1935

The preparation of methylene dimagnesium dihalide

BOSTON UNIVERSITY

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THESIS

THE PREPARATION OF METHYLENE DIMAGNESIUM DIHALIDE.

by

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TABLE OF CONTENTS

I - PURPOSE

The first aim of the work had been to prepare pentanediol-1,5 from methylene dihalide and ethylene oxide by the Grignard synthesis. Because of difficulty in isolating the compounds formed due to the small amount of reaction products present, and the expense of the reacting substances, the author has therefore attempted

(1) to increase the yield of methylene dimagnesium dihalide,

(2) to study the action of this Grignard reagent with acetone and endeavor to isolate the products formed.

II - SURVEY OF THE LITERATURE.

A. Early work with organo metallic compounds.

The use of organo metallic compounds as synthetic reagents has been known for many years. The zinc and mercury compounds were the first studied. Frankland worked with the zinc alkyls R_2Zn about 1849. These compounds ignite in air and the difficulties arising therefrom led to the study of other metals. Lohr prepared magnesium dimethyl, diethyl, and dipropyl by heating the alkyl halide with magnesium amalgam in sealed tubes. It is said that these compounds are likewise very reactive igniting even in carbon dioxide. Quite by accident in 1899, Barbier discovered that magnesium acting on methyl iodide and a ketone in presence of ether produced a tertiary alcohol. On observation of the reaction, it was found that magnesium reacted with the halide to form methyl magnesium iodide, CH_3MgI, and that this compound reacted with the ketone. Grignard studied this reaction and obtained the magnesium alkyl halide of several halides. These compounds are now known by his name. Grignard published a paper concerning these compounds in the year 1900 and since then there has been extensive work done in this field.

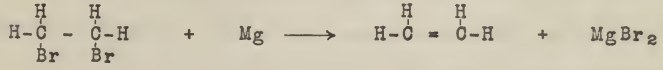
Some of the compounds with which this reagent enters into reaction are water, ammonia, aldehydes, ketones, esters,

ethylene oxide and similar substances, carbon dioxide, and amines.

B. The formation of the Grignard Reagent from alkyl dihalides.

Over one thousand articles have been written describing the Grignard reagent in regard to its preparation and uses, but there has been very little written concerning the alkyl dimagnesium dihalide compounds. The author has attempted to give a chronological survey of this literature.

1. In 1901 Grignard and Tissier[1] tried to form the dimagnesium compound of ethylene dibromide, but they found that ethylene was the chief product formed when the dihalide and magnesium reacted in the presence of ether.



2. In 1907 Zelinsky and Gutt[2] obtained the cyclic compound trimethylene $H_2C\langle^{CH_2}_{CH_2}$ and a small amount of hexamethylene dimagnesium dibromide $BrMg(CH_2)_6MgBr$ when they attempted to form the Grignard reagent trimethylene dimagnesium dibromide from 1,3-dibromopropane and magnesium in the presence of ether.

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1. C. I 999 (1901)

2. C.A. 1 2466 (1907)

$$Br(CH_2)_3Br + Mg \longrightarrow H_2C\begin{array}{l}\diagup\\\diagdown\end{array}\!\!\begin{array}{l}CH_2\\CH_2\end{array} + MgBr_2$$

$$Br(CH_2)_3Br + Mg\ Br(CH_2)_3Br \longrightarrow Br(CH_2)_6Br + MgBr_2$$

$$Br(CH_2)_6Br + 2Mg \longrightarrow BrMg(CH_2)_6MgBr$$

When carbon dioxide was added to the reaction mixture a yield of 20% of suberic acid was obtained.

$$BrMg(CH_2)_6MgBr \xrightarrow{CO_2} BrMgOOC(CH_2)_6COOMgBr$$

$$\xrightarrow[\text{acid}]{HOH} HOOC(CH_2)_6COOH$$

3. In 1907 Grignard and Vignon[1] worked with the dihalide 1,5-dibromopentane. When magnesium and this dihalide reacted in the presence of ether, and the reaction mixture was decomposed with water, they obtained pentane, decane, pentadecane, eicosane and a mixture of higher paraffins. They also found that carbon dioxide reacted with the Grignard reagent forming pimelic acid, decamethylenedicarboxylic acid, and cyclohexanone and when ethyl acetate was added to the Grignard reagent methylcyclohexanol was formed. The authors

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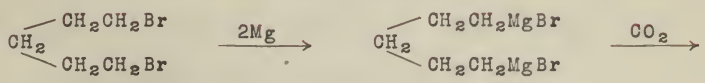
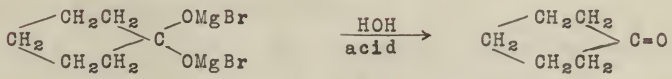
1. C II 631 (1907)

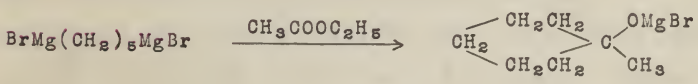
represented the reactions by the following equations:

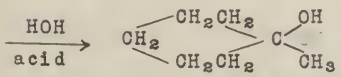




$$BrMg(CH_2)_5MgBr \xrightarrow{2CO_2} BrMgOOC(CH_2)_5COOMgBr \xrightarrow[\text{acid}]{HOH} HOOC(CH_2)_5COOH$$

$$Br(CH_2)_5Br + Mg + Br(CH_2)_5Br \longrightarrow Br(CH_2)_{10}Br \xrightarrow{2Mg} BrMg(CH_2)_{10}MgBr \xrightarrow{2CO_2} BrMgOOC(CH_2)_{10}COOMgBr \xrightarrow[\text{acid}]{HOH} HOOC(CH_2)_{10}COOH$$





4. Braun and Sobecki[1] worked with the alkyl dihalides of the methane series, in which the halogen atoms were attached to the end carbon atoms of the compounds. They studied the reaction of these dihalides with magnesium in order to determine to what extent the formation of the Grignard reagent and the Wurtz reaction took place.

By the Wurtz reaction many different compounds might be formed, the authors therefore aimed to investigate the following possibilities. One mol of dihalide might react with 1 atom of magnesium and magnesium bromide and a cyclic compound might be obtained. Two mols of dihalide and 1 atom of magnesium might react and a compound with the formula $Br(CH_2)_xBr$ might be formed and likewise 2 mols of this compound $Br(CH_2)_xBr$ might react with 1 atom of magnesium and $Br(CH_2)_{2x}Br$ might be formed. It may be seen that if this process continued, a series of compounds would be produced in which the number of CH_2 groups would be of varied length. The authors were also interested in finding out whether the Grignard reagent would be formed from these new formed dihalides producing compounds with the formulas $BrMg(CH_2)_xMgBr$, $BrMg(CH_2)_{2x}MgBr$, etc. The experimental work was carried out with the dibromides of butane, pentane, heptane, and decane.

(a) Tetramethylene dibromide or 1,4-dibromobutane reacted very easily with magnesium in the presence of ether. An oil was found which solidified when it was cooled. A

1. Ber. 44 1918 (1911)

considerable amount of magnesium remained. After completion of the reaction carbon dioxide was added to the reaction mixture and cyclopentanone C_4H_8CO, sebacic acid $(CH_2)_8(COOH)_2$, and dodecamethylene dicarboxylic acid $(CH_2)_{12}(COOH)_2$ were formed. The products were separated by aqueous alkali and the cyclopentanone was obtained by steam distillation of the alkali insoluble portion. A 35% yield of cyclopentanone which boiled at 130°C. was obtained. It was not possible to identify the products present in the residue because of insufficient quantity.

$$Br(CH_2)_4Br \xrightarrow{Mg} BrMg(CH_2)_4MgBr \xrightarrow{CO_2}$$

$$BrMgOOC(CH_2)_4COOMgBr \xrightarrow[acid]{HOH} (CH_2)_4CO$$

The alkali solution containing the organic acids was treated with hydrochloric acid and a colorless solid substance was obtained. A residue of solid snow white powder chiefly sebacic acid $(CH_2)_8(COOH)_2$ which had a melting point of 133°C. was obtained by extraction with ether. The ether was evaporated and there remained a viscous solution. It was not possible to identify the substance, but it was thought to be a mixture of dodecamethylenedicarboxylic acid and sebacic acid and possibly some higher homologues.

$$2\ Br(CH_2)_4Br \xrightarrow{Mg} Br(CH_2)_8Br \xrightarrow{Mg} BrMg(CH_2)_8MgBr$$

$$\xrightarrow{CO_2} BrMgOOC(CH_2)_8COOMgBr \xrightarrow[acid]{HOH} HOOC(CH_2)_8COOH$$

$$Br(CH_2)_4Br + Br(CH_2)_8Br \xrightarrow{Mg} Br(CH_2)_{12}Br$$

$$\xrightarrow{Mg} BrMg(CH_2)_{12}MgBr \xrightarrow{CO_2} BrMgOOC(CH_2)_{12}COOMgBr$$

$$\xrightarrow[acid]{HOH} HOOC(CH_2)_{12}COOH$$

(b) Pentamethylene dibromide or 1,5-dibromopentane reacted easily with magnesium in the presence of ether and an oil was formed similar in appearance to that obtained when 1,4-dibromobutane was used. The authors approximated the yield of the Grignard reagent $BrMg(CH_2)_5MgBr$ to be 50%. When the reaction mixture was decomposed with water, 35% of pentane, 15% of decane, 10% of pentadecane, and a small amount of eicosane were obtained. The residue was thought to be a mixture of higher paraffins.

The products were separated by distillation. The hydrocarbons were obtained from the ether layer which was previously treated with acid, washed, and dried with calcium chloride. At normal pressure, pentane distilled at 36°C. and decane at 175°C. At 16 mm. pressure, pentadecane distilled between 140-180°C. and eicosane at 230°C. The former was redistilled at normal pressure and the pure hydrocarbon obtained at 267°C. Eicosane is a solid melting at 37°C. This work was carried out chiefly to obtain cyclopentane if formed, as Grignard and

Vignon had already experimented with this compound. The authors could find no trace of the cyclic hydrocarbon.

Similar results have been obtained using 1,5-dichloropentane by E. v. Zappi[1].

(1) The reaction of acetone with the magnesium derivatives of 1,5-dibromopentane was studied and the following products were obtained[2].

(a) a glycol $(CH_3)_2C(OH)(CH_2)_5C(OH)(CH_3)_2$

(b) an alcohol $(CH_3)_2C(OH)(CH_2)_4CH_3$

(c) an unsaturated alcohol with either of the following formulas:

$$(CH_3)_2C(OH)(CH_2)_5C(CH_3)=CH_2$$

or

$$(CH_3)_2C(OH)(CH_2)_4CH=C(CH_3)_2$$

The reaction was carried out by allowing the acetone to drop on the Grignard reagent. The mixture was allowed to stand about twelve hours and then decomposed with acetic acid. A peculiar odor characterized the mixture. The greater

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1. C. II 660 (1916)
2. Ber. 44 1926 (1911)

portion, A, distilled between 60° - 180°C. at 12 mm. pressure and contained all the products. It amounted to approximately a 50% yield of products. The remaining residue in the flask decomposed at about 200°C. This was assumed to be reaction products of acetone with the multiple homologues of magnesium dibromopentane. From A, on slow distillation, the alcohol $(CH_3)_2C(OH)(CH_2)_4CH_3$ was obtained at 80°C. and 12 mm. pressure. At normal pressure it distilled between 160°- 162°C. This substance had a pleasant aromatic odor. An unsaturated alcohol distilled between 107°- 109°C. at 14 mm. pressure. It had the odor of citronellol. It was found to have the composition $C_{11}H_{22}O$. It was not possible to determine the formula by destructive oxidation. The authors assumed that this alcohol was formed by the elimination of a molecule of water from the glycol. The glycol $(CH_3)_2C(OH)(CH_2)_5C(OH)(CH_3)_2$ distilled between 135°- 145°C. at 12 mm. pressure and at room temperature was found to be a white crystalline solid melting at 77°C. It was recrystallized from ligroin and ether.

$$BrMg(CH_2)_5MgBr + 2(CH_3)_2CO \longrightarrow BrMgOC(CH_3)_2(CH_2)_5(CH_3)_2COMgBr$$

$$\xrightarrow[\text{acid}]{HOH} HOC(CH_3)_2(CH_2)_5(CH_3)_2COH$$

$$BrMg(CH_2)_5MgBr + (CH_3)_2CO \longrightarrow BrMgOC(CH_3)_2(CH_2)_5MgBr$$

$$\xrightarrow[\text{acid}]{HOH} HOC(CH_3)_2(CH_2)_4CH_3$$

(2) Cyclohexanone $(CH_2)_5CO$, acetophenone $\begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!CO$, and quinone  were found to react as easily as acetone, but isolation of the products was difficult and unsatisfactory. Formaldehyde was slow to react and the water soluble glycol formed was difficult to isolate from the mixture.

(c) Heptamethylene dibromide or 1,7-dibromoheptane reacted very slowly with magnesium and the authors recommended the use of the diiodide. The reaction mixture was decomposed with water and distilled. Normal-heptane distilled between 92°- 100°C. and tetradecane distilled at 250°C. No cycloheptane was obtained. Carbon dioxide was added to the Grignard reagent to find out if the higher homologues of this series would form cyclic ketones. Heptamethylene dicarboxylic acid was the only product identified.

(d) Decamethylene diiodide or 1,10-diiododecane reacted even more slowly with magnesium than 1,7-dibromoheptane. When the mixture was decomposed with water, decane, eicosane, and tetracontane $C_{40}H_{82}$ were separated and isolated, but no cyclodecane was formed.

Summary of Braun and Sobecki's Work.

1. The Wurtz reaction took place in all cases and compounds with the formulas $Br(CH_2)_xBr$, $Br(CH_2)_{2x}Br$ were formed, but there were no cyclic hydrocarbons obtained.

2. The Grignard reagent was formed in all cases, but

the yield was low. Compounds with the formulas $BrMg(CH_2)_xMgBr$, $BrMg(CH_2)MgBr$ were formed.

3. Cyclic ketones were obtained in each case when carbon dioxide was added to the Grignard reagent which was formed by the reaction of magnesium and 1,4-dibromobutane, or magnesium and 1,5-dibromopentane.

5. In 1924 Emschwiller became interested in the reaction of methylene iodide with magnesium while studying the behavior of free organic radicals.[1] Two years later he published an article[2] which gave an account of his work with this reaction. In the Grignard reagent formed, $CH_2(MgX)_2$, the two atoms of magnesium are attached to the same carbon atom.

Methylene dimagnesium diiodide, $CH_2(MgI)_2$, was prepared by the reaction of methylene iodide with magnesium in the presence of ether. The reaction was carried out under low pressure. It proceeded more easily after a light heating and continued with the evolution of sufficient heat to cause the ether to boil. It was found necessary to cool the reaction mixture as it tended to accelerate itself.

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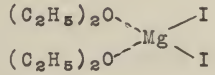
1. Compte rend. 179, 52 (1924)
2. Compte rend. 183, 665 (1926)

The reaction was accompanied by the formation of ethylene as represented by the following equation,

$$CH_2I_2 + 2Mg \longrightarrow CH_2(MgI)_2$$

$$CH_2(MgI)_2 + CH_2I_2 \longrightarrow C_2H_4 + 2MgI_2$$

After the reaction was completed, two liquid layers were apparent. The bottom layer was found to be an oil. The products were allowed to stand and white crystals were formed which the author believed to be an etherate of magnesium iodide.



When the mixture was decomposed with water, methane was evolved.

$$CH_2(MgI)_2 + 2H_2O \longrightarrow CH_4 + Mg(OH)_2 + MgI_2$$

Enschwiller obtained a yield of 22.09% of the Grignard reagent, $CH_2(MgI)_2$. The data given by him is as follows. One and four thousandths grams of magnesium and 1.843 grams of methylene iodide were used. Seventeen and eight tenths cc. of ethylene were formed. By hydrolysis of the Grignard reagent 33 cc. of methane were evolved and a quantity of magnesium hydroxide which was neutralized by 30.4 cc. of a 0.1N solution of sulfuric acid. The calculations for the amount of Grignard reagent formed are:

$30.4 \times .0049 = .14896$ grams of H_2SO_4

$$\frac{.14896}{X} = \frac{98}{315.88}$$

$X = .4802$ grams of Grignard reagent

or 1.52×10^{-3} gram mol.

$$\frac{1.843}{X} = \frac{267.88}{315.88}$$

$X = 2.173$ Theoretical yield of Grignard reagent.

$$\frac{.4802}{2.173} \times (100) = 22.09\% \text{ yield of Grignard reagent.}$$

Similar results were obtained when methylene dibromide reacted with magnesium. Due to the small amount of Grignard reagent obtained by the author, he caused it to react with dichloroformate and obtained diethyl malonate[1].

$$CH_2(MgI)_2 + 2ClCOOC_2H_5 \longrightarrow CH_2(COOC_2H_5)_2 + MgI_2 + MgCl_2$$

Although the yield of Grignard reagent obtained by the author was only 22.09%, there was no mention made of any attempt to increase it.

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1. Compte rend. 188 1555 (1929)

III. LABORATORY WORK.

A. PREPARATION OF REAGENTS.

1. Dry Ether.

Thin freshly cut pieces of sodium were added to the ether and allowed to remain in contact with it for several days. Just before using, the ether was distilled over the sodium, using an ordinary distillation apparatus.

2. Methylene Iodide.

(a) In some cases it was used as obtained from Eastman Kodak Co.

(b) The halide was treated with a saturated solution of sodium bisulfite to remove iodine and then allowed to remain in contact with calcium chloride for a day. It was distilled at 70 mm. pressure at 106°- 107°C.

3. Magnesium.

The magnesium was kept in a desiccator.

4. Activated Catalyst[1].

The activated catalyst was made by heating 12.75% Cu-Mg alloy with 20% of iodine in a vacuum at 300°C. for 8 to 10 minutes. The activity of the catalyst was destroyed by exposing it to the air for fifteen to twenty minutes.

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1. C.A. 22 1134 (1928)

It was kept in a rubber stoppered container. Just before using, 0.25 grams of the catalyst were placed in a test tube and heated until all the fumes were driven off. It was allowed to cool and while still slightly warm was added to the reaction flask. This was used in the preparation of pentanediol,1-5.

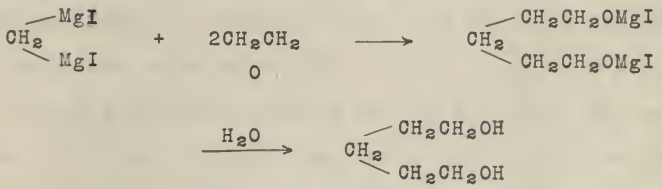
5. Acetone.

The acetone was dried over calcium chloride and then distilled.

B. ATTEMPTS TO PREPARE PENTANEDIOL 1-5

Pentanediol 1-5 was one of the products obtained by Kaufman and Adams[1] by the reduction of furfural (using platinum as the catalyst). It was isolated from the mixture by distillation. They found that it was a rather thick, water clear liquid, soluble in water and in alcohol, and boiled at 237°C. at 751 mm. pressure.

The author of this thesis attempted to form pentanediol 1-5 by the reaction of ethylene oxide $(CH_2)_2O$ with methylene dimagnesium dihalide, $CH_2Mg_2X_2$.



The procedure followed was similar to the one used in the synthesis of an alcohol by the reaction of the Grignard reagent with ethylene oxide[2]. Five and five-tenths grams of magnesium turnings and 0.25 grams of activated catalyst were placed in a 1-liter flask which was fitted with a mercury seal stirrer, dropping funnel, and a condenser, into the upper end of which

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1. J.A.C.S. 45 3043 (1924)
2. Organic Syntheses Vol. VI p. 54

was attached a drying tube containing calcium chloride. Twenty and eleven hundreths grams of methylene dibromide which had been previously dried over calcium chloride and distilled, were diluted with ether and poured into the dropping funnel. A small amount was added to the flask. The stirring was started as soon as liquid was present in the flask. After all the halide was added and the reaction completed, the flask was cooled. Five and one tenth grams of ethylene oxide were added to the mixture. The ethylene oxide tank was placed on a scale and balanced. The amount of ethylene oxide used was measured by the loss in weight. The gas was run through a tower of soda-lime and then through a spiral condenser surrounded with ice and salt. The ethylene oxide was added through a tube 4 mm. in diameter, the end of which was placed about 20 mm. above the surface of the liquid to prevent clogging. The flask was kept below 10°C. by cooling it in an ice and salt bath. The addition required about forty minutes. When all of the ethylene oxide had been added, the ice bath was removed, and the mixture was heated on a water bath for 15 minutes. The ether was removed by distillation and dry benzene was added. The distillation was continued until the temperature of the distilling vapor reached 65°C. The mixture was then refluxed with stirring for one hour. The solution became white and viscous. The mixture was allowed to cool and then decomposed with ice and water.

The precipitated magnesium hydroxide was dissolved by adding dilute sulfuric acid and enough ice to keep the mixture cold. The mixture was then distilled in a current of steam. The oily layer was separated and the watery portion put back into the reaction flask and redistilled, in order to obtain the glycol.

Three attempts were made to prepare pentanediol 1-5 by this method. From observation, the reaction proceeded normally. In each case a weighed amount of methylene dibromide, as near 20 grams as possible, was used. When the reaction mixture was hydrolyzed with water and sulfuric acid, a large amount of magnesium sulfate was formed. This caused bumping and distillation of the solution was made difficult. Considering the fact that Emschwiller obtained a yield of only 22.09% of the Grignard reagent, even if 100% addition of ethylene oxide took place, the yield of pentanediol 1-5 which would have been obtained would be about 2.49 cc. The expense of these reacting substances causes this synthesis to be of no use unless a better yield of Grignard reagent can be obtained. If this is found possible, many interesting compounds might be formed by its reaction with the wide variety of compounds with which it has been found that the Grignard reagent will react.

C. PREPARATION OF METHYLENE DIMAGNESIUM DIHALIDE.

From the account of Emschwiller's work, the reader obtains little knowledge of the procedure used by him in the preparation of methylene dimagnesium dihalide. One learns first that the reaction was carried out under reduced pressure, second, that it was found necessary to heat the reaction flask at first in order to start the reaction, and third, that the ether continued to boil of itself until the reaction was completed. There was no reference to the length of time necessary for completion of the reaction, or such valuable factors as the amount of ether used or how the reactants were added, that is, whether they were all placed in the reaction flask at the same time and caused to react, or whether the reaction was started with small quantities of the material and then the remainder added gradually.

It has been found that the amount of solvent which should be used varied with the halide[1] and that the yield of Grignard reagent may be increased by dilution and slow addition of the halide[2]. It is thought that by dilution and slow addition of the halide, it is not present in excess and reaction (b) is retarded.

(a) $RX + Mg \longrightarrow RMgX$

(b) $RMgX + RX \longrightarrow R\text{-}R + MgX_2$

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1. C. II 2555 (1929)
2. C.A. 22 2364 (1928)

A 500 cc. three-neck round bottom flask was attached to an apparatus consisting of a mercury sealed stirrer, a dropping funnel, and s condenser, which was provided at the upper end with a drying tube containing calcium chloride.

1. In the following cases the amount of solvent was not considered. The rate of addition of the halide and the effect of heat upon the reaction mixture were studied. In all of the experimental work, the calculated amount of magnesium was used.

1. The magnesium turnings and a crystal of iodine were placed in the flask. The methylene iodide previously weighed and diluted with ether was poured into the dropping funnel. About 15 cc. of the solution was added to the flask and stirring started. The stirring was continued as long as there was any evidence of reaction (which was shown by bubbling on the surface of the reaction mixture when stirring was interrupted). The flask was warmed on a water bath in order to start the reaction. The rest of the dihalide was added over a period of thirty minutes. After all of the dihalide was added, the mixture was heated on a hot water bath for one hour. This procedure was repeated several times, but in each case a white precipitate was formed. It was assumed that the precipitate was magnesium iodide and that the Wurtz reaction had taken place.

2. The magnesium turnings used in this experiment

(and in all of the following ones) were dried in a desiccator.

Eleven and nine hundredths grams of methylene iodide were diluted with 120 cc. of ether. About 15 cc. of this solution was added to the flask. Stirring was started as soon as liquid was present in the flask. The rest of the solution was added over a period of 30 minutes. The flask was warmed on a water bath at first, but after the reaction started, the ether continued to boil of itself until the reaction was completed. After all of the halide was added, the mixture was heated over a hot plate which was set at low heat, for twenty minutes. At the end of this period stirring was stopped and two layers were apparent, an ether layer and an oil. The two layers were separated and each was then hydrolyzed. When water was added to the oil, a violent reaction took place and a large quantity of $Mg(OH)_2$ was formed. Twelve and forty-five hundredths cc. of 0.5317 N HCl were required to neutralize the base. One and twenty-one hundredths cc. of acid were required to neutralize the base formed by hydrolysis of the ether layer. Phenolphthalein was used as the indicator. The total yield of Grignard reagent was 9.25%.

The method of calculation is based on the fact that by hydrolysis one mol of methylene dimagnesium dihalide forms one mol of magnesium hydroxide, which is neutralized by two mols of hydrochloric acid.

$$CH_2(MgI)_2 + H_2O \longrightarrow CH_4 + Mg(OH)_2 + MgI_2$$

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

The following data and calculations are for the preceding experiment.

Wt. of flask and methylene iodide	47.40 g.
Wt. of flask	36.31 g.
Wt. of methylene iodide	11.09 g.

Titration of ether layer.

0.5317 N HCl	0.5373 N NaOH
3.17 cc.	11.71 cc.
0.12 cc.	9.98 cc.
3.05 cc.	1.73 cc.

Titration of the oil.

0.5317 N HCl
15.50 cc.
3.05 cc.
12.45 cc.

$$\frac{0.5317}{0.5373} = \frac{1.73}{x}$$

X = 1.84 cc. of 0.5317 N HCl (excess)

15.5 - 1.75 = 13.75 cc. of HCl used.

$$\frac{36.5 \times 0.5317}{1000} = 0.019407 \text{ gm. HCl per cc.}$$

13.75 x 0.019407 = 0.2794 gm. of HCl used.

$$\frac{315.88}{73} = \frac{x}{0.2794}$$

x = 1.209 gms. of Grignard reagent formed (actual yield).

$$\frac{267.88}{315.88} = \frac{11.09}{x}$$

x = 13.07 gms. of Grignard reagent (theoretical yield).

$$\frac{1.209}{13.07} \times 100 = 9.25\% \text{ yield}$$

Similar calculations were used in the following experiments.

3. The same procedure as in (2) was repeated with 10.69 grams of methylene iodide and 110 cc. of ether. Twelve and ninety-five cc. of 0.5317 N HCl were required to neutralize the $Mg(CH)_2$ formed by hydrolysis of the Grignard reagent. An 8.59% yield of the Grignard reagent was obtained.

4. The same procedure as in (2) was used with two exceptions, the reaction mixture was heated over a hot plate (medium heat) during the reaction and about one hour after all of the halide had been added.

Sixteen and fifty-four hundredths grams of methylene iodide were diluted with 125 cc. of ether. Eleven and seventy-seven hundredths cc. of 0.5317 N HCl were used to neutralize the magnesium hydroxide formed by hydrolysis of the Grignard reagent. The yield of Grignard reagent was 5.45%.

5. In the following experiment, the methylene iodide and ether were placed in the flask and the magnesium was added over a period of thirty minutes. Twelve and seventy-one hundredths grams of the dihalide were diluted with about 120 cc. of ether. Ten and ninety-one hundredths cc. of 0.5317 N HCl were required to neutralize the magnesium hydroxide. The yield of Grignard reagent was 6.11%.

6. The same procedure as in (5) was used, but the magnesium in this case was added over a period of forty-five minutes. Thirteen and twenty-three hundredths grams of methylene iodide were used. Twenty-three and seven tenths cc. of 0.5317 N HCl were required. The yield of the Grignard reagent was 12.71%.

7. Eight and sixty-five hundredths grams of methylene iodide were diluted with 80 cc. of ether. In this case the dihalide was added over a period of 60 minutes and the reaction mixture was heated over a hot plate (at low heat) for 45 minutes, after the addition of all the dihalide. The magnesium hydroxide formed by hydrolysis was neutralized by 31.69 cc. of 0.5317 N HCl. The yield of Grignard reagent obtained was 26.13%.

8. As the previous yield was obtained using a 60 minute period for the addition of the dihalide, in the following case a forty-five minute period was used in order to determine whether such a long period of time was necessary. Nine and five hundredths grams of methylene iodide were diluted with 100 cc. of ether. The dihalide was added over a period of 45 minutes, and after all of the dihalide had been added, the reaction mixture was heated over a hot plate (at low heat) for 45 minutes. The magnesium hydroxide formed by hydrolysis of the Grignard reagent was neutralized by 15.58 cc. of 0.4576 N HCl. A 10.53% yield of Grignard reagent was obtained.

9. In the following experiments a smaller volume of ether was used. About 4 drops of the weighed methylene iodide (16.88 gms.) were diluted with 25 cc. of ether and added to the flask. The rest of the dihalide was diluted with 40 cc. of ether and added over a period of 45 minutes. The reaction mixture was heated on a water bath for 15 minutes after all of

the dihalide had been added. Thirty-eight and eighty-nine hundredths cc. of 0.4567 N HCl were used to neutralize the Magnesium hydroxide formed by hydrolysis. A 14.42% yield was obtained.

10. The same procedure as in (9) was followed, but the reaction was started without stirring. It was heated for thirty minutes after all of the dihalide was added. Twelve and thirty-seven hundredths grams of methylene iodide were used. Thirty-one and sixty-one hundredth cc. of 0.4567 N HCl were used to neutralize the magnesium hydroxide. A yield of 15.69% of Grignard reagent was obtained.

11. The same procedure as in (10) was repeated using 16.12 gms. of methylene iodide. Forty-two and seventeen hundredths cc. of 0.4567 N HCl were used to neutralize the magnesium hydroxide. A 16% yield of Grignard reagent was obtained.

12. About four drops of the weighed methylene iodide (10.87 gms.) were diluted with 15 cc. of ether and added to the flask. The reaction was started by warming with a hot water bath. Stirring was not started until the reaction had proceeded about four minutes. The rest of the dihalide was diluted with 30 cc. of ether, added over a period of forty-five minutes and heated on a hot plate (low heat) for thirty minutes. Forty-one and ninety-one hundredths cc. of 0.4939 N HCl were used to neutralize the magnesium hydroxide. A 25.45% yield of Grignard reagent was obtained.

13. The same procedure used in (12) was repeated using 11.07 grams of methylene iodide. Forty-three cc. of 0.4939 N HCl were used. A yield of 25.31% was obtained.

14. An example of greater dilution and slower addition was tried. Twelve and two-hundredths grams of methylene iodide were diluted with 150 cc. of ether. About 25 cc. of the solution were added to the flask. The rest of it was added over a period of ninety minutes. Only 0.9 cc. of 0.4939 N HCl were used. A yield of .61% was obtained. The methylene iodide used was obtained from Eastman Kodak Co. It had a very deep red color. The dihalide was shaken with a solution of sodium bisulfite in order to remove excess iodine. It was allowed to remain in contact with calcium chloride over night and then distilled at 70 mm. pressure. The liquid obtained at 106° C. still maintained the deep red color. Procedure (13) was repeated using 3.6 grams of this methylene iodide. An 8.996% yield of methylene dimagnesium diiodide was obtained. As the yield obtained in (13) could not be duplicated with this methylene iodide, it was impossible to check the result of (14).

The best yield of methylene dimagnesium diiodide obtained was only 4% higher than Emschwiller's results. It was found that the yield was lowered by the addition of magnesium to the dihalide and ether, and also, if the reaction mixture was heated too strongly. By allowing the reaction to start and proceed

for about four minutes without stirring, the yield was increased. The most favorable conditions for obtaining the best yield of methylene dimagnesium dihalide were a 60 minute period for the addition of the dihalide and about a 35 minute heating period (low heat) after all of the dihalide was added. In regard to the volume of ether similar results were obtained when either a 30 or 87% by weight, solution of ether was used.

Grams of CH_2I_2	Cc. of $(C_2H_5)_2O$	Rate of Addition of CH_2I_2	Period of Heating	% Yield
1. 11.09	120	30 min.	20 min.(low)	9.25
2. 10.69	110	30 min.	20 min.(low)	8.59
3. 16.54	125	30 min.	60 min.(hot)	5.45
4. 8.65	80	60 min.	45 min.(low)	26.13
5. 9.05	100	45 min.	45 min.	10.53
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1. 16,88	65	45 min.	15 min.	14.48
2. 12.37	65	45 min.	30 min.	15.69
3. 16.12	65	45 min.	40 min.	16.01
4. 10.87	45	55 min.	30 min.	25.45
5. 11.07	45	60 min.	30 min.	25.31
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1. 12.71	120	30 min.	20 min.	6.11
2. 13.23	129	45 min.	20 min.	12.71

The magnesium was added to the dihalide and ether.

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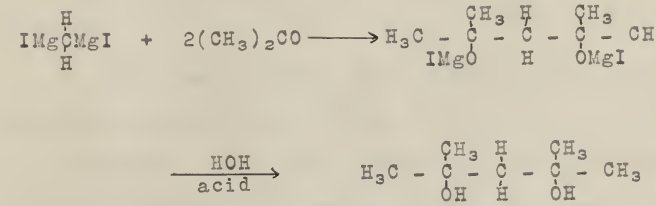
1. 12.02	150	75 mih.	30 min.	.61

Example of greater dilution and slower addition of the dihalide. The calculated amount of magnesium was used in all these cases.

D. ATTEMPTS TO PREPARE 2,4-DIMETHYL PENTANEDIOL, 2-4

Adolphe Frank prepared the glycol, 2,4-dimethyl pentanediol, 2-4 by the reaction of methyl magnesium iodide with diacetonealcohol[1]. It was described by him as a liquid with a weak camphor like odor which boiled at 98° C. at 13 mm. pressure. The diacetate[2] was formed by reaction of the glycol with acetic anhydride. The derivative was found to be a white crystalline substance which melted at 51° C. and boiled at 98° C. at 11 mm. pressure.

Instead of using ethylene oxide, acetone was added to the Grignard reagent, methylene dimagnesium diiodide, in order to form a glycol. Acetone was added as it was easier to work with and less expensive. The equation for the reaction of acetone with methylene dimagnesium diiodide is as follows+



The Grignard reagent was prepared using the conditions, with which the best yield had been obtained. After the

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1. C. I 1599 (1907)
2. C. II 862 (1914)

reaction was completed the flask was cooled in an ice bath and the acwrone diluted with ether was added, with stirring. The reaction proceeded with sufficientheat to cause the ether to biol when the ice bath was removed. A white precipitate was formed. The mixture was decomposed with water, and then ice and dilute acid were added. The mixture was kept cold during the addition of the acid by means of an ice bath.

1. Eight and six tenths grams of methylene iodide were used to form the Grignard reagent. The calculated amount (3.49 cc.) of acetone was diluted to 10cc. with ether and added to the flask. The reaction mixture was then decomposed with water and the ice and dilute acid added. The water layer was extracted with ether several times. The ether layer and the combined ether extractions were evaporated but no product was obtained. The water layer was distilled and no product was obtained.

2. The same procedure was repeated with 13.22 gms. of methylene iodide. The acetone (7.57 gms.) was diluted to 14 cc. with ether. The water layer was distilled and the small amount of residue which remained charred when heated. No product was obtained from the ether layer.

3. The Grignard reagent was formed from 9.12 gms. of methylene iodide. The acetone (4.99cc) was diluted to 10 cc. with ether. The reaction mixture was decomposed and allowed to remain over-night. The water layer was distilled under re-

duced pressure. A viscous liquid remained. It was allowed to stand and long needle-like crystals were formed. These were undoubtedly crystals of magnesium iodide. The mixture had a characteristic odor, which might be called camphor-like. It was distilled at 13 mm. pressure. A liquid was obtained which boiled between 80°-100° C. It was redistilled using an apparatus which consisted of two side-arm test tubes: one used as a flask, the other as a condenser. The container was cooled by allowing a stream of water to flow over it. About 1 cc. of liquid was separated. This was poured into a small test tube and acetic anhydride (1.5 cc.) was added. The test tube was heated for a few minutes and then allowed to cool. Cold water was added and a few white crystals were formed. However, when the solution was filtered, there were not enough of them to obtain a melting point.

The glycol 2-4, dimethyl pentanediol 2-4, was undoubtedly formed. The liquid obtained was impure, but it had a very strong camphor-like odor,. Apparently the diacetate was formed by the reaction of the liquid with acetic anhydride.

Summary

The yield of methylene dimagnesium diiodide was increased 4%. Emschwiller had reported a yield of 22.09%. The most favorable conditions for obtaining the best yield of methylene dimagnesium dihalide were a 60 minute period for the addition of the dihalide and about a 35 minute heating period (low heat) after all of the dihalide was added. In regard to the amount of ether similar results were obtained when either a 30 or 87%, by weight, solution of ether was used.

No product was isolated from the reaction of methylene dimagnesium dihalide with ethylene oxide.

It was thought that the glycol 2,4-Dimethyl Pentanediol, 2-4 was formed by the reaction of methylene dimagnesium diiodide with acetone. Due to the small quantity of the derivative formed by the reaction of the glycol with acetic anhydride, a melting point was not obtained.

BIBLIOGRAPHY.

Braun,J. and Sobecki,W.---Grignard Reaction and Its Application to Dihalogen Compounds.
Ber. 44 1918 (1911)

Emschwiller,G.---Action of Mg on CH_2I_2.
Compte rend. 183 665 (1926)

Emschwiller,G.---Action of Zn-Cu Couple on CH_2I_2
Compte rend. 188 1555 (1929)

Emschwiller,G.and Job A.---Behavior of Free Organic Radicals.
Compte rend. 179 52 (1924)

Gilman,H.---Activated Catalyst
C.A. 22 1134 (1928)

Gilman,H. and McCracken,R.---Yields of Some Grignard Reagents.
J.A.C.S. 45 2462 (1923)

Gilman,H. and West---Bibliography of the Grignard Reaction (1900-21)
National Research Coun l Pamphlet No. 24
Jan. 1922

Gilman,H. and Vandewal--- C. II 2555 (1929)

Gilman,J.-Editor---Organic Syntheses Vol. VI p. 54

Grignard,V. and Tissier---Alkyl Diiodides of Magnesium.
C. I 999 (1901)

Grignard,V. and Vignon---Dimagnesium Compounds of 1,5-Dibromo-pentane.
C. II 631 (1907)

Kaufman and Adams,R.---Use of Platinum as Catalyst in Reduction of Furfural.

J.A.C.S. 45 3043 (1928)

Meisenheimer,J.---C.A. 22 2364 (1928)

Pope,F.G.---Modern Research in Organic Chemistry. Methuen and Co. 1919

Runge,F.---Organic Metallic Compounds. Wissenschaftliche verlagsgeschlachaft 1932

Zappi,E.---Magnesium Derivatives of 1,5-Dichloropentane.
C. II 660 (1916)
C.A. II 2821 (1916)

Zelinsky and Gutt---Synthesis of Suberic Acid.
Ber. 40 3049 (1907)
C.A. I 2466 (1907)