

THE PREPARATION AND EXCHANGE  
REACTIONS OF CERTAIN DIALKYLMAGNESIUM COMPOUNDS

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A Thesis  
Presented to  
the Faculty of the Department of Chemistry  
Appalachian State University

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In Partial Fulfillment  
of the Requirements for the Degree  
Master of Arts


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by  
Gelene Andrews Atwood  
August, 1967

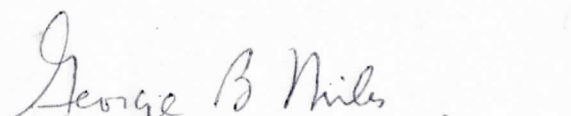
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TO BOYDEN AND THE FIVE LITTLE ATWOODS

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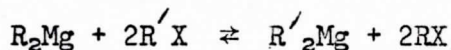
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ABSTRACT

Di-n-octylmagnesium was prepared in toluene in a nitrogen atmosphere using a two-step process. An ether solution of n-octylmagnesium bromide was prepared by the standard Grignard method. The ether was then removed by distillation as toluene was added dropwise to replace the ether. Solutions of di-n-octylmagnesium were obtained which showed a base/halide ratio as high as seven upon hydrolysis and analysis. This ratio for a Grignard reagent is one.

Exchange reactions were carried out between the prepared di-n-octylmagnesium in toluene and various halides at room temperature. The exchange product, the haloctane, was shown to be formed in most of the reactions by the use of vapor phase chromatograms. The 2:1 molar ratio of the reacted alkyl halide to the reacted di-n-octylmagnesium supports the following equilibrium:



In the limited number of systems studied the following trends in reactivity for the exchange reactions were observed: RI > RBr > RCl and tertiary halide > secondary halide > primary halide. Further study using more compounds would be needed to verify these observed trends.

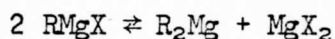


## CHAPTER I

### Introductory Survey

#### A. Preparation of Dialkylmagnesium Compounds

Since the preparation of diethylzinc by Frankland (1) in 1849 organometallic compounds have been the basis for numerous investigations. Organomagnesium compounds, first prepared by Grignard (2) and now called Grignard reagents, have been the most widely studied group. Studies have shown that these reagents usually represented as  $\text{RMgX}$  do not have this simple formula but actually exist as several species in solution (3). One of these species, the dialkylmagnesium compound represented in the equilibrium,



has been prepared by several methods. These include distillation under reduced pressure from solutions of Grignard reagents (4), heating of dialkylmercury with magnesium turnings in a sealed tube (4), and the addition of dioxane in ether to a Grignard reagent followed by centrifugation (5).

More recently Bryce-Smith and coworkers (6) made preparations of organomagnesium compounds in which the halogen content was much lower than that of the conventionally prepared Grignard reagent. An ether solution of n-butylmagnesiumiodide, prepared from magnesium and n-butyl iodide was slowly drawn by suction into isopropylbenzene which was refluxing under a reduced pressure of nitrogen at a temperature of  $130^\circ$ .

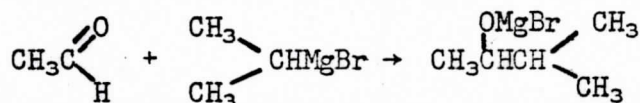
The ether was removed from the mixture through a Dufton Column. Hydrolyzed portions of this preparation gave a base/halide ratio of 3.0 as opposed to 1.0 for a Grignard reagent.

Using an adaptation of the above method, W. H. Glaze and C. M. Selman (7) prepared n-amylmagnesium compounds in which the alkyl/halide ratio for the bromide ranged from 12.3 to 18.2. In this preparation the n-amyl halide was added slowly to heated magnesium powder. When the reaction was complete, dry benzene was added and the mixture was filtered in a dry box. The clear benzene solution was then analyzed.

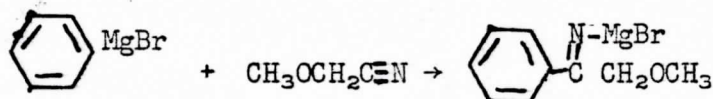
## B. Chemical Properties

The dialkylmagnesium compounds are usually assumed to undergo the same reactions as the very reactive Grignard reagents (3,8). The major types of reactions of the Grignard reagent are illustrated in the following list:

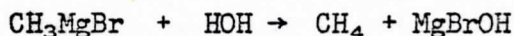
1. Addition reactions  
To carbonyl bond (9)



- To carbon-nitrogen unsaturation (10)



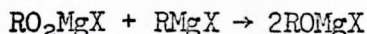
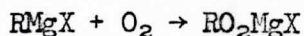
2. Reaction with active hydrogens (11)  
Reaction with water



This reaction explains why water or any species with an active hydrogen cannot be present when a Grignard reagent is prepared.

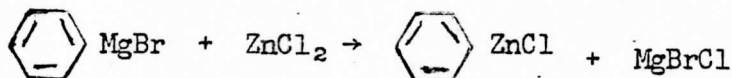
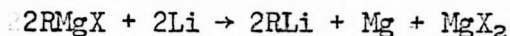
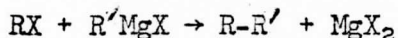
## 3. Oxidation (12)

When a Grignard reagent is exposed to air or oxygen, oxygen is absorbed and chemiluminescence is observed. The reaction is complex but has been represented by the following equations:



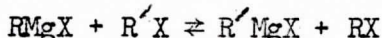
## 4. Reactions with metals and inorganic salts (13)

Organometallic compounds of metals more active than magnesium may be prepared from the Grignard reagent and the metal, while those of less active metals may be prepared from the Grignard reagent and the inorganic salt of the metal.

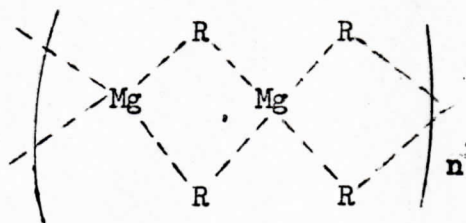
5. Reactions with alkyl halides  
Coupling reaction (14)

Practical application of this reaction is restricted to those alkyl halides having a highly reactive halogen such as allyl halides. The coupling reaction is not a simple union of the alkyl halide with the alkyl group of the Grignard reagent as three coupling products ( $\text{R-R}'$ ,  $\text{R-R}$ , and  $\text{R}'\text{R}$ ) are formed.

## Halogen-metal exchange (15)

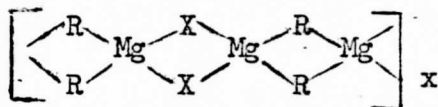
C. Structure and Bonding of Dialkylmagnesium Compounds

Very few studies of the structure and bonding of dialkylmagnesium compounds have been reported. Bryce-Smith (6) has postulated an electron deficient structure as shown on the next page.

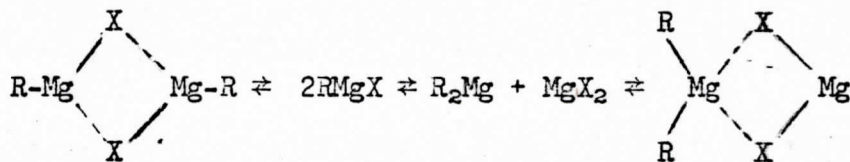


This structure is consistent with the structure of alkyllithium compounds proposed by Frank A. Settle (16) who presented evidence for a dimeric structure existing as a four-membered ring with electron deficient bonding.

Glaze and Selman (7) reported that di-n-amylmagnesium appeared to be dimeric in benzene at the freezing point of the solution, but they also state that the incorporation of magnesium halide seemed to cause polymerization to such complexes as shown below.

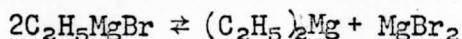


It is not surprising that the structure of dialkylmagnesium compounds have not been elucidated when the structure of the Grignard reagent is still being studied and contested. In a recent article, E. C. Ashby (17) suggested that the composition of the Grignard reagent in ether solution could best be described according to the equilibrium given below.



He based his conclusion on the preparation of ethylmagnesiumbromide in triethylamine. Since magnesium bromide did not precipitate ( $\text{MgBr}_2$  is insoluble in triethylamine), he concluded that the reaction product was a single species,  $\text{RMgX}$ .

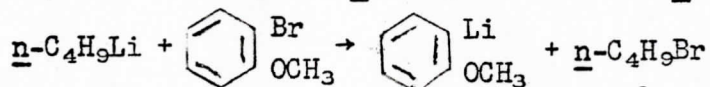
However, in an earlier investigation Raymond Dessey and coworkers (18) investigated the equilibrium



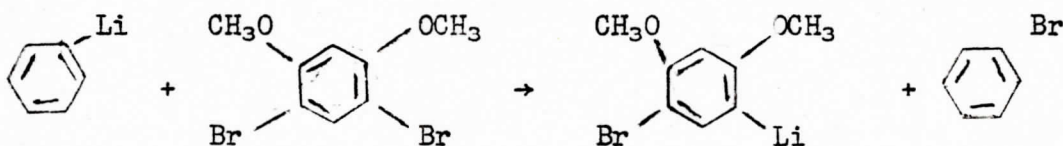
using  $\text{Mg}^{28}\text{Br}_2$ . Only a small amount of exchange was noted between  $(\text{C}_2\text{H}_5)_2\text{Mg}$  and  $\text{MgBr}_2$ . They concluded that the ethyl Grignard is better represented by a complex  $(\text{C}_2\text{H}_5)_2\text{Mg}\cdot\text{MgBr}_2$  than by  $\text{C}_2\text{H}_5\text{MgBr}$ .

#### D. The Halogen-Metal Exchange Reaction

The halogen-metal exchange reaction was independently discovered by Gilman and coworkers (19) who found that o-bromoanisole reacted with n-butyllithium to yield o-anisyllithium and n-butyl bromide,



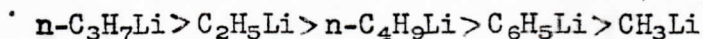
and by Wittig, Pockels and Dröge (20) who observed that 4, 6-dibromo-resorcinol dimethyl ether and phenyllithium reacted to yield 2-4- dimethoxy-5- bromophenyllithium and bromobenzene.



Although the mechanism for the halogen-lithium interconversion is not certain, it has been pictured as an exchange between lithium and an electro-positive halogen atom (21). Gilman and Jones (22) have stated that the reaction is confined almost entirely to bromides and iodides. Eastham, Settle, and Screttas (23) concluded from a kinetic analysis of this type of reaction that the exchange is general with iodides, occurs with some bromides and does not occur with chlorides.

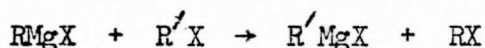
Other factors that affect the rate of the reaction for the  $\text{RLi-R}^1\text{X}$  systems are the nature of the organolithium compound and the solvent.

Gilman and Moore (24) reported that the order of decreasing effectiveness of some RLi compounds in diethyl ether solution of  $\alpha$ -bromonaphthalene was:



They also found that the reaction takes place most rapidly in diethyl ether, that di-n-butyl ether was a satisfactory solvent, but dimethylaniline, benzene, cyclohexane and petroleum ether were less effective. Eastham and coworkers (23) also noted the reaction to be slow in hydrocarbon media. They reported, however, that the reactions were catalyzed by relatively small amounts of ethers.

The reaction between organomagnesium compounds and alkyl and aryl halides has been studied only to a limited extent. Zakharkin and coworkers (15) found that an exchange reaction took place between Grignard reagents and alkyl or aryl halides. They represented the reaction with the following equation:



Their study showed that the rate of exchange was dependent on the solvating capacity of the solvent and polarizability of the halogen in the alkyl halide.

No work has been reported on exchange reactions involving dialkylmagnesium compounds.

#### E. Statement of Problem

The purpose of this study is to prepare dialkylmagnesium compounds in hydrocarbon solvents with as high a purity as possible and to study these compounds in various exchange reactions.

## CHAPTER II

### Materials and Equipment

#### A. Chemicals

Magnesium turnings for Grignard reaction secured from Fisher Scientific Company were used in the preparation of the alkylmagnesium compound. Anhydrous diethyl ether, analytical reagent, from Mallinckrodt Chemical Works was used. The 1-bromooctane used for the preparation of the organometallic reagents was the Eastman Organic Chemicals' white label product. Reagent grade toluene was obtained from Fisher and was dried over sodium metal before using.

The alkyl halides used in the exchange reactions were obtained either from Matheson, Coleman and Bell or Eastman. Vapor phase chromatograms of all the alkyl halides used in preparation of alkylmagnesium and in the exchange reactions showed them to be of high purity.

The sulfuric acid used for determining the hydroxyl content in a hydrolyzed sample of the alkylmagnesium compound was standardized with trishydroxyaminomethane using alizarin as indicator. The normality was 0.0988. A sodium hydroxide solution was used for back titration. One milliliter of the sodium hydroxide solution was equivalent to 0.910 ml. of the sulfuric acid solution.

The silver nitrate solution for determining the halide content of the organomagnesium compound was standardized using Fisher certified reagent sodium chloride with dichlorofluorescein as an indicator. The normality

was 0.1029.

All other chemicals used met ACS standards of purity and were used as received from the supplier.

#### B. Apparatus and Instruments

The reaction vessels for both the preparation of the organomagnesium compounds and the exchange reactions were Corning Glassware with ground glass joints. The joints were lubricated with Dow Corning stopcock grease.

Calibrated volumetric glassware was used for determining the volume of liquids.

A Carl Zeiss refractometer was used for determining the refractive index of liquids.

Components of reaction mixtures were identified by comparison of their vapor phase chromatography (v.p.c.) retention times with those of authentic samples chromatographed under identical conditions. The instrument used was the Varian Aerograph Model 1520. The columns used were commercially prepared 1/4 in. in diameter and 5 ft. in length and contained a silicone gum rubber (methyl) (SE-30) as a liquid phase. Helium was used as the carrier gas.

Concentrations of the materials in solution were determined from their relative peak areas without calibration. The peak areas were taken as one-half the peak height times the base width (25). To check the accuracy of the results obtained in this manner, representative samples were prepared containing the calculated percentages of the components. It was decided on the basis of these results that calibration would not be necessary for this study. Table I shows a comparison between the known concentrations and the concentrations calculated from v.p.c. data for several samples.



TABLE I

## V.P.C. Analysis Data

Sample	Components	Concentration in wt. %	
		Known	V.P.C. Data
1	Toluene	86	86
	Octane	14	14
2	Toluene	78	77
	Bromoethane	4.0	3.8
	Octane	19	19
3	Toluene	50	55
	2-Bromobutane	15	16
	Octane	17	17
	1-Bromooctane	18	12
4	Toluene	73	75
	1-Bromohexane	10	8.5
	Octane	15	17
	1-Bromooctane	2.0	0

## CHAPTER III

### Experimental

#### A. Preparation of the Dialkylmagnesium Compound

The method used for the preparation of di-n-octylmagnesium was an adaptation of that described by Bryce-Smith (6). Excess magnesium metal turnings were placed in a 250 ml. three-necked flask fitted with a condenser in reflux position, a dropping funnel, a magnetic stirrer, and a connecting adapter tube for a thermometer and nitrogen inlet. (Figure 1). Nitrogen was then swept through the system for several minutes. Approximately 20 ml. of an ether solution of 1-bromooctane were then added to the magnesium and stirred with a magnetic stirrer until the reaction started. When the initial reaction subsided the remaining 1-bromooctane-ether solution was added dropwise to the reaction flask. Stirring was continued during this addition. The mixture was then refluxed gently for thirty minutes. The condenser was then placed in position for distillation using a Claisen adapter. Dry toluene was placed in the dropping funnel and was added dropwise as the reaction mixture was heated in a steam bath. The distillation of ether was continued, with toluene being added to maintain constant volume, until the refractive index of the distillate was within 0.001 units of pure toluene. After most of the ether had been removed, the steam bath was replaced by a hot plate. Specific data for the seven preparations are given in Table II.

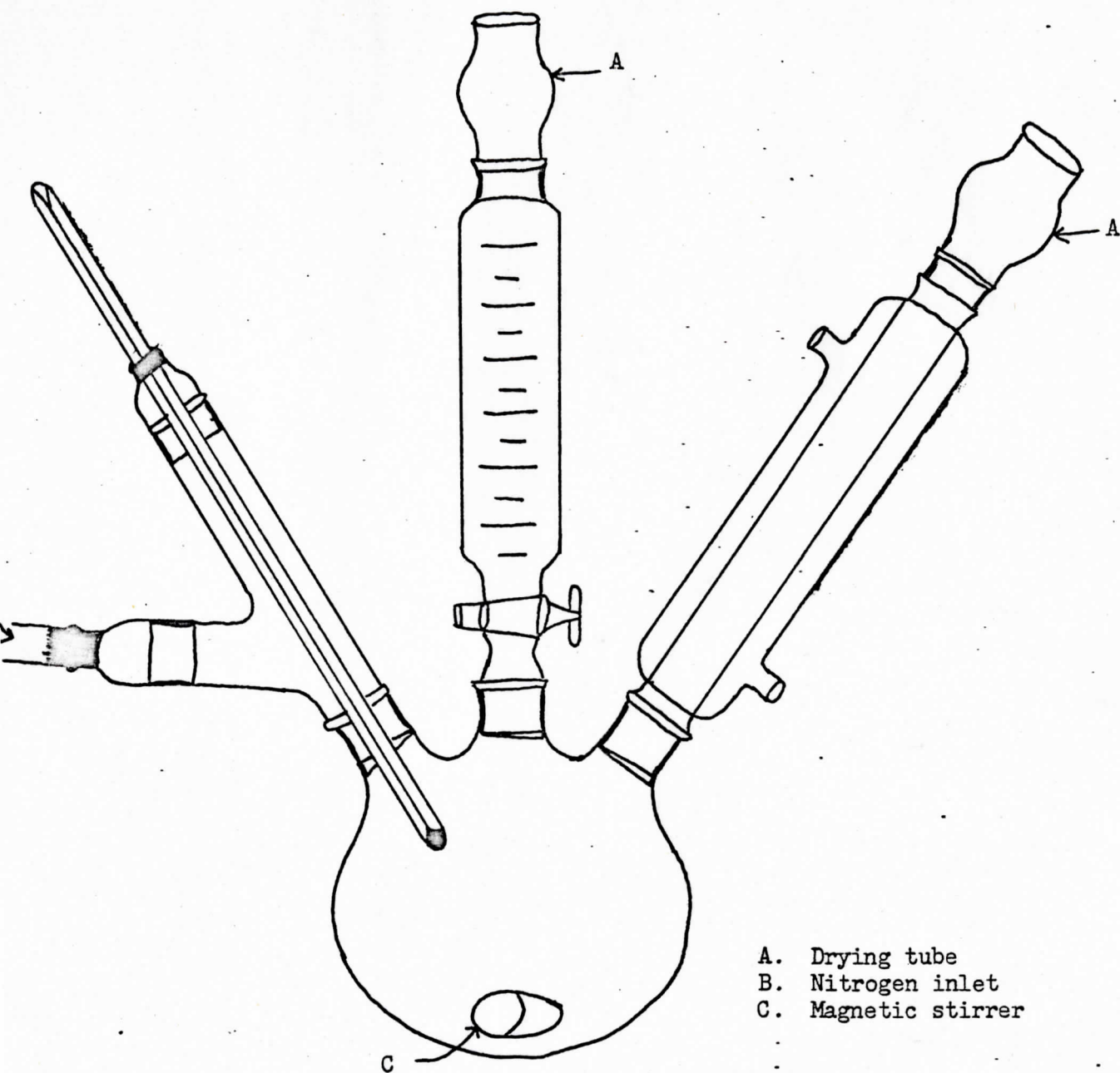


FIGURE 1. Apparatus for the preparation of organomagnesium compound.

TABLE II

## Preparation of Di-n-octylmagnesium

Preparation Number	1	2	3	4	5	6	7
Amount of Mg(g. atoms)	0.25	0.15	0.15	0.25	0.27	0.25	0.25
Amount of 1-bromooctane (moles)	0.23	0.13	0.13	0.23	0.25	0.23	0.23
Amount of ether (ml)	125	100	100	125	125	125	125
Time of addition of halide-ether mixture (min.)	60	45	40	45	45	45	45
Amount of toluene added (ml)	475*	200	225	275	400	300	300
Time of addition of toluene (min.)	300	225	195	225	240	210	210
Amount of distillate (ml)	455	165	210	280	380	305	310
Temperature range (°C)	40- 77	30- 105	43- 106	35- 106	31- 104	41- 107	36- 105

\* Benzene rather than toluene was used for this preparation.

When the process was completed the reaction mixture consisted of two phases, a white solid which settled to the bottom of the flask and a viscous liquid phase. The clear liquid phase was slightly yellow and much more viscous than the almost black ether solution of n-octylmagnesium-bromide.

Benzene rather than toluene was first tried in the preparation. A hydrolyzed portion of the product obtained gave a base / halide ratio of approximately 2:1 (Table III). After addition of large volumes of benzene, up to four times that of the ether used, the refractive index of the distillate indicated considerable ether in the benzene.

TABLE III

Analysis of the n-Octylmagnesium Compound

Preparation Number	ml. of 0.1029 N AgNO <sub>3</sub>	ml. of 0.0988N H <sub>2</sub> SO <sub>4</sub>	Base/halide ratio	Concentration* of R <sub>2</sub> Mg ( $\frac{\text{m moles}}{\text{ml}}$ )
1	1.30	2.40	1.85	0.12
2	1.70	6.82	4.01	0.34
3	1.66	8.58	5.17	0.43
4	3.50	14.90	4.26	0.74
5	2.36	12.78	5.42	0.63
6	2.44	17.12	7.02	0.85
7	2.50	16.94	6.87	0.84

\* The Concentration of di-n-octylmagnesium in m moles/ml. was calculated making the assumption that each mole on hydrolysis would give a mole of Mg(OH)<sub>2</sub> which would be neutralized by a mole of H<sub>2</sub>SO<sub>4</sub>.

## B. Analysis of Dialkylmagnesium Compound

One milliliter samples of the clear viscous liquid were hydrolyzed and then analyzed using the following procedure.

The halide content was determined by titrating the samples, without removing the organic material, with a standard solution of silver nitrate (0.1029N) using dichlorofluorescein indicator. Several samples were run and the average value was recorded.

The total hydroxide content was determined by titrating the total hydrolyzed sample with a standard solution of sulfuric acid (0.0988N) using phenolphthalein as an indicator. Excess acid was added and the solution was then back titrated with sodium hydroxide solution (1.00 ml NaOH equivalent to 0.910 ml. of  $H_2SO_4$ ). Table III gives the results of the analyses of the seven preparations for halide and hydroxide content.

Other hydrolyzed samples were centrifuged and the organic material was removed with a dropper and dried over Drierite. The dried samples were analyzed by vapor phase chromatography at  $100^\circ$ , 68 p.s.i. g. of helium and flow rate of 70 ml./min. Only two peaks, toluene and octane, appeared on the chromatograms. The percent of octane from preparations 4, 5, 6, and 7 respectively were 25, 17, 28.5, and 28. These values were used for calculating the percent of di-n-octylmagnesium initially present in the solutions for the exchange reactions.

## C. Di-n-octylmagnesium-alkyl Halide Exchange Reactions

A reaction vessel tube fitted with a nitrogen inlet, thermometer, and magnetic stirrer was used for the exchange reactions (Figure 2). Samples were obtained with a pipette by removing the thermometer. To reduce the amount of air entering the reaction tube, the nitrogen exit tube was closed during sampling. The samples were hydrolyzed in a centrifuge tube

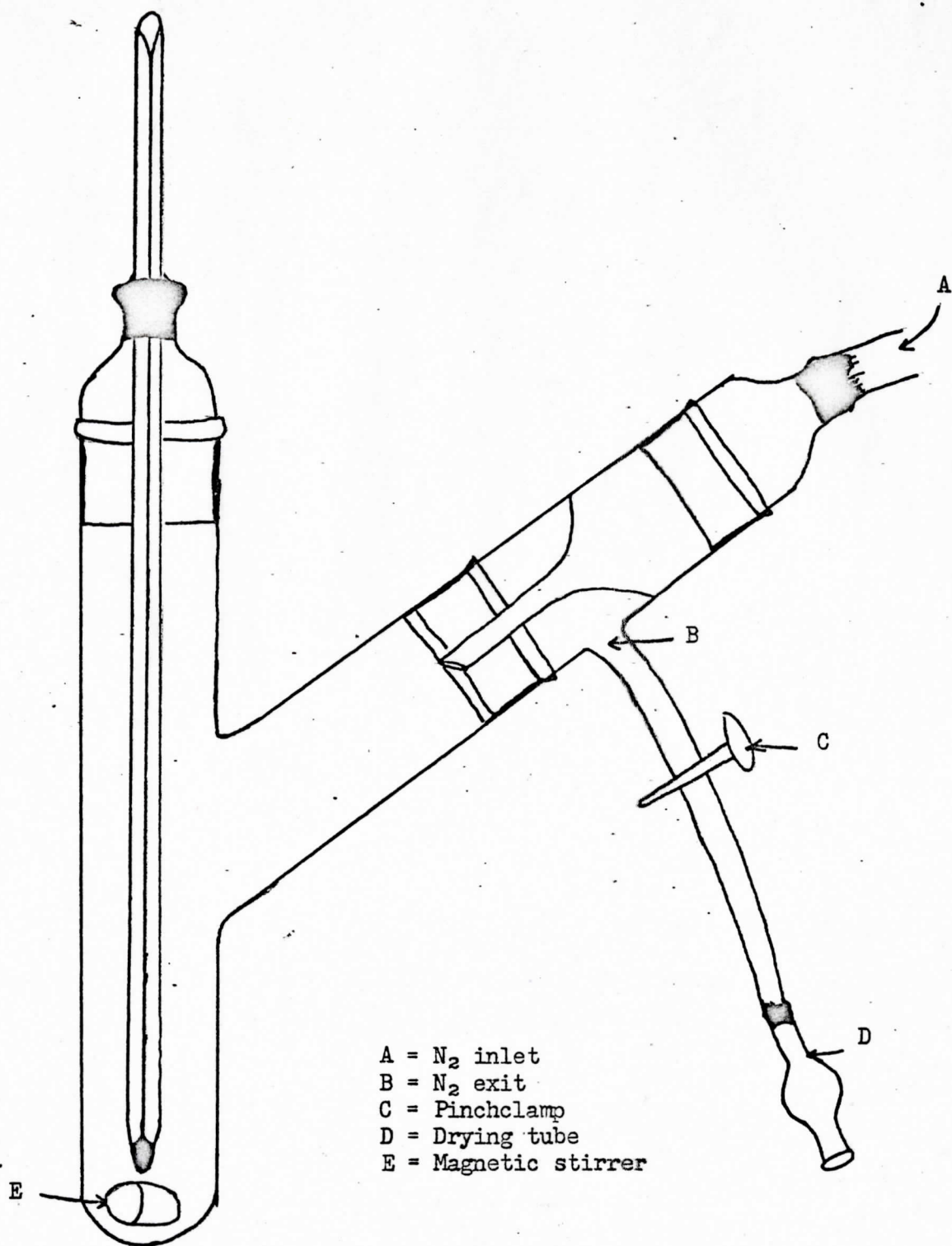


FIGURE 2. Apparatus for exchange reactions.



and then centrifuged for three minutes. The organic layer was removed and stored in a stoppered tube until analyzed by v.p.c. Any water in the organic layer was removed by drying over Drierite.

### 1. Exchange with Ethyl Bromide

Ten milliliters of the clear liquid from preparation four (Table III) and 0.81g (0.55 ml) of ethyl bromide were placed in the reaction tube at 30°C. The temperature increased to 32° on combining the materials. Samples were taken at 5 min., 1 hr., 2 hr., and 3 hr. These samples were analyzed by v.p.c. at 100°, 68 p.s.i. g of helium and gas flow of 70 ml./min. These chromatographic conditions were used for analyzing the samples from each of the exchange reactions. The chromatograms showed the presence of n-bromooctane indicating an exchange reaction had taken place. The bromooctane was not treated quantitatively as it gave a broad low peak. The retention time was much greater than that of the other components in the mixture.

### 2. Exchange with 1-Bromohexane

Ten milliliters of the clear liquid from preparation four and 1.2g(1.0ml) of 1-bromohexane were placed in the reaction tube at 33°. The temperature initially increased to 35°. Samples were taken at 5 min., 1 hr., 2 hr., and 3 hr. An exchange reaction was indicated by the presence of hexane and bromooctane as shown by the chromatogram. This reaction was repeated starting at a temperature of 50°. At this higher temperature equilibrium appeared to have been reached in the first hour as opposed to approximately two hours for the lower temperature.

### 3. Exchange with 1-Bromopropane

Ten milliliters of the clear liquid from preparation five and 0.77g (0.57ml) of 1-bromopropane were combined at 29.5°. The temperature increased

to 31.0°. Samples were removed at 5 min., 1 hr., 2 hr., and 2 1/2 hr. Bromooctane was present after two hours.

4. Exchange with 2-Bromobutane

Ten milliliters of the clear liquid from preparation six and 1.15g (0.80ml.) of 2-bromobutane were combined at 28°. The temperature increased to 30°. Samples were taken at 5 min., 1 hr., 2 hr. and 3 hr. Bromooctane was present in each of these samples.

5. Exchange with 2-Bromo-2-methylpropane

Ten milliliters of the clear liquid from preparation six and 1.15g (0.94ml) of 2-bromo-2-methylpropane were combined at 28°. Reaction was immediate with the temperature increasing to 85°. The chromatogram of the sample taken at 5 minutes showed the reaction to be complete as no 2-bromo-2-methylpropane was present. Bromooctane was present. This reaction was repeated starting at a temperature of 0°. Again reaction was rapid with temperature initially increasing to 21°. A trace of 2-bromo-2-methylpropane was present at five minutes but the reaction was complete within an hour.

6. Exchange with 1-Bromo-2-methylpropane

Ten milliliters of the clear liquid from preparation six and 1.15g (0.91ml) of 1-bromo-2-methylpropane were combined at 31°. No increase in temperature was noted. Samples were removed at 5 min., 1 hr., 2 hr., and 3 hr. Bromooctane was present after one hour.

7. Exchange with Benzyl Chloride

Ten milliliters of the clear liquid from preparation seven and 1.06g (0.96ml) of benzyl chloride were combined at 29°. Reaction was immediate with the temperature increasing to 55°. No benzyl chloride was shown by the chromatogram of a sample taken at 5 min. It was also noted that no chlorooctane, the exchange product, was present.

#### 8. Exchange with 1-Bromobutane

Ten milliliters of the clear liquid from preparation seven and 1.15g (0.90ml) of 1-bromobutane were combined at 31°. The temperature increased to 32°. Samples were taken at 5 min., 1 hr., 2 hrs. and 3 1/2 hrs. A trace of bromooctane was present at 2 hrs.

#### 9. Exchange with Ethyl Iodide

Ten milliliters of the clear liquid from preparation seven and 1.31g (0.67ml.) of ethyl iodide were combined at 29°. The temperature increased to 31°. Samples were taken at 5 min., 1 hr., 2 hrs., 3 hrs. and 22 hrs. The chromatograms of these samples showed a diminishing amount of ethyl iodide, but did not show any peak which could have been iodoctane. The exchange solutions were a violet color suggesting decomposition of an organic iodide.

#### 10. Exchange with 1-Chlorobutane

Ten milliliters of the clear liquid from preparation seven and 0.77g (0.91ml) of 1-chlorobutane were combined at 33°. The temperature increased to 34°. Samples were taken at 5 min., 1 hr., and 2 hrs. The exchange product, chlorooctane, was present in each sample as shown by v.p.c.

Table IV gives a summary of these reactions at two hours. Most of them appeared to reach equilibrium within this time. Table V gives the data for changes in concentrations of the reactants with time for two typical reactions.

TABLE IV

Degree of Reaction of Alkyl Halides with Di-n-octylmagnesium at Two Hours

Exchange Reaction No.	Concentration of alkyl Halide (Mole/100g) <sup>1</sup>		Concentration of R <sub>2</sub> Mg (Mole/100g) <sup>2</sup>		Mole/100g Rx Mole/100g R <sub>2</sub> Mg	Reacted
	Initial	2 Hrs.	Initial	2 Hrs.		
1	7.7	3.3	11.	8.7	2.3	1.9
2	7.3	6.1	11.	5.5	5.5	0.22
3	6.6	4.4	7.5	6.3	1.2	1.9
4	8.4	3.9	12.5	10.9	1.6	2.8
5	8.4	0	12.5	10.7	1.8	4.7
6	8.4	5.7	12.5	11.0	1.5	1.8
7	8.5	0	12.5	12.3	0.2	42
8	8.4	6.1	12.3	11.0	1.3	1.8
9	8.4	3.6	12.3	10.0	2.3	2.1
10	8.9	8.3	12.3	11.0	1.3	0.48

<sup>1</sup>The wt. % of the RX initially present was calculated from the weight of RX and the weight of the R<sub>2</sub>Mg solution. The wt. % was converted to moles/100g.

<sup>2</sup>The wt. % of the R<sub>2</sub>Mg initially present was calculated from the % octane in the hydrolysis product of the original preparation as determined from v.p.c. data. The wt. % of octane was converted to moles/100g. The moles/100g of R<sub>2</sub>Mg was taken as  $\frac{\text{moles/100g octane}}{2}$

TABLE V

Change in Concentration of Reactants with Time  
in Some Exchange Reactions

Exchange Reaction No.	Reactants	Concentration (Mole/100g)				
		Initial	5 min.	1 hr.	2 hr.	3 hr.
1	Ethyl Bromide	7.7	7.2	4.9	3.3	3.4
	di- <u>n</u> -octylmagnesium	11	10.5	9.3	8.7	8.7
4	2-Bromobutane	8.4	5.2	3.9	3.9	3.8
	di- <u>n</u> -octylmagnesium	12.5	11.4	11.0	10.9	11.0

## CHAPTER IV

### Discussion of Results

#### A. Preparation of Alkylmagnesium Compounds

Previous studies by Bryce-Smith (6) and Glaze and Selman (7) have shown that alkylmagnesium compounds can be prepared in hydrocarbon medium in which the halide content is less than that in a solution of a Grignard reagent. In this investigation such compounds have been prepared using an adaptation of the method of Bryce-Smith (6).

In the first of these preparations the hydrocarbon, benzene, was used. Benzene was successfully used by Glaze and Selman (7) but in their preparation the alkylmagnesium compound was prepared by direct reaction of heated magnesium and the alkyl halide followed by the addition of the benzene. The poor results obtained with benzene in the first preparation (Table III) was due to the incomplete removal of the ether from the Grignard preparation. Much better results were obtained using toluene as shown by the base/halide ratio for the hydrolysis mixture of these preparations in Table III. A high purity distillate was obtained much more readily than with the benzene. This presumably is due to the higher boiling point of toluene.

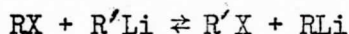
The best results (highest base/halide ratio) in the preparation of the dialkylmagnesium reagent were obtained by reacting 0.23 moles of the alkyl halide in 125 ml. of ether with excess magnesium, and then adding 300 ml. of toluene as the original volume was reduced slightly by distillation (Tables II and III): In each case with toluene solvent a greater base/halide

ratio was obtained than any achieved by Bryce-Smith (6).

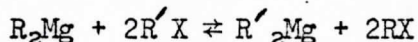
One of the difficulties encountered was in the removal of samples from the di-n-octylmagnesium solution. The viscous material often clogged the pipettes and drainage was poor. Also it was impossible to filter the di-n-octylmagnesium-toluene solution from the white precipitate as the organometallic compound would react with both moisture and oxygen in the air. In this study, samples of the solution were removed from the flask under a slight nitrogen pressure. Care was exercised to disturb the white precipitate as little as possible. Filtration in a dry box could be tried as a possible solution to some of these difficulties in future studies.

#### B. The Alkylmagnesium-Alkyl Halide Exchange Reactions

It has been shown by this investigation that an exchange reaction takes place between alkylmagnesium compounds, prepared in the manner described above and many alkyl halides. Such reactions for the alkyl-lithium-alkyl halide systems are represented by the following equilibrium:



The exchange reaction between dialkylmagnesium and alkyl halides can be represented by the following equilibrium:



The above equilibrium shows a molar ratio of 2:1 for RX:R<sub>2</sub>Mg. Table IV shows that for half of the reactions the molar ratio of RX: R<sub>2</sub>Mg was very close to 2:1. The large deviation from this ratio for the other reactions cannot be accounted for at this time. Two possible side reactions that are suggested from the alkylmagnesium-alkyl halide system cannot explain the results in these cases. One reaction, the formation of an alkene, has been noted in many lithium exchange systems (26). Chromatograms of both 1-octene and 2-octene were run, and no peaks at the retention times noted

were found in any of the studies recorded in this report. The other reaction, the coupling of the two alkyl groups to form alkanes, has been previously noted, but no evidence of the presence of hexadecane appeared in any of the above studies.

This investigation indicates that the rate of the exchange reaction is dependent upon the nature of the halide in the alkyl halide. Table IV shows that in general iodides exchange more readily than bromides and that chlorides exchange least readily. This is in agreement with the findings of Eastham and coworkers (23) for RLi-RX systems except in the case of the chlorides. These workers concluded that no exchange reaction took place between RLi and RCl. The present investigation indicates that alkyl chlorides react with di-n-octylmagnesium in an exchange reaction as the exchange product, chlorooctane, was present after reacting 1-chlorobutane with the di-n-octylmagnesium.

The rate of the exchange reaction is also affected by the nature of the R group in the alkyl halide, the following order of reactivity noted: tertiary > secondary > primary. (Table IV). No conclusions about the mechanism of the exchange reactions can be drawn from this study.

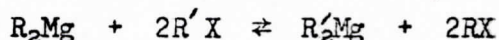


## CHAPTER V

### Summary and Conclusions

Di-n-octylmagnesium was prepared in toluene in a nitrogen atmosphere using a two-step process. An ether solution of n-octylmagnesiumbromide was prepared by the standard Grignard method. The ether was then removed by distillation as toluene was added dropwise to replace the ether. Solutions of di-n-octylmagnesium were obtained using this method which showed a base/halide ratio as high as seven upon analysis. This ratio for a Grignard reagent is one. A base/halide ratio of only two was obtained when benzene was used as the solvent. This suggests the study of other solvents as an approach to purer dialkylmagnesium solutions.

Exchange reactions were carried out between the prepared di-n-octylmagnesium and various alkyl halides at room temperature. These reactions were generally observed to be slow except for the tertiary bromide, 2-bromo-2-methyl propane, and benzyl chloride. The exchange product, the haloctane, was shown to be formed in most of the reactions by the use of vapor phase chromatograms. The 2:1 molar ratio of the reacted alkyl halide to the reacted di-n-octylmagnesium supports the following equilibrium:



In the limited number of systems studied the following trends in reactivity were observed in the exchange reaction: RI > RBr > RCl and tertiary halide > secondary halide > primary halide. Further study using more compounds would be needed to verify these observed trends.

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