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May 14 1941

I hereby recommend that the thesis prepared under my supervision by Leonard Edward Edelman

entitled Reduction of Organic Halides in Liquid Ammonia Solution.

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

Approved by:

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REDUCTION OF ORGANIC HALIDES IN LIQUID AMMONIA SOLUTION

A dissertation submitted to the

Graduate School

of the University of Cincinnati

in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

Leonard Edward Edelman

A.B. Hobart College 1936

A.M. University of Cincinnati 1939

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Introduction and Historical Background

Liquid ammonia, as a reaction medium, affords several advantages over other solvents. While its power to dissolve inorganic compounds is not as great as that of water, its degree of ionization is less. This lesser degree of ionization results in a lesser tendency to enter into reactions with the dissolved substances. In addition, liquid ammonia dissolves a great many organic substances for which, ordinarily, organic solvents would be employed. This diversified solvent power make it possible to carry out many reactions in a homogeneous phase. Consequently the reactions are more rapid, and may be studied quantitatively more easily than they could if they were heterogeneous. In homogeneous reactions the questions of the completeness of the reaction, possible catalysis, surface phenomena, and others are either obviated or minimized. The scope of ammonia's solvent power is extended even to metallic elements, notably the alkali and alkaline earth metals.

The solubility data for lithium, sodium, potassium and calcium are given in Table I.

Table I [1]

Metal	Temperature °C.	Grams of metal per 100 g. NH_3	Moles of NH_3 per gram-atom of metal
Lithium	- 34.4	11.3	3.61
Sodium	- 33.0	24.7	5.48
Potassium	- 33.0	46.5	4.95
Calcium	- 33.0	33.6	7.00

Rubidium, cesium, strontium, barium and magnesium are also soluble but to a less extent.

For some time a controversy was waged as to the nature of the solutions of the metals in liquid ammonia. Seely [2] first suggested that they were solutions of the metals while Joannis [3], Weyl [4] and others believed that they were solutions of the so-called "metal-ammoniums" to which they assigned the formulas $Na-NH_3$, $K-NH_3$, etc. Kraus [5], by applying the phase rule to available vapor pressure data of these solutions, showed that the suggestion of Seely was correct. Kraus [6] further postulated that the metals ionize in solution into positive and negative carriers:

$$1)\quad M \longrightarrow M^+ + e^-.$$

The positive carrier is identical with that formed by the solution of a salt of the particular metal in water, while the negative carrier is an electron which, in dilute solutions, is solvated by the ammonia:

$$2)\quad e^- + x\ NH_3 \longrightarrow e^-(NH_3)_x$$

The blue color characteristic of all these solutions is attributed to the equilibrium represented in equation 1).

Such a solution, containing free electrons, should be an excellent reducing medium, and as such has been used for the reduction of many and varied organic and inorganic compounds. The earliest work with organic halides was performed by Lebeau [7] and Chabley [8] working independently. Chabley investigated the reactions of carbon tetrachloride, chloroform, iodoform, and methyl chloride with sodium, while Lebeau used the lower alkyl monohalides. The former obtained a mixture of products, notably sodium halide, saturated and unsaturated hydrocarbons along with small amounts of sodium cyanide, hydrogen and nitrogen. Lebeau obtained the hydrocarbon and amine corresponding to the halide used. For example with propyl iodide he obtained propyl amine and propane. Their mechanism for the reactions, unfortunately, was based on the primary formation of sodium-ammonium.

An important result of the work of Lebeau and Chabley was the observation that the sodium always quantitatively removes halogens from the organic compound. This lead to the formulation of a quantitative method of determining halogens in organic compounds. The procedure was further developed by Dains [9], Vaughn [5], Brewster and Clifford [11].

Excellent summaries of the work of the above mentioned investigations and others on paraffin halides and polyhalides are given in a review by Fernelius and Watt in Chemical

Reviews[12]. The major portion of the summarized work, as well as the work with phenyl substituted alkyl halides and polyhalides, was not carried out quantitatively and all by-products were not identified. The investigation to date on the phenyl halogen derivatives are given in Table II[12].

Table II

Halide	Metal	Products	Reference
ϕ-CH_2-Cl	Na	Bibenzyl, toluene, etc.	14, 15, 18, 19.
ϕ-CH_2-Br	Na, K	Bibenzyl	20
ϕ_3-C-Cl	Na,K,Ca	ϕ_3-C-Na, ϕ_3-C-K. With Ca, an unstable reddish compd.	22
ϕ-CH-Cl_2	Na	Bibenzyl, benzylamine.	13, 18.
ϕ_2-C-Cl_2	Na	ϕ_2-C=C=ϕ_2 (90 %)	18
ϕ_2-CH-Cl	Na	ϕ_2-CH-CH-ϕ_2----65.6 % ϕ_2-CH_2---------27.6%	18
ϕ-C=Cl_3	Na	Bibenzyl, nitrogenous substances.	18
ϕ-(CH_2)-Br	Na	ϕ-C_2H_5 (38.3%) Styrene (1.3%)	16, 18.
ϕ_3-C-CH_2-Cl	Na	ϕ_2-C(Na)-CH_2-ϕ	21, 23.
ϕ-(CH_2)$_3$-Br	Na	ϕ-C_3H_7 (28.2%) ϕ-(CH_2)$_3$-NH_2 (17.9%)	19
ϕ-(CH_2)$_4$-Br	Na	ϕ-C_4H_9 (43.1%) ϕ-(CH_2)$_4$-NH_2 (16.5%) Unsaturates.	19

With a view to obtaining more quantitative information and to postulate a mechanism for the reactions, a study of the reduction of several organic halides was undertaken by

Burgess and co-workers[13,14,15,16]. The phenyl substituted halides were selected since the products were apt to be either solids or liquids. The reactions of benzyl chloride[14,15], benzal chloride[13] and phenyl ethyl bromide[16] have been studied in some detail.

Benzyl chloride has been reduced using both sodium and potassium; the products and yields are shown in Table III.

Table III

Products	Percentage yields	
	Na	K
Bibenzyl	70.62 %	87.3 %
Toluene	8.78	4.1
1,2,3-Triphenyl Propane	10.93	2.3
Benzyl amine	0.27	-----
Higher hydrocarbons	3.35	2.5
Totals	93.95%	96.2%

These reactions in contrast to earlier work on these compounds were carried out with precautions to exclude both air and moisture.

With benzal chloride the main products were benzyl amine, 1,2,3-triphenyl propane, and symmetrical diphenylethylenediamine in yields of 36.3%, 26.3%, and 19.3% respectively.

Styrene and phenylethane were the main products of the reaction between phenyl ethyl bromide and sodium. The yield of styrene was 40% and of phenyl ethane 30%. A hydrocarbon

of molecular weight 200 was also obtained. Styrene is known to polymerize in the presence of sodium in liquid ammonia (17) and the aforementioned unidentified hydrocarbon may be some such polymer.

The reactions described above show that there are several diverse types of reactions of the organic halides and metals in liquid ammonia depending both upon the type of organic radical and upon the metal used. In general, hydrocarbons and amines are formed. Saturated hydrocarbons corresponding to the halides used, unsaturated hydrocarbons which may be regarded as having been formed by the removal of HX from the organic halide, dimers formed by the Wurtz-Fittig type coupling of organic radical (saturated or unsaturated) and higher hydrocarbons are among the type of hydrocarbons to be expected. The amines may be primary, secondary, or tertiary and in some cases polyamines are formed.

An observation important in the establishment of a mechanism for the reactions of metals and organic halides in liquid ammonia, was the change of the blue color of the metal solution to red. This red end-point was observed when benzyl chloride, benzal chloride, and phenyl ethyl bromide were used. The nature of the compound causing this red color was further investigated in the case of benzyl chloride (14) and was shown to be sodium benzylide. This along with other experimental evidence to be cited later indicates that the first step in these reactions is the formation of an organo-alkali compound:

$$R\,X + 2\,M \longrightarrow R\text{-}M + M\,X$$

The next step in the reaction depends upon the stability and reactivity of these intermediates. To facilitate this discussion, a rough division of the organo-alkali compounds into three classes made by Zieglar and his co-workers[24] is given:

I. The very highly reactive, colorless simple alkyl M and aryl M types which are highly polar and insoluble in organic solvents.

II. The colored $R\text{-}CH_2\text{-}M$ types which have the metal attached to a carbon in direct union with aromatic rings or systems of double bonds. These are electrolytic conductors in many organic solvents, particularly in diethyl zinc which itself is non-conducting.

III. Numerous organo-lithium compounds which are colorless liquids or fusible solids, soluble in organic solvents, poor conductors and generally only slightly polar.

Examples of compounds that would give rise to organo-alkali compounds of Class I are propyl iodide and hexyl bromide. The reactions of each with sodium in liquid ammonia have been studied[7,25]. The products in each case are the corresponding hydrocarbon and the dimer. The mechanism is shown in the following equations:

1) $R\,X + 2\,Na \longrightarrow R\,Na + Na\,X$

2) $R\,Na + NH_3 \longrightarrow R\,H + NaNH_2$

3) $R\,Na + R\,X \longrightarrow R\,R + Na\,X$

While in the earlier work with alkyl halides, amines were formed, it has been shown[25] that these amines are formed after the above reactions occur and not concomitantly as was indicated in the usual mechanism. Any amines and unsaturated hydrocarbons arise from the reaction of the sodium amide formed, according to equation 2). This action of sodium amide is presented in equations 4) and 5).

4) $R\text{-}CH_2\text{-}CH_2\text{-}X + NaNH_2 \longrightarrow R\text{-}CH{=}CH_2 + Na\,X + NH_3$

5) $R\,X + NaNH_2 \longrightarrow R\text{-}NH_2 + Na\,X$

Equation 4) may be likened to the action of sodium hydroxide in alcoholic solution on alkyl halides to produce unsaturated hydrocarbons. Similar reactions have been obtained in liquid ammonia when pure sodium amide has been used. The amount of unsaturates obtained depends upon the length of the carbon chain and the halogen involved[26]. This conclusion can be drawn from a consideration of Table IV.

Table IV

Compound	% Unsaturates
$CH_3\text{-}CH_2\text{-}I$	5.4 %
$CH_3\text{-}CH_2\text{-}CH_2\text{-}I$	37.0
$CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$	69.6
$(CH_3)_2\text{-}CH\text{-}CH_2\text{-}I$	62.4
$(CH_3)_2\text{-}CH\text{-}CH_2\text{-}Cl$	83.6

Benzyl chloride, benzal chloride, and phenylethyl bromide give rise to organo-alkali compounds of Class II.. As has been

previously stated the formation of sodium benzylide has been demonstrated in liquid ammonia solution. It is red and the sodium is attached to a carbon directly hooked to an aromatic as befits members of this class.

6) $C_6H_5-CH_2-Cl + 2\ Na \longrightarrow C_6H_5-CH_2-Na + NaCl$

This compound is capable of at least transitory existence and the next step is the same as equation 2) above.

7) $\phi-CH_2-Na + \phi-CH_2-Cl \longrightarrow \phi-CH_2-CH_2-\phi + NaCl$

The subsequent steps are explained on the basis of the polarity of the organo-alkalis of this class. The sodium benzylide dissociates into benzyl radical and sodium:

8) $C_6H_5-CH_2-Na \longrightarrow C_6H_5-CH_2- + Na$

The other products can now be accounted for by the disproportionation of these free radicals, a theory first promulgated by Späth (27) to account for the complex hydrocarbons formed in the Grignard reaction.

Späth observed that, in the coupling action of the Grignard reagent, when two different R groups were used, dimers of each R group was formed

9-a) $R-MgX + R'X' \longrightarrow R + R' + MgX'X$

That is, in equation 9-a) two R radicals and two R' radicals could couple to form R-R and R'-R' respectively, as well as the compound R'-R which is the normally expected product. Moreover, the free alkyl groups could undergo other reactions, as a result of disproportionation. This disproportionation is, in effect, the transfer of a hydrogen atom from one radical

to the other. As a result one of the radicals is more saturated and the other less saturated. These new radicals thus formed, can undergo coupling with other radicals to form a wide variety of products. The equations for such reactions are 9-a), 9-b), 9-c), and 9-d).

9-b) $R + R' \longrightarrow R_{+H} + R_{-H}$

9-c) $R + R \longrightarrow R_{+H} + R_{-H}$

9-d) $R_{-H} + R' + R \longrightarrow R'\text{-}R_{-H}\text{-}R$

As experimental basis for the above free radical explanation he cites reactions of benzyl chloride with methyl magnesium bromide and on ethyl magnesium bromide. In the case of methyl magnesium bromide he obtained a hydrocarbon to which he assigned the formula of 1,2,3-triphenyl propane, which is formed according to the following equations:

9-e) $2\ \text{Ø-CH}_2\text{-} \longrightarrow \text{Ø-CH}_3 + \text{Ø-CH=}$

9-f) $\text{Ø-CH=} + 2\ \text{Ø-CH}_2\text{-} \longrightarrow \text{Ø-CH}_2\text{-}\underset{\text{Ø}}{\text{CH}}\text{-CH}_2\text{-Ø}$

With ethyl magnesium iodide he obtained this same hydrocarbon as well as 1,2-diphenyl butane.

9-g) $\text{Ø-CH=} + \text{C}_2\text{H}_5\text{-} + \text{C}_6\text{H}_5\text{-} \longrightarrow \text{Ø-}\underset{\text{C}_2\text{H}_5}{\text{CH}}\text{-CH}_2\text{-C}_6\text{H}_5$

The type of disproportionation represented in the equation of Späth is lateral rather than nuclear, i.e., the radicals combine to form chain compounds rather than by substitution in the aromatic ring. This, however, is not always the case. As just mentioned Späth thought he had prepared 1,2,3-triphenyl propane in the reaction of benzyl chloride upon

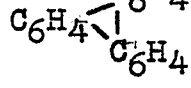
methyl magnesium iodide. However, Fuson[28] showed that this compound was p-benzyl dibenzyl, indicating nuclear rather than lateral disproportionation had occurred.

This theory of disproportionation of free radicals has been applied with success to other reactions of Grignard compounds by other investigators[29,30]. More closely allied to the work of this thesis is the Wurtz-Fittig reaction. Bachman and Clarke[31] and others[32,33] have applied the Späth theory to the problem of side reactions in the Wurtz-Fittig synthesis. Bachman and Clarke particularly studied the reactions of chlorobenzene and heptyl bromide. The equations for these are given since the reaction of chlorobenzene illustrates nuclear disproportionation and that of heptyl bromide illustrates the formation of an unsaturated hydrocarbon and lateral disproportionation:

10-a) $C_6H_5\text{-}Cl + 2\ Na \longrightarrow C_6H_5\text{-}Na + NaCl$

10-b) $C_6H_5\text{-}Na + C_6H_5\text{-}Cl \longrightarrow C_6H_5\text{-}C_6H_5 + NaCl$

10-c) $2\ C_6H_5\text{-} \longrightarrow C_6H_6 + C_6H_4=$

10-d) $3\ C_6H_4= \longrightarrow$ 

10-e) $C_6H_4= + 2\ C_6H_5\text{-} \longrightarrow C_6H_5\text{-}C_6H_4\text{-}C_6H_5$

Triphenylene formed in equation 10-d) and diphenyl benzene formed in equation 10-e) were both isolated products.

In the reaction of heptyl bromide and sodium in benzene the products are tetradecane, heptylene, and heneicosane. The equations for their formation follow:

11-a) $C_7H_{15}\text{-}Br + 2\ Na \longrightarrow C_7H_{15}\text{-}Na + NaBr$

11-b) $C_7H_{15}\text{-}Na + C_7H_{15}\text{-}Br \longrightarrow C_7H_{15}\text{-}C_7H_{15} + NaBr$

11-c) $2\ C_7H_{15}\text{-} \longrightarrow C_7H_{14}= + C_7H_{16}$

11-d) $C_5H_{13}\text{-}CH_2\text{-}CH= \longrightarrow C_5H_{13}\text{-}CH=CH_2$

11-e) $2\ C_7H_{15}\text{-} + C_7H_{14}= \longrightarrow C_7H_{15}\text{-}C_7H_{14}\text{-}C_7H_{15}$

We can now apply this mechanism to the reaction in liquid ammonia with benzyl chloride. The free benzyl radical formed according to equation 8) disproportionates:

12) $2\ C_6H_5\text{-}CH_2\text{-} \longrightarrow C_6H_5\text{-}CH_3 + C_6H_5\text{-}CH=$

The benzylidene free radical thus formed may react with other free radicals to form 1,2,3-triphenyl propane or it may react with the solvent ammonia forming benzyl amine:

13) $C_6H_5\text{-}CH= + 2\ C_6H_5\text{-}CH_2\text{-} \longrightarrow C_6H_5CH_2\text{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}\text{-}CH_2C_6H_5$

14) $C_6H_5\text{-}CH= + NH_3 \longrightarrow C_6H_5\text{-}CH_2\text{-}NH_2$

This now accounts for all the products formed in the reduction of benzyl chloride with sodium in liquid ammonia.

The source of the toluene, as shown in equation 12), is the disproportionation of the benzyl free radical. This is not analogous to the reactions in liquid ammonia of the organo-alkalis of Class I that form the corresponding hydrocarbon by ammonolysis. If the toluene had arisen by ammonolysis, sodium amide would be formed which in turn should react with additional benzyl chloride to give stilbene [34,35]. No stilbene was isolated in these reactions. It might be said that if any stilbene were formed it would be reduced to

bibenzyl by the excess sodium. However, the reduction requires a large excess of sodium.[36,37] a condition that would not hold in the above reaction, especially after most of the halide had been reacted. Another possibility is that the stilbene reacts with sodium benzylide in the following way:

15) $\phi\text{-CH=CH-}\phi + \text{Na-CH}_2\text{-}\phi \longrightarrow \phi\text{-CH(}\phi\text{-CH}_2\text{)-CH(Na)-}\phi$

An analogous reaction was reported by Zieglar and Bahr[38] using stilbene and potassium phenyl-dimethyl-methide, or the dimethyl derivative of potassium benzylide. The compound formed in equation 15) would then form 1,2,3-triphenyl propane on ammonolysis. However, this method of approach will not explain higher hydrocarbons and is not so well adapted to the other reactions in liquid ammonia as is the continuation of the disproportionation theory.

The mechanism applied to the reaction of benzal chloride is as follows:

16) $\phi\text{-CH-Cl}_2 + 4\ \text{Na} \longrightarrow \phi\text{-CH=(Na)}_2 + 2\ \text{NaCl}$

In this instance the organo-alkali compound is, as would be expected, extremely unstable and dissociates completely. No compounds are known with two strongly electro-positive groups on the same carbon atom.

17) $\phi\text{-CH=(Na)}_2 \longrightarrow \phi\text{-CH=} + 2\ \text{Na}$

This benzylidene free radical may then react with the solvent to form benzyl amine as in equation 14); benzyl amine represented 36% of the products isolated in this reaction. Another

possibility is that the free radical may disproportionate:

18) $2\ \phi\text{-}CH= \longrightarrow \phi\text{-}C\equiv + \phi\text{-}CH_2\text{-}$

The radicals necessary for the formation of another main product, 1,2,3-triphenyl propane, are now present (eq.13)). The triple-bonded free radical in reacting with the solvent forms symmetrical diphenyl ethylene diamine, the third important product of this particular reaction:

19) $2\ \phi\text{-}C\equiv + 2\ NH_3 \longrightarrow \phi\text{-}CH(NH_2)\text{-}CH(NH_2)\text{-}\phi$

Another example to which this mechanism may be applied is the reaction of phenyl ethyl bromide with sodium in liquid ammonia:

20) $\phi\text{-}CH_2\text{-}CH_2\text{-}Br + 2\ Na \longrightarrow \phi\text{-}CH_2\text{-}CH_2\text{-}Na + NaBr$

21) $\phi\text{-}CH_2\text{-}CH_2\text{-}Na \longrightarrow \phi\text{-}CH_2\text{-}CH_2\text{-} + Na$

22) $2\ \phi\text{-}CH_2\text{-}CH_2\text{-} \longrightarrow \phi\text{-}CH_2\text{-}CH_3 + \phi\text{-}CH_2\text{-}CH=$

This time the double-bonded free radical can be stabilized by simple rearrangement to form styrene:

23) $\phi\text{-}CH_2\text{-}CH= \longrightarrow \phi\text{-}CH=CH_2$

The high feasibility of disproportionations, such as given in the above examples, occurring is demonstrated in the work of Hein and his co-workers (39). They electrolyzed a solution of sodium ethide in diethyl zinc and obtained zinc at the cathode, and at the anode a mixture of hydrocarbons, chiefly ethane and ethylene along with small amounts of methane, butane and propane. The ethyl radical must have migrated to the anode and the disproportionation theory will

explain these products. When a lead anode was used, lead tetra ethyl was formed:

24) $4\ C_2H_5\text{-} + Pb \longrightarrow Pb(C_2H_5)_4$

The other types of free radicals represented in equations 10) and 16) have been prepared both photochemically (40) and by thermal decompositions (41,42) .. The methylene free radical was produced by the photochemical decomposition of ketene and the thermal decomposition of diazo methane:

$$CH_2{=}C{=}O \xrightarrow{h\nu} CH_2{=} + C{=}O$$

$$CH_2N_2 \xrightarrow[500°]{} CH_2{=} + N_2$$

These free radicals are absorbed on tellurium to exhibit their presence:

$$n\ CH_2{=} + n\ Te \longrightarrow (CH_2{=}Te)_n$$

The triple bonded free radicals are produced by photochemical decomposition of acetylene:

$$CH{\equiv}CH \xrightarrow{h\nu} 2\ CH{\equiv}$$

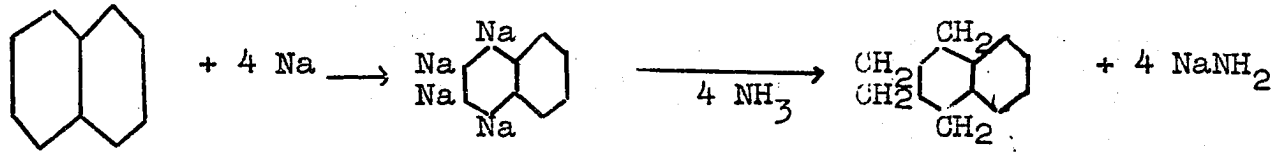
In equations 17) and 18), there are formed free radicals and in no instance do these radicals couple to form dimers. The expected compounds of bibenzyl, stilbene, or diphenyl acetylene are not formed as might well be expected. To explain this, Bachmann and Clarke (31) advance the hypothesis of electromeric forms, and consider that the radicals are of like "electron affinity" and therefore will not couple. Calingaert (55) and others have calculated upon the basis of free energies that the dimerization should occur more readily

than redistribution or disproportionation. As Calingaert points out, however, this takes no account of electrical charges.

In this connection, an interesting reaction carried out by Wimmer[16] should be cited. In neither the benzyl chloride nor the benzal chloride reaction with sodium in liquid ammonia is stilbene formed although both compounds give rise to the radicals that compose it. Wimmer added benzyl chloride to the benzal chloride reaction at the point where the color of the liquid ammonia solution changes from blue to red. This is the point at which all the sodium is in combination with halogen or organic radical. By this reaction, stilbene was obtained along with some bibenzyl. This result may be interpreted to mean that since the radicals arise from compounds of two different states of oxidation, they are two different electromeric forms and are therefore capable of reaction. The benzylidene free radical in one case arises by the loss of HCl from benzyl chloride and in the other case by the loss of two atoms of chlorine from benzal chloride.

The scope of the applicability of the mechanism is not limited to the reactions of organic halides. Evidence is abundant to show that nearly all reductions by alkali metals proceed with the initial formation of organo-metallics. As Gilman states[44], "It is interesting to note that those hydrocarbons[45,46,47] which are reduced by sodium in liquid

ammonia add alkali metals or organo-alkali compounds and those which are not reduced do not undergo such additions". As an isolated example, it has been shown that napthalene upon reduction with sodium in liquid ammonia yields tetrahydronapthalene [48,49]; further, that no matter how much excess sodium is used only four atoms will add to the napthalene ring. The mechanism is, therefore:



As a corrolary to this statement of Gilman, Wooster and Ryan [23] have formulated the benzohydrol rule for the particular case of the phenylated parrafins. This states that alkali metals and alkali metal amides will react with phenylated parrafins in liquid ammonia solution only when the benzohydrol group (ϕ_2-CH-) is present. Table V [20] summarizes the experimental work supporting this rule:

Table V

Hydrocarbon	Potassium	KNH_2
ϕ-CH_3	No action	No action
ϕ_2-CH_2	Reacts	Reacts
ϕ_3-CH	Reacts	Reacts
ϕ_4-C	No action	No action
ϕ-C_2H_5	No action	No action
ϕ-CH_2-CH_2-ϕ	No action	No action
ϕ_2-CH-CH_2-ϕ	Reacts	Reacts
ϕ_3-C-CH_3	Sl. reaction	No action
ϕ_2-CH-CH-ϕ_2	Reacts	Reacts
ϕ_3-C-CH_2-ϕ	Sl. reaction	No action
ϕ_3-C-C-ϕ_3	Adds	---------

An interesting extension of the benzohydrol rule is seen in Table VI (36); the action of sodium on olefins in liquid ammonia solutions is tabulated:

Table VI

Olefin	Product
ϕ-CH=CH_2	ϕ-C_2H_5 and polymers
ϕ-CH=CH-ϕ	ϕ-CH_2-CH_2-ϕ
ϕ_2-C=CH_2	ϕ_2-C(Na)CH_3
ϕ_2-C=C-ϕ_2	ϕ_2-C(Na)-C(Na)-ϕ_2
ϕ_2-C=CH-ϕ	ϕ_2-C(Na)-CH_2-ϕ
ϕ_2-C=CH-CH_3	ϕ_2-C(Na)-CH_2-CH_3

It will be observed that in each case two atoms of sodium add to the double bond but that only those atoms of sodium not attached to a benzohydrol group are ammonolyzed.

No examples of the members of Class III of organo-alkalis in liquid ammonia are available. Much has been done in other solvents and the work is excellently reviewed by Wooster in his paper on organo-alkalis.(50)

The work of this thesis was undertaken with a view to classifying the reactions of calcium into one of the general types. To compare its action with potassium and sodium, the benzyl and benzal chlorides were used. It was also desired to study a straight chain aliphatic compound and for this purpose heptyl bromide was used.

Only one mention is made in the literature of a reaction using calcium with organic halides in liquid ammonia solution. Kraus and Kawamura(22) report the reaction of triphenyl methyl chloride and calcium, stating that they obtained an unstable reddish brown solid, the nature of which was not further investigated.

The literature on the reactions of calcium with organic halides in solvents other than ammonia is also sparse. Some work has been done in ether and benzene. Usually the Wurtz-Fittig type of reaction is obtained but in some cases the calcium analogue to the Grignard reagent has been formed, i.e., R-Ca-X. Beckman(51) believed he had prepared these Grignard analogues with calcium from iodobenzene and ethyl

iodide in ether solution. However, Gilman[52] and his co-workers, with quantitative experimental evidence, showed that Beckman's compounds were not the R-Ca-I type. Gilman did succeed in preparing n-octyl calcium iodide, phenyl calcium iodide and n-butyl calcium iodide in ether solution. He also determined some of the properties of the compounds and used them in chemical reactions[53,54,55]. The compounds proved to be more reactive than the magnesium analogues and were in fact as active as the lithium organo-metallics.

EXPERIMENTAL WORK

This part of the thesis will be sub-divided into four main topics. A--Materials, B--Apparatus, C--Procedure, and D--Experimental Results and Discussion of these results.

A--MATERIALS.

The calcium used in these reactions was obtained from Kahlbaum in stick form. It was prepared for use by scraping off the oxide coating until a lustrous surface was obtained. The metal was then turned out on a lathe into pieces of 30-40 mms. thickness. The metal turnings were stored under anhydrous petroleum ether until used.

The purity of this calcium was determined by a permanganometric method. The procedure followed was to precipitate the calcium, dissolved in dilute hydrochloric acid, as the oxalate, which was redissolved in dilute sulfuric acid and titrated with standard potassium permanganate. The results of three determinations are shown in Table VII.

Table VII

Purity of calcium by permanganometric titration

Grams of metal	Cc. of .1036N $KMnO_4$	% Purity
0.1475	69.46	97.98
0.1574	74.10	97.90
0.1239	58.52	98.23

The average of these three determinations is 98.03 percent. If the impurity present were all calcium oxide, then the actual purity of the metal would be only 93.1 percent. To further check the purity, the calcium was dissolved in standard hydrochloric acid, and the excess acid was back titrated with sodium hydroxide. Assuming the acid consumed was due to calcium metal, the purity is as shown in Table VIII.

Table VIII

Purity of calcium by acid titration

Grams of metal	Cc. of .1001 N. acid	% Ca
0.1131	56.18	99.56
0.0985	48.97	99.59
0.0663	33.24	99.69

The average of these three determinations is 99.61 percent calcium. If the impurity found by permanganometric titration, were assumed to be calcium oxide, then this value determined by acid titration would be 98 percent. This lead to the conclusion that the impurity must be something beside calcium oxide.

The calcium was tested for magnesium by means of a titan yellow dye test (56). A drop of the test solution is put on a spot plate with a drop of dyestuff solution (0.1% aqueous) and a drop of dilute alkali. An orgnge or red color is formed according to the amount of magnesium present. When 0.1 gram of the calcium was dissolved in 25 cc. of distilled

water it gave a strong positive test. The magnesium would show up in the acid titration but not in the permanganate method. Iron was tested for as ferric ion using potassium thiocyanate, and as ferrous ion using potassium ferricyanide, but both tests were negative. The presence of carbon was indicated by the odor of acetylene upon dissolving the calcium in water.

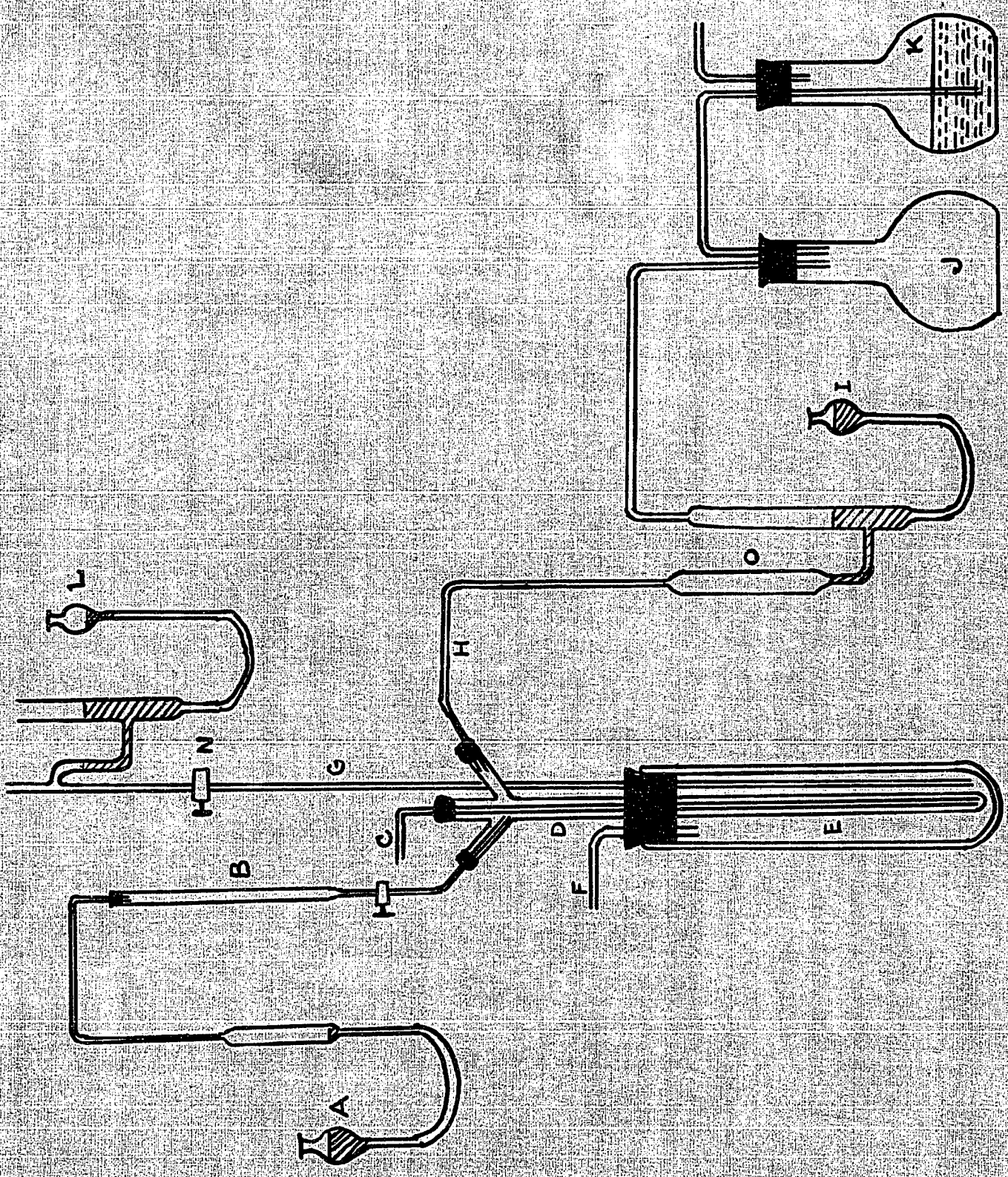
From these quantitative results and qualitative observations it was concluded that the purity of the calcium metal is 98 percent, and this figure is used in all subsequent calculations.

The benzyl chloride, benzal chloride, and heptyl bromide were all obtained from the Eastman Kodak Company. The benzyl chloride was redistilled twice before use and was a colorless liquid boiling between 176°-177.5° C. at 760 mm. The benzal chloride, redistilled once, had a boiling point of 95°-96° C. at 15 mm. The heptyl bromide was used without further treatment. The Eastman catalogue gives the boiling point as 177.5°-179.5° C. at 760 mm.

The liquid ammonia used was obtained from Mathieson Alkali Company in fifty pound cylinders. For the anhydrous ammonia, to be used in the reactions, smaller tanks in which were placed 2-3 grams of sodium were filled from the large cylinder.

B--APPARATUS

The apparatus used in this work is essentialy the same



as that used by White [57], Linford [14], and Wimmer [13]. A sketch of the set-up is shown in figure I.

The reaction tube D is immersed in a bath of liquid ammonia contained in a large Dewar flask E. The anhydrous liquid ammonia is admitted through inlet tube C. It condenses because of the lower temperature (about -50° C.) produced by causing rapid ebullition of the ammonia in the Dewar with a stream of air admitted through the tube G and because of the back pressure exerted by raising the leveling pear I, filled with mercury. The gas from the reaction tube passes out through tube H, through system O, safety flask J, and into the water in flask K. The gas from the cooling jacket passes out through the tube F into large bottles containing water.

The air admitted into the Dewar flask is first dried by passing through anhydrous calcium chloride. The rate of the passage of the air is regulated by leveling pear L and stopcock N. This is a modification of the original set-up and was found to be very satisfactory for regulation.

Leveling pear A is filled with mercury and is for the purpose of forcing liquid from the calibrated burette B into the reaction tube.

C--PROCEDURE

The reactions, described in this thesis, were carried out at atmospheric pressure and at the boiling point of liquid ammonia. The reaction tube was first cleaned thoroughly with

chromic acid cleaning solution, then rinsed with distilled water, alcohol and ether. A stream of dry nitrogen was passed through and the tube was put in place in the Dewar. Ammonia was then condensed in the tube until about 150 cc. had collected.

When sufficient ammonia was collected, a weighed amount of calcium was added through the side-arm. The burette was put in place, and the addition of organic halide started. This addition must be made slowly, especially of the first few drops. The reaction is a vigorous one and the calcium is apt to splash upon the sides of the tube. This may be washed down by condensing ammonia upon the walls of the tube.

As soon as a little organic halide is added a white solid separates out and as more halide is put in this precipitate becomes very thick. This is due to the formation of calcium halide, the bromide and chloride being only moderately soluble in liquid ammonia. This solubility is only 0.252 grams per 100 grams of ammonia in the case of calcium chloride[58]. Moreover, the calcium halides co-ordinate with eight molecules of ammonia[59], which makes them heavy and voluminous precipitates.

Addition of the organic halide was continued until the blue color of the calcium metal in liquid ammonia solution disappears. At this point the reaction ratio can be computed. The reaction ratio is the number of gram moles of halide added at the end-point divided by the number of gram atoms

of calcium used. In some of the runs additional halide was added after the first end-point had been reached, and these runs are referred to as the secondary reaction.

At the conclusion of the reaction, the bath of liquid ammonia was removed and the ammonia in the reaction tube allowed to evaporate off. The residue, a heavy, white solid mass, was extracted with anhydrous ether giving an ether soluble and ether insoluble portion, which were investigated separately.

D--EXPERIMENTAL RESULTS AND DISCUSSION

In all, five different reactions were run using calcium in liquid ammonia solution and they will be reported in the following order:

1). Benzyl chloride, primary reaction.

2). Benzyl chloride, secondary reaction.

3). Heptyl bromide, primary reaction.

4). Heptyl bromide, secondary reaction.

5). Benzal chloride.

The experimental results will include, a) reaction ratios, b) separation of the products, c) identification of the products, d) quantitative estimation of the products, and e) discussion of the data.

Each reaction will be more definitely defined by its reaction ratio than it is in the arbitrary classification given for purposes of organization. These reaction ratios and other data are discussed specifically for each reaction,

because of the interdependency of the results of each reaction, i.e., to understand reaction 2), the results of reaction 1) should be understood.

1). Benzyl chloride, primary reaction.

a). Reaction ratios. The reaction ratios are computed using the purity of calcium as 98 percent and the density of the benzyl chloride as 1.103 gm/cc. at 18° C. The reaction ratios for several representative runs are given in Table IX.

Table IX

Reaction Ratios in Benzyl Chloride Reaction.

Run	Moles Benzyl Chloride	Gm-atoms Calcium	Ratio
13	0.0506	0.0456	1.13
14	0.0573	0.0500	1.15
15	0.0494	0.0422	1.16
16	0.0378	0.0318	1.19
17	0.0448	0.0379	1.20
18	0.0348	0.0297	1.18
20	0.0364	0.0305	1.19
21	0.0377	0.0324	1.16
22	0.0278	0.0233	1.19
23	0.0335	0.0303	1.13
24	0.0380	0.0322	1.18
25	0.0368	0.0319	1.16
26	0.0408	0.0341	1.19

The reaction ratio is obtained by dividing the moles of benzyl chloride by the gram atoms of calcium. The average reaction ratio for the runs listed is 1.17. No red end-point was observed as in the reaction of sodium and potassium with benzyl chloride in liquid ammonia. The reaction ratio with sodium and potassium was nearly one in each case and if the reaction of calcium were comparable its ratio would be expected to be two. Preliminary observations, then, indicate a different type of reaction when calcium is used as the reducing metal.

b). Separation of products. The ether soluble portion of the reaction products, usually about 300 cc. in volume, was distilled through a Hempel distilling column packed with glass beads. Two main fractions were obtained. The first (A) was a colorless oil boiling between 105°-115°; the second (B) was a liquid boiling between 275°-295° and solidifying upon cooling.

The ether insoluble portion consisted of calcium salts with ammonia of crystallization. The material was dissolved in excess acid and back titrated with standard alkali to determine the basicity. Then the ammonia was distilled off in the presence of saturated sodium hydroxide using a Kjeldahl set-up. The ammonia was absorbed in standard acid and its quantity determined by titration. In each run there was a decided difference between the amount of total base and the amount of ammonia; i.e., there must have been some other acid

consuming substance present.

c). Identification of products. The colorless oil (A) was redistilled and it boiled between 108°-110°. Its refractive index was 1.4968 ($N_d^{20°}$) which is very close to that of toluene ($N_d^{20°} = 1.4955$) [60]. To check, the dinitro derivative was prepared according to Millikan [61], and the compound thus obtained had a melting point of 70°-71°, the same as reported by him. As a result of these tests, it was concluded that the colorless oil (A) was toluene.

The crystalline compound (B) had a melting point of 51-52° C. It was recognized as being bibenzyl and the only further check was a mixed melting point with some repurified bibenzyl, prepared by the action of potassium on benzyl chloride in liquid ammonia. There was no change in the melting point so that compound (B) must have been bibenzyl.

d). Quantitative estimation of products. When the ammonia was allowed to evaporate after the conclusion of the reaction, the greater part of the toluene collected in the flask of water used to absorb the exhaust ammonia. Toluene apparently distils out of the reaction flask with ammonia vapors. Some of the toluene excapes from this catch flask also, as was demonstrated by connecting a tube from this flask into a pneumatic trough over which was an inverted bottle filled with water. The water was displaced during the course of the reaction. The gas collected had the odor of toluene and burned with the characteristic smoky flame of

a hydrocarbon. As was demonstrated in the separation of the products of the reaction some toluene also remains behind. For these reasons, the toluene yield could not be obtained quantitatively. The amount of toluene, however, could be estimated indirectly as will be explained in the discussion of this reaction. For the bibenzyl determination, the residue left in the reaction tube, after the ammonia had evaporated off, was dissolved in water and just neutralized with hydrochloric acid. The small amount of toluene was distilled off. Then the bibenzyl was steam distilled from the mixture, filtered, dried, and weighed. Results are given in Table X. The yields are based upon the amounts of benzyl chloride used. The yield is calculated by multiplying the moles of bibenzyl formed by two, and dividing by the moles of benzyl chloride used.

Table X

Yields of Bibenzyl

Run	Gm-moles Benzyl chloride	Gm-moles Bibenzyl	% yield
14	0.0573	0.0079	27.4
16	0.0378	0.0053	28.1
17	0.0448	0.0067	29.8
19	0.0282	0.0037	26.2
20	0.0364	0.0047	26.0
21	0.0377	0.0050	26.4

The average yield of bibenzyl from the six runs is 27.3 % .

Acid-base titration of the ether insoluble portion revealed that there was a basic compound present other than just calcium chloride with ammonia of crystallization. The number of equivalents of this base is given for several runs in Table XI. Also shown is the ratio of the number of equivalents of base to the number of moles of benzyl chloride used. The benzyl chloride is used as a reference since it was used as the limiting factor in determination of bibenzyl yields.

Table XI

Ratio of equivalents of base to moles of Benzyl chloride

Run	Gm-Equivalents base	Gm-moles Bz-Cl	Ratio
20	0.0248	0.0364	0.681
21	0.0264	0.0377	0.700
22	0.0205	0.0278	0.738
23	0.0259	0.0335	0.773
24	0.0270	0.0380	0.711
25	0.0278	0.0368	0.756
26	0.0272	0.0408	0.666

The average ratio for the seven runs tabulated is 0.718.

e). Discussion of the results. From the quantitative data obtained, the reaction of calcium with benzyl chloride in liquid ammonia can be shown to proceed according to two distinct reactions, one in which bibenzyl is formed, and the other in which toluene and a basic calcium compound is

obtained. The first, which will be assumed for the time being but will be substantiated by the experimental evidence, represents the formation of bibenzyl according to the equation:

$$\text{I.}\quad 2\ \phi\text{-}CH_2\text{-}Cl + Ca \longrightarrow \phi\text{-}CH_2\text{-}CH_2\text{-}\phi + CaCl_2$$

Since we know how much bibenzyl is formed we can calculate the amount of benzyl chloride and calcium that were required to form it. By subtracting these amounts from the original quantities of calcium and benzyl chloride used, we can calculate a new reaction ratio, which excludes bibenzyl formation. These results are shown in Table XII.

Table XII

Reaction Ratios exclusive of Bibenzyl formation.

Run No.	Original Moles BzCl	Ca	Exclusive of Bibenzyl BzCl	Ca	Reaction Ratio
14	.0573	.0500	.0415	.0421	0.99
16	.0378	.0318	.0272	.0265	1.03
17	.0448	.0379	.0314	.0313	1.00
19	.0282	.0254	.0208	.0217	0.96
20	.0364	.0305	.0270	.0258	1.05
21	.0377	.0324	.0277	.0274	1.01

This new reaction ratio approaches closely to that of one gram mole of benzyl chloride to one gram atom of calcium.

Since the inorganic product formed in this reaction (I) is calcium chloride, it would not enter into the titration

of the basicity of the ether insoluble portion. Table XIII presents the ratio of the equivalents of base, exclusive of ammonia, to the number of equivalents of calcium not entering into bibenzyl reaction.

Table XIII

Relation of equivalents of base to equivalents of calcium exclusive of bibenzyl reaction

Run No.	Equivalents of Base	Equivalents of Ca (not entered into Bibenzyl)	Ratio
20	0.0248	0.0516	0.481
21	0.0264	0.0548	0.482
22	0.0205	0.0376	0.545
23	0.0259	0.0498	0.520
24	0.0270	0.0528	0.511
25	0.0278	0.0540	0.515
26	0.0272	0.0548	0.496

It can be seen from a consideration of this table that the equivalents of base is always about one-half of the equivalents of calcium not converted to calcium chloride in the bibenzyl reaction. This fact, coupled with the reaction ratio of one as calculated in Table XII led to the postulation that the second reaction occurring was as follows:

II. $\phi\text{-}CH_2\text{-}Cl + Ca \longrightarrow \phi\text{-}CH_2\text{-}CaCl$

This fulfills the condition of having a 1:1 reaction ratio. The product, benzyl calcium chloride, would on ammonolysis or

hydrolysis yield toluene:

III. $\phi\text{-}CH_2\text{-}CaCl + NH_3 \longrightarrow \phi\text{-}CH_3 + Ca(NH_2)Cl$

IV. $\phi\text{-}CH_2\text{-}CaCl + H_2O \longrightarrow \phi\text{-}CH_3 + Ca(OH)Cl$

In either III or IV a base would be formed, the number of equivalents of which would be one-half of the number of equivalents of calcium entering into the reaction. Moreover, the number of equivalents of this base would be equal to the number of equivalents of toluene formed. Table XI then can be regarded as showing the total yield of toluene based on benzyl chloride. It must be pointed out that, as yet, we have no way of telling whether III occurs exclusively or whether some of the toluene is formed, according to IV, when we dissolve the ether insolubles in water. The quantitative data would be the same in either case. This question will be clarified in the study of the completed reaction.

We can calculate from the reaction ratio the extent to which reactions I and II occur.

Let 1.17 = moles of benzyl chloride used.

1.00 = gram atoms of calcium used.

The reaction ratio is then 1.17.

I. $2\ \phi\text{-}CH_2\text{-}Cl + Ca \longrightarrow \underset{a}{\phi\text{-}CH_2\text{-}CH_2\text{-}\phi} + CaCl_2$

II. $\phi\text{-}CH_2\text{-}Cl + Ca \longrightarrow \underset{b}{\phi\text{-}CH_2\text{-}CaCl}$

Let a = moles of bibenzyl formed.

b = moles of benzyl calcium chloride formed.

Then,

$$2a + b = 1.17 \quad \text{(The benzyl chloride used)}$$
$$a + b = 1.00 \quad \text{(The calcium used)}$$

Therefore, $a = 0.17$

and, $b = 0.83$

The yield of bibenzyl is $\frac{2 \times 0.17}{1.17} = 29.1\%$, and the yield of benzyl calcium chloride is $\frac{0.83}{1.17} = 70.9\%$. The average yield of bibenzyl determined experimentally was 27.3%. The average ratio of the equivalents of base to the moles of benzyl chloride was 0.718, or as has been stated, this figure can be regarded as the yield of toluene, 71.8%. The sum of the average yields of bibenzyl and toluene represents 99.1% of the total benzyl chloride added. In runs number 20 and 21, in which the yield of each was determined, this total was 94.1% and 96.4% respectively.

Before concluding the discussion of the reaction of benzyl chloride and calcium, note should be made of the observation of a red colored solid in some of the runs, after the ammonia had evaporated off. Since the amounts of this solid were small, and they disappeared immediately upon exposure to air, they were not isolated. As to their nature, then, there can only be conjecture. Gilman and Fothergill (62) found in the hydrolysis of alkyl magnesium halides that a small amount of hydrogen was given off. They stated that this

hydrogen probably comes from the reaction of the sub-bromide of magnesium and water. This sub-bromide arises from the dissociation of the Grignard reagent:

$$R\text{-}MgBr \longrightarrow R\text{-} + MgBr$$

$$MgBr + H_2O \longrightarrow Mg(OH)Br + \tfrac{1}{2} H_2$$

The free radical then undergoes disproportionation and coupling to various degrees. Now if a like dissociation of the benzyl calcium chloride took place, then the sub-chloride of calcium would be formed. This sub-chloride has been made (63) by the electrolysis of calcium chloride, the sub-chloride being formed as red crystals at the anode. In the reduction of benzyl chloride and the other halides with calcium, hydrogen was tested for but in no case was any evolved.

A qualitative test for the benzyl calcium chloride as described by Gilman and Schulze (55), was tried on the reaction residue, after evaporation of ammonia. In some of the runs on which this was tried, positive results were obtained, and in others, negative results. Briefly, the test is to react the benzyl calcium chloride in ether solution with a 1% benzene solution of Michler's ketone. This reaction product is then hydrolyzed, followed by the addition of several drops of 0.2% solution of iodine in glacial acetic acid. If there is a compound of the Grignard type present, a characteristic blue-green color will be produced.

2). Benzyl chloride, secondary reaction

a). Reaction ratios. The solution of the problem of the completeness of the ammonolysis of the benzyl calcium chloride at the end-point, was the purpose of running this reaction, termed the secondary benzyl chloride reaction. In these runs, enough benzyl chloride was added to make the reaction ratio two. If any benzyl calcium chloride were present it should couple with the additional benzyl chloride to form bibenzyl. If the benzyl calcium chloride were completely ammonolyzed any reaction occurring would be between the calcium amido chloride and the benzyl chloride.

b). Separation of products. Preliminary investigation of the ether soluble portion of the reaction mixture showed it to contain an amine and an unsaturated compound. These findings aided in formulating the plan of separation.

The solution of ether solubles was warmed gently to drive off any ammonia. Then the solution was extracted with dilute hydrochloric acid three times with fifty cubic centimeter portions. This dilute acid solution on evaporation yielded a white crystalline solid (C).

The ether solution left after extraction with acid was then dried using anhydrous sodium sulfate, and allowed to evaporate. A large amount of white solid was left as a residue, which was dissolved in carbon tetra chloride. The carbon tetrachloride solution was heated to boiling and bromine was added dropwise until it no longer was decolorized upon

further addition. When the solution was cooled, glistening, white needles separated out. These were filtered and dried (D). The filtrate was evaporated to dryness and a solid residue remained (E).

The ether insolubles were dissolved in water and the procedure outlined under the study of the primary benzyl chloride reaction was followed.

c). Identification of products. The solid (C) was water soluble. It was suspected, from preliminary tests, of being a monoamine hydrochloride. The percentage of chloride in the compound was determined gravimetrically by silver nitrate precipitation. From this percentage, the molecular weight of the compound can be determined by dividing the atomic weight of chlorine by the percent of chlorine in the compound. The results of two determinations are given in Table XIV.

Table XIV

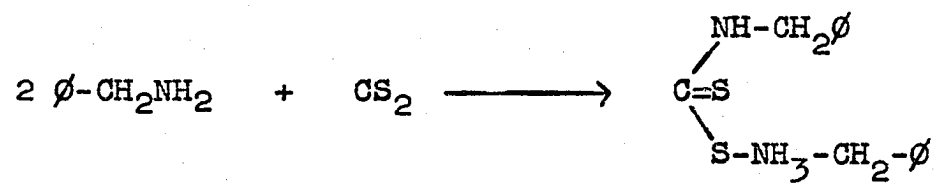
Molecular weight of amine hydrochloride

Determination	Weight of Sample	Weight of AgCl	Calculated Molecular Weight
I	.3522	.3531	142.7
II	.3243	.3250	142.8

These values agree quite will with the formula weight of benzylamine hydrochloride, which is 143.5.

A sample of the solid (C) was placed in a test tube with a few cubic centimeters of concentrated sodium hydroxide. A

light oil separated out which was extracted with 10 cc. of ether. This ether solution was dried with anhydrous sodium sulfate. One cc. of carbon disulfide was added, whereupon a white crystalline precipitate settled out. This precipitate, after being dried, had a melting point of 126-7° which compares very favorably with the literature melting point of the dithiocarbamic acid derivative of benzylamine which is 127°. The formation of this derivative is represented by the following equation:



The amine hydrochloride had a melting point of 246-48° as compared with the literature-given melting point of 248° for benzylamine hydrochloride. It was concluded that solid (C) was benzylamine hydrochloride.

The solid (E), obtained by complete evaporation of the ether solution, was recrystallized from ethyl alcohol and it had a melting point of 52°. A mixed melting point with bibenzyl identified solid (E) as being bibenzyl.

The compound (D) had a melting point of 235-7°. This is the compound which was obtained by bromination. The compound which gives rise to it was isolated in several runs by steam distilling the bibenzyl from the ether soluble portion. This left as a residue a substance which melted at 118-20°. Molecular weight determinations were made on this compound using

the freezing point method with benzene as the solvent. The results are given in Table XV.

Table XV

Molecular Weight of Solid Melting as 118-20°

Determination	Grams sample	Grams C_6H_6	T	Mol. Wt.
I	.1500	21.76	.191	184.8
II	.1460	21.76	.185	185.8

The above properties and molecular weight indicate the compound was stilbene (Ø-CH=CH-Ø). The compound (D), which was formed by bromination would then be stilbene dibromide, which has a reported melting point of 237°.

d). Quantitative extimation of products. The separation of products was carried out as already described. The benzylamine was weighed as the hydrochloride, the stilbene as stilbene dibromide and the bibenzyl as such. The yields of stilbene and benzylamine are calculated in two ways, first, on the basis of the total benzyl chloride used, then, on the basis of the additional benzyl chloride added at the end-point required to make the reaction ratio 2. The yields are presented in Tables XVI and XVII.

Table XVI

Yield of Benzylamine

Run	Total Moles BzCl	Excess Moles BzCl	Moles Amine	Yield on excess	Yield on total
37	.1062	.0452	.0167	37.0	15.7
38	.1084	.0451	.0145	32.1	13.4
44	.0842	.0372	.0135	36.3	16.0

Table XVII

Yield of Stilbene

Run	Total Moles BzCl	Excess Moles BzCl	Moles Stilbene	Yield on excess	Yield on total
37	.1062	.0452	.0091	40.2	17.1
38	.1084	.0451	.0097	43.0	18.8
39	.1378	.0630	.0113	36.0	16.4

The yields of bibenzyl are given in Table XVIII. In this table, the yields are reported on the basis of the total benzyl chloride used and on the amount of benzyl chloride added at the end-point. The latter calculation is made in order to compare the result with the yield of bibenzyl when no excess is added. No calculation of yield for bibenzyl is made upon the basis of the excess benzyl chloride, since bibenzyl is not formed exclusively from the excess as are stilbene and benzyl amine.

Table XVIII

Yield of bibenzyl, secondary reaction

Run	Moles Benzyl Chloride		Moles	% Yield	
	End-point	Total	Bibenzyl	On end-point	On total
36	.0609	.1072	.0131	43.0	24.4
37	.0610	.1062	.0141	46.7	26.6
38	.0633	.1084	.0128	40.3	23.6
43	.1040	.1712	.0205	40.0	23.9

The yield based on the end-point is calculated by multiplying the moles of bibenzyl formed by two and dividing by the moles of benzyl chloride added at the end-point. These yields would correspond to the yields in the primary reaction given in Table X. The moles of bibenzyl multiplied by two and divided by the total moles of benzyl chloride give the yield based on the total.

The results of the titration of the ether insolubles for the secondary reaction are given in Table XIX. The ratio of the equivalents of base, exclusive of ammonia, to the total moles of benzyl chloride used is considerably less in the secondary reaction than it was in the primary reaction.

Table XIX

Ratio of equivalents of base to moles of benzyl chloride

Run	Moles of benzyl chloride used	Equivalents of base	Ratio
35	.1084	.0066	.061
37	.1062	.0064	.060
38	.1084	.0030	.028

e). Discussion of results. In the discussion of the reaction of the benzyl chloride and calcium to the end-point, it was pointed out that benzyl calcium chloride was formed. From the quantitative data, it could not be stated whether this compound was completely ammonolyzed or not.. If there remained some benzyl calcium chloride, then it ought to couple with additional benzyl chloride to form bibenzyl, as follows:

$$\text{Ø-CH}_2\text{-CaCl} + \text{Ø-CH}_2\text{Cl} \longrightarrow \text{Ø-CH}_2\text{-CH}_2\text{-Ø} + \text{CaCl}_2$$

If, however, it were completely ammonolyzed according to equation III, then no more bibenzyl would be formed, and any reaction occurring would be between the excess benzyl chloride and the product of ammonolysis, calcium amido-chloride.

The Table XIX, giving the data on basicity shows that the reaction which occurred in adding excess halide removed the compounds contributing to the basicity. Tables XVI and XVII giving the yields of stilbene and benzylamine show that the greater portion of the base-forming compound of the reaction

mixture was calcium amido-chloride, since stilbene and benzylamine are the usual products of the reaction of a metal amide on benzyl chloride in liquid ammonia[35]. Their formation may be represented as follows:

$$2\ \text{ø-CH}_2\text{Cl} + 2\ \text{Ca(NH}_2\text{)Cl} \longrightarrow \text{ø-CH=CH-ø} + 2\text{CaCl}_2 + 2\text{NH}_3$$

$$\text{ø-CH}_2\text{Cl} + \text{Ca(NH}_2\text{)Cl} \longrightarrow \text{ø-CH}_2\text{NH}_2 + \text{CaCl}_2$$

The formation of these two products accounts for about 80% of the excess benzyl chloride added. The rest of the excess goes to form additional bibenzyl as can be seen from inspection of Table XVIII. The yield of bibenzyl as reported in this table is about 40% based on the benzyl chloride used at the end-point. When no excess benzyl chloride was used, this figure was approximately 27%. Therefore the benzyl calcium chloride is not completely ammonolyzed at theend-point and it will couple with excess benzyl chloride to form bibenzyl.

In order to present a material balance on the excess benzyl chloride we will assume, using data in Table X, that the yield of bibenzyl up to the end-point is 27.3%. We can then calculate the amount of bibenzyl formed by the addition of excess benzyl chloride. This calculation is illustrated using run number 37. The total number of moles of bibenzyl formed was .0141 moles. The amount of bibenzyl formed at the end-point would be 27.3% of the .0610 moles of benzyl chloride added at the end-point, or 0.0082 moles. Therefore, .0141 - .0083, or .0058 moles were formed from the .0452 moles

of excess benzyl chloride. The .0058 moles represents 12.8% of the excess benzyl chloride used. The material balance for the excess benzyl chloride for runs 37 and 38 is given in Table XX using the values of benzylamine and stilbene given in Tables XVI and XVII.

Table XX

Product	Run 37--% Yield	Run 38--% Yield
Bibenzyl	12.8	9.3
Benzylamine	37.0	32.1
Stilbene	40.2	43.0
Total	90.0	84.4

The products account for 84% and 90% of the excess benzyl chloride. The loss is partly due to manipulative errors, and partly due to the fact that all the benzyl chloride does not react as indicated in Table XIX. In this table, the amount of base not ammonia is given for three runs. If all the additional benzyl chloride had reacted there should be no residual base; the figures given in this table then represent the amount of unreacted benzyl chloride. In run 37, 6.5% was unreacted, and in run 38, 14.3% was unreacted.

3). Heptyl bromide, primary reaction

a). Reaction ratio. The reaction of the heptyl bromide was carried out exactly as was the benzyl chloride reaction. The reaction was less vigorous and the halide could be added fairly rapidly. The reaction ratios for several representative runs are given in Table XXI

Table XXI

Reaction Ratios for Primary Heptyl Bromide Reaction

Run	Moles Ca	Moles Heptyl Bromide	Reaction ratio
1	.0355	.0440	1.24
2	.0396	.0487	1.23
3	,0536	.0671	1.25
4	.0530	.0657	1.24
5	.0533	.0697	1.31
6	.0451	.0557	1.24
8	.0361	.0465	1.30
9	.0376	.0477	1.27
10	.0516	.0620	1.20
11	.0537	.0655	1.22

The average for these runs is 1.25, a little higher than in the case of benzyl chloride. The ratio indicates, however, that the course of the reaction is similar.

b). Separation of products. On the surface of the flask designed to catch the ammonia escaping from the reaction tube, there collected a small amount of an oil. This oil (F) was

separated off and investigated.

The solution containing the ether soluble portion of the reaction mass was evaporated and there was left as a residue a clear, colorless oil (G).

The ether insoluble portion was dissolved in water and titrated for basicity as described under the benzyl chloride reaction.

c). Identification of products. The oil (F) isolated in but very small amounts had a refractive index of 1.3852 ($N_d^{20°}$). Its boiling point, taken in a capillary tube, was 96,4° (corrected). The values of these constants for n-heptane are $N_d^{20°}$ = 1.3879 and the boiling point 98.3°C. It was concluded that the compound (F) was normal-heptane.

The boiling point of the oil (G), taken in a capillary tube, was 248° (uncorrected). Two determinations of the molecular weight were made using the Beckmann freezing-point method with benzene as a solvent. The results are given in Table XXII

Table XXII

Molecular Weight of oil (G)

Determination	Grams sample	Grams C_6H_6	T	Mol. Wt.
I	.1773	21.76	.206	201.5
II	.1214	21.76	.143	200.6

The above properties of oil (G) led to the conclusion that it was tetradecane. The literature (64) values for the boiling

point if 245° at 750 mm. and for the refractive index (61) $N_d^{20°} = 1.4459$. The formula weight of tetradecane is 198.2.

d). Quantitative estimation of products. The yields of tetradecane were obtained by direct weighing of the oil left on evaporation of the ether solution. It is calculated on the basis of the amount of heptyl bromide used.

Table XXIII

Yield of Tetradecane

Run	Moles Heptyl bromide	Moles Tetradecane	% Yield
4	.0657	.0106	32.2
5	.0697	.0123	35.5
9	.0477	.0073	30.8
10	.0630	.0103	33.2

The average yield of tetradecane for the four runs tabulated is 33.9%, based upon the heptyl bromide added.

The determination of the yield of n-heptane offers the same difficulties as the determination of the yield of toluene did in the benzyl chloride reaction. However, as explained in the discussion of experimental results, the yield can be estimated indirectly.

When the ether insolubles were dissolved in water and titrated for total basicity and for ammonia it was again found that there was considerable base other than ammonia. Table XXIV gives the number of gram-equivalents of the base and the relation to the moles of heptyl bromide used.

Table XXIV

Ratio of equivalents of base to moles of heptyl bromide

Run	Moles Heptyl bromide	Equivalents of base	Ratio
9	.0477	.0273	.581
10	.0620	.0386	.623
11	.0655	.0403	.615

The average ratio of the equivalents of base to the number of moles of heptyl bromide used is .606 for runs 9,10 and 11.

e). Discussion of results. Reactions occur with heptyl bromide and calcium in liquid ammonia solution similar to those with benzyl chloride and calcium. The products of the reaction are the dimer, tetradecane, and the hydrocarbon corresponding to the organic radical, n-heptane.

Again, as has been done with the benzyl chloride reaction, we can calculate from the reaction ratio (1.25), the extent to which each of the two reactions occur.

$$C_7H_{15}\text{-}Br + Ca \longrightarrow C_7H_{15}\text{-}CaBr$$

$$2\ C_7H_{15}\text{-}Br + Ca \longrightarrow C_7H_{15}\text{-}C_7H_{15} + CaBr_2$$

The formation of heptyl calcium bromide represents 60% of the reaction, and the formation of tetradecane, 40%. These agree quite well with the experimentally determined values of 60.6% and 33.9% respectively.

4). Heptyl bromide, secondary reaction

At the end-point of the heptyl bromide reaction, sufficient halide was added to bring the ratio to two. However, when the ammonia was evaporated off, nearly all of the heptyl bromide was recovered unchanged. It was found, however, that the oil that collected in the flask containing water would absorb a small amount of bromine, indicating unsaturation. This oil had a boiling point of 94° (uncorrected). The boiling points of n-heptane and n-heptene, the probably products are almost the same,,98° and 96° respectively, so that s separation on such a small amount could not be effected.

In another run benzyl chloride was added to the heptyl bromide reaction at the end-point and stilbene and benzylamine were isolated as reaction products. This indicates the presence of calcium amido-bromide.. The heptyl bromide is apparently not sufficiently reactive to react appreciably with the calcium amido-bromide.

5)..Benzal chloride reaction

a). Reaction ratios. The benzal chloride reacted with calcium even more vigorously than did benzyl chloride. In these runs, a red end-point was observed, i.e., the point at which the blue color of the calcium solution disappeared and was replaced by a red color. The reaction ratio at the red end-point is tabulated for several runs in Table XXV.

Table XXV

Reaction Ratios for Benzal Chloride Reaction

Run	Gram atoms Ca	Gram moles $BzCl_2$	Ratio
1	.0269	.0185	.69
3	.0124	.0085	.69
5	.0279	.0184	.66
6	.0224	.0141	.63
7	.0313	.0198	.63
8	.0275	.0182	.66
9	.0440	.0280	.64
10	.0465	.0290	.63

The average reaction ratio for these eight runs is .65.

The reaction was not stopped at this point but sufficient halide was added to make the reaction ratio one. The red color slowly disappeared upon the addition of the benzal chloride, but the change was not sharp, and for this reason the reaction ratio at the colorless end-point could not be determined.

b). Separation of products. In analyzing the products for these runs the method used by Wimmer[16] in separating the products of the reaction of sodium on benzal chloride was followed. Briefly, this method is as follows. The reaction mass is extracted several times with ether. This ether solution is extracted, first with several portions of distilled water, then with several portions of dilute

hydrochloric acid. These two solutions are kept separate. The ether solution is then dried with anhydrous sodium sulfate and evaporated, which process yields a viscous oil.

c). Identification of products. The three products found by Wimmer were as follows:

Water soluble----------benzylamine

Dilute acid soluble-------diphenyl ethylene diamine

Ether soluble----------1,2,3-triphenyl propane

That these same products were here obtained was established by the following tests, again using the methods of Wimmer (16).

The water solution was acidified with a few cubic centimeters of hydrochloric acid. This solution was then evaporated to dryness on a water bath and the crystalls remaining were recrystallized from a small amount of absolute ethyl alcohol. The melting point of these crystals was 245°7°. The value given in the literature is 246-8°. The dithiocarbamic acid derivative, prepared as described under identification of benzylamine in the benzyl chloride reaction, had a melting point of 126-7°, the same as that given in the literature. These properties were taken as sufficient proof of the presence of benzylamine.

The evaporation of the dilute hydrochloric acid soluble portion left white crystals, which after recrystallization from ethyl alcohol, were identified as symmetrical diphenyl ethylene diamine dihydrochloride. The tests used were the preparation of the dithiocarboxy acid derivative whose

melting point was 131° (literature--132°), of the symmetrical diphenyl ethylene diamine whose melting point was 92° (literature--92°), and the melting point of the dihydrochloride itself, 245-6° (literature---246-8°).

The yellow oil was identified as 1,2,3-triphenyl propane by its boiling point and by its refractive index. The refractive index ($N_d^{20°}$) was 1.6037 and its boiling point 340-350° at 750 mm. These are very close to values obtained by Wimmer and others. Wimmer's values were for boiling point, around 350° C., and for refractive index, $N_d^{20°} = 1.6015$.

d). Quantitative estimation of products. The products were separated as briefly outlined, and the benzylamine weighed as the hydrochloride, the symmetrical diphenyl ethylene diamine as the dihydrochloride, and the triphenyl propane as such. The yields are given in Tables XXVI, XXVII, and XXVIII.

Table XXVI

Yield of Benzylamine

Run	Gram Moles $BzCL_2$	Gram Moles Benzylamine	% Yield
7	.0319	.0060	17.5
10	.0471	.0100	21.0
16	.0442	.0077	18.2

The average yield of benzylamine, based on the amount of benzal chloride used, is 18.9%.

Table XXVII

Yield of Diamine

Run	Gram Moles $BzCl_2$	Gram Moles of Diamine	% Yield
7	.0314	.0032	20.6
16	.0442	.0040	18.1

The average yield for these two runs is 19.4%. There was considerable resinous gum mixed with this portion of the products. This necessitated recrystallization from ethyl alcohol. For this reason losses do occur in this determination.

Table XXVIII

Yield of Triphenyl Propane

Run	Moles $BzCl_2$	Moles Triphenyl Propane	% Yield
8	.0281	.0032	34.2
9	.0449	.0056	37.4
10	.0475	.0052	32.9
12	.0502	.0060	35.9
14	.0517	.0055	31.9

The average yield for the five runs listed is 34.5%. This oil was tested with bromine in boiling carbon tetrachloride to see if any stilbene were present. No bromine was absorbed.

The average yield obtained with calcium is tabulated in Table XXIX along with the average yields of the same compounds when sodium was used as the metal (13).

Table XXIX

Product	Ca Yield	Na Yield
Benzyl amine	18.9%	35 %
Sym. Diphenyl ethylene diamine	19.4	20
1,2,3-Triphenyl propane	34.5	26
Total percent	72.8	81

The amount of material lost is large, partly due to large manipulative errors, and partly to the resinous material formed. This resinous material necessitated the recrystallization of both of the amines formed.

SUMMARY OF EXPERIMENTAL RESULTS

Benzyl chloride reacts with calcium in liquid ammonia solution in the ratio of 1.17 gram moles of halide to one gram-atom of calcium. The main products of the reaction are toluene and bibenzyl; the former was formed in 73% yield and the latter in 27% yield. These yields are based upon the amount of benzyl chloride used. If an excess of benzyl chloride is used, i.e., two moles of benzyl chloride to one atom of calcium, bibenzyl, stilbene, toluene, and benzyl-amine can be isolated from the reaction mixture. The yields based on benzyl chloride are as follows:

Benzyl amine----------15%

Stilbene----------17.6%

Bibenzyl----------24.6%

The toluene accounts for the remainder of the benzyl chloride, about 40%.

Benzal chloride is reduced in liquid ammonia solution using calcium in the same general manner that it is reduced when sodium is the reacting metal. An intermediate red end-point, the point at which the color of the solution changes from blue to red, is observed when the ratio of gram moles of benzal chloride to gram-atoms of metal of .67. The main products of this reaction are diphenyl ethylene diamine (symmetrical), benzyl amine, and 1,2,3-triphenyl propane. They are obtained in yields of 19.4%, 18.9%, and 34.5%

respectively, based on the amount of benzal chloride used.

The heptyl bromide reaction is akin to that of the benzyl chloride. Tetradecane is formed in about 34% yields, and the rest of the organic radical is converted into heptane. Heptyl bromide is not reactive enough to react with calcium amido-bromide to an appreciable extent when added in excess.

MECHANISM OF REACTIONS

The reactions of calcium with organic halides in liquid ammonia solution proceed, as was postulated in the case of the alkali metals, with the intermediate formation of an organo-alkali compound, the nature of which governs the subsequent reaction. With benzyl chloride and heptyl bromide an organo-metallic is formed that exhibits the reaction of members of Class I of the organo-alkali eompounds, outlined in the introduction to this thesis. This equation for its formation is as follows:

$$C_6H_5\text{-}CH_2Cl + Ca \longrightarrow C_6H_5\text{-}CH_2\text{-}CaCl$$

This may then couple with more halide to form the dimer:

$$C_6H_5\text{-}CH_2Cl + C_6H_5\text{-}CH_2\text{-}CaCl \longrightarrow C_6H_5\text{-}CH_2CH_2\text{-}C_6H_5 + CaCl_2$$

Or it may react with the solvent to give the corresponding hydrocarbon:

$$C_6H_5\text{-}CH_2\text{-}CaCl + NH_3 \longrightarrow C_6H_5\text{-}CH_3 + Ca(NH_2)Cl$$

If additional benzyl chloride is added the presence of the calcium amido-chloride is shown by the following reactions, characteristic of amides:

$$2\ C_6H_5\text{-}CH_2Cl + 2\ Ca(NH_2)Cl \longrightarrow C_6H_5\text{-}CH{=}CH\text{-}C_6H_5 + 2NH_3Cl + 2CaCl_2$$

$$C_6H_5\text{-}CH_2Cl + Ca(NH_2)Cl \longrightarrow C_6H_5\text{-}CH_2NH_2 + CaCl_2$$

The reaction of the benzal chloride is illustrative of the reactions given by members of Class II of the general classification of organo-alkalis. The reaction, according

to the mechanism, proceeds with the initial formation of a benzylidene free radical:

$$C_6H_5\text{-}CHCl_2 + Ca \longrightarrow C_6H_5\text{-}CH= + CaCl_2$$

This may react with the solvent or disproportionate:

$$C_6H_5\text{-}CH= + NH_3 \longrightarrow C_6H_5\text{-}CH_2NH_2$$

$$2\ C_6H_5\text{-}CH= \longrightarrow C_6H_5\text{-}CH_2\text{-} + C_6H_5\text{-}C\equiv$$

Coupling of the benzylidene and benzyl radicals will produce 1,2,3-triphenyl propane:

$$C_6H_5\text{-}CH= + 2\ C_6H_5\text{-}CH_2\text{-} \longrightarrow C_6H_5\text{-}CH_2\text{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}\text{-}CH_2\text{-}C_6H_5$$

The reaction of the triple bonded free radical with the solvent ammonia produces the third main product, symmetrical diphenyl ethylene diamine:

$$2\ C_6H_5\text{-}C\equiv + 2\ NH_3 \longrightarrow C_6H_5\text{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{---}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{-}C_6H_5$$

A definite conclusion can be drawn, namely, that neither the metal involved nor the type of organic radical employed alone determine the type of reaction. Benzyl chloride gives one reaction with sodium and potassium, and another with calcium. Calcium gives one type of reaction with benzyl chloride and another with benzal chloride. The type of reaction occurring with the metals in liquid ammonia proceeds first with the formation of an intermediate organo-metallic compound whose stability and reactivity determine the nature of subsequent reactions.

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