THE CONSTITUTION OF ORGANO-MAGNESIUM COMPOUNDS AND
THE MECHANISM OF GRIGNARD REACTION.

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DISSERTATION

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for the Degree of Doctor of Philosophy in the
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By

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PREFACE

The organo magnesium compounds have assumed an importance in synthetic organic chemistry unsurpassed by any other synthetic process. The constitution of the Grignard reagents and the mechanism of their condensing actions have formed a fascinating field of research for the past twenty years. Notwithstanding the enormous amount of research along these lines no general mechanism has been discovered which will serve to explain all the reactions alkyl magnesium halides are known to undergo.

During the progress of this research about eighteen hundred journal articles have been reviewed. In the following pages a general reaction mechanism has been evolved and applied which serves to correlate and clarify many heretofore unrelated facts regarding the reactions of organo magnesium halides. The results of almost three years of experimental research are offered in support of the ideas advanced.

The author wishes to acknowledge his indebtedness to the Ohio State University for a University Scholarship during the years 1923-24 and 1924-25 also for the Graduate Assistantship 1925-26 which has made it possible for him to carry on the investigation. He also desires to express his thanks to Prof. C.E. Boord for the constructive suggestions and valuable advice given during the progress of the research and preparation of the dissertation.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td><strong>Part I</strong></td>
<td></td>
</tr>
<tr>
<td>The Constitution of Grignard Reagents</td>
<td>3</td>
</tr>
<tr>
<td>The Action of RMgX upon Aldehydes and Ketones</td>
<td>16</td>
</tr>
<tr>
<td>The Action of RMgX upon Olefine Oxides</td>
<td>21</td>
</tr>
<tr>
<td>The Action of RMgX upon Malohydins</td>
<td>32</td>
</tr>
<tr>
<td>The Action of CH3MgI upon -Hydroxy-, Amino-, and Imino-Derivatives</td>
<td>39</td>
</tr>
<tr>
<td>The Action of ROMgX upon ROMgX</td>
<td>42</td>
</tr>
<tr>
<td><strong>Part II</strong></td>
<td></td>
</tr>
<tr>
<td>The Action of RMgX upon Alkyl and Aryl Halides</td>
<td>47</td>
</tr>
<tr>
<td><strong>Part III</strong></td>
<td></td>
</tr>
<tr>
<td>The Mechanism of &quot;Olefinic Splitting&quot; by RMgX</td>
<td>67</td>
</tr>
<tr>
<td>Olefinic Splitting by the Separation of RMgX</td>
<td>67</td>
</tr>
<tr>
<td>Olefinic Splitting by the Separation of ROMgX</td>
<td>70</td>
</tr>
<tr>
<td>Olefinic Splitting by the Separation of R2MgX</td>
<td>72</td>
</tr>
<tr>
<td>Olefinic Splitting by the Separation of MgX2</td>
<td>76</td>
</tr>
<tr>
<td><strong>Part IV</strong></td>
<td></td>
</tr>
<tr>
<td>The Action of RMgX upon Simple Ethers</td>
<td>81</td>
</tr>
<tr>
<td><strong>Part V</strong></td>
<td></td>
</tr>
<tr>
<td>The Reducing Action of RMgX upon Aldehydes and Ketones</td>
<td>86</td>
</tr>
<tr>
<td>The Reduction of Aldehydes by Compounds of Type ROCHOMgX &quot;Ketonic Splitting&quot;</td>
<td>96</td>
</tr>
<tr>
<td>Other Forms of Ketonic Splitting</td>
<td>99</td>
</tr>
<tr>
<td>&quot;Ketonic Splitting&quot;</td>
<td>103</td>
</tr>
<tr>
<td>&quot;Aldehydic Splitting&quot;</td>
<td>106</td>
</tr>
<tr>
<td>&quot;Ester Splitting&quot;</td>
<td>106</td>
</tr>
<tr>
<td>Reduction of Compounds with Two Functional Groups</td>
<td>113</td>
</tr>
<tr>
<td>General Summary and Conclusions</td>
<td>118</td>
</tr>
</tbody>
</table>
THE CONSTITUTION OF ORGANOMAGNESIUM COMPOUNDS AND
THE MECHANISM OF THE REACTIONS OF GRIGNARD REAGENTS

INTRODUCTION

During the progress of some earlier researches in this laboratory a series of normal primary alcohols was required. In attempting to apply the reaction of Grignard reagents upon ethylene oxide to the preparation of this material the previously recognized difficulties of the method were more forcibly impressed upon us. The yield, which is never high, becomes smaller as the molecular weight of the alkyl magnesium halide is increased. This decrease in yield of the 'normal' condensation product is accompanied by a marked increase in the yield of the by-product, ethylene halohydrin. It is true that increasing the molecular proportions of the Grignard reagent in part remedies this defect but the desirability of finding a reaction mechanism which would explain more clearly the vagaries of the reaction led to a study of the problem. The success of this attempt was so satisfying that the application of the same ideas had been extended to other types of Grignard reactions and form the primary purpose of the present research.

Not all of the ideas involved in this discussion are new and copious references to the literature are given.
About eighteen hundred articles from the original literature were reviewed. Such data as seemed pertinent to this discussion has been included in tabular form. Each type reaction has been treated in a separate section. The experimental work performed by the author has been included in each section in order to enable the reader to follow more closely the argument as presented.
THE CONSTITUTION OF GRIGNARD REAGENTS

The Free, Separate and Independent Existence of Compounds of the Type RMgX.

From the properties of the organo-magnesium compounds, Grignard at first concluded that they were formed accordingly to the equation:

\[ \text{Mg} + \text{RX} \rightarrow \text{RMgX} \]

This is true of those complexes formed in indifferent solvents. Tschelinzewff has shown that benzene, toluene, xylene, hexane, petroleum ether, benzine, and terpenic hydrocarbons can be used as solvents for preparing Grignard reagents. A trace of dimethyl aniline greatly facilitates the reaction and iodine assists in starting it. The complexes formed in these solvents are compounds of the type R - Mg-X.

These complexes, R-Mg-X, can be directly prepared from RX and Mg in the absence of a solvent or of any catalyst. Spencer and his students showed that aryl bromides and iodides react directly with magnesium when heated. Aryl chlorides and all the lower alkyl halides up to the butyl derivatives, only react with magnesium when heated to about 270° in a sealed tube for several hours.

1. Thesis (L'Univ. de Lyon, 1901) 2. Ber. 37, 4535-4540 (1904)
Alkyl halides higher in the series than the butyl derivatives react with magnesium when they are heated with it at their boiling point for a few minutes.

These individual complexes can also be obtained from ethereal complexes by the complete elimination of ether in vacuo as shown by Jolibois. 4

The Separate And Independent Existence Of The Mono- And Di-Etheral Complexes.

Grignard 5 observed that the reaction between CH₃I and Mg was much facilitated in the presence of ether, and that an addition product having the composition Et₂O·CH₃Mg-I remains after the excess of ether has been removed by heating for several days in a vacuum.

Blaise 6 showed that Et₂O·C₂H₅-MgI began to partially lose ether in vacuo at 100-125°C, while Et₂O·C₂H₅-Mg-Br began to lose one half of ether at 145°C.

Zerewitinoff 7 succeeded to isolate a crystalline compound of CH₃-MgI with amyl ether (C₅H₁₁)₂O. CH₃-Mg-I.

Tschechinzeff showed that the addition of ether to a benzene solution of R-MgX caused the evolution of definite and equal amounts of heat for each of the first two

molecular quantities of ether added; the subsequent addition of ether caused little thermal disturbance. He also determined that the amount of ethyl ether which will combine with one mole of $R\cdot Mg\cdot X$ to be exactly two moles. These facts led him to announce the existence of derivatives of the type $2\cdot Et\cdot O\cdot R\cdot Mg\cdot I$.

Pickard$^9$ and Kenyon found that tribenzyl-phosphine oxide may replace ether in the formation of $R\cdot Mg\cdot X$ and succeeded in obtaining a compound having, in the crystalline form, the composition: $2\cdot (C_6H_5CH_2)_3PO\cdot CH_3MgI$.

The Present Knowledge of The Structure of
The Ether Complexes.

A definite idea regarding the distribution of valences in the ether addition products was first put forward by Baeyer and Villiger, who, with the work of Collie and Tickle in mind, believed that they had in this class of compounds further evidence to strengthen their belief in the existence of tetravalent oxygen. Three years previously Collie and Tickle had found that dimethyl pyrone formed a well defined addition product with \( \text{HCl} \) to which they assigned an oxonium structure:

\[
\begin{align*}
\text{H} & \quad \text{Cl} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{CH} & \quad \text{CH}
\end{align*}
\]

Accordingly, Baeyer and Villiger represented the substance \((\text{C}_2\text{H}_5)_2\text{O} \cdot \text{C}_6\text{H}_3\cdot\text{Mg-I}\) by a somewhat analogous oxonium arrangement:

\[
\begin{align*}
\text{C}_2\text{H}_5 & \quad \text{O} \\
\text{C}_2\text{H}_5 & \quad \text{Mg-}\text{H}_3
\end{align*}
\]

The work of Archibald and McIntosh on the basic properties of oxygen showed that ethyl ether forms definite crystalline substances with \( \text{HCl}, \text{HBr}, \) and \( \text{HI} \) having the

composition, $\text{Et}_2\text{O} \cdot 0.5\text{HCl}$, $\text{Et}_2\text{O} \cdot \text{HBr}$, and $\text{Et}_2\text{O} \cdot \text{HI}$ respectively. This would seem to lend support to the Baeyer and Villiger method of formulation. It is shown in the experimental part of this paper that magnesium does not act upon an ethereal solution of hydrochloride, but with an ethereal solution of $\text{HBr}$ yields hydrogen and $\text{MgBr}_2$. This would seem to indicate the formation of $\text{Et}_2\text{O} \cdot \text{H-Mg-X}$ which acts immediately on $\text{Et}_2\text{O} \cdot \text{HBr}$ giving $\text{H}_2$ and $\text{MgBr}_2$.

Further support is given to the Baeyer and Villiger structure by the work of Blaise$^{13}$ who formulated the complex $2\text{Et}_2\text{O} \cdot \text{MgI}_2$ as

\[
\begin{array}{c}
\text{Et} \quad \text{I} \\
\text{Et} \quad \text{Mg} \\
\text{Et} \quad \text{I} \\
\text{Et}
\end{array}
\]

In its reaction with benzoyl chloride the products are ethyl iodide, ethyl benzoate, and magnesium chloride and the following equation is suggested by Blaise as representing the reaction:

\[
\text{Et} \quad \text{I} \\
\text{Et} \\
\text{Et}
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 2\text{PhCOCl} = 2\text{Et} \quad \text{I} + 2\text{PhCOEt} \quad \text{MgCl}_2
\]

The fact of oxonium salt formation between ethers and halogen acids and the formation of an analogous dithyl ether complex by magnesium halides seems to lend positive support to the Baeyer type of formulation. One can then

13. Compt. rend., 138, 1211-1213 (1904);
with some plausibility make the placement of an ether molecule upon the salt side of the simple complex, R-Mg-X.

Grignard\textsuperscript{14} himself adopted an oxonium structure, but distributed the four valences of oxygen in a different manner:

$$\begin{array}{c}
R \quad \text{C}_2\text{H}_5 \\
\text{I-Mg} \quad \text{C}_2\text{H}_5
\end{array}$$

The absence of evidence of oxonium salt formation between ethers and alkyl halides and of the formation of analogous diether complexes by magnesium dialkyls are the principle objections to the Grignard's structure for the mono-ether complex.

G. Stadnichoff\textsuperscript{15} has undertaken to defend the Grignard formula. His theory concerning the mechanism of the reaction involves first the formation of an oxonium compound as shown in (a). This product is then reacted upon by magnesium to form a mono-etherate as in (b). Upon hydrolysis (c) a new oxonium compound is formed which undergoes decomposition in several directions as indicated in (d).

$$\begin{array}{c}
R^* \quad 0 + R' \quad X \quad \rightarrow \quad R'^* \quad O \quad X' \\
R^* \quad 0 \\
\text{R}^* \quad \text{O} \quad \text{X}
\end{array} \quad \text{(a)}$$

Apparent strength is given to the hypothesis of Staudnikoff by the very multiplicity of products obtained. As a concrete example of which the following case may be cited: The reaction product of magnesium and propyl iodide formed in the presence of diphenyl-carbinol butyl ether upon decomposition with dilute sulfuric acid yielded Ph₂CH-CHPh₂, Ph₂CHPh, H₂ and unchanged Ph₂CH-0-Bu.

A. I. Gorski, in his criticism of the work of Staudnikoff, pointed out the possibility of interpreting his results on the basis of hydrolysis and reduction, or of direct reaction, of the ethers from analogy to the behavior of the zinc alkyls.

\[
(Ph)_3C-O-C_2H_5 + PrMgI = (Ph)_3CH + EtOMgI + C_3H_6
\]

His argument is further strengthened by a consideration of

the behavior of RMgX towards other oxygenated compounds.

The Baeyer formulation is unsatisfactory in that it does not explain the general mechanism of the reaction. Either replacement or addition takes place in the first step of the reaction between R-MgX-Et₂O and an aldehyde or ketone in the formation of an oxonium complex¹⁷ which may or may not undergo rearrangement into

\[
\begin{align*}
\text{R} & \overset{\text{H}}{\longrightarrow} R \overset{\text{C} = 0}{\longrightarrow} R \\
\text{R} & \overset{\text{OMgX}}{\longrightarrow} R \overset{\text{C} = 0}{\longrightarrow} R
\end{align*}
\]

the reaction takes place

If by replacement, Baeyer's formula can not explain the principle products obtained.

\[
\begin{align*}
\text{Et} & \overset{0}{\longrightarrow} \overset{\text{X}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \\
\text{Et} & \overset{0}{\longrightarrow} \overset{\text{Mg-R}}{\longrightarrow} \overset{\text{X}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R}
\end{align*}
\]

\[
\begin{align*}
\text{H₂O} & \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R}
\end{align*}
\]

If it begins by addition, the addition product itself has a structure in agreement with the formulation used by Grignard to explain the principle product obtained.

\[
\begin{align*}
\text{Et} & \overset{0}{\longrightarrow} \overset{\text{X}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \\
\text{Et} & \overset{0}{\longrightarrow} \overset{\text{Mg-R}}{\longrightarrow} \overset{\text{X}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R}
\end{align*}
\]

\[
\begin{align*}
\text{Et} & \overset{0}{\longrightarrow} \overset{\text{Mg-R}}{\longrightarrow} \overset{\text{O=C}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{Et}}{\longrightarrow} \overset{0}{\longrightarrow} \overset{\text{X}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{H₂O}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{C} = 0}{\longrightarrow} \overset{\text{R}}{R} \overset{\text{R}}{\longrightarrow} \overset{\text{OH}}{R}
\end{align*}
\]

¹⁷. Klages, Ber. 36, 2633-2648 (1902); Neisenheimer, Ann., 442, 180, (1925); Hess Ann., 437, 258 (1924); Aborn and Stapler, Ber. 38, 3264 (1904); Hess and Tischer, Ber. 45, 912 (1912); J. Leriche, Compt. rend. 148, 1611 (1909).
Baeyer and Villiger's formula suggests the existence of two isomers, 
\[
\text{R}_\text{MgR}^1 \quad \text{R}_\text{MgR}^2 \\
\text{R}^1 > \text{X} \quad \text{R} > \text{X}
\]
which would be identical according to Grignard formula. Both Tscheliningoff\(^{18}\) and Thorp\(^{19}\) and Kamml claimed to have obtained evidence of isomerism. Grignard,\(^{20}\) however, has claimed that his formula also admits of the existence of isomerides, since the two addition valences of the oxygen atom have not the same value as the original two.

Other workers have preferred to refrain from giving these new ether complexes a definite structure and have represented them merely as molecular combinations. Werner\(^{21}\) prefers to regard them as co-ordinated compounds analogous to the cobaltamines.

\[\begin{bmatrix}
\text{Et} \\
\text{Et} > 0 & \text{---MgR} \\
\text{Et} > 0 & \text{---MgR}
\end{bmatrix}_x\]

While Thorp and Kamml regard them as loose molecular combinations.

\[\begin{bmatrix}
\text{Et} \\
\text{Et} > 0 & \text{---Mg} \\
\text{Et} > 0 & \text{---Mg}
\end{bmatrix}_x\]

Considerations such as those above have led other workers to formulate the diether complexes in the following ways: Tscheliningoff\(^{23}\) regards the second ether molecule.

---

as an addition to the iodine atom to form an iodoxy type of derivative.

\[
\begin{align*}
\text{Et} & \quad \text{>0} \quad \text{MgR} \\
\text{Et} & \quad \text{I=0} \quad \text{Et}_2
\end{align*}
\]

Meisenheimer on the other hand believes both ether molecules to be loosely bound to magnesium.

\[
\begin{align*}
\text{Et}_2\text{O} & \quad \text{>Mg} \quad \text{R} \\
\text{Et}_2\text{O} & \quad \text{>Mg} \quad \text{X}
\end{align*}
\]

Grignard\textsuperscript{25} has suggested that these dietherates may be represented as follows:

\[
\begin{align*}
\text{Et} & \quad \text{>0} \quad \text{R} \quad \text{I=0} \quad \text{Et} \\
\text{Et} & \quad \text{>0} \quad \text{Mg} \quad \text{Et}
\end{align*}
\]

In addition to the considerations recited above the attention should be directed to the thermal data compiled by Tschinzeff which does not seem to have been given all the consideration to which it is probably entitled. This investigator measured carefully the heat evolved by the addition of various ethers and tertiary amines in molar and dimolar quantities to benzene solutions of propyl magnesium iodide. The results are set forth below in tabular form. Table I shows the heat evolved when the additions

25.Loc. cit.
are made directly to the solution of the free alkyl magnesium halide in benzene solution. Table II shows the heat involved by various replacements.

Table I

Heats evolved in the formation of mono and di-complexes of n-propyl magnesium iodide (Tschelinzeff 26).

\[
\begin{align*}
\text{NC}_3\text{H}_7\text{Mgl} + 1(\text{C}_2\text{H}_5)\text{I}_2 & = \text{C}_3\text{H}_7\text{Mgl} \cdot (\text{C}_2\text{H}_5)\text{I}_2 \quad \text{0} + 6.23 \text{ Cal.} \\
\text{NC}_3\text{H}_7\text{Mgl} + 2(\text{C}_2\text{H}_5)\text{I}_2 & = \text{C}_3\text{H}_7\text{Mgl} \cdot 2(\text{C}_2\text{H}_5)\text{I}_2 \quad \text{0} + 12.60 \text{ Cal.} \\
\text{NC}_3\text{H}_7\text{Mgl} + \text{I}(\text{C}_6\text{H}_{11})\text{I}_2 & = \text{C}_3\text{H}_7\text{Mgl} \cdot (\text{C}_6\text{H}_{11})\text{I}_2 \quad \text{0} + 5.91 \text{ Cal.} \\
& + 2(\text{C}_6\text{H}_{11})\text{I}_2 = \text{C}_3\text{H}_7\text{Mgl} \cdot 2(\text{C}_6\text{H}_{11})\text{I}_2 \quad \text{0} + 10.31 \text{ Cal.} \\
& + (\text{C}_2\text{H}_5)_\text{I}_3 = \text{C}_3\text{H}_7\text{Mgl} \cdot (\text{C}_2\text{H}_5)_\text{I}_3 \quad \text{0} + 11.70 \text{ Cal.} \\
& + (\text{C}_6\text{H}_7)_\text{I}_3 = \text{C}_3\text{H}_7\text{Mgl} \cdot (\text{C}_6\text{H}_7)_\text{I}_3 \quad \text{0} + 10.32 \text{ Cal.} \\
& + (\text{C}_5\text{H}_{11})\text{I}_3 = \text{C}_3\text{H}_7\text{Mgl} \cdot (\text{C}_5\text{H}_{11})\text{I}_3 \quad \text{0} + 9.00 \text{ Cal.} \\
& + \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 = \text{C}_3\text{H}_7\text{Mgl} \cdot \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 \quad \text{0} + 3.81 \text{ Cal.} \\
& + \text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 = \text{C}_3\text{H}_7\text{Mgl} \cdot \text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \quad \text{0} + 0.98 \text{ Cal.}
\end{align*}
\]

Table II

Heats evolved by mono or di-complexes by further addition or replacement: R= NC3H7 (Tschelinzeff 26)

\[
\begin{align*}
\text{RMgl} \cdot 2(\text{C}_5\text{H}_{11})\text{I}_2 & \rightarrow \text{RMgl} \cdot 2\text{Et}_2 \quad \text{0} + 2.09 \text{ Cal.} + 2(\text{C}_5\text{H}_{11})\text{I}_2 \\
\text{RMgl} . \text{N}-(\text{CH})_3\text{NC}_3\text{H}_7 & \rightarrow \text{RMgl} . \text{N}(\text{CH}_3)_3 \quad \text{6.43 Cal.} + \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2
\end{align*}
\]

26. Ber. 41, 646-655 (1908)
RMgI. (C₆H₅)N-(CH₃)₂ 1 (Et₂O) → RMgI. C₆H₅N-(CH₃)₂ Et₂O + 5.22 Cal.
RMgI. C₆H₅N-(CH₃)₂ Et₂O 1Et₂O → RMgI. 2Et₂O + 3.56 Cal. + C₆H₅N(CH₃)₂
RMgI. C₆H₅N(CH₃)₂ 2Et₂O → RMgI. 2Et₂O + 8.66 Cal + C₆H₅N(CH₃)₂

RMgI. N(C₆H₅)₃ 1Et₂O → RMgI. N(C₂H₅)₃ Et₂O + 3.91 Cal.
RMgI. N(C₂H₅)₃ Et₂O 1Et₂O → RMgI. N(C₂H₅)₃ Et₂O + 0 Cal + Et₂O
RMgI. N(C₂H₅)₃ 2Et₂O → RMgI. N(C₂H₅)₃ Et₂O + 3.91 Cal. + Et₂O

RMgI. N(C₃H₇)₃ 1Et₂O → RMgI. N(C₃H₇)₃ Et₂O + 3.82 Cal.
RMgI. N(C₃H₇)₃ Et₂O 1(Et₂O) → RMgI. N(C₃H₇)₃ Et₂O + 0 + Et₂O
RMgI. N(C₃H₇)₃ 2Et₂O → RMgI. N(C₃H₇)₃ Et₂O + 3.88 Cal + Et₂O

The above thermal data seems to indicate two things clearly.

First, the individual complex RMgX is endowed with a definite quantity of molecular free energy which in the case of C₃H₇MgI is equal to 12.60 calories. The sum of molecular free energy of two molecules of ether is about equal to 12 calories. This may be the explanation for the excellence of ethyl ether as a solvent for the preparation of R-MgX. 2Et₂O. Second, this molecular free energy while not rigidly fixed is localized about two points upon the molecular structure of the alkyl magnesium halide. An ether molecule can be added to each of these points, while an amine molecule can be added to only one. More than one half of molecular free energy may be neutralized by one mole of a given neutralizing agent. The remaining
free energy can then be neutralized by our mole of another neutralizing agent which would normally release a greater amount.

From a consideration of all the evidence at hand the author is inclined to agree with Grignard as to the constitution of the diether complex. This dietherate probably stands in equilibrium with both the Baeyer and Grignard monoetherate forms as is indicated below. Hibbert\(^2\)\(^7\) has also suggested that the Baeyer and Grignard forms stand in dynamic equilibrium but not in the manner indicated here.

\[
\begin{align*}
\text{Et}_2\text{O} & \xrightleftharpoons{\text{Mg}} \text{Et}_4\text{O} \\
\text{Et}_2\text{O} & \xrightleftharpoons{\text{Mg}} \text{Et}_2\text{O} \\
\text{Et}_2\text{O} & \xrightleftharpoons{\text{Mg}} \text{Et}_2\text{O}
\end{align*}
\]

Justification of this viewpoint is to be found in the following facts.

First, the ether complexes can be readily decomposed with the loss of first one mole and finally both moles of ether. When such a decomposition takes place it always does so with the separation of the original individual complex, \(\text{R-Mg-X}\).

Second, in some cases viz. ethylene oxide, as will be shown in the experimental part of this paper, a definite energy change is observed which may be attributed to the rearrangement of the structural valency bonds.

Third, the work of Tschelinzerl seems to show that the first reaction between a Grignard reagent and any reactant is addition to form a molecular complex analogous to the ether complexes. The second phase of the reaction consists of a readjustment of the true structural bonds.

Application of the above equilibrium to an analysis of the results obtained when Grignard's reagents are caused to react with aldehydes, ketones or related compounds.

1. Attention should be called to the fact that in the above formulation the Baeyer and Grignard type of monoether complexes exist in equilibrium through the dietherate. Hibbert has also suggested that these two forms exist in dynamic equilibrium.

2. The relative amounts of these two forms will depend directly upon the nature of R- and the nature of λ.

3. If we now consider for a moment the reaction which will take place when any reactant such as acetone is added to the above equilibrium mixture, addition seems
to be the first and logical consequence.

The logical phase of the reaction would seem to be a rearrangement of the structure bonds to form $A_2$ and $B_2$. The hydrolysis will then yield in either case the normal condensation products or the original ketone as the case may be.

4. Since the point of equilibrium between $A$ and $B$ depends directly upon the nature of $R$ and of $X$, the yield of normal product may be expected to vary in precisely the same manner. That such is the case is evident by reference to the following tabulation of the yields.
Table III
(Paul Ablemann, Ber. 40, 4589-4590 (1907))

<table>
<thead>
<tr>
<th>Grignard reagent</th>
<th>reactant</th>
<th>Principal product</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃MgI</td>
<td>CH₃-CH=C(Me)CH₀</td>
<td>CH₃-CH=C(Me)CH(Me)OH</td>
<td>70%</td>
</tr>
<tr>
<td>C₂H₅MgBr</td>
<td>&quot;</td>
<td>CH₃-CH=C(Me)CH(Et)OH</td>
<td>64%</td>
</tr>
<tr>
<td>NC₃H₇MgBr</td>
<td>&quot;</td>
<td>CH₃-CH=C(Me)CH(Pr)OH</td>
<td>48%</td>
</tr>
<tr>
<td>isoc₃C₇H₇MgBr</td>
<td>&quot;</td>
<td>CH₃-CH=C(Me)CH(isoPr)OH</td>
<td>49%</td>
</tr>
<tr>
<td>isoc₄C₉H₁₇MgBr</td>
<td>&quot;</td>
<td>CH₃-CH=C(Me)CH(isobu)OH</td>
<td>45%</td>
</tr>
</tbody>
</table>

Table IV

<table>
<thead>
<tr>
<th>Grignard reagent</th>
<th>Reactant</th>
<th>Normal product</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tert. C₄H₉MgCl²⁸</td>
<td>paraformaldehyde (CH₃)₂C₂H₂-OH</td>
<td>30-40%</td>
<td></td>
</tr>
<tr>
<td>Tert. C₄H₉MgBr²⁹</td>
<td>&quot;</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>Tert. C₄H₉MgI²⁹</td>
<td>&quot;</td>
<td>2%</td>
<td></td>
</tr>
</tbody>
</table>

Table V

[Petellier, Compt. rend. 146, 843 (1908)]

<table>
<thead>
<tr>
<th>Grignard reagent</th>
<th>Reactant</th>
<th>Normal product</th>
<th>yield %</th>
<th>considerable</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrMgCl</td>
<td>(CH₃)₃CCOR</td>
<td>(CH₃)₂OC(Pr)₂OH</td>
<td></td>
<td>smaller</td>
</tr>
<tr>
<td>PrMgBr</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td>amount.</td>
</tr>
<tr>
<td>PrMgI</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Table VI

Tissier and Grignard, *compt. rend.* 134, 107-108 (1902)

<table>
<thead>
<tr>
<th>Grignard reagent</th>
<th>Reactant</th>
<th>Normal Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅MgBr</td>
<td>H₂C=O</td>
<td>NC₃H₇=OH</td>
<td>65</td>
</tr>
<tr>
<td>N-C₃H₇MgBr</td>
<td></td>
<td>NCH₄H₉=OH</td>
<td>55</td>
</tr>
<tr>
<td>(CH₃)₂CH-C₆H₄-CH₂MgBr</td>
<td></td>
<td>isoc₆H₁₃OH</td>
<td>70</td>
</tr>
</tbody>
</table>

From the above tables it is evident that the yield of normal condensation product is greatest for RMgCl intermediate for RMgBr and least for RMgI. It is also apparent that the yield of normal product is greatest when R is methyl and gradually diminishes as the number of carbon atoms in R is increased. In the latter case an exception must be made to include the remarkable influence exercised by isomerization in any given alkyl grouping. Iso compounds always give higher yields than the corresponding normal compounds and the same ordering of groupings is formed as was found by Conant and others in determining the reactivity of alkyl halides.

5. Attention should also be called to the fact that the yield of normal condensation product while varying slightly with the nature of the compound with which the reagent is condensed it remains remarkable constant for any given compound, RMgI.
**Table VII**


<table>
<thead>
<tr>
<th>Grignard reagent</th>
<th>Oxygenated Compounds</th>
<th>Normal products yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH₃MgI</td>
<td>PhCO₉H₁₀⁺ M⁻</td>
<td>PhCH₂OH₂⁺ C₆H₅⁺ M⁻</td>
</tr>
<tr>
<td>2. &quot;</td>
<td>CH₃COOCH₃</td>
<td>(CH₃)₂COH</td>
</tr>
<tr>
<td>3. &quot;</td>
<td>CH₃COO⁻ C₁₀H₈⁺</td>
<td>(CH₃)₂COH₆⁺ C₁₀H₈⁺</td>
</tr>
<tr>
<td>4. &quot;</td>
<td>PhCO⁻</td>
<td>Ph(CH₃)₂COH</td>
</tr>
<tr>
<td>5. &quot;</td>
<td>PhCOO⁻ C₃H₇⁻</td>
<td>Ph(CH₃)₂COH</td>
</tr>
<tr>
<td>6. &quot;</td>
<td>CH₃COO⁻ C₃H₇⁻</td>
<td>(CH₃)₃COH</td>
</tr>
<tr>
<td>7. &quot;</td>
<td>CH₃CHO</td>
<td>(CH₃)₂COH</td>
</tr>
<tr>
<td>8. &quot;</td>
<td>CH₃CO⁻ Ph</td>
<td>(CH₃)₂PhCOH</td>
</tr>
<tr>
<td>9. &quot;</td>
<td>EtCH=CMcCHO</td>
<td>(Et-CH=CMc)CH(Me)OH</td>
</tr>
</tbody>
</table>

**Table VIII**

(Grignard, Loc. cit.)

<table>
<thead>
<tr>
<th>Grignard reagent</th>
<th>Oxygenated Compounds</th>
<th>Normal Products</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. EtMgBr</td>
<td>(Me)₂C=C(CH₂)₂CH(Me)CH₂CHO</td>
<td>(Me)₆C=C(CH₂)₆CH</td>
<td>78%</td>
</tr>
<tr>
<td>2. &quot;</td>
<td>EtOCHO</td>
<td>(Et₂CHOH)</td>
<td>73%</td>
</tr>
<tr>
<td>3. &quot;</td>
<td>Ph-CHO</td>
<td>(Ph)(Et)CHOH</td>
<td>70-83%</td>
</tr>
<tr>
<td>4. &quot;</td>
<td>H₂CO</td>
<td>C₃H₇OH</td>
<td>65%</td>
</tr>
</tbody>
</table>

**Table IX**

(Grignard, Loc. cit.)

<table>
<thead>
<tr>
<th>Grignard reagent</th>
<th>Oxygenated compound</th>
<th>Normal Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. IsoAmMgBr</td>
<td>PhCHO</td>
<td>(Ph)(C₅H₁₁)CHOH</td>
<td>56%</td>
</tr>
<tr>
<td>2. &quot;</td>
<td>(Me)₂C₆O</td>
<td>(Me)₂(C₅H₁₁)COH</td>
<td>46%</td>
</tr>
</tbody>
</table>
3. IsoAmMgBr \rightarrow MeCOOR \rightarrow Me(C_6H_{11})_2COH

4. " \rightarrow MeCH=CH-CHO \rightarrow (MeCH=CH)(C_5H_{11})CHOH

5. " \rightarrow HOC-CH || || HOC-O-C-CHO \rightarrow (C_3H_5O)(C_5H_{11})CHOH

The ACTION of R-Mg-X UPON ETHYLENE OXIDES

Following the mechanism indicated in the previous pages, ethylene oxide may be expected to react with the two members of the equilibrium mixture of monoetherates to form first addition products as indicated by A and B.
The second phase of the reaction will be a rearrangement of the structural bonds in A. and B. to form the addition products indicated. The product from A. upon hydrolysis will yield the normal condensation product, a primary alcohol. The product from B. will yield the halohydrin of the olefine oxide used.

Blaise\textsuperscript{1} was apparently the first to point out that the halohydrin was one of the products of the reaction between RMgX and an olefine oxide. Grignard\textsuperscript{2} seems to have been the first to use the method for preparing primary alcohols. The latter worker is inclined to attribute the formation of the halohydrin to the reaction between unchanged ethylene oxide and anhydrous magnesium halide.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{O} + \text{MgBr}_2 & \rightarrow \text{CH}_2\text{Br} \text{MgBr}_2 \\
\text{CH}_2\text{OH} + \text{Br}_2 \text{Mg} & \rightarrow \text{CH}_2\text{Br} \text{MgBr}_2 \\
\end{align*}
\]

Accepting for the moment the validity of the mechanism outlined above it is evident the relative amounts of A. and B. formed will depend upon the nature of R- and the nature of X-. If this is true the yield or normal product, primary alcohol, may be expected to diminish as the number of carbon atoms in the alkyl group R-is increased. Reference to the tables below

---

1. Compt. rend., 134, 551-53 (1902) 2; Compt. rend., 136, 1280-62 (1903)
shows this to be true. Here again the alkyl groups containing branching chains give the highest yield but within any given structural series the rule may be rigidly applied.

\[ X \text{ and } X \]

The data collected in tables are drawn from original experimental results obtained by applying the experimental procedures used by Atwedge and by Grignard respectively in condensing alkyl magnesium halides with ethylene oxide.

Table X

<table>
<thead>
<tr>
<th>Results obtained by the Atwegg Procedure.</th>
<th>RX</th>
<th>RX (gms)</th>
<th>Normal Product</th>
<th>Yield (gms)</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (a) EtBr</td>
<td>54.5</td>
<td></td>
<td>N(CH$_2$OH)</td>
<td>18.0</td>
<td>49%</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td></td>
<td></td>
<td>20.5</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td>(c)</td>
<td></td>
<td></td>
<td>21.0</td>
<td>57%</td>
</tr>
<tr>
<td>2. (a) PrBr</td>
<td>61.5</td>
<td></td>
<td>N(CH$_3$OH)</td>
<td>19.5</td>
<td>44%</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td></td>
<td></td>
<td>18.5</td>
<td>42%</td>
</tr>
<tr>
<td>3. (a) BuBr</td>
<td>68.5</td>
<td></td>
<td>N(CH$_3$OH)</td>
<td>17.0</td>
<td>33%</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td></td>
<td></td>
<td>15.0</td>
<td>30%</td>
</tr>
<tr>
<td>4. (a) Iso-C$_3$H$_7$Br</td>
<td>61.5</td>
<td></td>
<td>Iso-C$<em>5$H$</em>{11}$OH</td>
<td>26.5</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td></td>
<td></td>
<td>25.0</td>
<td>57%</td>
</tr>
<tr>
<td>5. (a) Iso-C$_4$H$_9$Br</td>
<td>68.5</td>
<td></td>
<td>Iso-C$<em>6$H$</em>{13}$OH</td>
<td>23.5</td>
<td>46%</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td></td>
<td></td>
<td>22.0</td>
<td>43%</td>
</tr>
</tbody>
</table>

2. Compt. rend., 136, 1260-62 (1903)
<table>
<thead>
<tr>
<th></th>
<th>6. (a) isoC₅H₁₁Br</th>
<th>75.5</th>
<th>isoC₇H₁₅OH</th>
<th>WQ</th>
<th>21.5</th>
<th>37%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>C₆H₅Br</td>
<td>78.5</td>
<td>C₆H₅C₆H₂C₆H₂OH</td>
<td>48.5</td>
<td>75%</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>C₆H₅C₆H₂Cl</td>
<td>63.5</td>
<td>C₆H₅(CH₂)₃OH</td>
<td>35.5g</td>
<td>52%</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>C₆H₁₁I</td>
<td>60.0</td>
<td>C₆H₁₁(CH₂)₂OH</td>
<td>27.0g</td>
<td>42%</td>
<td></td>
</tr>
</tbody>
</table>

**Table XI**

Results obtained by the Grignard Procedure.

<table>
<thead>
<tr>
<th>Rₐ</th>
<th>Rₐ(gms)</th>
<th>Normal product</th>
<th>Yield (gms)</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (a)</td>
<td>EtBr</td>
<td>54.5</td>
<td>Nu₄H₉OH</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. (a)</td>
<td>PrBr</td>
<td>61.5</td>
<td>Nu₅H₁₁OH</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. (a)</td>
<td>BuBr</td>
<td>63.5</td>
<td>Nu₆H₁₄OH</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. (a)</td>
<td>isoC₅H₁₁Br</td>
<td>75.5</td>
<td>isoC₇H₁₅OH</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>C₆H₅Br</td>
<td>78.5</td>
<td>C₆H₅(CH₂)₂OH</td>
<td>20.5</td>
</tr>
</tbody>
</table>

**The Grignard Procedure**

Thirteen grams magnesium shavings, one gramule iodine, and 200cc of absolute ether are placed in a 1-liter triple-necked flask. The central neck of the flask is fitted with an efficient stirrer provided with a mercury seal. One of the side necks is provided with a long refluxed condenser carrying a calcium chloride tube, the other is fitted with a 50cc burette containing
the alkyl bromide to be added. The end of the burette is provided with a drying tube. Five cc of the bromide is added at the beginning to start the reaction. Soon after the brisk reaction begins, the remainder of the bromide is added drop by drop in the course of two hours. No cooling is necessary; after the reaction begins, the flask may be placed in a warm water bath (35-40°C) so as to accelerate the speed of the reaction. From beginning to end, the stirring is used. After the addition of bromide is completed, the stirring is continued for half an hour. The reaction mixture is then cooled to 0°C. Eleven grams of liquid ethylene oxide is condensed in an inverted burette the open end of which has been sealed. A few pieces of porous plates are placed at the bottom of the burettes so as to facilitate the evaporation. The tip of the burette is connected to a delivery tube which is fixed by a rubber stopper to the side neck of the flask. The end of the delivery tube is directed towards the center of the flask about five centimeters from the surface of the reaction mixture. The burette containing ethylene oxide is surrounded by water at a temperature 2 or 3 degrees above the boiling point of ethylene oxide. It takes usually three or four hours to vaporize the ethylene oxide which is gradually and completely absorbed by Grignard's reagent. After
standing over night, the reaction mixture is transferred from the reaction flask to a two-liter round-bottom flask. The unchanged magnesium is completely removed. The solvent ether is gradually distilled off by heating on the water bath. As the thermometer indicates above 45°C, the mass swells up and fills the whole flask, a phenomenon which is attended by the evolution of much heat and the complete expulsion of ether. After cooling, this solid porous mass is treated with 50cc. ice water; this produces no heat effect. A calculated amount of dilute sulfuric acid is gradually added. After the distinct separation of two layers, the alcohol is removed by repeated extractions with ether. The ethereal extract is neutralized with sodium carbonate solution and dried with anhydrous sodium sulfate. The ethereal solution is then subjected to practical distillation. In the preparation of n-Butyl alcohol and n-amyl alcohol, steam distillation is applied immediately after the decomposition with ice water and dilute sulfuric acid.

The Atwegg's Procedure

The procedure is exactly as the one described above, excepting that previous to the distillation of the ether 100cc of dry benzene is added. The ether is then distilled off until the temperature registers 75°C. The distillation is discontinued and the solution is allowed
to reflux for two hours at the temperature of the water bath. In this method 22 grams of ethylene oxide are used, and it is not necessary to remove the unchanged magnesium.

The essential difference between these two procedures lies in the fact that Grignard uses about two moles of R-MgX for each mole of ethylene oxide while Atwege uses these reagents mole for mole. As will be shown in the following section the increased yield obtained by Grignard may be accounted for by the action of the excess of RMgX upon the addition product from R₂.

A second interesting feature of the condensation of Grignard reagent upon ethylene oxide is that at 10⁰C, apparently little rearrangement of either type takes place. If the ether is distilled off in vacuo at this temperature, and the grey solid obtained is then treated with a small amount of water; a quantitative yield of a resinous product is obtained. The resinous product is apparently a polymerized form of the olefine oxide.

The rearrangement of R₂ into its stable form takes place smoothly and completely in ethereal solution below 35⁰C the boiling point of ether. The rearrangement

---

or A', however into its stable form has only taken place to a very limited extent at this temperature but is quite complete at 75°C.

The experimental basis for these statements is to be found in the six test experimental runs designed on the Atweeg procedure and described in detail below. The results are summarized in table.XII.

On adding acetyl chloride to the condensation products which have been refluxed at the boiling point of ether for half an hour, one obtains 8% of normal butyl acetate and 42% of brom-ethylacetate. If the heating is prolonged for two hours, the yield of butyl acetate can be increased up to 15%, while the yield of brom-ethyl acetate remains almost constant. If the ether is distilled off, after the addition of benzene to the condensation product, so as to raise the temperature high enough to affect the complete rearrangement of A', the yield of N-butyl acetate can be increased up to 53%. This increase in the normal condensation product is accomplished with a diminution in yield of by-product.

Water can be used in place of acetyl chloride in the above experiments.

Six reaction products prepared separately by adding 22g. of ethylene oxide to one half mole of ethyl magnesium bromide.
The first two reaction products are both refluxed at the boiling point of ether for half an hour and then cooled to 0° C. One of them is carefully treated with 200 cc of ice water, while the other is added drop by drop 39.5 g. of acetyl chloride (freshly distilled) in the course of two hours, and then 157 g. of acetyl chloride at one time. The temperature is maintained at 0° C in this process. The reaction product is then also treated with 200 cc of ice water.

The second two reaction products are both refluxed in the same way for two hours and then cooled to 0° C, one of them is treated with ice water while the other with acetyl chloride as the above procedure.

The third two reaction products are both treated with 200 cc of benzene and the solvent ether is then distilled off from both of them until the thermometer registers 75° C. One of them is then treated with ice water while the other with acetyl chloride as the above procedure.

These six reaction products are then separately purified, dried, and fractionally distilled as described in the general procedure.
Table XII

<table>
<thead>
<tr>
<th>No</th>
<th>reagents used</th>
<th>Butyl acetate</th>
<th>Butyl alcohol</th>
<th>yield</th>
<th>Brom</th>
<th>Bromethyl hydrid</th>
<th>acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>H₂O</td>
<td>2g</td>
<td>5</td>
<td>26g</td>
<td></td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Ib</td>
<td>CH₃COCl</td>
<td>4.5g</td>
<td>8</td>
<td></td>
<td>35g</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>H₂O</td>
<td>4g</td>
<td>10</td>
<td>26g</td>
<td></td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Ib</td>
<td>CH₃COCl</td>
<td>8.5g</td>
<td>15</td>
<td></td>
<td>35g</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>H₂O</td>
<td>18g</td>
<td>49</td>
<td>27.5g</td>
<td></td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Ib</td>
<td>CH₃COCl</td>
<td>31g</td>
<td>53</td>
<td></td>
<td>38g</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

Attention must be called to the reaction phenomenon that the rearrangement of $A_i$ is attended with the evolution of large amount of heat and, in case the Grignard procedure is followed, by an enormous swelling or volume change in the reaction product. The more negative the radical $R$, the more readily and calmly is the rearrangement of $A_i$ into its stable form. Thus the rearrangement of $A_i$ takes place more violently and with more difficulty as the number of carbon atoms in the alkyl group, $R$, is increased. Thus the rearrangement of $A_i$ in which $R$ is an aromatic radical takes place more calmly and readily than that in which $R$ is an aliphatic radical. The facts just indicated throw light on the explanation of the rapid rearrangement of $B_i$ in which the negative halogen is taking the position of $R$ in $A_i$. 
It is to be regretted that the data is not available to prove that the yield of halohydrin is inversely proportional to that of the normal product. A research with this purpose in mind should be carried out. Attention should also be called to the fact that it probably would be possible to measure the decomposition temperatures of the several addition products of the type \( A_1 \) which would be produced as the number of carbon atoms in the alkyl group, \( R \), is increased. Likewise that if a sufficiently low temperature could be obtained it should be possible to observe similar transformations for aldehydes and ketones.

Henry Louis together with Bourneau and Tiffeneau undertook to study the action of Grignard's reagents on alkyl substituted ethylene oxides. The results of their investigation showed that the mono-substituted ethylene oxide behaves similar to ethylene oxide towards RMgX, while di- or poly-substituted ethylene oxides give rise to isomeric change in the following manner:

\[
\begin{align*}
R_2C & \xrightarrow{0} R^1MgX \rightarrow R_2CH-CH(R')OMgBr.
\end{align*}
\]

The present author is inclined to believe that the action of Grignard reagents on di- or poly-

\[4. \text{Compt. rend., 142, 406-8 (1907); 145, 154 (1907).} \]
\[5. \text{Compt. rend., 145, 437-39 (1907).} \]
substituted ethylene oxides give first the olefine
oxidic complexes which readily pass over into aldehydic
or ketonic complexes, and by rearrangement yield the
secondary or tertiary alcohols.

\[
\begin{align*}
R_2C\xrightarrow{O}R' & \quad \rightarrow \quad R_2CH-CH\_--R' \quad \rightarrow \quad R_2CH-CH-R' \\
H_2C\_O\MgX & \quad \rightarrow \quad \MgX & \quad \rightarrow \quad \MgX
\end{align*}
\]

\[
\begin{align*}
RHC\_O\_R & \quad \rightarrow \quad R_2CH-CH\_--R' \quad \rightarrow \quad R_2CH-CH-R' \\
R_2C\_O\_MgX & \quad \rightarrow \quad \MgX & \quad \rightarrow \quad \MgX
\end{align*}
\]

The transformation from an addition complex
which is difficult of undergoing rearrangement to an
isomeric addition complex which is capable of undergoing
is the rapid rearrangement characteristic of Grignard reaction.

The Action of Organon Magnesium Halides
upon Halohydrins.

By even a casual examination one is convinced
that a halohydrin is likely to undergo reaction with
only the A. type of monoetherate.

\[
\begin{align*}
H\_O\_R & \quad \xrightarrow{OEt}_2 \quad \rightarrow \quad XCH_{\alpha}CH_{\alpha}-O-Mg-X\cdot Et_{\alpha}O + RH
\end{align*}
\]

The structural rearrangement in this case will
probably be spontaneous with an evolution of the hydro-
carbon, RH. The resulting decomposition product may be
thought of as a mono-etherate similar to but not identical with the rearrangement product of the α type in the case of ethylene oxide. It may yield a normal condensation product in either of two ways. First it may undergo further decomposition to yield ethylene oxide which then reacts with a further quantity of \( R \cdot MgX \) as described in the preceding section or; second it may react directly with a further quantity of \( \alpha \) as follows:

\[
\begin{align*}
Et_2O \cdot X & \quad R \quad -CH_2CH_2O \quad X \quad OEt_2 \\
& \quad Mg \quad - X \quad Mg \quad OEt_2
\end{align*}
\]

\[
\begin{align*}
Et_2O \cdot XMgX & \quad + \quad RCH_2CH_2O \quad X \quad OEt_2 \\
& \quad Mg \quad - X \quad Mg \quad OEt_2
\end{align*}
\]

Here again the yield of normal product will depend upon the relative amounts of \( \alpha \) and \( \beta \) which in turn depend upon the nature of \( R \) and \( X \). The work of Conant and Kirner\(^1\) shows this to be true.

---

Table XIII

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Grignard reagent</th>
<th>Normal product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClCH$_2$CH$_2$OH</td>
<td>PhCH$_2$MgCl</td>
<td>Ph(CH$_2$)$_3$OH</td>
<td>64</td>
</tr>
<tr>
<td>Cl(CH$_2$)$_2$CH$_2$OH</td>
<td>&quot;</td>
<td>Ph(CH$_2$)$_5$OH</td>
<td>50</td>
</tr>
<tr>
<td>&quot;</td>
<td>Ph(CH$_2$)$_3$MgBr</td>
<td>Ph(CH$_2$)$_5$OH</td>
<td>36</td>
</tr>
<tr>
<td>&quot;</td>
<td>Ph(CH$_2$)$_3$MgBr</td>
<td>Ph(CH$_2$)$_6$OH</td>
<td>33</td>
</tr>
<tr>
<td>&quot;</td>
<td>Ph(CH$_2$)$_4$MgBr</td>
<td>Ph(CH$_2$)$_7$OH</td>
<td>21</td>
</tr>
</tbody>
</table>

In a perfectly analogous manner it is now easy to explain why, as the results in table XIII above show, an excess of RMgX increases the yield of normal product when condensation is made with ethylene oxide. The stable form of the addition product of B, will react with the A type of monoetherate to yield a normal condensation product:

$$
\text{Et}_2\text{O} \cdot \text{RMgOC}_2\text{H}_2\text{XR} + \text{RMgXEt}_2\text{O} \rightarrow \text{Et}_2\text{ORMgOC}_2\text{H}_2\text{CH}_2\text{BR}$$

$$
\text{H}_2\text{O} \rightarrow \text{Et}_2\text{O} \cdot \text{Mg(OH)}_2 \cdot \text{RCH}_2\text{CH}_2\text{OH} + \text{RH}.$$

The reader will now recall the statement previously made that ClCH$_2$CH$_2$OMgX may undergo decomposition to yield ethylene oxide which acts upon RMgX to give the primary alcohol. The products obtained by Grignard\textsuperscript{2} in the action of RMgX on ClC(OH)(OmgBr)(OmgBr)CH$_2$Cl, by Louis Henry\textsuperscript{3} in the action of RMgX on Me$_2$C(Cl)CH(Me)(OMgBr) and by Bourneau and Tiffeneau\textsuperscript{4} in the action of

---

NMgX on chloracetone point to the possible intermediate formation of olefine oxides resulting from the decomposition of compounds of the type Cl-C-C-OMgX.

The present author now finds that if the chlorine atom in Cl-C-C-OMgX is directly bound to a tertiary radical, the olefine oxidic type of splitting can readily take place. The olefine oxide formed acts on RMgX to give an olefine oxidic addition complex. The latter passes readily over into an aldehydic or ketonic addition complex which in turn rearranges into the final product.

\[
\begin{align*}
\text{MeC(Et)Cl} & \quad \text{Et} \quad \text{MeC(Et)Cl} \quad \text{MeCET} \quad \text{Cl} \\
\text{CH}_2\text{OH} & \quad \text{MgBr} \quad \text{CH}_2\text{OMgBr} \quad \text{H}_2\text{C} \quad \text{MgBr}
\end{align*}
\]

\[
\begin{align*}
\text{MeCET} \quad \text{Cl} \quad \text{OEt}_2 \quad \text{Et} \quad \text{OEt}_2 \quad \text{MeCET} \quad \text{Et} \quad \text{OEt}_2 \quad \text{H}_2\text{C} \quad \text{Mg}
\end{align*}
\]

\[
\begin{align*}
\text{MeCH(Et)-CHCH(OH)} & \quad \text{MeCH(Et)-CHCH(OH)} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

(Tiffeneau's Alcohol)

If the chlorine atom in Cl-C-C-OMgX is directly bound to a primary radical, the olefine oxidic type of splitting does not readily take place, and hence aliphatic Grignard reagents give poor yields with primary halo-hydrins.
Aromatic Grignard reagents however give good yield. This may be readily explained by the facts that they form practically only a type of mono-etherates and their addition complexes with olefine oxides can readily undergo rearrangement as shown in the previous section.

Attention is finally called to the fact that the phenomena exhibited by the action of Grignard reagents on the ethylene chlorohydrin and on ethylene oxide are very similar in character. Frequently in working with chlorohydrins a resinous product is obtained similar to that obtained in the case of ethylene oxide.

Direct evidence that the increased yield of normal product obtained, when more than one mole of ethyl magnesium bromide is allowed to act upon ethylene oxide, is not due to the action of $RMgX$ upon $ClCH_2CH_2OMgBr$ but to the intermediate formation of ethylene oxide is to be found in the results of the following experiments.

Two isomeric chlorohydrins having the structural relationship indicated in formulas I and II were prepared and submitted to the action of ethyl magnesium bromide and the results compared

$\text{MeEtC(OH)CH}_2\text{Cl} \quad \text{I.}$  $\text{MeEtC(Cl)CH}_2\text{OH} \quad \text{II.}$
Preparation of the Chlorohydrin of Asym. Methyl Ethyl Glycol I. Ethyl magnesium bromide is prepared from 123 gms. C₂H₅Br, 26.8 gms. Mg in 400cc absolute ether. The mixture is diluted with 160cc ether, cooled to 10°c and 32gms. of chloracetone dissolved in 2000cc ether is slowly added with thorough stirring. The reaction product purified in the usual manner gives 71gms pure chlorohydrin of methyl ethyl glycol (B.pt. 152-153°c) or 58% of the theoretical.

Preparation of Asymmetrical methyl ethyl ethylene oxide. The above experiment is repeated using half the amount mentioned. The reaction product, after distilling off the ether is cooled with ice water and treated slowly, and with constant shaking, with a cooled solution of 60gms. KOH in 30cc water. After continued shaking for a short time, the upper layer is separated and dried over K₂CO₃ and the oxide is obtained by fractionation through a column. The portion boiling between 80-83°c, weighed over 28 gms. or 35% of the theoretical. Two grams of Tiffeneau's secondary alcohol, \( \text{CH(Me)(Et)} - \text{CH(Et)(OH)} \), is obtained as a by product. (B.pt. 150°c, benzoate B.pt. 178, 147°c)

Preparation of the S chlorohydrin of asym. methyl ethyl glycol II. One adds 22gms. of the olefine oxide obtained in the preceding experiment drop by drop to concentrated hydrochloric acid which has been well cooled
in freezing mixture. The reaction product is extracted with ether, dried over anhydrous sodium sulfate, and subjected to fractional distillation. One obtains 23gms. of a pure chlorohydrin (B.pt. 149-150°c) which has been definitely proved by Louis Henry to consist chiefly of the halohydrin isomeric with that described above as boiling at 152-153°c.

General procedure for the condensation of halohydrins with ethyl magnesium bromide. The halohydrin is dissolved in twice its volume of ether and the solution is added drop by drop to the Grignard reagent. Each drop produces a lively effervescence without the evolution of much heat. After all the solution has been added the stirring is continued for one hour and the ether is then distilled off on water bath. As the thermometer registers 49°c, a violent reaction takes place with the swelling of the mass and the effusion of the remaining ether. The product purified in the usual manner, consists of Tiffeneau's secondary alcohol (A) boiling at 147°c. (Butyrate, B.pt. 145-8°c, Benzoate B.pt. 17 147°c.) The results one obtains are clearly set forth in the table XIV. The halohydrin used in (3) was freshly prepared material, while in (4) it had been prepared one week before its use. Tertiary halohydrins seem to be capable of undergoing transformation into the isomeric primary halohy-
drins on standing.

Table XIV

<table>
<thead>
<tr>
<th>Halohydrin</th>
<th>Mole C₂H₅MgBr (mole)</th>
<th>Halohydrin regenerated gms.</th>
<th>yield of (A) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.165</td>
<td>0.33</td>
<td>71%</td>
</tr>
<tr>
<td>II</td>
<td>0.6</td>
<td>1.2</td>
<td>64%</td>
</tr>
<tr>
<td>II</td>
<td>0.165</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>0.165</td>
<td>0.165</td>
<td>considerable</td>
</tr>
</tbody>
</table>

A similar study was made of the action of C₂H₅MgBr upon CH₂CH₂OH. In every case excepting exp. (1) after a larger part of the ether is removed by distillation, 100cc of toluene is added and the reaction product heated on the water bath for three hours. The results are set forth in Table XV.

Table XV

<table>
<thead>
<tr>
<th>halohydrin</th>
<th>NMX (mole)</th>
<th>Mol. C₂H₅MgBr</th>
<th>Normal product</th>
<th>yield gms</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>C₂H₅MgBr</td>
<td>0.5</td>
<td>MC₄H₉OH</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>&quot;</td>
<td>0.4</td>
<td>&quot;</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>&quot;</td>
<td>0.6</td>
<td>&quot;</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>C₆H₅MgBr</td>
<td>0.6</td>
<td>C₆H₅(CH₂)₂OH</td>
<td>20</td>
</tr>
</tbody>
</table>

The Action of CH₃MgI upon Hydroxy-, Amino-, and Imino Derivatives.

Hibbert found that most hydroxy compounds give low values of CH₄ in their reaction with CH₃MgI.
when phenetole is used as the solvent. The lower alcohols, up to and including propyl alcohol, behave in this respect quite abnormally not only in phenetole, but also in amyl ether. The deviations from the theoretical values in the quantity of methane evolved from methyl, ethyl, and propyl alcohols are 43, 71, and 83% respectively. The aromatic amines also give low values in phenetole solution. In the case of the lower amines both in phenetole and amyl ether solution, there is a slow continuous evolution of gas extending over many hours, which is only completed in some cases by heating.

This abnormal behavior can be readily explained by considering the fact that we are dealing in solution with two isomerides $A$, and $B$, in equilibrium with each other thru $A$ and $B$ from which they are derived. only the isomeride $A$ decomposes with evolution of methane:

$$
B \quad \underset{\text{R}_2\text{NH}}{\overset{\text{ROH}}{\rightleftharpoons}} \quad \underset{\text{H}^{\prime}\text{O}^\text{R}}{\overset{\text{Mg}_{\text{R}}}{}}, \quad A
$$

$$
R \quad \overset{\text{O-Mg}^\text{X}}{\text{R}} \quad \overset{\text{X}}{\text{R}} \quad \overset{\text{Mg}^{-}}{\text{R}} \quad \overset{\text{H}^{\prime}\text{O}^\text{R}}{\text{R}}
$$

$$
B, \quad R^{\prime}\text{H}^+\text{ROMg}^+\text{R}_{2}^0 \quad R^{\prime}\text{H}^+\text{R}_{2}\text{NMG}^+\text{R}_{2}^0
$$

Zerewitinoff\textsuperscript{2} surmounted this difficulty by using the sparingly soluble compound, \((\text{C}_5\text{H}_5\text{N})_2\text{CH}_3\text{MgI}\) \((\text{C}_5\text{H}_{11})_2\text{O}\), as a reagent for the determination of the "reactive" hydrogen. By so doing he obtained normal results with both aromatic and aliphatic hydroxy compounds and amines including the lower aliphatic alcohols. His determinations in many cases show a surprisingly small deviation from the theoretical. Zerewitinoff's compound can be shown to have the following structure:

\[
(\text{C}_5\text{H}_{11})_2\text{O} \quad \text{CH}_3 \quad \text{I} \quad \frac{\text{Mg}}{\text{CH}_3} \quad (\text{C}_5\text{H}_5\text{N})_2
\]

Pyridine may add itself either on \(\text{CH}_3\)-Mg\text{I-side} or on \(\text{Mg}-\text{X}\) side. If pyridine adds\textsuperscript{3} itself on \(\text{CH}_3\)-Mg\text{I}\text{-side}, an alkylated base is obtained after decomposing the reaction product with water.

\[
\text{N} \quad \text{CH}^- \quad -\text{R} \quad \text{X} \quad \text{Mg}\text{-side} \quad \text{H}_2\text{O} \quad \text{CH}-\text{R} \quad \text{N} \quad \text{MgX} \quad \text{CH}-\text{R} \quad \text{K} \quad \text{MgX} \quad \text{K} \quad \text{H} \quad \text{N} \quad \text{MgX}
\]

One, two, or three molecules of pyridine may be added to the salt side, \(-\text{Mg}-\text{X}\), by the action of pyridine on an ethereal solution of \(\text{RMgX}\). The complexes thus formed regenerate pyridine when treated with water (Ber., 37, 3088-92).

---

2. Ber. 40, 2033 (1907); 41, 2233 (1908); 43, 3590 (1910); 45, 2384 (1912). 3. Atti. Accad. Lincei (5), 10, 1, 538-545 (1907).
Two pyridine molecules occupy the salt side of Zerewitnoff's compound. So stable is the combination that there is little or no dissociation, on this side of the di-complex. On the alkyl-metallo side, however, the amyl ether is readily detached forming an A type of mono-complex.

\[
(C_5H_{11})_2O + MgCH_3 \rightarrow (C_5H_{11})_2O + Mg(CH_3)I
\]

A.

Solutions containing the Zerewitnoff's compound readily react with hydroxyl, amino, and amino derivatives to form addition products of the A type which readily decompose with a quantitative evolution of methane. The excellency of Zerewitnoff's reagent is thus clearly explained.

**The Action of \textit{RO}Mg\textit{X} upon \textit{RO}Mg\textit{X}**

Compounds of the type \textit{R}-\textit{O}-Mg\textit{X} have been shown to form only the mono ether complex\textsuperscript{1}. It seems logical to assume that this mono ether complex is of the A form, \textit{RO}Mg\textit{X}Et\textsubscript{2}O. Doubtless there is residual affinity upon the oxygen atom of the \textit{RO}Mg\textit{X} molecule but probably the tendency to add ether molecules at this point is not greater than that of the ether molecules to associate with each other. The mono-etherate will doubtless undergo partial dissociation and exist in equilibrium.
with the free nonetherated complex, ROMgX. Under the conditions described the free ROMgX may unite with another molecule of its own kind or with a molecule of the mono etherated form to set up a system such as is

\[
\begin{align*}
\text{RO} & \quad \text{X} \quad \text{Et}_2\text{O} \quad \rightarrow \quad \text{RO} \quad \text{X} \quad \text{Mg}^+ \quad \text{Et}_2\text{O} \\
\text{Mg}^+ & \quad \text{O} \quad \text{Et}_2\text{O} \quad \rightarrow \quad \text{RO} \quad \text{X} \quad \text{Mg}^+ \quad \text{Et}_2\text{O} \\
\text{R} & \quad \text{OR} \quad \rightarrow \quad \text{RO} \quad \text{X} \quad \text{Mg}^+ \quad \text{Et}_2\text{O} \\
\text{X} & \quad \text{Mg}^+ \quad \text{O} \quad \text{Et}_2\text{O} \\
\text{R} & \quad \text{OR} \quad \rightarrow \quad \text{RO} \quad \text{X} \quad \text{Mg}^+ \quad \text{Et}_2\text{O} \\
\text{X} & \quad \text{Mg}^+ \quad \text{O} \quad \text{Et}_2\text{O} \\
\end{align*}
\]

When two different compounds ROMgX and R'OMgX are brought into the same reaction mixture, or when the conditions are such that both are formed in the course of the reaction, then both alkyl halides RX and R'X may be produced. These in turn by virtue of their action upon ROMgX and R'OMgX may result in the formation of all three of the ethers R-0-R', R-0-R', and ROR'.

These reactions are quite general when at least one or the compounds contains the heavy negative phenyl radical; such as PhOMgX, PhCH₂OMgX, Ph₂CHOmgX, Ph₃COMgX or Ph(R)CHOMgX. In such a compound the bond between the oxygen and the magnesium is apparently

Weaker than that between the magnesium and the halogen. The rearrangement of the structural bonds resulting in the splitting off of RX requires a high temperature. The absence of ether therefore greatly favors the reaction. The alkyl halide reacts more readily with alkylxy magnesium halides containing an aliphatic radical such as C_2H_5OMgI than with those having an aromatic radical such as Ph_2CHOMgI.

Evidence that compounds of this type react with the production of ethers is to be found in the work of Stadnikof, Spath, Klages and Carre and is set forth in Table XVI.

**Table XVI**

**Action of R'OMgX upon R'OMgX**

<table>
<thead>
<tr>
<th>No.</th>
<th>R'OMgX</th>
<th>Product yield</th>
<th>R-O-R</th>
<th>Product yield</th>
<th>R-O-R'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph_2CHOMgI</td>
<td>EtOMgI</td>
<td>(Ph_2CH)_2</td>
<td>25 gms, Ph_2CHEt</td>
<td>45 gms</td>
</tr>
<tr>
<td>2</td>
<td>Ph_3COMgI</td>
<td>EtOMgI</td>
<td></td>
<td></td>
<td>Ph_3COEt</td>
</tr>
<tr>
<td>3</td>
<td>Ph_3COMgI</td>
<td>EtOMgI</td>
<td></td>
<td></td>
<td>Ph_3COEt</td>
</tr>
<tr>
<td>4</td>
<td>Ph_3COMgI</td>
<td>PhCH_2OMgI</td>
<td></td>
<td></td>
<td>Ph_3COCH_2Ph</td>
</tr>
<tr>
<td>5</td>
<td>Ph_3COMgI</td>
<td>CH_3OMgI</td>
<td></td>
<td></td>
<td>Ph_3COME</td>
</tr>
<tr>
<td>6</td>
<td>C_6H_5CH_2O MgBr</td>
<td></td>
<td></td>
<td></td>
<td>(PhCH_2)_2</td>
</tr>
<tr>
<td>7</td>
<td>CH_3C_6H_5CHET 0 MgBr</td>
<td></td>
<td></td>
<td></td>
<td>(CH_3C_6H_5CHET)_2</td>
</tr>
<tr>
<td>8</td>
<td>Sym. (CH_3)_3C_6H_2CH_2OMgBr</td>
<td></td>
<td></td>
<td></td>
<td>(Sym. (CH_3)_3C_6H_2CH)_2</td>
</tr>
</tbody>
</table>

The technique of bringing together two alkyloxy magnesium halides is quite simple. The two substances may be synthesized and brought together or they may be simultaneously produced in the same reaction mixture as follows:

1. \( 2\text{PhMgBr} + \text{HCOOEt} \rightarrow \text{Ph}_2\text{CHOMgBr} + \text{EtOMgBr} \)
2. \( 2\text{Ph}_2\text{CHOMgBr} + \text{HCOOEt} \rightarrow \text{HCOOCHPh}_2 \text{EtOMgBr} + \text{Ph}_2\text{CHOMgBr} \)

Stadnikof has shown that 9.2 mole of \( \text{Ph}_2\text{CHOMgI} \) acts upon \( \text{HCOOEt} \) (0.3mole) giving one gram of tetraphenyl ethane, twenty three grams of \( \text{Ph}_2\text{CHOEt} \) and eight grams of \( \text{Ph}_2\text{CHOCPh}_2 \). He further showed that the same reactions products can also be obtained by the action of \( \text{PhMgBr} \) upon \( \text{HCOOEt} \).

The essential step in the proof of the mechanism by which the ethers are formed in the above reactions would seem to turn upon the possibility of proving that an alkylhalide, \( \text{RX} \) is formed as an intermediate product. The second phase of the reaction is only a generalized case of the Williamson synthesis. This the author has succeeded in doing by the following experiments.

Thirty-six grams of diphenyl carbinol dissolved in 20cc of dry ether were added to 0.2 mole of \( \text{EtMgBr} \), prepared from 22 grams of \( \text{EtBr} \) and 5 grams of \( \text{Mg} \) in 50cc of ether. Fifteen grams of ethyl formate dissolved in 25cc of ether were then added. After distilling off the ether under diminished pressure the
reaction mixture was heated for 24 hours. The decomposition products yielded 10 grams of the Ph₂CHBr which upon treating with metallic sodium formed tetraphenylethane, mpt. 209°C.

In a second experiment the reaction between Ph(Me)CHOMgI and EtOMgI was carried out by a procedure analogous to that given above. A 15% yield of Ph(Me)CHI was obtained and the product identified by its action on metallic sodium to give Ph(Me)CH—CH(Me)Ph, mpt. 123.5⁰.
PART II

The Action of Alkyl Magnesium Halides upon Alkyl and Aryl Halides.

Let us again assume the two forms of the monoo-etherate to be in equilibrium through the medium of the dietherate. There will be two orientations by which the alkyl halide may come into combination with the mono-etherates A and B, namely $A_1, A_2$ and $B_1, B_2$ respectively.

\[
\begin{align*}
E_2O \cdot RMgR + I_x & \quad E_2O \cdot RMgX + RX \\
A_1 & \quad B_2 \\
R \cdot R + X MgX \cdot E_2O & \quad R \cdot R + X MgX \cdot E_2O
\end{align*}
\]

The simplest case will be that in which the alkyl halide is the same as that used in the preparation of the Grignard reagent. In the case of $B_1$ a rearrangement of the structural bonds would result in the formation of magnesium of dialkyl and free halogen. There is no experimental evidence that such a phenomenon ever takes place. A rearrangement of the structural bonds in $B_2$ and $A_1$ results in a reproduction of the original
alkyl halide and monoetherate and does not disturb the equilibrium. Rearrangement of A<sub>2</sub> alone results in the condensed hydrocarbon, R-R. In the simple case then the condensed hydrocarbon finds its origin entirely through A.

Now it is common knowledge that Grignard reagents prepared from alkyl halides with fewer than four or five carbon atoms do not yield appreciable amounts of the condensed hydrocarbon. In such cases a mixture of hydrocarbon gases is obtained which seems to consist essentially of equal volumes of unsaturated and saturated hydrocarbons having the same carbon content as the alkyl group of the alkyl halide.

Considerations such as those enumerated above lead to the second assumption. Namely, any mono-complex having free residual valence upon the organo-metallic side, as in the A form of mono-etherate, may undergo spontaneous decomposition with the separation of the olefines as indicated below.
This spontaneous decomposition is of such frequent occurrence in reactions involving Grignard reagents that a separate section of this paper will be devoted to a discussion of the mechanism of the phenomenon in detail. The phenomenon will hereafter be referred to as "olefine splitting" and is accompanied by the simultaneous formation of an Mgx complex which exercises a powerful reducing action. This reducing action is also a frequent accompaniment of reactions involving organomagnesium compounds and a section will also be devoted to its discussion in detail.

The most prolific worker in this field has been Späh.\textsuperscript{1} Much of his work has been tabulated in table III. Späh has quantitatively examined the gaseous products evolved by the action of ethyl iodide upon ethyl magnesium iodide and shown ethane and ethylene to be present in almost equal amounts and butane to be present in traces. The gas evolved by the action of methyl iodide upon methyl magnesium iodide was found to be almost pure ethane.

\textsuperscript{1} Monat. 34, 1965-2014 (1913).
Following the procedure of Späth we have systematically carried out a series of reactions in which one fifth mole of alkyl halide was allowed to react with an equimolar quantity of the corresponding alkyl magnesium halide, under such conditions that the gaseous products could be quantitatively collected and examined. The olefins were absorbed in bromine, in carbon tetrachloride and the dihalides separated and determined. The saturated products were only quantitatively determined. The solid and liquid condensation products were identified by their melting and boiling points respectively. The results are summarized in Table I.

Table I

<table>
<thead>
<tr>
<th>No.</th>
<th>RX</th>
<th>R MgX</th>
<th>Gaseous products</th>
<th>Condensed products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NCH₃I</td>
<td>NCH₃MgI</td>
<td>C₂H₆</td>
<td>C₂H₄ + C₂H₆ C₄H₁₀(trace)</td>
</tr>
<tr>
<td>2.</td>
<td>NC₂H₅I</td>
<td>NC₂H₅MgI</td>
<td>C₃H₆ + C₃H₆ (?)</td>
<td>C₆H₁₄ (trace)</td>
</tr>
<tr>
<td>3.</td>
<td>NC₃H₇Br</td>
<td>NC₃H₇MgBr</td>
<td>C₄H₈ + C₄H₁₀</td>
<td>C₆H₁₂ (3%)</td>
</tr>
<tr>
<td>4.</td>
<td>NC₄H₉Br</td>
<td>NC₄H₉MgBr</td>
<td>C₅H₁₀ + C₅H₁₂(?)</td>
<td>C₅H₁₂ (7%)</td>
</tr>
<tr>
<td>5.</td>
<td>IsoC₅H₁₁Br</td>
<td>IsoC₅H₁₁MgBr</td>
<td>C₆H₁₀ + C₆H₁₂(?)</td>
<td>C₆H₁₀ + C₆H₁₂(7%)</td>
</tr>
<tr>
<td>6.</td>
<td>C₆H₅Br</td>
<td>C₆H₅MgBr</td>
<td>-- --</td>
<td>(C₆H₅)₂ (9%)</td>
</tr>
<tr>
<td>7.</td>
<td>C₆H₅I</td>
<td>C₆H₅Mg I</td>
<td>-- --</td>
<td>(C₆H₅)₂ (11%)</td>
</tr>
<tr>
<td>8.</td>
<td>C₆H₅CH₂Cl</td>
<td>C₆H₅CH₂MgCl</td>
<td>-- --</td>
<td>(C₆H₅CH₂)₂ (38%)</td>
</tr>
<tr>
<td>9.</td>
<td>C₆H₅CH₂Cl</td>
<td>C₆H₅MgBr</td>
<td>C₆H₅ CH₂C₆H₅ (43.4%)</td>
<td></td>
</tr>
</tbody>
</table>

The above table reveals the fact that the yield of condensed hydrocarbon increases with the number of
carbon atoms in the alkyl group. Attention should also be called to the fact that the yield does not rise above 45% and is lower than the amount of the mono-etherate as indicated by the yield of normal alcohol as shown in the previous section.

Attention should also be directed to the possibility of measuring the speed of the decomposition in reactions by measuring the volume of gaseous evolved. Experiments having for their object a preliminary survey of this possibility were carried out as follows: The alkyl magnesium halide solutions were prepared by allowing one fifth mole of the corresponding alkylhalide to act upon five grams of magnesium in the presence of 75cc of absolute ether. One fifth mole of the appropriate alkyl halide, R¹X was then added, all in one portion. The gas evolved was collected over water; its volume measured and corrected. The results are summarized in Table II.

<table>
<thead>
<tr>
<th></th>
<th>RX</th>
<th>Mol</th>
<th>RMgX</th>
<th>Mol</th>
<th>Rate of evolution of gas (cc/per hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₃I</td>
<td>.2</td>
<td>CH₃MgI</td>
<td>.2</td>
<td>104</td>
</tr>
<tr>
<td>2</td>
<td>C₂H₅I</td>
<td>&quot;</td>
<td>C₂H₅MgI</td>
<td>&quot;</td>
<td>612</td>
</tr>
<tr>
<td>3</td>
<td>C₂H₅Br</td>
<td>&quot;</td>
<td>C₂H₅MgBr</td>
<td>&quot;</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>C₂H₅I</td>
<td>&quot;</td>
<td>C₂H₅MgBr</td>
<td>&quot;</td>
<td>425</td>
</tr>
<tr>
<td>5</td>
<td>C₂H₅Br</td>
<td>&quot;</td>
<td>C₂H₅MgI</td>
<td>&quot;</td>
<td>563</td>
</tr>
</tbody>
</table>
6. C₂H₅I .4 C₂H₅MgI n 1633
7. C₂H₅I .2 C₂H₅MgI .4 400

It is apparent from table II that the speed of the reaction between RX and RMgX₁ is increased more by an excess of RX than by an excess of RMgX₁. The speed is however more dependent upon the nature of RMgX₁ than of RX.

In the more complex case where R¹X¹ is permitted to react with RMgX many additional possibilities are developed.

Here again the diplex, B₁, probably never reaches the stage of structural rearrangement. The diplex, B₂, by rearrangement reproduces the same type of mono-etherate with the simple exchange of halogen. This interchange will only take place when X¹ is a lighter halogen atom than X. For, it will be recalled, metallic bromides and iodides readily exchange halogens with chlorine substituted organic compounds. We have to do with just such an exchange in the structural rearrangement of B₂. The sig-
nificance of this interchange will be apparent when it is recalled that in the principal equilibrium between A and B the relative amount of the A form varies Cl\Br\I. The net result of the structural rearrangement of B\(2\) therefore is to increase the amount of the A-form of monoetherate.

Diplex, \(A_1\), by structural rearrangement produces a new alkyl magnesium halide, by the interchange of alkyl groups. At the same time the free alkyl halide containing the alkyl group of the original Grignard reagent is produced. Out of these two products a completely new system is now set up. The significance of this is very great. For through the structural rearrangement of \(A_1\) it will now be seen that all mixed systems such as \(RX + R^1\text{MgX}^1\) or \(R^1X^1 + RMgX\) converge toward the same equilibrium composition.

There will exist then in any complex reaction mixture of this type four diplex derivatives of type \(A_2\):

These four forms of \(A_2\) will by structural rearrangement yield three condensed hydrocarbons \(R-R, R-R^1\) and \(R^1-R^1\). The final reaction products of such a system will therefore be; the two olefines \(R(-H)\) and \(R^1(-H)\), the two paraffins \(RH\) and \(R^1H\) and the three condensed hydrocarbons, \(R-R, R-R^1, R^1-R^1\).
R-R' and R'R'. The experimental justification of the arguments is to be found in the work of Späth; some of whose results are set forth in Table III.

Table III

(Annalen 34, 1905-2014(1913))

<table>
<thead>
<tr>
<th>RMgX</th>
<th>R'X'</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH₃MgI + NC₃H₇I</td>
<td>C₃H₆C₂H₄C₂H₆+CH₃C₃H₇CH₃, (considerable) &amp; large</td>
<td></td>
</tr>
<tr>
<td>2. CH₃MgI + Tert. C₄H₉Br</td>
<td>C₄H₈(38%)CH₄, C₂H₂, quantity &amp; CH₃C₂H₉,</td>
<td></td>
</tr>
<tr>
<td>3. CH₃MgI + Sec. Octyl-I (Hexadecyl)</td>
<td>CH₄(81.5%)+C₂H₆(18.5%)+C₈H₁₆+C₆H₁₈+CH₃C₈H₁₇(31.4%)</td>
<td></td>
</tr>
<tr>
<td>4. CH₃MgI + Sec. Iodide</td>
<td>CH₂(6.9%)+C₁₁H₂₄, (considerable)+C₁₆H₃₄+</td>
<td></td>
</tr>
<tr>
<td>5. C₂H₅MgBr + Sec. Octyl Br.</td>
<td>C₂H₆(53.8%)+C₂H₄(38.3%)+C₈H₁₈+C₈H₁₆</td>
<td></td>
</tr>
<tr>
<td>6. NC₃H₇MgBr + Sec. Octyl Br.</td>
<td>C₈H₁₈(22.1%)+C₈H₁₆(18%)+C₁₆H₃₄(29%)+gaseous mixture.</td>
<td></td>
</tr>
<tr>
<td>7. Sec. C₃H₇MgCl + Sec. Octyl Br.</td>
<td>C₈H₁₈(24.1%)+C₈H₁₆(18.6%)+C₁₆H₃₄</td>
<td></td>
</tr>
<tr>
<td>8. NC₃H₇MgI + Tert C₅H₁₁ Cl</td>
<td>C₃H₆C₅H₁₂, C₅H₁₀C₅H₁₁+C₅H₁₁</td>
<td></td>
</tr>
</tbody>
</table>

The present analytical technique is not sufficient.
to enable one to quantitatively or qualitatively prove with certainty the existence of all of these products in a reaction mixture. The work of Späth is sufficient, however, to show the multiplicity of the products obtained.

Späth has also shown that the products obtained by the action of $\text{RX}$ upon $\text{R'MgX}$ are qualitatively and quantitatively the same as the products of the reaction of $\text{R'X}$ upon $\text{R MgX}$. The results of his experiments are shown in Table IV.

### Table IV.

<table>
<thead>
<tr>
<th>RMgX</th>
<th>R'X</th>
<th>Products obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_5\text{MgI}$</td>
<td>$\text{NC}_3\text{H}_7\text{I}$</td>
<td>$2400\text{cc}$ $\text{C}_2\text{H}_4 (45.8%) + \text{C}_3\text{H}_6$ + gas collected (54.2%) $\text{C}_2\text{H}_6 (66%) + \text{C}_3\text{H}_8 (34%)$</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_7\text{MgI}$</td>
<td>$\text{NC}_2\text{H}_5\text{I}$</td>
<td>$2410\text{cc}$ $\text{C}_2\text{H}_4 (47.1%) + \text{C}_3\text{H}_6$ + gas collected (52.9%) $\text{C}_2\text{H}_6 (66%) + \text{C}_3\text{H}_8 (34%)$.</td>
</tr>
</tbody>
</table>
In view of the slow rate at which these decom-
positions take place as shown by Table II and that the
diplex, \(A_2\), tends to bring all reaction mixtures to the
same composition these results are not surprising and
are fully explained.

From a consideration of the above mechanism
we arrive at the conclusion that the reaction products of
an alkylmagnesium halide upon an aryl halide should
consist of \(R(-H), RH, R-R, Ar-R\) and \(Ar-Ar\). With a view
to testing this prediction the following series of ex-
periments was made. Solutions of the alkyl magnesium
halide were prepared by allowing one half mole of the
alkyl halide, \(RX\), to react with 12.2 grams of magnesium
in 120cc of absolute ether using a small amount, or gran-
ule of iodine to initiate the reaction. One half mole of
the aryl halide, \(ArX'\), was dissolved in 80cc of ether and
slowly added to the Grignard reagent. The gaseous pro-
ducts were collected and examined as previously de-
scribed. The solid products were recrystallized and the
melting points determined as a method of establishing
their identity. The results are summarized in table V. The yield of diaryl is calculated upon the basis of
aryl halide used.
Table V

<table>
<thead>
<tr>
<th>RMgX</th>
<th>RX</th>
<th>Gaseous products</th>
<th>Solid products</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. C₂H₅MgBr</td>
<td>C₆H₅CH₂Cl</td>
<td>C₂H₄+C₂H₆+C₄H₁₀+(C₆H₅CH₂)₂</td>
<td></td>
<td>16.3%</td>
</tr>
<tr>
<td>2. C₂H₅MgI</td>
<td></td>
<td></td>
<td></td>
<td>80.3%</td>
</tr>
<tr>
<td>3. NC₃H₇MgBr</td>
<td></td>
<td>C₃H₆+C₆H₈(?)+C₆H₁₄</td>
<td></td>
<td>23.5%</td>
</tr>
<tr>
<td>4. NC₄H₉MgCl</td>
<td></td>
<td>C₄H₈+C₄H₁₀+C₈H₁₈</td>
<td></td>
<td>38.4%</td>
</tr>
<tr>
<td>5. NC₄H₉MgBr</td>
<td></td>
<td></td>
<td></td>
<td>42.0%</td>
</tr>
<tr>
<td>6. NC₄H₉MgI</td>
<td></td>
<td></td>
<td></td>
<td>71.0%</td>
</tr>
<tr>
<td>7. C₂H₅MgBr</td>
<td>C₆H₅Br</td>
<td>not observed (C₆H₅)₂</td>
<td></td>
<td>5.0%</td>
</tr>
<tr>
<td>8. C₂H₅MgI</td>
<td>C₆H₅Br</td>
<td></td>
<td></td>
<td>8.0%</td>
</tr>
<tr>
<td>9. C₂H₅MgBr</td>
<td>C₆H₅Cl</td>
<td></td>
<td></td>
<td>3.0%</td>
</tr>
</tbody>
</table>

It is interesting to note in the above table the yield of dibenzyl increases with the carbon content of the alkyl group of the Grignard reagent. An increase in this product is also noted as the halogen of the reagent changes from chlorine to bromine to iodine. A simple explanation of these facts would be to say that this condensed hydrocarbon finds its origin through the mono-etherate, R. This is probably true in part but only indirectly so. The author prefers to attribute the large yield of dibenzyl to two factors: first a relatively high speed in the A₁; second the additional assumption that the diplex structural rearrangement of the diplex compounds B₁ and B₂ undergo dissociation with the loss of ether to form new monoplex derivations of the A type. These in turn reacting with a second molecule of benzyl chloride form new diplex derivatives analogous to A₁ and A₂. The type A₁
derivatives by rearrangement yield benzyl magnesium halides thus increasing the yield of dibenzyl.

The question now arises; can one justify on both experimental and theoretical grounds the interchange of hydrocarbon residues as represented by the structural rearrangement of diphenoxy from table 1? one has the evidence of high yields of dibenzyl. The formation of this product is difficult to account for excepting through the intermediate formation of C_9H_8O/2Cl/2Br unless one is prepared to accept with Späth complete dissociation into a system of free radicals and leave their recombination to the law of chance.

A search of the literature reveals also the following experimental facts:

(a) \[ C=O + 2MgBr \rightarrow Mg-C=O+2MgI \]

(b) \[ \text{eq.} \quad C=C-C=O+2MgBr \rightarrow Mg-C=O+2MgI \]

(c) \[ \text{eq.} \quad C=C-C=O+2MgBr \rightarrow Mg-C=O+2MgI \]

The following experiments were carried out and the results clearly indicate an interchange of acyl groups.

1. Action of benzyl magnesium chloride upon ethylene dibromide.
One quarter mole of PhCH₂MgCl was added to 47 grams of BrCH₂-CH₂Br. The reaction mixture was heated eight hours on the water bath. Eighteen hundred cc of gas was collected which proved to be pure ethylene. Decomposition of the reaction mixture yielded 8.5 grams of toluene, 26 grams of unchanged BrCH₂-CH₂-Br, twelve grams of dibenzyl (Mpt. 52°C and equivalent to 55% of the benzyl chloride used) and one gram of residue.

The simplest explanation of the formation of the products indicated is shown by the following series of equations:

\[ \text{BrCH}_2\text{-CH}_2\text{Br} + \text{C}_6\text{H}_5\text{CH}_2\text{MgCl} \rightarrow \text{BrCH}_2\text{CH}_2\text{MgCl} + \text{C}_6\text{H}_5\text{CH}_2\text{Br} \]

(a) \[ \text{BrCH}_2\text{CH}_2\text{MgCl} + \text{C}_6\text{H}_5\text{MgClBr} \]

(b) \[ \text{C}_6\text{H}_5\text{CH}_2\text{MgCl} + \text{C}_6\text{H}_5\text{CH}_2\text{Br} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5\text{MgClBr} \]

(c) \[ \text{C}_6\text{H}_5\text{CH}_2\text{MgCl} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{CH}_3\text{-MgClOH} \]

II. Action of Phenyl Magnesium Bromide upon Ethylene Dibromide.

The experimental procedure was analogous to that used in the preceding case. Decomposition of the reaction mixture yielded 33 grams of unchanged ethylene dibromide, 6.5 grams of diphenyl (equivalent to 3.4% of the C₆H₅Br used to prepare the reagent), 5.1 grams of benzene and 2 grams of C₆H₅Br. The evolution of ethylene
was also observed. The following equations may be used to explain these facts

\[ \text{BrCH}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{BrCH}_2\text{CH}_2\text{MgBr} + \text{C}_6\text{H}_5\text{Br} \]

(a) \[ \text{BrCH}_2\text{-CH}_2\text{MgBr} \rightarrow \text{C}_2\text{H}_4\text{MgBr}_2 \]

(b) \[ \text{C}_6\text{H}_5\text{MgBr} + \text{C}_6\text{H}_5\text{Br} \rightarrow \text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{MgBr}_2 \]

(c) \[ \text{C}_6\text{H}_5\text{MgBr} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{MgBr(OH)} \]

Having now presented the experimental evidence one is prepared to answer the question propounded above. Carbon is a labile element. Being in the middle of the first series of elements in the Periodic System its compounds partake largely of chemical characteristics of the elements with which it is combined. Hydrocarbon-carbons are reducing agents like hydrogen. Carbon tetrachloride is a chlorinating agent like chlorine. Organic combinations containing numerous halogen substituents partake of the negative character of the halogens. Unsaturation in an organic nucleus seems to also give it a negative character as is evidenced in acetylene and the phenyl group. Combination with oxygen produces an analogous effect as is shown in the negative character of carbonyl, carboxyloxy, acetyl, carboxyl, and phenoxy groups. Methyl groups on

3. Ibid., 44, 1395-1406.
the other hand having an accumulation of hydrogen atoms are more positive (less negative) than hydrogen. This effect apparently is rapidly diminished as one passes from methyl to amyl residues.

Now as has been cited above it is common knowledge that metallic iodides react with organic chlorides and bromides by an interchange of halogens. The motivating force underlying these reactions is undoubtedly the greater chemical neutralization produced by bringing the more positive metal into combination with the more negative chlorine or bromine. These same forces operate to produce the interchange of organic residues in diplex A₁. The more negative phenylated residues such as C₆H₅, C₆H₅CH₂, (C₆H₅)₂CH, (C₆H₅)₃C—, C₆H₅O— and C₆H₅OCH₂CH₂—or the halogenated acetylene or polyhalogenated paraffin residues such as I—C=C—Br—C=C— and X₂CH—CHX— easily replace the simple aliphatic residues from their metallo-alkyls.

C₆H₅CH₂Br + CH₃MgBr → C₆H₅CH₂MgBr + CH₃Br, etc.

That the diaryl is not the only condensed hydrocarbon found in such a reaction mixture is shown by the data in table IV. These experiments were carried out by the same procedure as these the results of which are listed in table I, excepting that the evolved gases were not determined. In experiments 1, 6, 7, 9 and 10 the
ether was removed by distillation. Each reaction mixture was heated on the boiling water bath (100°C) for the time indicated. Under these conditions even though the ether was not distilled off it was gradually lost by evaporation through the condenser. The propyl benzene and dibenzyl were separated by fractional distillation.

| Table VI |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| RMgX       | Mol           | RX              | Ether Mol (coosed) | Time of heating 1. | PhCH₄R | PhCH₄R         |
| C₂H₅MgBr   | .2            | C₆H₅CH₂Cl      | .2                | 50               | 5 hours | 32              | 19              |
| 2.         |               |                 |                   |                  |         |                 |                 |
| 3.         |               |                 |                   |                  |         |                 |                 |
| 4.         |               |                 |                   |                  |         |                 |                 |
| 5.         |               |                 |                   |                  |         |                 |                 |
| C₂H₅MgI    |               |                 |                   |                  |         |                 |                 |
| 6.         |               |                 |                   |                  |         |                 |                 |
| C₂H₅MgBr   |               |                 |                   |                  |         |                 |                 |
| 7.         |               |                 |                   |                  |         |                 |                 |
| C₂H₅MgCl   | .4            | C₆H₅CH₂Br      | 100               | 9                | 3       | 32              |                 |
| 8.         |               |                 |                   |                  |         |                 |                 |
| 9.         | .4            | .2              | 50                | 5                | 37      | 16              |                 |
| 10.        | .2           | .2              | 50                |                  |         |                 |                 |

These results show clearly that a diminution in the quantity of ether used and an increase in the decomposition temperature favor the formation of alkyl benzenes. In absence of ether, one is mainly dealing with the action of RX on individual R MgX which can readily undergo double decomposition with RX at high temperatures to give R-R and
MgX₂.

The work of Spencer on the direct interaction of magnesium and alkyl or aryl halides verifies this statement.

Table VII

( * J. Chem. Soc. 93, 68-72, 1821-26 (1908) *)

<table>
<thead>
<tr>
<th>RX</th>
<th>RR</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅I</td>
<td>C₆H₅C₆H₅</td>
<td>54%</td>
</tr>
<tr>
<td>C₆H₅Br</td>
<td>C₆H₅ C₆H₅</td>
<td>54%</td>
</tr>
<tr>
<td>Iso C₄H₉Cl</td>
<td>(IsoC₅H₉)₂</td>
<td>40%</td>
</tr>
<tr>
<td>Iso C₅H₁₁Br</td>
<td>(IsoC₅H₁₁)₂</td>
<td>67%</td>
</tr>
<tr>
<td>C₂H₅Cl</td>
<td>(C₂H₅)₂</td>
<td>(45% of gaseous product)</td>
</tr>
<tr>
<td>Br CH₂CooMe</td>
<td>CH₂CooMe</td>
<td>48%</td>
</tr>
<tr>
<td></td>
<td>CH₂CooMe</td>
<td></td>
</tr>
</tbody>
</table>

The data tabulated in table VIII indicates the yield of alkyl benzenes obtained when phenyl-magnesium halide is treated with alkyl halides in the proportions indicated. The experimental procedure followed is perfectly analogous to that previously described and closely follows that of Spath. Those experiments marked by an asterisk (*) were borrowed from Spath's work. It will be noted that the yield of alkyl benzene varies as follows: I > Br; NC₄H₉ > NC₃H₇ > C₂H₅ > CH₃; tert C₄H₉ > iso C₄H₉ > NC₄H₉. 
### Table VIII

<table>
<thead>
<tr>
<th>RMgX</th>
<th>Mol RX</th>
<th>Mol Reaction condition</th>
<th>Reaction product</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅MgBr</td>
<td>2 CH₃I</td>
<td>.2</td>
<td>C₆H₅CH₃ (10%)</td>
</tr>
<tr>
<td>C₂H₅I</td>
<td></td>
<td>.2</td>
<td>C₆H₅C₂H₅ (13%)</td>
</tr>
<tr>
<td>C₂H₅Br</td>
<td></td>
<td>.2</td>
<td>C₆H₅C₂H₅ (5%)</td>
</tr>
<tr>
<td>NC₃H₇Br</td>
<td></td>
<td>.2</td>
<td>C₆H₅C₃H₇ (10%)</td>
</tr>
<tr>
<td>NC₄H₉Br</td>
<td></td>
<td>.2</td>
<td>C₆H₅C₄H₉ (15%)</td>
</tr>
<tr>
<td>IsoC₄H₉Br</td>
<td>1.3</td>
<td>.1 IsoC₄H₉Br</td>
<td>C₆H₅C₄H₉ (20%)</td>
</tr>
<tr>
<td>C₆H₅C₅H₁₁</td>
<td></td>
<td>1.3</td>
<td>C₆H₅C₅H₁₁ (20%)</td>
</tr>
<tr>
<td>2CH₃I</td>
<td></td>
<td>.2</td>
<td>C₆H₅C₉H₇ (33%)</td>
</tr>
<tr>
<td>TertC₄H₉Br</td>
<td>13.7</td>
<td>1 TertC₄H₉Br</td>
<td>(50cc ether)</td>
</tr>
<tr>
<td>2CH₃I</td>
<td></td>
<td>.2</td>
<td>C₆H₅C₉H₇ (3%)</td>
</tr>
<tr>
<td>Et₂CHBr</td>
<td>7.6g</td>
<td>1.05 Et₂CHBr</td>
<td>C₆H₅C₉H₇ (51%)</td>
</tr>
<tr>
<td>C₆H₅MgI</td>
<td>1.1</td>
<td>4.5 Et₂CHI</td>
<td>C₆H₅C₉H₇ (5.4%)</td>
</tr>
</tbody>
</table>

It is known that α-chloro ethers ⁶ and allyl halides ⁷ react with RMgX to give good yield of normal product. The action of magnesium upon allyl halide gives a quantitative yield of diallyl and no residual allyl magnesium halide. Attention is called to the fact that these halides all contain two functional groups adjacent one to each other. The mechanism of their reaction can be readily explained in the following way:-

---

6. Compt. rend., 133, 813-975 (1904)
7. Compt. rend., 139, 481 (1904)
8. Ber., 54, (B) 1655-65 (1921)
So complete is this directive action of a second residual valence group in the same molecule that the data of Späth (loc. cit.) on the action of R-MgX on P-methoxy benzyl bromide may be taken as a basis for determining the relative amounts of the two types of monoether complexes of different Grignard reagents. The mechanism of the reaction is shown as follows:
Table IX
The action of $R \text{MgX}$ on $\text{CH}_3 \text{O} \text{C}_6\text{H}_4\text{CH}_2\text{Br}$

<table>
<thead>
<tr>
<th>$R\text{MgX}$</th>
<th>Normal Product</th>
<th>Yield (%)</th>
<th>Side Product Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{MgBr}$</td>
<td>$\text{CH}_3\text{O} \text{C}_6\text{H}_4\text{CH}_2\text{CH}_3$</td>
<td>90</td>
<td>$(\text{CH}_3\text{O} \text{C}_6\text{H}_4\text{CH}_2)_2$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{MgI}$</td>
<td>&quot;</td>
<td>13.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{MgCl}$</td>
<td>$\text{CH}_3\text{O} \text{C}_6\text{H}_4\text{CH}_2\text{Et}$</td>
<td>88</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{MgBr}$</td>
<td>&quot;</td>
<td>85</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{MgI}$</td>
<td>&quot;</td>
<td>26.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{NC}_3\text{H}_7\text{MgBr}$</td>
<td>$\text{CH}_3\text{O} \text{C}_6\text{H}_4\text{CH}_2\text{Pr}$</td>
<td>68.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{IsoC}_3\text{H}_7\text{MgCl}$</td>
<td>$\text{CH}_3\text{O} \text{C}_6\text{H}_4\text{CH}_2\text{Pr(iso)}$</td>
<td>30.6</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{IsoC}_3\text{H}_7\text{MgBr}$</td>
<td>&quot;</td>
<td>29.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>$\text{IsoC}_4\text{H}_9\text{MgBr}$</td>
<td>$\text{CH}_3\text{O} \text{C}_6\text{H}_4\text{CH}_2\text{Bu(iso)}$</td>
<td>50</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
10. TertC₄H₉MgCl CH₃O C₆H₄CH₂Bu(tert) 24.9 (CH₃O C₆H₄CH₂)₂ 50
11. Iso-C₅H₁₁MgBr CH₃O C₆H₄CH₂Amyl(iso) 50 " ?
12. (Et)₂CH MgBr CH₃O C₆H₄CH₂CH(Et)₂ 50 " 40
13. (Et)₂CH MgI " very little " ?
14. C₆H₅MgBr CH₅O C₆H₄CH₂Ph 78 " ?
15. C₆H₅MgI " very little CH₃O C₆H₄CH₂ 69
   (Ph)CH C₆H₄ 0CH₃
16. C₆H₅CH₂MgCl CH₃O C₆H₄CH₂CH₂Ph 62% (crude product)

From the above table it is again evident that the yield of normal condensation product is greatest for RMgCl intermediate for RMgBr and least for RMgI, when R is methyl and gradually diminishes as the number of carbon atoms in R is increased. Attention is called to the fact that the yield of normal product varies inversely as the yield of side product. The action of R-MgX on OCH₃O C₆H₄CH₂Br reveals the same truth.

Table X

<table>
<thead>
<tr>
<th>RMgX</th>
<th>Normal product</th>
<th>Yield%</th>
<th>Side product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅MgCl</td>
<td>OCH₃O C₆H₄CH₂Et</td>
<td>34.5</td>
<td>(CH₃O C₆H₄CH₂)₂</td>
<td>36%</td>
</tr>
<tr>
<td>C₂H₅MgBr</td>
<td>&quot;</td>
<td>32.6</td>
<td>&quot;</td>
<td>43%</td>
</tr>
<tr>
<td>C₂H₅MgI</td>
<td>&quot;</td>
<td>9.7</td>
<td>&quot;</td>
<td>58%</td>
</tr>
</tbody>
</table>
PART III

THE MECHANISM OF "OLEFINIC SPLITTING" BY ORGANO MAGNESIUM HALIDES.

Olefinic Splitting by the Separation of $\text{HMgX}$.

Attention was called to the fact, in a previous section, that a free monocomplex of the $A$ type such as $A^1, A^{11}$ and $A^{111}$.

\[
\begin{align*}
\text{A'} & \quad \text{A''} & \quad \text{A'''} \\
\begin{array}{c}
\text{R} \\
\text{Mg} \\
\text{X}\end{array} & \quad \begin{array}{c}
\text{R} \\
\text{Mg} \\
\text{X}\end{array} & \quad \begin{array}{c}
\text{R} \\
\text{Mg} \\
\text{X}\end{array}
\end{align*}
\]

might and frequently does undergo spontaneous decomposition with the separation of an olefine.

A common form of this decomposition is the separation of an olefine from the simple alkyl magnesium halides. The $\text{-MgX}$ grouping separates with a $H$ atom from the $H$ carbon atom with the simultaneous formation of an olefine having the same carbon content as the alkyl group of the Grignard reagent and $\text{HMgX.Et}_2\text{O}$.

\[
\begin{align*}
\text{C} & \quad \text{H} \\
\text{C} & \quad \text{MgX.Et}_2\text{O} \\
\text{C} & \quad \text{MgX.Et}_2\text{O} \\
\text{C} & \quad \text{MgX.Et}_2\text{O} \\
\text{C} & \quad \text{MgX.Et}_2\text{O}
\end{align*}
\]

The $\text{HMgX}$ complex is a powerful reducing agent.
In reaction mixtures containing aldehydes or ketones they are instantly reduced to the corresponding alcohols, a phenomenon, which will be discussed in detail in a later section. In the absence of a more easily reducible substance a second molecule of the alkyl halide is reduced with the separating of a paraffin. This has given rise to the frequent observation that from a Grignard reaction mixture equal volumes of isomeric olefine and paraffin gases are evolved.

\[
\begin{align*}
\text{Et}_2\text{O} & \xrightarrow{-X} \text{Me} \xrightarrow{+RX} \text{Et}_2\text{O} & \xrightarrow{-X} \text{Me} \xrightarrow{+R} \text{Et}_2\text{O} & \xrightarrow{+X} \text{Me} \xrightarrow{+RX}
\end{align*}
\]

Gomberg and Cone\textsuperscript{1} have actually verified this relationship quantitatively, in the action of ethyl magnesium iodide upon triphenylmethyl chloride.

\[(\text{C}_6\text{H}_5)_3\text{C}l (1\text{mol}) + \text{C}_2\text{H}_5\text{MgI} (2\text{mol}) \rightarrow (\text{C}_6\text{H}_5)_3\text{CC}_2\text{H}_5 (74\%) +\]

\[\text{C}_2\text{H}_4 (18\%) + (\text{C}_6\text{H}_5)_3\text{CH} (18\%) + \text{MgBrI}.
\]

Olefinic splitting takes place more readily when either or both the \(\alpha\) and \(\beta\) carbon atoms are secondary or tertiary in character. Under these conditions splitting frequently occurs quite rapidly even at room temperatures.

\[1.\text{Ber.} 39, 1461-3075 (1906)\]
This is the principle reason why a side reaction is frequently encountered in working with secondary or tertiary Grignard reagents. The following table cites some of the cases in which simultaneous formation of unsaturated and hydrogenated residues have been recorded.

Table I

<table>
<thead>
<tr>
<th>No.</th>
<th>Alkyl halides</th>
<th>Unsaturated Product</th>
<th>Hydrogenated Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Iso C₃H₇I + MgEt₂₀ → CH₃CH = CH₂ + CH₃CH₂CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>Tert. C₄H₉Cl → C₄H₈ + C₄H₁₀ above 150°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>Tert. C₅H₁₁Cl → C₅H₁₀ + C₅H₁₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>C₆H₅CH₂ C(Me)(Et)Br → C₆H₅CH = CMeEt + C₆H₅CH₂CHMeEt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td>Br(Me)(Ph)C=CooEt → CH₂=C(Ph)CooEt + C₆H₅CH(Ph)CooEt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(f)</td>
<td>CHBr-CooEt → CH-CooEt ! + CH₂-CooEt</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂ - CooEt ! + CH₂ - CooEt</td>
<td></td>
</tr>
<tr>
<td>(g)</td>
<td>C₆H₅CH = CHBr → C₆H₅CH = CH₂ + C₆H₅CH = CH₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Attention should be called to the fact that in four of the above cases the magnesium is attached directly to a tertiary carbon atom. In other words we have to do, in this phenomenon, with ethylene and not methylene dissociation. As will be shown in a later section of this

paper a hydrogen atom is required in the position in order that a Grignard reagent shows reducing action. In other words reaction mixtures containing $\text{CH}_3\text{MgX}$, $\text{C}_6\text{H}_5\text{CH}_2\text{MgX}$ or $\text{R}_3\text{C CH}_2\text{MgX}$ as the alkyl magnesium halide do not form the $\text{HMgXEt}_2\text{O}$ complex.

Olefinic splitting frequently takes place through the separation of a complex other than $\text{HMgX}$, among the complexes which split off in this way are $\text{HOMgX}$, $\text{ROMgX}$ and $\text{XMgX}$. Obviously these splittings are not accompanied by any reducing action.

Olefinic Splitting by the Separation of $\text{HOMgX}$.

Grignard, Ehrlich and Sache, Hell and Klages have each observed this type of splitting.

$$\begin{align*}
\text{HC} & \rightarrow \text{H} \quad \text{X} \quad \text{OEt}_2 \\
\text{HC} & \rightarrow \text{OMg} \quad \text{OEt}_2 \\
\text{HC} & \rightarrow \text{HOMg} \\
\text{HC} & \rightarrow \text{OMg} \\
\text{HC} & \rightarrow \text{HOMg}
\end{align*}$$

The author has repeated some of the experiments of Klages excepting that the conditions have been kept uniform in order that the results might be compared.

One fifth mole of the Grignard reagent, in ether solution, was treated with one tenth mole of acetophenone, the ether distilled off and the reaction mixture heated for six hours at 100°C. The results are summarized in the following equations.

1. $2\text{CH}_3\text{MgI} + \text{CH}_3\text{COCH}_3 \rightarrow \text{C}_6\text{H}_5\text{C} = \text{CH}_2 \quad 45\%$

2. $2\text{C}_2\text{H}_5\text{MgI} + \text{CH}_3\text{COCH}_3 \rightarrow \text{C}_6\text{H}_5\text{C} = \text{CHCH}_3 \quad 65\%$

3. $2\text{C}_3\text{H}_7\text{MgI} + \text{CH}_3\text{COCH}_3 \rightarrow \text{trace of product.}$

The mechanism of the dehydration of $R_3\text{COMgI}$ in the presence of $R'\text{MgI}$ may be pictured in either of the two following ways.

I. (a) $\text{Ph(Me)(Et)C} - \text{OMgI} + \text{EtMgI} \rightarrow \text{EtOMgI} + \text{Ph(Me)(Et)C-MgI}$

(b) $\text{Ph(Me)(Et)C-MgI} \rightarrow \text{Ph(Me)C} = \text{CHCH}_3 + \text{MgI}$

(c) $\text{Ph(Me)EtC-OMgI} + \text{HMgI} \rightarrow \text{Ph(Me)(Et)CH-MgO-MgI}_2$

(d) $\text{EtOMgI} + \text{HMgI} \rightarrow \text{EtH} + \text{MgO} + \text{MgI}_2$

(e) $\text{EtOMgI} + \text{H}_2\text{O} \rightarrow \text{EtOH + HOMgI}$

II (a)

(b) $\text{EtMgX} + \text{HOMgX} \rightarrow \text{EtH} + \text{MgO} + \text{MgX}$

Neither $\text{Ph(Me)(Et)CH}$ nor ethyl alcohol were found in the reaction products. And although when only two molecules of Et MgI were used for each molecule of Ph(Me)(Et)COMgI only small quantities of ethane were evolved the author is inclined to believe that decomposition proceeds according to II. The function of the
excess of Grignard reagent then is merely to hasten the process of dehydration.

This mechanism seems to be supported by the fact that Ph(Et)CHO+MgX, which is more difficult to dehydrate than Ph(Me)(Et)COMgX, can be readily dehydrated by increasing the temperature as is shown by the following experiments.

A solution of ethyl magnesium bromide was prepared by allowing 22 grams of ethyl bromide to react with 4.8 grams of magnesium with presence of 50cc of absolute ether. To this solution 25 grams of phenyl ethyl carbinol was added slowly. After heating on the water bath for two hours the ether was distilled off and 150cc of dry benzene added. The reaction mixture was then refluxed on the water bath for eight hours. The reaction product after vacuum distillation yielded phenyl propylene (bpt.173-176 C) as the chief product and four grams of the carbinol, regenerated.

In another experiment 25 grams of phenyl ethyl carbinol was added to a solution of ethyl magnesium iodide (0.2' mols) prepared directly in benzene. The mixture was heated on the water bath for five hours. The yield of phenyl propylene was quantitative.

Olefinic Splitting by the Separation of ROMgX

The phenomenon of olefinic splitting with the
separation of R0MgX has been observed by Grignard\textsuperscript{11} by the action of alkyl magnesium halides upon \(\beta\) bromophenetole. The results of his experiments may be summarized by the following equations.

1. \(\text{PhO-CH}_2\text{CH}_2\text{Br} + \text{Mg} \rightarrow \text{C}_2\text{H}_4 + \text{PhOMgBr} \rightarrow (\text{PhOCH}_2\text{CH}_2)_2\text{MgBr}\)

2. \(\text{PhO-CH}_2\text{CH}_2\text{Br} + \text{C}_5\text{H}_11\text{MgBr} \rightarrow \text{C}_2\text{H}_4 + \text{PhOMgBr} + \text{C}_5\text{H}_11\text{OMgBr}\)

3. \(\text{PhO-CH}_2\text{CH}_2\text{Br} + \text{PhCH}_2\text{MgBr} \rightarrow \text{C}_2\text{H}_4 + \text{PhOMgBr} + \text{PhO(CH}_2\text{)}_3\text{Ph} + \text{PhCH}_2\text{OMgBr}\)

4. \(\text{PhO-CH}_2\text{CH}_2\text{Br} + \text{PhMgBr} \rightarrow (\text{PhOCH}_2\text{CH}_2)_2\text{MgBr}(83\%) \rightarrow \text{PhMgBr}(\text{trace})\)

The reaction mechanism of this decomposition can best be formulated as follows:

\[
\begin{align*}
\text{Br} & \text{PhOCH}_2\text{CH}_2\text{Mg} + \text{Et}_2\text{O} \rightarrow \text{PhOCH}_2\text{CH}_2\text{Mg} - \text{Mg} - \text{Et}_2\text{O} + \text{C}_5\text{H}_11\text{Br} \\
\text{CH}_2\text{CH}_2\text{Br} & \text{PHMgBr} \rightarrow \text{C}_2\text{H}_4 + \text{PhOMgBr} \cdot \text{Et}_2\text{O} + \text{C}_5\text{H}_11\text{Br} \\
\text{Et}_2\text{O} & \text{PHMgBr} \rightarrow \text{C}_2\text{H}_4 + \text{PhOMgBr} \cdot \text{Et}_2\text{O} + \text{PhMgBr} + \text{Et}_2\text{O}
\end{align*}
\]

It is interesting, the fact that compounds of the type \(\text{R}_0(\text{CH}_2)_n\text{MgX}\) are only unstable when \(n=2\). The works of Braun and Sobeck\textsuperscript{12}, Hamonet\textsuperscript{13}, Dioneau\textsuperscript{14}, and Tarassov\textsuperscript{15}

\textsuperscript{12} Ber., 44, 1039 (1911); 13, Compt. rend., 138, 813-814; 975-977 (1904);
\textsuperscript{14} Ibid., 142, 91, 92 (1906); 15, Ber., 43, 941-948 (1910).
\textsuperscript{11} Compt. rend., 138, 1048-1050 (1904).
all indicate that compounds of the \( \text{RO} \left( \text{CH}_2 \right)_n \text{MgX} \) type 
\((R = \text{aliphatic or Ph radical})\) are stable when \( n=1, 3, 4, 5, \text{or } 6 \).

The following experiments were carried out by the author to test the validity of the above mechanism.

1. Two grams of \( \beta \) ethoxyethyl iodide were added in one portion to two grams of magnesium covered with 30cc of ether. More than one liter of ethylene was evolved. By adding an excess of acetyl chloride to the reaction product a considerable portion of ethyl acetate was obtained.

2. \( \beta \) ethoxyethyl chloride was found to be inactive with magnesium even in the presence of iodine.

3. Eight and one half grams of \( \beta \) ethoxyethyl iodide were added slowly to 27 grams of \( \text{EtMgI} \). A vigorous reaction followed with the evolution of a large volume of gas. The gas was found to consist of ethylene and a saturated hydrocarbon probably ethane. The reaction mixture upon treatment with acetyl chloride yielded ethyl acetate and three grams of unchanged \( \beta \) ethoxyethyl iodide.

4. A solution of 36 grams of \( \text{C}_2\text{H}_5\text{MgI} \) in ether was added slowly to 10 grams of \( \text{C}_2\text{H}_5\text{OH} \text{CH}_2\text{CH}_2\text{Cl} \). The ether was removed by distillation and the temperature gradually raised. A point was reached when a violent
reaction occurred with a swelling of the mass. The mixture was heated on the oil bath at 120°C for two hours. Upon working up the reaction mixture 6.8 grams of EtOCH₂CH₂I (b.p. 150-155°C) was obtained and 3.5 grams of EtOCH₂CH₂Cl (b.p. 108°C) recovered.

5. Experiment #4 was repeated excepting that the reaction mixture was heated at 180-200°C for 5 hours. Seven and eight tenths grams, or a 50% yield, of β-ethoxyethyl iodide was obtained.

Experiment #1 shows that EtOCH₂CH₂MgI decomposes with the formation of ethylene and EtOMgI. The reaction between EtOCH₂CH₂I and EtMgI as shown in experiment #3 yields these same products together with another gas, probably ethane.

Experiments #2, 4 and 5 show that β-ethoxyethyl chloride does not form a Grignard reagent directly and reacts with EtMgI by the usual exchange of halogens to form EtOCH₂CH₂I.

L. C. Swallen working in this laboratory has shown conclusively that EtOCH₂CH₂I reacts almost quantitatively with PhMgBr yielding EtOCH₂CH₂Ph. These results are in accord with those of Grignard cited above both tending to show that PhMgBr does not react with ROCH₂CH₂X to form ROCH₂CH₂MgX and hence no olefinic splitting can
occur.

The work of Swallen also shows that the reaction
\[ C_2H_5OCH-CH_2MgBr \rightarrow R-CH=CH-C_2H_50MgBr \]
\[ R \quad \text{is a general method for producing} \]
olefins.

All of these results seem to point strongly to correctness of the proposed mechanism.

**Olefinic Splitting by the Separation of \text{MgX}_2**

Braun and his students\(^{16}\) have shown that compounds of the type \( \text{X}(\text{CH}_2)_n \) are stable when \( n=4,5,6 \) and that compounds of the type \( \text{X}-\underset{\text{X}}{\text{C}}-\text{MgX} \) are extremely unstable, readily undergoing decomposition with the formation of olefine and \( \text{MgX}_2 \).

Grignard and Tissier\(^{17}\) have shown the instability of \( \text{BrCH}_2\text{C}_2\text{MgBr} \).

Ahrens and Stapler claim that the existence of \( \text{BrCH}_2\text{C}_2\text{MgBr} \) can be analytically proved. The author was unable to duplicate their experiments. The author found however that \( \text{Br(Ch}_2)_3\text{MgBr} \) was perfectly stable in ether solution.

All of these facts seem to indicate the peculiar instability of compounds of the type \( \text{X}-\underset{\text{X}}{\text{C}}-\text{Mg-X} \). This same tendency to undergo decomposition can be shown to

16. Ber. 44, 1039, 3699; 52, (B) 1713-16 (1919); 17. Compt. rend., 152, 836-7 (1901).
be a general property of organo metallic compounds of the type \( \textit{X-C-C-Me-X} \). (\( \textit{Me} = \text{Metal} \))

\[
\text{X-C-C-Me-X} \quad \text{C=C} + \text{MeX}_2
\]

Manchot\(^{19} \) has found that organo mercuri compounds such as \( \textit{R-O-CH}_2\textit{CH}_2\textit{HgX}, \textit{H-O-CH}_2\textit{CH}_2\textit{HgX} \) and \( \textit{X-Hg-CH}_2\textit{CH}_2\textit{O-CH}_2\textit{CH}_2\textit{HgX} \) are decomposed quite readily by the action of mineral acids, especially hydrochloric acid even when very dilute, to give a mercuric salt, ethylene and a residual product.

Green and Price\(^{20} \) have shown the compounds such as \( \text{Cl-CH=CH-AsCl}_2 \) react with cold \( \text{NaOH} \) solution to give not \( \text{Cl-CH}_2=\text{CH} \text{ AS}=0 \), but the quantative regeneration of acetylene.

These peculiar phenomena: of olefinic splitting can each be explained by the intermediate formation of the compounds of \( \textit{X-C-C-MeX} \) type which undergo the "olefinic splitting" as soon as they are formed in the following mechanism:

\[
\begin{align*}
\text{CH}_2\text{--X} & \rightarrow \text{CH}_2\text{--X} \\
\text{CH}_2\text{--Me--X} & \rightarrow \text{CH}_2\text{--Me--X} \\
\rightarrow \text{CH}_2 & \rightarrow \text{CH}_2 + \text{MeX}_2
\end{align*}
\]

When an alkyl mono-chloride is passed over a layer of various anhydrous metal chlorides in a tube

\(^{19} \) Ber., 38, 1296, 3259 (1905); \(^{20} \) Ber., 54, 964 (1920); \(^{20} \) J. Chem. Soc., 119, 448 (1921).
maintained at above 260°C, there is rapid decompo-
sition into unsaturated hydrocarbon and hydrochloride:

\[ C_{2n+1}H_{2n-1}Cl = HCl + C_nH_{2n} \]

Methyl chloride alone does not decompose in this way.  
Barium, nickel, cobalt, lead, cadmium, and ferrous chlo-
rides are suitable for effecting the decomposition.  
Primary chlorides are decomposed above 260°C and rapidly  
at 300°C while secondary and tertiary chlorides are  
still more easily acted upon. The same metallic chlo-
rides decompose ethyl alkyl mono-bromides or mono-
iodides with the separation of HBr or HI, but higher  
temperatures are required.\(^{21}\) Dry BaCl\(_2\) gives very  
good results and can effect the decomposition indef-
initely. The chlorides of mono-valent metals, Ag, Na  
and K are inactive. The process applies to monochlor  
derivatives of cyclohexane and cyclopentane. It  
succeeds with unsaturated mono-chloride and even  
halogenated alcohols\(^{22}\) as well as with dichlorocy-
clohexane which is converted to dihydrobenzene.\(^{23}\) Anhy-
\[ \text{drous AlCl}_3 \] acts vigorously in the same propyl chlo-
ride into propylene.\(^{24}\) At 300°C, ferric chloride  
causes the elimination of HCl from IsoC\(_4\)H\(_3\)Cl, but

\(^{21}\) Compt. rend., 141, 238 (1905); \(^{22}\) German patent 255,519  
(1913); \(^{23}\) French patent 441,203. \(^{24}\) Ann., 231, 306 (1885);
no isobutylene is formed; a solid of high molecular weight being produced. Chromic chloride is not active. All of these phenomena of "olefinic splitting" can be explained by the assumption of the intermediate formation of the compound of $X-C=C=MeX$ type derived from the alkyl chloride:

$$
\begin{align*}
H-C-C-Cl & \quad H-C-C-Cl & \quad H-C-C-Cl \\
X-Me-X & \quad X-Me-X & \quad X-Me-X \\
\rightarrow & \quad HX & \quad C-Cl \\
& \quad C=Me-X
\end{align*}
$$

The complex thus formed rapidly undergoing olefinic splitting:

$$
\begin{align*}
X-C-Cl & \quad \rightarrow \quad \rightarrow \quad \rightarrow \quad \rightarrow \\
\quad C=Me-Cl & \quad \quad \quad C=Me-Cl & \quad \quad \quad C=Me-Cl
\end{align*}
$$

The regenerated chloride can repeat the cycle of reactions indefinitely. The formation of such a mixed complex can actually be observed in the case of anhydrous AlCl₃. If this metallic chloride is mixed with $\text{IsoC}_4\text{H}_9\text{Cl}$ at $-100^\circ$, no reaction takes place but if the mixture is warmed to $0^\circ$, HCl and $\text{IsoC}_4\text{H}_8$ are evolved and an intensely colored liquid is formed.

Attention is also called to the interesting fact that the more electrochemically negative the

---

halogen, \( X \), the more electrochemically positive the metal(Me), the greater is the mutual attraction and between them therefore the more unstable is the compound of \( X-\underline{\text{C}}-\underline{\text{C}}-\text{MeX} \) type.

The same form of mechanism is found in ketonic and aldehydic splitting to be discussed in a later section.
PART IV

The Action of Alkyl Magnesium Halides upon Simple Ethers.

From the previous discussion one may expect the two types of mono ether complex to rearrange their structural bonds at high temperatures in the following manner:

The R'X obtained as a decomposition product of A reacts with RMgX to give R'MgX and RX. RX then acts on R-MgOR" to give R H \_ \_ , R(-H) and R"OMgX if R is an aliphatic radical; while R'MgX acts upon R'X to give R'-R' if R' is an aromatic radical. (The mechanism of the action of RX on R-MgX has been thoroughly discussed and proved in a previous section).

The above prediction is completely confirmed by the work of Stadnikoff on the action of Grignard reagents upon ethers. The following data may be tabulated:-
<table>
<thead>
<tr>
<th>R'O Bu</th>
<th>RMgX</th>
<th>gaseous products evolved during heating.</th>
<th>R'R</th>
<th>R'R'</th>
<th>ether regenerated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (Ph)₂CHOBu</td>
<td>CH₃MgCl(Et₂O)</td>
<td>No</td>
<td>0</td>
<td>42%</td>
<td>42%</td>
</tr>
<tr>
<td>2. &quot;</td>
<td>EtMgI(Et₂O)</td>
<td>C₂H₄ and C₂H₆</td>
<td>24%</td>
<td>23%</td>
<td>50%</td>
</tr>
<tr>
<td>3. &quot;</td>
<td>PrMgI(Et₂O)</td>
<td>C₃H₆ and C₃H₈</td>
<td>16%</td>
<td>33%</td>
<td>46%</td>
</tr>
<tr>
<td>4. Ph₂CHOEt</td>
<td>PrMgI(benzene)C₃H₆ and C₃H₈</td>
<td>38.5%</td>
<td>14.5%</td>
<td>21%</td>
<td></td>
</tr>
</tbody>
</table>

Gorski¹ obtained C₆H₅CH₂ Pr and (C₆H₅CH₂)₂ by the action of propyl magnesium bromide on C₆H₅CH₂OEt. His results may be similarly explained.

Attention is now called to the fact that the molecular free energy of most ethers is usually smaller in amount in comparison with that of ethyl ether, so they can not form any oxonium complex with RMgX in presence of ethyl ether. In order to cause the ethers to react with RMgX, ethyl ether must be removed and high temperatures used to cause the rearrangement of the structural bonds. High temperatures favor the spontaneous decomposition of RMgX into HMGX and R(-M). The HMGX formed will reduce R-OMgX to form RH + MgO + MgX₂.

The results obtained by Grignard² in the action of R-MgX on aromatic ethers, by Stadnikoff³ in the action of RMgX on (Ph)₃C-0Et and by Spath⁴ in the action of RMgX on both aliphatic and aromatic ethers may be readily explained either by the general mechanism previously outlined or by the process of reduction just mentioned.

PART V

THE REDUCING ACTION OF GRIGNARD REAGENTS UPON ALDEHYDES AND KETONES

Having discussed in detail the mechanism of the condensation processes involving Grignard reagents and their dependence upon the equilibrium between the two mono-etherate forms A and B, and having definitely established the nature of the spontaneous decomposition of these same reagents to give an olefine and RMgX, we are now in position to consider the reduction phenomena which so frequently accompany reactions involving these same reagents. These reduction phenomena may be divided into three distinct classes:

1. The reduction of aldehydes and ketones by alkyl magnesium halides.

II. The reduction of aldehydes by compounds of the type R'OMgX, especially R₂CHOMgX.

III. The action of alkyl magnesium halides upon compounds containing two adjacent, active functional groups.

The Reducing Action of Grignard Reagents upon Aldehydes and Ketones.

In Part I of this paper we discussed in detail the reaction of alkyl magnesium halides with aldehydes and ketones to yield the normal condensation products, secondary and tertiary alcohols, respectively. It was pointed out that these
normal condensation products had their origin through A and $A_1$ by a rearrangement of the structural bonds. It was also pointed out that a similar rearrangement applied to B through $B_1$ would result in a regeneration of the original aldehyde or ketone. There is no direct experimental evidence in the case of aldehydes and ketones that such a rearrangement ever occurs. An analogous rearrangement was proven for ethylene oxide.

A further extension of this mechanistic process may now be formulated to include the reduction phenomena.

\[
\begin{align*}
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{Mg} \quad \rightarrow \\
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{RCH} \quad \text{Mg} \quad 0 \\
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{RCH} \quad \text{Mg} \quad 0 \\
\text{CH}_2 \quad \text{H} \quad \text{X} \quad \text{RCH} \quad \text{Mg} \quad 0 \\
\text{CH}_2 \quad \text{H} \quad \text{X} \quad \text{RCH} \quad \text{Mg} \quad 0 \\
\end{align*}
\]

\[
\begin{align*}
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{Mg} \quad \rightarrow \\
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{Mg} \quad 0 \\
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{Mg} \quad 0 \\
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{Mg} \quad 0 \\
\text{Et}_2\text{O} \quad \text{R} \quad \text{X} \quad \text{Mg} \quad 0 \\
\end{align*}
\]
\[
\text{RCH}_2 \xrightarrow{X - \text{HCR}} 0 \xrightarrow{\text{Mg} \quad \|} 0 \xrightarrow{\text{H}_2\text{O}} \text{RCH}_2\text{OH} + \text{RCHO} + \text{ROMgX}
\]

It will be noted that the product arising by the loss of ether from B₁ is an A type of complex. Olefinic splitting of either this product or of A results in the formation of an olefine and the strongly reducing HMgX complex. Upon the basis of this mechanism the following rules of performance may be predicted.

1. The reducing action will depend upon the nature of R⁻ and the nature of X⁻.

2. Where R is CH₃⁻, Ph⁻ or R₃C-CH₂⁻ incapable of olefinic dissociation no reduction can take place.

3. Free aldehyde is necessary to combine with the HMgX complex and thus form the reduction product. An excess of the Grignard reagent will tend to prevent reduction.

4. Conversely, an excess of aldehyde enhances the chances for reduction.

5. The reducing action is dependent upon the amount of B; that is upon the equilibrium, B ⇌ A. The reduction will therefore vary: \text{RMgCl} < \text{RMgBr} < \text{RMgI} and \text{CH}_3\text{MgX}(\text{C}_2\text{H}_5\text{MgX} < \text{NC}_3\text{H}_7\text{MgX} < \text{NC}_4\text{H}_9\text{MgX} etc.

6. That radical R⁻, the reagent of which most readily undergoes olefinic dissociation will give the highest reducing action. Reduction therefore will vary \text{RCH}_2 < \text{R}_2\text{CH} < \text{R}_3\text{C}-.
7. Those experimental conditions which favor olefinic splitting will also favor reduction, i.e., absence of ether and high temperatures.

8. Since the total reducing action is largely dependent upon the nature of $R\text{MgX}$, it should be quite constant for any given alkyl magnesium halide.

These predictions are susceptible to experimental verification and the results of fifty test runs carried out according to the following procedure are shown in tables I and II.

An $X$ number of moles of the alkyl halide were dissolved in $2X$ moles of absolute ether and the solution added gradually to $(X + 0.2)$ moles of magnesium covered with 20cc of ether. One drop of bromine was used to start the reaction. The unchanged magnesium was removed by decantation and carefully washed with ether. The ether washings were added to the prepared reagent. A $X$ number of moles of freshly distilled benzaldehyde were dissolved in an equal volume of absolute ether and this solution added drop by drop to the Grignard reagent well cooled in a freezing mixture.

After completion of the reaction under the conditions indicated in the tables the reaction product was decomposed with 10% hydrochloric acid. The ether solution was shaken several times with concentrated sodium bisulfite solution and the recovered benzaldehyde calculated from the weight
of bisulphite compound obtained. The ethereal solution was then washed with dilute sodium carbonate and dried. After evaporation of the ether the residue was distilled in vacuo. The yield of benzyl alcohol was calculated from the weight of the p-nitrobenzoyl ester which could be obtained from a weighed portion of the distillate.

Table I

<table>
<thead>
<tr>
<th>R-Mg-X</th>
<th>Mol</th>
<th>C₆H₅CH =O(mol)</th>
<th>Reduction product(%) (C₆H₅CH₂OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH₃MgI</td>
<td>.2</td>
<td>.2</td>
<td>0</td>
</tr>
<tr>
<td>2. C₂H₅MgBr</td>
<td>.2</td>
<td>.2</td>
<td>18</td>
</tr>
<tr>
<td>3. C₆H₅MgI</td>
<td>.2</td>
<td>.2</td>
<td>25</td>
</tr>
<tr>
<td>4. NC₃H₇MgCl</td>
<td>.2</td>
<td>.2</td>
<td>0</td>
</tr>
<tr>
<td>5. NC₃H₇MgBr</td>
<td>.2</td>
<td>.2</td>
<td>20</td>
</tr>
<tr>
<td>6. NC₃H₇MgI</td>
<td>.2</td>
<td>.2</td>
<td>30</td>
</tr>
<tr>
<td>7. NC₄H₉MgCl</td>
<td>.2</td>
<td>.2</td>
<td>.5</td>
</tr>
<tr>
<td>8. NC₄H₉MgBr</td>
<td>.2</td>
<td>.2</td>
<td>22</td>
</tr>
<tr>
<td>9. NC₄H₉MgI</td>
<td>.2</td>
<td>.2</td>
<td>32</td>
</tr>
<tr>
<td>10. IsoC₃H₇MgBr</td>
<td>.2</td>
<td>.2</td>
<td>32</td>
</tr>
<tr>
<td>11. IsoC₄H₉MgBr</td>
<td>.2</td>
<td>.2</td>
<td>40</td>
</tr>
<tr>
<td>12. SecC₄H₉MgBr</td>
<td>.2</td>
<td>.2</td>
<td>25</td>
</tr>
<tr>
<td>13. Tert. C₄H₉MgBr</td>
<td>.2</td>
<td>.2</td>
<td>10(No normal product)</td>
</tr>
<tr>
<td>14. IsoC₅H₁MgBr</td>
<td>.2</td>
<td>.2</td>
<td>10</td>
</tr>
<tr>
<td>15. C₆H₁₁MgCl</td>
<td>.2</td>
<td>.2</td>
<td>15</td>
</tr>
<tr>
<td>16. C₆H₅MgBr</td>
<td>.2</td>
<td>.2</td>
<td>0</td>
</tr>
<tr>
<td>17. C₆H₅MgI</td>
<td>.2</td>
<td>.2</td>
<td>0</td>
</tr>
<tr>
<td>RMgX</td>
<td>mol C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CHO</td>
<td>Reaction condition</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH=0 (re-generated) (%)</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------------------</td>
<td>----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>-3°C</td>
<td>20</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0°C</td>
<td>20</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0°C (standing 1hr)</td>
<td>18</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0°C (standing 5hr)</td>
<td>12</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0°C (standing 24hr)</td>
<td>10</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>Boiling water bath (1hr)</td>
<td>5</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>(2hr)</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>(3hr)</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>Distill off ether, add C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;(100cc) and heat to boiling (1hr)</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>Ether solution (1 hr at room temperature)</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>Ether solution boiling water bath (3 hrs)</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;MgBr</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table II (continued)

<table>
<thead>
<tr>
<th>RMgX</th>
<th>mol C₆H₅CHO</th>
<th>Reaction condition</th>
<th>C₆H₅CH=0 (re- generated) (%)</th>
<th>C₆H₅CH₂OH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22. C₆H₅MgBr</td>
<td>0.5</td>
<td>1:0</td>
<td>Ether solution boiling water bath (3 hrs)</td>
<td>12</td>
</tr>
<tr>
<td>23. &quot;</td>
<td>&quot;</td>
<td>1.5</td>
<td>&quot;</td>
<td>15</td>
</tr>
<tr>
<td>24. &quot;</td>
<td>&quot;</td>
<td>4.5</td>
<td>Ether solution room temperature (10 days)</td>
<td>0</td>
</tr>
<tr>
<td>25. &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>10 days later boiling water bath (2 hrs)</td>
<td>0</td>
</tr>
<tr>
<td>26. &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Distill off ether, add C₆H₅CH₃, and heat to boiling (3 hrs)</td>
<td>0</td>
</tr>
<tr>
<td>28. &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Aldehyde to Grignard reagent in boiling benzene</td>
<td>0</td>
</tr>
<tr>
<td>27. &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Aldehyde to Grignard reagent in boiling ether</td>
<td>0</td>
</tr>
<tr>
<td>29. &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Aldehyde to Grignard reagent in boiling toluene</td>
<td>0</td>
</tr>
<tr>
<td>30. &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Grignard reagent to boiling aldehyde</td>
<td>0</td>
</tr>
<tr>
<td>31. &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Grignard reagent to boiling ethereal solution of aldehyde</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: papers recently published by Meisenheimer, Hess and Rheinboldt agree with the results of the author in many points but they differ as to the mechanism by which the alcohol is supposed to be formed in the reaction.

Discussion of Results

That those alkyl magnesium halides which cannot undergo olefinic dissociation will give no reducing action (prediction #2) is shown by test runs #1, 16, 17, 18 and 19 of Table I.

The effect of an excess of the Grignard reagent to largely prevent reduction (prediction #3) is borne out by runs 12, 13, 14, 15, 16, and 17 of Table II.
The increase in reduction product by the presence of free aldehyde (prediction #4) is shown by the series #s 18, 19, 20, 21, 22, and 23 of Table II.

That the reducing action is dependent upon the amount of R and therefore varies; RMgCl < RMgBr < RMgI is evident from the series #s 4, 5, 6; and 7, 8, 9 of Table I. Also that the alkyl series varies CH₃ < C₂H₅ < NC₃H₇ < N C₄H₉ - is shown by a comparison of test runs # 1, 3, 6, 9 or of 2, 5, and 8. Thus prediction 5 is fulfilled.

The series : NC₄H₉, Iso-C₄H₉/ sec-C₄H₉ and tert-C₄H₉ run through a maximum as shown by #5, 8, 11, 12 and 13 of Table I and do not support prediction #6. The underlying cause of this deviation from the theoretical is the unstability and low yield of those Grignard reagents.

The effects of varying reaction conditions such as reaction temperature and water concentration are shown by test runs # 1-12 and 24-31, both inclusive, of Table II. In the main they support prediction 7 that these conditions which favor olefinic splitting also favor reduction.

Prediction #8 that the total reducing action of any alkyl magnesium halide is proportional to the amount of the B form cannot be verified from the data at hand because in no case was the reducing action of the reagent exhausted.

In general the first and most fundamental prediction that the reducing action is a function of the nature of R- and the nature of X- is sustained.
The results obtained by Sabatier and Mahile in studying the action of R-Mg-X upon cyclohexanone as shown in Table III support the above conclusions.

Table III.

(Compt. rend. 141, 298-301 (1905))

<table>
<thead>
<tr>
<th>R</th>
<th>Mg X</th>
<th>Reduction product yield</th>
<th>Condensation Product yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃MgI</td>
<td></td>
<td>very slight</td>
<td>---</td>
</tr>
<tr>
<td>C₂H₅MgI</td>
<td></td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>NC₃H₇MgI</td>
<td></td>
<td>50%</td>
<td>---</td>
</tr>
<tr>
<td>IsoC₃H₇MgI</td>
<td></td>
<td>75%</td>
<td>---</td>
</tr>
<tr>
<td>IsoC₅H₁₁MgI</td>
<td></td>
<td>20%</td>
<td>---</td>
</tr>
<tr>
<td>SecC₈H₁₇MgI</td>
<td></td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>Cyclo-C₆H₁₁MgCl</td>
<td></td>
<td>large amount</td>
<td>20%</td>
</tr>
</tbody>
</table>

A careful survey of the literature¹ shows that the aldehydes CCl₃CHO, C₆H₅CHO and (CH₃)₃C-CHO; the ketones C₆H₅CO-C₆H₅, (CH₂)₅CH-CO-CH(CH₂)₅, (CH₃)₆CO, (iso-C₃H₇)₂CO, iso-C₄H₉CO-C₆H₅, Ph₃COC-Ph and aliphatic ketones of the type R₃C-CO-R are all easily reduced by alkyl magnesium halides.

These facts indicate that reduction takes place most readily

when the aldehyde or keto grouping is bound to a tertiary or secondary radical.

These radicals weaken the residual affinity of \( \text{C}=0 \) group to such an extent that \( \text{B}_1 \) can not rearrange themselves into \( \text{R} \text{C}^\text{X} \text{R} \text{OEt}_2 \), but remain as an oxonium complex which undergoes olefinic splitting following the loss of ether to bring about the reducing action. In certain cases the residual affinity of \( \text{C}=0 \) group is so weakened that \( \text{A}_1 \) cannot rearrange itself at high temperatures, while \( \text{B}_1 \) readily undergoes reduction; one therefore obtains a reduction product from \( \text{B}_1 \) and the recovered ketone from \( \text{A}_1 \). In the case of \( (\text{CH}_3)_3 \text{C}=(\text{CH}_3)_3 \), the residual affinity of \( \text{C}=0 \) group is so masked that it can have no action with \( \text{RMgX} \) under any conditions. (Ann. Chim. Phys. (8) 30, 349-453 (1913), The data summarized in Table IV illustrates those points.

The data was obtained by an experimental procedure similar to that previously described. In all cases the ether was distilled off, 100cc of benzene added and the reaction mixture heated at the boiling point for three hours. The separation of the products was made by fractional distillation.

<table>
<thead>
<tr>
<th>RMgX</th>
<th>Ketone</th>
<th>Condensation product (yield)</th>
<th>Reduction product (yield)</th>
<th>Ketone Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1. \text{isoC}_4\text{H}_9\text{MgX} )</td>
<td>( \text{CH}_3\text{CHO} )</td>
<td>52%</td>
<td>0%</td>
<td>large</td>
</tr>
<tr>
<td>( 2. )</td>
<td>( \text{CH}_3\text{CO CH}_3 )</td>
<td>50%</td>
<td>Small</td>
<td>33%</td>
</tr>
<tr>
<td>( 3. )</td>
<td>( \text{C}_6\text{H}_5\text{CHO} )</td>
<td>43%</td>
<td>40%</td>
<td>6%</td>
</tr>
<tr>
<td>( 4. )</td>
<td>( \text{C}_6\text{H}_5\text{CO C}_6\text{H}_5 )</td>
<td>Trace</td>
<td>38%</td>
<td>42%</td>
</tr>
</tbody>
</table>
REDUCTION OF ALDEHYDES BY COMPOUNDS OF THE TYPE

ROMgX. "KETONIC SPLITTING".

Joseph Marshall has definitely proven that the formation of a ketone is frequently the accompaniment of the reduction of an aldehyde. In such a case the reducing action is due to the separation of H3Mg X from the compound ROMgX. This decomposition seems to take place most readily when the radical, R- of ROMgX is secondary so that one of the splitting products is a ketone. The phenomenon may therefore be called "Ketonic Splitting". The mechanism is indicated below:

\[
\begin{align*}
R & \quad R \\
\text{C} & \quad \text{N} \\
& \quad \text{0Et}_2 \\
& \quad \text{Mg}
\end{align*}
\]

\[
\begin{align*}
R & \quad R \\
\text{C} & \quad \text{H} \\
& \quad \text{X} \\
& \quad \text{H}_2\text{O}
\end{align*}
\]

"Ketonic Splitting"

The author has been able to show that R(R')CHOgMgX, prepared by any one of the three methods indicated is almost equally efficient in reducing benzaldehyde to benzyl alcohol.

2. J. Chem. Soc. 105, 527-534 (1914); 107, 509-523 (1915); 127, 2187 (1925)
1. $R(R')\text{CHOM} + \text{C}_2\text{H}_5\text{MgBr} \rightarrow R(R')\text{CHOMgBr} - \text{C}_2\text{H}_5$

2. $\text{RCHO} + R'\text{MgBr} \rightarrow R(R')\text{CHOMgBr}$

3. $R'\text{CHO} + R\text{MgBr} \rightarrow R(R')\text{CHOMgBr}$

Rheinboldt and Roleff have shown that $R_2\text{CHOMgX}$ and $R_3\text{COMgX}$ remain unchanged after heating either in ether or benzene solution. This seems to indicate that ketonic splitting occurs after the addition of the aldehyde to the type B monoplex as formulated in the mechanism above.

The experimental procedure was the ordinary one. An ether solution containing 0.2 moles of $\text{Ph(Ent)CHOMgBr}$ was treated with 0.2 moles of benzaldehyde. The ether was then distilled off, 200cc of benzene added and the reaction mixture heated at the boiling point for 3 hours. The ketone formation was not measured but the benzyl alcohol was determined as previously described. The results are summarized in table V.

**Table V**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $[\text{Ph(Ent)CHO}(0.2 \text{ mole}) + \text{C}_2\text{H}_5\text{MgBr}(0.2 \text{ mole})]$</td>
<td>$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$</td>
<td>63%</td>
</tr>
<tr>
<td>2. $[\text{PhCHO}(0.2 \text{ mole}) + \text{EtMgBr}(0.2 \text{ mole})]$</td>
<td></td>
<td>51%</td>
</tr>
<tr>
<td>3. $[\text{EtCHO}(0.2 \text{ mole}) + \text{PhMgBr}(0.2 \text{ mole})]$</td>
<td></td>
<td>70%</td>
</tr>
<tr>
<td>4. $[\text{PhCHO}(0.2 \text{ mole}) + \text{EtMgI}(0.2 \text{ mole})]$</td>
<td></td>
<td>60%</td>
</tr>
<tr>
<td>5. $[\text{EtCHO}(0.2 \text{ mole}) + \text{PhMgI}(0.2 \text{ mole})]$</td>
<td></td>
<td>68%</td>
</tr>
</tbody>
</table>

Analogous results were obtained from $(\text{CH}_3)_2\text{CHOMgI}$ as shown by Table VI.
Table VI

\[
\text{(CH}_3\text{)}_2\text{CHO} \text{MgI} \quad \text{yield} \quad \text{C}_6\text{H}_5\text{CH}_2\text{OH}
\]

1. \[ \text{(CH}_3\text{)}_2\text{CHOH} \quad (. 2 \text{ mole}) + \text{C}_2\text{H}_5\text{MgI} (. 2\text{mole}) \] 33%

2. \[ \text{(CH}_3\text{)}_2\text{CHO} \quad (. 2 \text{ mole}) + \text{CH}_3\text{MgI} (. 2 \text{mole}) \] 35%

By Marshall

A summary of the results obtained is shown in Table VII.

Table VII

<table>
<thead>
<tr>
<th>RMgX</th>
<th>RCNO</th>
<th>Reaction Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhMgBr(1mole)</td>
<td>PhCHO(2mole)</td>
<td>PhCOPh + Ph CH\text{2} OH</td>
</tr>
<tr>
<td>p-CH\text{3}C\text{6}H\text{4} MgBr&quot;</td>
<td>PhCHO &quot;</td>
<td>PhCOC\text{6}H\text{4}CH\text{3} + PhCH\text{2} OH</td>
</tr>
<tr>
<td>CH\text{3}MgI (1mole)</td>
<td>PhCHO &quot;</td>
<td>PhCOCH\text{3} + PhCH\text{2} OH</td>
</tr>
<tr>
<td>C\text{2}H\text{5}MgI &quot;</td>
<td>PhCHO(1-1/2mole)</td>
<td>PhCOC\text{2}H\text{5} + PhCH\text{2} OH (30%)</td>
</tr>
<tr>
<td>CH\text{3}MgI &quot;</td>
<td>PhCH=CHCHO(2mole)</td>
<td>PhCH=CHCOCH\text{3} + PhCH=CHCH\text{2} OH</td>
</tr>
<tr>
<td>C\text{2}H\text{5}MgI &quot;</td>
<td>PhCH=CHCHO &quot;</td>
<td>PhCH=CHCOC\text{2}H\text{5} + PhCH=CHCH\text{2} OH</td>
</tr>
</tbody>
</table>

Meisenheimer\textsuperscript{3} in a recent paper has proved that by the action of isobutyl magnesium bromide upon benzaldehyde, mole for mole, benzyl alcohol is formed partly by olefinic splitting and partly by ketonic splitting. Further work should be done to determine the relative amounts of reducing action coming from the two sources.

**Conclusions**

One may conclude that aldehydes are reduced in the presence of compounds of the type R\text{2} CHO MgX by virtue of a

---

"ketonic splitting" with the separation of \( R\text{MgX} \). This process is quite analogous to the reduction of both aldehydes and ketones in the presence of compounds of the type \( R\text{MgX} \) by virtue of "olefinic splitting" and the two reduction processes are mechanically alike.

Other forms of "Ketonic Splitting". Separation of \( R\text{-O-MgX} \) and \( X\text{MgX} \).

If one is prepared to accept the validity of the reasoning by which the above conclusions have been drawn it is easy to understand the formation of ketones as intermediate products of the action of Grignard reagents upon esters (I) and acyl chlorides (II).

I. \[
\begin{align*}
R & \quad \text{OR'} \\
\downarrow & \quad \downarrow \\
0 & \quad \text{Mg} \\
\text{Cl} & \quad 0_{\text{Et}_2} \\
\end{align*}
\]

II. \[
\begin{align*}
R & \quad \text{Cl} \\
\downarrow & \quad \downarrow \\
0 & \quad \text{Mg} \\
\text{Cl} & \quad 0_{\text{Et}_2} \\
\end{align*}
\]

Tschelinzeff found that the heats evolved by the addition of esters to solutions containing \( R\text{OMgX} \) are higher than those obtained by the addition of the corresponding alcohols or ethers. The addition of the second and third molecule of

esters or acyl chlorides produce very low heat effects. These facts led to the belief, by the author, that the larger portion of the residual affinity of esters and acyl chlorides is resident in the carbonyl group and that the first point of attack of an alkyl magnesium halide $\text{RMgX}$, upon such derivatives is through this group.

The peculiar results obtained by Stadnikoff$^5$ who studied the action of $\text{PrMgI}$ upon $\text{CH}_3\text{COOCHPh}_2$ are easily explained upon this basis. He reported 12.5% of $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_6$, 12.5% of $\text{Ph}_2\text{CH-CHPh}_2$ and five grams of $\text{CH}_3(\text{Pr})_2\text{C-OH}$. The formation of $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_6$ directly from $\text{C}_3\text{H}_7\text{MgI}$ is easily understood upon the basis of "olefinic splitting" and reduction. By addition of N-$\text{C}_3\text{H}_7\text{MgI}$ to the ester and ketonic splitting, $\text{CH}_3\text{CO C}_3\text{H}_7$ and $\text{Ph}_2\text{CHOMgI}$ are formed. The original $\text{NC}_3\text{H}_7\text{MgI}$ acting upon $\text{Ph}_2\text{CHOMgI}$ gives $\text{Ph}_2\text{CHI}$ and the whole series of products then becomes clear through the following series of equations.

(a) $\text{CH}_3\text{COOCHPh}_2 + \text{NC}_3\text{H}_7\text{MgI} \rightarrow \text{Ph}_2\text{CHOMgI} + \text{CH}_3\text{CO C}_3\text{H}_7$

(b) $\text{Ph}_2\text{CHOMgI} + \text{NC}_3\text{H}_7\text{MgI} \rightarrow \text{Ph}_2\text{CHI} + \text{NC}_3\text{H}_7\text{MgO-MgI}$

(c) $\text{Ph}_2\text{CHI} + \text{NC}_3\text{H}_7\text{MgI} \rightarrow \text{Ph}_2\text{CHMgI} + \text{NC}_3\text{H}_7\text{I}$

(d) $\text{Ph}_2\text{CHI} + \text{Ph}_2\text{CHMgI} \rightarrow \frac{\text{Ph}_2\text{CH-CHPh}_2(r.5\%)}{\text{MgI}} + \text{MgI}_2$

(e) $\text{NC}_3\text{H}_7\text{I} + \text{NC}_3\text{H}_7\text{MgI} \rightarrow \frac{\text{C}_3\text{H}_6 + \text{C}_3\text{H}_6(r.5\%)}{\text{MgI}} + \text{MgI}_2$

(f) $\text{CH}_3\text{CO C}_3\text{H}_7 + \text{NC}_3\text{H}_7\text{MgI} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3(\text{NC}_3\text{H}_7)\text{C-OH (5 grams)+HOMgI.}$

An interesting series of experiments were devised to test this theory of "ketonic splitting". In any

5. Ber. 47, 2132-2142 (1914)
case where the ketone $R'\text{COR''}$ is readily reduced by the alkyl magnesium halide, $R''\text{MgX}$, then if in the reaction of this same reagent upon the ester, $R'\text{COOR}$, or the acyl chloride, $R'\text{COCl}$, a ketone is the first reaction product, reduction will follow and the secondary alcohol $R'(R'')\text{CHOH}$ will be the final product and not the tertiary alcohol $R'(R'')_2\text{COH}$ as one would normally suppose.

Experimental Procedure.

A solution of isobutyl magnesium bromide was prepared by causing 14 grams of isobutyl bromide to react with 2.4 grams of magnesium in 50cc of ether. Sixteen grams of isobutyl phenyl ketone were added and the reaction mixture allowed to stand at room temperature for five hours. Upon working up the reaction mixture in the usual way phenyl isobutyl carbinol was obtained as the sole product. This was identified by oxidation to the ketone, bpt. 225-226°C, which was in turn converted into its oxime, mpt. 73-74°C.

$$(\text{CH}_3)_2\text{CH-CH}_2\text{MgBr} \rightarrow (\text{CH}_3)_2\text{C} = \text{CH}_2 + \text{HMgBr}$$

$$(\text{CH}_3)_2\text{CH-CH}_2\text{COPh} + \text{HMgBr} \xrightarrow{\text{H}_2\text{O}} (\text{CH}_3)_2\text{CH-CH}_2\text{CHOH-Ph} + \text{HMgBr}$$

In a second experiment 0.2 mole of isobutyl magnesium bromide was allowed to react with 15 grams of ethyl benzoate. The reaction mixture after standing over night at room temperature yielded 38% of phenyl isobutyl carbinol. No tertiary carbinol could be isolated.

A similar experiment in which isobutyl magnesium
bromide was allowed to react with benzyl chloride yielded 42% of phenyl isobutyl carbinol and no tertiary alcohol.

Ketonic Splitting by the Separation of $R_3C\cdot MgX$

Another interesting case of ketonic splitting is to be found in the work of Lerodeo$^6$. This worker found that the reaction mixture obtained by the action of normal propyl magnesium chloride upon dimethyl malonic acid ethyl ester yielded; $(CH_3)_2CH\cdot COEt, NC_3H_7COC_3H_7iso, NC_3H_7COC_3H_7N, (N-C_3H_7)_2CHON, (NC_3H_7)_3COH$ and a little $NC_3H_7CHOH\cdot C(Me)_2CHON\cdot C_3H_7N$. The origin of these products is easily understood upon the basis of a series of "ketonic splittings" if in one instance one is prepared to admit the separation of a tertiary alkyl magnesium halide.

I. $EtOOC\cdot C(CH_3)_2\cdot C\cdot OEt\xrightarrow{\text{EtOOC\cdot C(CH}_3)_2\cdot C\cdot OEt2} C_3H_7$  
$0\xrightarrow{\text{MgX\cdot OEt2}} C_3H_7$  

II. $C_3H_7CO\cdot C\xrightarrow{\text{EtOOC\cdot C(CH}_3)_2\cdot C\cdot OEt2} C_3H_7$  
$0\xrightarrow{\text{EtOmgX\cdot OEt2}} C_3H_7$  

III. $EtOOC\cdot C(CH_3)_2\cdot C\cdot OEt\xrightarrow{\text{EtOOC\cdot C(CH}_3)_2\cdot C\cdot OEt2} C_3H_7$  
$0\xrightarrow{\text{MgX\cdot OEt2}} C_3H_7$
III. (continued)

\[
\text{EtOOC} \\
\text{CH}_3 - C - \text{MgXOEt}_2 + \text{C}_3\text{H}_7\text{CO.C}_3\text{H}_7
\]

IV.

\[
\text{Et}_2\text{O}_2\text{Mg} \\
\text{CH}_3 - C - C - \text{Et} \\
\text{CH}_3 - \text{C} - \text{Mg} + \text{X} - \text{Et}_2 \Rightarrow \text{CH}_3 - C - \text{OEt} \\
\text{CH}_3 - \text{C} - \text{OEt} \\
\rightarrow \text{C}_3\text{H}_7\text{CO-C- MgXOEt}_2 + \text{EtO}_2\text{MgXOEt}_2
\]

Reactions I, II and IV are simple Ketonic Splittings by the separation of ROMgX. Reaction III occurs with the separation of the tertiary alkyl magnesium halide EtOOC·(CH₃)₂C-MgXOEt₂. All the products are now easily accounted for by simple reactions:

1. EtOOC·C(CH₃)₂-MgXOEt₂+H₂O \rightarrow (CH₃)₂CH·COOEt + HOMgXOEt₂
2. C₃H₇CO-C(CH₃)₂ MgXOEt₂+H₂O \rightarrow (CH₃)₂CH·COC₃H₇ + HOMgXOEt₂
3. C₃H₇CO-C₃H₇ is found in III
4. C₃H₇MgXOEt₂ \rightarrow C₃H₇ + HMgXOEt₂
   C₃H₇ CO C₃H₇+ HMgXOEt₂ → C₃H₇CHOH.C₃H₇ + HOMgX.OEt₂
5. C₃H₇CO.C₃H₇+ C₃H₇MgXOEt₂ \rightarrow (C₃H₇)₂CÓN + HOMgXOEt₂
6. C₃H₇CO·C(CH₃)₂CO-C₃H₇+ 2HMgXOEt₂ \rightarrow C₃H₇CHOH-C(CH₃)₂CHOH-C₃H₇ + 2HOMgXOEt₂

"Ketonic Splitting" by the Separation of R₂M-MgX

Roger Adams⁷ has found that RCO-CO-N(CH₃)Ph is formed by

⁷ J. Am. Chem. Soc., 42, 2369 (1920)
by the action of RMgBr upon Ph(Me)N-(CH₃)Ph. The mechanism of this reaction is readily understood by an analogous formulation.

\[
\begin{align*}
\text{Ph} & \quad \text{N} \quad \text{C} \quad \text{O} \\
\text{Me} & \quad \text{O} \quad \text{O} \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{N} \quad \text{C} \quad \text{N} \\
\text{Me} & \quad \text{O} \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{N} \quad \text{C} \quad \text{N} \\
\text{Me} & \quad \text{O} \quad \text{Me}
\end{align*}
\]

"Ketonic Splitting"

In closing the discussion of these conditions under which ketones are formed in the course of reactions involving alkyl magnesium halides one can scarcely resist the temptation to point out a few instances in the literature where the formation of the products obtained in the application of a Grignard reaction has never been explained. These cases fit into the above scheme if one assumes the temporary formation of a ketone or analogous compound with the separation of HOMgX, XMgX or HMgX respectively.

1. Houben⁸ has found that phenylamino magnesium iodide absorbs carbon dioxide with the formation of phenylisocyanate.

\[
\begin{align*}
\text{Ph+NH-MgI} & \quad \text{CO}_2 \rightarrow \text{Ph-N-CO} \\
\text{N-OMgI} & \quad \text{HOMgI}
\end{align*}
\]

⁸Ber. 37, 3978 (1904), 42, 3815 (1909)
II. McKenzie and Boyle⁹ have shown that phenyl magnesium bromide reacts with diphenyl chloro acetyl chloride to give a product isomeric with diphenyl-methyl phenyl ketone, together with the simultaneous formation of diphenyl.

\[
\begin{align*}
1. \text{Ph}_2\text{C} & \quad + \quad \text{MgX} \quad \rightarrow \quad \text{Ph}_2\text{C} \quad - \quad \text{C} = \text{O} \quad + \quad \text{PhCl} \\
\text{COCl} & \\
\rightarrow & \\
\text{Ph}_2\text{C} & \quad = \quad \text{C} = \text{O} \quad + \quad \text{MgXCl}
\end{align*}
\]

2. \[\text{Ph}_2\text{C}=\text{C}=\text{O} + \text{Ph}:\text{MgX} \rightarrow \text{Ph}_2\text{C} = \text{C}^0\text{MgX} \quad \text{Ph} \quad \text{Ph}_2\text{C}=\text{C}^0\text{MgX} \quad \text{Ph}
\]

3. \[\text{PhCl} + \text{PhMgCl} \rightarrow \text{PhPh} + \text{MgXCl}.
\]

III. Tschenko¹⁰ found that magnesium reacts with acetyl bromide in dry ether to give 25% of acetic acid, 30% ethyl acetate and 40% of diacetyl. In dilute ether the yield was 30% ethyl acetate and 30% diacetyl. And in concentrated ether solution 80% ethyl acetate with only a trace of diacetyl. The mechanism by which these products are formed may be indicated as follows:

1. \[\text{CH}_3\text{COBr} + \text{Mg} + \text{Et}_2\text{O} \rightarrow \text{CH}_3\text{CO} \quad \text{MgBrEt}_2\]

\[\rightarrow \quad \text{CH}_2=\text{C}=\text{O} + \text{HMgBrEt}_2\]

2. \[\text{CH}_3\text{COMgBrEt}_2 + \text{HMgBrEt}_2 \rightarrow \text{CH}_3 - \quad \text{C}^0\text{MgBrEt}_2\]

\[
\text{H} \\
\text{CH}_2\text{COBr} \quad \text{CH}_3 \quad \text{C}^0\text{MgBrEt}_2 + \text{BrMgBrEt}_2 \quad \text{0-CO-CH}_3
\]

3. \( \text{CH}_3\text{CO-CH-CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{HOMgBr} \cdot 0\text{Et}_2 \)
\( \text{MgBr}0\text{Et}_2 \)

4. \( \text{CH}_2=\text{C}=0 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{=C=O} \cdot \text{OH} \)

5. \( \text{CH}_2=\text{C}=0 + \text{CH}_3\text{CO MgBr} \rightarrow \text{CH}_2=\text{C}-\text{CO}-\text{CH}_3 \)
\( \text{OMgBr} \cdot 0\text{Et}_2 \)

\( \text{H}_2\text{O} \rightarrow \text{CH}_3\text{=C-}0\text{CO-CH}_3 + \text{HOMgBr} \cdot 0\text{Et}_2 \)

Conclusions

From the preceding discussion the following conclusions may be drawn.

1. The formation of ketones by the action of alkyl magnesium halides upon esters and acyl chlorides may be explained upon the same general mechanism as "olefinic" and "ketonic splitting", which is accompanied by reduction, through the separation of \( \text{ROMgX or AMgX} \), respectively.

2. "Ketonic Splitting" may also occur with the separation of \( \text{R}_3\text{C-MgX} \) or \( \text{R}_2\text{N-MgX} \).

3. "Ketonic Splitting" analogous to ketonic splitting may also occur and gives a basis of explaining many heretofore unexplained reactions.
"Aldehydic Splitting" of Compounds of the Type R-CH$_2$OMgX.

Just as we have formation of olefines by the splitting of alkyl magnesium halides, RMgX, and of ketones by the splitting of the alkyloxy magnesium halides R$_2$CHO$_2$OMgX so can we also have formation of aldehydes by the splitting of the alkyloxy magnesium halides RCH$_2$OMgX.

The experimental verification of this type of splitting is to be found in the work of Marshall$^1$ who showed benzaldehyde to be one of the products of the reaction between phenyl magnesium bromide and formaldehyde.

$$\text{PhMgBr} + \text{CH}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OMgBr}$$

Splitting with the formation of an Ester,

"Ester Splitting".

Grignard and his students$^2$ have repeatedly found that a reaction takes place between an aldehyde and an alkyl-}

---

1. J. Chem. Soc., 127, 2187 (1925);
phenomena is easily understood upon the basis of a mechanism perfectly analogous to those given above.

\[
\begin{align*}
\text{(a)} & \quad \text{C}_3\text{H}_7 \quad \text{H} \\
& \quad \text{C} + \text{OEt} \quad \text{I} \\
& \quad \text{0} \quad - \quad \text{Mg} \\
& \quad \text{0} \quad - \quad \text{Mg} \\
\text{C}_3\text{H}_7 \quad \text{OEt} \\
& \quad \rightarrow \quad \text{C} \quad \text{H} \quad \text{I} \\
& \quad \text{0} \quad - \quad \text{Mg} \\
\text{(b)} & \quad \text{C}_3\text{H}_7 \quad \text{H} \\
& \quad \text{C} + \text{OEt} \quad \text{I} \\
& \quad \text{0} \quad - \quad \text{Mg} \\
& \quad \text{0} \quad - \quad \text{Mg}
\end{align*}
\]

\[
\begin{align*}
\text{(c)} & \quad \text{C}_3\text{H}_7 \quad \text{OEt} \quad \text{C}_4\text{H}_9 \\
& \quad \text{C}_3\text{H}_7 \quad \text{OEt} \quad \text{I} \\
& \quad \text{0} \quad - \quad \text{Mg} \\
& \quad \text{0} \quad - \quad \text{Mg}
\end{align*}
\]

\[
\begin{align*}
\text{C}_3\text{H}_7\text{COOEt} + \text{EtMgI} \quad \text{OEt}_2
\end{align*}
\]

Grignard and Dubien found that 0.5 mole of 
\[\text{N-} \text{C}_3\text{H}_7\text{CHO}\] reacting with 0.1 mole of \[\text{C}_2\text{H}_5\text{OMgI}\] yielded 45% of ethyl butyrate, and a considerable amount of butyl butyrate, together with the aldol condensation product, \[\text{CH}_3\text{CH}_2\text{CH}_2-\text{CHON-CHEt-CHO}\]. In the case where acetone was substituted for the aldehyde only an aldol type of condensation product, \[\text{(CH}_3\text{)}_2\text{C(OH)}-\text{CH}_2-\text{CO-CH}_3\], was produced. This is easily understood
since the ketone addition product formed with EtOMgI could undergo only ketonic splitting.

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\
\uparrow & \quad \uparrow \\
\text{C--OEt} & \quad \text{C} \\
\text{I--OEt}_2 & \quad + \\
\text{0--Mg} & \quad \text{EtOMgI, OEt}_2 \\
\end{align*}
\]

The above mechanism would indicate that there is a dynamic equilibrium set up in the action of R'OMgX upon an ester R''-CO-OR.

\[
\begin{align*}
\text{R''} & \quad \text{OR} \quad \text{OR'} \quad \text{X} \\
\text{C--} & \quad \downarrow \quad \text{OEt}_2 & \quad \text{C--} & \quad \text{Mg} \\
\text{0--} & \quad \text{Mg} & \quad \text{0--} \\
\end{align*}
\]

The work of Stadnikoff\(^3\) indicates that this equilibrium is largely dependent upon the nature of R''\(^\text{3}\). It is also dependent however upon the nature of R and R'. When R' is C\(_6\)H\(_5\) or (C\(_6\)H\(_5\))\(_3\)C-- the oxygen of R'OMgX has almost no residual affinity and there is therefore no reaction with an ester. A secondary radical (R') can easily replace a primary radical (R) to form a new ester.

A number of experiments along this line were carried out by the author and the results are summarized in the Table I. An ether solution containing 0.2 moles of the alkylxoxy magnesium halide, R'OMgX was prepared by allowing a Grignard reagent to react with the appropriate alcohol, or

aldehyde and an equivalent portion of the ester added. After standing at room temperature for two hours the reaction mixture was decomposed and examined in the usual manner. The \(\text{CH}_3\text{COOCH(Me)}\text{Ph} \) (bpt. 217-220 °C, spg. 1.06 at 17°) was further identified by hydrolysis in alcoholic potash solution to give acetic acid and phenyl methyl carbinol, bpt 202-204 °C. The identity of \(\text{CH}_3\text{COOCHPh}_2 \) (bpt 301-320° at 739 mm, spg 1.5 at 22°) was proven in a similar manner.

### Table I

<table>
<thead>
<tr>
<th>R&quot;COOR</th>
<th>R'OMgX</th>
<th>R&quot;COOR'</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (\text{CH}_3\text{COOC}_2\text{H}_5)</td>
<td>Ph(Me)CHOMgI</td>
<td>(\text{CH}_3\text{COCH(Me)}\text{Ph})</td>
<td>68%</td>
</tr>
<tr>
<td>2. (\text{CH}_3\text{COOC}_2\text{H}_5)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>62%</td>
</tr>
<tr>
<td>3. (\text{CH}_3\text{COOCH(Me)}\text{Ph})</td>
<td>&quot;</td>
<td>no reaction</td>
<td>---</td>
</tr>
<tr>
<td>4. (\text{CH}_3\text{COOC}_2\text{H}_5)</td>
<td>PhCHOMgI</td>
<td>(\text{CH}_3\text{COOCHPh}_2)</td>
<td>72%</td>
</tr>
<tr>
<td>5. (\text{CH}_3\text{COOC}_2\text{H}_5)</td>
<td>PhOMgI</td>
<td>no reaction</td>
<td>---</td>
</tr>
<tr>
<td>6. (\text{CH}_3\text{COOC}_2\text{H}_5)</td>
<td>Ph_3COMgI</td>
<td>&quot;</td>
<td>---</td>
</tr>
</tbody>
</table>

In experiment #1 the R'OMgX was prepared by the action of C_2H_5MgI upon Ph(Me)CHOH while in experiment #2 it was prepared by the action of CH_3MgI upon C_6H_5CHO. The results sustain the conclusions stated above.

One further reduction phenomenon peculiar to ROMgX, remains to be elucidated. It has been repeatedly shown by different investigators that an aldehyde R"CHO is frequently easily reduced to the corresponding alcohol R"CH_2OH in the presence of absolute alcohol and a very small
amount of \( \text{C}_2\text{H}_5\text{OMgX} \). This reduction is easily understood if we assume the following mechanism.

\[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{Mg} \cdot \text{Et}_2} \text{CH}_3 \\
\text{CH} & \quad \text{X} \\
\text{O} & \quad \text{Mg} \\
\end{align*}
\]

\[
\begin{align*}
\text{R''} & \quad \text{H} \\
\text{C} & \quad \text{X} \\
\text{O} & \quad \text{Mg} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{OCH}_2\text{R''} \quad \text{X} \\
\text{C}_2\text{H}_5 & \quad \text{Mg} \\
\end{align*}
\]

The above reaction was subjected to experimental investigation as follows: One tenth mole of \( \text{C}_2\text{H}_5\text{OMgCl} \) was prepared by adding 75cc of absolute alcohol to an ether solution of \( \text{N-C}_4\text{H}_9\text{MgCl} \). One hundred cc of the appropriated aldehyde or ketone mixed with 200cc of absolute alcohol was then added and the reaction mixture was heated to boiling under a reflux condenser. A stream of deoxidized air was led through the reaction mixture throughout the process. The acetaldehyde evolved was condensed in a series of bulbs immersed in a freezing mixture. In one experiment the yield of acetaldehyde was equal to about 75% of the reduced alcohol obtained. The reaction mixture after distilling off the alcohol was acidified with dilute \( \text{H}_2\text{SO}_4 \), extracted with
ether, dried over K₂CO₃ and fractionated. The results are summarized in Table II.

**Table II.**

<table>
<thead>
<tr>
<th>Aldehyde or Ketone</th>
<th>Reduction Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. C₆H₅CHO</td>
<td>C₆H₅CH₂OH</td>
<td>65%</td>
</tr>
<tr>
<td>2. C₆H₆CH = CH - CHO</td>
<td>C₆H₆CH = CH-CH₂OH</td>
<td>70%</td>
</tr>
<tr>
<td>3. CH₃CH= CH - CHO</td>
<td>CH₃CH= CH-CH₂OH</td>
<td>53%</td>
</tr>
<tr>
<td>4. C₆H₅-COCH₃</td>
<td>C₆H₅CHOH - CH₃</td>
<td>0%</td>
</tr>
<tr>
<td>5. CCl₃CHO</td>
<td>CCl₃CH₂OH</td>
<td>0%</td>
</tr>
</tbody>
</table>

Joseph Houben⁴ has described a reaction by which hydropipinen magnesium chloride reacts with methyl formanilide to produce hydropipinen aldehyde. The mechanism of the reaction can be understood if one assumes the separation of Ph(Me)N-MgX as in the case of "ketonic splitting" described by Adams and referred to previously in this paper.

\[
\begin{align*}
\text{Ph(CH₃)N} & \quad \text{H} \\
\text{C} & \quad - \text{C₃₀H₁₇Cl} \\
\text{0} & \quad + \text{Mg} \quad \rightarrow \quad \text{C} \quad - \text{C₃₀H₁₇} \\
\text{0} & \quad \rightarrow \quad \text{MgClOEt₂}
\end{align*}
\]

\[
\begin{align*}
\text{C₃₀H₁₇} & \quad \text{H} \\
\text{C} & \quad - \text{N(CH₃)Ph} \quad \rightarrow \quad \text{C₃₀H₁₇CHO + Ph(CH₃)N-MgClOEt₂} \\
\text{0} & \quad \rightarrow \quad \text{MgClOEt₂}
\end{align*}
\]

**Summary**

It has been shown that the alkylxoy magnesium halides R₂CHOMgX and RCH₂OMgX undergo ketonic and aldehydic splitting, respectively, to cause the reduction of aldehydes to primary
alcohols. These reducing actions can in every case be formulated upon a common mechanism.

These conclusions are supported by the fact that tertiary alkyloxy magnesium halides have no action upon either aldehydes or ketones as was demonstrated by a very considerable number of negative experiments carried out in this laboratory.

The work of Marshall supported also by the results of this research indicate that ketones are not reduced by alkyloxy magnesium halides.

The work of Verley and Nakai shows that compounds of the type $\text{Mg(OR)}_2$ show reducing action both in the presence and absence of alcohol. While the work of Meerwein and Schmidt shows that $\text{Al(OEt)}_3$, $\text{Mg(OEt)}_2$ and $\text{NaOEt}$ behave in a similar manner although they differ in degree of reactivity.

It will be of interest to take up in a mechanistic way a comparison of the condensations and reductions which take place in the presence of sodium alcoholates and alkyloxy magnesium halides, except that the problem extends beyond the scope of this thesis.

III. Reduction of Compounds Two Adjacent Functional Groups.

Many other interesting cases have been recorded in which reduction occurs in the presence of a Grignard reagent. It will suffice to mention here a few of these. Quite recently the reduction of azobenzene has been discussed by Gilman and his students. (Gilman and Pickens-J. Am. Chem. Soc. 47, 2406 and Gilman and Adams-J. Am. Chem. Soc. 47, 2816)

They have shown the reduction of azo compounds to be accompanied by the formation of large amounts of the condensed hydrocarbon R-R where the Grignard reagent is R-Mg-X. These facts can be readily explained by the following mechanism.

\[
\begin{align*}
C_6H_5-N-\text{Br} & \rightarrow C_6H_5-N-Br \\
(\text{a}) & \\
C_6H_5-N-\text{MgPh} & \rightarrow C_6H_5-N-\text{MgPh} \\
(\text{b})
\end{align*}
\]

\[
\begin{align*}
\text{PhMg} & + \text{Br} \rightarrow \text{PhMg} + \text{Br} \\
\text{N} & \rightarrow \text{N} + \text{Mg-Br} \\
\text{Ph} & \rightarrow \text{Ph} + \text{Ph}
\end{align*}
\]

(c) PhBr + PhMgBr \rightarrow Ph-Ph + MgBr₂

(d) \[
\begin{align*}
\text{Ph-N-MgPh} + 3\text{H}_2\text{O} & \rightarrow \text{Ph-NH} + C_6H_6 + \text{Mg(OH)}_2 + \text{MgBr(OH)} \\
\text{Ph-N-MgBr} & \rightarrow \text{Ph-NH}
\end{align*}
\]

This mechanism accounts for the fact that when an acyl chloride is added to the reaction mixture large quantities

1. Ber. 43, 1298-1303 (1910); Ann. 400, 55-72 (1913); Ber. 48, 1081-1101 (1922); Ann. Chem. J. 35, 69 (1906).
of a \textit{mono} acyl derivatives is formed.

\[
\begin{align*}
\text{Ph} - \text{N} - \text{MgBr} & \quad \xrightarrow{+ \text{AcCl}} \quad \text{Ph} - \text{N} - \text{Ac} + \text{MgBrCl} \\
\text{Ph} - \text{N} - \text{MgPh} & \quad \text{Ph} - \text{N} - \text{MgPh}
\end{align*}
\]

Diacyl derivatives are formed in an analogous manner.

\[
\begin{align*}
\text{Ph} - \text{N} - \text{MgBr} & \quad \xrightarrow{+ 2\text{BzCl}} \quad \text{Ph} - \text{N} - \text{Bz} + \text{MgClBr} + \text{PhMgCl} \\
\text{Ph} - \text{N} - \text{MgPh} & \quad \text{Ph} - \text{N} - \text{Bz}
\end{align*}
\]

The action of Grignard reagents upon organic peroxides are equally well explained. Dibenzyl peroxide reacts with phenyl magnesium bromide to yield phenyl benzoate, bromomagnesium benzoate, triphenyl carbinol, and phenol. Gilman says benzophenone may also be present. All of these products are easily accounted for as follows:

(a) \[\text{PhCO} - \text{O} \rightarrow \text{Ph} + \xrightarrow{+ \text{Ph}} \text{PhCOOPh} + \text{PhCOOMgBr}\]

(b) \[\text{PhCOOPh} + \text{PhMgBr} \rightarrow \text{Ph}_2\text{C}(\text{OPh})\text{OMgBr}\]

(c) \[\text{Ph} - \text{C} - \text{Ph} \xrightarrow{\text{OMgBr}} \text{Ph} - \text{Ph} + \text{PhOMgBr}\]

(d) \[\text{Ph} \xrightarrow{\text{C}} \text{Ph} \xrightarrow{\text{OMgBr}} \text{Ph} - \text{Ph} \xrightarrow{\text{H}_2\text{O}} \text{Ph}_3\text{COH} + \text{HOMgBr}\]

(e) \[\text{PhOMgBr} + \text{H}_2\text{O} \rightarrow \text{PhOH} + \text{HOMgBr}\]

Ethyl peroxide yields phenetole and diphenyl but very
little phenol.

\[ C_2H_50\text{Ph} + C_2H_5\text{MgBr} \rightarrow C_2H_5\text{Ph} + C_2H_50\text{MgBr} \]

(b) \[ \text{PhBr} + \text{MgPh} \rightarrow \text{PhBr} + C_2H_50\text{MgBr} \]

(c) \[ \text{PhBr} + \text{PhMgBr} \rightarrow \text{Ph-PH} + \text{MgBr}_2 \]

The peculiar reduction phenomenon described by Gomberg and Bachmann\(^2\) in which benzophenone and related ketones are largely reduced to pinacols by the action of magnesium and iodide but not by either magnesium or magnesium halide alone, is easily understood.

(a) \[ \text{Ph-PH} \rightarrow \text{Ph} - \text{I} \]

(b) \[ \text{Ph-PH} \rightarrow \text{Ph} - \text{MgI} \]

In the reaction of bischoff\(^3\) by the action of \(\text{Br-CH}_2\text{CH}_2\text{MgBr}\) upon benzil.

obtained benzoin as the principal product.

(a) \[ \text{Br} - \text{CH}_2 - \text{CH}_2 - \text{Mg-Br} \rightarrow \text{C}_2\text{H}_5 + \text{MgBr}_2 \]

(b) \[ \text{PhC} = 0 \quad \text{Me} \quad \text{PhC} = 0 - \text{Br} \]

\[ \text{PhC} = 0 \quad \text{Mg-Br} \rightarrow \text{PhC} = 0 \text{MgBr} \]

(c) \[ \text{Br} - \text{C}_2\text{H}_5\text{Br} \]

\[ \text{PhC} = 0 \quad \text{MgBr} \rightarrow \text{PhC} = 0 \text{MgBr} \]

\[ \text{PhC} = 0 \text{MgBr} \quad \text{BrCH}_2\text{CH}_2\text{Br} \]

(d) \[ \text{PhC} = 0 \text{MgBr} \rightarrow \text{PhC-OMe} \rightarrow \text{PhC=0} \]

\[ \text{PhC} = 0 \text{MgBr} \rightarrow \text{PhC-OMe} \rightarrow \text{PhCHOH} \]

One must conclude, therefore, that the few unusual cases involving reduction in the presence of Grignard reagents, and apparently not involving \( \alpha - \beta \) splitting with the separation of \( \text{HMGX} \), may be explained upon the same mechanism as used to explain other reactions of alkyl magnesium halides.
GENERAL SUMMARY AND CONCLUSIONS.

1. Ether solutions of alkyl magnesium halides contain the Baeyer type of monoetherate \( A \) and the Grignard type of monoetherate \( B \) in equilibrium through the dietherate.

\[
\begin{align*}
B & \xleftrightharpoons[0.50]{Mg} \xrightarrow[0.50]{Et_2O} A \\
R & \xrightarrow[0.50]{X} R & \xrightarrow[0.50]{X} R & \xrightarrow[0.50]{Et_2O} R & \xrightarrow[0.50]{X} R & \xrightarrow[0.50]{Et_2O} R & \xrightarrow[0.50]{Mg} OEt_2
\end{align*}
\]

2. The relative amounts of \( A \) and \( B \) will depend upon the nature of \( R \) and the nature of \( X \).

3. Aldehydes, ketones, and ethylene oxide form their normal condensation products, secondary, tertiary and primary alcohols, respectively, through addition to \( A \) and subsequent rearrangement or structural bonds.

4. The yield of the normal condensation products derived through \( A \) varies:

\[
RMgCl > R MgBr > RMgI \quad \text{and also CH}_3\text{MgX} > \quad C_2H_5\text{MgX} > NC_3H_7\text{MgX} > NC_4H_9\text{MgX} \text{ etc.}
\]

5. In the case of ethylene oxide in particular addition and rearrangement also takes place through \( B \) to form the halo-hydrin.

6. The yield of halo-hydrin varies in the diametrically opposite way as the yield of normal product:-
RMgCl < RMgBr < RMgX and also CH₃MgX < C₂H₅MgX < N-C₃H₇MgX < NC₆H₄MgX etc.

7. Halo hydrins probably react with Grignard reagents by first forming the olefine oxides and subsequently show the reaction products of these compounds.

8. The failure of some alcohol, amines and imines to yield the theoretical amount of RH by their reaction with RMgX is explained upon the basis of this equilibrium. The value of Zerewitinoff’s reagent is made clear.

9. Ether synthesis by the action of ROMgX upon R'OMgX is explained.

10. The same equilibrium is used in devising a mechanism for the reaction of alkyl halides upon alkyl magnesium halides.

11. Upon the basis of this mechanism the formation of equivalent quantities of olefine and paraffin hydrocarbon having the same carbon content as the alkyl group is made clear.

12. The mechanism also explains the formation of a multiplicity of condensed hydrocarbons R-R, R-R', R'-R' etc.

13. The origin of the multiplicity of products is clarified and a basis given for predicting which will be found in the greater amount in any given reaction.
14. It is pointed out that Spath's data, obtained in a study of the action of alkyl magnesium halides upon p-methoxy benzyl bromide, may be used for calculating the equilibrium point between A and B in any given case.

16. This same mechanism is applied to R-MgX, RCH₂OMgX and R₂CHOMgX with the formation of olefines, aldehydes and ketones, respectively. These phenomena are termed "olefinic splitting", "aldehydic splitting" and "ketonic splitting" respectively.

17. A mechanism is devised for explaining the reducing action of the Grignard reagents. This mechanism involves an α-β splitting of organo-magnesium halide with the separation of H₂MgX.

17. "Ketonic Splitting" is shown to be very general and the same mechanism is applied to account for the formation of ketones by the action of Grignard reagents upon esters and acid chlorides.

18. "Ketonic Splitting" is proposed as an explanation of many reactions not heretofore understood.

19. The splitting of ethers is explained.

20. A similar mechanism is applied in explanation of complex reactions involving Grignard reagents and organic compounds having more than one functional group.
Autobiography

I, Ciong Coh Sung, was born in Ninghua, Fukien, China, August 15, 1901. I received practically all of my secondary school education at Guthrie Memorial High School. I came to the United States in the fall of 1920 and attended Ohio Wesleyan University from which I received the degree of Bachelor of Arts in 1923. I entered the Ohio State University in the fall of 1923 and obtained the degree of Master of Science in 1924. While in residence at Ohio State University I was awarded a University Scholarship for two years 1923-1924 and 1924-1925 and was Graduate Assistant in Chemistry for one year 1925-1926. I completed all the requirements and received the degree of Doctor of Philosophy in March 1926 after three years of residence.