THE REACTION OF MONOCHLOROMETHYL ETHER
WITH ORGANO METALLIC COMPOUNDS

by

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I. **INTRODUCTION**

The carbon-halogen bond in alpha-halogenated ethers is easily ruptured. When this bond is subject to attack by organometallic compounds, usually an ether with a longer carbon chain is formed. In the case of monochloromethyl ether, the following generalized equations may be used to describe the reactions:

\[
2\text{ClCH}_2\text{OCH}_3 + 2\text{RMX} \rightarrow 2\text{RCH}_2\text{OCH}_3 + \text{MX}_2 + \text{Cl}_2
\]

\[
2\text{ClCH}_2\text{OCH}_3 + \text{R}_2\text{M} \rightarrow 2\text{RCH}_2\text{OCH}_3 + \text{MCl}_2.
\]

The purpose of this investigation is to study the relative ease of reaction of monochloromethyl ether with dialkyl zinc and cadmium compounds as compared to that with the more familiar Grignard reagents.

The dialkyl cadmium compounds are prepared through the reaction of the corresponding Grignard reagents with anhydrous cadmium chloride.

The dialkyl zinc compounds are prepared from the reaction of the alkyl halide and a zinc-copper couple. As this method of preparation often results in low yield or failure due to the difficulty in initiating the reaction between the alkyl halide
and the zinc-copper couple generally used, an investigation is made for a more satisfactory method of preparing the couple.

The reactions of monochloromethyl ether with the organometallic compounds are carried out under conditions as similar as possible so that the reactions can be favorably compared.
II. LITERATURE REVIEW

The purpose of this review is to present a necessary historical background to the present investigation. It is not within the scope of the present investigation to review in its entirety the large field of organometallic compounds and their many reactions. Those publications which directly relate to the reaction of monochloromethyl ether with organometallic compounds are carefully reviewed. Special emphasis is placed upon those investigations describing the preparation of dialkyl zinc compounds.

Monochloromethyl Ether

By virtue of its very reactive chlorine atom, monochloromethyl ether has been used to introduce the methoxy-methyl group in place of the reactive hydrogen atoms\(^{(21,30,31)}\), in certain organic compounds. Its reaction with organometallic compounds furnishes a general method of preparation of various methyl ethers. As early as 1891, Henry\(^{(20)}\) had reported the reaction of monochloromethyl ether with dimethyl, diethyl, and di-n-propyl zinc to form respectively methyl ethyl, methyl n-propyl, and methyl n-butyl ether. The first reaction was
reported to give almost 90 per cent yield. No yields were reported for the latter two reactions.

Since 1936, reactions of monochloromethyl ether with many different Grignard reagents were reported. Those with n-butyl, sec-butyl, and tert-butyl magnesium bromides gave yields of 69, 31, and 0 per cent, respectively (2).

No investigation of the reactions of monochloromethyl ether with dialkyl cadmium compounds has been reported.

Monochloromethyl ether is generally prepared by the action of hydrogen chloride on a mixture of formaldehyde and methanol (11),

\[ \text{HCHO} + \text{CH}_3\text{OH} + \text{HCl} \rightarrow \text{ClCH}_2\text{OCH}_3 + \text{H}_2\text{O}. \]
Organometallic Compounds

Ever since the discovery of diethyl zinc by Frankland in 1849, organometallic compounds have been increasingly valuable in the field of organic chemistry. They have been used chiefly in synthesis and in the study of reaction mechanisms (9).

The preparation of organometallic compounds can be classified into three groups.

(A) The action of a metal or an alloy of the metal on a halide.

\[ RX + M \rightarrow R M X \]

or

\[ 2 R X + 2 M \rightarrow R_2 M + M X_2 \]

(B) The action of a metal on the organometallic compound prepared from another metal.

\[ R_2 M + M' \rightarrow R_2 M' + M \]

M' is generally of a higher potential or above M in the electromotive series.

(C) The action of a metal halide on the organometallic compound prepared from another metal.

\[ R_2 M + M' X_2 \rightarrow R_2 M' + M X_2 \]

M' is generally below M in the electromotive series.
The organometallic compounds of the Group II elements, especially those of magnesium (Grignard reagents), zinc and cadmium, are particularly interesting. Systematic studies of the compounds of these three metals by Grignard, Gilman, Blaise, Noilé, Cason, and other workers, have shown the compounds to be invaluable in the synthesis of not only other organic compounds but also the less known organometallic compounds.

**Organozinc Compounds**

Frankland first reported the isolation of an organometallic compound in 1849. Trying to prepare the free ethyl radical, he obtained diethyl zinc from the reaction of ethyl iodide and zinc. The organozinc compounds were used in the preparation of many compounds until being largely replaced by the Grignard reagents. They are now used chiefly in the synthesis of ketones with acyl halides, of quaternary hydrocarbons with tertiary halides and in the Reformatsky reaction.

Dialkyl zinc compounds can be prepared by either of the three methods mentioned above, but are usually prepared by the action of zinc metal on a halide. A mixture of one-half
alkyl bromide and one-half alkyl iodide reacting with a zinc-copper couple is found to be most satisfactory\textsuperscript{(27)}.

\[
\begin{align*}
RX + Zn & \rightarrow RZnX \\
2RZnX & \xrightarrow{\text{heat}} R_2Zn + ZnX_2
\end{align*}
\]

Different methods increasing the reactivity of the zinc were tried by several investigators. Aside from one report of using a zinc-sodium alloy\textsuperscript{(28)}, most investigators favored the use of a zinc-copper couple. The following methods for the preparation of zinc-copper couples have been reported.

(A) A solution of 1.5 per cent cupric sulfate was poured on zinc foils\textsuperscript{(16)}. The foils were then washed with water, alcohol, and ether, respectively, and dried in carbon dioxide.

(B) Copper was precipitated from a cupric sulfate solution with zinc\textsuperscript{(29)}. The precipitate was mixed with zinc dust and heated in an atmosphere of hydrogen.

(C) Cupric oxide was mixed with zinc dust and heated in an atmosphere of hydrogen until it was completely reduced to copper\textsuperscript{(27)}.

(D) A zinc-copper alloy containing 5 to 10 per cent copper was lathed into turnings and used\textsuperscript{(33)}. 
Dialkyl zinc compounds are generally prepared by using (C) and (D), above. However, the yield largely depends upon the technique of the worker in the preparation of the zinc-copper couple. The preparation of a highly active zinc-copper couple has been described as "an art rather than a science" (29). Experimenters with little experience will often find the yield of the dialkyl zinc very poor or even void.

The spontaneously flammable nature of dialkyl zinc compounds in air is overcome by the addition of an equal volume of an inert solvent (27). The compounds thus treated can be handled in air with reasonable safety.

**Grignard Reagents and Organocadmium Compounds**

Grignard reagents are the best known and most studied of all organometallic compounds. Their ease of preparation and reaction with many functional groups makes them ideal for the synthesis of other compounds.

Hallwachs and Shafaric first reported the isolation of what was thought to be diethyl magnesium (13). Barbier and Grignard in 1899 effected the Grignard reaction by treating methylheptenone with methyl iodide and magnesium and got the corresponding dimethylhepenol. In 1900, Grignard divided the synthesis into two steps, the first of which bears his
name, and made a systematic study of its reactions during the following years.

Grignard reagents are usually prepared by the reaction of a halide with magnesium in ethyl ether.

\[ RX + Mg \rightarrow HMX \]

\[ 2RMgX \leftrightarrow R_2Mg + MgX_2 \]

Before 1936, little was known about organocadmium compounds other than their preparation. In that year, Gilman and Nelson\(^{14}\) recommended the reaction between organocadmium compounds and acyl halides for the preparation of ketones. However, the importance of this method was not recognized until several years later. In 1941, De Benneville\(^{1}\) reported the preparation of ketones and keto-acids with organocadmium compounds. Subsequent investigations by Cason\(^{4,5,6}\) showed that this method compares favorably with other methods of preparation of ketones. Since then, the organocadmium compounds have also been used for the preparation of a number of other compounds\(^{22,32}\).

Dialkyl cadmium compounds are usually prepared by the reaction of anhydrous cadmium chloride with corresponding Grignard reagents\(^{7}\).

\[ 2RMgX + CdCl_2 \rightarrow R_2Cd + MgCl_2 + MgX_2 \]
III. EXPERIMENTAL

Preliminary Remarks

In the preparation of monochloromethyl ether, the procedure described by Marvel and Porter (11) was used.

The preparations of the Grignard reagents and the dialkyl cadmium compounds followed that of Gason and Prout (7).

Dialkyl zinc compounds were prepared by the modification of procedures described by Noller (27), and Soroo and Morgan (33).

Under the headings, Preparation of Reactants and Reaction with Monochloromethyl Ether, only those procedures that were found to give the best results are described.

Preparation of Reactants

Monochloromethyl Ether

Three hundred and fifty grams (10.9 moles) of methanol and 900 g. of technical formalin containing 252 g. (8.4 moles) of formaldehyde were placed in a two-liter round-bottom flask to which were attached a reflux condenser and a glass tube reaching to the bottom of the flask. Hydrogen chloride was run into the solution, which was cooled with running water. After a period of time, two distinct layers appeared. The flow of
hydrogen chloride was continued until it was no longer absorbed. The two layers were separated. The water layer was saturated with calcium chloride. Again, two layers appeared. The monochloromethyl ether layer was separated and added to the main portion. It was then dried over calcium chloride and distilled. The portion boiling from 57 to 60 °C. was considered sufficiently pure and was used in later reactions.

In generating hydrogen chloride, two methods were tried. One was the addition of concentrated hydrochloric acid to concentrated sulfuric acid; the other was the addition of concentrated sulfuric acid to a paste of sodium chloride and concentrated hydrochloric acid. Both were found to be unsatisfactory as the hydrogen chloride streams thus generated were slow and uneven. Frequent refilling of the generator was necessary. The usual time needed to complete the reaction was 40 hours. The yield was low (usually about 350 g. or 52%). By using dry hydrogen chloride from a commercial cylinder, the flow of gas could be controlled at much higher rates. The reaction was completed in 10 hours. The yield was 596 g. or 88%.

Grignard Reagents

Twenty-four and three-tenths grams (1 g. atom) of magnesium turnings were covered with 150 ml. of dry ether in a one-liter
three-necked flask to which were connected a mechanical stirrer, a reflux condenser, and a dropping funnel. One mole of alkyl bromide in 250 ml. of dry ether was placed in the dropping funnel. A few milliliters of the bromide were added to the flask which was warmed with stirring. The rest of the bromide was added dropwise during one and one-half hours. Heating was discontinued as soon as the reaction started. After the addition of the bromide, the mixture was refluxed for 15 more minutes to complete the reaction. During the reaction, a protective nitrogen atmosphere was used.

**Dialkyl Cadmium Compounds**

One mole of alkyl bromide in 250 ml. of dry ether was added to 24.3 g. (1 g. atom) of magnesium turnings and the Grignard reagent was prepared as above.

The flask was then cooled in an ice bath and the dropping funnel removed. Ninety-eight grams (0.54 mole) of anhydrous cadmium chloride were added over a period of 10 minutes under nitrogen atmosphere with stirring. The ice bath was removed and the mixture was refluxed for 45 minutes. The mixture was then tested for the presence of the Grignard reagent. If the test was positive, the mixture was refluxed until further tests indicated the absence of the Grignard reagent.
The test for the presence of Grignard reagents (Gilman test)\(^{(10)}\) was made as follows: a small portion of the reaction mixture was added to one-half milliliter of 1% Michler’s ketone in dry benzene. After shaking the mixture, one milliliter of water and a few drops of 0.2% iodine in glacial acetic acid were added. The development of a greenish-blue color shows the presence of a Grignard reagent.

**Dialkyl Zinc Compounds**

1. **Preparation of Zinc-copper Couples**

   Three different methods of making zinc-copper couples had been used in the preparation of dialkyl zinc. All of the couples contained 5 to 8% of copper by weight.

   (a) One hundred and twenty grams of zinc dust and 10 g. of powdered cupric oxide in a 500 ml. three-necked flask were heated gently over a free flame in a current of hydrogen with shaking until the cupric oxide was reduced. Care must be taken not to heat to the point of fusion. All moisture must be driven off.

   (b) Pure zinc and copper metals were mixed and melted to form an alloy containing 5 to 8% of copper by weight. The alloy was then lathed to small turnings.
(c) A modified method of (a) was employed as follows: one hundred and thirty grams of zinc dust were mixed thoroughly with 25 g. of cupric citrate powder and placed in a 500 ml. three-necked flask. The contents of the flask were heated with a free flame under a protective current of nitrogen until all of the cupric citrate decomposed. This was shown by the fact that gases and moisture ceased to be evolved. Furthermore, the powder changed in appearance from a green color to a rusty color.

All couples prepared, except in the case of the alloy turnings, must be used directly and without exposure to the air.

2. Preparation of Dialkyl Zinc

A 500 ml. three-necked flask containing approximately 130 g. of zinc-copper couple was equipped with a reflux condenser, a mercury sealed stirrer, and a dropping funnel (Figure 1). The apparatus was thoroughly flushed with nitrogen and warmed over a water bath. Half a mole each of the alkyl bromide and iodide were placed in the dropping funnel. A few milliliters of the halide were added to the zinc-copper couple and the rest added dropwise over a period of 2 to 3 hours with stirring under an atmosphere of nitrogen. The mixture was allowed to stand overnight.
The flask was then quickly connected with a vacuum distillation system (Figure 2) and distillation was attempted at a pressure of 2 to 30 mm.

All of the connections that were exposed to the dialkyl zinc vapor had to be made with cork stoppers.

Whenever the reaction seemed too vigorous, heating was discontinued and if needed, an ice bath was used to cool the flask until the reaction subsided.

**Reaction with Monochloromethyl Ether**

**Grignard Reagents**

Thirty-six grams (0.44 mole) of monochloromethyl ether in an equal volume of ether were added dropwise to the previously prepared Grignard reagent. The reaction flask was cooled with running water. After the addition the contents of the flask were heated to reflux conditions for 30 minutes. The flask was cooled to room temperature and then placed in an ice bath. One hundred milliliters of water and subsequently 200 ml. of 1:1 concentrated hydrochloric acid were added slowly. The water and ether layers were separated. The ether layer was dried over Drierite and fractionally distilled.
Dialkyl Cadmium Compounds

Solvent ether was first partially removed by distillation from the mixture containing the dialkyl cadmium. Thirty-six grams (0.44 mole) of monochloromethyl ether in an equal volume of ether were added dropwise into the flask. The reaction flask was cooled with running water during the addition. The contents of the flask were then refluxed for 30 minutes, cooled to room temperature, and placed in an ice bath. One hundred milliliters of water and then 200 ml. of 1:1 concentrated hydrochloric acid were added slowly. The water and ether layers were separated. The ether layer was dried over Drierite and fractionally distilled.

Dialkyl Zinc Compounds

Twenty-five grams (0.31 mole) of monochloromethyl ether in an equal volume of n-butyl ether were added dropwise to the dialkyl zinc also in an equal volume of n-butyl ether. During the addition, the flask was cooled in running water. The contents were then refluxed for 30 minutes, after which time 100 ml. of water were added to hydrolyze any unreacted dialkyl zinc. The ether layer was separated from the water layer, and dried over Drierite. It was then fractionally distilled.
Results

Owing to the close boiling points and refractive indices of methyl n-butyl ether and methyl iso-butyl ether with respectively hexane and 2,3-dimethyl butane, which may be produced by the coupling reaction of the organometallic compounds (25) (Table I), the fractions within 3° of the boiling points of the pure compounds were combined and added slowly into a flask of concentrated sulfuric acid in an ice bath.

<table>
<thead>
<tr>
<th>Compound</th>
<th>B. P.</th>
<th>N\textsuperscript{20} D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl n-butyl ether</td>
<td>71°</td>
<td>1.38</td>
</tr>
<tr>
<td>Hexane</td>
<td>68.7°</td>
<td>1.3749</td>
</tr>
<tr>
<td>Methyl iso-butyl ether</td>
<td>59°/741 mm</td>
<td>--</td>
</tr>
<tr>
<td>2,3-dimethyl butane</td>
<td>58°</td>
<td>1.3750</td>
</tr>
</tbody>
</table>

The insoluble product, if any, was separated and weighed. The weight of the combined portions minus the weight of the insoluble product was considered to be the weight of the ether obtained. The sulfuric acid layer was then poured slowly into a flask of cracked ice. The ether recovered was dried over Drierite and the boiling point and refractive index taken.
From two to five runs were made of each of the magnesium, cadmium, and zinc derivatives of n- and iso-propyl halides. The observations and the results are summarized as follows (Table II):

**TABLE II**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of Runs</th>
<th>Ease of Preparation</th>
<th>Reaction with Chloromethyl Ether</th>
<th>Yield* ( \text{RCH}_2\text{OCH}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{n-C}_3\text{H}_7\text{MgBr} )</td>
<td>4</td>
<td>easiest</td>
<td>vigorous</td>
<td>68%</td>
</tr>
<tr>
<td>iso-( \text{C}_3\text{H}_7\text{MgBr} )</td>
<td>2</td>
<td>easiest</td>
<td>vigorous</td>
<td>42%</td>
</tr>
<tr>
<td>( \text{n-C}_3\text{H}_7\text{Cd} )</td>
<td>5</td>
<td>easy</td>
<td>less vigorous</td>
<td>32%</td>
</tr>
<tr>
<td>(iso-( \text{C}_3\text{H}_7\text{Cd} )</td>
<td>3</td>
<td>easy</td>
<td>less vigorous</td>
<td>16%</td>
</tr>
<tr>
<td>( \text{n-C}_3\text{H}_7\text{Zn} )</td>
<td>3</td>
<td>difficult</td>
<td>vigorous</td>
<td>63%</td>
</tr>
<tr>
<td>(iso-( \text{C}_3\text{H}_7\text{Zn} )</td>
<td>2</td>
<td>difficult</td>
<td>vigorous</td>
<td>32%</td>
</tr>
</tbody>
</table>

* Based on monochloromethyl ether.

In the reactions of the magnesium and cadmium compounds, no attempt was made to isolate the compounds before the addition of monochloromethyl ether.

An investigation of the activities of the zinc-copper couples was made. Methyl, ethyl, n-propyl and isopropyl halides were reacted with zinc-copper couples prepared by three different methods. The results are shown in Tables III and IV.
TABLE III

<table>
<thead>
<tr>
<th>Couple Type</th>
<th>Initiation Period</th>
<th>Runs</th>
<th>Evidence of Reaction</th>
<th>R$_2$Zn Distilled</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5-2.5 hr.</td>
<td>11</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>2-10 min.</td>
<td>8</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>0.5-5 min.</td>
<td>7</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

TABLE IV

<table>
<thead>
<tr>
<th>Couple Type</th>
<th>% Yield R$_2$Zn</th>
<th>Methyl</th>
<th>Ethyl</th>
<th>n-Propyl</th>
<th>iso-Propyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>80</td>
<td>10</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>38</td>
<td>13</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

A represents couples made from the reduction of cupric oxide in the presence of zinc.

B represents the zinc-copper alloy.

C represents couples made from the decomposition of cupric citrate in the presence of zinc.
With the equipment available, oxidation of the dialkyl compounds could not be avoided during the vacuum distillation. The yields of the dialkyl zinc compounds were much lower than the percentage conversions of the alkyl halides based on the amounts of unreacted materials.

The reaction of the halides with the type C couples was much more vigorous in comparison with the other couples.

The reaction of monochloromethyl ether with diethyl zinc gave 82% yield of methyl n-propyl ether. The yield of methyl ethyl ether from the reaction of monochloromethyl ether and dimethyl zinc was greater than 70%. The low boiling point of methyl ethyl ether (4°C.) made the recovery of this material extremely difficult.
Reactions of Monochloromethyl Ether with Organometallic Compounds

The carbon to chlorine bond in some organic compounds is easily ruptured. For instance, allyl chloride and benzyl chloride possess carbon to chlorine bonds which are easily cleaved. Such compounds have a tendency to dissociate a chloride ion when an outside force such as a nucleophilic reagent is present. In the case of allyl chloride in a non-ionizing solvent, the following reaction may occur when an iodide is present:

\[
\text{CH}_2 = \text{CH-CH}_2 \rightarrow \delta^+ \cdot \delta^- + \text{I}^- \rightarrow \text{CH}_2 = \text{CH-CH}_2 \rightarrow \delta^+ \cdot \delta^- + \text{I}^-.
\]

Monochloromethyl ether under similar conditions, may react as follows:

\[
\text{CH}_3\text{-O-CH}_2 \rightarrow \delta^+ \cdot \delta^- + \text{I}^- \rightarrow \text{CH}_3\text{-O-CH}_2 \rightarrow \delta^+ \cdot \delta^- + \text{I}^-.
\]

It has been demonstrated that the carbon to chlorine bond in the ether is more reactive in a nucleophilic displacement reaction such as the above than is the case for allyl chloride.
In recent years, some evidence has been presented to show that alpha-halo ethyl alkyl ethers form tautomERICALLY an oxonium ion and a halide ion.*

\[
\begin{align*}
\text{Cl} & \quad \text{CH}_3\text{-CH-O-R} \quad \overset{\text{CH}_2 = \text{CH-OH}}{\longleftrightarrow} \quad \left[\text{CH}_2 = \text{CH-OH}\right]_R^+ \quad \text{Cl}^- \\
\end{align*}
\]

Such evidence offers additional proof of the reactivity of the carbon to chlorine bond in alpha-halo ethers.

The over-all reaction of monochloromethyl ether with organometallic compounds can be expressed in the following two equations:

\[
\begin{align*}
2\text{RM}X + 2\text{ClCH}_2\text{OCH}_3 & \quad \longrightarrow \quad 2\text{RCH}_2\text{OCH}_3 + MX_2 + \text{MCl}_2 \\
\text{R}_2\text{M} + 2\text{ClCH}_2\text{OCH}_3 & \quad \longrightarrow \quad 2\text{RCH}_2\text{OCH}_3 + \text{MCl}_2.
\end{align*}
\]

The yields of methyl n-butyl ether in the n-propyl series appeared in the order RMgBr > R2Zn > R2Cd. The yields of methyl iso-butyl ether in the iso-propyl series also follow the same order. The primary organometallic compounds gave higher yields of ethers than the corresponding secondary compounds. The

* Original article by Shostakovskii and Bogdanova abstracted in C. A., 42, 4519d (1948) was not seen.
lower yields of ethers from secondary organometallic compounds may be due to competing side reactions.

Better yields were obtained when the monochloromethyl ether was slowly added to the organometallic compounds.

From the results of this investigation, Grignard reagents and dialkyl zinc compounds are recommended over the dialkyl cadmium compounds in the preparation of ethers from monochloromethyl ether. The best yields were obtained by using the organometallic compounds prepared from primary halides.

A Comparison of the Performance of Different Zinc-Copper Couples

In the following discussion, the zinc-copper couples prepared from zinc dust and cupric oxide will be referred to as type A couples, the alloy as type B, and that prepared from zinc dust and cupric citrate as type C.

The investigation of the performance of the couples was made because of the unsatisfactory results often obtained with the commonly used type A couples by the investigator and by others. The three types of couples were compared on the basis of (1) ease of preparation of the active couple, (2) length of the initiation period for the formation of the alkyl zinc halide, and (3) the yield of the dialkyl zinc compound.
Type A is hazardous to prepare as it involves heating the mixture of zinc dust and cupric oxide with a free flame under an atmosphere of hydrogen near the point of fusion of the metals. Furthermore, the cupric oxide, when well mixed with zinc dust, is hard to reduce, probably because of its small chance of contact with hydrogen. There is no way of knowing when the couple is ready for use. Heating for as long a period as one and one-half hours with constant shaking sometimes failed to give reactive couples. Type B involves tedious work in melting, casting, and latheing the alloy and is, therefore, impractical for use in just a few small scale experiments. Type C is made simply by heating with a free flame a mixture of cupric citrate and zinc dust below the point of fusion with occasional shaking. It is ready for use in 10 to 30 minutes, depending upon the amount of heat applied.

The initiation period of the type A couple is usually longer than one and one-half hours. Type B usually reacts within 10 minutes. The reaction of type C couple in some cases has been almost instantaneous. The initiation period is usually less than five minutes.

The yields of the dialkyl zinc compounds obtained by the use of type A couples are usually good, while those from type B are considerably lower in most instances. Examination of the
residue from the type B couple often shows unreacted zinc in the center of the turnings, especially when the larger turnings are used. The yields of the dialkyl zinc compounds from the type C couples are superior to those obtained from the other types of couples.

In view of the above facts, type C is considered to be superior and is strongly recommended for laboratory use in place of the other two types.

The preparation of a zinc-copper couple by the decomposition of cupric tartrate or other cupric salts of organic acids has not been investigated. The thermal decomposition of such salts has been used to prepare copper catalysts. These salts will probably give the same results as obtained with cupric citrate.

The high reactivity of the couple was believed to be due to the formation of extremely reactive minute particles of copper, that is, particles of high specific surface.
V. SUMMARY

1. The reactions of monochloromethyl ether with the magnesium cadmium and zinc derivatives of normal propyl and isopropyl halides were investigated.

2. In both the normal propyl and iso-propyl series, the yields of the expected condensation products $RCH_2OCH_3$ appeared in the order $RMgX > R_2Zn > R_2Cd$.

3. The primary organometallic compounds reacted with monochloromethyl ether in higher yields than did the corresponding secondary compounds.

4. A new method was developed for preparing a zinc-copper couple by heating a mixture of zinc dust and powdered cupric citrate under an atmosphere of nitrogen.

5. This method gave a couple superior in laboratory use to the zinc-copper couples now generally employed.
VI. ACKNOWLEDGMENT

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VII. BIBLIOGRAPHY

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VIII. VITA

The author was born near Shanghai, China, in March 1929. He attended St. John's University in Shanghai, China, in September, 1946. He was transferred to Indiana University in September, 1947, and was graduated in June, 1950, with a major in chemistry. In September, 1950, he entered Virginia Polytechnic Institute for graduate study in chemistry.
IX. APPENDIX

Figure 1. Preparation of Dialkyl Zinc Compounds
Figure 2. Vacuum Distillation and Reaction System