 grams.

The portion of the $C_6H_5CH<$ that went to form the benzylamine can be computed by multiplying the weight of benzylamine hydrochloride, as determined, by the factor $\frac{C_6H_5CH<}{C_6H_5CH_2NH_2.HCl} =$

$\frac{90}{143.57} = .6272$. The figure 1.27 grams, in Column VII, gives this weight for Reaction 1., and was obtained thus:

$.6272 \times 2.03 = 1.27$ grams

The weight of the $C_6H_5CH<$ residue that formed diphenyl ethylene diamine is obtained by multiplying the weight of diphenyl ethylene diamine hydrochloride found by the factor $\frac{2\ C_6H_5CH<}{\underset{\substack{NH_2\\HCl}}{C_6H_5CH} - \underset{\substack{NH_2\\HCl}}{CHC_6H_5}} =$

$\frac{180}{285} = .6316$ Thus in Reaction 1., $.6316 \times 1.45 = .915$ grams.

The .915 grams recorded in Column VIII therefore gives the weight of $C_6H_5CH<$ that went into the formation of diphenyl ethylene diamine. Since the weight of α, β, γ triphenyl propane, as recorded in Column VI, differed from the weight of the $C_6H_5CH<$, going to form it, by only 2 parts in 273, or $\frac{2\ H}{C_6H_5CH_2\underset{C_6H_5}{CH}CH_2C_6H_5}$, the difference was not computed as the error introduced does not exceed the accuracy of the method employed.

The percentage of the theoretical $C_6H_5CH<$ shown in Column III, that forms benzylamine, is shown in Column IX. This was computed by dividing the value in Column VII by the value in Column III and multiplying by 100. For Reaction 1., $\frac{1.27}{3.70} \times 100 =$ 34.5% Columns X and XI record the percentage of $C_6H_5CH<$ going to form diphenyl ethylene diamine and α, β, γ triphenyl propane respectively and are computed as was the benzylamine. For the example, the values are 24.7% and 22.5%. Column XII gives the total percentage of the $C_6H_5CH<$ which is accounted for by the formation of benzylamine, diphenyl ethylene diamine, and

α, β, γ triphenyl propane. In Reaction 1. the total $C_6H_5CH<$ accounted for in the formation of the above compounds was 81.7% of the theoretical $C_6H_5CH<$ as listed in Column III.

In the last horizontal line in the table is given the average value for each column and is listed in Column I as Average. These values may then be considered a summary of the quantitative estimation of the ether soluble reaction products.

The fact that approximately 20% of the $C_6H_5CH<$ cannot be accounted for by analysis is largely due to loss in extraction. A considerable amount of product is lost in this method of separation.

V.

STUDY OF THE INTERMEDIATE COMPOUND.

In the introduction of this thesis, various type equations were developed which were to serve as a basis of classification for the reaction of the dihalides of the class $RCHX_2$ with sodium in liquid ammonia solution. Several of the type equations depended on the formation of intermediate sodium organo compounds. Therefore, since there was every indication that an intermediate compound was formed in the reaction of benzal chloride and sodium in liquid ammonia, as will be shown later, a study of this intermediate compound formation was necessary to classify this reaction. This study will be divided into three parts, preparation, nature of the intermediate compound and identification of this compound.

A.

Preparation.

In the description of the reaction as it takes place, as given under Procedure, it was noted that the appearance of a bright red coloration occurred shortly after the addition of benzal chloride was started. It was also noted that the intensity of this red coloration increased until 80% of the benzal chloride had been added. At this point, the last indication of the characteristic opaque blue color of the free sodium in solution disappeared, and the solution became transparent.

Since the disappearance of the characteristic opaque blue color of metallic sodium in liquid ammonia indicates the absence of free sodium in solution and since only 80% of the theoretical benzal chloride necessary to furnish chlorine for the formation of sodium chloride, has been added, it is logical to assume that a sodium organo-compound has been formed by combination of the sodium and the organic residue, $C_6H_5CH<$. This assumption is further substantiated by the bright red color of the solution at this point, this color being characteristic of sodium organo-compounds [(24), (25)].

The red end point was not distinct unless small amounts of sodium were employed in the reaction. This red end point could not be determined accurately in reactions even when only two grams of sodium were used, the heavy precipitate formed rendering the end point indistinct. Therefore to determine this red end point accurately and thus determine the ratio of benzal chloride to sodium, dilute solutions of sodium were employed which gave sharp end points. The table which follows gives the results of these end point determinations.

Table 7.

Molar Ratio at Red End Point.

I. Reaction Number	II. Sodium Grams	III. Theoretical $C_6H_5CHCl_2$	IV. $C_6H_5CHCl_2$ at red end point Grams	V. $C_6H_5CHCl_2$ at red end point Grams	VII. Molar Ratio of $C_6H_5CHCl_2$ to sodium at red end point
1.	.1380	.392	.31	79.49	4 : 5
2.	.3360	.956	.76	79.50	4 : 5
3.	.3110	.885	.71	80.23	4 : 5
Average	.2617	.744	.59	79.74	4 : 5

Column I lists the number of the reaction. In Column II is recorded the weight of sodium used in the reaction. Column III records the number of c.c. computed from the weight of sodium used which would be necessary for a complete reaction of one mol of benzal chloride to two mols of sodium. The number of c.c. of benzal chloride necessary to reach the red end point in each reaction is shown in Column IV. In Column V appears the percentage of the theoretical benzal chloride, necessary for the complete reaction, that was used to produce the red end point. The molar ratio of benzal chloride to the sodium for formation of the red compound is shown in Column VI. The last horizontal line gives the average values for the three reactions.

From the results of the above determinations the conclusion was reached that, within the limits of experimental error, the molar ratio of benzal chloride to sodium for formation of the intermediate sodium organo-derivative was 4 to 5. This ratio was then applied in carrying out the reaction with larger amounts of sodium.

B.

Nature of Intermediate Compound.

The intermediate compound is soluble in liquid ammonia, the solution being bright red in color. In liquid ammonia solution, it reacts with benzyl chloride, exhibiting a sharp color change to white when the benzyl chloride is added in a ratio of one mol to one mol to the sodium in the sodium organo-compound, namely 20% of the weight used in the reaction.

When the liquid ammonia is allowed to evaporate after 80% of the theoretical benzal chloride has been added, a dark purple red residue remains. This dark colored residue immediately becomes decolorized on exposure to air or moisture. When anhydrous ether is added to the residue with careful exclusion of air, a deep red solution is formed, thus indicating solubility of the intermediate compound in ether. On exposure to air, this red solution immediately changes to a light yellow. An ether insoluble product is present and when removed by filtration, washed thoroughly with ether and dried, has a decided pink color. The examination of this pink product will be discussed later.

In order to postulate the identity of this sodium organo-compound, it is necessary to consider the groups available for reaction. As the benzal chloride is added to the sodium solution, the sodium removes the chlorine atoms with the formation of sodium chloride and the $C_6H_5CH<$ group is thus available. There also exists in the solution, Na^+ ions, and the solvent NH_3. The following equations represent possible reactions that may occur.

I. $C_6H_5CH\langle + 2\ Na \rightarrow C_6H_5CH\langle^{Na}_{Na}$

II. $4\ C_6H_5CH\langle + 2\ Na + 2\ NH_3 \rightarrow 2\ C_6H_5CH\langle^{Na}_{H}$

$+\ C_6H_5\underset{NH_2}{C}H - \underset{NH_2}{C}HC_6H_5$

III. $2\ C_6H_5CH\langle + 2\ Na \rightarrow C_6H_5\underset{Na}{C}H - \underset{Na}{C}HC_6H_5$

Since no compounds have ever been prepared containing the two strongly electropositive sodium atoms attached to the same carbon atom, reaction listed as Equation I is not probable.

The sodium compounds listed as products in Equations II and III have been prepared by Schlenk and his co-workers, and their properties studied [25]. Both compounds react with water forming sodium hydroxide. Both react with alkyl halides with the formation of the sodium halide. When sodium benzyl reacts with an alkyl halide, it does so according to the following equation.

(A) $C_6H_5CH_2Na + RX \rightarrow NaX + C_6H_5CH_2R$ [24] [25]

The reaction of disodium stilbene with alkyl halides is peculiar in that two hydrocarbons are formed as shown by the following equation:

(B) $C_6H_5\underset{Na}{C}H - \underset{Na}{C}HC_6H_5 + 2\ RX \rightarrow C_6H_5CH{=}CHC_6H_5 + R{-}R + 2\ NaX$

These reactions and properties of known sodium organo-compounds were of value in determining the identity of the intermediate compound.

C.

Identification of Intermediate Compound.

The identification of the intermediate compound was accomplished by a study and analysis of the ether insoluble pink reaction product and a study of the reaction of the red intermediate with benzyl chloride.

1. Analysis of Ether Insoluble Reaction Product.

It has been mentioned previously that an ether insoluble product was formed when the liquid ammonia solvent was allowed to evaporate after 80% of the theoretical quantity of benzal chloride had been added. This compound was separated by extracting the reaction product with ether, thus removing the ether soluble products of the reaction. After complete washing with ether this product was dried in air. When wet with ether, this compound was a deep rose color and when dry was pink. Since it was logical to assume that the sodium chloride that was formed in the reaction would be present in this ether insoluble product, it was concluded that this pink substance consisted of sodium chloride crystals in which some of the red intermediate compound had been mechanically enclosed.

Therefore, if the above conclusion is correct, the weight of the sodium chloride present plus the weight of the intermediate compound should be equal to the weight of the pink compound obtained in the reaction. The weight of sodium chloride could be determined by titration of a solution of a sample of the pink compound with standard silver nitrate. Since a sodium organo-compound reacts with water to form sodium hydroxide, the weight of sodium hydroxide formed in a solution of the sample could be determined by titration with standard acid and from this the weight of the sodium organo-compound computed. In the table following are given the results of such an analysis of the pink substance from three different reactions, and a comparison of the sum of the weights of sodium chloride and sodium organo-compound, computed as $(C_6H_5CHNa)_x$, with the weight of sample.

Table 8.

Analysis of Ether Insoluble Product.

I. Sample Number	II. Product Grams	III. $AgNO_3$ Solution c.c.	IV. NaCl Grams	V. Acid c.c.	VI. $(C_6H_5CHNa)_x$ Grams	VII. NaCl and $(C_6H_5CHNa)_x$ Grams	VIII. Variation from Sample Grams	IX. Variation %
1A	.7950	36.65	.5486	42.50	.2423	.7909	.0041	0.515
1B	.4166	19.50	.2919	21.80	.1243	.4162	.0004	0.096
2A	.3592	20.00	.2994	9.50	.0542	.3536	.0056	1.559
3A	.6287	26.50	.3967	40.10	.2286	.6253	.0034	0.504
3B	.5246	22.00	.3293	34.20	.1950	.5243	.0003	0.057
Ave.	.5448					.5421	.0027	0.495

In Column I is shown the sample number. This number also shows the reaction from which the sample is taken. Thus in samples 1A and 1B the figures indicate the reaction and the letters indicate separate samples from the same reaction. Column II is a record of the weight of the samples analyzed in grams. The volume in c.c. of standard silver nitrate (1 c.c.$\approx$ .01497 grams NaCl) necessary to precipitate the chloride as silver chloride, potassium chromate being used as the indicator, is shown in Column III. The weights of sodium chloride in grams, which are equivalent to the standard silver nitrate used, are shown in Column IV. Column V records the number of c.c. of standard sulfuric acid (1 c.c.$\approx$.005701 grams $(C_6H_5CHNa)_x$) necessary to neutralize the sodium hydroxide formed in the solution of the sample, methyl orange being used as the indicator. In Column VI is shown the number of grams of the compound $(C_6H_5CHNa)_x$ which is equivalent to the weight of sodium hydroxide as determined in the acid titration. The weight thus determined is independent of the value of x, within the limit of experimental error, thus representing either sodium benzyl or disodium stilbene. In Column VII is recorded the sum of the weights, in grams, of the sodium chloride and $(C_6H_5CHNa)_x$ as determined by the analysis. In Columns VIII and IX are shown the deviation of this sum shown in Column VII from the weight of sample taken, shown in Column II, in grams and percentage respectively.

Thus, the remarkable agreement shown between the sum of the sodium chloride plus the computed weight of $(C_6H_5CHNa)_x$ gives strong support to the assumption that the pink product consisted of sodium chloride in which was mechanically enclosed the red intermediate compound, and that this red compound could be disodium stilbene or sodium benzyl.

2. Reaction of Benzyl Chloride with Intermediate Compound.

It was decided to study the intermediate compound by the preparation of derivatives using benzyl chloride as the organic halide. Benzyl chloride was chosen for the following reasons:

1. The addition to the reaction tube could be made conveniently from the buret.
2. The reaction of the benzyl chloride took place readily with the intermediate compound, a distinct end point occurring when the theoretical amount had been added.
3. The products of the reaction should be ctystalline solids.

This reaction will be studied under two heads, procedure and identification of products.

(a). Procedure. In carrying out the reaction of benzyl chloride with the intermediate compound, the procedure followed up to the red end point where 80% of the theoretical benzal chloride had been added, was identical with that followed in carrying out the complete reaction. At this point the buret containing the benzal chloride was removed, emptied, washed with alcohol and ether, dried, and refilled with benzyl chloride. The buret was then replaced in the apparatus and the theoretical quantity of benzyl chloride was added. The liquid ammonia solvent was then allowed to evaporate and the product extracted with anhydrous ether. The ether was then evaporated from the solution. On cooling, crystals separated, mixed with a viscous yellow oil.

The crystals were separated from the yellow oil as completely as possible by suction filtration. After crystallization several times from ethyl alcohol the crystals were obtained as glistening white plates. The above crystallization was carried out from concentrated solutions and the crystals obtained consisted of all the crystalline substances formed in the reaction.

Fractional crystalization was then employed in an endeavor to separate crystals of two different substances if present in the purified crystals from the reaction. Dilute ethyl alcohol solutions were now used instead of concentrated and the first, second, and third crops of crystals carefully separated. After a number of separations of this type, two distinct crystalline compounds were isolated.

(b). Identification of products. The first crop of crystals which were obtained in the fractional crystallization melted sharply at 123 degrees C. When boiled with acid potassium permanganate solution, benzaldehyde was formed, recognized by its characteristic odor. A solution of these crystals in carbon tetrachloride, to which bromine had been added, when boiled and cooled, deposited white crystals that melted at 236 degrees C.

The properties of this crystalline reaction product as described above are identical with stilbene whose melting point is 124 degrees C. The bromine derivative which was prepared was stilbene dibromide whose melting point is 237 degrees C. A melting point of a mixture of equal parts of the crystals obtained in the reaction with the crystals of pure stilbene secured from the Eastman Company was determined as 123 degrees C., thus completing the identification of the compound as stilbene.

The other crystalline compound obtained in the fractional crystallization possessed a sharp melting point of 52 degrees C. This compound mixed with an equal amount of dibenzyl which also has a melting point of 52 degrees C. showed no change in melting point, the mixture also melting sharply at 52 degrees C. Thus, this compound was identified as dibenzyl.

The identification of stilbene and dibenzyl in this reaction leads to the conclusion that the intermediate compound is disodium stilbene, $C_6H_5\underset{Na}{C}H - \underset{Na}{C}HC_6H_5$, as the reaction of this compound with benzyl chloride would take place according to the equation (B) in the following manner:

$$C_6H_5\underset{Na}{C}H - \underset{Na}{C}HC_6H_5 + 2\ C_6H_5CH_2Cl \rightarrow \begin{array}{l} C_6H_5CH{=}CHC_6H_5 \\ C_6H_5CH_2CH_2C_6H_5 + 2\ NaCl \end{array}$$

<u>3. Conclusions.</u>

From the general properties exhibited by the intermediate compound formed in the reduction of benzal chloride with sodium in liquid ammonia solution, a sodium organo-compound is indicated. The results obtained by the analysis of this compound, mechanically enclosed in the sodium chloride crystals formed in the reaction, limited the identification to compounds having the formula $(C_6H_5CHNa)_x$. Further study in which the reaction of benzyl chloride with the compound was carried out, showed characteristic properties of disodium stilbene and thus x = 2.

VI.

Summary of Experimental Results

The facts derived from the experimental results of this investigation lead to the following general conclusions:

1. Benzal chloride reacts with sodium in liquid ammonia solution in the ratio of one mol of the chloride to two mols of sodium.

2. Sodium Chloride is formed in the reaction in the amount equivalent to the weight of sodium used in the reaction.

3. Benzylamine is a major reaction product and is formed to the extent of approximately 35% of the organic group $C_6H_5CH<$ added, as determined in the experimental estimation.

4. Diphenyl ethylene diamine is a major reaction product and is formed to the extent of approximately 20% of the organic group $C_6H_5CH<$ added.

5. α, β, γ triphenyl propane is a major reaction product and is formed to the extent of approximately 26% of the organic group $C_6H_5CH<$ added.

6. Strong evidence has been presented to show that disodium stilbene is formed as an intermediate compound in the reaction

and that when the molar ratio of benzal chloride to sodium is 4 to 5, all the sodium that had not formed sodium chloride is combined with the organic residue.

7. The approximate 20% loss of the organic group $C_6H_5CH<$ as determined in the experimental procedure, was due to loss of material during separation of the individual components of the reaction mixture.

VII.

MECHANISM OF THE REACTION AND FORMULATION OF EQUATIONS

The investigation has shown that the products, sodium chloride, benzylamine, diphenyl ethylene diamine, and α, β, γ triphenyl propane are formed when sodium in liquid ammonia reacts on benzal chloride in the molar ratio of 2 to 1. It has also shown that an intermediate atage occurs in the reaction in which disodium stilbene is formed as an intermediate product.

If this reaction is compared qualitatively to the type reactions which were presented in the introduction, it is found to fall under type XIII, which follows:

$$6\ RCHX_2 + 12\ Na + 3\ NH_3 \rightarrow \underset{NH_2}{RCH} - \underset{NH_2}{CHR} + RCH_2\underset{R}{C}HCH_2R$$

$$+ RCH_2NH_2 + 12\ NaX$$

Type XIII is the completed reaction of the intermediate stage represented by type equation VII:

$$2\ RCHX_2 + 6\ Na \rightarrow \underset{Na}{RCH} - \underset{Na}{CHR} + 4\ NaX$$

If the stoiciometrical relations of type XIII are compared to the quantitative estimation of reaction products as shown in the experimental results (page 47), it is found that the two do not agree. This comparison may be shown as follows.

Table 9.

Comparison of Stoiciometrical Relations.

Percentage of Original $C_6H_5CH<$

	I. Benzylamine	II. Diphenyl Ethylene Diamine	III. α,β,γ Tri-Phenyl Propane	IV. Total
Type equation XIV	16.67%	33.33%	50%	100%
Experimental Determination	36.3%	19.3%	26.3%	81.9%

From the results of this comparison, the conclusion is reached that the reaction of benzal chloride and sodium in liquid ammonia does not permit classification under type equation XIII. It is also concluded that the reaction must take place in more than one way and must therefore be compared to a combination of types.

When the benzal chloride is added to the sodium solution it was noted that the characteristic red color of the disodium stilbene appeared almost immediately. This indicates that the reaction is taking place, at least partly, according to type equation VII. It is, nevertheless, logical to think that another reaction is occurring simultaneously, probably according to type equation I or II with formation of stilbene or benzylamine respectively. The results of the analysis of the reaction product lead to the conclusion that type II is representative of that action as follows:

$$RCHX_2 + 2Na + NH_3 \rightarrow RCH_2NH_2 + 2\ NaX$$

Therefore types II and VII may be combined in the following way to represent the first stage of the reaction between benzal chloride and sodium in liquid ammonia.

$$6\ C_6H_5CHCl_2 + 16\ Na + 2\ NH_3 \rightarrow 2\ C_6H_5\underset{Na}{C}H-\underset{Na}{C}HC_6H_5$$

$$+ 2\ C_6H_5CH_2NH_2 + 12\ NaCl$$

In the second step of the reaction, the two molecules of the disodium stilbene formed, can then be assumed to react as in type equation XIII as follows:

$$2\ C_6H_5\underset{Na}{C}H-\underset{Na}{C}HC_6H_5 + 2\ C_6H_5Cl_2 \rightarrow 2\ C_6H_5\dot{C}H\dot{C}HC_6H_5 \quad 2\ C_6H_5CH< \quad + 4\ NaCl \qquad (a)$$

$$2\ C_6H_5\dot{C}H\dot{C}HC_6H_5 + 2\ C_6H_5CH< + 3\ NH_3 \rightarrow C_6H_5\underset{NH_2}{C}H - \underset{NH_2}{C}HC_6H_5$$

$$+ C_6H_5CH_2\underset{C_6H_5}{C}HCH_2C_6H_5 + C_6H_5CH_2NH_2 \qquad (b)$$

The summation of the first and second stages of the reaction give the following equation as representing the completed reaction:

$$8\ C_6H_5CHCl_2 + 16\ Na + 5\ NH_3 \rightarrow 3\ C_6H_5CH_2NH_2 + C_6H_5\underset{NH_2}{CH} - \underset{NH_2}{CH}C_6H_5$$

$$+\ C_6H_5CH_2\underset{C_6H_5}{CH}CH_2C_6H_5 + 16\ NaCl$$

If the stoiciometrical relations are now examined, they are found to compare favorably as may be seen in the following table.

Table 10.

Comparison of Stoiciometrical Relations.

Percentage of Original $C_6H_5CH<$ Group Present in

	I. Benzylamine	II. Diphenyl Ethylene Diamine	III. α,β,γ Tri-Phenyl Propane	IV. Total
Equations as Presented Combination of II and XIV	37.5%	25%	37.5%	100%
Experimental Determination	36.3%	19.3%	26.3%	81.9%
Percent Deviation	3.2%	22.8%	29.9%	18.1%

The distribution of the 18.1% loss in the quantitative estimation of the reaction products is very logical in this study of the stoiciometrical relationships. In the experimental procedure of separation of these products by extraction, the benzyl amine was first obtained with little opportunity for loss. The estimation of the diphenyl ethylene diamine was subject to greater error in the extraction due to loss during the extraction of the benzylamine. Likewise the

α, β, γ triphenyl propane was subject to the greatest loss during the extraction. These facts are logical reasons for the increasing deviation from the theoretical percentages as noted in the stoiciometrical comparison. From the evidence presented, the reducing action of sodium in liquid ammonia on benzal chloride can be classified under the type reactions II, VII, and XIII.

VIII.

SUMMARY.

1. Type reactions have been developed for dihalogen derivatives of aliphatic hydrocarbons in which the two halogen atoms are attached to the same carbon atom in the α position.

2. A mechanism for the reducing action of sodium in liquid ammonia on benzal chloride has been presented, based on experimental investigation of this reaction.

IX.

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