

THE PREPARATION OF A GRIGNARD REAGENT  
" IN THE ABSENCE OF A SOLVENT.

A Thesis Submitted to the Faculty of the  
Virginia Polytechnic Institute  
In partial fulfillment of the requirements for the  
Degree of Master of Science.

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Acknowledgement.

The inspiration that caused this investigation was an observation made under the direction of Dr. R. E. Hussey. With his guidance and helpful counsel this research was carried out. Therefore to him the author expresses deep appreciation.

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## INTRODUCTION

This work is a study of the product formed by the reaction of magnesium on bromobenzene in the absence of a solvent, and the results of hydrolysing this product.

Ormerod (1) discovered that by refluxing bromobenzene with magnesium a substance was obtained which gave a positive test for a Grignard reagent. The production of a Grignard reagent in such a manner, without the use of ether or any solvent, deserved investigation because of the importance of the Grignard reagent in organic synthesis, and because of the theories of its formation.

Therefore it was decided to study the reaction to determine to what extent the reagent was formed by this method, to consider its hydrolysis and reactions in absence of a solvent, and finally to make a comparison of the production of Phenyl magnesium bromide by this method with that by traditional methods.

A great deal of work has been done on the subject of the Grignard reaction. Many products were prepared for the first time through its use. It is the standard method of manufacturing many fine chemicals.

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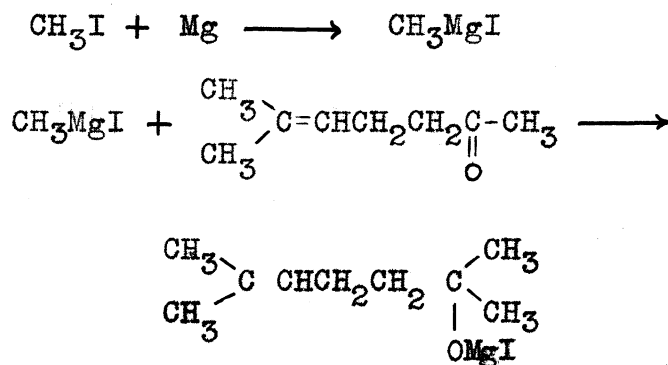
(1) D.F.Ormerod. B.S. Chemical Thesis V.P.I. (1938)

Numerous theories have been advanced as to the nature of the organo magnesium compound, and its relation to ether.

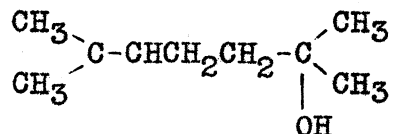
Of the voluminous literature on the subject of the Grignard reaction, we will first review those articles bearing relation to the subject of this thesis.

## HISTORICAL.

In 1899 Phillip Barbier (1) heated together methyl heptanone, anhydrous ether, magnesium metal, and methyl iodide. The reaction that occurred has become one of the most important and best known in organic chemistry. It is called the Grignard reaction, and expressed simply is :



The product on hydrolysis with water yields the tertiary alcohol, di-methyl heptanol.

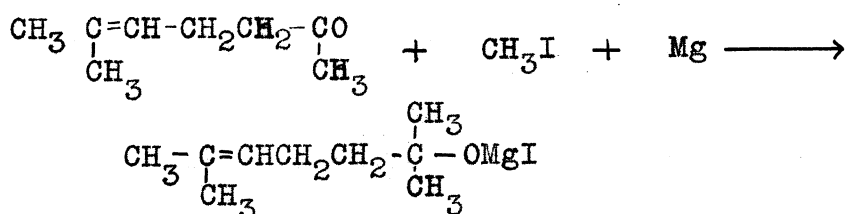


That Barbier had no conception of the mechanism of this reaction is indicated by his method of

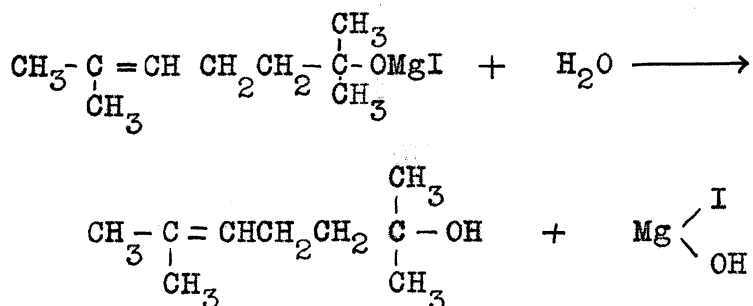
(1) Compt. rend. 128: 110-111 (1899).

preparation. He mixed the heptonone, ether, and magnesium, added dropwise the methyl iodide, and left these in contact for twelve hours.

The equations that he wrote to express his reaction shows a somewhat better understanding of the mechanism than his method would indicate. He wrote



For the water hydrolysis he wrote



Barbier wished to see the reaction tried on other homologous substances. He assigned (1) to his pupil Victor Grignard the task of doing this.

Grignard (2) resolved the reaction into its

(1) E. Bodtker Chem. Ztg. 34 : 150 (1910)

(2) Compt. rend. 130 : 1322-1324 (1900).

two steps. He studied the active alkyl magnesium halide. He found that by the addition of aldehydes and ketones he could prepare many secondary and tertiary alcohols, which were previously unknown.

At first the reaction was quite justly called the Barbier Grignard reaction. Contemporary articles (1) discussed the question of which man deserved credit for the discovery.

Grignard stated that it was necessary for the reaction to be carried out in ethyl ether. If one attempts to drive off the ether, he said, there remains a greyish mass, which absorbs moisture. But the great advantage of this reaction is that it is useless to isolate the combination obtained. (2) An aldehyde or ketone added to the combination produced, on hydrolysis with water containing a small amount of acid, a secondary or tertiary alcohol.

The grey mass that Grignard had left when the volatile ether was driven off still contained a molecule of

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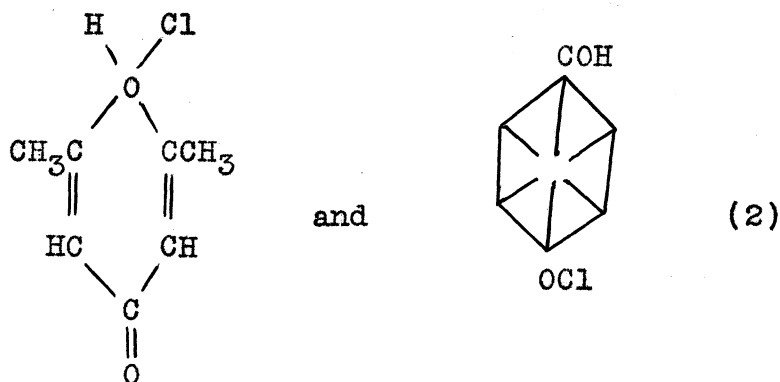
(1) Chem. Ztg 34 : 150  
ibid. 34 : 529  
Bull. Soc. Chim. 7 : 453

(2) Compt. rend 130 : 1323 (1900)

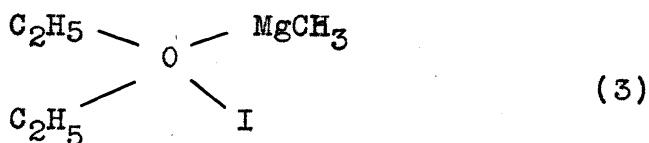


ether. This was considered ether of crystallization.

The work of Grignard came to the attention of Baeyer and Villiager (1), who were collecting evidence of the existence of tetra valent oxygen. A compound, di-methyl pyrone hydrochloride had been found which had been assigned formulae with tetra valent oxygen.



Using the Grignard reagent as another example of a compound with a tetra valent oxygen, they gave it the formula




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(1) Ber. 35 : 1201-1212 (1902)

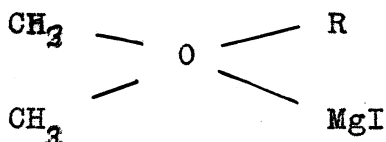
(2) Ber. 34 : 3615 (1901)

(3) Ber. 35 : 1201-1212 (1902)

## 8.

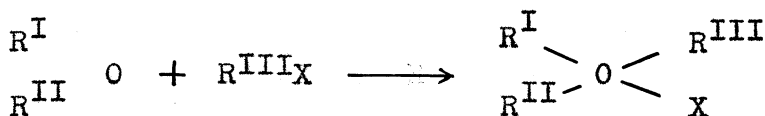
The reagent tied on to the ether gave oxygen a valence of four, and the complex was an example supporting their theory.

Later Grignard (1) adapted an oxonium structure, but he distributed the valences differently.



This formula, he claimed, explained the observed activity.

Stadnikoff (2) set forth a theory of the mechanism of the reaction, which supports Grignard's formula. His theory involves the formation of an oxonium compound, as follows:



(1) Compt. rend 136 : 1260-1262 (1903)

(2) Stadnikoff, G.

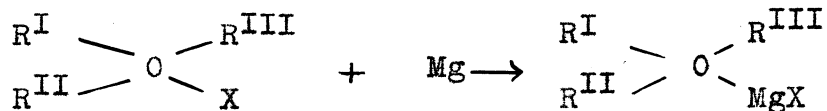
J. Russ. Phys. Chem. Soc. 43 : 1244 (1911)

ibid 44 : 1219 ; 44 : 1256 (1912)

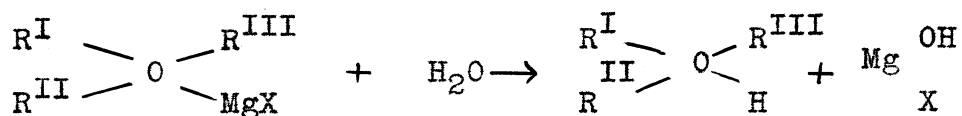
J. pract. chem. 88 : 1 (1913)

Through Thorp and Kamm J.A.C.S. 36 : 1023 (1914)

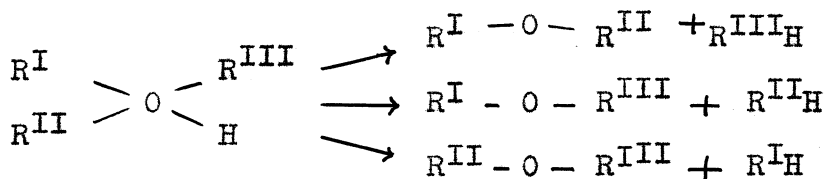
This adds magnesium to give Grignard's formula:



On treatment with water

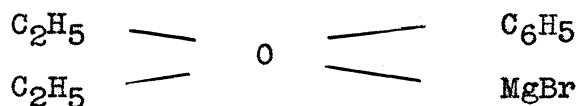


Stadnikoff said this may break up in several ways:



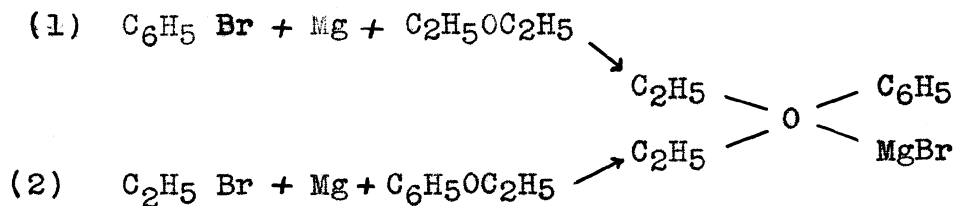
Using such ethers as diphenyl methyl butyl and diphenyl methyl propyl ether, and hydrolysing with dilute sulfuric acid, he found all of the products indicated by the above equations.

Thorp and Kamm's experiment (1) <sup>WAS AN</sup> attempt to prove the Grignard formula by producing



by two methods. First from reacting bromo benzene, magnesium, and di ethyl ether; and second from ethyl bromide, magnesium and ethyl phenyl ether.

(1) J.A.C.S. 36 : 1022-1028



Then if this formula were correct, the same compound would be formed in each case, and on hydrolysis the same products should be obtained. They found that this was not the case. The first reaction gave benzene and diethyl ether, and the second ethane and ethyl phenyl ether.

On hydrolysis the ether started with is the one that is obtained, and the hydrocarbon is the hydrocarbon of the bromide started with.

This lead Thorp and Kamm to conclude that the Grignard representation was incorrect, and they stated that it is unnecessary to assume any oxonium formula, but, they said, if one is desired, the Baeyer-Villiger is preferable.

The preliminary formation of free radicals in the preparation of the Grignard reagent has been considered. (1) The formation of di p tolyl in very small quantities incidental to the formation of benzyl magnesium chloride is advanced as evidence for free radical formation.

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(1) Gilman and Kirby J.A.C.S. 51 :1571 (1929)

The Grignard reagent has been prepared successfully using ethers other than di ethyl ether. Majima and Kotake (1) found that better yields of the product of the action of magnesium indol iodide on carbon dioxide are obtained in the presence of anisole than ethyl ether.

Tschelnizeff (2) found that organo magnesium compounds may be prepared in the presence of benzene to which ether had been added. They may also be prepared in benzene alone, at a higher temperature.

In 1930 Gilman and Brown (3) at Iowa State teachers College heated .1 mole chloro benzene and .1 atom magnesium in a sealed, evacuated bomb tube to a temperature of 150-160° c. After three hours the liquid had disappeared, and a brown powder was left in the tube. They said this was phenyl magnesium chloride. The powder was dissolved in a mixture of ether and benzene. Unreacted magnesium was filtered out. Aliquot portions of the solution were taken for titration to determine the amount of Grignard reagent formed.

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- (1) Ber 55 : 3865-3872 (1922)  
J. Chem. Soc. Japan 43 : 936-948 (1922)  
Through J.C.S. 124 Part 1 : 150,428
- (2) Ber 37 : 4534-4540 (1904)  
U.C.S. 88 a 1 : 40
- (3) J.A.C.S. 52 : P 3330 (1930)

This method of analysis was based on a previous work by Gilman and his associates. (1) They found that an ether solution of the Grignard reagent could be titrated with standard acid, using phenolphthalein as indicator. An accuracy within one percent was claimed for this method. Another similar method was to heat the reagent with a known amount of standard sulfuric acid, and titrate the excess acid with standard base.

Using the above method of analysis, the yield of Grignard reagent in the sealed tube preparation was calculated to be 85%.

There is a sensitive qualitative test for the Grignard reagent. (2) .5cc of the reagent is treated with a 1% solution of Michler's ketone in dry benzene. One cc of water is added, and several drops of a 2% solution of iodine in acetic acid. A characteristic blue color indicates the presence of a Grignard reagent.

Ormerod (3) in a study of the preparation of phenyl magnesium bromide in various solvents, made the

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(1) Gilman, Wilkinson, Fishel, Meyers J.A.C.S. 43 : 150 (1923)

(2) Gilman and Schultz J.A.C.S. 47 : 2002 (1925)

(3) Ormerod, B.S. Chemical Thesis V.P.I. (1938)

observation that if bromo benzene was boiled with magnesium in a Claisen flask, while stirring rapidly, a reaction takes place. The product gave a positive test with the Michler's ketone reagent described above. He dissolved the mixture of Grignard reagent, unreacted magnesium and unreacted bromo benzene, in ether, and filtered through glass wool to remove the unreacted magnesium.

This ether solution was treated with carbon dioxide. A yield of organic matter resembling benzoic acid was so small that a melting point could not be made.

No tertiary alcohol was isolated after he reacted the ether solution of the Grignard reagent with acetone.

## Experimental.

## Description of the apparatus used.

The apparatus for the condensation consisted of a 500 cc claisen flask. This was equipped with a mechanical stirrer and mercury seal. A thermometer extended into the reagent. A water cooled reflux condenser was used. On top of the condenser was a calcium chloride tube.

The flask was heated with an electric burner. The heat could be regulated.

For hydrolysis the calcium chloride tube was removed, and a dropping funnel supported over the condenser. The liquid to be added was dropped slowly down through the condenser. The flask was kept cool during hydrolysis by being immersed in cold water.

Steam distillation was carried out in the customary apparatus.

A Soxhlet extractor was used for extraction.



## Reaction of Bromobenzene and Magnesium.

The bromobenzene (Eastman Kodak Co. B.P. 154-155°) was first distilled, and the middle fraction, boiling at 153°/715 mm was used:

12.5 g powdered magnesium, 52 cc (78<sup>g</sup>) bromobenzene and a small crystal of iodine were placed in the flask, and the stirrer made to rotate slowly, just sufficient to keep the mixture well stirred. The mixture was heated at 153°c. It refluxes at this temperature.

After about twenty minutes the volume of the mixture began to increase, and white fumes rose above it. A yellow color was noticed in the grey mixture.

When heating was stopped soon after this change in appearance, the reaction continued for a short time. Then the mixture thickened to a brownish grey mass, with considerable clear liquid still present. This product gave all of the tests to be described, but the yield of the reaction products were found to be lower than when heating is continued.

If the heating is continued at a reduced rate, the temperature begins to fall slowly, but the reaction continues. Even when the heating was not reduced the temperature of the reacting mixture was observed to

fall slowly, but the refluxing became more vigorous, and even violent. Also continued strong heating caused excessive charring at the bottom of the flask.

Hence it was considered best to continue the heating at a reduced rate. Then after two hours the mixture had condensed to a brownish grey plastic mass. This was allowed to cool. The material solidified to a hard solid.

This material reacts violently with water.

It gives a positive test for a Grignard reagent (1) with Michler's ketone. The test was made as follows. (1) A little of the brownish grey solid was dissolved in ether. One cc. of this solution was added to one cc of a 1% solution of Michler's ketone in benzene. 1 cc of water is added slowly. Then a few drops of a 2% solution of iodine in glacial acetic acid. A greenish blue color develops. This test color is shown only by organo magnesium halides having the Mg X groups attached to carbon. (2)

If the brownish grey solid is left exposed to air, it slowly turns white, and becomes crumbly.

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(1) Gilman and Schultz. J.A.C.S. 47 : 2002 (1925)

(2) Gilman and Schultz. J.A.C.S. 47 : 2005 (1925)

Hydrolysis with dilute acid and identification of products.

Bromobenzene was reacted with magnesium as already described. The product was allowed to cool. The reaction flask was then partially immersed in cold water. Dilute sulfuric acid containing one part acid to four parts water was added dropwise through the condenser from a separatory funnel placed above the condenser. As each drop came into contact with the solid material, it caused a vigorous reaction. White fumes rose up. The reaction from each drop was allowed to subside before another drop was added. After several cc were added in this manner, the rest could be added more rapidly. As soon as the solid mass was sufficiently decomposed to free the stirrer, stirring was started. A total of 200 cc of the dilute acid was added. This produced a mixture of oily material and water

This was allowed to stand for several hours. Then it was steam distilled. The distillate separated into an oily layer and a water layer. A white solid formed in the condenser tube of the steam distillation apparatus, and had to be flushed out several times by running the water out of the condenser jacket, and letting the uncondensed steam through the tube carry the solid

down into the receiving flask. The oily layer of the distillate dissolved this material.

A sample of this white solid was taken for analysis. It was found to melt at  $69^{\circ}\text{C}$ . It was insoluble in water, dilute hydrochloric, dilute sodium hydroxide, and cold concentrated sulfuric acid. It gave no test for halogen. These characteristics were found to coincide with di phenyl. The boiling point was found to agree, and a comparison with di phenyl proved that the white solid was di phenyl.

The oily layer from another run, in which none of the di phenyl had been removed was fractionated. The first distillate came off at  $77^{\circ}$ , and the temperature rose slowly and steadily to  $88^{\circ}$ . After that only a few drops came over until vapor at  $150^{\circ}$  reached the thermometer. It rose slowly and steadily from that point on. and fractions were taken off up through  $240^{\circ}$ . At this temperature there seemed to be considerable decomposition in the flask, so distillation was stopped.

In another run, this distillation was stopped at  $190^{\circ}$ , and the residue poured out on a watch glass. It solidified. The solid was white, with a slightly brown tinge. It melted over a two degree range, at the di phenyl melting point. Solubility data, crystallization, and

odor agreed with di phenyl.

The fraction of the distillate which came over between  $77^{\circ}$  and  $88^{\circ}$  was redistilled. It appeared to be benzene. It was identified by making the nitro derivative. (1) Three drops of the liquid, 1cc Nitric acid and 1cc sulfuric acid were mixed in a test tube. This was heated to boiling and boiled for one minute. The liquid was poured into cool water. Yellow crystals formed. These were filtered out and washed well. Then they were dissolved in hot 1 : 1 alcohol. On standing long needle like crystals formed. These were filtered and dried. The melting point was found to be  $88^{\circ}$ . Theoretical melting point of m di nitro benzene  $89^{\circ}$ . Therefore this fraction was benzene.

The fraction that came over above  $150^{\circ}$  was redistilled. The boiling range narrowed down. Most of the liquid came over and around  $153^{\circ}\text{c}$ . This liquid gave a positive Beilstein test for halogen. It was a colorless liquid, identical with bromobenzene in odor and solubility. An approximate determination of the density also agreed. It was concluded that this was unreacted bromo benzene.

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(1) Mulliken : Identification of organic compounds P.200

Then the products in the oily layer of the steam distillate were benzene, di phenyl, and unreacted bromo benzene.

Based on the weights of the fractions of the first fractional distillation of the oily layer, the amount of each of the products were as follows:

7 — 8.5 g benzene

5 — 5.5 g di phenyl

21 — 15 g unreacted bromo benzene

These figures are the results of several separate preparations and determinations. Probably each of the above contained a small amount of the others, because they are the results of the first fractionation.

The water layer of the steam distillate was clear. It was distilled with a high column. All of it distilled at 98-99°. No residue was left.

Then the material not volatalized by steam was considered. This consisted of an aqueous solution and a brown-black solid adhering to the walls of the flask and in the liquid. On warming the flask and mixture the solid became tar-like. It was removed with a spatula.

The aqueous solution measured 250 cc. Of this 75 cc was taken and distilled, using a long fractionating column. The water came over at 98°/715 mm, leaving

3 cc of a yellow liquid, which came over at  $124^{\circ}$ . A white solid was left in the flask.

The yellow liquid from this and other runs was examined. It was soluble in water and insoluble in ether. It was acid to litmus. Silver nitrate caused a precipitate. The liquid apparently was inorganic. It was identified as  $\text{H Br}^{\text{H}}$ , which forms a constant boiling mixture with water. Theoretical B.P.  $126^{\circ}$ .

The white solid was an inorganic magnesium salt. It was soluble in water and gave a good qualitative test for magnesium.

The brown-black tarry material was examined. It was found to be very soluble in hot benzene. Nothing could be crystallized out by cooling, or by allowing the solvent to evaporate slowly. When all of the benzene had evaporated, the tar was recovered. The tar was soluble in hot acetone also, but nothing could be crystallized.

Boiling ligroin extracted most of the tar, leaving some inorganic material and carbonized product that was in the tar. On cooling the hot ligroin solution in ice water a brownish-yellow solid was thrown out. This was filtered and washed with cold ligroin. It was too sticky to get into a melting point tube.

The brownish-yellow solid was recrystallized from hot ligroin. A bright yellow solid was obtained. It melted over a wide range. Melting points on samples of this yellow material from several separate runs ranged from 95 to 148°. After several more recrystallizations from ligroin the color had become almost white with a slightly yellow tinge. M.P. 180 - 190° : The amount of product from the series of recrystalization was very small/.

A slight modification of this method of purification resulted in better results. The tarry residue was extracted with boiling ligroin. The beaker containing the hot ligroin solution was placed inside of a larger beaker which had been warmed. Both beakers were covered. In this way the cooling was very slow, and was not carried below room temperature.

The crystals formed were filtered, washed with cold ligroin, dried, and recrystallized four more times from boiling ligroin in the same manner. An almost white solid with a slightly yellow tinge resulted. M.P. 193°-196° C .

This solid was insoluble in water, dilute hydrochloric acid, dilute sodium hydroxide and cold concentrated sulfuric acid. It showed a negative Beilstein test for halogen. It burned completely in the Bunsen flame.



The ceric nitrate test for a hydroxyl group (1) was negative.

The permanganate test (2) showed no results.

The phenyl hydrazine test for aldehydes or ketones was negative.

Metallic sodium (3) produced no reaction.

There was no apparent reaction with acetyl chloride or benzoyl chloride.

On the basis of these tests it was suspected that the compound was terphenyl. From the literature on terphenyl it was found that terphenyl sublimed at  $427^{\circ}$ .

A small quantity of the compound was placed in a 10 ml. beaker covered with a watch glass and heated on a small hot plate set at  $430^{\circ}$ . The solid first melted, then pure white leaflets began to form on the sides of the beaker above the liquid level. The leaflets were examined under the microscope. The melting point was determined. M.P.  $210 - 211^{\circ}$  corrected. Theoretical M.P.  $212^{\circ}$ .

A benzene solution of terphenyl shows a blue fluorescence.

Nitration of terphenyl produces a mixture of nitrates.

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(1) Shriner and Fuson-Identification of Organic Compounds

(1940) P 52.

(2) *ibid* P 38.

(3) Kamm- Qualitative Organic Analysis, Second edition P 148.

## Hydrolysis with water, and Identification of Products.

In order to be sure that the products obtained by the dilute acid hydrolysis of the Grignard reagent prepared without a solvent were not due in any way to the sulfuric acid, it was decided to attempt a pure water hydrolysis. This gave rise to several difficulties, and made necessary some modification of the separation procedure already described.

The Grignard reagent prepared as described under preparation was hydrolyzed by adding dropwise through the condenser pure water. The reaction observed was the same as that observed when the dilute acid was used.

The product of the hydrolysis was steam distilled. The oily layer of the distillate was fractionated as before, and the benzene, di phenyl and bromo benzene identified.

From a typical run, the following were isolated:

Benzene	6.4	g
Di phenyl	4.6	g
Bromo benzene	26.11	g

The flask containing the material not volatized by steam contained a considerable quantity of brown and solid material.

This was filtered, and the solid on the filter paper allowed to dry. This produced a hard mass which was reduced to powder in a mortar. The powder was evidently

composed of organic and inorganic material.

A small amount of the powder was treated with dilute acid. Some of it dissolved, and a black tarry precipitate was left. This resembled the tarry material from the acid hydrolysis.

To avoid completely the use of acid, the powder from another run was placed in a Soxhlet extractor and extracted with benzene. The benzene solution was a dark brown color. The powder on drying became white. It dissolved in acid and the solution showed a test for magnesium. It was a magnesium salt.

The benzene extraction was distilled on a water bath and the benzene removed. This left a dark brown tar.

This tar was extracted with boiling 95% ethyl alcohol. The hot alcohol solution was decanted into a warm beaker. This was placed inside of a larger beaker that had been warmed. Both beakers were covered. The solution cooled slowly, and a voluminous yellow solid crystallized out. This was filtered and washed with ethyl alcohol. As much of the alcohol was removed by suction as was possible. The solid was allowed to dry. As it dried the color became lighter. The dry solid was a very pale yellow color M.P.  $180^{\circ}$  -  $185^{\circ}$  (uncorrected). The weight of this crude terphenyl was .3 grams. Part of this was placed in a 10 cc beaker covered with a watch glass and heated on

a small hot plate set at  $430^{\circ}$  c. White leaflets sublimed up on the side of the beaker. The melting point of these was found to be  $210^{\circ}$  (corrected) It was pure terphenyl.

The alcohol mother liquor from the first crystallization was evaporated to half its volume, and allowed to cool to room temperature as before. A second crystallization was obtained. The crystals were washed, dried and sublimed as were the first. More terphenyl was formed.

## Analysis of the Bromo benzene reagent.

In order to determine whether or not the bromo-benzene reagent used contained di bromo benzene, the bromine content of the bromo benzene was determined.

The bromo benzene was manufactured by the Eastman Kodak Company Research Laboratory. (Organic chemical #43 B.P. 154- 155° .)

The bromine was determined by the Carins method (1) .7 g of silver nitrate free from halogen and 2 cc of fuming nitric acid were placed in the bottom of a bomb tube. About .5 g of the bromo benzene was weighed out exactly to the fourth decimal place in a small test tube. This test tube was slid into the tube. The bromo benzene and nitric acid were not in contact. Then the tube was carefully sealed with the end drawn out to a small capillary. After the seal had cooled the tubes were placed in a tube furnace. The temperature was raised slowly to 235° and kept between 235-240° for four hours. Then the tubes in the furnace were allowed to cool.

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(1). Kingscott and Knight. Methods of Quantitative Organic Analysis (1914) P<sub>p</sub> 50-52.

After the furnace and tubes were cold, the capillary was gently heated with the bunsen flame to drive out any liquid. Then the tip was heated more strongly, and the pressure within blew the tube open. The end of the tube was then cut off.

The contents of the tube were rinsed out thoroughly with distilled water into a beaker. The solution and precipitate was digested for one hour at 80° c. Then it was filtered through a prepared tarred Gooch crucible.

The precipitate was washed with alcohol and dried at 110°. Crucible and contents were weighed and the weight silver bromide was determined.

$$\text{Weight silver bromide} \times \frac{\text{Br}}{\text{Ag} + \text{Br}} = \text{weight bromine.}$$

$$\text{Weight silver bromide} \times .42555 = \text{weight bromine.}$$

$$\frac{\text{Weight bromine}}{\text{Weight of sample}} \times 100 = \% \text{ bromine}$$

Trial 1	50.71 % Br.	)	
2	50.52% Br.	)	
3	51.05 % Br.	)	
			Average 50.76%.

Br. in Bromo benzene calculated from formula = 50.91%.

## Discussion of Results.

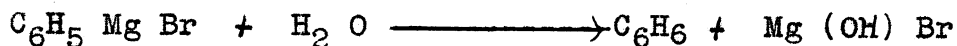
A Grignard reagent has been prepared and hydrolysed in the complete absence of ether or any other solvent. Its presence was proven qualitatively by the Michler's ketone test, and by its activity.

Hydrolysis was accomplished with dilute sulfuric acid, and with distilled water. Both produced the same organic compounds. The only difference was that the sulfuric acid produced an inorganic salt which was soluble in water (magnesium sulfate) and this simplified separation.

The yields of the products of hydrolysis were calculated on the basis of the bromo benzene taken for the reaction. The results of several runs follow:

Benzene	17- 22 %
Di phenyl	12- 15%
Terphenyl	1 - 2%
Amorphous residue	9- 15%
Bromobenzene(recovered)	33 - 28%

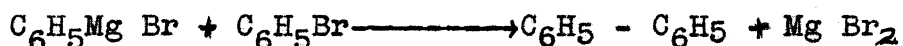
Benzene is produced by hydrolysis of the Grignard reagent.



The Benzene represents hydrolysed Grignard reagent. This indicated 17-22%  $\text{C}_6\text{H}_5 \text{ Mg Br}$ .

The formation of di phenyl is an unusual side reaction in the preparation of phenyl magnesium bromide. In the absence of a solvent it was shown that this side reaction consumes 12 - 15% of the bromo benzene. This is a much larger amount than is consumed by this reaction when ether is used as a solvent. Evidently ether hinders the di phenyl formation, although it always does form to some extent.

From the equation for the di phenyl formation:



it is apparent that one half of the di phenyl is the product of already prepared Grignard reagent. The other half represents bromo benzene.

Then the amount Grignard reagent taken up in di-phenyl formation is 6 - 8%.

The quantity of  $\text{C}_6\text{H}_5\text{Mg Br}$  represented by the terphenyl is uncertain, since the exact mechanism of formation is not known. It is believed that at least one molecule of phenyl magnesium bromide and probably two is used in its formation. This means .6 to 1.3%  $\text{C}_6\text{H}_5\text{Mg Br}$  went to terphenyl formation.

From the above representation, the amount of  $\text{C}_6\text{H}_5\text{Mg Br}$



formed in the absence of a solvent is indicated to be 24 - 30 % of the possible yield.

The formation of terphenyl in this reaction deserves further consideration. No observation of its formation in Grignard reactions was found in the literature.

The possibility of this product being formed from p di bromo benzene present in the bromo benzene was eliminated when analysis of the bromo benzene showed that there was no di bromo benzene present.

Gilman and Kirby (1) identified di p tolyl an extremely minor product of reactions involving the Grignard reagent benzyl magnesium chloride. Di benzyl was also formed. They attributed the di p tolyl formation to free radicals. There appears to be a slight analogy between the p di tolyl production and terphenyl production. Both are produced by reaction of a Grignard reagent where the reaction is at a position on the ring para to the Mg X position. Di benzyl is the product of the reaction at the Mg X linkage in the benzyl magnesium bromide preparation made by Gilman and Kirby. Diphenyl is the product of the reaction at the Mg X linkage in the preparation of phenyl magnesium bromide studied in this thesis.

The coupling in a position para to the Mg Br position on the ring is p-di tolyl in Gilman and Kirby's reaction, and p-di phenyl benzene in the reaction studied in this thesis.

Bachman and Clark(1) found that the action of sodium on boiling chloro benzene leads to the formation of benzene, bi phenyl, o-di phenyl benzene, p di phenyl benzene, tri phenylene, o-o'-di phenyl bi phenyl, together with unidentified resinous and tarry hydrocarbons.

The action of free radicals of phenyl and phenylene is advanced to explain this reaction. Such action may be responsible for ter phenyl formation in the case of phenyl magnesium bromide.

## Conclusion.

1. By refluxing bromo benzene and magnesium, reaction takes place to form phenyl magnesium bromide, di phenyl and terphenyl. The yield of phenyl magnesium bromide was found to be 24- 30 %.
2. The quantity of di phenyl formed is several times the amount formed when ether is used as a solvent.
3. Terphenyl was isolated from this reaction.