ISSN: 0974 - 7516 Volume 11 Issue 8

Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 11(8), 2015 [288-292]

The grignard synthesis of triphenylmethanol

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ABSTRACT

The goal of this experiment is to synthesize a Grignard reagent phenyl magnesium bromide, and use it to synthesize the alcohol triphenylmethanol via Grignard reaction.This Grignard reaction was performed through the reaction between phenyl magnesium bromide and benzophenone, followed by an acid work-up.Laboratory techniques such as: reflux, vacuum filtration, decantation were involved in this experiment.The product triphenylmethanol will then be purified by recrystallization, and percentage yield is used to measure the success of reaction, in which a 29.08% yield was obtained.The melting point of triphenylmethanol was measured to be128-130 °C, comparing to the literature value of 162 °C, indicating a substantial amount of impurity.Its IR, ^{1}H NMR and ^{13}C NMR spectra will also be obtained and compared to the standard, in order to further confirm its identity.Since the experimental results were generally similar to literature values, this experiment was considered successful.

KEYWORDS

Triphenylmethanol;
Identity;
Grignard reaction.

INTRODUCTION

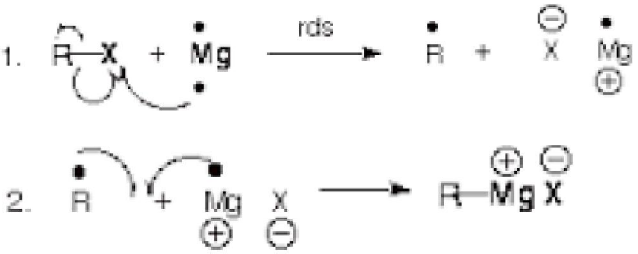
Grignard reaction is a nucleophilic addition reaction.A Grignard reagent, which usually is an alkyl magnesium halide will function as a nucleophile and attack the electrophilic carbon in a carbonyl group, facilitating the formation of new C-C bond [1].

Grignard reagent has a formula RMgX where X is a halogen, and R is an alkyl or aryl.R group is strongly nucleophilic and in charge of nucleophilic addition[2].

Some general characteristics of Grignard reagent includes

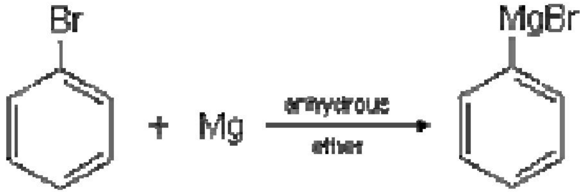
1. Strongly basic, therefore cannot mix with water
2. Useful for the C-C bond formation
3. Used in reduction where C in it is a nucleophile

Grignard reagent is prepared by reacting an alkyl halide with magnesium metal in a non-water condition[3].Ethyl ether is often used as solvent since it is very non-reactive and protective:



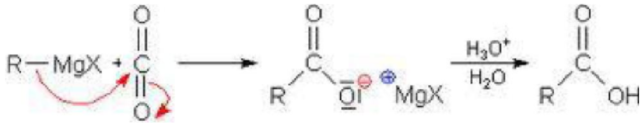
In this experiment, bromobenzene is reacting with magnesium, forming phenyl magnesium bromide, with anhydrous ethyl ether as solvent:

The reaction condition has to be dried since the

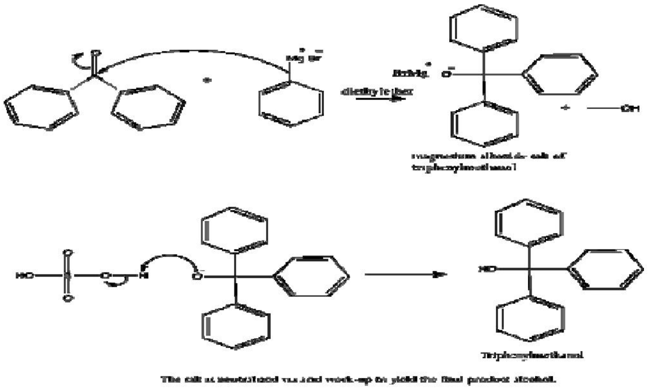


R part in Grignard reagent is very basic that it can grabs one H in water molecule.This prevents any further reaction with other substances.The same rule applies to carboxylic acid, where Grignard reagent will only grab the acidic H instead of attack the nucleophilic carbon in carboxyl group.

Another common reaction regarding Grignard reagent is with carbon dioxide.The R part would be added to the C carbon dioxide due to nucleophilic addition.After an acid work-up, a carboxylic acid will form.The mechanism is as following:



This experiment involves Grignard reagent reacting with a ketone, in which the carbonyl compound is reduced.The "R" portion acts as a nucleophile and attack the electrophilic carbon in carbonyl.The electron in double bond is then pushed to the carbonyl oxygen.After an acid work-up with sulfuric acid, the oxygen is protonated and alcohol is finally formed[4].



IR, 1H NMR and 13C NMR technique were all used in this experiment for substance determination.IR is used to detect functional groups within a molecule based on different bond vibration frequency, but it's not enough to deduce the exact structure.NMR could identify the exact structure of molecule.1H NMR identified the structure by interpreting degree of unsaturation, integration number, chemical shifts and multiplicity (slitting pattern).13C NMR interprets number of signals, and chemical shifts (0-240ppm)[5].

EXPERIMENTAL

Phenyl Magnesium bromide was prepared at first: 1.5g of magnesium metal were stirred in a dry 250mL round bottom flask over a stir plate for 10 minutes, before adding a small iodine crystal.Preparing a drying tube at the same time with anhydrous CaCl2 and cotton.Assemble the entire reflux apparatus with a 125mL dropping funnel attached to the curved arm of the Claisen adapter.40mL anhydrous ethyl ether was added via dropping funnel and color change was observed.

5.3mL bromobenzene and 15 mL anhydrous ethyl ether was added into dropping funnel and half mixture were transferred to flask at one time with stirring.

The remaining half of bromobenzene solution was added drop wise, and refluxing for 10 minutes.

Triphenylmethanol was prepared then: 9.1g benzophenone in 100mL anhydrous ethyl ether was transferred to dropping funnel and added to phenyl magnesium bromide drop wise with stirring.After addition, replaced stir plate with a steam bath and refluxed for 15 minutes before cooled in ice bath.At the same time, prepare cold acidic solution: Poured 4.5mL concentrated sulfuric acid onto ice, which had filled a 50mL beaker.The icy acid was then transferred to a 250 mL beaker and diluted to 75mL with tap water.Keeping beaker on ice.

Added acid solution drop wise via pipette through condenser while stirring.

Pouring whole mixture into a 500mL Separatory Funnel and saving organic layer.Extracting aqueous layer twice with 50mL ethyl ether and combining ether layer before drying over MgSO4.Vacuum filtration was performed to collect yellow ethereal solution.

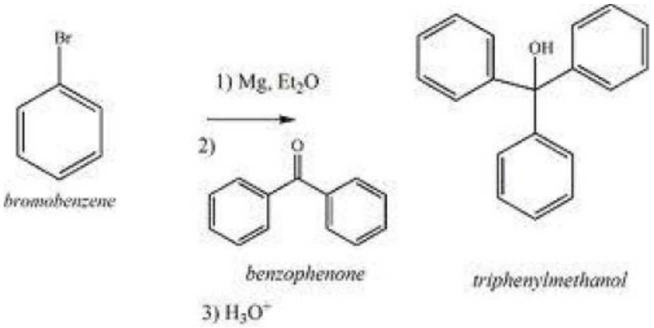
Reagent table

Reagent	MW (g/mol)	Density (g/ml)	Concentration(M)	M(g) or V (mL)	MP (°C)	BP(°C)	Safety
Phenyl magnesium bromide	181.31	1.14	N/A	N/A	N/A	N/A	Flammable, volatile
Bromobenzene	157.01	1.495	N/A	5.3mL	-30.8	156	Flammable, hazardous
Magnesium	24	1.738	N/A	1.5g	650	1091	Irritant
Benzophenone	182.22	1.11	N/A	9.1g	48.5	305.4	Flammable
Sulfuric acid	98.1	1.84	N/A	4.5mL	10	337	Hazardous, reactive
Magnesium sulfate	120.4	2.66	N/A	N/A	1124	N/A	Irritant
Triphenylmethanol	260.3	1.2	N/A	N/A	162	370	Irritant
Methanol	32.04	0.79	N/A	N/A	-97.6	64.7	Flammable
Ethyl ether	74.12	0.706	N/A	215mL	-116	34.6	Flammable, irritant
Calcium chloride	110.98	2.15	N/A	N/A	773	1935	Hazardous

In the second week, ethereal solution was evaporated over steam bath to dryness then cooled on ice.It was then recrystallized with 100ml hot methanol.Hot gravity filtration and vacuum filtration were performed to collect pure triphenylmethanol, which was weighed later on.In the third week, Melting point, IR spectrum, 1H NMR and 13C NMR spectra of collected triphenylmethanol were all obtained for further analysis.

RESULTS

Overall reaction



Observation

In the first part, solution turned brown after adding 40 mL ethyl ether to magnesium.Next, after the first half addition of bromobenzene to mixture, color of solution blackened then turned to light green, and finally became white, greyish.Further addition of remaining bromobenzene turned the solution to brown, and finally dark coffee color.

During the preparation of triphenylmethanol, the addition of benzophenone turned mixture into purple, with white brownish particles at bottom initially.After a while, solution turned pink.Finally, the solution had white color on top and pink at bottom with continuous bubbling.The addition of acid later on made the both layer clearer, and pink part started to disappear, and bubbling still existed.Finally solution had light yellow color on top and colorless at bottom.

The mass of recrystallized triphenylmethanol was: 43.13-39.35= 3.78 grams

The melting point was measured to be: 128-130°C

Calculation 1: Theoretical Yield of Triphenylmethanol

Moles of Bromobenzene: n1= (1.495g/ml)(5.3ml)/(157.01g/mol)= 0.05mol

Moles of Magnesium: n2= (1.5g)/ (24g/mol)= 0.0625mol

Moles of benzophenone: n3= (9.1g)/(182.22g/mol)= 0.05mol (limiting reagent)

Mass (triphenylmethanol)= (Moles)(Molecular weight)= (0.05mol)(260.3g/mol)= 13 grams

Calculation 2: Percent Yield of Triphenylmethanol

% Yield= (Mass of actual yield/ Mass of theoretical yield) × 100%= (3.78g/13g) × 100%= 29.08%

DISCUSSION

The purpose of this experiment was to reduce the carbonyl-containing compound benzophenone to the alcohol compound trimethylmethanol.This reduction was done by the nucleophilic addition of the Grignard reagent: phenyl magnesium bromide, in a nonreactive ethyl ether solution.One of C=O double bond in benzophenone was cleaved and electron density was dumped to the electronegative O after initial attack.Then after an acid work-up with H2SO4, the species was protonated to an alcohol: trimethylmethanol.

The color change in solution indicated the progress of reaction.After the addition of bromobenzene to Mg, color changed several times to dark coffee finally, indicating the formation of a new species: Phenyl magnesium bromide.The mixing of benzophenone with phenyl magnesium bromide turned solution to pink, and acid addition turned top layer into yellow, indicating the formation of trimethylmethanol based on the mechanism.

The IR, ^{1}H NMR and ^{13}C NMR spectra provided further evidence for the successful conversion.On IR, peaks at 3455/cm, 2960/cm, 2873/cm showed the presence of alcohol, aromatic C-H, and sp3 C-H bond respectively, all of which were in structure of triphenylmethanol.However, there was a peak 1734/cm, which corresponded to C=O bond.Therefore, there might be some unreacted benzophenone reagent remained.On ^{1}H NMR, the multiplets around 7.3ppm indicated the aromatic ring, and the singlet at 3 ppm proved the presence of hydroxyl group.Information from ^{13}C NMR reached similar conclusion: peaks around 124ppm stood for aromatic C, and the one at 78ppm stood for alcohol C.

The experimentally obtained melting point range: 128-130 °C was lower than literature of 162°C, indicating s substantial amount of impurities.This difference could be due to the unreacted benzophenone, which was detected by IR spectra, or glassware contamination.The percentage yield was calculated to be 29.08%, which was fairly low.It could be caused by the incomplete reaction of benzophenone, solution loss during vessel transfers, incomplete reaction during Grignard reagent synthesis, or residual solid left on Buchner funnel during filtration.

However, this experiment was still considered successful due to the color change observed, and IR, ^{1}H NMR, ^{13}C NMR results.

TABLE 1 : Infrared spectra analysis of triphenylmethanol

Peak#	Wavenumbers (/cm)	Analysis
1	3455	-OH bond (broad peak)
2	2960	C (aromatic) -H bond
3	2873	C (sp3 hybridized)-H bond
4	1734	C=O double bond

TABLE 2 : 1H NMR analysis of triphenylmethanol

Multiplicity	Chemical shift(ppm)	Analysis
Singlet	2.544	Hydroxyl
Multiplet	7.0	Aromatic
Multiplet	7.3	Aromatic

TABLE 3 : ^{13}C NMR analysis of triphenylmethanol

Chemical shift (ppm)	Analysis
78	Alcohol
123.6	Aromatic
124.3	Aromatic

ACKNOWLEDGMENTS

This research was supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions and Jiangsu Co-innovation Center for Prevention and Control of Important Animal Infectious Diseases and Zoonoses.

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