

THE REACTION OF ETHYLENE OXIDE
WITH
VARIOUS ALKYL MAGNESIUM CHLORIDE SOLUTIONS

By
Cecil Chester Langham

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INTRODUCTION

INTRODUCTION

The reactions that Grignard reagents undergo are manifold and diversified.

As with so many other chemical phenomena, the organic chemist has been all too ready to generalize concerning these compounds. Thus, in the past there has perhaps been too little attention given to the nature of the halogen component of a Grignard reagent in respect to its influence on certain types of reactions.

This work was, therefore, undertaken in an attempt to compare the reactions of ethylene oxide and alkylmagnesium chloride solutions with those of the analogous bromide compounds.

HISTORICAL

HISTORICAL

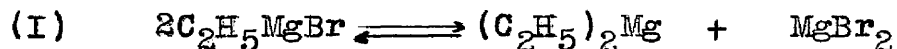
Very little previous work has been done in respect to the reactions of alkylmagnesium chloride compounds with ethylene oxide.

In 1902 Blaise (1) treated ethylmagnesium bromide with ethylene oxide and obtained as the principal product ethylene bromohydrin.

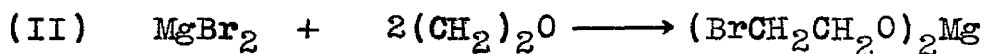
Grignard (2) in 1903 found that after the initial reaction, heating of the addition product gave n-butyl alcohol.

Ribas and Tapia (3) treated ethylmagnesium bromide with ethylene oxide at -20° C. From their analysis of the addition product they concluded that it consisted of a mixture of $(\text{BrCH}_2\text{CH}_2\text{O})_2\text{Mg}$ and $\text{BrCH}_2\text{CH}_2\text{OMgBr}$.

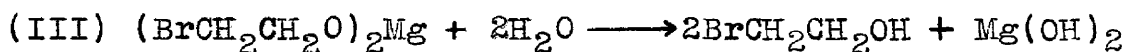
Huston and Agett (4) showed that, although both MgBr_2 and $(\text{C}_2\text{H}_5)_2\text{Mg}$ are found in the Schlenk (5) equilibrium:



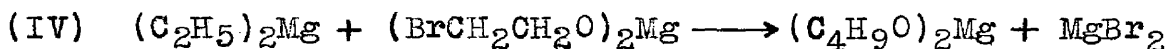
when one mole of ethylene oxide is added to one mole of ethylmagnesium bromide, the main reaction is with magnesium bromide:



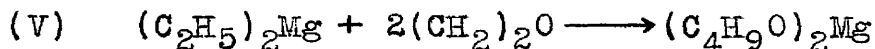
Direct hydrolysis of the addition product, without heating, gave sixty to seventy percent yield of ethylene bromohydrin and little or no n-butyl alcohol. The principal reaction may be represented according to the equation:



Excellent yields of n-butyl alcohol may be obtained either by heating the reaction mixture:



or by adding a second mole of ethylene oxide:



Hydrolysis of the addition product obtained by use of two moles of ethylene oxide gives a mixture of n-butyl alcohol and ethylene bromohydrin.

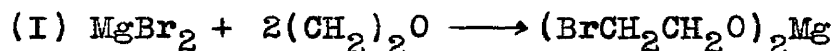
Huston and Agett (4) also found that when one mole of benzylmagnesium chloride reacted with one mole of ethylene oxide, phenylpropyl alcohol was obtained as the principal product. They concluded that either dibenzylmagnesium reacts at room temperature with $(ClCH_2CH_2O)_2Mg$ to form $(C_6H_5CH_2CH_2CH_2O)_2Mg$, or that benzylmagnesium chloride reacts directly with ethylene oxide to give $C_6H_5CH_2CH_2CH_2OMgCl$.

THEORETICAL

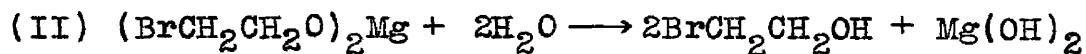
THEORETICAL

Work in this laboratory has revealed fundamental differences between the reactions of ethylene oxide with bromide Grignard reagents (4) and with the corresponding chloride compounds.

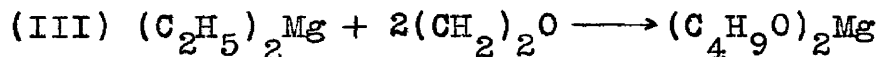
In a mole per mole ratio, without heating, the reaction of ethylene oxide with the Grignard reagent of ethyl bromide may be represented by the equation:



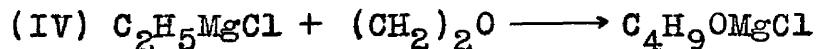
The addition product upon hydrolysis gives ethylene bromohydrin:



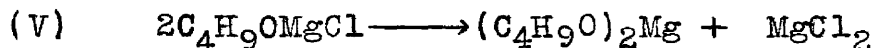
If the Grignard reagent is ethylmagnesium chloride, the main reaction, under similar conditions, may be represented according to one of the following equations:



or

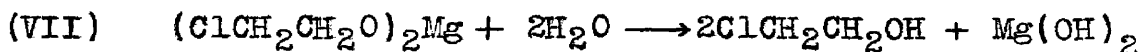
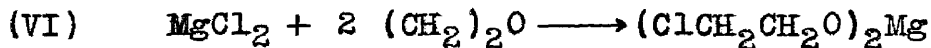


Reaction according to equation (IV) necessitates a subsequent rearrangement;

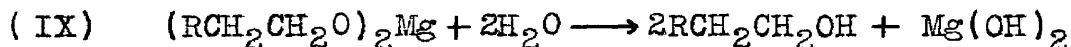
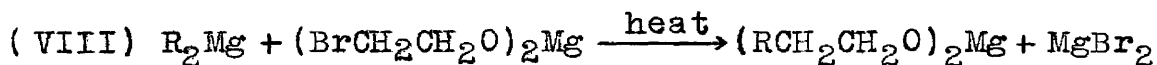


Hydrolysis of the addition product yields n-butyl alcohol.

Ethylene chlorohydrin is also formed in the previously described reaction of ethylene oxide with the Grignard reagent of ethyl chloride:



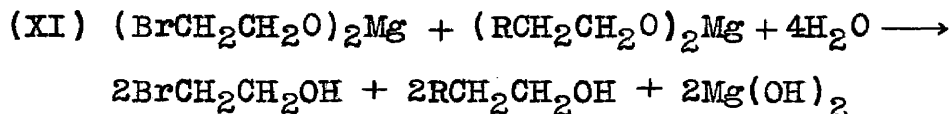
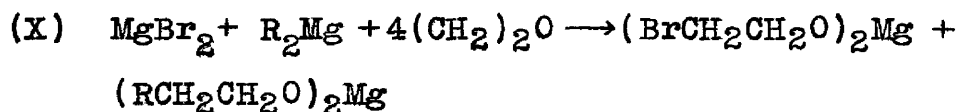
A good yield of the alcohol may be obtained by treatment of an alkylmagnesium bromide with one mole of ethylene oxide and heating the addition product:



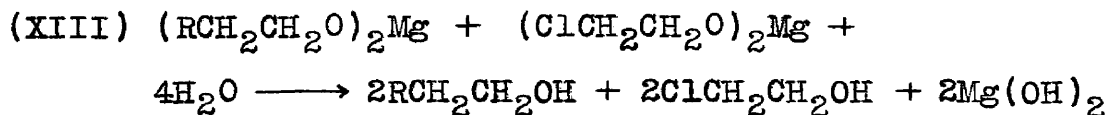
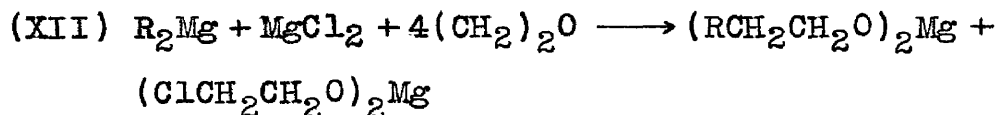
There is little evidence that heating a mixture of R_2Mg and $(ClCH_2CH_2O)_2Mg$ gives a

considerable yield of $(RCH_2CH_2O)_2Mg$.

When two moles of ethylene oxide are added to one mole of alkylmagnesium bromide, both ethylene bromohydrin and the alcohol are formed:



Addition of two moles of ethylene oxide to one mole of an alkylmagnesium chloride enhances the yield of both the alcohol and ethylene chlorohydrin. Assuming that dialkylmagnesium leads to the formation of the alcohol, the reactions may be represented by the following equations:



EXPERIMENTAL

EXPERIMENTAL

I. Materials

Ethyl chloride was obtained from the Ohio Chemical Company.

The following alkyl chlorides were obtained from the Columbia Organic Chemicals Company:

n-propyl chloride
isopropyl chloride
n-butyl chloride
s-butyl chloride
t-butyl chloride

Isobutyl chloride was prepared from the corresponding alcohol and thionyl chloride in the presence of pyridine (6).

All of the alkyl halides, except ethyl chloride, were fractionated through a twelve inch Fenske-type column packed with 3/32 inch glass helices and dried over calcium chloride.

The isobutyl alcohol was Eastman Technical.

Ethylene oxide was obtained from the Dow Chemical Company and was dried over soda lime.

Pure magnesium turnings were supplied by

the Dow Chemical Company and dried over calcium chloride.

The anhydrous ether was dried over sodium for at least a week before it was used in the reactions.

Partially anhydrous magnesium chloride was obtained from the Dow Chemical Company. Last traces of moisture were removed by treatment with anhydrous hydrogen chloride (7) at 400° C. The reaction was carried out in a pyrex glass tube which was placed in an electric furnace and maintained at the desired temperature. The magnesium chloride was finely ground, placed in a glass boat which in turn was inserted into the pyrex tube. Anhydrous hydrogen chloride was introduced into one end of the tube and the other end closed by means of a large calcium chloride tube. The anhydrous magnesium chloride was stored over phosphorus pentoxide in an evacuated desiccator.

Grignard reagents prepared and studied were:

ethylmagnesium chloride
n-propylmagnesium chloride
isopropylmagnesium chloride
n-butylmagnesium chloride

s-butylmagnesium chloride

isobutylmagnesium chloride

t-butylmagnesium chloride

II. Preparation of Grignard Reagents

A. Preparation of Ethylmagnesium Chloride

Two and one-quarter moles (54.7g.) of magnesium turnings were placed in a dry¹ two-liter three-necked round-bottomed flask. The flask was fitted with a mercury-sealed stirrer which was equipped with an inlet tube for nitrogen, a dry-ice condenser and an inlet tube for ethyl chloride. The ethyl chloride tube extended nearly to the bottom of the flask. After flushing out the system with dry nitrogen and ethyl chloride, one liter of anhydrous ether was added to the flask and the reaction catalyzed by the addition of a small amount of ethylmagnesium bromide. Dry ice was then placed in

¹The flask was dried in an oven for twenty-four hours. The reaction must be protected from carbon dioxide, water vapor and oxygen of the air.

the condenser. Ethyl chloride was bubbled through concentrated sulfuric acid and added at such a rate as to maintain a moderate rate of reaction. After most of the magnesium had reacted, addition of the ethyl chloride was discontinued and stirring maintained until the reaction mixture reached room temperature. This latter stage of the reaction was carried out in a very slow stream of nitrogen. The flask was sealed off from air and allowed to stand over night.

B. Preparation of Other Grignard Reagents

Two and one-quarter moles (54.7g.) of magnesium turnings were placed in a dry two-liter, three-necked, round-bottomed flask. The flask was fitted with a mercury-sealed stirrer which was equipped with an inlet tube for nitrogen, a reflux condenser and a dropping-funnel. After flushing out the system with dry nitrogen,

four or five grams of the alkyl halide mixed with one hundred ml. of anhydrous ether was added to the flask. The reaction was started by the addition of a small amount of ethylmagnesium bromide and an additional hundred ml. of ether added. The balance of the alkyl halide to make a total of two moles was mixed with eight hundred ml. of ether and added at such a rate as to maintain moderate refluxing. After addition was complete, a slow stream of nitrogen was introduced and stirring continued for two hours. The product was allowed to stand overnight. The preparation of t-butylmagnesium chloride was carried out very slowly; addition of the halide required about eight hours for a two mole run.

Each Grignard reagent was treated in three different ways. A typical run for each of the three procedures will be described:

III. Reaction of Ethylene Oxide and Grignard Reagents

A. Reaction of one mole of ethylene oxide with one mole of Grignard reagent

The concentration of the Grignard reagent was determined by means of an acid-base titration (8). Five ml. aliquot samples were taken for analysis. The samples were placed in four hundred ml. beakers and covered with watch glasses. Sufficient water (about ten ml.) was carefully added from a pipette to cause complete hydrolysis. A measured excess of .1 N hydrochloric acid was added and the mixture heated on the steam bath until all the basic magnesium chloride was dissolved. The excess hydrochloric acid was finally titrated with .1 N sodium hydroxide using phenolphthalein as an indicator.

The total volume of the solution was measured in a liter graduated cylinder from which the air had been displaced by nitrogen. A stream of nitrogen was used to drive the Grignard reagent from the

reaction flask into the graduated cylinder. The solution was transferred through a bent glass tube, one end of which extended nearly to the bottom of the flask and the other end to the bottom of the cylinder. The Grignard reagent was then placed in another dry, three-necked flask which had been previously filled with nitrogen. This flask was also fitted with a mechanical stirrer, reflux condenser and a dropping-funnel equipped with an outer metal jacket to permit the use of dry ice as a cooling agent. The Grignard reagent was cooled in an ice-salt-bath. One hundred ml. of anhydrous ether was placed in the dropping-funnel and surrounded with dry ice. A calcium chloride tube was used to protect the contents of the funnel from moisture of the air. The calculated amount of ethylene oxide which had been previously

dried over soda lime was weighed out and quickly placed in the dropping-funnel. The ethylene oxide-ether mixture was cautiously added to the Grignard reagent. As soon as addition was complete, the ice-salt-bath was removed and the mixture allowed to stir for an hour. The product was hydrolyzed by carefully adding it to chipped ice. After hydrolysis the ether layer was decanted. The pasty magnesium hydroxide was extracted three times with small portions of ether, neutralized with ice, dilute hydrochloric acid and again extracted three times with ether. The ether extracts were combined, dried over anhydrous sodium sulfate and fractionated through the Fenske-type column described in Section I.

B. Reaction of one mole of ethylene oxide with one mole of Grignard reagent followed by heating

Addition of the ethylene oxide to the Grignard reagent was accomplished according

to the procedure described in III A. After addition was complete the condenser was set for distillation. The reaction flask was placed in a Glas-Col heating mantle and about seven hundred ml. of ether removed. The temperature of the reaction mixture was not allowed to exceed 45°. ¹ Five hundred ml. of anhydrous benzene was added and gentle refluxing continued for six hours with stirring. The product was hydrolyzed, extracted, dried and fractionated as described in III A.

C. Reaction of two moles of ethylene oxide with one mole of Grignard reagent

The calculated amount of ethylene oxide was mixed with one hundred ml. of anhydrous ether and added to the Grignard reagent according to the procedure described in III A.

¹This was a precautionary measure to guard against violent decomposition of the addition product.

Since the ethylene oxide tended to polymerize, it was usually not possible to stir the mixture for an hour after addition was complete. The product was hydrolyzed immediately, extracted, dried and fractionated as described in III A.

IV. Preparation and Analysis of the Intermediate Product from the Reaction of Ethylene Oxide and Grignard Reagent

The Grignard reagent (C_2H_5MgCl) was prepared according to the procedure given in II A. Ethylene oxide was added as described in III A, except that if an excess was used, stirring was discontinued at once after addition was complete. Part of the reaction mixture was placed in centrifuge tubes and diluted with an equal volume of anhydrous ether. The tubes were tightly stoppered and centrifuged for ten minutes at 1800 r.p.m. The precipitate was washed with ether, transferred quickly to a weighing-bottle which was placed in a desiccator¹ and evacuated with a

¹The white solid hydrolyzed quickly if exposed to the moisture of the air.

water-pump for three hours and with an oil-pump at about 2 mm. pressure for twelve hours. Total chlorine was determined by means of a Parr bomb fusion (9).

In a Parr bomb fusion cup were placed seventy-five hundredths gram (.75 g.) of powdered potassium nitrate, four-tenths gram (.4 g.) of finely ground cane sugar, two-tenths gram (.2 g.) of the sample, also in the form of a fine powder and, finally, fourteen grams (14 g.) of sodium peroxide. The Parr bomb was assembled and the contents carefully mixed by shaking. The sample was ignited by heating two to three minutes with a Bunsen burner. The bomb was allowed to cool, opened and the fusion cup placed in a six hundred ml. beaker. The top was thoroughly rinsed with distilled water. A cover glass was then placed on the beaker and two hundred ml. of water added. The excess sodium peroxide was decomposed by boiling and the fusion cup removed and rinsed with distilled water. After cooling, the

solution was carefully acidified with concentrated nitric acid and then boiled to remove the hydrogen peroxide. A measured excess of .1 N silver nitrate was added to the cold solution, after which it was boiled to coagulate the precipitate. The solution was cooled, the silver chloride removed by filtration and the precipitate washed free of silver nitrate. Chlorine was then determined by the Volhard method for chlorine (10).

Magnesium was determined by decomposing weighed samples with a Meker burner and weighing as MgO. The sample was placed in a silica crucible which had been brought to constant weight by a Meker burner. It was necessary to heat the material very carefully at first to prevent it from taking fire. The temperature was gradually increased until the maximum capacity of the Meker burner was reached. The sample was allowed to cool in a desiccator and weighed. The sample

was reheated for a half hour at the highest temperature of the burner, allowed to cool and re-weighed. This process was repeated until the crucible attained constant weight. The percent of magnesium was calculated from the formula:

$$\frac{\text{Wt. of MgO} \times 0.6032 \times 100}{\text{Wt. of sample}} = \% \text{ magnesium}$$

V. The Reaction of Ethylene Oxide with Magnesium Chloride

While attempts to prepare $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{Mg}$ in the pure state were unsuccessful, it was shown that ethylene oxide will react with magnesium chloride to give ethylene chlorohydrin.

Forty-two hundredths mole (40.3g.) of anhydrous magnesium chloride and five hundred ml. of anhydrous ether were placed in a one-liter, three-necked, round-bottomed flask. The flask was equipped with a glycerine-sealed mechanical stirrer, a reflux condenser and a dropping-funnel

fitted with an outer metal jacket. The system was completely protected from moisture of the air by use of calcium chloride tubes. An ice-salt-bath was used to cool the reaction mixture. One hundred ml. of anhydrous ether was placed in the dropping-funnel and surrounded with dry ice. Forty-two hundredths mole (18.6 g.) of ethylene oxide was added to the dropping-funnel and the ethylene oxide-ether mixture added to the reaction flask over a period of one half hour with vigorous stirring. The ice-salt-bath was removed and the reaction mixture allowed to come to room temperature with stirring. The contents of the flask were poured on chipped ice, neutralized with iced, dilute hydrochloric acid and extracted three times with ether. The ether extracts were dried over anhydrous sodium sulfate and fractionated from a Claisen flask modified by a fifteen inch Vigreux column. Both the ether and the water layers were

investigated. The ethylene chlorohydrin in the water layer was determined by a method described by Gomberg (11). The aqueous solution was distilled until the temperature reached sixty degrees when it was assumed that all the ether had been removed. A fraction was then collected which comprised approximately half of the total water solution. This latter fraction was neutralized with a saturated solution of sodium carbonate. The resulting solution was fractionated, saving a fraction with a boiling point range of 60 - 99.8° and weighing 100.5 g. After determining the refractive index of the solution, the amount of ethylene chlorohydrin was computed by reference to a curve in which index of refraction was plotted against percent chlorohydrin.

From the ether layer there was obtained a fraction of 1.5 g. having a boiling point range of 125 - 128° at 741 mm. The refractive index of the water solution

indicated an ethylene chlorohydrin content of 1.6 g. This represented a total of 3.1 g. of the halohydrin and corresponded to a 9.1 percent yield.

VI. Determination of Ethylene Chlorohydrin and Alcohol

When the boiling points of the ethylene chlorohydrin and the alcohol were too close together to allow a good separation by fractionation, the two fractions were collected together. After determining the total weight of the distillate, it was placed in a one-liter, three-necked flask. The flask was equipped with ground-glass joints and fitted with a mercury-sealed stirrer, a condenser and a ground-glass stopper. Five hundred ml. of .3 M sodium hydroxide was added and the mixture refluxed with stirring for a half hour. The contents of the flask were cooled, placed in a separatory funnel and the water-layer drawn off into a liter volumetric flask. The solution was made up

to volume and five ml. samples taken for analysis. Chlorine was determined by means of the Volhard method (10). The amount of ethylene chlorohydrin was calculated from the results of the chloride analysis and the weight of the alcohol obtained by difference.

VII. Identification of n-Butyl Alcohol

The alcohol was identified from its boiling point (117° at 740 mm.) and the 3, 5 - dinitrobenzoate derivative (12).

One-half g. of 3, 5 - dinitrobenzoic acid was mixed with 1 g. of phosphorus pentoxide in a test tube. The mixture was warmed gently to start the reaction. After the initial rapid reaction had subsided, the mixture was heated for about four minutes at such a rate as to cause vigorous bubbling. While still liquid the mixture was poured on a watch glass and the mass allowed to solidify. The material was transferred to a clean clay plate and rubbed with a spatula to

remove phosphorus oxychloride. About .5 g. of the 3, 5 - dinitrobenzoyl chloride thus prepared was mixed with one ml. of the alcohol in a test tube and the mixture boiled gently for five minutes. Then ten ml. of distilled water was added and the solution cooled in an ice bath until the precipitate solidified. The precipitate was collected on a filter and washed with ten ml. of two percent sodium carbonate solution. It was then recrystallized from five to ten ml. of a mixture of ethyl alcohol and water of such proportions that the ester dissolved in the hot solution but separated when the solution was cooled. After the crystals had been removed by filtration and dried on a porous plate the melting point was determined.

Melting point of the ester	61°
Mixed melting point	61°

VIII. Identification of Ethylene Chlorohydrin

The ethylene chlorohydrin was also identified from its boiling point (128 - 129° at 740 mm.) and the 3, 5 - dinitrobenzoate derivative.

The ester was prepared according to the procedure described in Section VII.

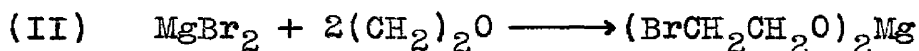
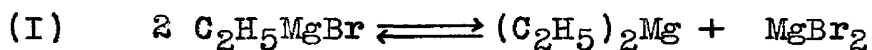
Melting point of the ester 89 - 90.5°

Mixed melting point 89 - 90°

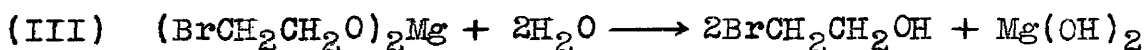
DISCUSSION

DISCUSSION

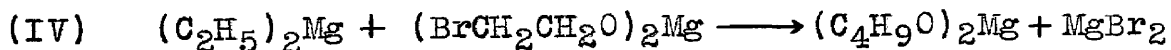
Earlier work by Schlenk and Schlenk (5), Ribas and Tapia (3) and Huston and Agett (4) indicated that the reactions which take place when one mole of ethylene oxide is added to one mole of ethylmagnesium bromide may be represented by the following equations:



Hydrolysis of the addition product gives ethylene bromohydrin:

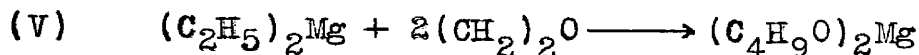


Heating the reaction mixture obtained by the addition of one mole of ethylene oxide to one mole of ethylmagnesium bromide leads to n-butyl alcohol:



n-Butyl alcohol also results from the use of two moles of ethylene oxide to one mole of

ethylmagnesium bromide:



In this case hydrolysis of the addition product gives a mixture of n-butyl alcohol and ethylene bromohydrin.

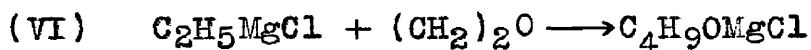
The purpose of the present investigation was to examine the behavior of alkylmagnesium chloride solutions and ethylene oxide under similar conditions.

Hydrolysis of the reaction mixture formed by adding ethylene oxide to ethylmagnesium chloride in a 1:1 molar ratio, without heating, gave a 54.6 percent yield of n-butyl alcohol and 22.0 percent of ethylene chlorohydrin based upon the titrated Grignard reagent (8). These results represent only the amounts actually recovered from the ether layer. They do not take into account the appreciable quantity of ethylene chlorohydrin destroyed during hydrolysis and that remaining in the water layer after extraction with ether.

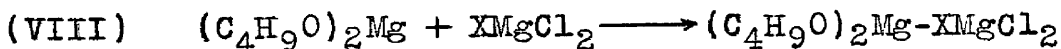
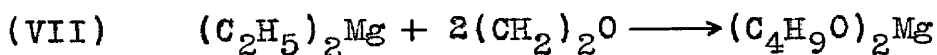
A precipitate was formed by adding ether to

the reaction mixture obtained from equal molecular quantities of ethylmagnesium chloride and ethylene oxide. This precipitate was analyzed for chlorine and magnesium content. The results of several such analyses are given in Table I, Page 35.

Since C_4H_9OMgCl contains 26.7 percent chlorine and 18.3 percent magnesium, the values given in Table I indicate that the precipitate may have consisted largely of either C_4H_9OMgCl resulting from the reaction:



or $(C_4H_9O)_2Mg-XMgCl_2$ formed by the reactions:



Hydrolysis of either intermediate would yield n-butyl alcohol.

However, when the molar ratio of ethylene oxide to ethylmagnesium chloride was 2:1, there was obtained an 80.3 percent yield of n-butyl alcohol and a 69.4 percent yield of ethylene chloro-

hydrin. If the intermediate leading directly to the formation of a large amount of n-butyl alcohol were C_4H_9OMgCl , insufficient magnesium chloride would be left in solution to give this yield of ethylene chlorohydrin.

Even so, C_4H_9OMgCl may still be considered a possible intermediate if it is assumed that as the solution becomes depleted of magnesium chloride, decomposition of C_4H_9OMgCl occurs according to the equation:



Thus it seems evident that the immediate precursor of the n-butyl alcohol is $(C_4H_9O)_2Mg$, which could be formed by the reaction of ethylene oxide with either ethylmagnesium chloride or diethylmagnesium.

The reaction of the epoxide with diethylmagnesium appears more probable in view of the fact that ethylmagnesium chloride, according to Schlenk (13), is approximately eighty-five percent dissociated into diethylmagnesium and magnesium chloride.

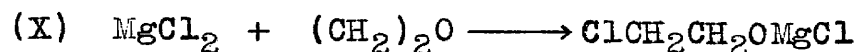
Evidence submitted by Noller and Castro (14) substantiates the theory that $(C_4H_9O)_2Mg$ combines

with varying amounts of magnesium chloride. They observed that the precipitate formed by the oxidation of n-butyilmagnesium chloride removed magnesium chloride from solution. Noller and Castro suggested that if C_4H_9OMgCl is the product of oxidation, it should have the property of forming a complex with magnesium chloride, probably by virtue of the unshared electrons on the oxygen atom. Obviously, $(C_4H_9O)_2Mg$ should behave like C_4H_9OMgCl in this respect.

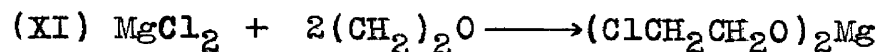
Further evidence for the precipitation of $(C_4H_9O)_2Mg-XMgCl_2$ was provided by analysis of the precipitate formed by the use of one half mole of ethylene oxide to one of ethylmagnesium chloride. In this case the chloride content was found to be 40.8 percent and the magnesium content was 19.6 percent. These are much higher values than the ones obtained when equimolecular quantities of the reactants were used. This is the result that should be expected under these conditions since more magnesium chloride would be available to precipitate with $(C_4H_9O)_2Mg$. Theoretical values for $(C_4H_9O)_2Mg-2MgCl_2$ are 39.3 percent chlorine

and 20.2 percent magnesium.

There are two possible intermediates for ethylene chlorohydrin - $\text{ClCH}_2\text{CH}_2\text{OMgCl}$, formed by the reaction:



or $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{Mg}$, formed by the reaction:



According to equation (X) the theoretical yield of ethylene chlorohydrin per mole of Grignard reagent is one-half mole. However, if the percentage yield is calculated on this basis, when ethylene oxide and ethylmagnesium chloride are reacted in a 2:1 molar ratio the amount of halohydrin actually obtained leads to far more than a hundred percent. Hence, we feel justified in the assumption that the intermediate leading to ethylene chlorohydrin is $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{Mg}$.

A survey was made of the reaction of ethylene oxide with the Grignard reagents of several alkyl chlorides. Each Grignard reagent was treated in three different ways as described in part III of the Experimental Section and the yield of the

alcohol and halohydrin determined in each case. Results from the three methods of procedure are compared in Table III, Page 37.

Column 1 of Table III shows that four of the Grignard reagents reacted with ethylene oxide in a mole per mole ratio, without heating, to give the alcohol as the principal product. *n*-Butylmagnesium chloride and isobutylmagnesium chloride gave somewhat higher yields of halohydrin than of the alcohols. In agreement with results reported by Whitmore (15), *t*-butylmagnesium chloride when treated with ethylene oxide yielded only ethylene chlorohydrin.

The data recorded in column 2 reveals that in respect to the two secondary Grignard reagents and isobutylmagnesium chloride, heating the reaction product before hydrolysis appears to enhance somewhat the yield of the alcohol at the expense of the halohydrin. In other cases the result of heating was to increase the yields of both the alcohol and of the ethylene chlorohydrin. The reaction product from ethylmagnesium chloride and ethylene oxide could not be heated successfully because the mixture solidified upon attempting to

distill off the ether prior to heating with benzene. This resulted in considerable decomposition of the intermediate product due to excessive heating near the side-walls of the flask.

In most cases addition of two moles of ethylene oxide to one mole of the Grignard reagent greatly increased the yield of both the alcohol and the ethylene chlorohydrin.

Attempts to prepare $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{Mg}$ in the pure state by treating a stirred suspension of dry magnesium chloride with ethylene oxide were not successful. However, it was possible to prepare a small amount of ethylene chlorohydrin by this reaction.

SUMMARY

SUMMARY

1. The main reaction between one mole of ethylene oxide and one mole of Grignard reagents formed by the treatment of alkyl chlorides with magnesium is between the epoxide and either R_2Mg or $RMgCl$. With Grignard reagents formed from alkyl bromides and magnesium the principal reaction is with $MgBr_2$.
2. The intermediate in the formation of n-butyl alcohol from $(C_2H_5)_2Mg$ is $(C_4H_9O)_2Mg$. From C_2H_5MgCl it is C_4H_9OMgCl which by rearrangement gives $(C_4H_9O)_2Mg$ and $MgCl_2$. The high yield of both alcohol and chlorohydrin when excess of ethylene oxide is used indicates in all cases $(C_4H_9O)_2Mg$.
3. Analytical results indicate that the composition of the precipitate formed when the reaction mixture of one mole of ethyl Grignard reagent and one mole of ethylene oxide is diluted with ether corresponds to $(C_4H_9O)_2Mg-MgCl_2$. When the ratio of Grignard reagent to ethylene oxide

is 2:1 it approaches the composition of $(C_4H_9O)_2Mg-2MgCl_2$.

4. Evidence submitted in this thesis indicates that the precursor of the ethylene chlorohydrin is $(ClCH_2CH_2O)_2Mg$.
5. Results obtained by heating the reaction mixture from equal molecular quantities of alkylmagnesium chloride and ethylene oxide do not indicate a high degree of reactivity between $(ClCH_2CH_2O)_2Mg$ and R_2Mg to give $(RCH_2CH_2O)_2Mg$.
6. Addition of two moles of ethylene oxide to one of alkylmagnesium chloride greatly increased the yields of both the alcohol and ethylene chlorohydrin.

TABLES

TABLE I

Analysis of Addition Product from $(\text{CH}_2)_2\text{O}$
and $\text{C}_2\text{H}_5\text{MgCl}$
Mole per Mole Ratio

Reaction Number	% Chlorine	% Magnesium
1	34.86	16.47
2	31.85	17.85
3	31.57	18.21
4	34.31	17.96
5	31.97	18.12
6	33.27	17.52
7	36.34	17.49
8	27.03	16.84
9	30.52	17.85

TABLE II

Analysis of Addition Product from
 $(\text{CH}_2)_2\text{O}$ and $\text{C}_2\text{H}_5\text{MgCl}$

One half Mole of $(\text{CH}_2)_2\text{O}$ to One Mole of $\text{C}_2\text{H}_5\text{MgCl}$		
Reaction Number	% Chlorine	% Magnesium
1	40.85	19.66
One and One half Moles of $(\text{CH}_2)_2\text{O}$ to One Mole of $\text{C}_2\text{H}_5\text{MgCl}$		
1	24.68	16.04
2	32.16	17.21

TABLE III

Percent Yields of Alcohols and Ethylene Chlorohydrin

Based upon the Titrated Grignard Reagents

	1.	2.	3.
	$\text{RMgCl} + (\text{CH}_2)_2\text{O}$ No heat	$\text{RMgCl} + (\text{CH}_2)_2\text{O}$ Heat	$\text{RMgCl} + 2(\text{CH}_2)_2\text{O}$ No heat
Ethylmagnesium Chloride			
1-Butanol	54.6	45.9	80.3
Chlorohydrin	22.0	16.4	69.4
n-Propylmagnesium Chloride			
1-Pentanol	39.5	49.9	66.4
Chlorohydrin	31.5	32.0	54.0
Isopropylmagnesium Chloride			
3-Methyl-1-butanol	34.5	46.5	54.8
Chlorohydrin	25.1	19.5	58.0
n-Butylmagnesium Chloride			
1-Hexanol	39.0	45.8	69.6
Chlorohydrin	25.5	36.8	60.1
s-Butylmagnesium Chloride			
3-Methyl-1-pentanol	25.6	35.1	40.9
Chlorohydrin	30.9	23.9	61.5
Isobutylmagnesium Chloride			
4-Methyl-1-pentanol	23.6	29.8	35.2
Chlorohydrin	34.6	25.0	60.4
t-Butylmagnesium Chloride			
3,3 Dimethyl-1-butanol	0.0	0.0	0.0
Chlorohydrin	21.3	23.3	48.1

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BIBLIOGRAPHY

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