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An Investigation of the Reaction Between Ethylene Bromide and Magnesium

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AN INVESTIGATION OF THE REACTION BETWEEN
ETHYLENE BROMIDE AND MAGNESIUM

A THESIS
presented in partial fulfillment
of requirements for the degree of
MASTER OF SCIENCE
from South Dakota State College

prepared by

CHARLES E. HEACOCK

1933

INTRODUCTION

Synthetic Organic Chemistry received a great impetus with the discovery by Franklund in 1849(1), that zinc would react with alkyl iodides to give compounds of the type ZnR_2 . The ease of their formation and the readiness with which they react with other substances to form such products as hydrocarbons, alcohols, ketones and alkyl derivatives of other metals made them almost indispensable to the organic chemist. Their disadvantage lay in the fact that they had disagreeable odors, caused severe burns when in contact with the skin, and were very explosive in air, necessitating keeping them in an atmosphere of carbon dioxide.

Grignard, in 1900(2), found that magnesium, in anhydrous ether, reacts with various alkyl halides, especially the iodides and bromides, to form mixed organo-metallic compounds of the type $R-Mg-X$. In a series of communications(3), he demonstrated that this was a typical reaction of alkyl halides and that the products thus formed, known as Grignard reagents, resembled the activity of the zinc alkyls and could be used in place of them in the synthesis of organic compounds. These so-called "Grignard reagents" had the distinct advantage in retaining their activity in ether solutions, where it is not necessary to provide for them an inert atmosphere.

By reason of their extraordinary reactivity, the Grignard reagents aroused great interest, and the original investigations

(1) Franklund, Ann. 71, 213, (1849)

(2) Grignard, Compt. rend. 130, 1322, (1900)

(3) Grignard, *ibid.* 132, 336, 558, 683, (1901)

or Grignard were immediately followed by those of other workers. It was soon apparent that, for synthetic purposes, magnesium compounds of the type R-Mg-X could be more conveniently manipulated and gave better yields than other metal alkyls. Consequently, these compounds of magnesium have attained a position in synthetic chemistry unrivalled by that of any other class of compounds. The following is a list of some of the important reactions of the Grignard Reagents:

Grignard Reagent treated with:	Product formed after hydrolysis:
water	hydrocarbons
formaldehyde	primary alcohols
other aldehydes	secondary alcohols
ketones	tertiary alcohols
carbon dioxide	carboxylic acids
sulfur dioxide	sulfinic acids
carbon disulfide	carbithionic acids

These are but a few of the typical reactions of Grignard reagents. A detailed discussion of these reactions and many others will be found in the monograph by H. Wren(4).

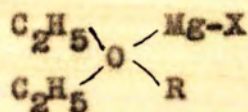
Considerable work has been done on the theory of the formation of Grignard reagents. The role of the solvent, ether, has been the source of considerable controversy. At first, it was believed that ether was an absolute essential to the preparation of organo-magnesium compounds. There are

(4) Wren, "Organometallic Compounds of Zinc and Magnesium", (1913)

instances of Grignard formation in the absence of any solvent. Spencer and Stokes(5) found that magnesium would react with various aryl iodides at their boiling points. Spencer and Crewdson(6) brought about similiar reactions with the lower alkyl halides at high temperatures in sealed tubes. The yields in both cases were unsatisfactory. The use of solvents other than ether were investigated by Tschelinzeff(7), Hepworth(8) and others. In all cases it was found that solvents with atoms of unsaturated residual valences such as oxygen, nitrogen and sulfur could be used.

Tschelinzeff in 1904(7) came to the conclusion that the action of the solvent was catalytic. He showed that the formation of the Grignard reagents took place in the presence of such inert solvents as benzene, toluene and xylene, with the presence of a trace of ether. The amount of Grignard reagent formed was out of all proportions to the quantity of ether employed.

Ever since Blaise' original analysis(9), the fact has been accepted that the ether forms a loose chemical union with the Grignard reagent in the form of an etherate. Because of the apparent stability of the ether union, Baeyer and Villiger(10) believed these to be oxonium compounds of the probable formula:



- (5) Spencer and Stokes, J. Chem. Soc. 93, 68, (1908)
 (6) Spencer and Crewdson, *ibid.* 93, 1822, (1908)
 (7) Tschelinzeff, Ber. 37, 4534, (1904)
 (8) Hepworth, J. Chem. Soc. 119, 1249, (1921)
 (9) Blaise, Ber. 46, 2163, (1913)
 (10) Baeyer and Villiger, Ann. chim. (7) 24, 441, (1901)

The literature abounds with examples of the formation of Grignard reagents from monohalogen compounds and magnesium. Scarcely a single monohalide exists which does not react normally in ether solution with magnesium. Relatively little mention is made in the literature, however, of the action of magnesium on polyhalogen derivatives. M. Guy Emschwiller(12) was apparently the first to study the action of magnesium on methylene halides. He demonstrated the formation of a small quantity of an organo-magnesium compound of the formula $\text{CH}_2(\text{MgX})_2$. In the case of the iodide, about 3% of the magnesium was converted into this compound. The remainder is accounted for in ethylene.

Zelinsky and Gutt(13) demonstrated that when magnesium reacts with 1,3-dibrom-propane, trimethylene and propylene are produced. Only a trace of $\text{Br.Mg.}(\text{CH}_2)_3.\text{Mg.Br}$ was formed. In the case of the corresponding compounds of butane, pentane, and heptane(14), a larger amount of the Grignard reagent is obtained. In the case of the dihalogen derivatives of benzene, it has been pointed out that they react quite readily with magnesium. Usually one molecule of magnesium is introduced but Gilman(15) has demonstrated conditions wherein about 23% of the dimagnesium compound can be formed. He mentions that the reaction is complicated by a large number of side reactions.

Relatively little study has been made of the action of magnesium on ethylene bromide and other 1,2-dihalogen deriv-

(12) Emschwiller, Compt. rend. 183, 665, (1926)

(13) Zelinsky and Gutt, Ber. 40, 3049, (1907)

(14) Von Braun and Sobelcke, Ber. 44, 1911, (1918)

(15) Gilman, Beaber and Jones, Rec. trav. chim. 48, 597, (1929)

atives. Tissier and Grignard(16) pointed out that when magnesium is treated with ethylene bromide in anhydrous ether, magnesium bromide crystallizes out in voluminous crystals and ethylene is evolved.

Ahrens and Stapler(17) studied the reaction. The large crystals that were formed were treated with benzaldehyde, whereupon a vigorous reaction took place. The substance formed they analyzed as $C_6H_5 \cdot CH(OMgBr) \cdot CH_2 \cdot CH_2Br \cdot C_4H_{10}O$. They also believed that they separated another product which reacted with benzaldehyde to yield a dimagnesium compound. Similar results were obtained when their crystals were condensed with toluylaldehyde and nitrobenzaldehyde. Later(18) they state that perhaps the principle product was magnesium bromide with a small quantity of the organomagnesium compound.

Richter makes mention of the fact that, in the cold, ethylene bromide and magnesium yield $Br \cdot CH_2 \cdot CH_2 \cdot MgBr$ (19). He does not, however, give the source of his information.

As far as we have been able to ascertain, these are the only references in the literature, of the possible formation of a Grignard reagent with ethylene bromide and its homologs. Meisenheimer(20) pointed out the confusion in our knowledge of this action. He was not able to duplicate the work of Ahrens and Stapler(17) and he believed that the conversion

(16) Tissier and Grignard, *Compt. rend.* 132, 835, (1901)

(17) Ahrens and Stapler, *Ber.* 38, 1296, (1905)

(18) Ahrens and Stapler, *ibid.* 38, 3259, (1905)

(19) Richter, "Organic Chemistry", (Spielmann), Vol. 1, page 322, (1919)

(20) Meisenheimer, *Ber.* 61B, 708, (1928)

of benzil to benzoin by the product of the action of ethylene bromide and magnesium discovered by Bischoff(21), was not due to the reducing action of a Grignard reagent, but to magnesium bromide itself. Gomberg and Bachmann(22) have actually demonstrated the reducing action of magnesium bromide in this reaction.

If it were possible to prepare a Grignard reagent from ethylene bromide and magnesium, a large field would be opened in synthetic organic chemistry. A relatively simple method could then be devised wherein the more complex aldehydes and ketones, as well as derivatives of succinic acid could be synthesized. It is the purpose of this investigation, therefore, to study this action of magnesium on ethylene bromide. We carried out the reaction first in the conventional methods of Grignard synthesis, making use of some of the newer methods of identifying Grignard reagents. We then altered the conditions of the reaction, hoping in this way that we could notice some trend that would give us a key to the possible formation of a Grignard reagent.

(21) Bischoff, Ber. 39, 3964, (1906)

(22) Gomberg and Bachmann, J. Am. Chem. Soc. 46, 2339, (1924)

MATERIALS

Care was taken that all chemicals used were water free. All reagents were taken from newly opened containers. Ether was dried with sodium, and kept in bottles in contact with strips of freshly cut sodium, protected with calcium chloride tubes. Its state of dehydration was checked from time to time with fresh shavings of metallic sodium.

The halogen derivatives were dried over phosphoric anhydride, and kept in dark bottles until used.

All other reagents were tested for dehydration with strips of sodium.

EXPERIMENTAL

Part 1 (Normal Conditions). 0.0116 mols of ethylene bromide, an equal volume of ether and an equivalent amount of magnesium were introduced into a 50 cc bottle provided with a delivery tube arranged to catch any gas evolved by displacement of water contained in a buret. An exactly identical duplicate was made, substituting ethyl bromide for ethylene bromide. After a short period of induction, the reaction proceeded readily, with the evolution of gas. The ethylene bromide generated about 300 cc of gas, compared with 50 cc from the ethyl bromide.

The liquid remaining in the generating flask gradually separated into distinct layers. In the case of ethylene bromide, three layers were formed. These were a clear top layer, a middle layer consisting of a heavy brown liquid, and a solid bottom layer. Ethyl bromide, on the other hand, formed

one clear liquid layer and a solid layer.

Analysis of the Products. The gas generated from ethylene bromide decolorized permanganate immediately and burned with a luminous flame, typical of ethylene. The gas generated from ethyl bromide showed no unsaturation with permanganate and burned with the almost colorless flame of the saturated hydrocarbons. The former also decolorized bromine, while the latter reacted slowly, with evidence of the formation of hydrogen bromide.

In order to obtain larger quantities of the liquid layers, a duplicate experiment was carried out, using about ten times the quantities used above. The apparatus was provided with a mechanical stirrer.

The liquid layers separated out as before. When this mixture was accidentally left exposed to direct sunlight after all apparent reaction had ceased, a vigorous reaction immediately ensued, until all of the ether seemed to be transformed into this brown liquid of the middle layer. This liquid, when left standing overnight in a room slightly above freezing, formed large, clear cut rhombic crystals. These crystals reacted violently with water.

Analysis of the Crystals formed in the Brown Liquid Layer. In the hope that these crystals might contain some of the Grignard reagent, they were analyzed for the presence of the latter. Approximately a two gram sample was introduced into a gelatine capsule, and placed in a large inverted test tube filled with ice water. When the capsule dissolved, a

violent reaction took place with the formation, however, of a negligible amount of gas. This seemed to demonstrate that a highly volatile liquid, undoubtedly ether, was evolved and condensed in the cold water.

The method of Gilman and Meyers(23) and Gilman, Wilkinson, Fishel and Meyers(24) was next used to detect the presence of a Grignard reagent. This depends upon the fact that any Grignard reagent, when hydrolyzed, produces basic magnesium halide. This substance is sufficiently ionized in water that it may be titrated by adding an excess of standard acid and titrating the excess with standard base, using methyl orange as indicator. This showed decidedly positive results in the case of the product of reaction of ethyl bromide and magnesium. However, no indication of alkalinity was demonstrated, when solutions of the crystals were similarly treated.

We believed, then, that the crystals must simply be etherates of magnesium bromide. A quantitative study of the etherates of magnesium bromide was made recently by Evans and Rowley(25). They demonstrated the existence of three etherates, containing 1, 2 and 3 molecules of ether per molecule of magnesium bromide. The monoetherate is very stable, the dietherate fairly stable under ordinary conditions, while the trietherate is unstable, its transition temperature being 13° C. Accordingly, we should be able to isolate both the monoetherate

(23) Gilman and Meyers, *Rec. trav. chim.* 45, 314, (1926)

(24) Gilman, Wilkinson, Fishel and Meyers, *J. Am. Chem. Soc.* 45, 150, (1923)

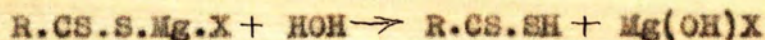
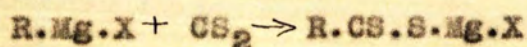
(25) Evans and Rowley, *J. Am. Chem. Soc.* 52, 3523, (1930)

Analysis of the Lower Solid Layer. The analysis of the two upper liquid layers have demonstrated the absence of any Grignard reagent in them. The solid layer was next investigated.

The solid layer was washed thoroughly with dry ether until the washings showed the absence of any etherate, when subjected to the tests described above. A portion of this residue was treated with water in an apparatus set up for gas collection. A violent reaction immediately took place and just as quickly subsided. No more than a negligible amount of gas was given off. In a control reaction with ethyl bromide, the solid residue evolved large quantities of gas when hydrolyzed. The water solution was titrated by the method of Gilman described above, with negative results.

It was found that, after the first violent reaction had ceased, a very slow reaction persisted. It was found that, after a time, the solution had acquired some alkalinity. The gas was collected for several days over water and proved to be hydrogen. This must be a reaction, therefore, between unused magnesium and water.

The Use of Carbon Disulfide as a Grignard Indicator. Carbon disulfide reacts much like carbon dioxide with Grignard reagents, yielding, on hydrolysis, carbithionic acids(26).



These acids have a characteristic repulsive odor and are,

(26)Cohen, "Organic Chemistry", Part 1, (1928). Page 254.

therefore, easily identified. We have made use of this reaction as a test for the Grignard reagent. Since these acids are all made by the action of a Grignard reagent on carbon disulfide(27), we can assume it to be a general test.

When used with the Grignard reagent formed from ethyl bromide, even traces of the Grignard are easily detected.

Applying this test to all parts of the solution formed in the action of magnesium on ethylene bromide, negative results were obtained in every case.

Discussion of Results of Part 1. All of our tests for the possibility of a Grignard reagent being formed in the reaction between magnesium and ethylene bromide have been negative. These results include: 1. The only gas evolved when magnesium reacts with ethylene bromide in anhydrous ether is ethylene, as indicated by the readiness with which it reacts with permanganate, and its luminous flame when ignited. 2. The solution, on hydrolysis, showed no alkalinity. 3. Hydrolysis of the solutions was accompanied by a violent reaction, but with the formation of no more than a negligible amount of gas. 4. The crystals formed as a result of the reaction were proved by analysis to be etherates of magnesium bromide. 5. Carbon disulfide, when treated with the solutions, showed no indication of the formation of a carbithionic acid.

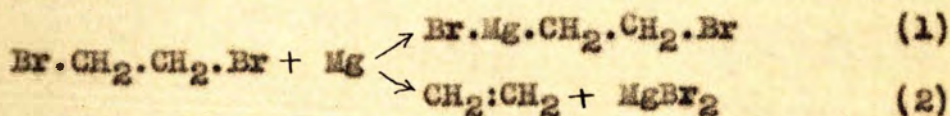
We have not eliminated the possibility of some substance other than ethylene being formed. Thus we might have such products as cyclobutane, cyclohexane, etc., formed by a

(27) Schmidt, "A Textbook of Organic Chemistry", (1932), Page 200.

reaction similar to Freund's synthesis. Our results show that most of the gas evolved was ethylene, and the possibility of higher homologs seem irrelevant to this problem and was not investigated.

Part 2. (Abnormal Conditions.) Having established fairly well the absence of any Grignard reagent in the reaction between magnesium and ethylene bromide under normal conditions, we next attempted to alter the conditions of the experiment, to see if we could detect some difference in the reaction.

Effect of Pressure. This experiment was carried out with the assumption that the reaction between magnesium and ethylene bromide might involve a side reaction with the formation of a Grignard. Under normal conditions, however, the formation of ethylene is so rapid that the formation of the Grignard is masked(28). This is indicated by the following equation:



If such is the case, the second reaction, involving a gaseous product, should be diminished or entirely stopped by the application of pressure, allowing the first to be observed.

A preliminary determination was carried out in a sealed glass tube. Upon attempting to break the tube to study the products, the enormous pressure that was built up shattered

(28) Getman and Daniels, "Outlines of Theoretical Chemistry", Fifth Edition, (1931), Page 334.

the tube with detonating force, and an alternative method had to be devised.

The reagents were introduced into a small bottle, and the bottle filled to the brim with anhydrous ether. A rubber stopper was inserted, and held in place by the plunger of a pellet press. In this way, no free space was left above the liquid.

In such a system, there was no indication of any reaction taking place, even after heating. It was found that, by removing the stopper, the reaction would soon start, but it could be stopped by stoppering tightly again. Thus we found that we could start and stop the reaction at will by releasing and applying pressure, respectively.

The reaction was then allowed to start at atmospheric pressure. After it had reached a point of continuous reaction, the stopper was tightly inserted, until no free space was left. The reaction was then observed behind a thick plate of glass as precaution against explosion. It was observed in every case that the clear ether layer would separate into two phases, with a more or less indistinct line of demarcation.

The bottles were then opened under water, and the solution tested for alkalinity. Results paralleled exactly those of normal conditions.

If the tube, while still under pressure, was placed in a freezing mixture, crystals of the same form as in part 1 of this study appeared. These crystals were subjected to the same tests as those of part 1, and were found to be identical with them.

Effect of Temperature. Freezing mixtures of snow and calcium chloride were next used to lower the temperature of the reaction mixtures. In this way, temperatures could be held at -15° C. In all cases, the results were identical to those already observed.

Reaction mixtures were then heated to temperatures a little above the boiling point of ether, again with no positive results.

Effect of Solvent. As was pointed out before, the solvent plays an important part in the formation and action of Grignard reagents. There is the possibility that the free energy of magnesium bromide etherate is so low, that the tendency to form this etherate completely masks any tendency towards Grignard formation.

Recalling the work of Spencer and coworkers(5)(6), an attempt was first made to prepare the substance in the absence of any solvent. Pure magnesium has no tendency to react with ethylene bromide even at temperatures sufficiently high to decompose the compound by pyrolysis. Believing that this might be due to the presence of a protective layer of basic carbonate, the reaction was allowed to start in the presence of ether. When the reaction was well under way, a vacuum was applied to the system and the ether evaporated. As soon as the ether had disappeared, all reaction ceased. When fresh portions of ether were added, the action would be resumed. Subsequent evaporation would again stop it. We would have to conclude, therefore, that a solvent is absolutely necessary.

Next was taken up a study of the possibility of a reaction in solvents other than those which have a "solvate" action. Those considered were: chloroform, carbon disulfide, carbon tetrachloride and benzene. The effect of addition of iodine and small quantities of ether were studied. A summary of the experimental results is given in the table on the following page.

In each case, 5 cc of solvent was taken, unless otherwise stated. 0.0232 mols of magnesium was used, and 0.0116 mols of ethyl bromide. Small crystals of iodine, of uniform size, were used, one crystal in each case unless otherwise stated.

It will be observed, from the table of the results, that ethylene bromide and magnesium do not react with any of the solvents, even when heated to the boiling point of the solvents. The addition of a crystal of iodine initiates a reaction immediately. The reaction, however, is slight and apparently one of combination between magnesium and iodine. Thus, we found that increasing the amount of iodine, increased the reaction. Also that the reaction ceased as soon as the yellow color of iodine was no longer apparent in the solution.

The poisonous effect of carbon disulfide is interesting. Two drops of carbon disulfide in 5 cc of solution was sufficient to noticeably retard any reaction. One-half cc of carbon disulfide in a mixture of 5 cc of ether, with the regular mixture, completely stopped the reaction. Thus, carbon disulfide has a remarkable tendency to inhibit the reaction between magnesium and ethylene bromide.

Table Showing the Reaction Between Magnesium and Ethylene Bromide in the presence of Various Solvents.

Solvent	Magnesium	Iodine	Ethylene Bromide	Ether	Action
Chloroform	x				None
"	x	x			Slight
"	x	x	x		Slight
"	x	x	x(2 cc)		Slight
"	x	x	x(2 cc)	4 cc	Greater
"		x	x		None
"	x	x	x		Slight
"	x	x	x	½ cc	Slight
"	x	x	x	5 cc	Greater
"	x	x	x		Slight
"	x	x(2)	x		Greater
"	x	x	x	1 drop	Slight
Carbon disulfide (2 drops)	x	x	x	1 drop	Less
" (½ cc)	x	x	x	1 drop	None
" (½ cc)	x	x	x	5 cc	None
"	x	x		1 drop	None
Carbon Tetrachloride	x				None
"	x	x			Slight
"	x	x	x		Slight
"	x	x	x	2 drops	Slight
"	x	x	x	2 cc	Greater
Benzene	Identical in every respect with carbon tetrachloride.				

In this connection, it is interesting to recall the work of Freundler and Damond(29). They found, in the reaction between trioxymethylene and the Grignard reagent from secondary butyl bromide in ether solution, that the violence of the reaction could be diminished by the addition of a few drops of carbon disulfide. The role of the carbon disulfide in these reactions would be an interesting problem for further investigation.

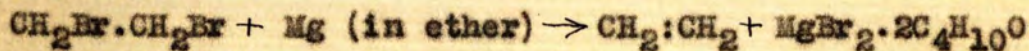
(29)Freundler and Damond, Compt. rend. 141, 830, (1905)

DISCUSSION OF RESULTS

In any scheme of research, where the purpose of the investigation is to find a relation between cause and effect, it is necessary to establish a system of reliable controls. Then when one of the factors in the experiment is varied, the corresponding effect can be reliably attributed to that variation and to nothing else.

To establish a reliable control, therefore, was the purpose of carefully observing the results obtained in carrying out the reaction of ethylene bromide, magnesium and ether under conditions identical to those in which Grignard reagents are normally prepared from simple alkyl halides. Fortunately, results obtained were of such nature that they could be exactly explained and accounted for, not only from theory but from experiment.

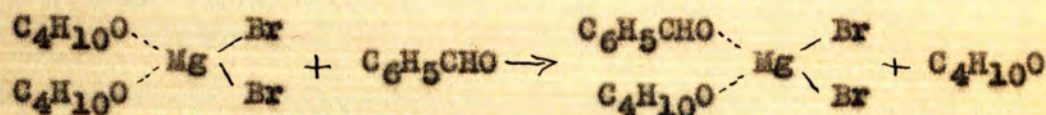
The fact that the following reaction took place repeatedly under conditions suitable for Grignard reagent formation, gave us a basis from which to measure any other effect when conditions were varied:



In studying variations in temperature and pressure, we had facilities to apply pressures up to three atmospheres and to give us a temperature range from -15°C up to 50°C . In every case of a variation in conditions, we obtained products which could be easily identified as identical with those products of our control or standard. There was no change in

reactions secured under these abnormal conditions which did not have its parallel in our control. We feel confident, therefore, that no compound escaped us and that every step of our investigation gave results which we could reliably check.

We feel that we can definitely say, therefore, that Ahrens and Stapler(17) did not have the Grignard reagent that they claimed to have. Their observations paralleled those of this research, except for the formation of a compound with benzaldehyde, of the formula $C_6H_5.CH(OMgBr).CH_2.CH_2Br.C_4H_{10}O$. Their only proof for the actual existence of this compound was the analysis of it. There is a possibility of explaining this as a reaction between the etherate of magnesium bromide and benzaldehyde. The substance which they believed to be the Grignard reagent, was actually the crystalline compound which has been proved in this research to be simply the dietherate of magnesium bromide. Since, as pointed out by Meisenheimer, benzaldehyde has a greater "reaction energy" than ether, the reaction that one would expect to take place would be:



where the ether is displaced on the residual valence of the magnesium by the molecule of benzaldehyde. The percentage composition of this final compound would not be far from that believed to be formed by Ahrens and Stapler:

Calculated for:	Carbon	Magnesium	Bromine
$C_6H_5CH(OMgBr) \cdot CH_2 \cdot CH_2Br \cdot C_4H_{10}O$	39.57%	6.21%	40.74%
$MgBr_2 \cdot (C_6H_5CHO)(C_4H_{10}O)$	36.30%	6.68%	43.90%
Actually Observed by Ahrens and Stapler	40.58%	6.32%	40.90%

Although the check is not as good as would be desired, such analyses of substances as unstable as these etherates seem to be, would introduce considerable error in one's results. It might seem possible that experimental error would cause such a misinterpretation, and that, instead of the Grignard complex, they actually had simply magnesium bromide with one molecule each of ether and benzaldehyde of solvation. Further work should be done on this particular problem.

A thorough survey of the literature did not reveal the source of the information from which Richter(19) stated that, at low temperatures, a Grignard reagent would be formed from ethylene bromide and magnesium. We assume, therefore, that he must have discovered this statement from an unpublished investigation. From this study, we feel safe in saying that the statement is in error, and that there is no indication of such Grignard formation. At temperatures 35 degrees below room temperatures, we found absolutely no indication that a Grignard reagent might have been formed.

Several topics not altogether relevant to this problem have been discovered during this work. I do not believe it to be out of place to include them with this thesis.

A survey of literature regarding etherate synthesis mentions nothing of etherate formation in the manner that we encountered in our work. As described previously in detail, the

reaction of ethylene bromide and magnesium, in a large quantity of ether, mechanically stirred, gave a mixture which, on standing in direct sunlight, formed a large quantity of a heavy "etherate liquid". This liquid, on standing in temperatures around 10° C, is converted almost entirely into well defined crystals. Since this accidental discovery was incidental to our work, nothing further than an analysis of the crystals was made.

The use of carbon disulfide as a reagent to detect Grignard reagent formation was used in this work with some degree of success. The presence of even traces of the R-Mg-X structure, will give the typical repulsive odor of the carbithionic acids. Outside of the color test for Grignard reagents discovered by Gilman and Schultze(30), using Michler's Ketone, there is apparently no other simple qualitative test. This had the advantage of that test in that it is more sensitive and not so readily affected by other substances.

Another branch of this work which could be made the basis of some very interesting and worthwhile study, is the reaction between magnesium bromide etherates and other organic substances. Apparently, we have discovered a reaction wherein molecules of solvation can be displaced by other substances. It would be interesting to see if it would be possible to make up a "displacement series" of organic compounds, giving their relative abilities to displace ether of solvation from magnesium bromide. Such a series should enable one to predict the readiness with

(30) Gilman and Schultze, J. Am. Chem. Soc. 47, 2002, (1925)

which a substance would react with a Grignard reagent. Such a study is beyond the scope of this research.

In conclusion, the author wishes to acknowledge his great indebtedness to Professor L. S. Guss, under whose guidance this problem was developed and, also, to thank other members of the Chemistry Department of State College, especially Professor E. R. Binnewies, who have, in many ways, generously given their assistance in various matters of detail relating to this problem.

SUMMARY

A study was made of the possibility of formation of a Grignard reagent from magnesium and ethylene bromide.

Under normal conditions of Grignard reagent formation, no evidence of any Grignard reagent could be detected. This is contrary to the work of Ahrens and Stapler and in agreement with that of Grignard and Meisenheimer.

Under varying conditions of temperature, pressure and solvent, no Grignard reagent was detected.

Methods of detection of Grignard reagents were investigated and discussed.

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