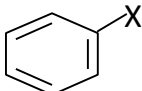
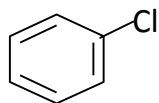


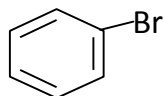
## AROMATIC HALIDES

They have a general structure  Where X is Cl, Br or I

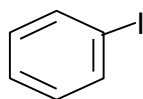
### Examples



Chlorobenzene



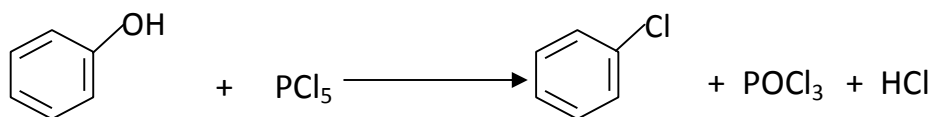
Bromobenzene



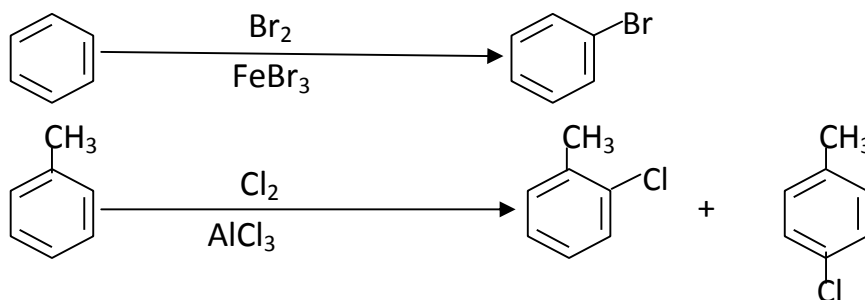
Iodobenzene

### Methods of preparation

1. Reacting a phenol with Phosphorus pentachloride ( $\text{PCl}_5$ ).

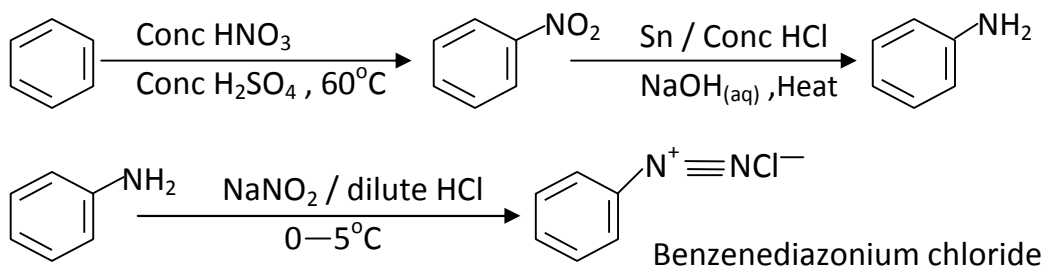


2. Reacting aromatic compounds with halogens in presence of a halogen carrier

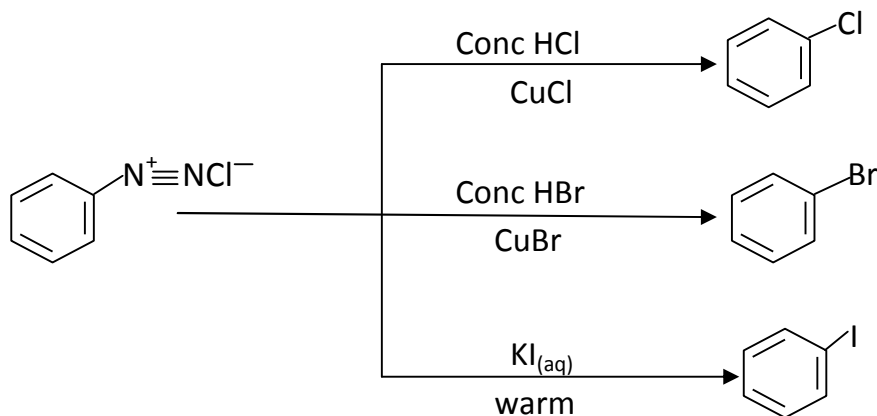


3. From benzene diazonium salt.

**N.B** The diazonium salt is first prepared from benzene as follows



The diazonium salt can be converted to any of the aromatic halides as shown below.



**Qn. Explain why Bromobenzene does not easily react with sodium hydroxide solution while Bromoethane easily react with sodium hydroxide solution.**

**Explanation;**

Bromobenzene does not easily react with sodium hydroxide solution. This is because the lone pair of electrons on the bromine atom interacts (associates) with the delocalised pi-electrons of the benzene ring. This leads to the formation of a partial double bond between the carbon atom of the benzene ring and the bromine atom. The carbon bromine bond is therefore made stronger and not easily broken.

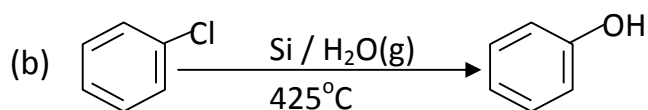
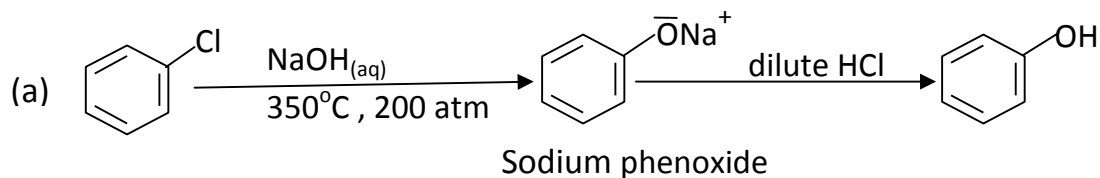
Bromoethane easily reacts with sodium hydroxide solution. This is because the carbon-bromine bond is polar since the bromine atom is more electronegative than the carbon atom. The bromine atom pulls the electrons of the bond more towards itself. This weakens the carbon-bromine bond creating a partial positive charge on the carbon atom and so it is easily attacked by the hydroxide ion.

**N.B** The same explanation applies for Chlorobenzene and any alkyl halide containing the chloride atom e.g Chloroethane and Iodobenzene with any alkyl halide containing the iodide atom e.g Iodobutane but while explaining, use the corresponding halide.

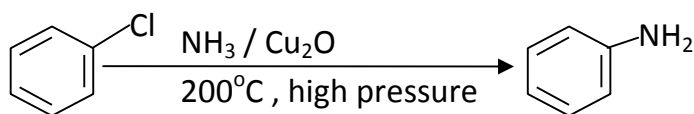
## Reactions of aromatic halides

The following reactions involve replacement of the halogen atom with another group.

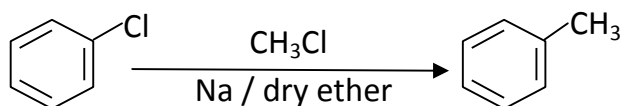
### 1. Conversion to a phenol.(C<sub>6</sub>H<sub>5</sub>OH)



### 2. Conversion to Phenylamine. (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)

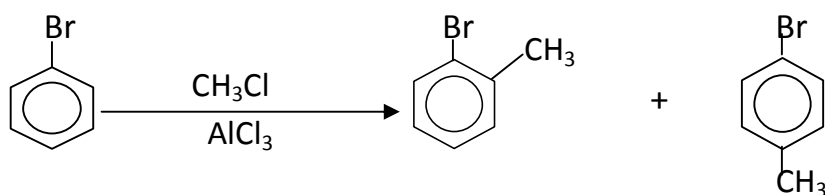


### 3. Conversion to methylbenzene.(C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)

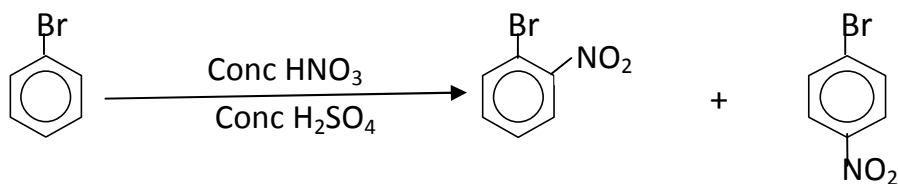


The reaction of aromatic halides below involves electrophilic substitution in the benzene ring.

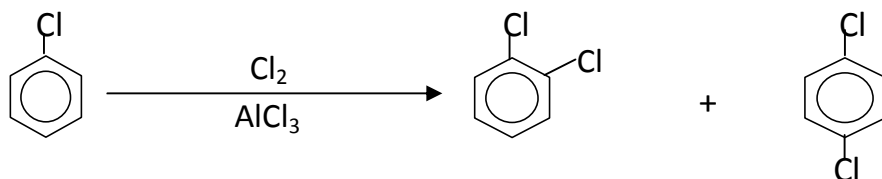
#### (a) Friedel craft alkylation.



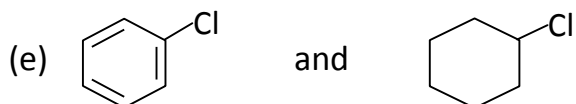
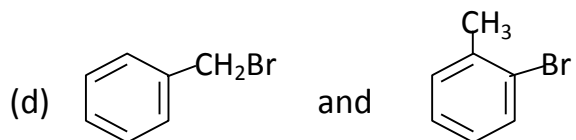
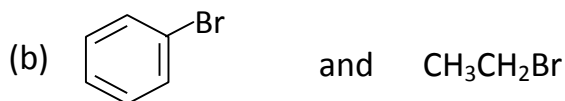
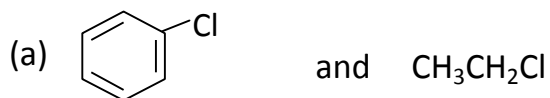
#### (b) Nitration



(c) Halogenation

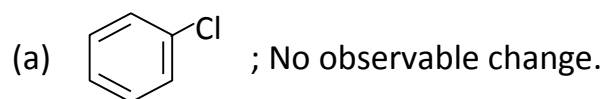


**Qn.** Name the reagent(s) that can be used to distinguish between the following pairs of compounds. In each case state what is observed when each member of the pair is treated with the named reagent(s) and write an equation (s) for the reaction that takes place.

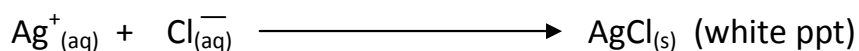
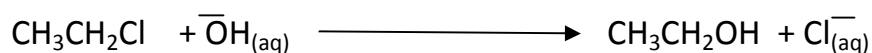
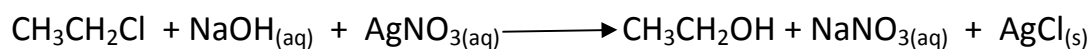
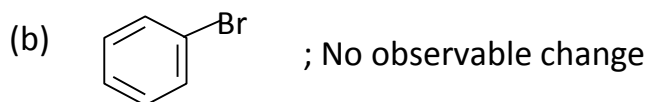


**Reagent(s)****Hot Sodium hydroxide solution followed by acidified silver nitrate solution.**

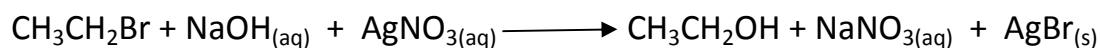
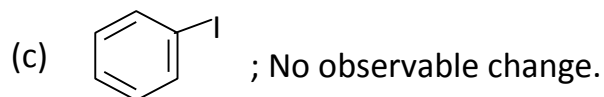
(Hot Sodium hydroxide solution followed by dilute nitric acid followed by silver nitrate solution).

**Observation(s)**

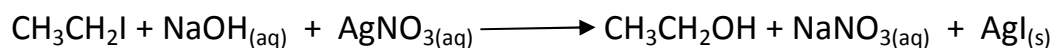
$\text{CH}_3\text{CH}_2\text{Cl}$  ; white precipitate is formed.

**Equation(s)****Or****Observation(s)**

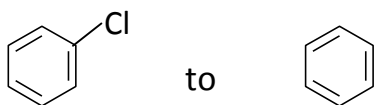
$\text{CH}_3\text{CH}_2\text{Br}$  ; a pale yellow precipitate is formed.(cream ppt)

**Equation****Observation(s)**

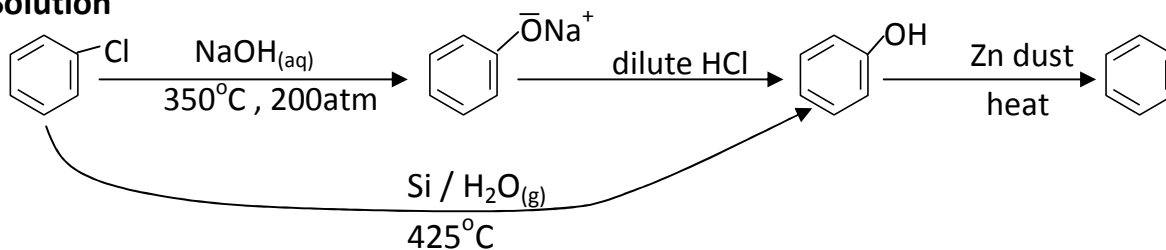
$\text{CH}_3\text{CH}_2\text{I}$  ; a yellow precipitate is formed.

**Equation**

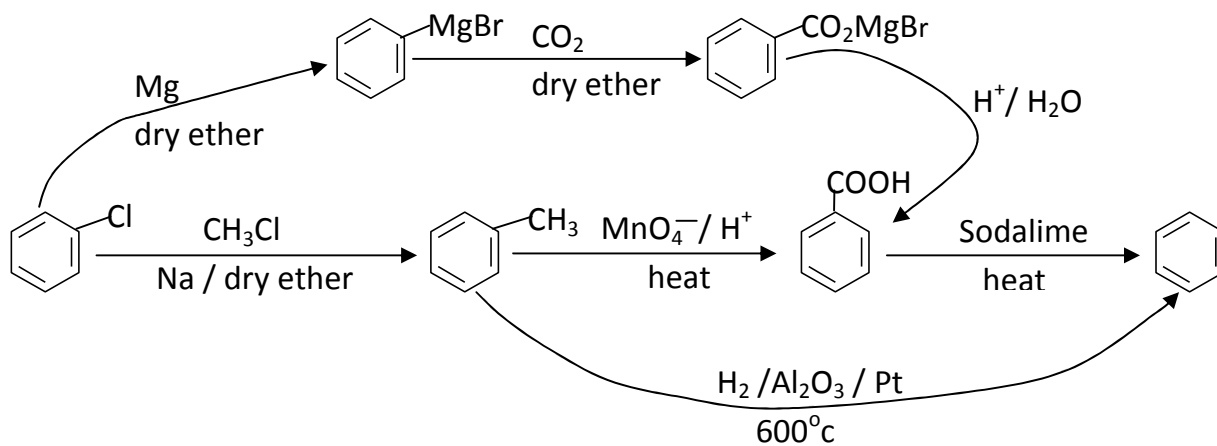
Qn. Using equations only show how the following conversions can be made.



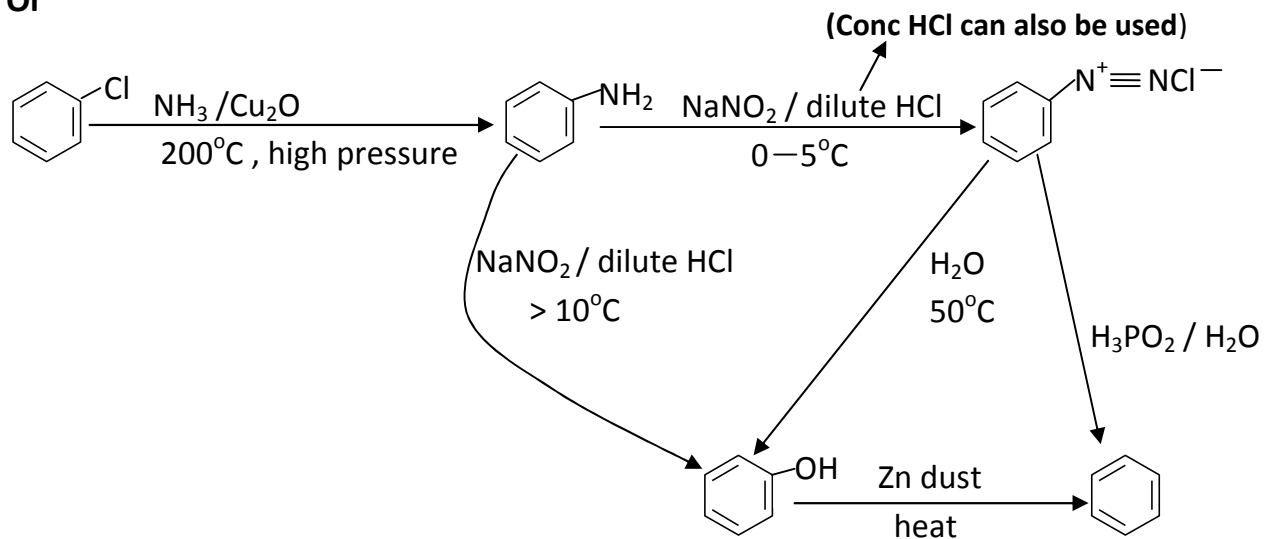
**Solution**



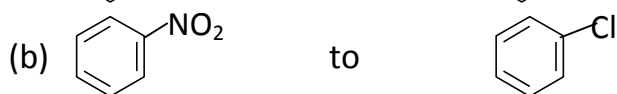
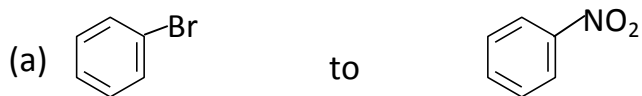
**Or**



**Or**



## Qn. Synthesize



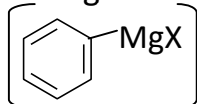
(c) Methylbenzene to Bromobenzene

(d) Phenol to Phenylamine

(e) Chlorobenzene from Phenylamine

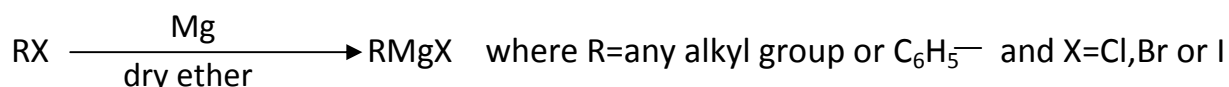
## GRIGNARD REAGENTS

A Grignard reagent is an alkyl magnesium halide (RMgX) or aromatic magnesium

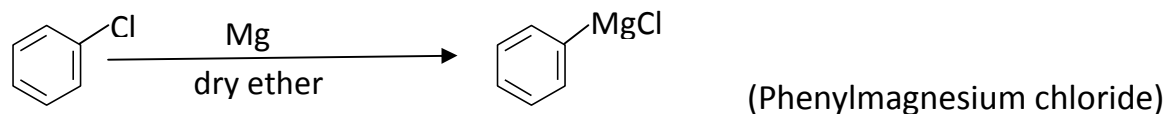
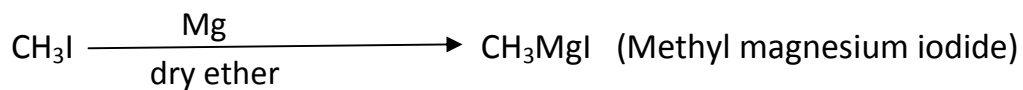
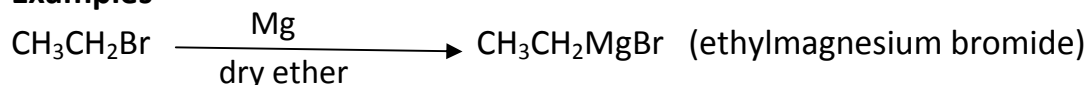
halide  Where X = Cl, Br or I

### Method of preparation

A Grignard reagent is prepared by reacting an alkyl halide or an aromatic halide with magnesium in presence of dry ether. i.e



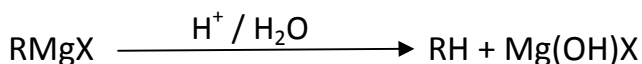
### Examples



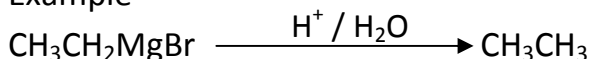
## Reactions of Grignard reagents (importance of Grignard reagents in Organic synthesis)

1. Conversion to an alkane.

Hydrolysis of a Grignard reagent forms an alkane.

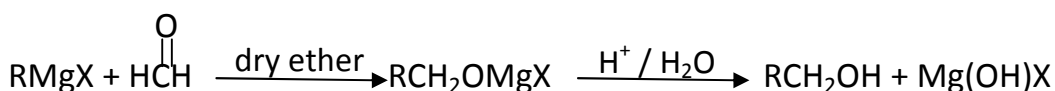


Example

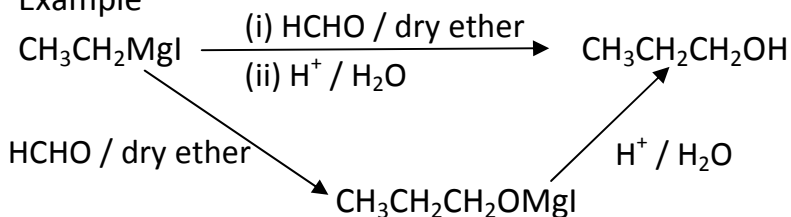


2. Conversion to a primary alcohol.

When a Grignard reagent is treated with methanal (HCHO) and the product hydrolysed, a primary alcohol is formed. i.e



Example

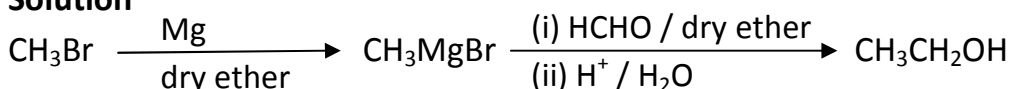


N.B This reaction increases the length of the carbon chain.

### Qn. Synthesis

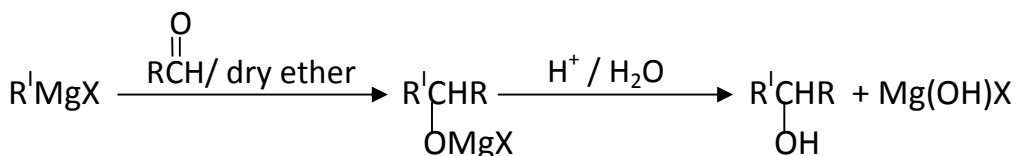
CH<sub>3</sub>Br to CH<sub>3</sub>CH<sub>2</sub>OH

**Solution**



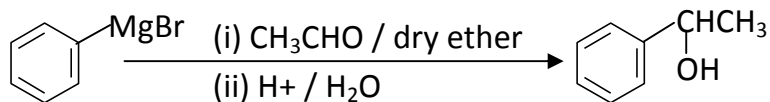
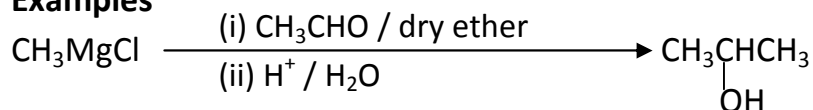
3. Conversion to a secondary alcohol.

When a Grignard reagent is treated with other aldehydes and then the product hydrolysed, a secondary alcohol is formed. i.e



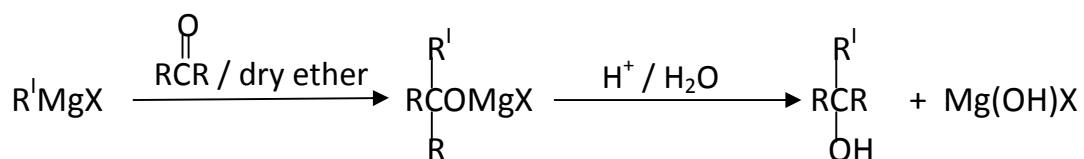


### Examples

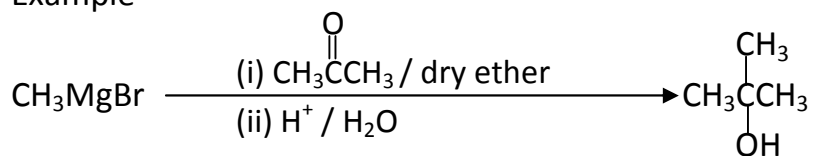


#### 4. Conversion to a tertiary alcohol.

Tertiary alcohols are formed when Grignard reagents are reacted with ketones and the products formed hydrolysed. i.e

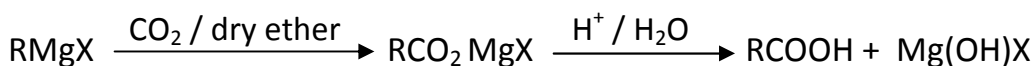


#### Example

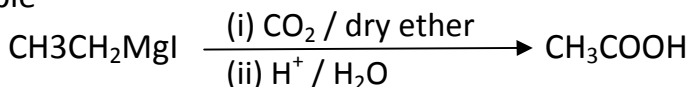


#### 5. Conversion to a carboxylic acid .

A carboxylic acid is formed when a Grignard reagent is reacted with carbon dioxide and the product formed hydrolysed. i.e

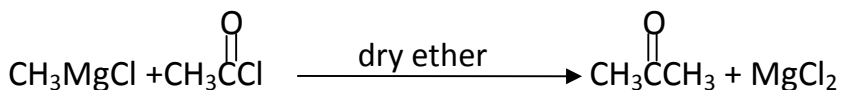


#### Example

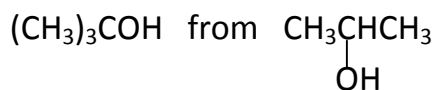


#### 6. Conversion to ketones.

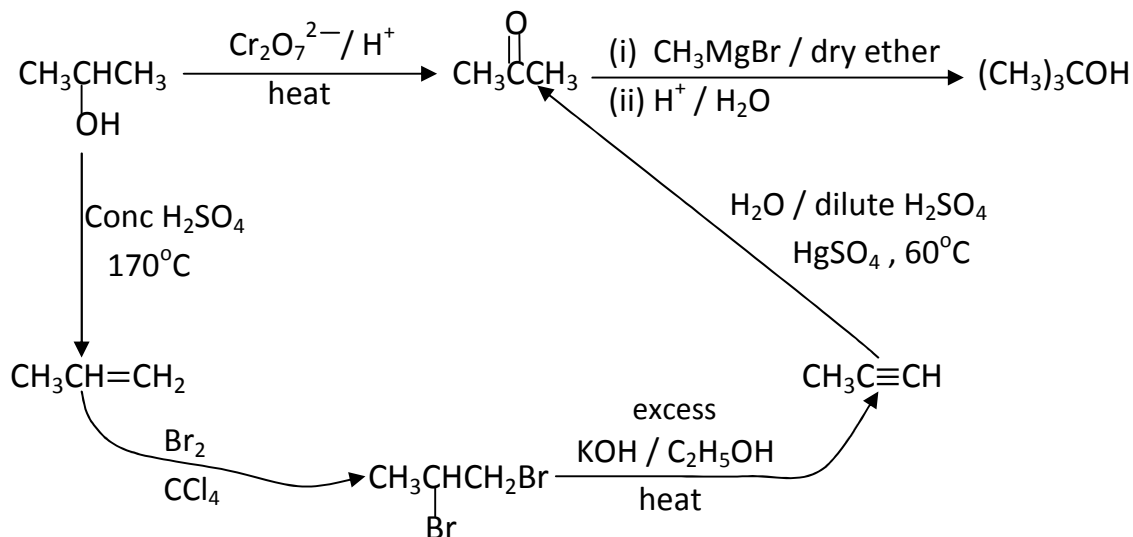
A ketone is formed when a Grignard reagent is reacted with an acid chloride. e.g



## Qn. Synthesis



### Solution



Qn. Using equations only show how the following compounds can be synthesised.

- $\text{C}_6\text{H}_5\text{Br}$  to  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- $\text{C}_6\text{H}_5\text{MgBr}$  to  $\text{C}_6\text{H}_5\text{COCl}$
- $\text{HC}\equiv\text{CH}$  to  $\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_3$
- $\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_3$  from  $\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_3$
- $\text{CH}_3\text{Br}$  to  $(\text{CH}_3)_3\text{COH}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  from  $\text{CH}_3\text{C}\equiv\text{CH}$
- Methylbenzene to  $\text{C}_6\text{H}_5\text{MgCl}$
- 2,2-dibromobutane to propan-1-ol
- Carbon to 2-methylpropan-2-ol
- Phenylmagnesium iodide to Phenylamine.

## ALCOHOLS