

# **Chapter 1: Introduction to Organic chemistry**

## **What is organic Chemistry**

Organic is the study of the chemistry of carbon. Carbon out of 112 elements of the Periodic Table forms a branch of chemistry called organic chemistry; it must be unique.

## **Uniqueness of carbon**

Carbon **forms very many useful** compounds of different chemical and physical properties.

## **Uses of organic compound**

Organic compounds are used for making:

- Plastic chairs,
- Plastic tables,
- drugs,
- perfumes
- pens
- paper
- Herbicides.

## **Terminologies**

### **1. Hydrocarbons**

These are compounds that contain carbon and hydrogen only.

### **2. Functional groups**

Is an atom or groups of atoms that impart chemical properties to organic compounds. For instance, a double bond in alkenes ( $-C=C-$ ), a triple bond in alkynes ( $-C\equiv C-$ ), hydroxyl group

in alcohols (-OH), a halogen atom in alkylhalides, carbonyl (-CO-) group and a carbocyclic group (-COOH).

### 3. **Homologous series**

is group of organic compounds that

- (i) Can be represented by similar general formula,
- (ii) Have similar functional group and hence similar chemical properties
- (iii) Are prepared by similar chemical methods
- (iv) show varying chemical properties. For instance, members of a given homologous series may vary from gases to liquids to solids.

## Chapter 2: Alkanes

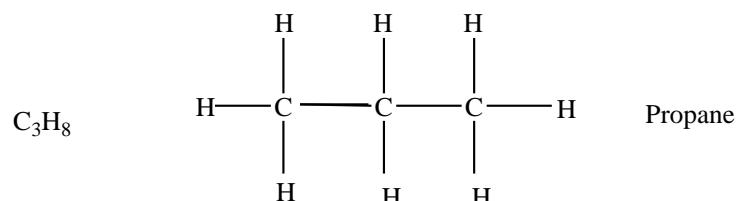
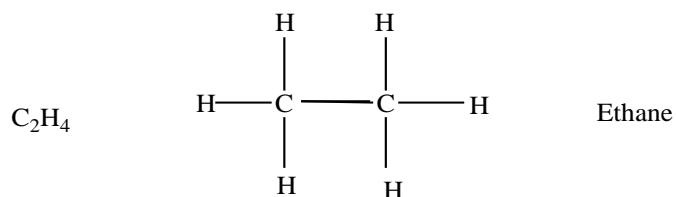
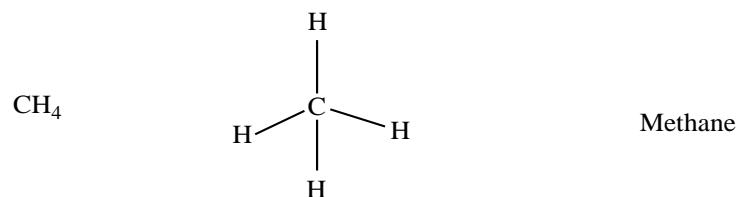
### Alkanes

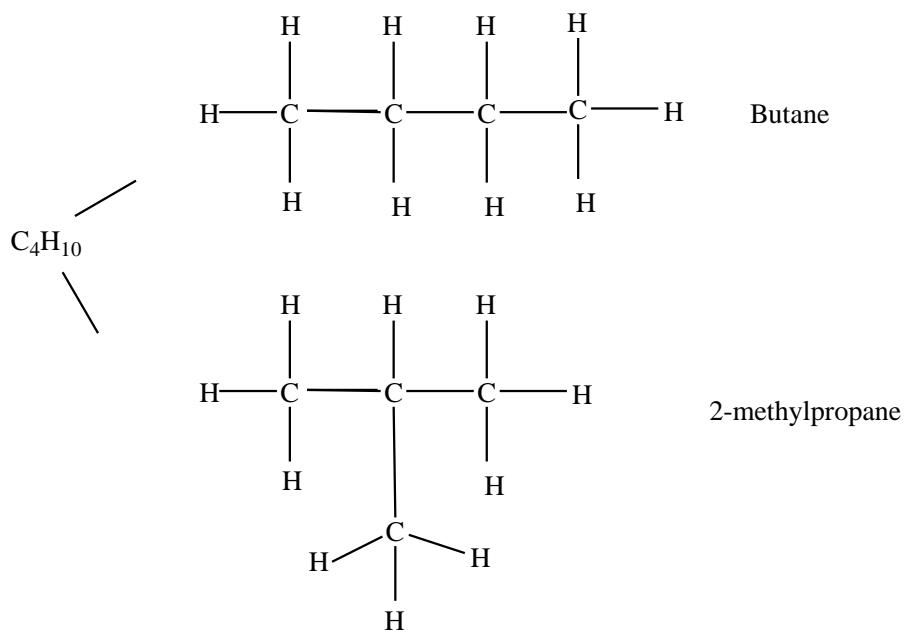
This is the simplest homologous series

General formula:  $C_nH_{2n}$  where  $n \geq 1$

### Examples

Molecular Formula	Structural Formulae	Names
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Compounds that contain the same molecular formula but different structural formulae like butane and 2-methylpropane are called **isomers**.

### Definitions.

Isomerism is the existence of compound with the same molecular formulae but different arrangement of atoms in a compound.

### Types of isomerism

1. Structural isomerism
2. Optical isomerism

### Structural isomerism

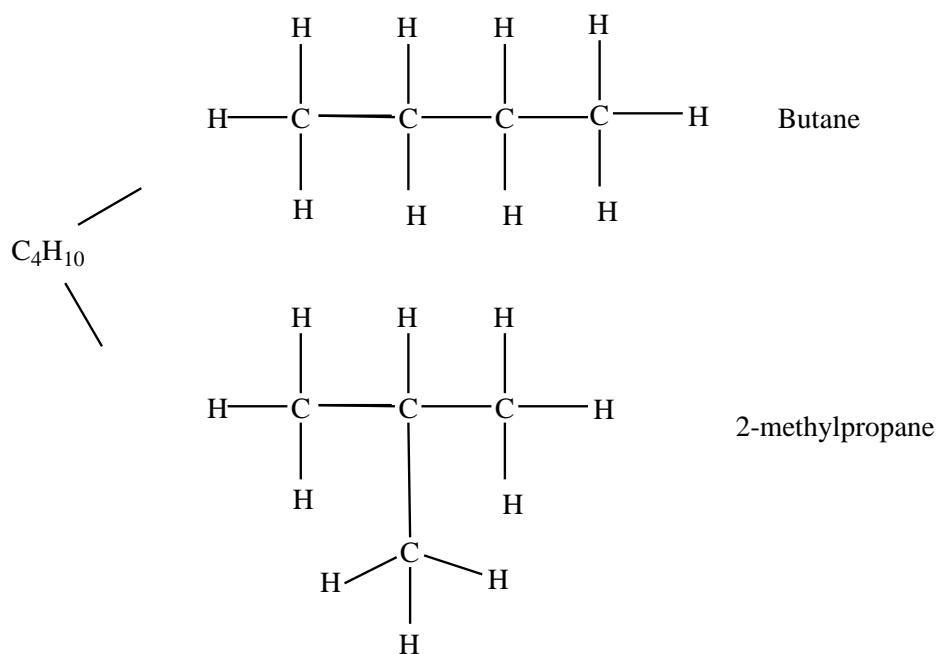
Here compounds differ in arrangement of atoms in a compound.

- (a) **Chain isomerism:** compound have the same molecular formula but different arrangement of atoms in the chain.

### (i) Structure isomers:

These are common to alkanes, isomers differ in arrangement of atoms in the chain

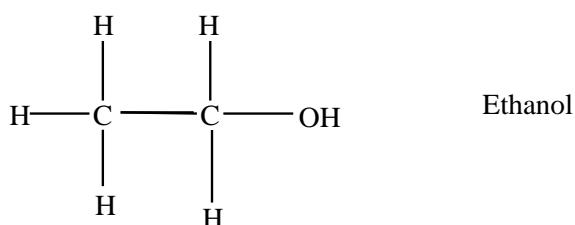
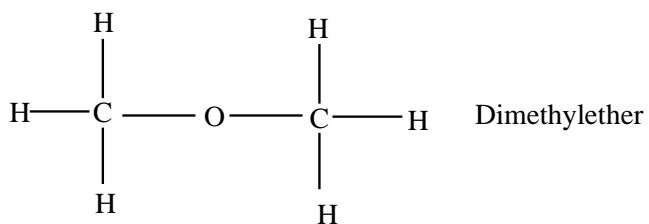
#### Examples



### (ii) Functional isomerism

Compounds have the same molecular formula but different functional groups such as alcohols and ether.

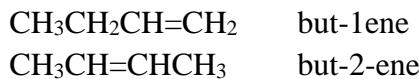
#### Example



(iii) **Positional Isomer:**

The isomers have the same molecular formula, same functional group but different positions of the functional group on a molecule.

**Examples**

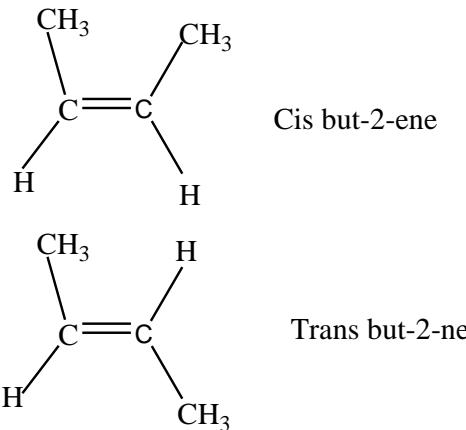


**(b) Stereo isomerism**

Compounds have the same molecular formula, the same functional group but different arrangement of atoms in space.

- (i) **Geometrical isomerism:** atoms, molecules are arranged differently about a double bonds:

**Example**



- (ii) **Optical isomers:**

Compounds have the same molecular formula, the same functional group but differ in optical properties towards plane polarised light. Those that rotate light towards the right are called **dextro** isomers and those that rotate light towards the left are called **levo** isomers.

# Nomenclature

## (a) Straight chain isomers

Straight chain isomers are named according to the number of carbon atoms in the chain.

The names of the first ten straight chain isomers are given below;

$\text{CH}_4$	Methane
$\text{CH}_3\text{CH}_3$	Ethane
$\text{CH}_3\text{CH}_2\text{CH}_3$	Propane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	Butane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Pentane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Hexane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Heptane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Octane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Nonane
$\text{CH}_3\text{CH}_3\text{CH}_3\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Decane

## An alkyl group

is an alkane less one hydrogen atom.

Example

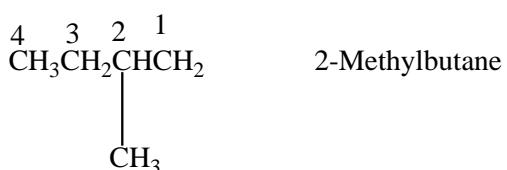
$\text{CH}_4$	Methane	$\text{CH}_3-$	methyl group
$\text{CH}_3\text{CH}_3$	Ethyl	$\text{CH}_3\text{CH}_2-$	Ethyl group
$\text{CH}_3\text{CH}_2\text{CH}_3$	Propane	$\text{CH}_3\text{CH}_2\text{CH}_2-$	Propyl group
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	Butane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	Butyl group

Because alkyl group do not have chemical properties, they are generally represented by a letter R,

## (a) Naming branched alkanes

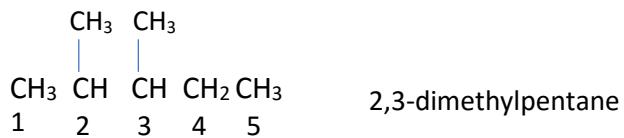
- Determine the number of carbon atoms in the longest carbon chain that contain the branch.
- Number the carbon atoms from the side nearest the branch.

Example



- (iii) If there are more than one similar alkyl groups on the longest chain; use di, tri, tetra to indicate the number of such groups on the main chain.

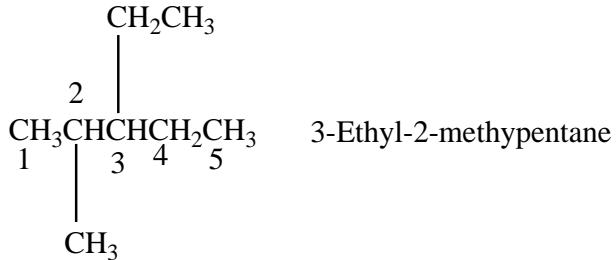
**Example.**



**Note that**

- This name implies that there is a methyl group attached to carbon 2 and another to carbon 3 of the pentane.
- When writing the name of organic compound, a coma (,) is placed between figures and a dash (-) between a figure and a letter.

- (iv) If different branches name them alphabetically

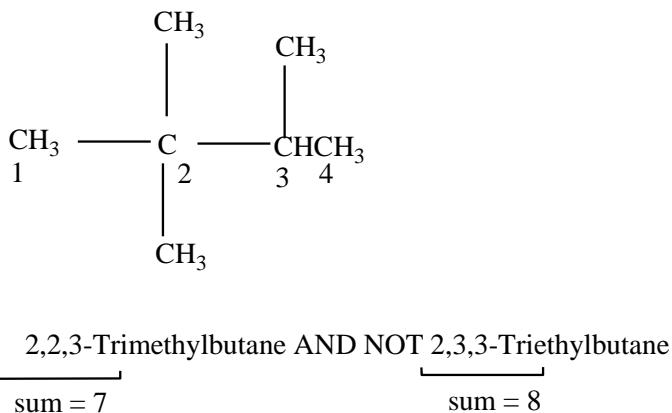


**Note that**

"E" for ethyl group comes before "M" for methyl group in the alphabets.

- (v) If branching occurs equal distance from either side, choose a name that gives the least sum of combination of numbers.

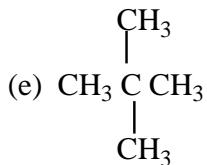
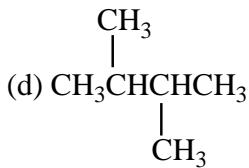
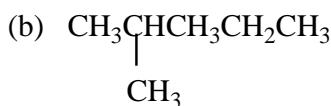
## Example



2,2,3-trimethylbutane is the correct name because it gives the least sum for the combination of numbers.

## Exercise

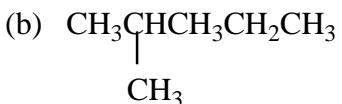
Name the following compounds



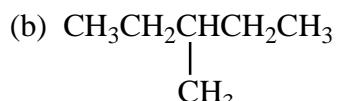
## Solution



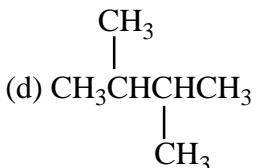
Hexane



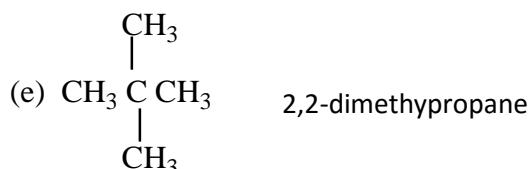
2-methylpentane



3-methylpentane



2,3-dimethylbutane



2,2-dimethylpropane

## Physical properties of alkane

- they are insoluble in water
- they are soluble in organic solvents
- they range from gases to liquids to waxy solides

## Chemical properties

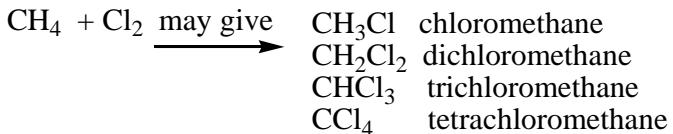
1. They burn in air to produce carbon dioxide, water and heat. Due to production of heat they are used as fuel.

Example



2. Chlorination: they react with chlorine in presence of sunlight or u.v-light to produce chlorinated alkanes.

Example

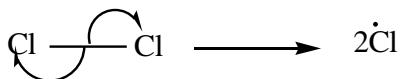


## Mechanism

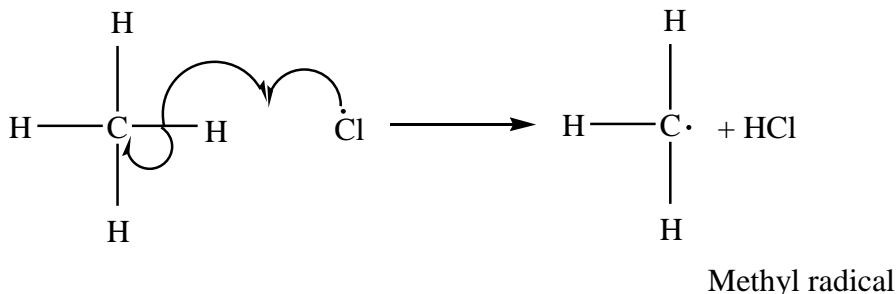
A mechanism are steps followed by a reaction from the reactant to the products.

The following are steps followed in chlorination of methane

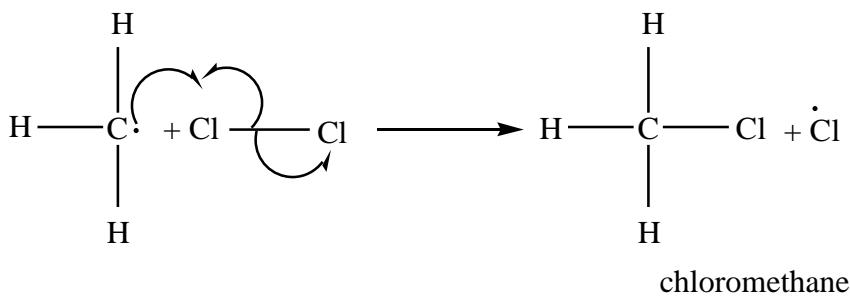
- Chlorine molecules dissociates into atoms with unpaired electron. Atoms or molecules with unpaired electron are called free radicals. Free radicals are indicated by a dot on the atom that posses un paired electron



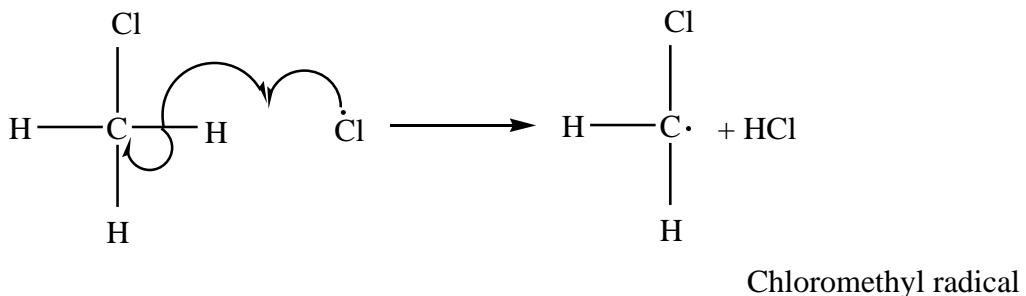
- Chlorine radical attacks a methane to produce hydrogen chloride and a methyl radical.



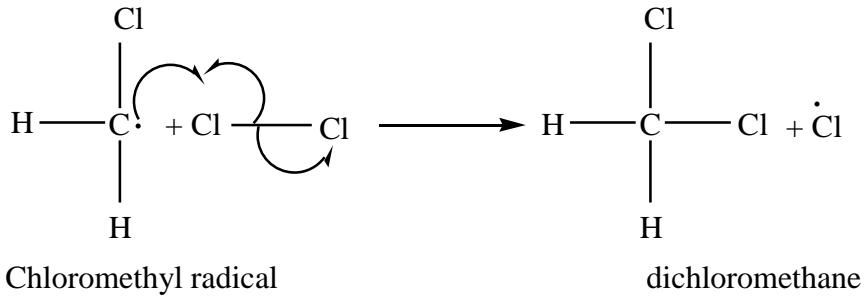
- Methyl radical reacts with a chlorine molecule to form chloromethane and a chlorine radical



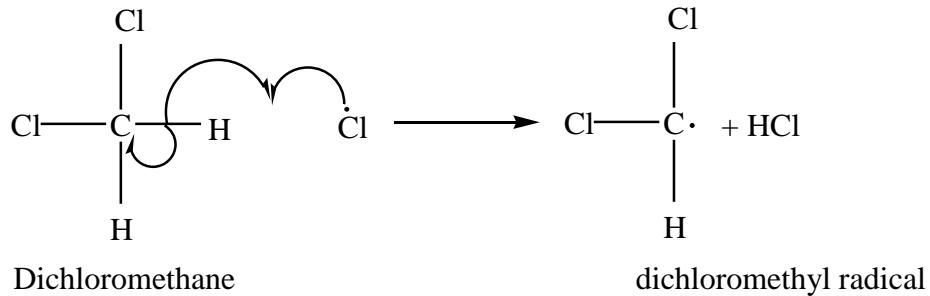
- Chlorine radical attacks a chloromethane to produce hydrogen chloride and a chloromethyl radical.



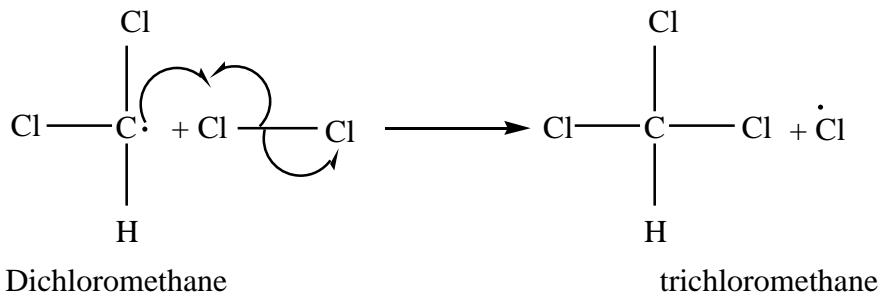
5. Chloromethyl radical reacts with a chlorine molecule to form dichloromethane and a chlorine radical



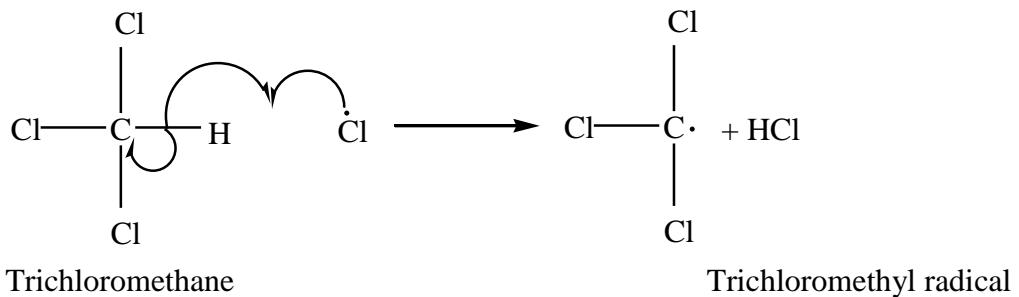
6. Chlorine radical attacks a dichloromethane to produce hydrogen chloride and a dichloromethyl radical.



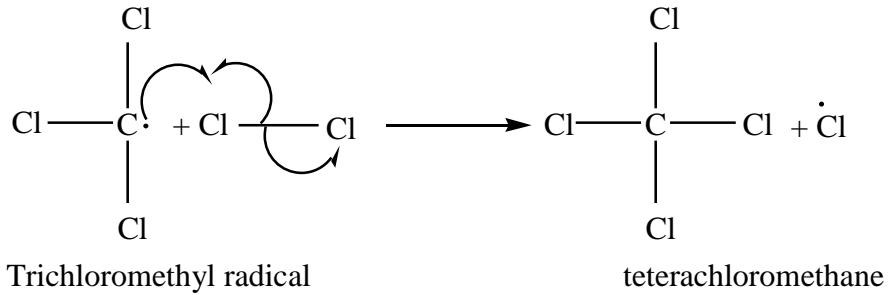
7. Dichloromethyl radical reacts with a chlorine molecule to form trichloromethane and a chlorine radical



8. Chlorine radical attacks a trichloromethane to produce hydrochloride and a trichloromethyl radical.



9. Trichloromethyl radical reacts with a chlorine molecule to form tetrachloromethane and a chlorine radical



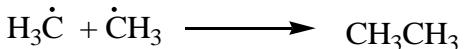
## Terminating steps

Meanwhile the radicals may combine to produce molecules. The reactions where radicals react to produce molecules is called terminating steps i.e, they prevent the reaction from continuing. Some of the terminating steps are:-

1. Chlorine radical + chlorine radical produces chlorine molecule



2. Methyl radical + methyl radical produces ethane



3. Methyl radical reacts with chlorine radical to form chloromethane and so on.



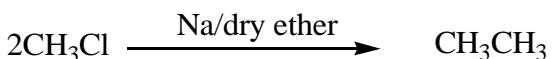
## Sources of alkanes

1. Petroleum product
  2. Biogas

Biogas is produced by anaerobic decomposition of organic matter (such as cow dung, plant remains, faeces) in presence of water. The main component of biogas is methane.

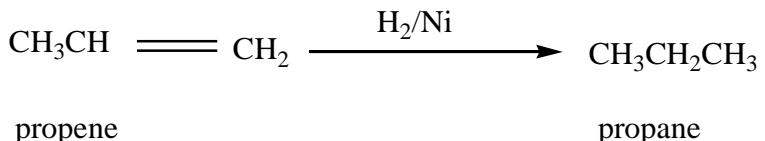
## Laboratory preparation

1. By coupling reaction of alkylhalide in presence of sodium and dry ether. For instance chlomethane couple with chloromethane to form ethane



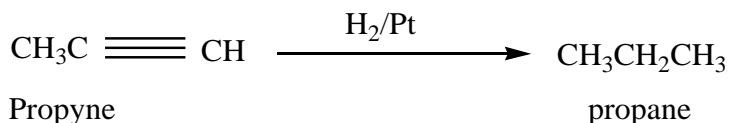
## 2. By reduction of alkenes

## Example



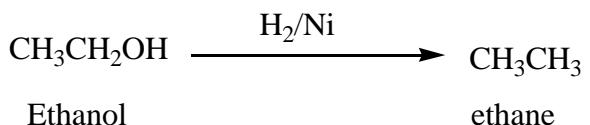
### 3. Reduction of alkynes

## Example



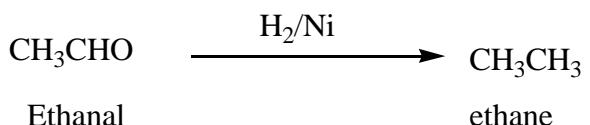
#### 4. Reduction of alcohols

## Example



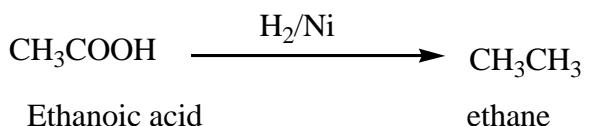
## 5. Reduction of carbonyl compound

## Example



## 6. By reduction of carboxylic acid

## Example



7. By cracking long alkane

Cracking is the breakdown of long chain hydrocarbons into short alkanes.

Cracking may be catalytic where a catalyst is used or thermal when heat is used.

Thank you for choosing Dr. Bbosa Science

## Alkenes

These are hydrocarbons that contain a double bond →

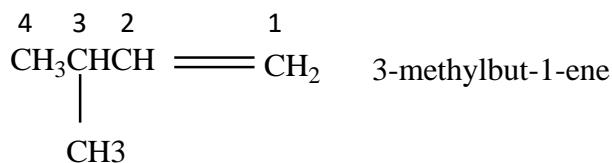
General formula is  $C_nH_{2n}$   $n \geq 2$

Examples are



For branched alkene we number the carbon atoms from the side nearest the double bond

For example



## Physical properties

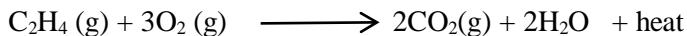
They like those of alkane

- they are insoluble in water
- they are soluble in organic solvents
- they are solvents
- they range from gases to liquids to waxy solids

# Chemical properties

## 1. Combustion

They burn in air to produce carbon dioxide, water and heat.

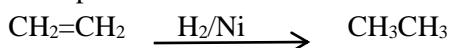


Because they produce heat they are used as fuel.

## 2. Reduction

They are reduced by hydrogen in presence of catalysts; nickel or platinum to alkenes

Example

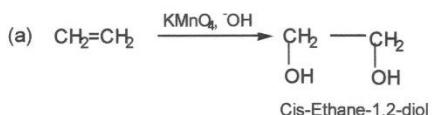


## 3. Hydratation reaction

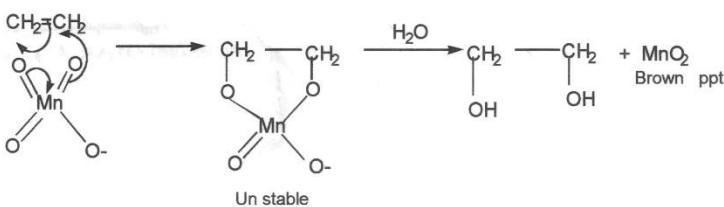
(i) Reaction of alkenes with  $\text{KMnO}_4$  solution

Dilute alkaline  $\text{KMnO}_4$  solution converts alkenes into compounds called GLYCOLS (dihydroxy alcohol)

Examples



MECHANISM



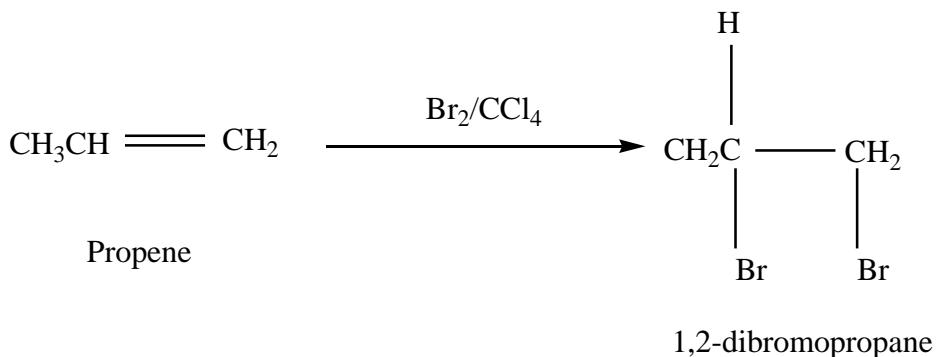
**NB.** (a) Since oxidation of alkenes with  $\text{KMnO}_4$  proceeds with decolorisation of solution, this can be used as a test for unsaturation.

### (i) Addition of halogens

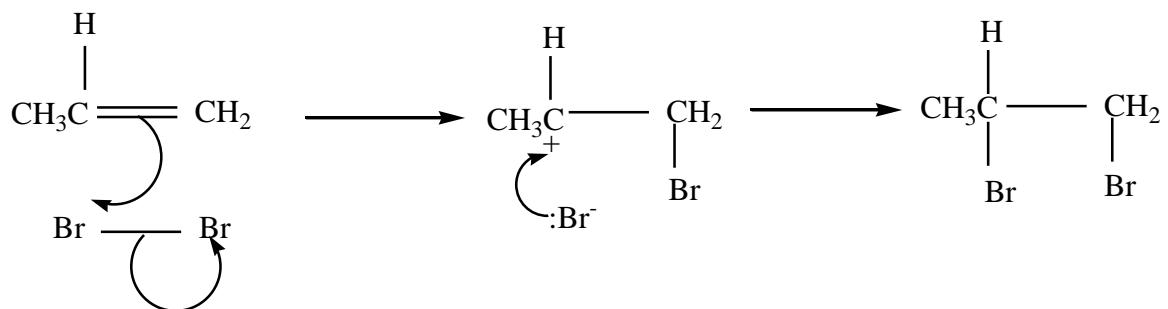
Halogens add across a double bond to form dihalogeno compounds. The reaction is carried out in an inert solvent (like tet

### Example 1

Propene reacts with bromine in presence of inert solvents (tetrachloromethane) to form 1,2-dibromopropane

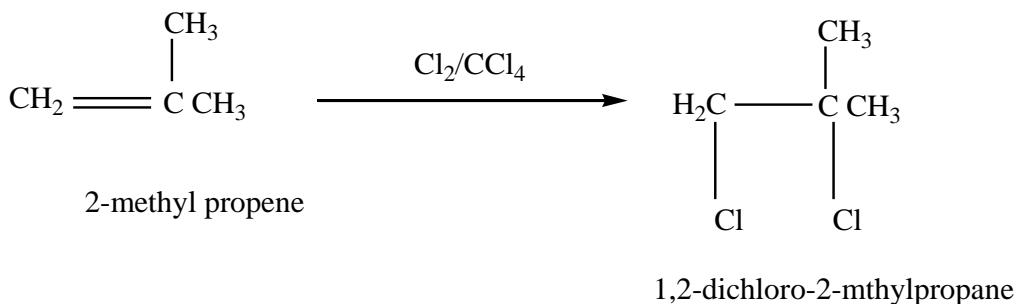


### Mechanism

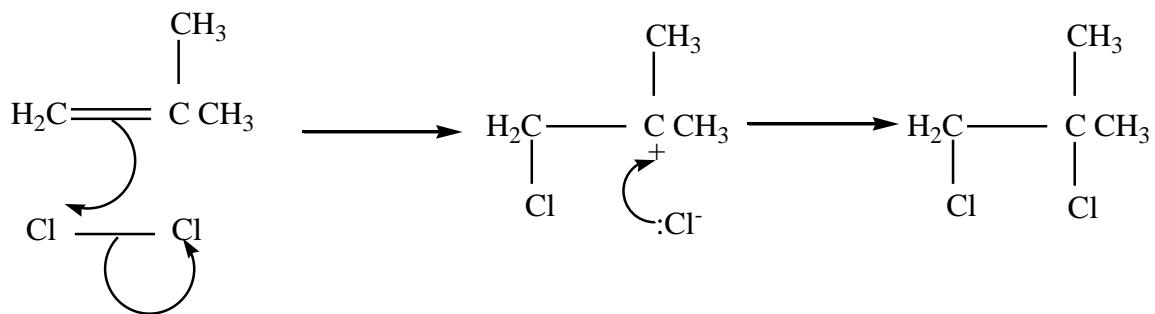


### Example 2

2-methylpropene plus chlorine in presence of tetrachloromethane give 1,2-dichloro-2-methylpropane

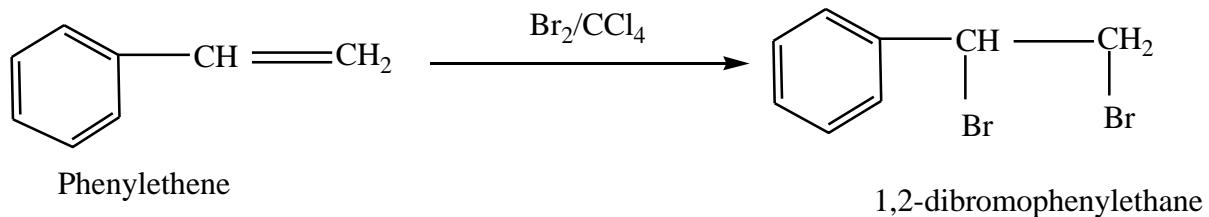


### Mechanism

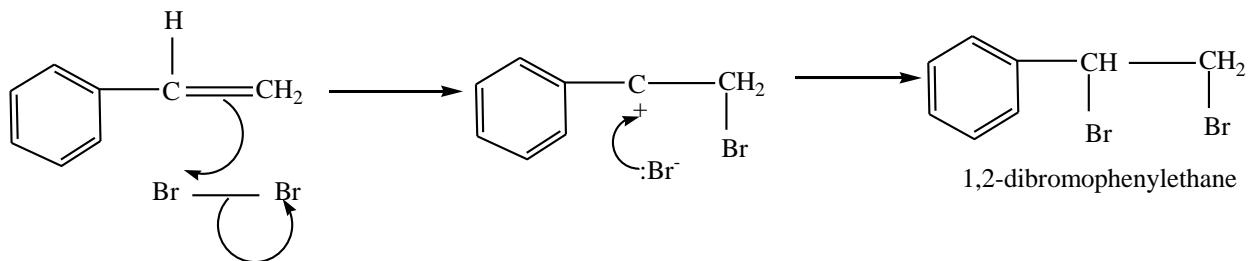


### Example 3

Phenylethene plus bromine in presence of tetrachloromethane give 1,2-dibromophenylethane

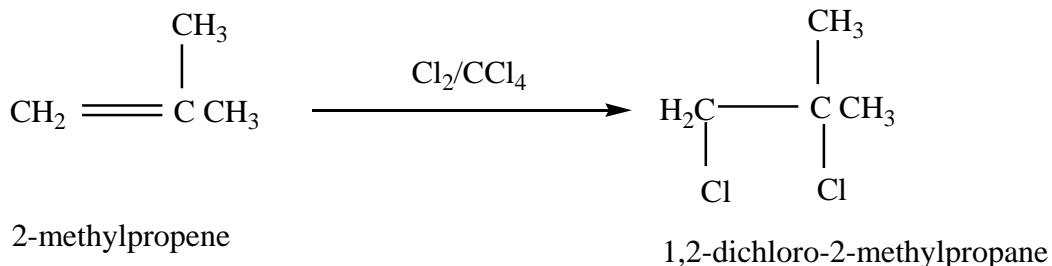


### Mechanism

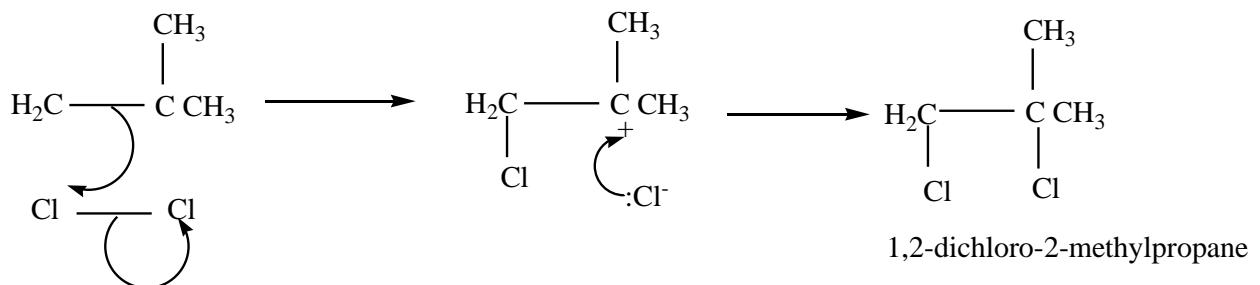


### Example 4

2-methylpropene plus chlorine in presence of tetrachloromethane gives 1, 2-dichloro-2-methylpropane



## Mechanism

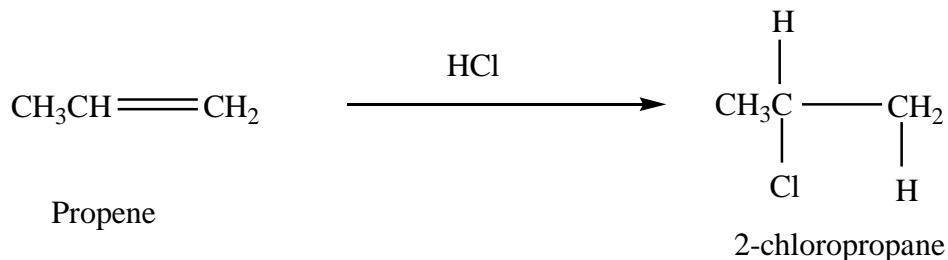


## (ii) Reaction of alkenes with HX (X = Cl, Br, I)

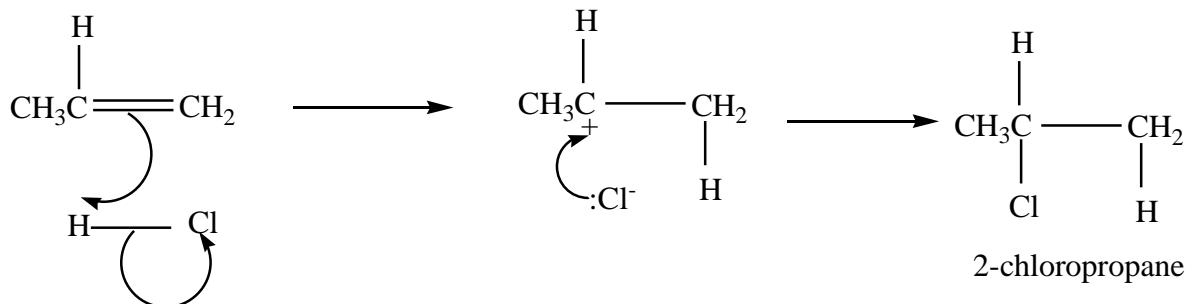
The reaction is carried out by bubbling HX through alkenes.

### Example 5

Propene plus hydrochloric acid gives 2-chloropropane

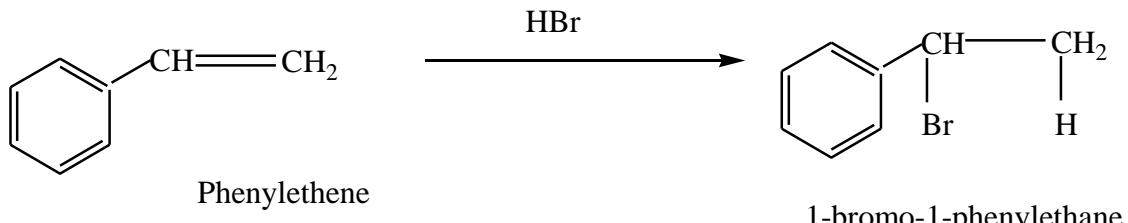


## Mechanism

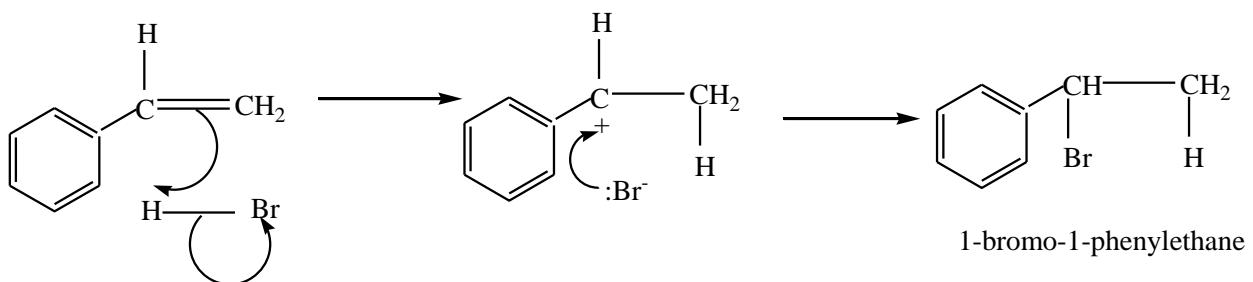


### Example 6

Phenylethene plus hydrogen bromide give 1-bromo-1-phenylethane

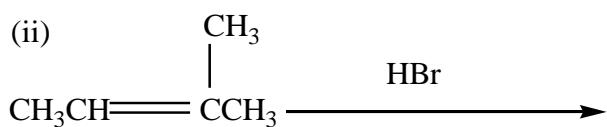
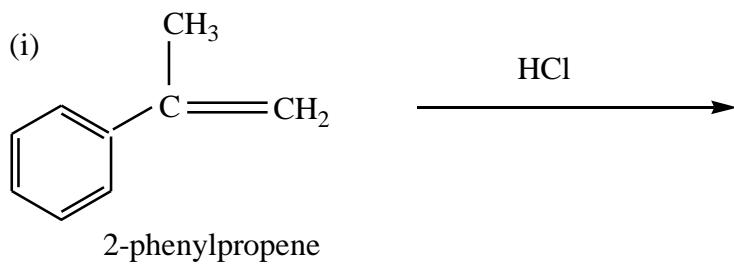


Mechanism



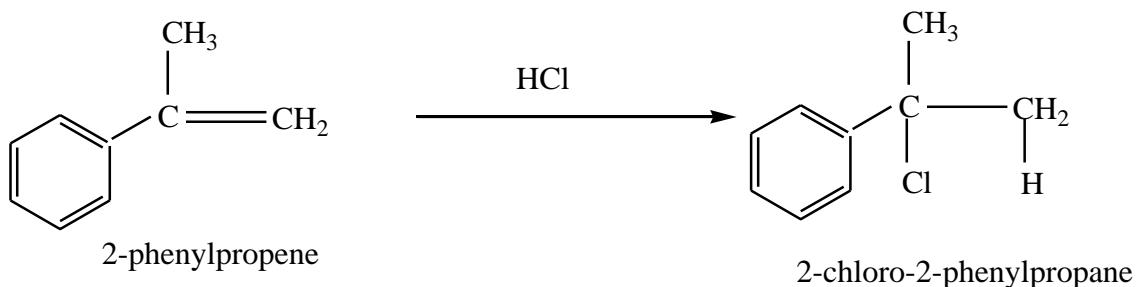
### Trial 1

Complete and write a mechanism

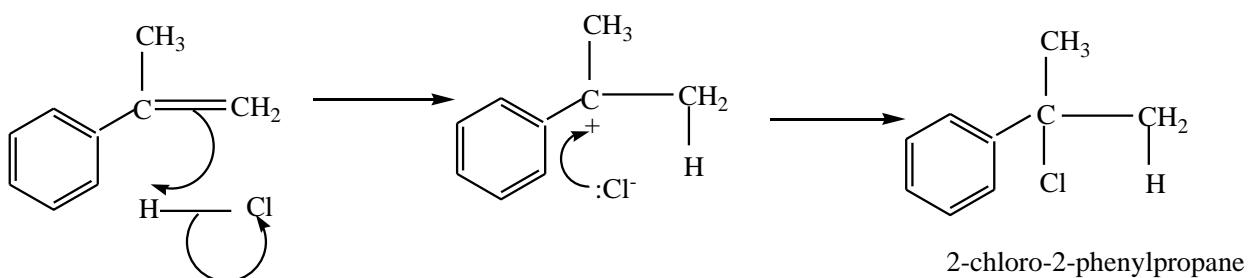


## Solution to the exercise

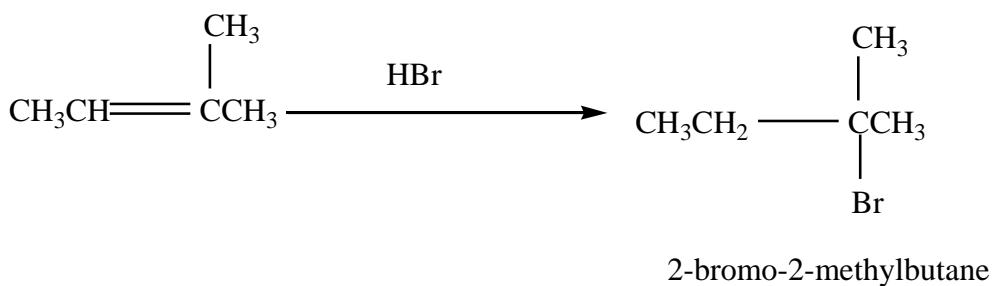
(i) 2-phenylpropene plus HCl gives 2-chloro-2-phenylpropane



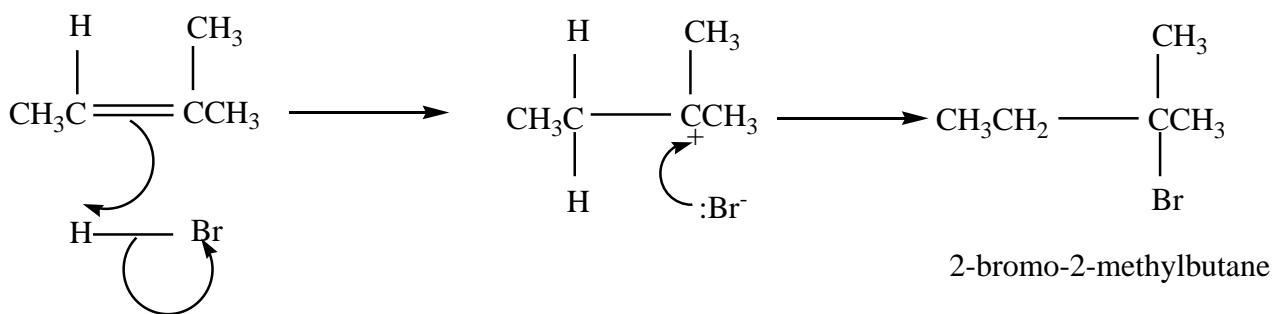
### Mechanism



(ii) 2-methylbut-2-ene plus HBr gives 2-bromo-2-methylbutane



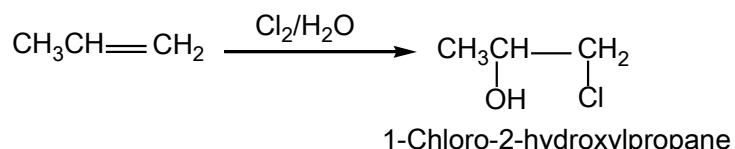
### Mechanism



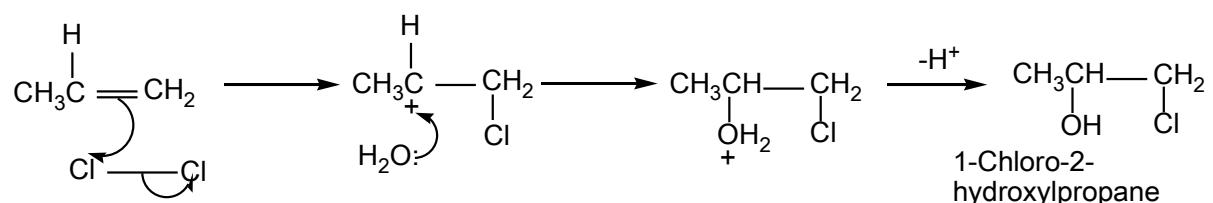
(ii) Reaction of alkenes with halogens in presence of water.

The reaction is carried out by bubbling alkenes through aqueous halogens.

### Example 7

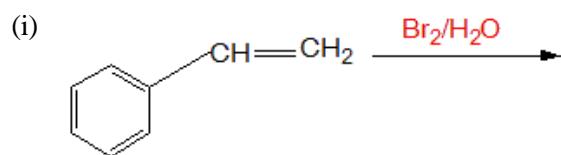


#### MECHANISM

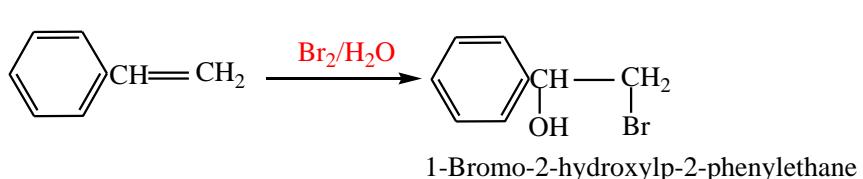


### Trial 2

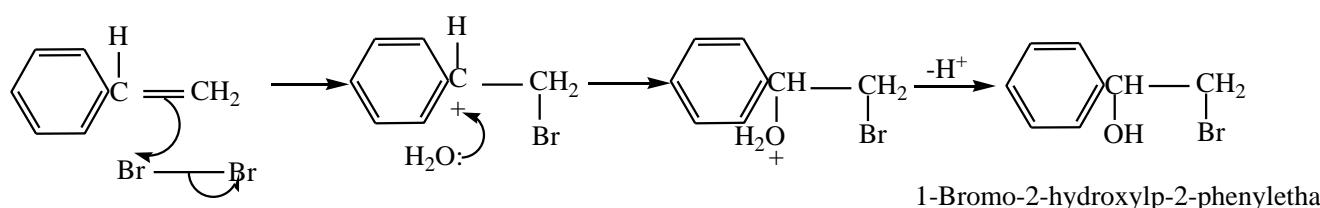
Complete the following and write meachnaism (do not look at the answer before)



#### Solution

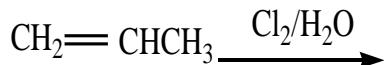


#### MECHANISM



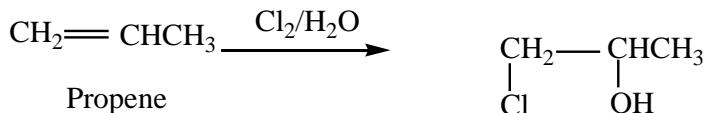
### Trial 3

Complete and write a mechanism

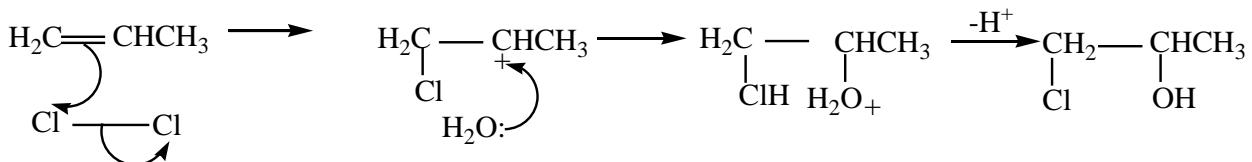


Propene

Solution



### MECHANISM

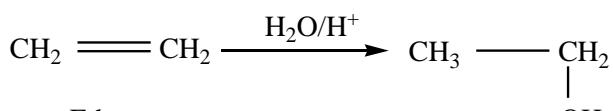


(d) Reaction of alkene with water.

The reaction is catalysed by an acid sulphuric acid or phosphoric acid. Alcohols are produced

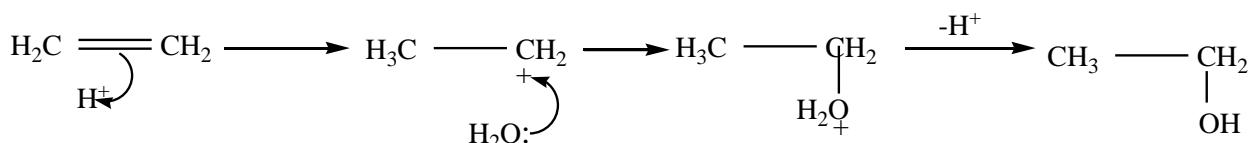
Example

Ethene reacts with acidified water to produce ethanol.



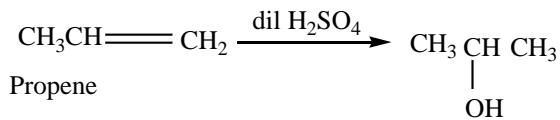
Ethanol

### MECHANISM



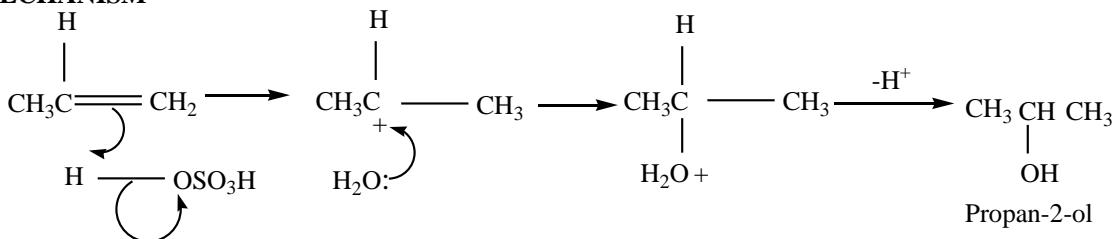
## Example 8

Propene reacts with dilute sulphuric acid to form propan-2-ol



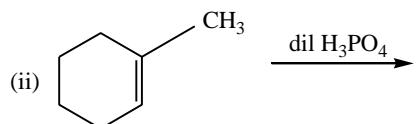
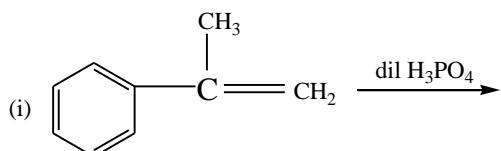
Propan-2-ol

### MECHANISM

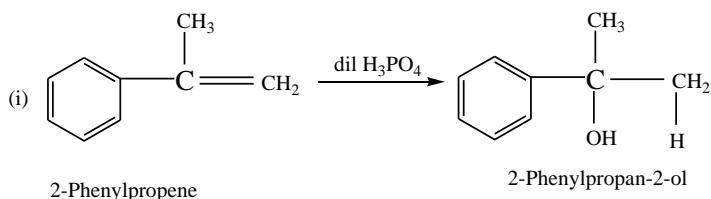


## Trial 4

Complete the following equations and suggest mechanisms



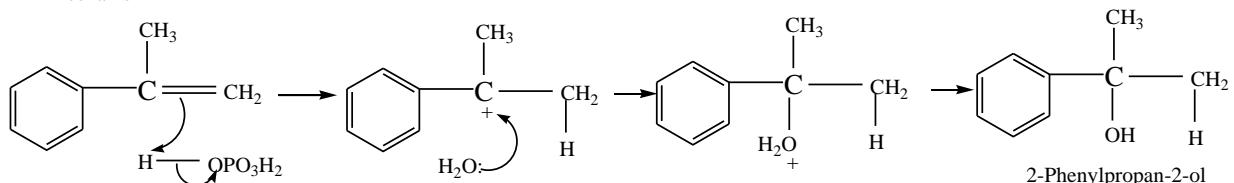
### Solution

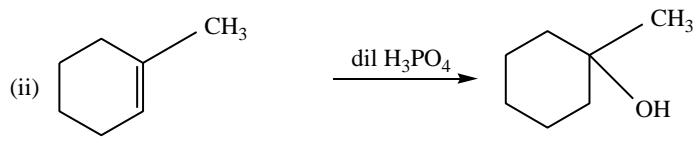


2-Phenylpropene

2-Phenylpropan-2-ol

### Mechanism

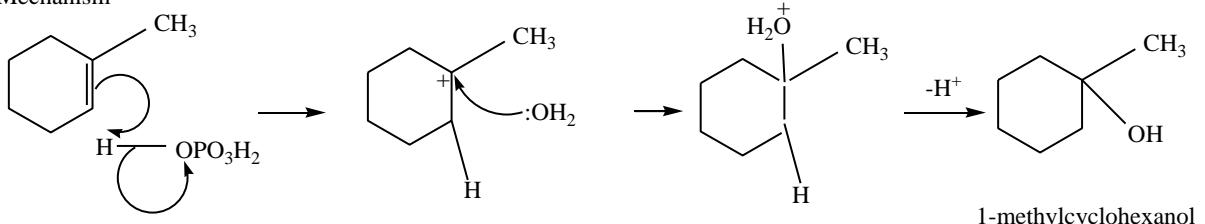




1- Methylcyclohexene

1-methylcyclohexanol

Mechanism

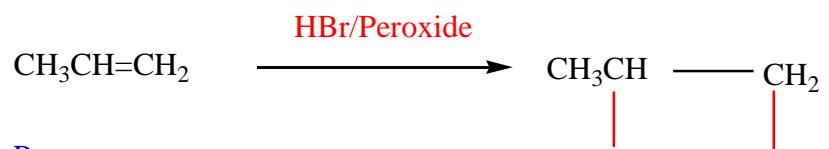


NB. The charges must be accounted for at every stage

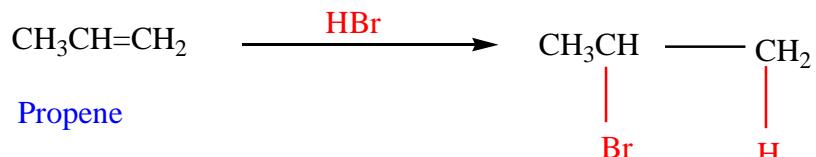
(e) Addition of hydrogen bromide in presence of a peroxide

In presence of a peroxide, alkenes react with HBr by free radical mechanisms; but in this case hydrogen atom goes to a carbon atom that carry the least number of hydrogen atoms of those that form a double bond otherwise the bromine atom goes to a carbon with the highest number of hydrogen atoms.

**Examples 9**

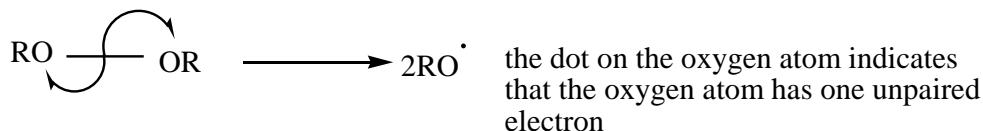
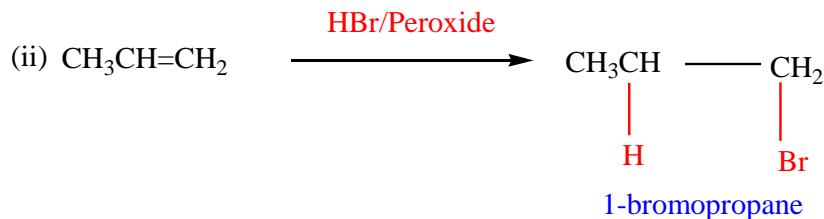


Instead of

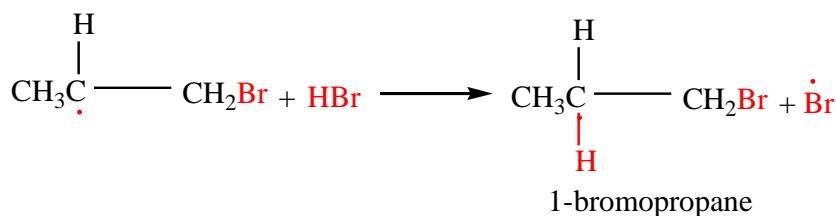


2-bromopropane

## Mechanism

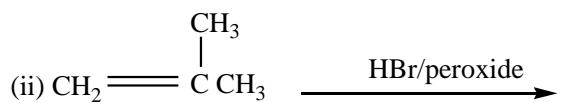


Then

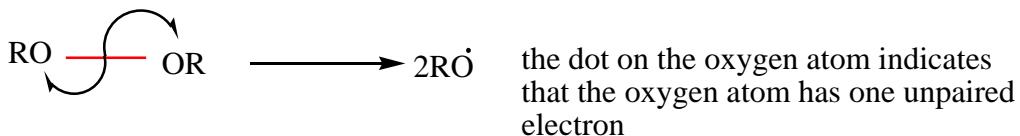


## Trial 4

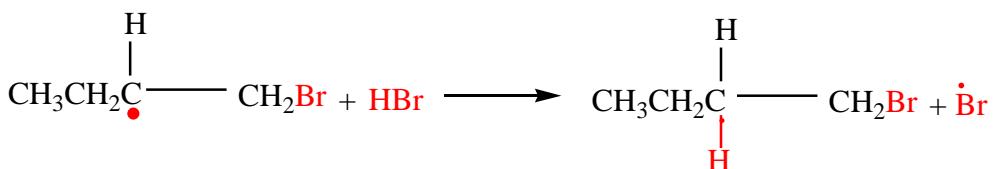
Complete and write a mechanism (it advisable you attempt these questions and mark yourself)

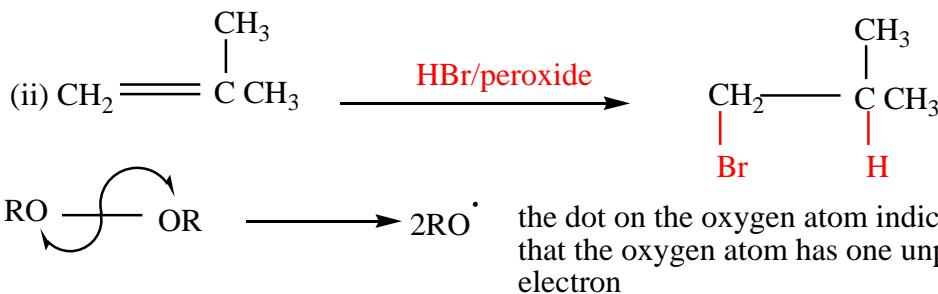


Solutions to the exercise

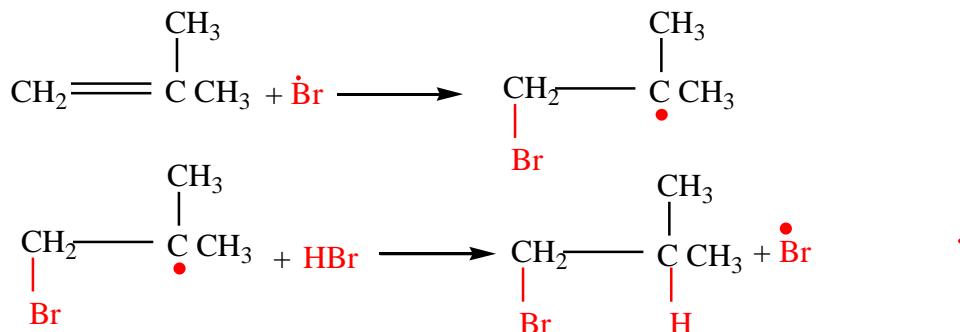


Then





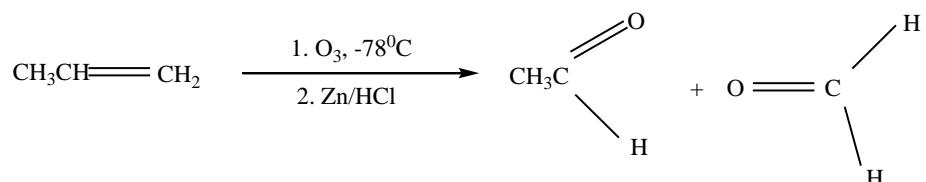
Then



#### (f) Ozonolysis (reaction of ozone with alkenes)

Ozone reacts with alkene to form unstable ozonide that is reduced by zinc in presence of hydrochloric acid to form carbonyl compounds.

Example



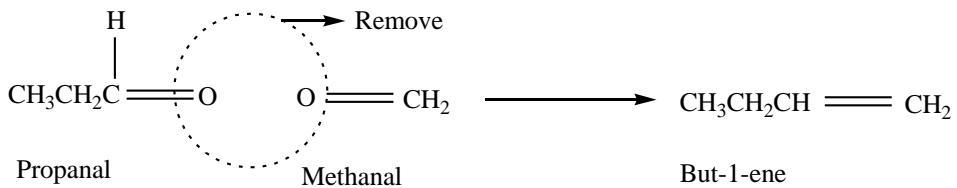
From the products of ozonolysis, it is possible to tell the position of the double bond in the compound that was ozonolysed because ozonolysis breaks a compound at the double bond.

#### Example 10

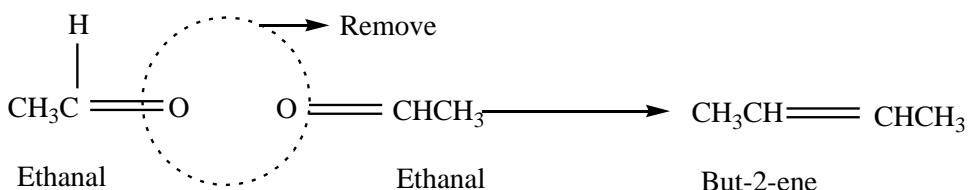
Write the structure of an alkene which on ozonolysis gave

- (i) Propanal ( $\text{CH}_3\text{CH}_2\text{CHO}$ ) and methanol ( $\text{HCHO}$ )

By removing the oxygen atoms from each compound create a double bond and hence the compound.



(ii) One product ethanal



Trial 5

An alkene X has molecular formula  $C_4H_8$

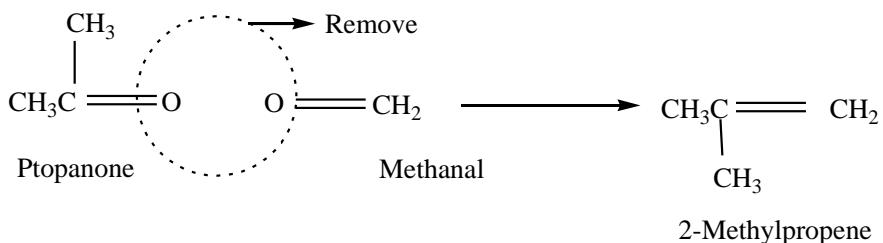
- (a) Write the name and structural formula of compound X.  
(b) On ozonolysis X gave propanone ( $\text{CH}_3\text{COCH}_3$ ) and methanal ( $\text{HCHO}$ ). Identify X.

## Solution

(a)



- (b) By removing oxygen atoms from the products of ozonolysis, the position of a double bond is created.



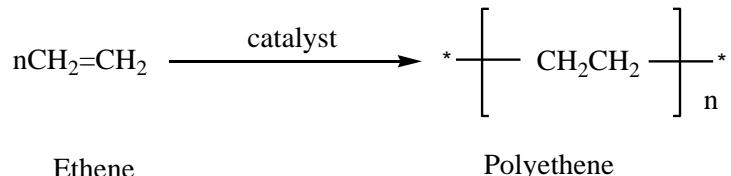
Therefore X is 2-methylpropene.

## Polymerization

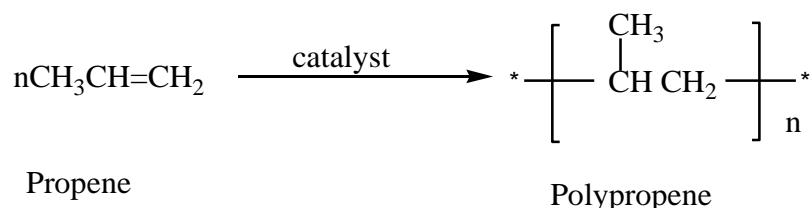
This is the joining of very many small molecules called monomers to form big molecules called polymers

In presence of a catalyst, (acid) alkenes polymerize to form polyalkenes.

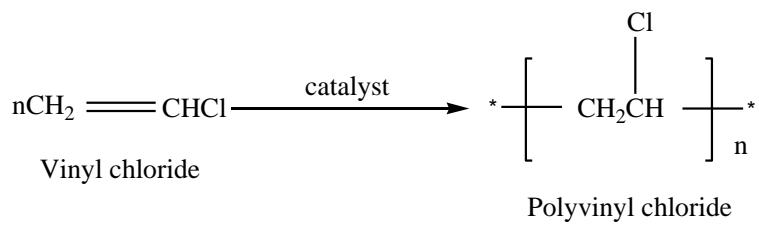
For example ethane plus a catalyst you get polyethene



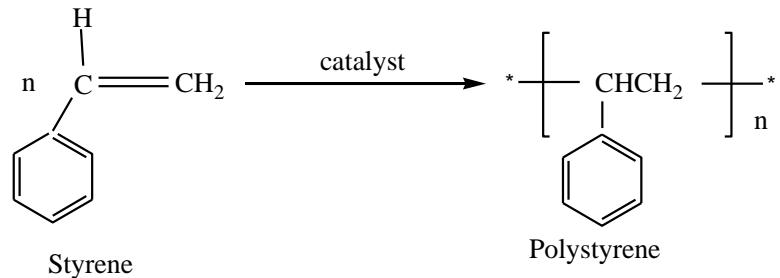
(ii) Propene polymerize to form polypropene



(iii) Vinyl chloride polymerizes to form polyvinylchloride (PVC)



(iv) Styrene polymerizes to form polystyrene.



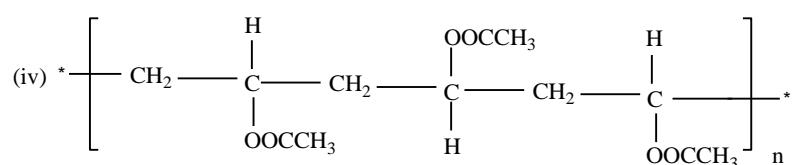
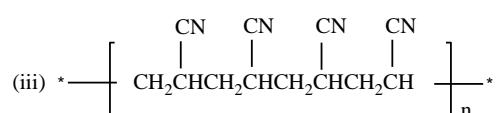
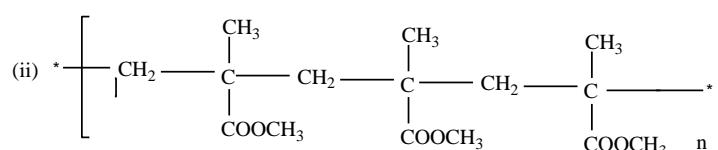
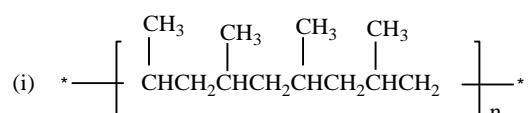
All polyalkenes can be used as insulators, packing materials and pipes.

Alkenes undergo a type of polymerization called addition polymerization in that when the monomers of alkenes add to form a polymer, there is no loss of any atom, or particle from them.

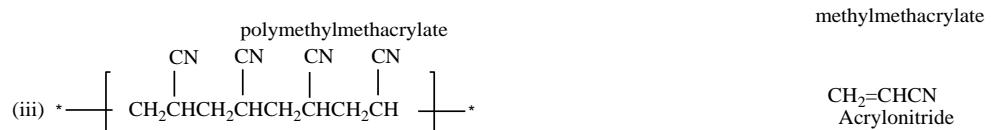
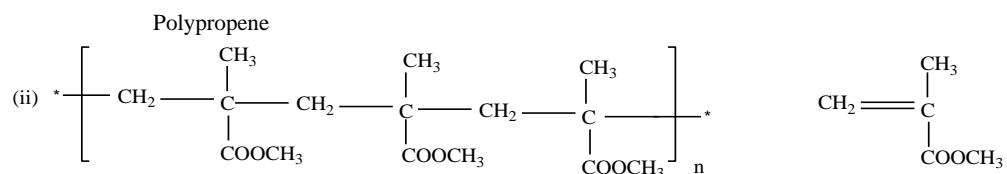
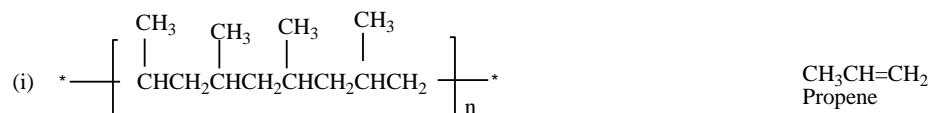
Note that when given a polymer without a double bond the monomer is a substituted two carbon compound with a single double bond.

### Exercise 11

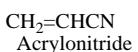
Write the structure and the names of monomer for the following polymers

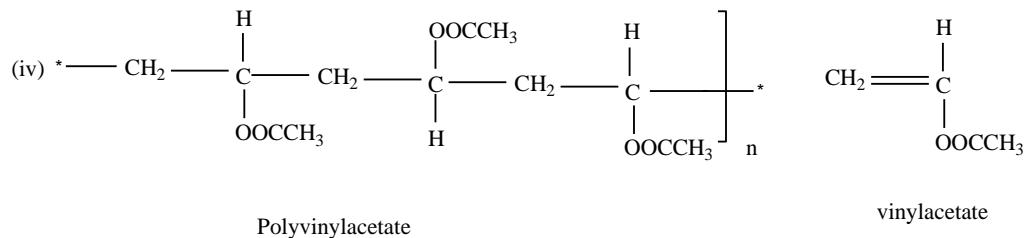


### Solutions



Polyacrylonitrile





### Uses of polyalkenes

- packing materials
- water pipes
- insulators

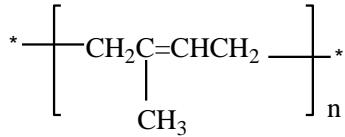
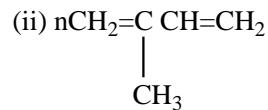
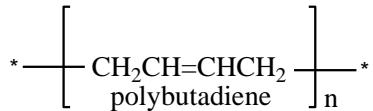
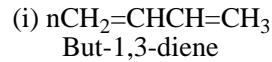
Alkenes undergo a type of polymerization called addition polymerization because monomers add to form a polymer without loss of any atom.

Polyalkenes are also called thermoplastics because they soften on heating and can be remolded.

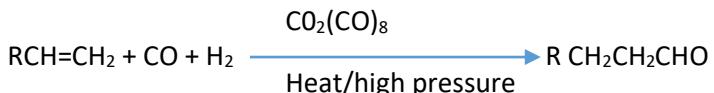
### Polymerization of dienes

Alkenes with conjugated double bond undergo polymerization to form polyalkenes with double bonds

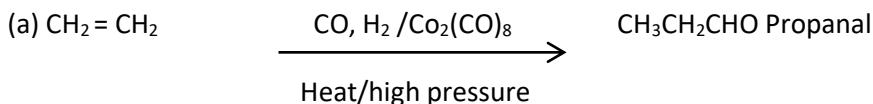
#### Example



### Reaction with carbon monoxide



#### Example



## Preparation of alkenes

### 1. From alcohols

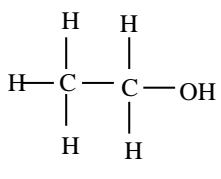
Alkenes are produced by dehydration of alcohols by hot sulphuric or phosphoric acid. Alcohols are organic compounds that contain hydroxyl group (-OH). The mechanism depends on the class of alcohol.

#### Classification of alcohols,

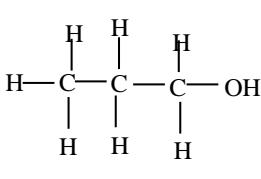
They are **three** classes of alcohols according to the number of alkyl groups attached to a carbon atom that carry -OH group.

- (a) Primary alcohols have one alkyl group on the carbon atom that carry OH group

#### Examples 11



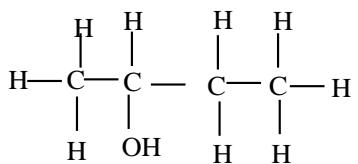
Ethanol



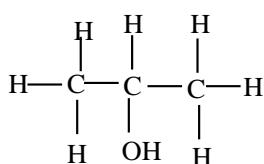
Propan-1-ol

- (b) Secondary alcohols have two alkyl groups attached to a carbon atom that carry OH group

#### Examples 12



Butan-2-ol

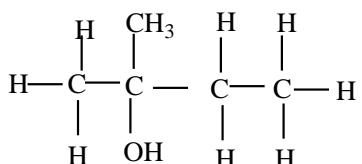


Propan-2-ol

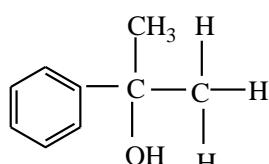
- (c) Tertiary alcohols

Tertiary alcohols have three alkyl groups attached to the carbon atoms that carry OH group

#### Examples



2-methylbutan-2-ol



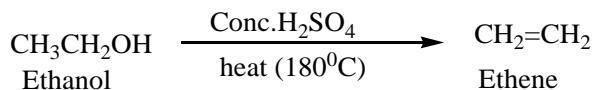
2-phenylpropan-2-ol

#### Mechanism

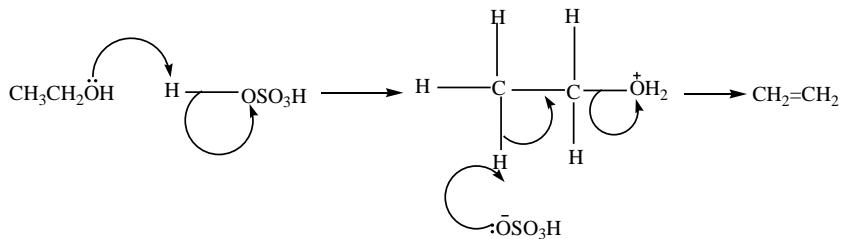
Depends on the class of alcohol.

- (a) Primary alcohol: undergo a mechanism called elimination bimolecular(E2). It is an elimination reaction because water molecule is removed from the alcohol. It bimolecular because the slow step involves two species.

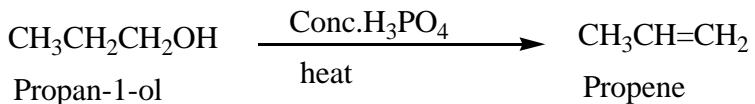
## Example 12



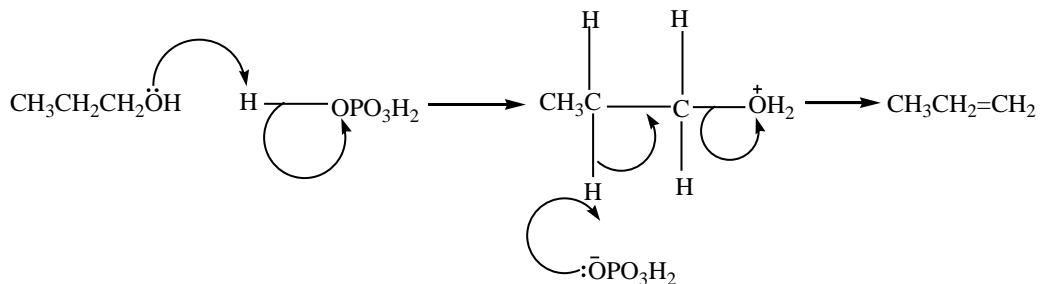
## Mechanism



### Example 13

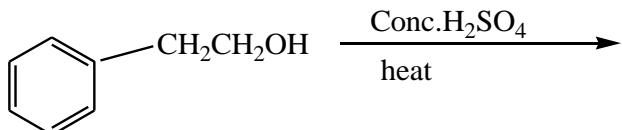


## Mechanism

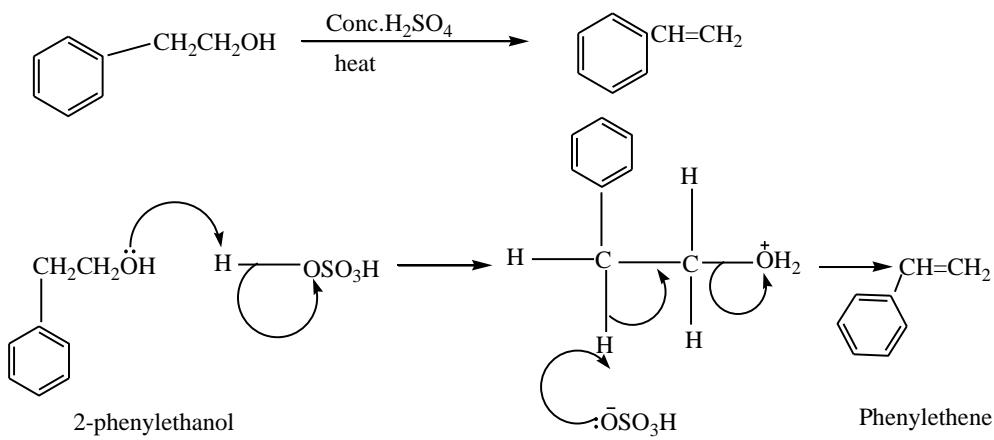


## Trial 6

Complete and write a mechanism

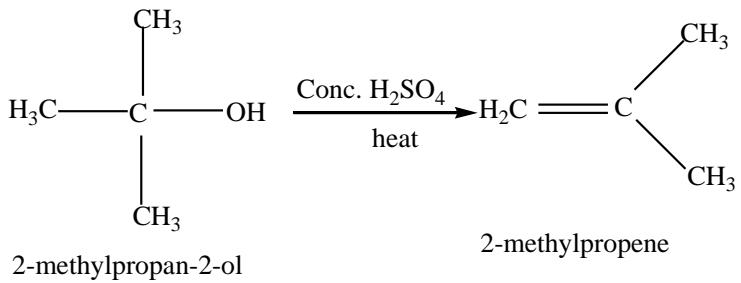


## Solution

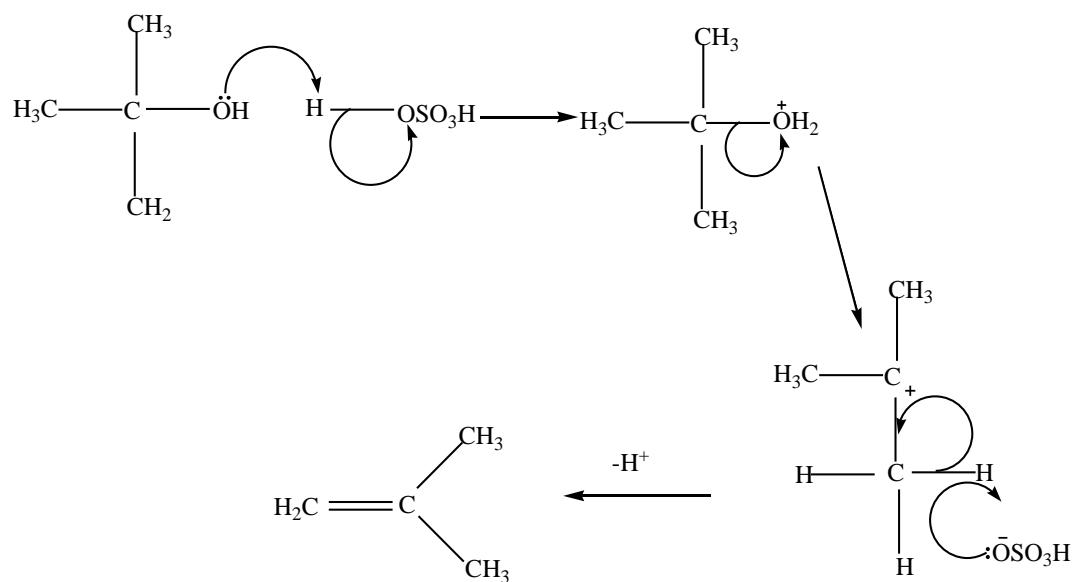


- Secondary alcohols undergo the same mechanism as primary alcohol or that of tertiary alcohol
  - Tertiary alcohol undergo a mechanism called E1 or elimination unimolecular because a water molecule is eliminated and the slowest step involve one molecule only.

## Example 16

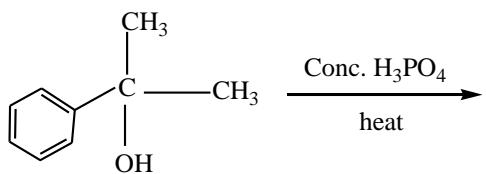


### Mechanism

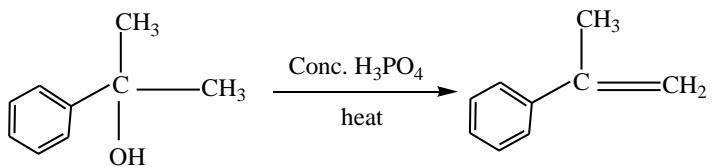


Trial 17

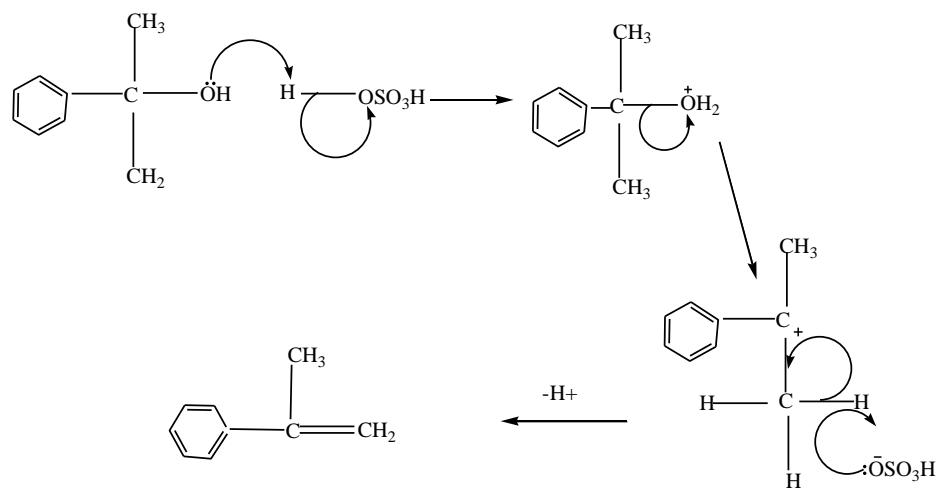
Complete and write a mechanism



Solution



## Mechanism



Preparation of alkenes from alkylhalide (R-X where R is alkyl group and X is Cl, Br or I)

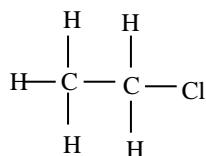
The mechanism depends on the class of alkylhalide

## Classification of alkyl halide

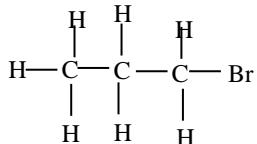
They are **three** classes of alkylhalide according to the number of alkyl groups attached to a carbon atom that carry a halide

- (a) Primary alkylhalide have one alkyl group on the carbon atom that carries a halide.

Examples

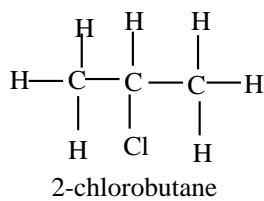
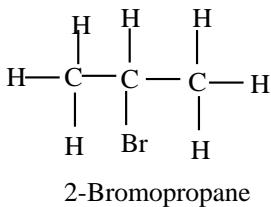


Chloroethane



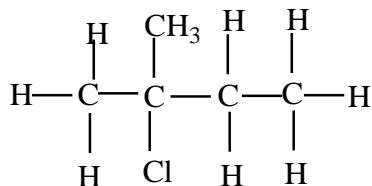
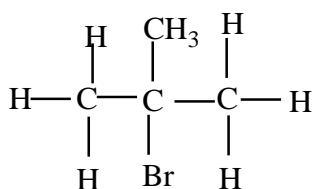
1-Bromopropane

Examples



(c) Tertiary alkylhalide

Tertiary alkylhalide have three alkylgroups attached to the carbon atoms that carry OH group  
Examples

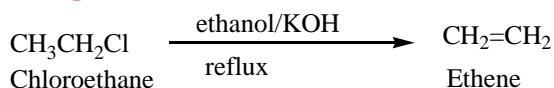


### Mechanism

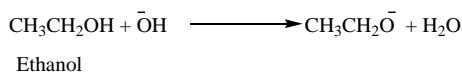
Depend on the class of alcohol.

- (a) Primary alkyl halide: undergo a mechanism called elimination bimolecular(E2). It is an elimination reaction because HX is removed from the alkylhalide. It bimolecular because the slow step involves two species.

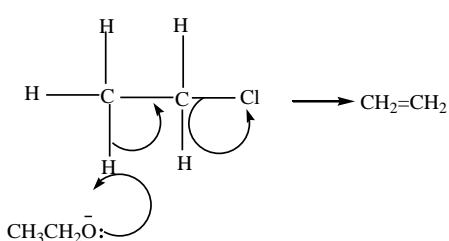
#### Example 17



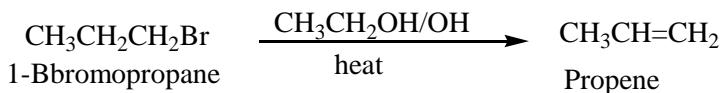
### Mechanism



Then



### Example 18

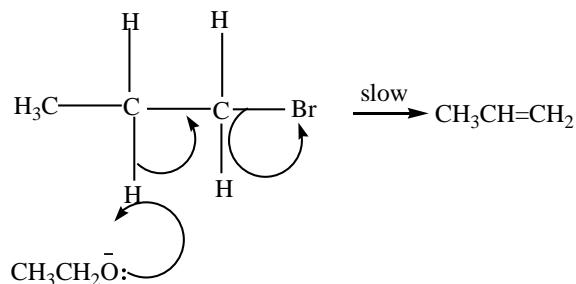


## Mechanism



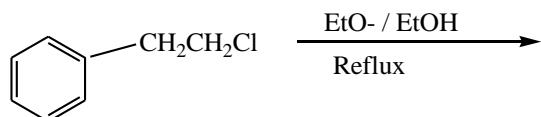
### Ethanol

Then

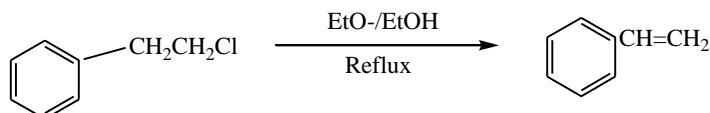


## Trial 7

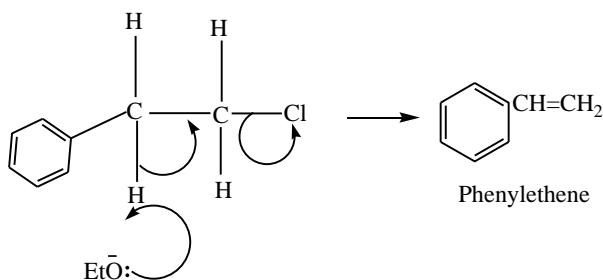
Complete and write a mechanism



## Solution

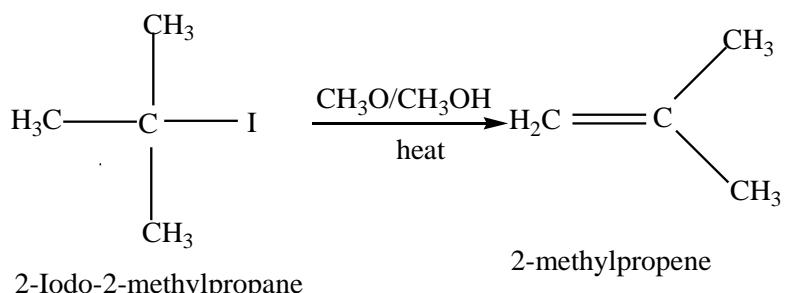


### Mechanism

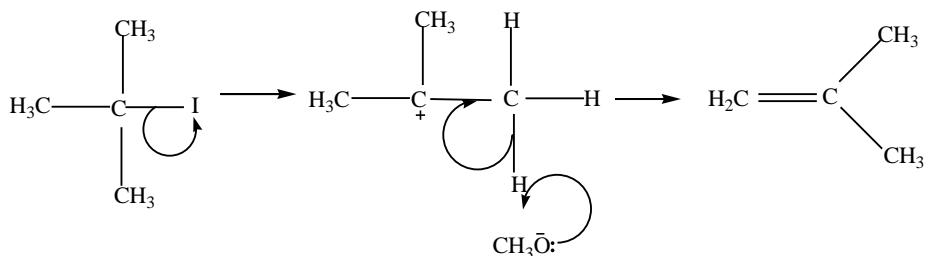


- Secondary alkylhalides undergo the same mechanism as primary alcohol or that of tertiary alcohol
- Tertiary alkylhalides undergo a mechanism called E1 or elimination uni-molecular because a water molecule is eliminated and the slowest step involve one molecule only.

Example

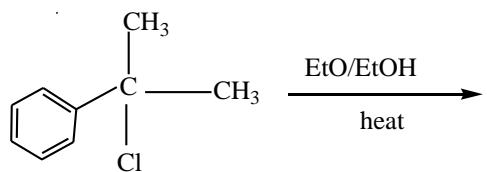


Mechanism

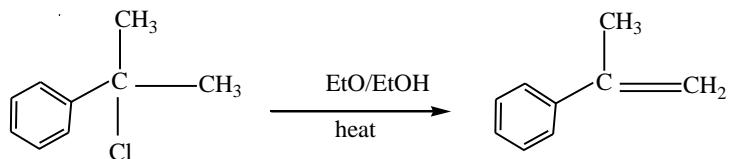


### Trial 8

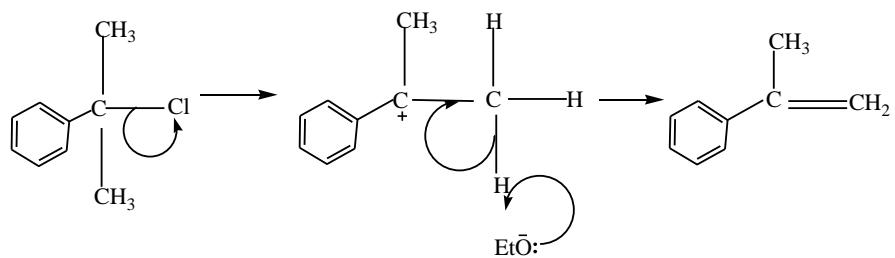
Complete and write a mechanism



### Solution



### Mechanism



## Chapter 3: Alkynes

T

### Alkynes

Alkynes

General formula  $C_nH_{2n-2}$  where  $n \geq 2$

T

hey contain a triple bond

Examples



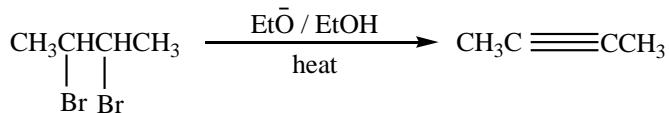
### Preparation

#### 1. From vicinal dihalides.

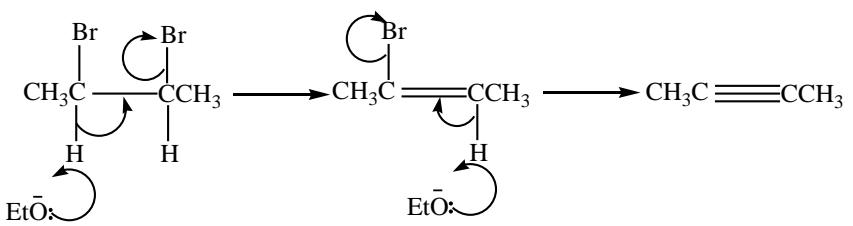
Vicinal dihalides are halides with two halogen atoms on adjacent carbon atoms

The reaction is carried out by refluxing vicinal dihalides with a mixture of an alcohol with its sodium or potassium salt.

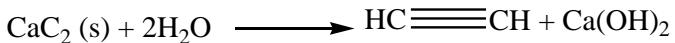
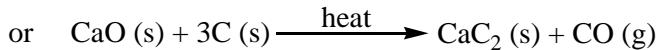
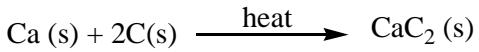
#### Example



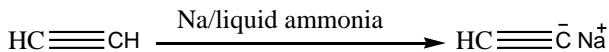
## Mechanism



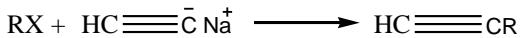
### 2. Preparation of alkyne from carbon



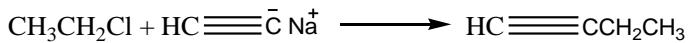
### 3. Preparation of long chain alkyne from ethyne



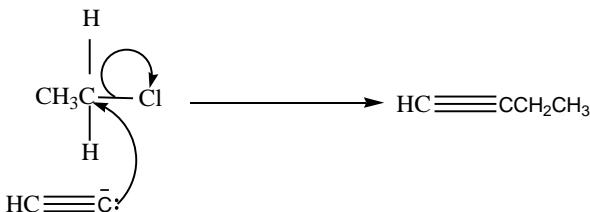
Then



Example



Mechanism



## Exercise

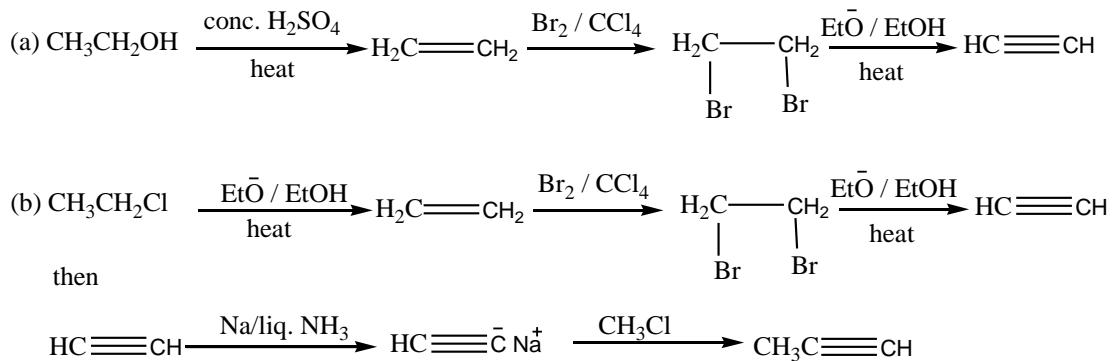
### 4. Synthesize



Questions involving synthesis requires a student to write a series of reactions leading the formation of products from the reactant(s). Most time more than one equation is required because reactions of organic compounds are specific that we may need to convert the reactants into intermediate compounds before a product can be obtained.

For instance, before baking bread, wheat flour is first converted to dough. Usually think of the intermediates to enable you complete a synthesis equation.

### Solution



### Physical properties

- They range from gases to liquids to solids
- They are insoluble in water but soluble in organic solvents

### Chemical properties.

- They burn in oxygen to give carbon dioxide, water and heat.

Example

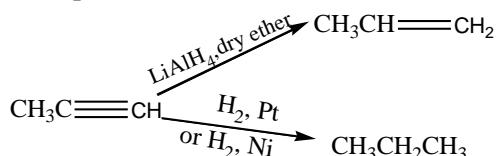


They are used as fuel because they produce heat

- Reduction

Depending on conditions, alkyne may be reduced to alkenes or alkanes

Example



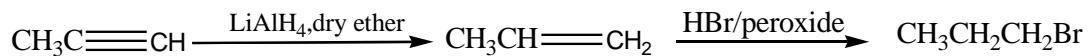
Note that reduction of alkyne to alkene has synthetic value because alkenes are more reactive than alkanes.

Example

Synthesize



### Solution



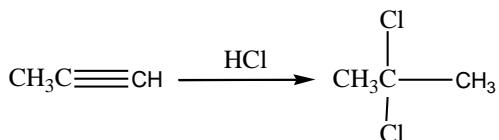
Note that the first part of the synthesis involves **reduction alkynes** to alkene.

### 3. Addition reactions

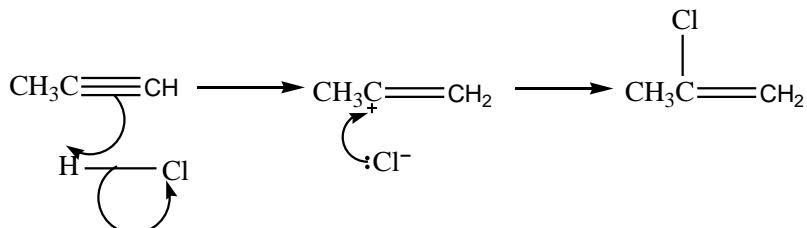
Alkyne undergo addition reactions like alkenes except that the addition occurs twice.

#### (a) Addition of HX (X= Cl, Br, and I)

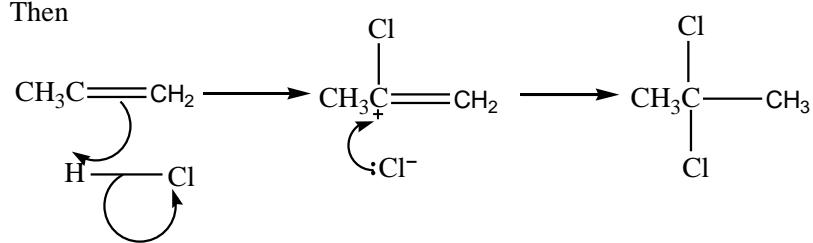
Example



Mechanism



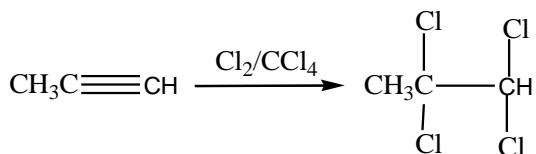
Then



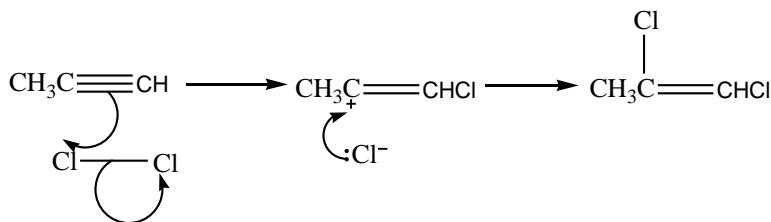
#### (b) Addition of halogens

The halogen is diluted with carbon tetrachloromethane (to prevent explosion)

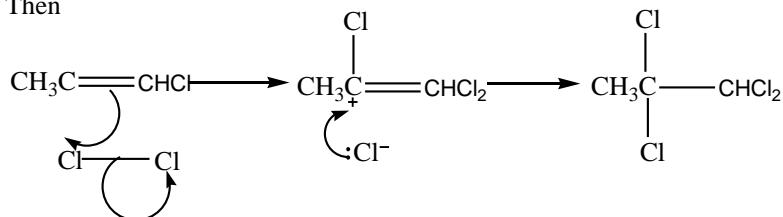
Example



### Mechanism



Then

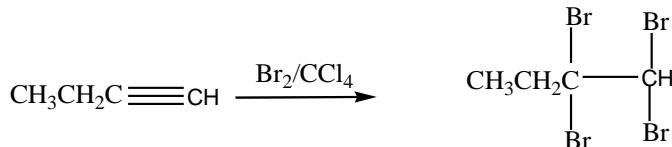


### Exercise

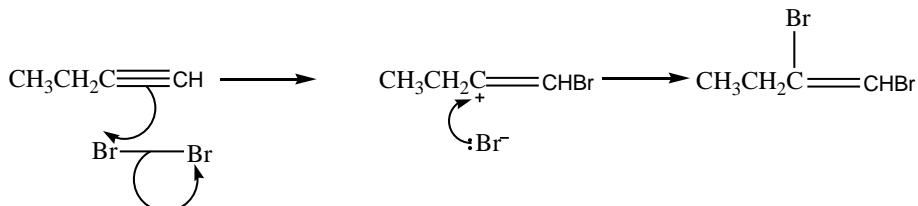
Complete and write a mechanism



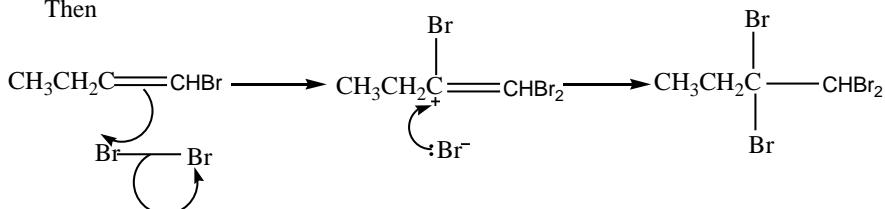
### Solution



### Mechanism



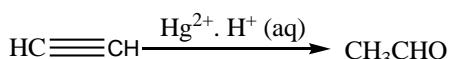
Then



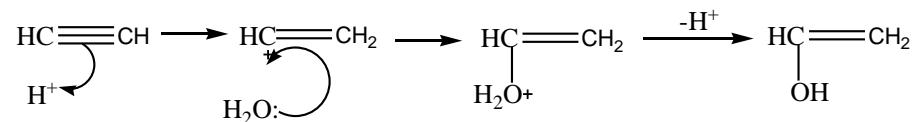
- (c) Addition of water.

The reaction is catalyzed by mercury (II) sulphate and dilute sulphuric acid. Carbonyl compounds are formed.

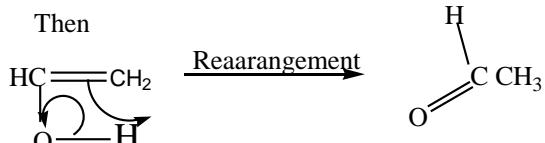
### Example



### Mechanism



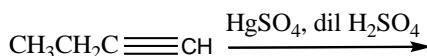
Then



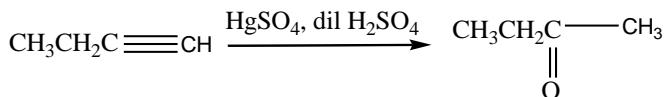
then

### Exercise

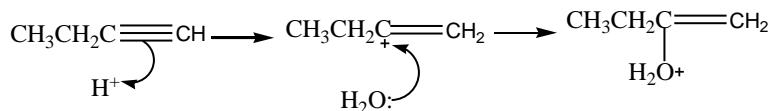
Complete and write a mechanism



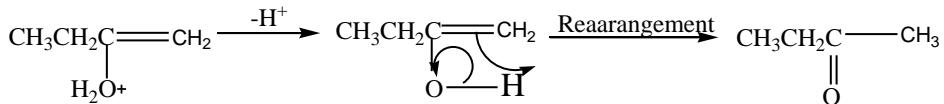
### Solution



### Mechanism



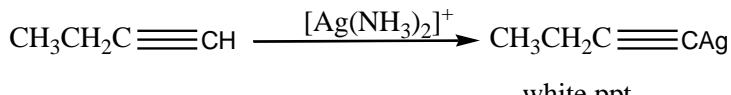
Then



### (d) Reaction of terminal alkyne

Alkynes with a triple bond at the end of the chain react with ammoniacal silver nitrate or ammoniacal copper I chloride to form white precipitate or red precipitate respectively.

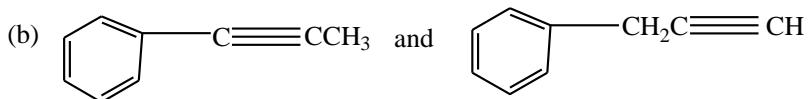
Example



This reaction is used to distinguish alkynes with a triple bond at the end from those with a triple bond in the middle of the chain.

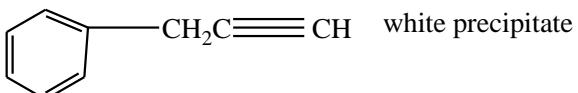
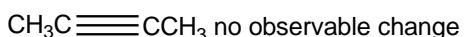
### Exercise

Name one reagent that can be used to distinguish between the following pairs of compounds. In each case state what will be observed when the reagent is treated with each of the compound of the pair.



Reagent: ammoniacal silver nitrate

Observation



### Revision questions

1.  $10\text{cm}^3$  of a hydrocarbon X was exploded with  $70\text{ cm}^3$  of Oxygen and cooled, the final volume was  $55\text{cm}^3$ . The volume of the mixture reduced to  $15\text{cm}^3$  when shaken with concentrated potassium hydroxide solution.
  - Determine the molecular formula of X.
  - Write and name all isomers of X.
  - X formed a red precipitate with ammonial copper 1 chloride,
    - Identify X.
    - Write equations and suggest mechanism for the reaction between X and acidified water, hydrogen in presence of palladium catalyst and hydrogen peroxide.
  - Write equations and conditions to show how X can be prepared from a named
    - Alcohol
    - Alkyl halide.

## Our country, our future

Any consultation Contact: Dr. Bbosa Science +256 776 80 27 09, digitalteachers.co.ug

### Chapter 4: Alkylhalides (R-X, X = Cl, Br, I)

These are compounds with atleast one halogen atom attached to the parent chain.

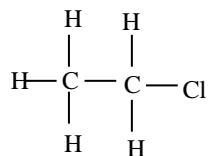
#### Classification of mono substituted alkylhalide

As seen earlier, they are classified like alcohols.

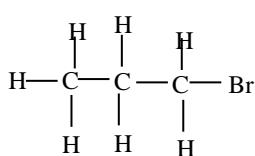
They are **three** classes of alkylhalide depending on the number of alkyl groups attached to a carbon atom that carry a halide.

(a) Primary alkylhalide have **one** alkyl group on the carbon atom that carries a halide.

Examples



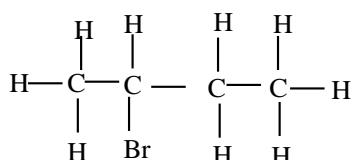
Chloroethane



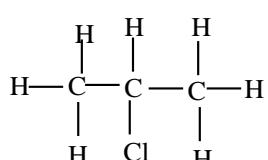
1-Bromopropane

(b) Secondary alkylhalide have **two** alkyl groups attached to a carbon atom that carry a halide

Examples



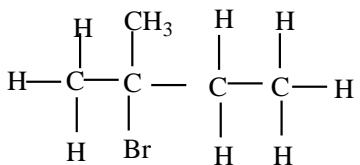
2-Bromobutane



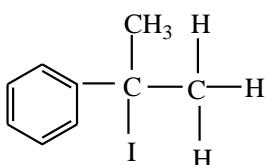
2-chloropropane

(c) Tertiary alkylhalide

Tertiary alkylhalide have **three** alkylgroups attached to the carbon atoms that carry OH group  
Examples



2-bromo-2-methylbutanane

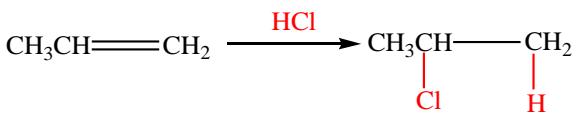


2-iodo-2-phenylpropane

### Preparation of alkylhalide

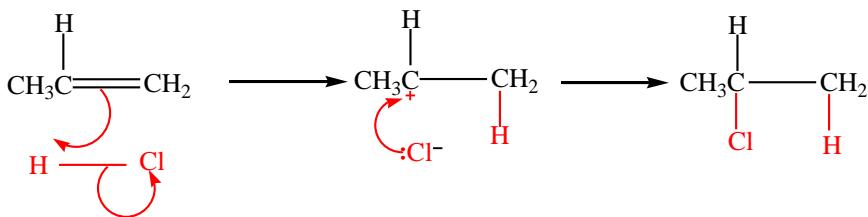
1. By reacting alkenes with halogenhalide

Example



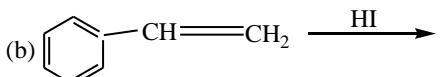
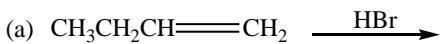
### Mechanism

Remember: the reaction occurs at **the double bond** and hydrogen atom goes to a carbon that carries highest number of hydrogen atoms.



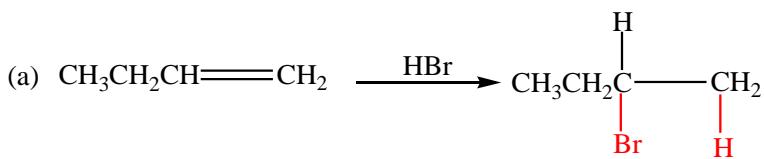
### Exercise

Complete and write a mechanism for the following reactions (mark yourself after)

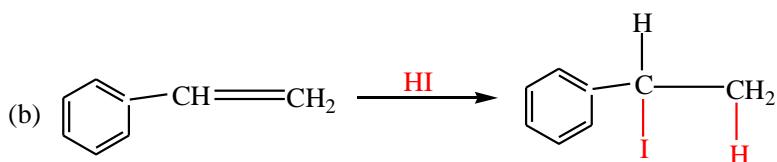
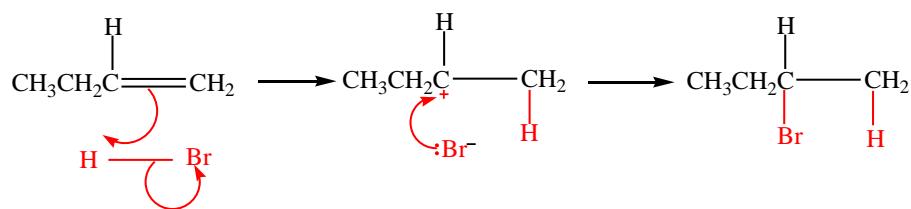


### Mark yourself

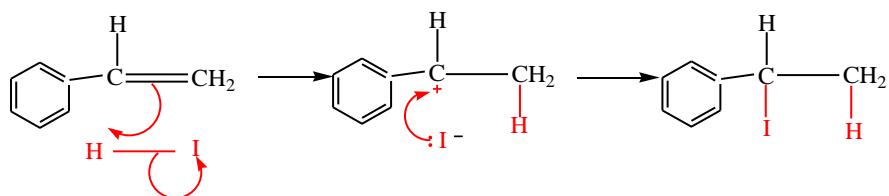
In these reactions, the double bond breaks and hydrogen halide adds itself across the carbon atoms that were forming the double bond. Hydrogen atom add to a carbon atom the carries the highest number of hydrogen atom of those that form a double bond. Make sure you account for the charges.



Mechanism

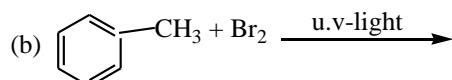
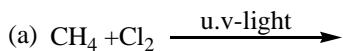


Mechanism



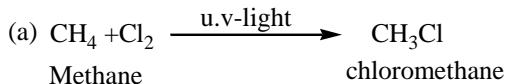
2. By reacting chlorine gas or bromine with alkanes. The reaction occurs in the presence of u.v light. This was dealt with when dealing with reactions of alkanes.

Complete the following equation and write a mechanism

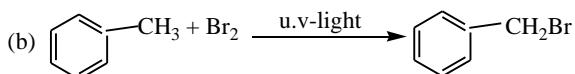
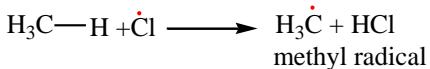
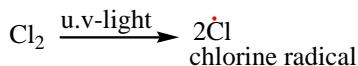


Mark yourself

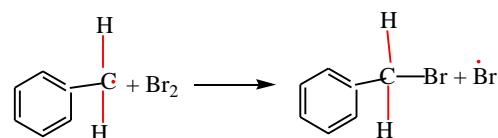
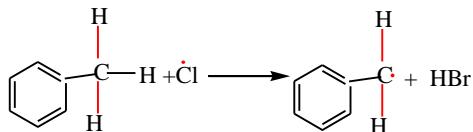
These reactions follow a free radical mechanism, be keen to observe the initiation and formation of free radicals as the reaction proceeds. Every dot (un paired electron) must be accounted for.



### Mechanism



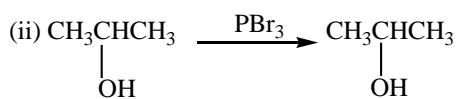
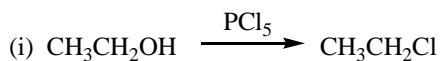
### Mechanism



### 3. By reacting alcohols with

(a) Phosphorus halide

## Examples



(b) With HX (X= Cl, Br, I)

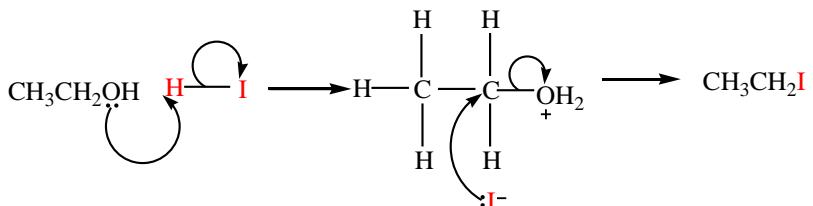
HI and HBr react readily with alcohols but the reaction of HCl is catalyzed with anhydrous zinc chloride. The mechanism of the reaction depends on the class of alcohol. Though secondary alcohols react like either primary or tertiary alcohols.

## Examples

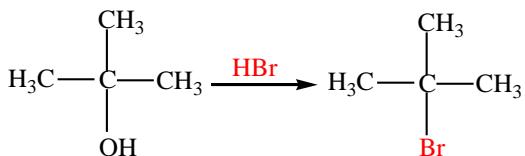
### Primary alcohol



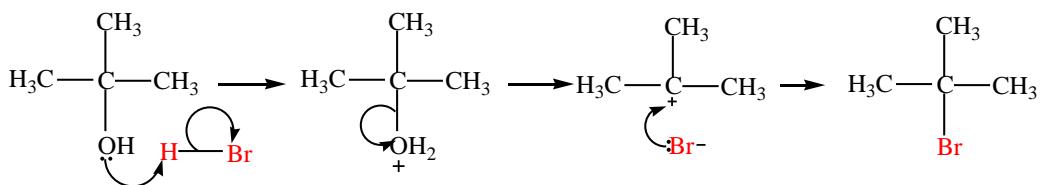
### Mechanism



## Tertiary alcohol

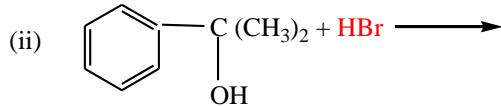
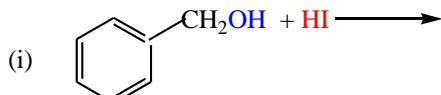


### Mechanism

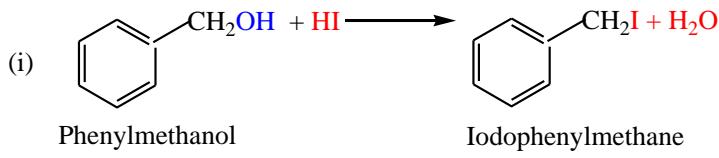


## Exercise

Complete and write a mechanism, thereafter mark yourself

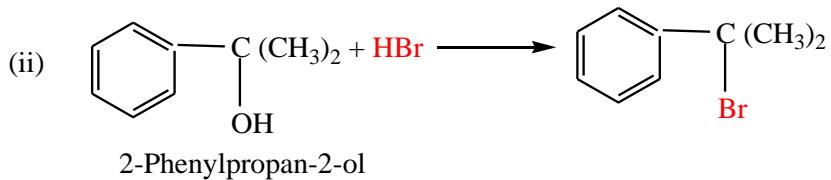
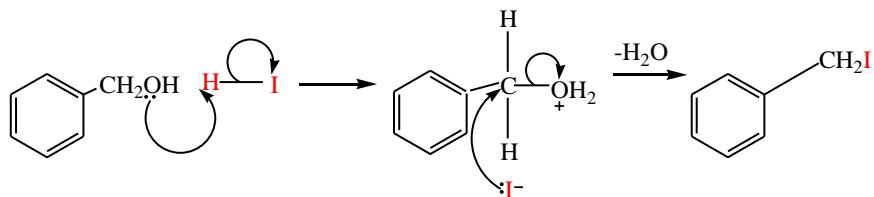


## Mark yourself



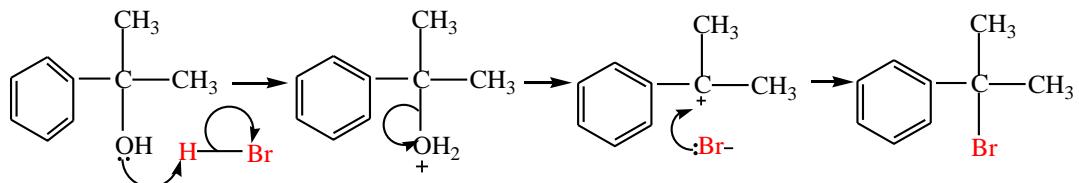
## Mechanism

Note that phenylmethanol is a primary alcohol



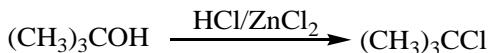
### Mechanism

Please note that 2-phenylpropan-2-ol is a tertiary alcohol

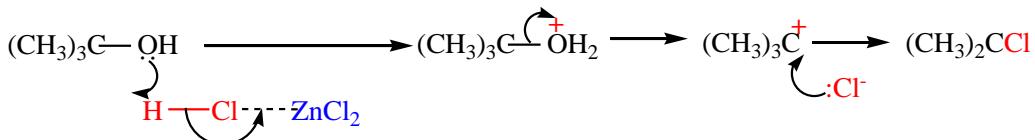


- (c) Reaction of HCl with alcohols is catalyzed by anhydrous zinc chloride because HCl bond is strong. Primary alcohol does not react, secondary alcohol reacts slowly, and tertiary alcohol reacts faster.

Example

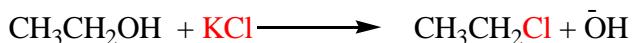


Mechanism

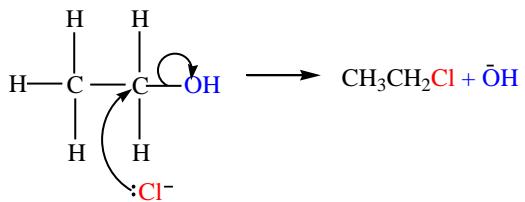


- (d) Reaction of alcohol with KX (X= Cl, Br, I)

The mechanisms depend on the class of alcohols. The mechanism of secondary alcohols  
Primary alcohol



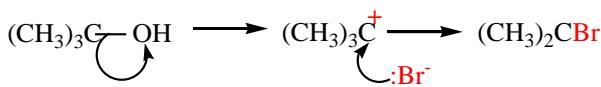
Mechanism



Tertiary alcohol



Mechanism

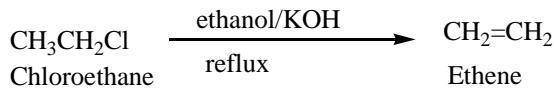


### CHEMICAL PROPERTIES

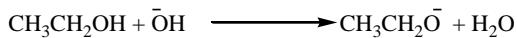
#### (a) Formation of alkenes

Alkylhalides react with hot alcoholic potassium hydroxide to form alkenes. The mechanism depend on the class of alkylhalide but mechanism of reaction for secondary alkylhalide is similar to that of the primary or tertiary alkylalide. These reactions were also considered when we dealt with preparation of alkene

#### (i) Example for primary alkylhalides,

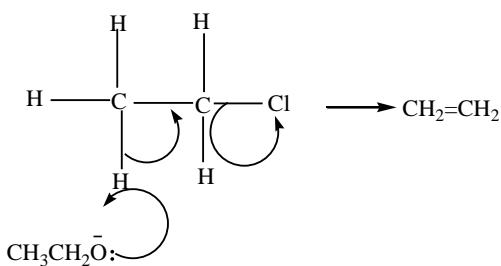


Mechanism

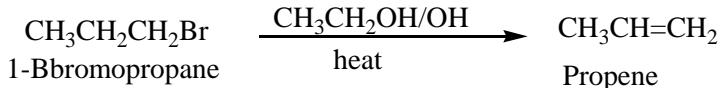


Ethanol

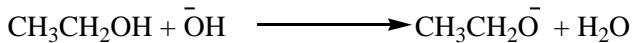
Then



#### Example II

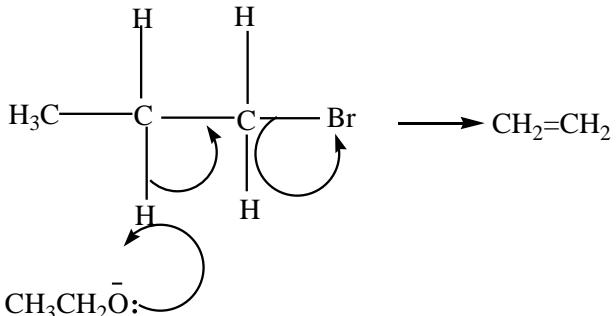


## Mechanism



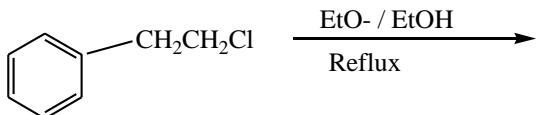
### Ethanol

Then

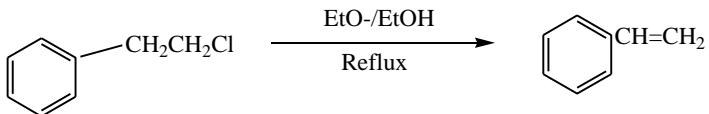


## Exercise

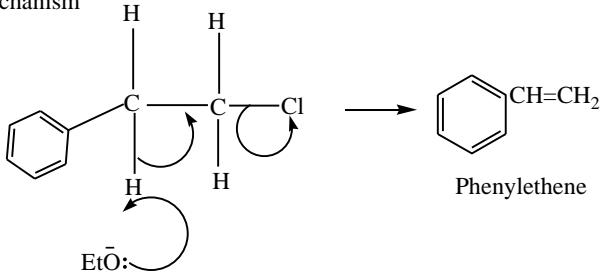
Complete and write a mechanism



## Solution

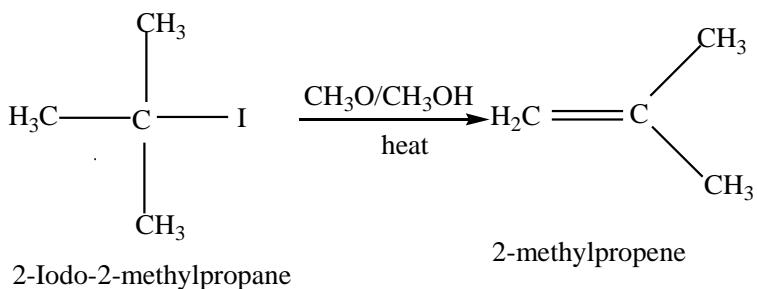


## Mechanism

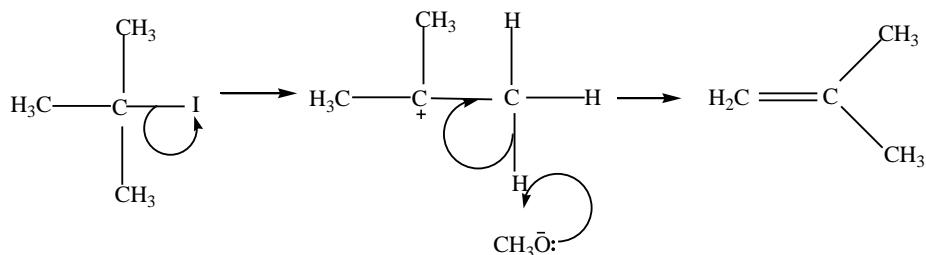


- (ii) Secondary alkyl halides undergo the same mechanism as primary alkyl halides or that of tertiary alkyl halides
  - (iii) Tertiary alkyl halides undergo a mechanism called E1 or elimination unimolecular because a water molecule is eliminated and the slowest step involves one molecule only.

### Example

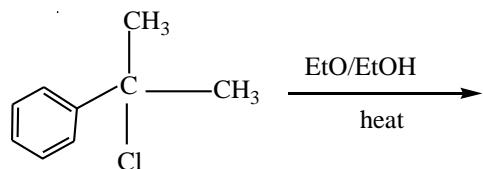


### Mechanism

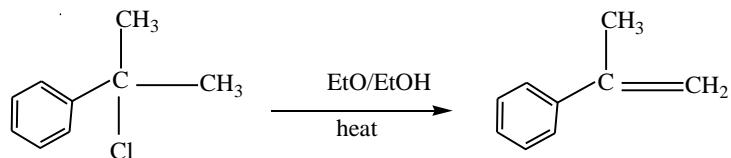


### Exercise

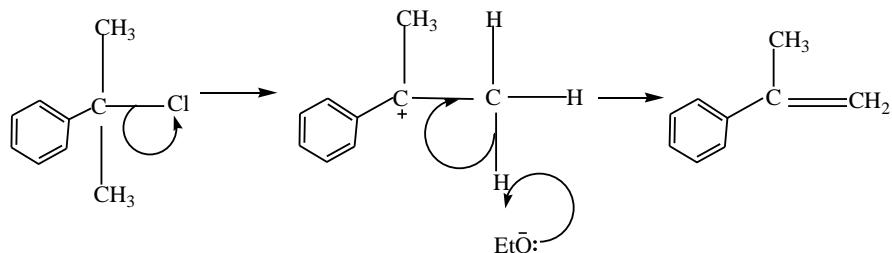
Complete and write a mechanism



### Solution



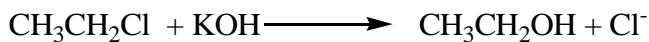
### Mechanism



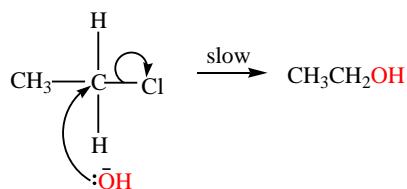
### (b) Reaction of alkyl halide with alkalis (NaOH or KOH)

Alkyl halides react with hot alkalis to form alcohols. The secondary alkyl halides react by either mechanism of primary or tertiary alkyl halides.

## Primary alkyl halide



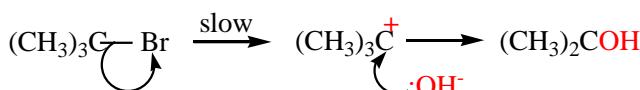
### Mechanisms



The mechanism is described as  $\text{S}\text{N}^2$  (substitution nucleophilic bimolecular) because a nucleophile ( $-\text{OH}$ ) substitutes a halide atom and the slow step in the reaction involved to species i.e.  $-\text{OH}$  and alkylhalide.

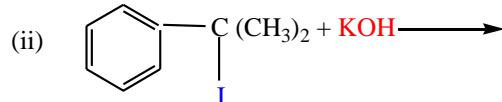
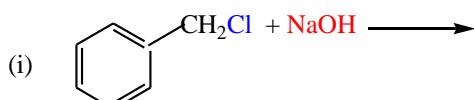


### Mechanism

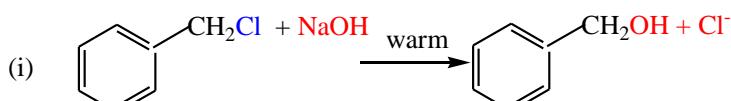


### Exercise

Complete and write a mechanism, thereafter mark yourself



### Mark yourself

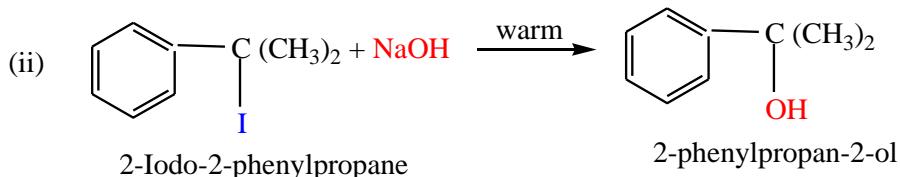
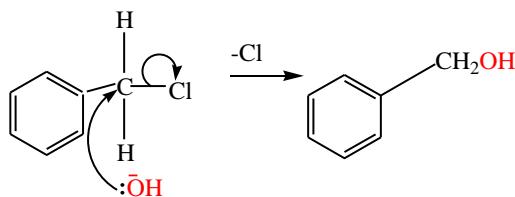


Chlorophenylmethane

Phenylmethanol

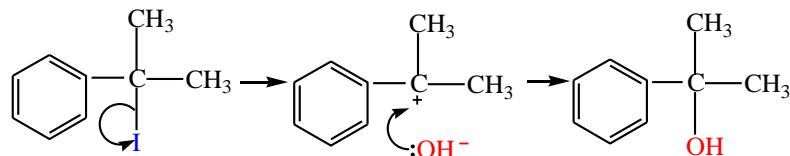
## Mechanism

Note that chlorophenylmethane is a primary alkyl halide



## Mechanism

Note that 2-iodo-2-phenylpropane is a tertiary alkyl halide



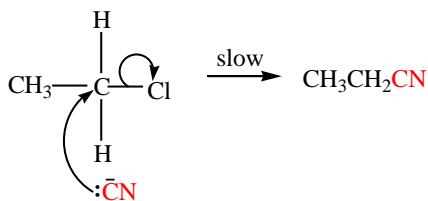
### (c) Reaction with potassium cyanide

Alkyl halides react with potassium cyanide to form nitrile. This reaction is important because it increases the carbon chain by one carbon atom. Primary alkyl halide undergo  $SN^2$  while tertiary alkyl halide undergo  $SN^1$  mechanism whereas secondary alkyl halides undergo either mechanism.

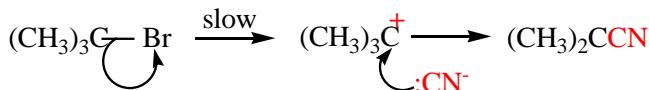
### Examples



Mechanism (note that chloroethane is a primary alkyl halide)

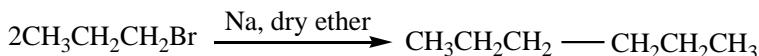
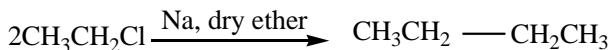


Mechanism (2-bromo-2-methylpropane is tertiary alkyl halide)



(d) Coupling reaction

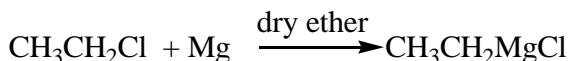
Two alkyl halides couple in presence of sodium and dry ether or zinc-copper couple to form alkane of twice the number of carbon atoms as the parent alkyl halide.



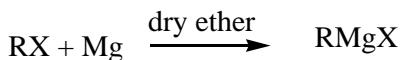
(e) Formation of Grignard's reagent

Alkyl halides react with magnesium in presence of dry ether to form compound called Grignard's reagent.

Example

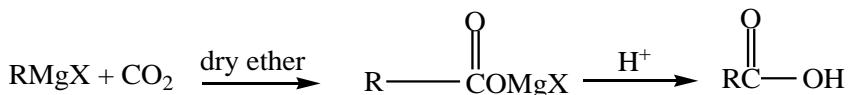


Generally



Grignard's reagents are important synthetic molecules that enable us to increase the parent carbon chain by unlimited number of carbon atoms in synthesis.

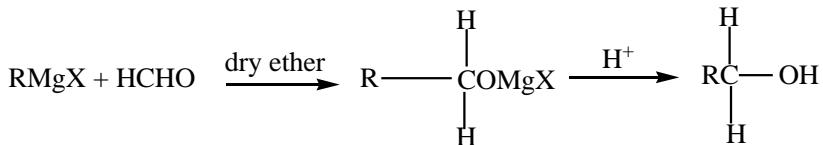
- (i) Grignard's reagent reacts with carbon dioxide to produce carboxylic acid. The parent chain increase by one carbon atom.



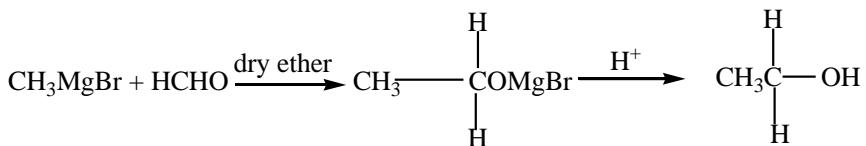
Example



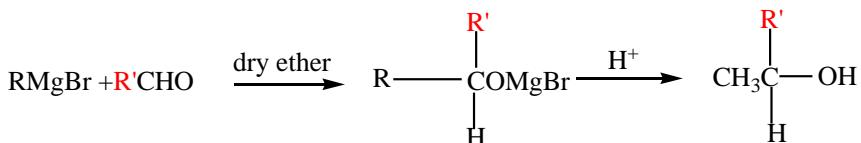
- (ii) Gridnard's reagent reacts with methanal to produce primary alcohols. The parent chain increase by one carbon atom.



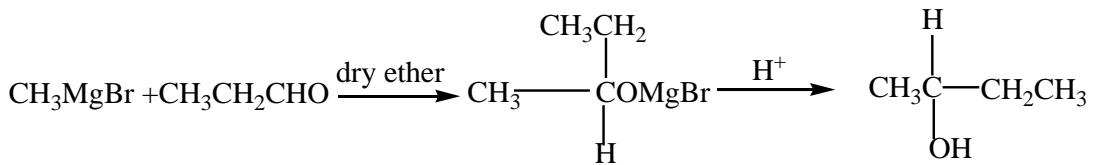
Example



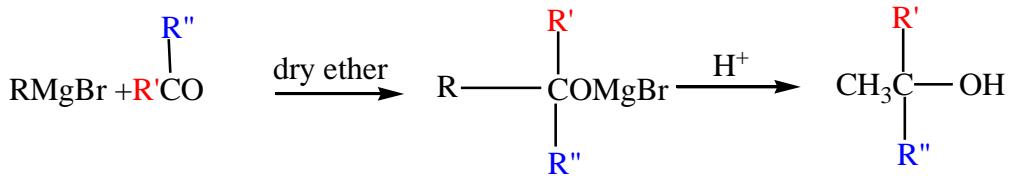
- (iii) Gridnard's reagent reacts with aldehydes to produce secondary alcohols.



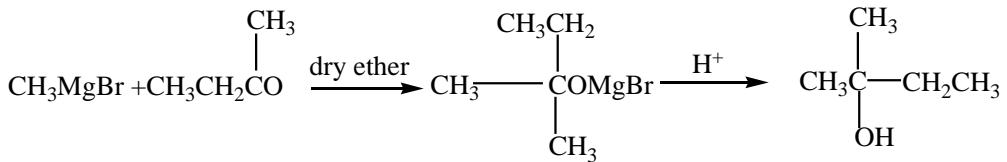
Example



- (iv) Gridnard's reagent reacts with ketones to produce secondary alcohols.



Example





## Chapter 5: Amines

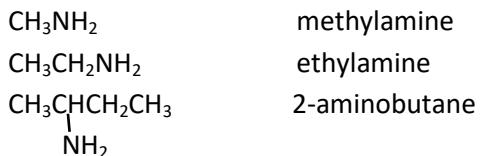
These are organic derivatives of ammonia

### Classification

According to the number of alkyl groups attached to the nitrogen atom

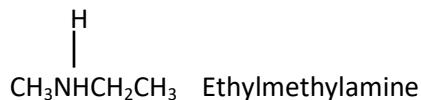
- (a) Primary amines: have only one alkyl group attached. i.e.  $\text{RNH}_2$

Example



- (b) Secondary amines: have two alkyl groups attached to a nitrogen atom,  $\text{R}_2\text{NH}$

Examples



(in alphabetical order)

- (c) Tertiary amine: have 3 alkyl groups on the nitrogen atom i.e.,  $\text{R}_3\text{N}$ , where R is an alkyl group.



## Physical properties

### 1. Boiling and melting points

- (a) Amines are polar compounds and therefore higher melting and boiling points than non-polar compounds of similar molecular mass due to dipole-dipole intermolecular forces or hydrogen bonding,
- (b) Primary and secondary amines have higher melting points and boiling points than tertiary amines because tertiary amine do not form intermolecular hydrogen bonds
- (c) Primary amines have higher melting and boiling points than secondary amines because they form many hydrogen bonds per molecule.

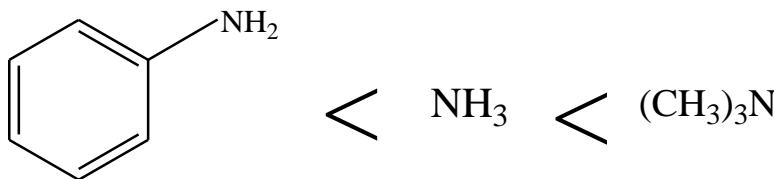
### 2. Solubility

Amines are soluble in water because they can form hydrogen bonds with water but the solubility decrease with alkyl chain length.

### 3. Basicity of amines

Like ammonia, amines dissolve in water to form alkaline solution.

The strength of the alkaline solution is measured by the function  $K_b$



$$K_b = \frac{[RN^-][OH^-]}{[RNH_2]}$$

The higher the  $K_b$  the stronger the base.

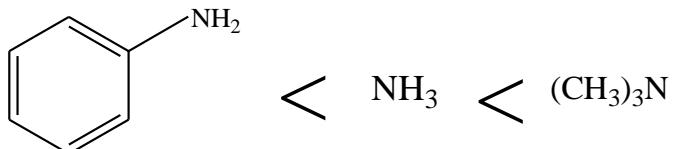
The ability to form alkaline solution, by amines, is due to the presence of a lone pair of electron on the nitrogen atom.

- (i) Groups (such as alkyl groups) that donate electrons increase the electron density of the lone pair on the nitrogen atom. This increases the ability of alkylamine to abstract a proton from water and form stronger alkaline solutions. Thus, secondary amines are stronger bases than primary amines than ammonia because secondary amine has two electron donating groups, primary amines one, whereas, amines have none. However, tertiary amines are weaker bases than either secondary or primary amines because their iminium ions are poorly solvated or hydrated.
- (ii) Groups that withdraw electrons from nitrogen atoms like phenyl group, make amines weaker bases because they reduce the ability of the lone pair of electron on the nitrogen atom and its ability to abstract a proton from water.

## Exercise

Explain the following observations

- (i) The basic strength of the following amine is in order.



- (ii) The boiling points of the following amines are

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 = 66.8^\circ\text{C}$$

$$\text{CH}_3\text{CH}_2\text{NCH}_3 = 45.4$$

$$(\text{CH}_3)_3\text{CN} = 7.7^\circ\text{C}$$

- (iii) The acid constants  $K_a$  for the following amines are:

Amine	$K_a$ (mol dm <sup>-3</sup> )
-------	-------------------------------

$$(\text{CH}_3)_3\text{N} \quad 9.70$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \quad 10.67$$

## Chemical properties

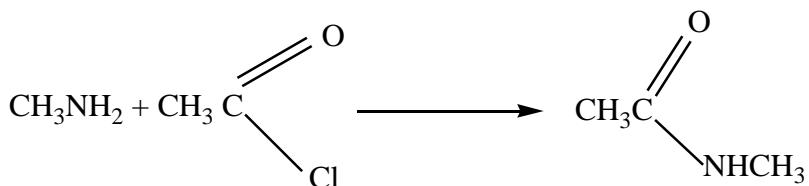
1. They react with acids to form salts

Example

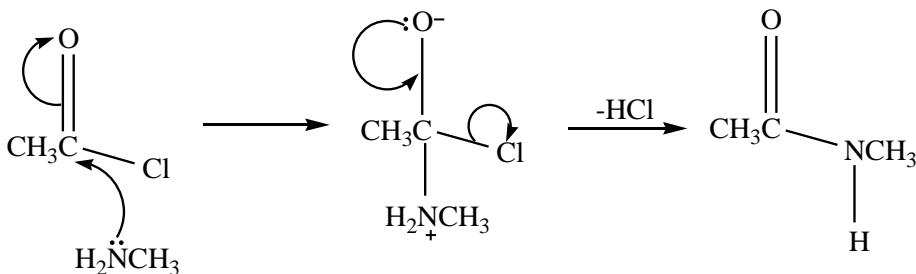


2. Primary and secondary amines react with alkanoyl halides to form amides

Example

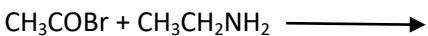


## Mechanism



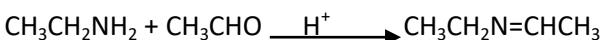
## Exercise

Complete and write a mechanism

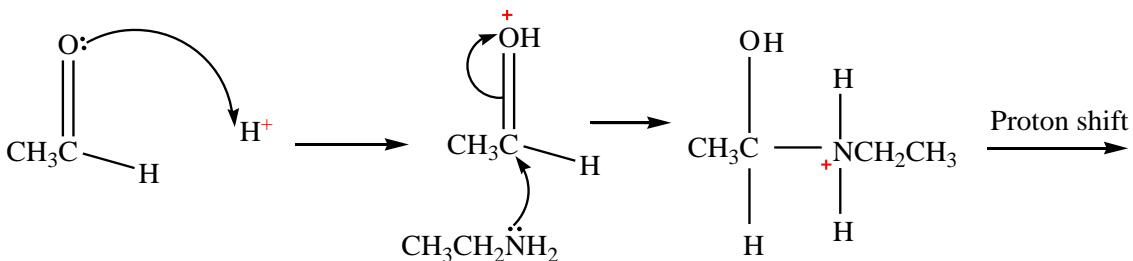


3. Primary amines undergo condensation reaction with carbonyl compounds between pH 4 -5 to form **imines**. At lower pH the **amine is protonated** as well making it a weaker nucleophile.

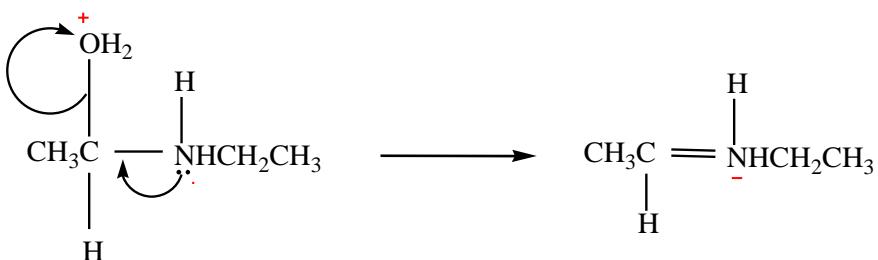
Example



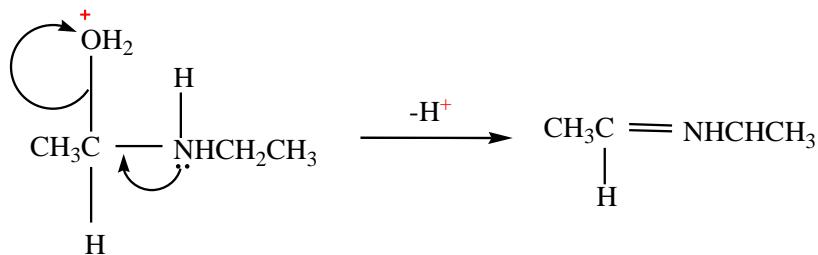
## MECHANISM



Then



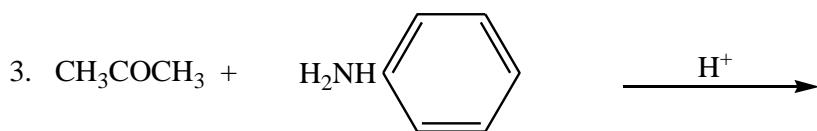
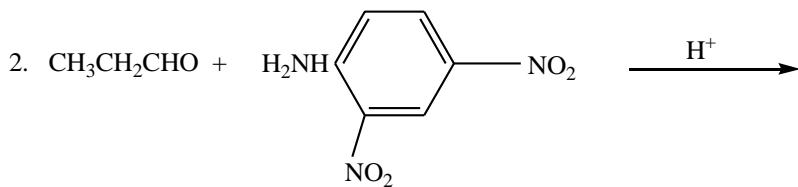
Then,



**NB:** Take note of the movement of the proton

## Exercise

Complete the following equations and write appropriate mechanism.



## Distinguishing between primary, secondary and tertiary amines

A. Reagent: nitrous acid ( $\text{NaNO}_2$ ,  $\text{HCl}$  ( $0\text{-}5^\circ\text{C}$ ))

## Observation

(i) Primary amine: effervescence

## Equation



(ii) Secondary amines: yellow oil liquid

Equation



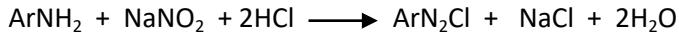
(iii) Tertiary amines: no observable change due to the formation of soluble diazonium salts

Equation

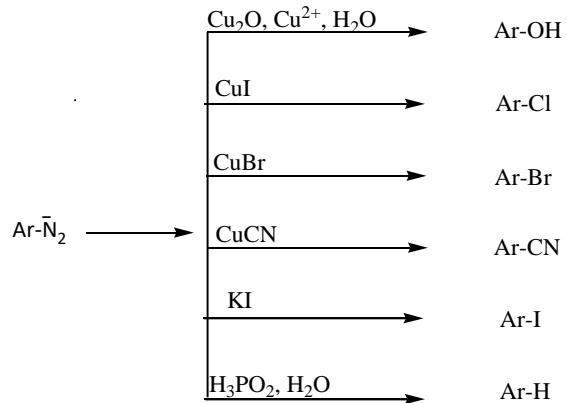


(iv) Aromatic amine: no observable change due to the formation of soluble diazonium salts

Equation



Reaction of aromatic diazonium salts



## B. The Hinsberg test

Procedure: a mixture of small amount of the amine and benzenesulfonyl chloride is shaken with potassium hydroxide, time allowed for the reaction to take place and then the mixture is acidified.

Primary amine: forms a colorless solution with potassium hydroxide, forming a precipitate when the mixture is acidified.

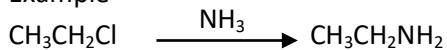
Secondary amine: forms a precipitate with potassium hydroxide insoluble when the mixture is acidified

Tertiary amine: no observable change

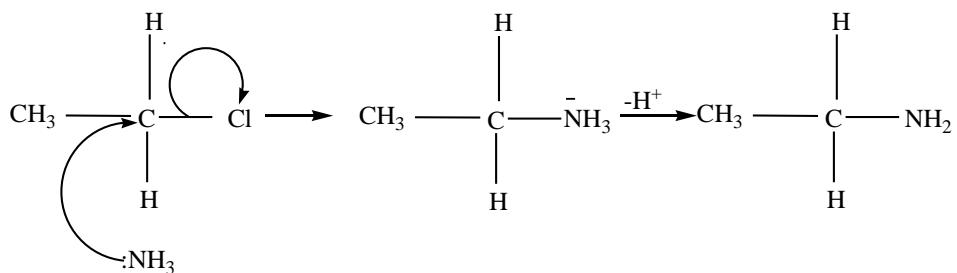
## PREPARATION OF AMINES

### 1. Reaction of alkyl halides with ammonia

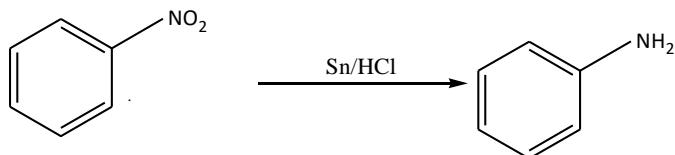
Example



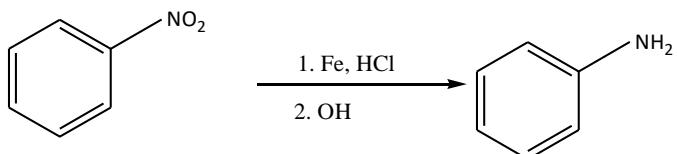
#### Mechanism



### 2. By reduction of nitroalkane

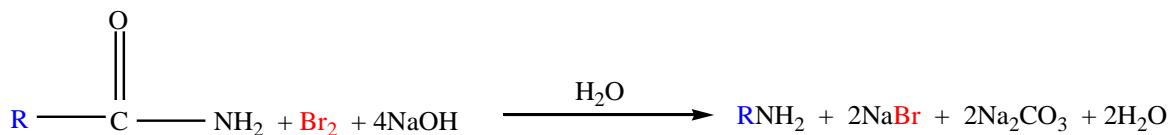


Or

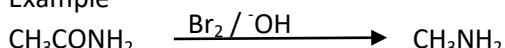


### 3. By Hofmann degradation

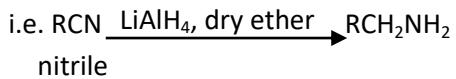
Amides with no substituent on the nitrogen atom react with solution of bromine or chlorine in sodium hydroxide to yield amines.



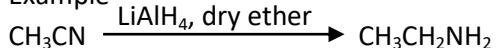
Example



4. By reduction of nitriles



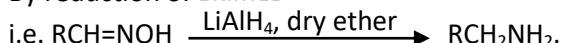
Example



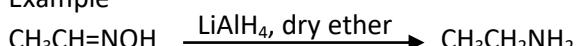
Nitrile can be obtained by reacting alkyl halides with potassium cyanide.



5. By reduction of oximes



Example



thanx

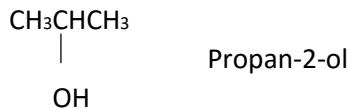
# Alcohols/Alkanols

These are organic compounds that contain at least one hydroxyl group (-OH) attached to saturated carbon atom.

## Classification

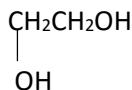
### (a) According to the number of -OH group

- (i) Monohydric alcohols have one hydroxyl (-OH) group Example

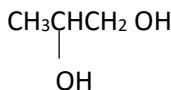


- (ii) Dihydric alcohols or glycols have two hydroxyl groups

Examples

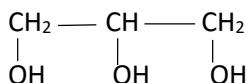


Ethan-1,2-diol



Propane-1,2-diol

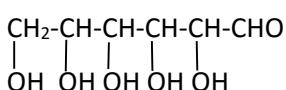
- (iii) Trihydric alcohols have three hydroxyl groups.



Propane-1,2,3-triol

- (iv) Polyhydric alcohols or polyol contain more than three hydroxyl groups

e.g. Sugar



### (b) Classification of monohydric alcohols

They are classified according to the number of alkyl groups attached to the carbon atom that bear a hydroxyl (OH) group.

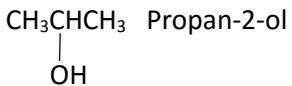
- (i) Primary alcohols have one alkyl group attached to the carbon atom that carry OH group, i.e. ROH.

Example



- (ii) Secondary alcohol: have two alkyl groups attached to the carbon atom that bear OH group, i.e.  $\text{R}_2\text{CHOH}$

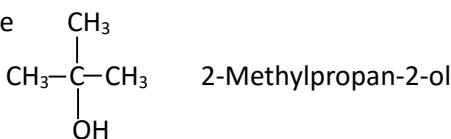
Example



- (iii) Tertiary alcohols: have three alkyl groups attached to a carbon atom that bear OH group

i.e.  $\text{R}_3\text{COH}$

Example



## Nomenclature

- (a) Are named by replacing the final “e” in the corresponding alkanes with “ol”
- (b) The hydroxyl group is taken as a substituent group, and its position is given by numbering the carbon atoms in the chain from the side nearest to the carbon atom that carry OH group.

Examples



## Physical properties

1. Alcohols have high melting and boiling points than corresponding hydrocarbons of similar molecular masses due to intermolecular hydrogen bonds.consequently alcohols ate either liquids or solids.

Example

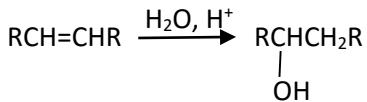
Propane (44) Bpt =  $-42^{\circ}\text{C}$

Ethanol (46) Bpt =  $78^{\circ}\text{C}$

2. Lower members are completely soluble in water due to the formation of hydrogen bonds withwater. But solubility of alcohols decrease as alkyl group lengths increase due to increase in “alkane like” character.

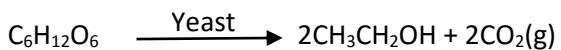
## Preparation of alcohols

- (a) Industrial preparation
  - (i) From petroleum products,e.g. alkenes

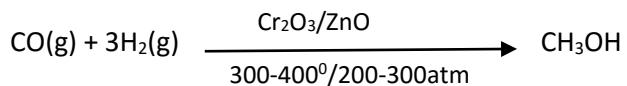


(ii) Fermentation of sugars

Ethanol can be made by fermentation of sugars. Fermentation is usually carried out by adding yeast to a mixture of sugar and water.

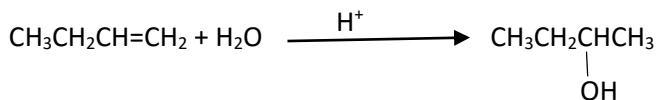


(iii) Methanol is produced by catalytic reduction of carbon monoxide.

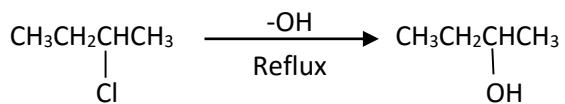


(b) Laboratory preparation

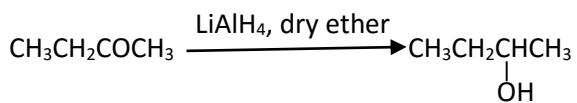
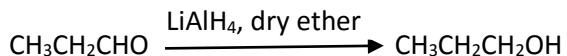
(i) Hydration of alkenes in presence of acid catalyst



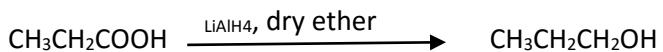
(ii) By hydrolysis of alkyl halides using aqueous alkali



(iii) By reduction of carbonyl compounds (aldehyde and ketones) using lithium aluminium hydride ( $\text{LiAlH}_4$ ) in presence of dry ether.



(iv) Reduction of carboxylic acids using  $\text{LiAlH}_4$  in dry ether



## Absolute ethanol

All aqueous solutions of ethanol yield, on fractional distillation a constant boiling mixture (azeotrope) of 96% ethanol and 4% water known as rectified spirit.

- (i) In the laboratory rectified spirit is stored over quick lime overnight. Quick lime dehydrates the mixture; then pure ethanol called absolute ethanol is distilled.



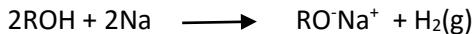
- (ii) In industry, benzene is added to the rectified spirit. Distillation yields three fractions  
At  $65^\circ\text{C}$  a constant boiling mixture of ethanol, benzene and water.  
At  $68^\circ\text{C}$  a constant boiling mixture of ethanol and water  
At  $78^\circ\text{C}$  pure ethanol distills of

## Reactions of monohybrid alcohol

- a. Cleavage of O-H bond
- b. Cleavage od C-O bond
- c. Oxidation
- d. Dehydration

### (a) Cleavage of O-H bond

- (i) Behavior as a weak acid



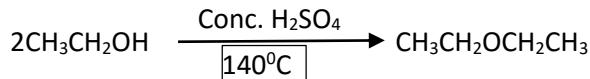
Acidity: primary alcohol > secondary alcohol > tertiary alcohol

- (ii) Behavior as a base

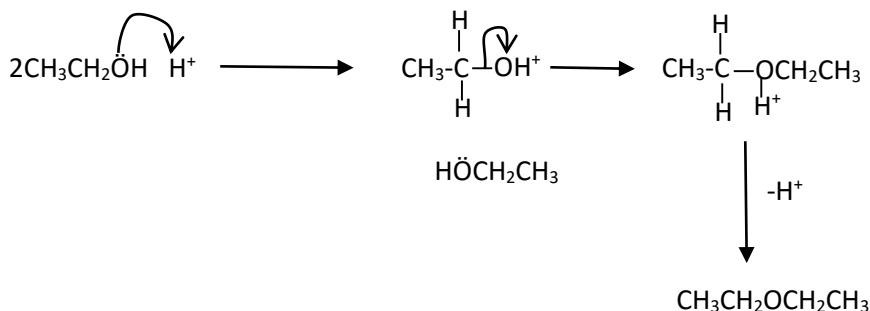


- (iii) Formation of ether

Ethanol reacts presence of concentrated sulphuric acid at  $140^\circ\text{C}$  to form diethyl ether.



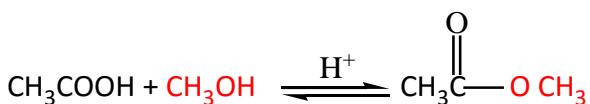
Mechanism



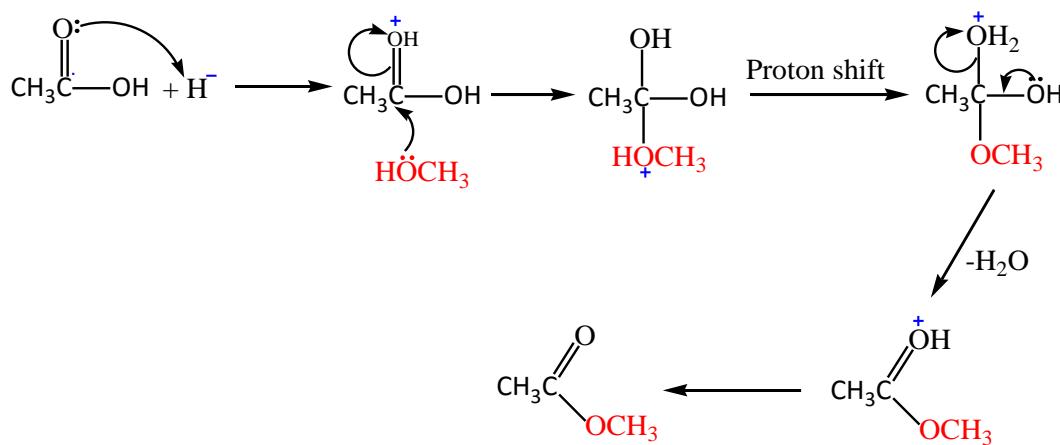
(iv) Formation of esters

- (a) Alcohols react with carboxylic acids in the presence of a mineral acid (phosphoric or sulphuric acid) to form esters. However, this is not a good method because the reaction is reversible and does not go to completion.

Example



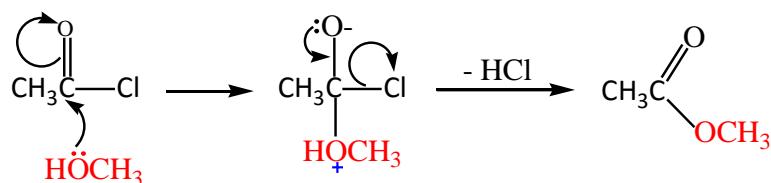
Mechanism



- (b) Alcohols react with acid halides to form esters.

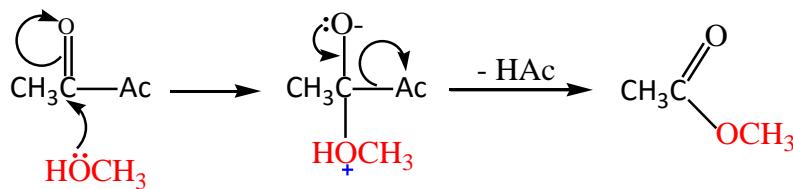


Mechanism



- (c) Alcohols react with acid anhydride to form esters.



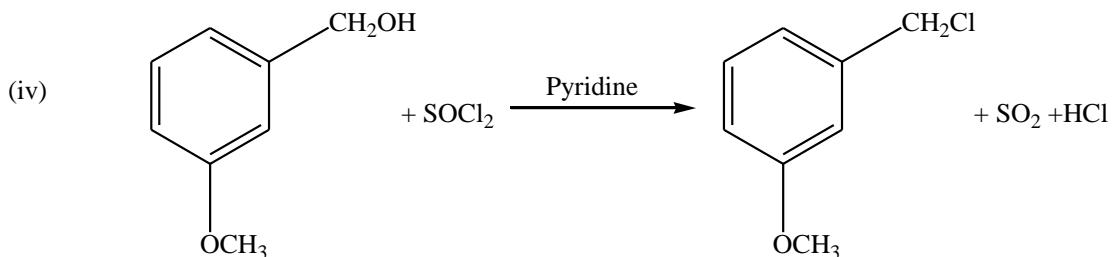
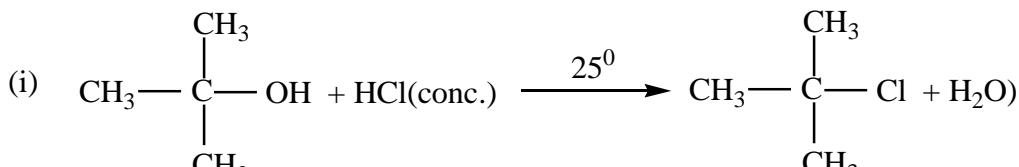


### (b) Cleavage of C-O bond

Formation of alkyl halide

Alcohols react with a variety of reagents to yield alkyl halides. The most commonly used reagents are hydrogen halides (HCl, HBr and HI) phosphorus tribromide (PBr<sub>3</sub>) and thionyll chloride.

Examples



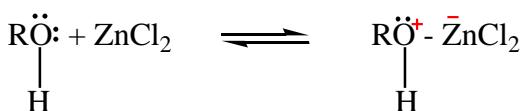
The order of reactivity of hydrogen halides is HI > HBr > HCl whereas the order of reactivity of alcohols is 3° > 2° > 1°. The reaction of HCl with alcohol is catalyzed by anhydrous zinc chloride. The reaction is used to distinguish between primary, secondary and tertiary alcohols.

Tertiary alcohol react readily with HCl in presence of anhydrous zinc chloride to form an insoluble chloride giving two layers immediately.

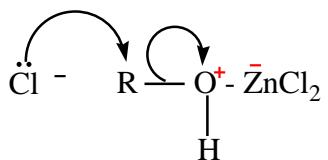
Secondary alcohol form two layer in 50 -10minutes

Primary alcohol do not form layers at room temperature.

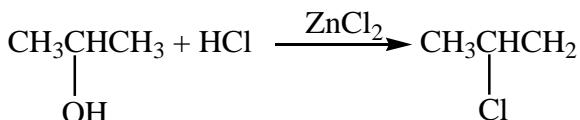
Mechanism



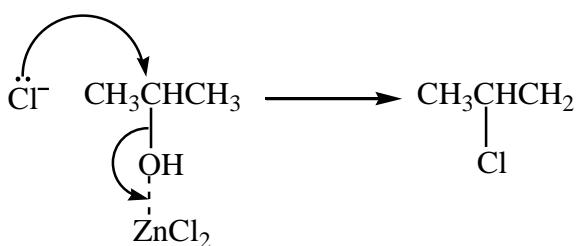
Then,



Example



Mechanism



### (c) Oxidation

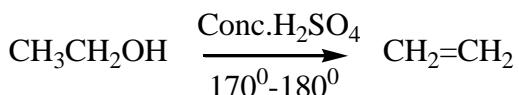
- (i) Alcohols are burnt in oxygen to produce carbon dioxide, water and heat. Due to production of heat on combustion, alcohols are used as fuel.
- (ii) Mild oxidizing agents like acidified potassium dichromate oxidize primary alcohols to aldehydes and then, to carboxylic acids. Secondary alcohols are oxidized to ketones.

Tertiary alcohols are not oxidized by potassium dichromate and therefore acidified potassium dichromate is used to distinguish tertiary alcohols from primary or secondary alcohols. When reacted with primary or secondary alcohol, the color of acidified potassium dichromate changes from orange to green.

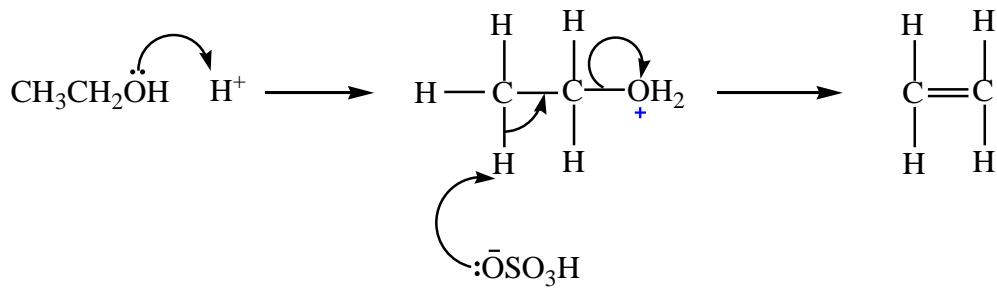
### (d) Dehydration of alcohol

Alcohols are dehydrated by hot concentrated sulphuric or phosphoric acid to form alkenes. The mechanisms depend on the class of alcohols.

- (i) Primary alcohol undergo elimination bimolecular; E2.
- Example

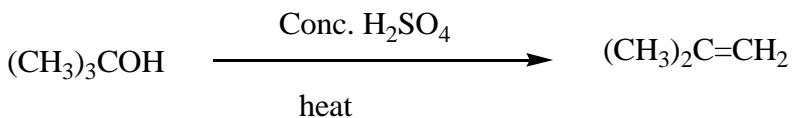


Mechanism

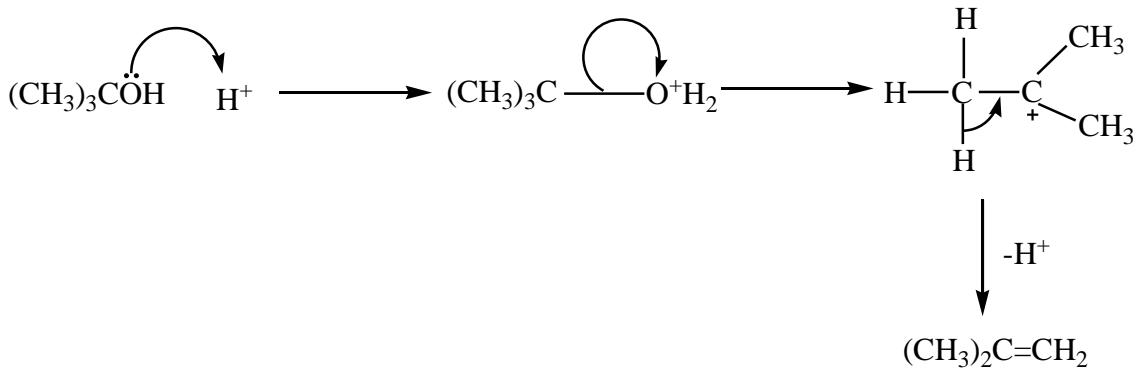


(ii) Tertiary alcohols undergo elimination unimolecular; E1.

Example



Mechanism

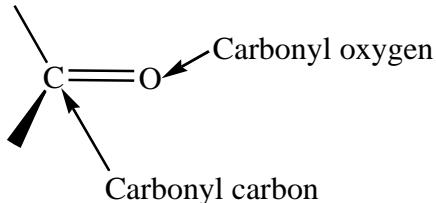


(iii) Secondary alcohol undergo either E2 or E1 mechanism

.....end

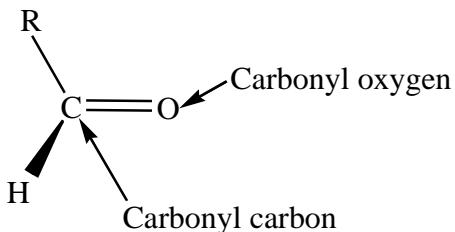
# Carbonyl compounds

The are compounds that contain carbonyl group



## Aldehydes

These are carbonyl compounds with the following structure.



R = alkyl group

## Nomenclature of aldehydes

1. Aldehydes are named by replacing the final “e” of the names of corresponding alkanes with “al.”
2. Since the aldehyde group must be at the end of the chain its position is not indicated.
3. When other substituents are present, the carbonyl carbon is assumed to occupy position one.

Example

HCHO	Methanal (40% solution is called formalin) or formaldehyde
CH <sub>3</sub> CHO	Ethanal or Acetaldehyde
CH <sub>3</sub> CH <sub>2</sub> CHO	Propanal or propionaldehyde
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	Butanal or butyraldehyde
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	Pentanal or veraldehyde

## Nomenclature of ketones

1. Their names end in suffix “one”
2. The position of the ketone group (-CO-) is given the lowest number.

CH<sub>3</sub>COCH<sub>3</sub> Propanone

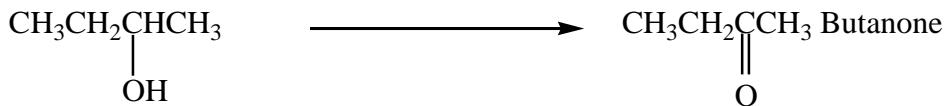
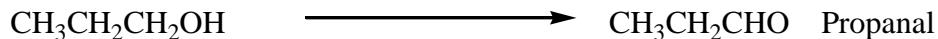
CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub> Butanone



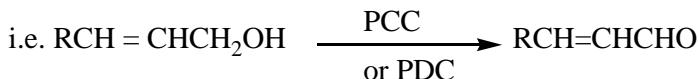
## Preparation of carbonyl compounds

- a. Oxidation of alcohol with acidified potassium dichromate, sodium dichromate or potassium permanganate. Primary alcohols give aldehydes whereas secondary alcohols give ketones.

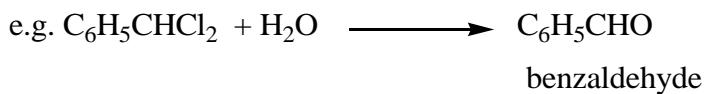
## Example



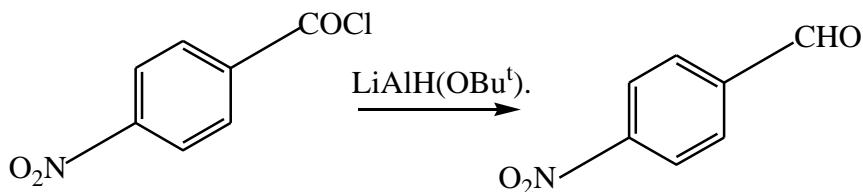
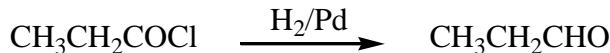
- b. Oxidation of alcohols using pyridinium chlorochromate [PCC,  $\{C_5H_5NH^+\}Cl.CrO_3$ ] and pyridinium dichromate [ PDC,  $\{C_5H_5NH^+\}_2Cl.Cr_2O_7^{2-}$ ] are currently the reagents of choice, particularly for oxidation of  $\alpha,\beta$ - unsaturated primary and secondary alcohols to give aldehydes and ketones respectively.



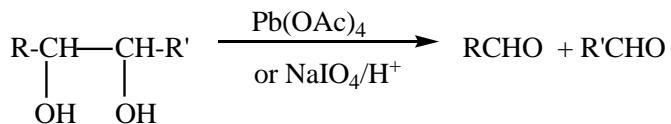
- ### 3. Hydrolysis of gem dihalide, ( $\text{RCHCl}_2$ , $\text{R}_2\text{CCl}_2$ )



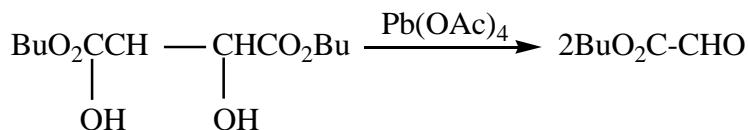
4. Reduction of acid chloride by hydrogen on palladium which is supported on barium sulphate or by using  $\text{LiAlH}(\text{OBu}^t)$ .



5. Cleavage of 1,2-diol using either lead tetraacetate or sodium metaperiodate

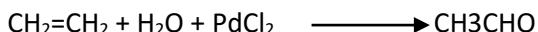


Example

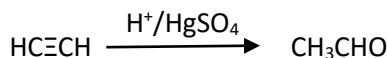


6. Preparation of ethanol

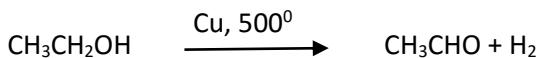
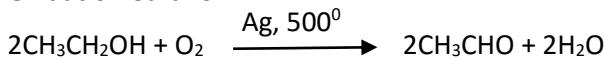
- (i) By oxidation of ethane with palladium chloride in water



- (ii) Passing ethyne through dil sulphuric acid in presence of mercury sulphate as a catalyst.



- (iii) Oxidation ethanol

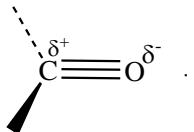


## Physical properties

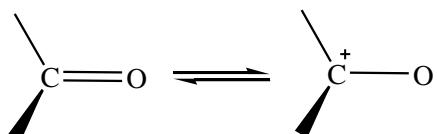
- (a) The polar carbonyl group makes carbonyl compounds polar and therefore, they have melting and boiling points than non-polar compounds with similar molecular mass.
- (b) Lower members are soluble in water but the solubility decreases with the increase in chain length.

## Chemical properties

The structure of carbonyl compound is sp<sup>2</sup> hybridized

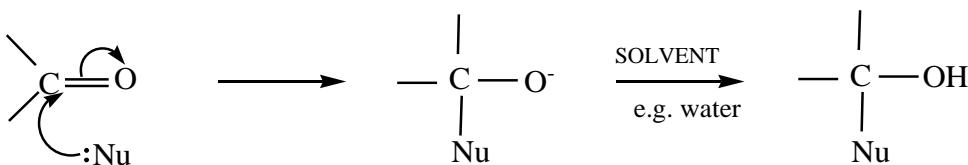


Possible structure

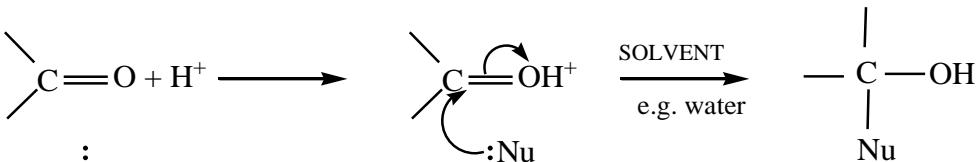


As a result of the partial positive charge, the carbonyl carbon is subjected to nucleophilic attack by a large number of nucleophiles. This results in nucleophilic addition reaction across the carbon-oxygen double bond. The nucleophilic addition to the carbon-oxygen double bond, can be regarded to occur in two possible ways generally.

- (i) In presence of a strong nucleophile.



- (ii) Weak nucleophile, the carbon oxygen bond has to be protonated first.



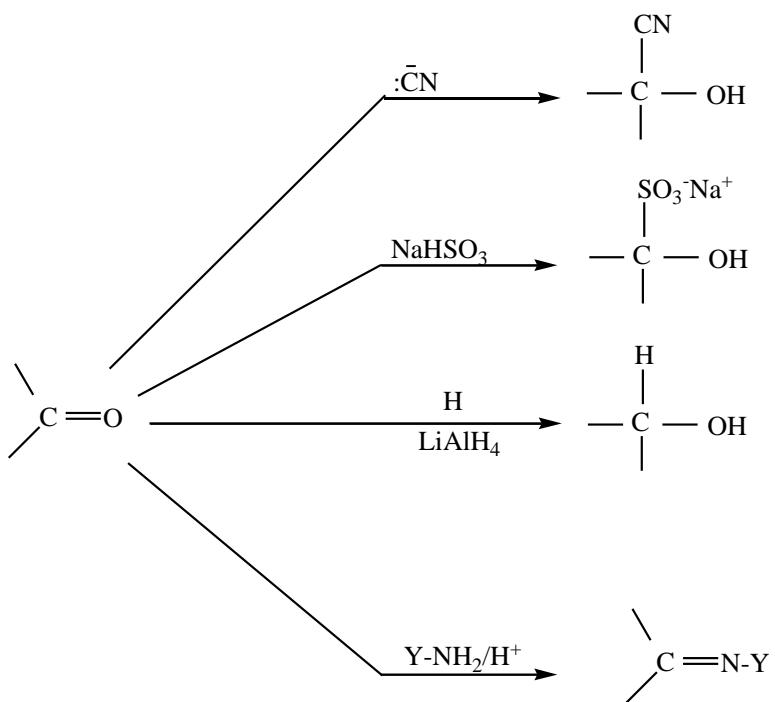
Generally, aldehydes undergo nucleophilic addition reaction more readily than ketones

Reasons

- (i) Steric effect: the bulkiness of the alkyl groups attached to the carbonyl carbon hinders the approach of nucleophile.
- (ii) Inductive effect: the positive inductive effect of the alkyl groups attached to the carbonyl carbon in ketones, reduce the positivity of the carbonyl carbon thus rendering it less reactive towards nucleophiles.

NB. Presence of an electron withdrawing group on the alkyl carbon make the carbonyl carbon more reactive towards nucleophilic addition reaction. For example,  $\text{CCl}_3\text{CHO}$  is more reactive than  $\text{CH}_3\text{CHO}$ .

### General scheme of nucleophilic reaction to carbonyl compounds

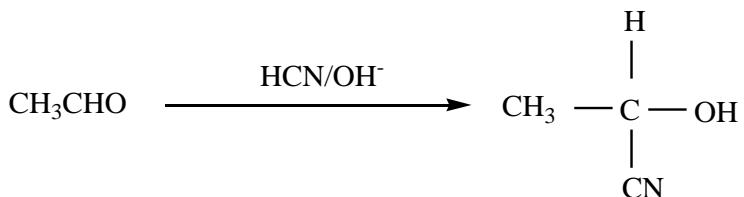


### Mechanism

#### (a) Addition of HCN or KCN

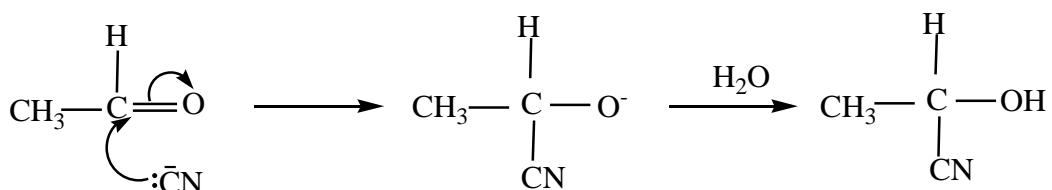
The reaction for addition of HCN is catalyzed by NaOH or KOH

Example



### Mechanism





This reaction can be used to increase the carbon chain by one carbon atom

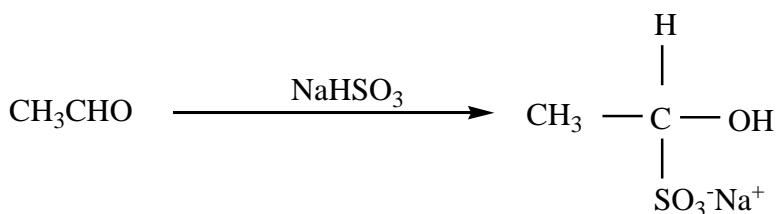
### Exercise

Complete and write a mechanism

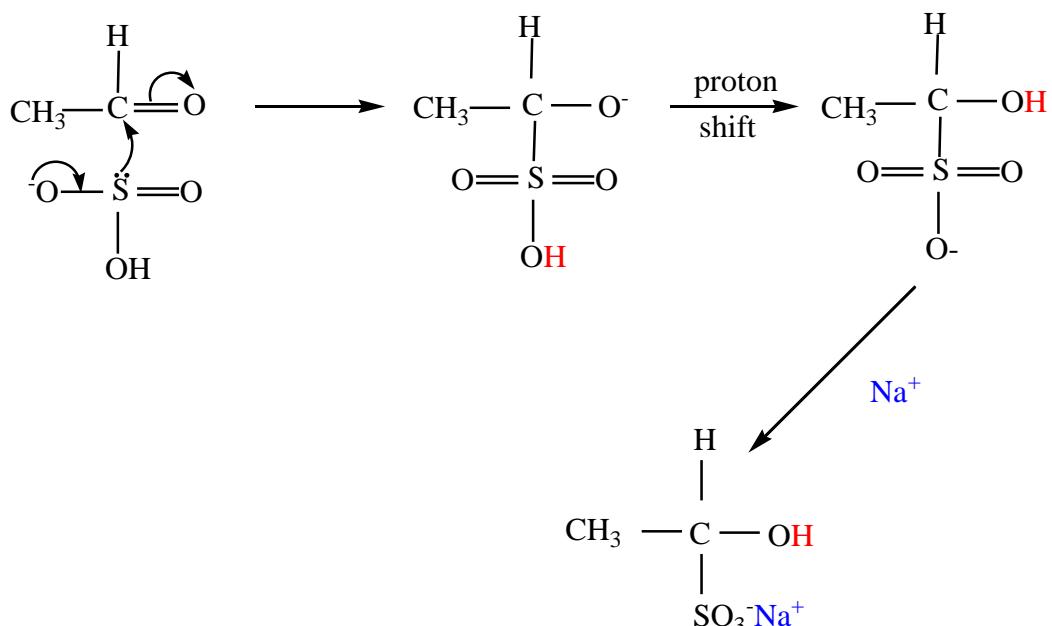


- (b) Addition of sodium hydrogensulphite,  $\text{NaHSO}_3$ .

Example



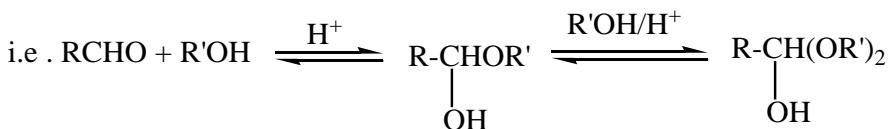
Mechanism



The reaction can be used to purify carbonyl compound since the products formed are solid. After crystallization, the can be redissolved.

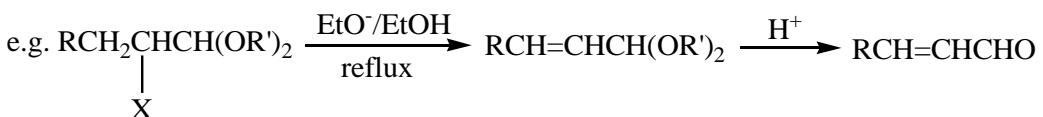
(c) Addition of alcohols

- 1mole of aldehyde + 1mole of alcohol in presence of an acid the product is hemiacetal
- 1mole of aldehyde + 2moles of alcohol in presence of an acid is acetal.

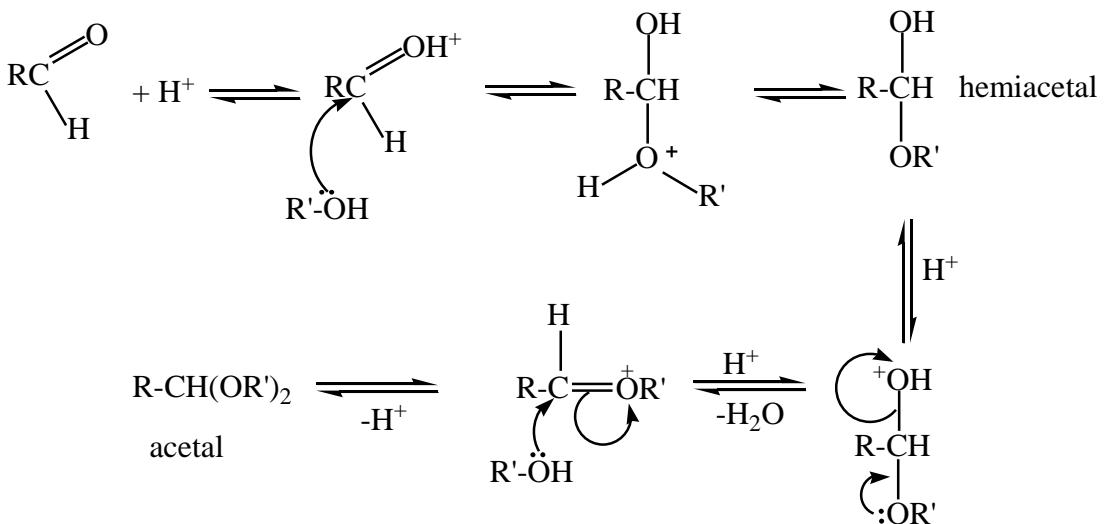


The reaction is used to protect the aldehyde group in chemical synthesis.

Example



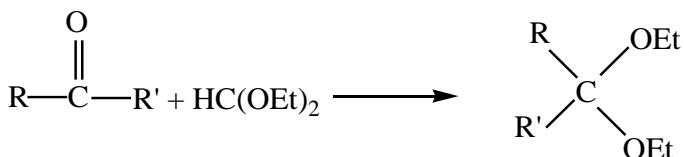
Mechanism



NB (i) Formation of acetals is sensitive to steric hindrance, i.e. depends on the size of groups attached to carbonyl carbon and the size of alcohol. Simple compounds give up to 80% yield, but the yield decrease with the increase in the size of the groups.

(ii) Reaction is reversible; therefore, it's necessary to reduce the concentration of the acid to minimize the reversibility of the reaction.

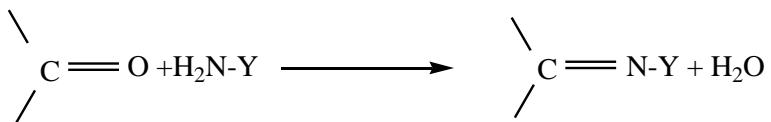
(iii) Ketals are not prepared by direct reaction between ketones and alcohol. This is because the equilibrium of the reaction lies mainly to the left. In this case **orthoformate** is used.



## 2. Addition of ammonia derivatives

Carbonyl compounds react with compounds of the general formula  $\text{H}_2\text{N}-\text{Y}$  with elimination of water. The reaction is catalyzed by acids. A reaction in which two molecules combine with elimination of small molecules e.g. water is called **condensation reaction**.

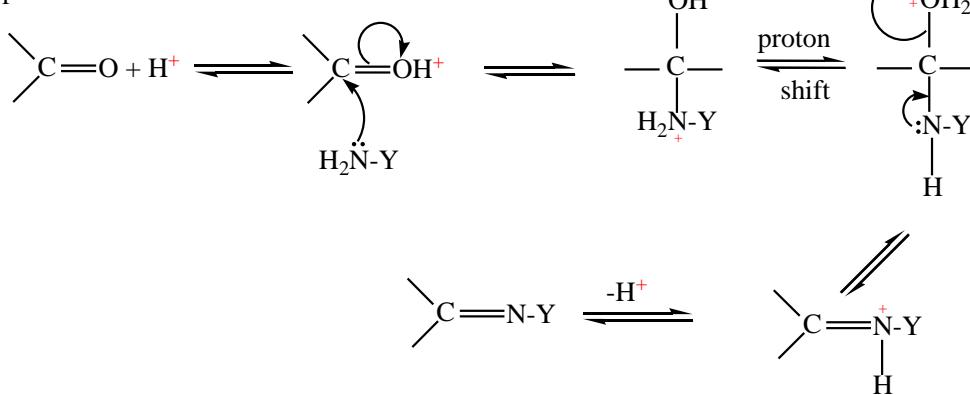
General equation



Y	REAGENTS	PRODUCTS
-OH	$\text{H}_2\text{N}-\text{OH}$	$\begin{array}{c} \backslash \\ \text{C}=\text{OH} \end{array}$ (Oxime)
-NH <sub>2</sub>	$\text{H}_2\text{N}-\text{NH}_2$	$\begin{array}{c} \backslash \\ \text{C}=\text{N}-\text{NH}_2 \end{array}$ (Hydrazone)
		$\begin{array}{c} \backslash \\ \text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_5 \end{array}$ Phenylhydrazone
		$\begin{array}{c} \backslash \\ \text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \end{array}$ 2,4-dinitrophenylhydrazone
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{NH}-\text{C}-\text{NH}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{NH}-\text{C}-\text{NH}_2 \end{array}$	$\begin{array}{c} \backslash \\ \text{C}=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2 \end{array}$ Semicarbazone

Mechanism

pH should be about 5

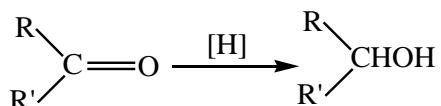
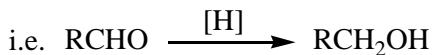


The products of these condensation reactions, i.e. oxime and hydrazones are orange crystalline solids with sharp melting points. Thus, they can be used to characterize carbonyl compounds. The most commonly used ammonia derivatives to characterize carbonyl compounds is 2,4-dinitrophenyl hydrazine (Brady's reagent). Reaction of carbonyl compounds with this reagent produces orange colored crystalline solids.

### 3. Reduction of carbonyl compounds

#### (i) Reduction of carbonyl compounds to alcohols

Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols

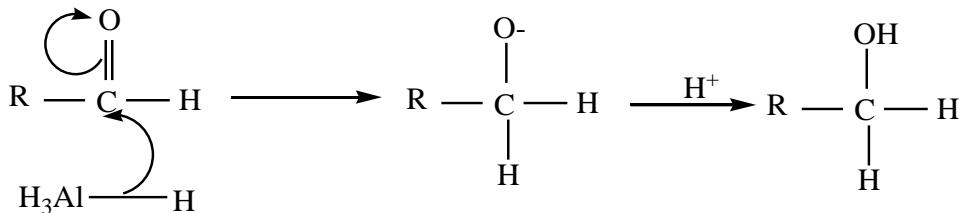


#### Reducing agents include

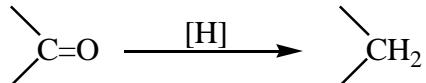
- (a) H<sub>2</sub>/catalyst (Ni, Pt, Pd): the disadvantage with this reagent is that it reduces double bonds when present.
- (b) LiAlH<sub>4</sub>, NaBH<sub>4</sub> – do not reduce double bonds



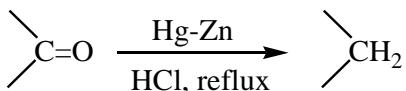
Mechanism



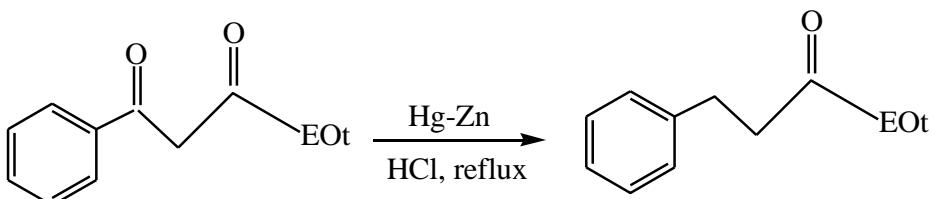
#### (ii) Reduction of carbonyl compounds to methylene. i.e.



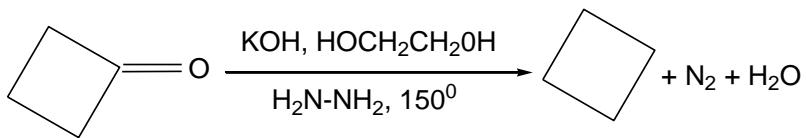
- (a) Clemmensen's reduction: it is useful for compounds that are stable under acidic conditions. It is carried out by refluxing a ketone with hydrochloric acid containing amalgamated zinc. Zinc and hydrochloric acid also reduces nitro groups to amines.



Example

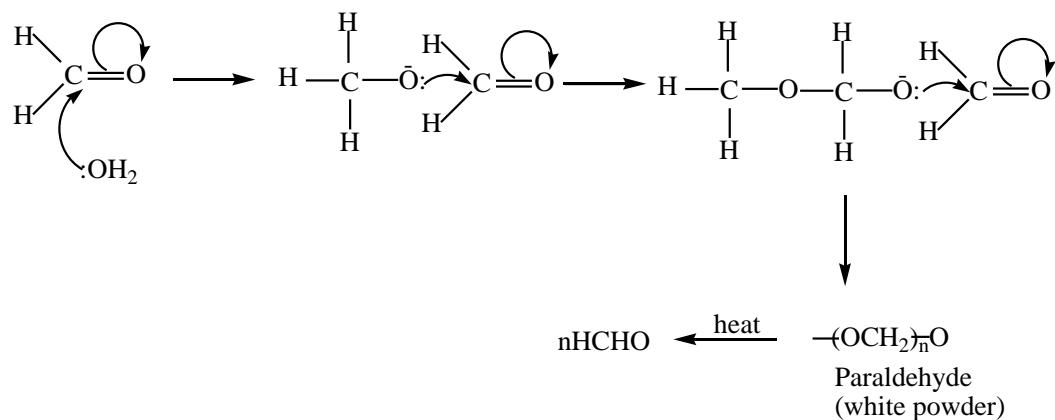


- (b) Hong-Mislon modification of Walf-Kishner reaction: a carbonyl compound is heated in presence of high boiling polar solvent, e.g. ethane-1,2-diol with hydrazide + KOH



#### 4. Polymerization of aldehyde

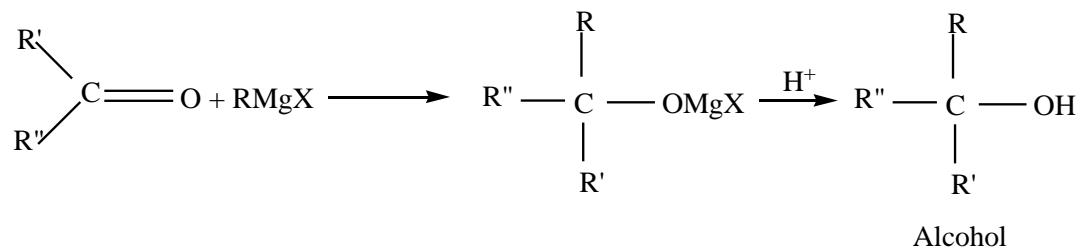
Aldehyde(methanol) polymerizes, mainly under basic conditions.



Paraformaldehyde is a useful form for transportation of methanal

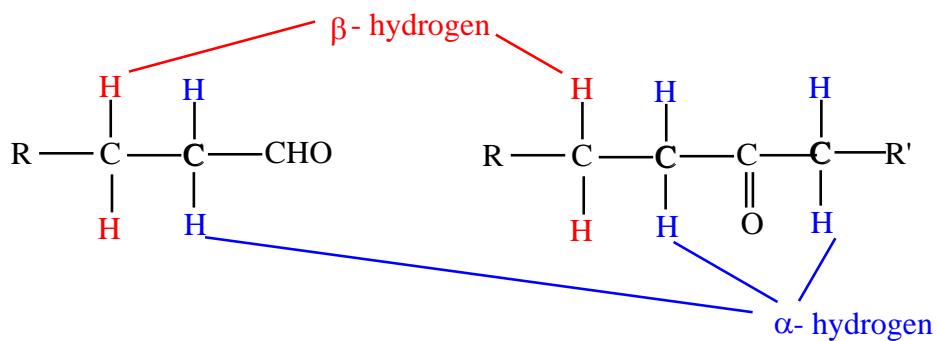
#### 5. Reaction of Grignard's reagents

Reaction of carbonyl compounds with Grignard's reagents produces all the three types of alcohols. Thus this is an important reaction for the preparation of alcohols.

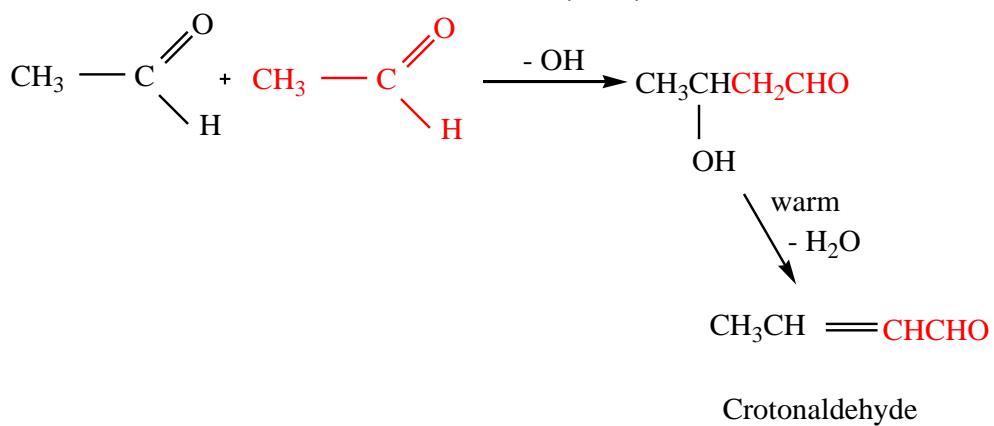


#### 6. Aldol condensations

Carbonyl compounds which contain at least one alpha hydrogen, react in presence of alkali to form hydroxyl carbonyl compounds called Aldol

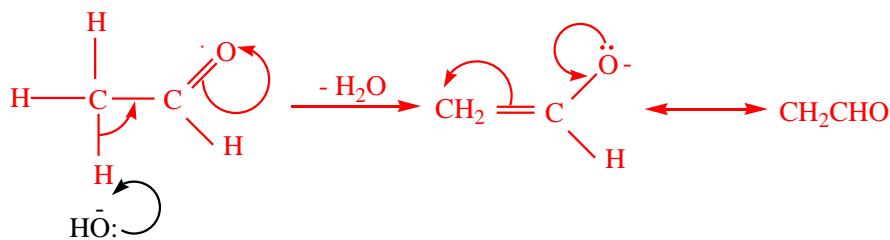


- (i) Two molecules of ethanal combine to form 3-hydroxybutanal

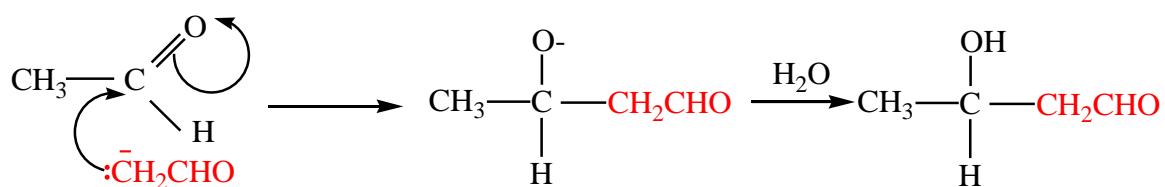


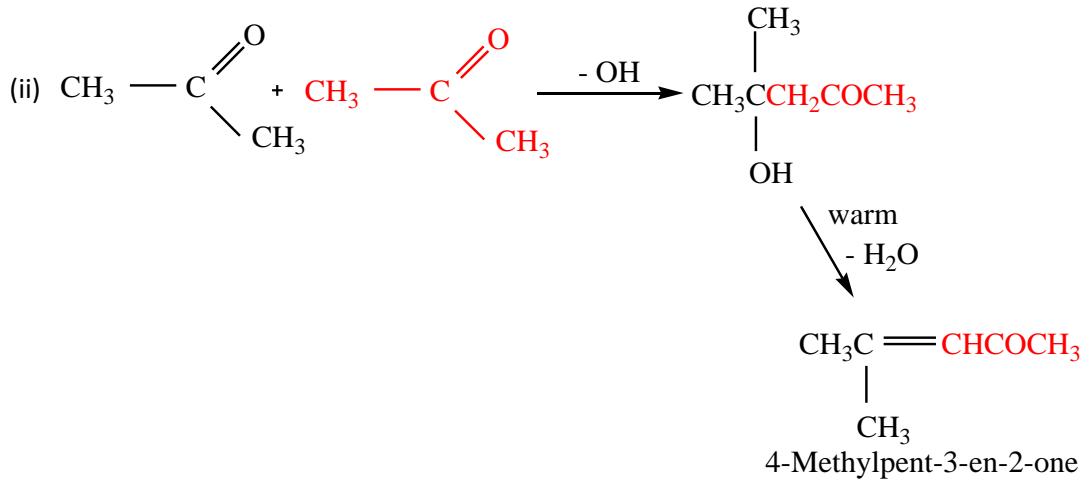
Crotonaldehyde is used to calibrate spectrometer because it's absorbance is known

Mechanism

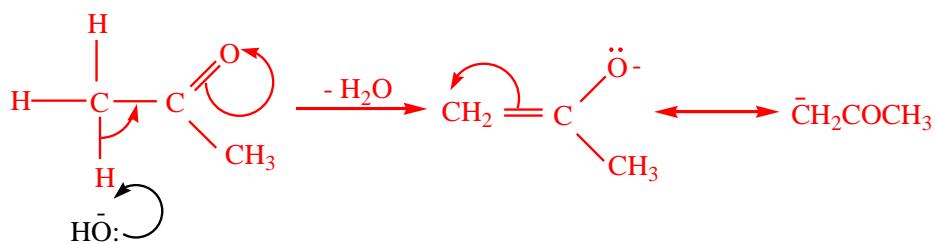


Then,

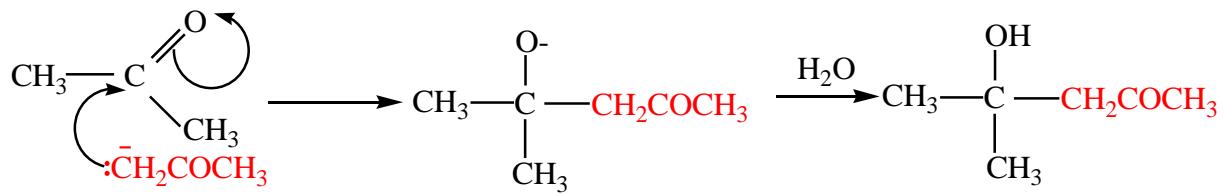




Mechanism



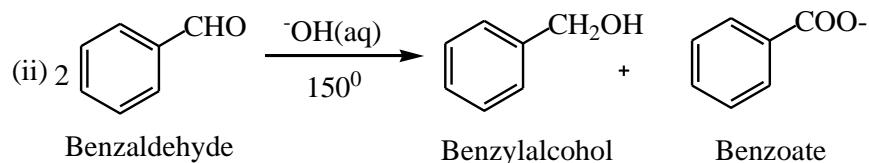
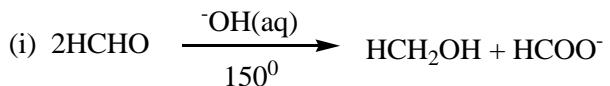
Then



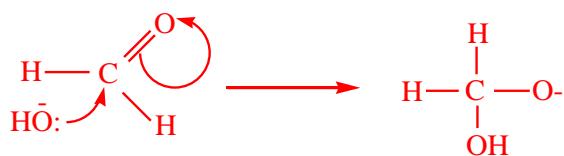
## 7. Cannizzaro reaction

This is a reaction between sodium hydroxide solution and aldehydes with no  $\alpha$ -hydrogen  
It's a self-oxidation – reduction reaction

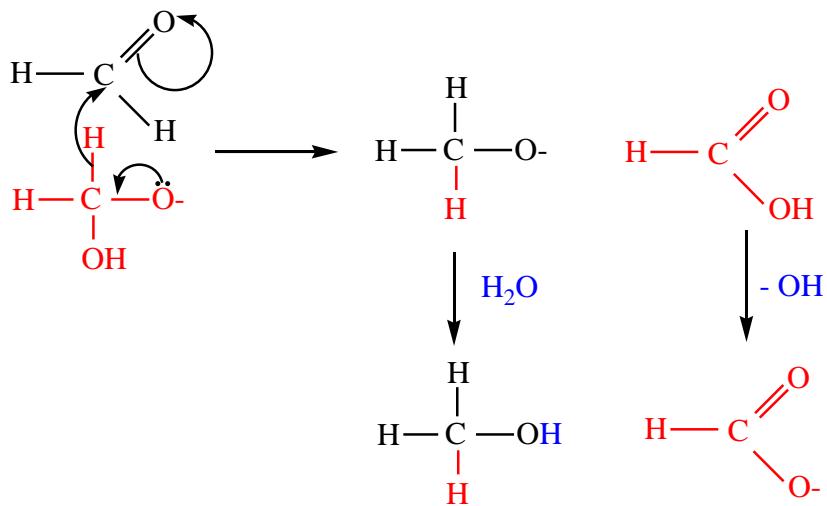
Examples



Mechanism

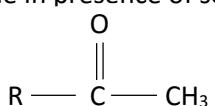


Then,



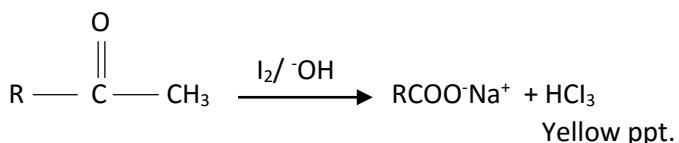
## 8. Iodoform reactions

Iodine in presence of sodium hydroxide solution react with carbonyl compounds with structure



to form a yellow ppt.

i.e.



**NB** (i) the reaction is useful when identifying compound with the group  $\begin{array}{c} \text{O} \\ || \\ \text{R} - \text{C} - \text{CH}_3 \end{array}$

- (ii) Ethanal is the only aldehyde that gives a positive iodoform test
- (iii) All ketone with the structure  $\text{RCOCH}_3$  give positive iodoform test
- (iv) Secondary alcohols of the group  $\text{RCHOHCH}_3$  give positive iodoform test
- (v) Ethanol is the only primary alcohol that gives a positive iodoform test.

### Exercise

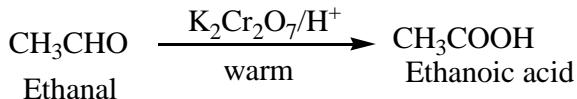
Give one reagent that can be used to distinguish between the following pairs of substances. In each case state what would be observed the reagent is treated separately with the reagent you have mentioned.

- (i)  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CH}_2\text{OH}$
- (ii)  $\text{HCHO}$  and  $\text{CH}_3\text{CHO}$
- (iii)  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

### 9. Oxidation of carbonyl compounds

Aldehydes are easily oxidized to carboxylic acid. The oxidizing agent, normally used are  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ,  $\text{KMnO}_4/\text{H}^+$ .

Example



Ketones are not oxidized under mild condition

### Distinguishing between aldehydes and ketone

Reagent	Observation	
	Aldehydes	Ketones
Fehling's solution	Brown ppt	No observable change
Tollen's reagent or ammoniacal silver nitrate	Black ppt or silver mirror	No observable change
Acidified potassium dichromate	Orange solution turns green	No observable change

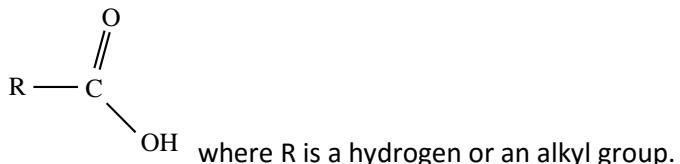
### Exercise

Give one reagent that can be used to distinguish between the following pairs of substances. In each case state what would be observed the reagent is treated separately with the reagent you have mentioned.

- (i)  $\text{CH}_3\text{CH}_2\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$

## Carboxylic acid or alkanoic acids

These are compounds with the formula



The carboxylic group is a combination of carbonyl group and an hydroxyl group(OH): the name carboxylic group.

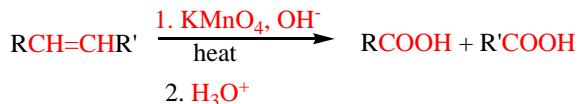
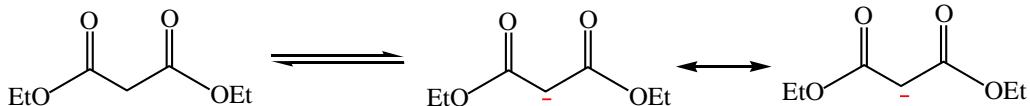
### Nomenclature

1. Their names end with suffic “oic” followed by the word acid.
2. The carboxylic group must always be at the end of the chain and therefore its position need not to be specified. Take longest chain that contain the carboxylic group and start numbering from the carboxylic carbon

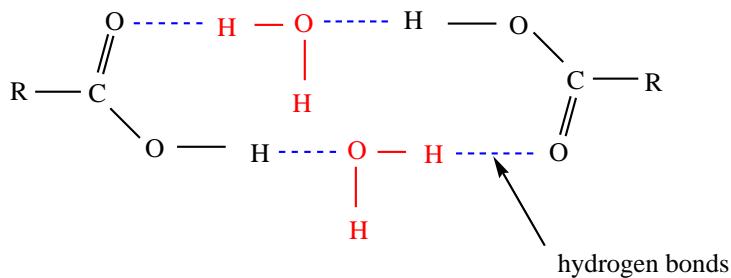
Examples	Systematic name	Common name
HCOOH	Methanoic acid	Formic acid
CH <sub>3</sub> COOH	Ethanoic	Acetic acid
CH <sub>3</sub> CH <sub>2</sub> COOH	Propanoic acid	Propionic acid
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Butanoic acid	Butyric acid
CH <sub>3</sub> CH(CH <sub>3</sub> )COOH	2-methylpropanoic acid	Isobutyric acid

### Physical properties

1. Lower member are liquids and higher members are waxy solids. With boiling points which are higher than expected, this because, their molecules are associated by hydrogen bonds.



2. Lower members are soluble in water but the solubility decreases with the increasing molecular mass of carboxylic acid. This is because carboxylic acids are capable of formation of hydrogen bonds with water



### 3. Melting points

Compounds	Mpt (°C)	Bpt (°C)	Ka
HCOOH	8	100.5	$1.7 \times 10^{-4}$
CH <sub>3</sub> COOH	16.6	118	$1.77 \times 10^{-5}$
CH <sub>3</sub> CH <sub>2</sub> COOH	21	141	$1.34 \times 10^{-5}$
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	-6	164	$1.54 \times 10^{-5}$
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	-34	187	$1.52 \times 10^{-5}$
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	-3	205	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COOH	16	259	

Generally the melting point increase with the molecular mass. However, the melting points of lower carboxylic acids are relatively higher than those of higher carboxylic acids because they form stronger hydrogen bonds.

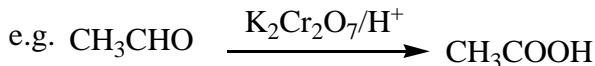
4. The acidity of carboxylic acids decrease with the increase in molecular mass due to positive inductive effect of alkyl group. Electron with drawing groups make carboxylic acid more acidic. For example CCl<sub>3</sub>COOH is more acidic than CH<sub>3</sub>COOH.

#### Methods of preparation

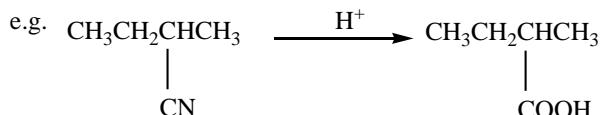
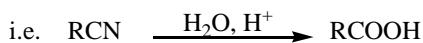
1. By oxidation of primary alcohols using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sup>+</sup>, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sup>+</sup>, or KMnO<sub>4</sub>/H<sup>+</sup>



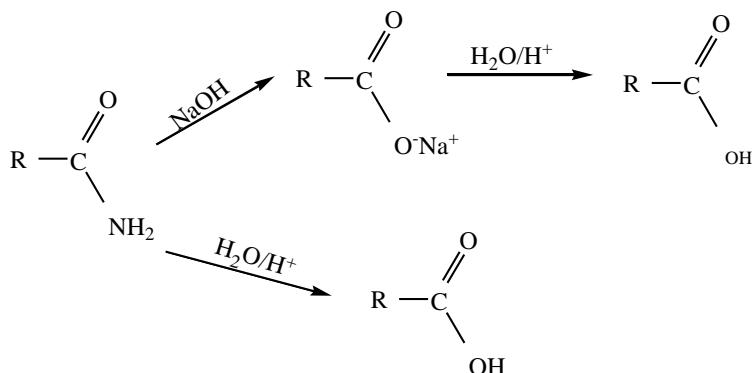
2. Oxidation of aldehyde using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sup>+</sup>, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sup>+</sup>, or KMnO<sub>4</sub>/H<sup>+</sup>



3. Hydrolysis of nitrile in presence of a mineral acid.



4. Hydrolysis of acid amide with a mineral acid or alkali

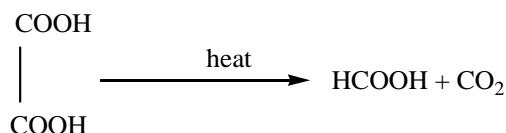


5. Reaction of carbon dioxide with a grignard reagent followed with hydrolysis.

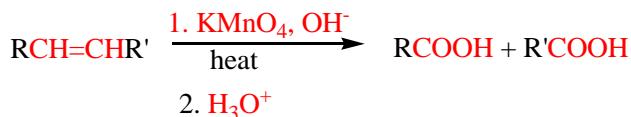


6. Preparation of methanoic acid

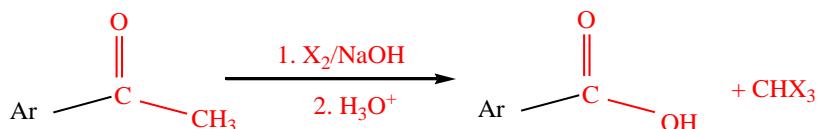
By heating a solution of ethane dioic acid in propane-1,2,3-triol



7. Oxidation of alkenes using hot alkaline  $\text{KMnO}_4$ .



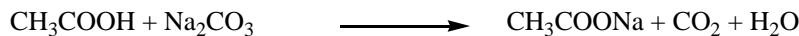
8. Oxidation of methyl ketone



### Chemical properties

- Carboxylic acid react with base to form salts and even liberate carbon dioxide from carbonates.

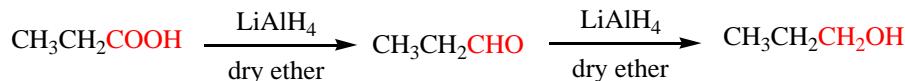
### Examples



### 2. Reduction of carboxylic acid

Carboxylic acids are resistant to reduction by mild reducing agents. However, can be reduced through aldehydes to primary alcohols by LiAlH<sub>4</sub> in presence of dry ether.

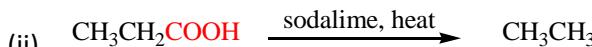
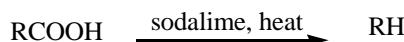
#### Example



### 3. Decarboxylation

This is a reaction in which a molecule of CO<sub>2</sub> is removed from carboxylic acids.

- (i) Simple carboxylic acids are not easily decarboxylated but their salts are easily decarboxylated in presence of soda lime.

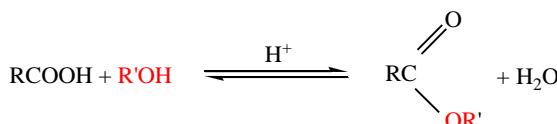


- (iii) Acids with electron withdrawing groups on α-carbon are easily decarboxylated on heating.

#### Example



- (iv) Esterification: Carboxylic acids react with alcohol in presence of mineral acids to form esters.



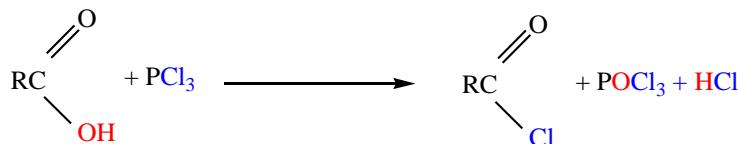
Esters have got sweet smell; this is why this reaction is used in identification of carboxylic acids.

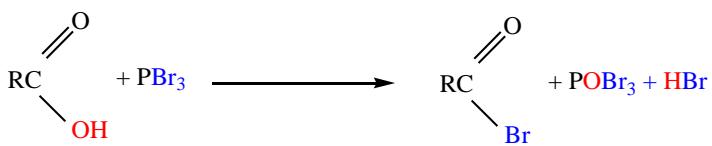
Reactivity of alcohols is in order 1<sup>0</sup> > 2<sup>0</sup> > 3<sup>0</sup>, and the reactivity of carboxylic acids is in order

HCOOH > CH<sub>3</sub>COOH > RCH<sub>2</sub>COOH > R<sub>2</sub>CHCOOH > R<sub>3</sub>CCOOH, due to steric hindrance. i.e. the presence of bulky groups near the site of reaction, whether in the alcohol or in acid slows esterification.

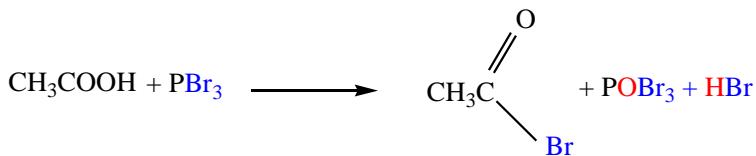
### 4. Formation of acid halides

Carboxylic acids (except methanoic acid) react with phosphorus halides to form acid halides



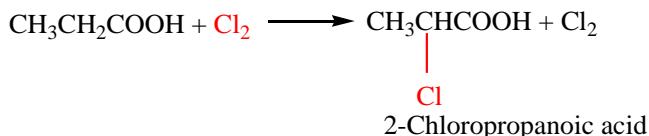


Example



### 5. Halogenation of aliphatic acids

- (a) Carboxylic acids (except methanoic acid) react with chlorine in presence of sunlight or u.v light, thereby a chlorine atom replacing an  $\alpha$ -hydrogen.



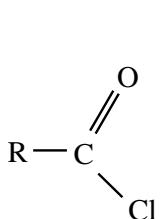
- (b) Bromine replaces an  $\alpha$ -hydrogen in presence of red phosphorous (hell-vohlard zelensky reaction)



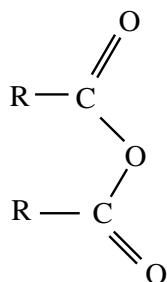
END

## Functional derivatives of carboxylic acids

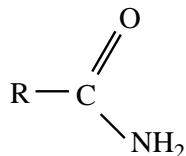
Closely related to carboxylic acids and to each other are a number of chemical families known as functional derivatives of carboxylic acids : Acid halide, anhydride, amide and esters. These derivatives are compounds in which the OH of the carboxylic acid has been replaced by X(Cl, Br, I), OOCR, NH<sub>2</sub> or OR.



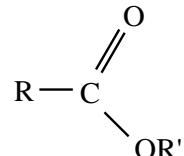
Acid chloride



Acid hydride

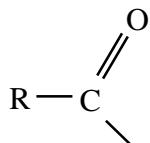


Acid amide



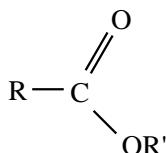
Ester

The all contain the group



### 1. Esters

They have a general formula



Examples



Methylmethanoate



Ethylethanoate



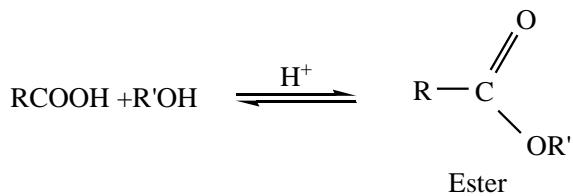
Ethylpropanoate

### Physical properties

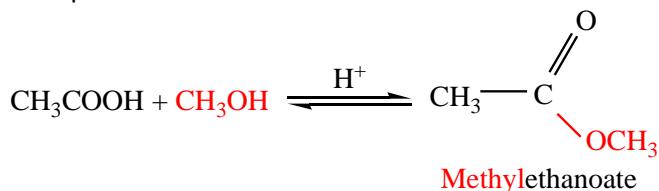
- (i) Insoluble in water but soluble in organic solvent
- (ii) They are neutral liquids with pleasant smell
- (iii) They have low boiling points compared to carboxylic acids of comparable molecular mass.

### Preparation

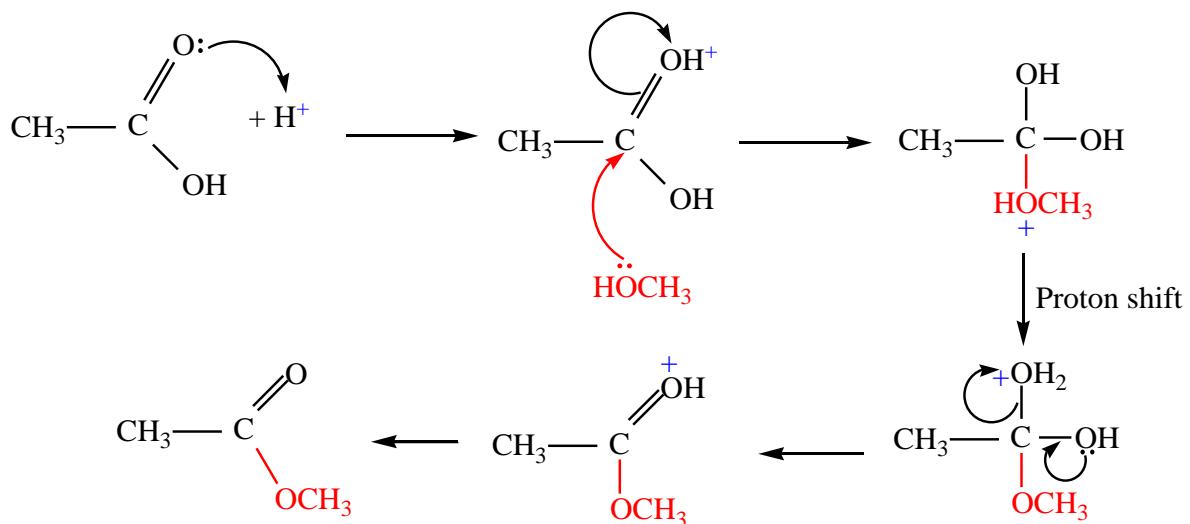
- (a) By reacting carboxylic acids with alcohol in the presence of mineral acids



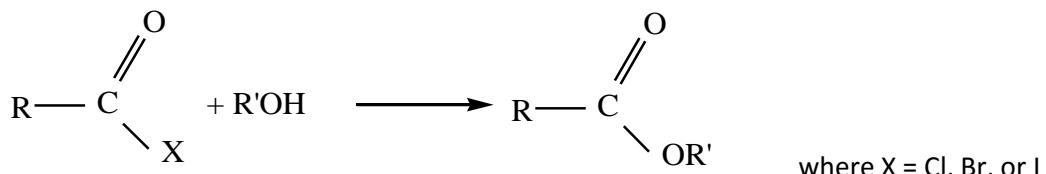
Example



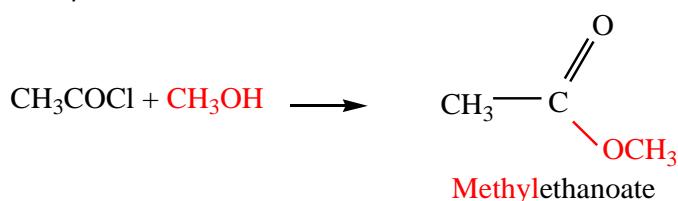
Mechanism



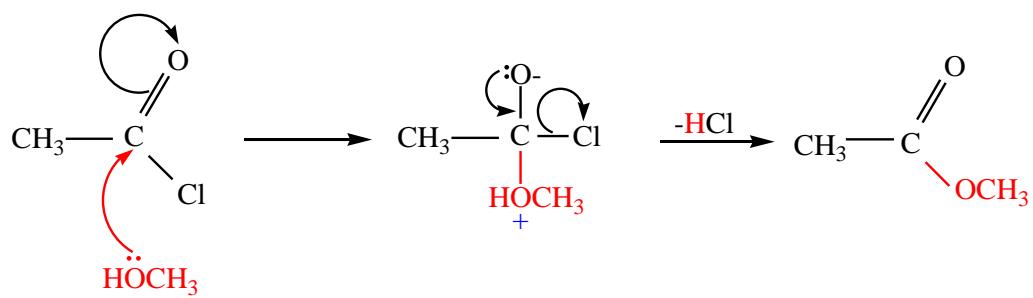
(b) reaction of alcohols with acid halides



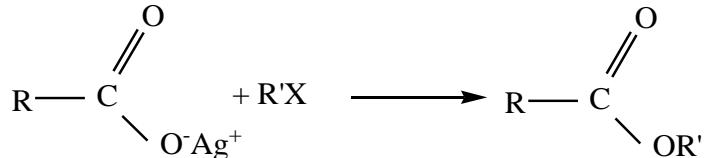
Example



### Mechanism



(c) By reacting silver salts of carboxylic acid with alkyl halide

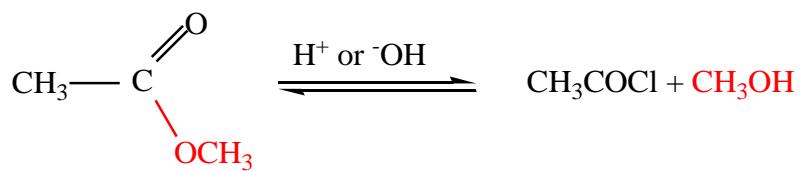


### Chemical properties

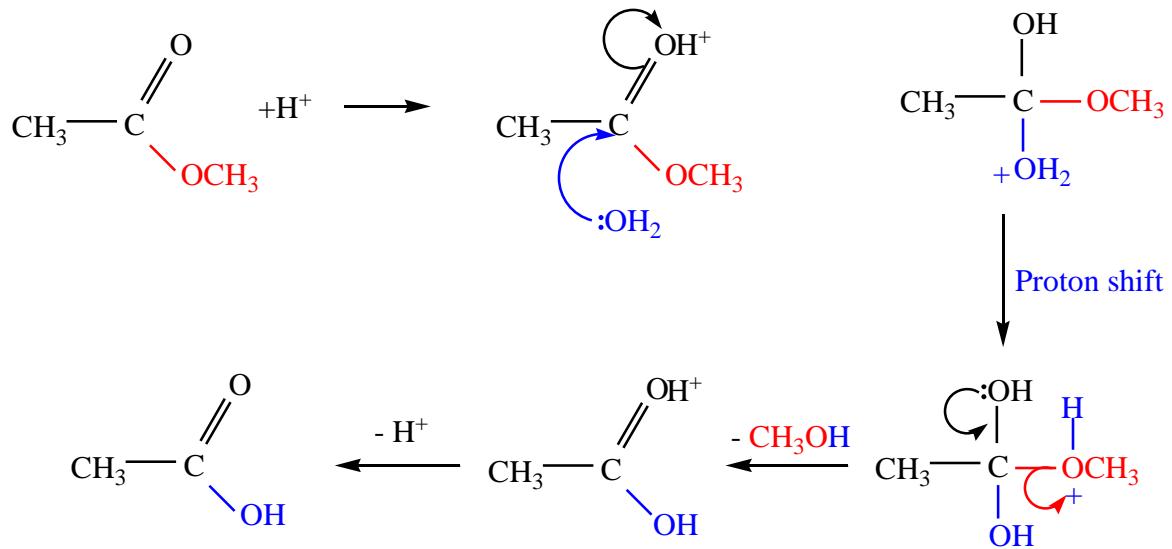
#### 1. Hydrolysis

Esters are hydrolyzed by mineral acids or alkalis

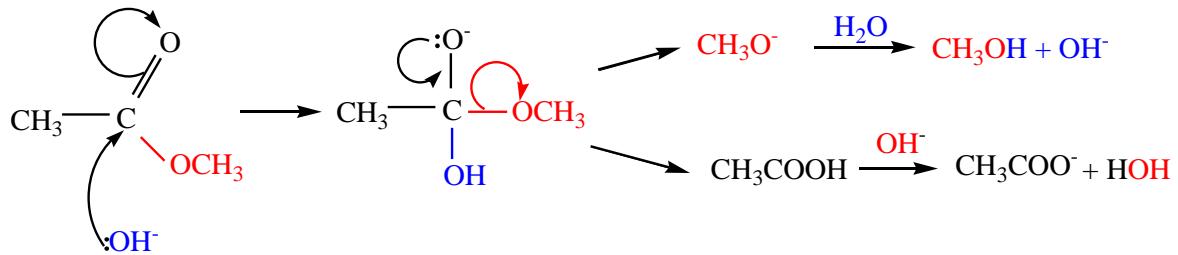
Example



Mechanism (acid catalyzed)

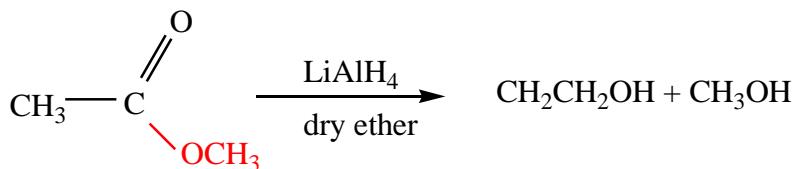


(ii) base catalyzed

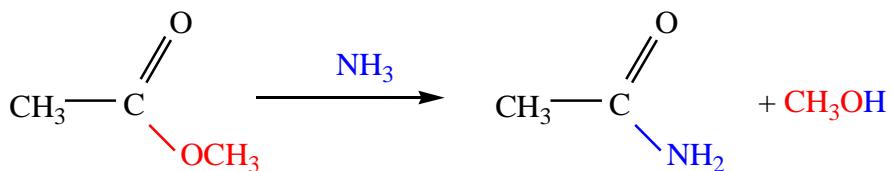


2. Esters are reduced by  $\text{LiAlH}_4$  to alcohols

Examples



3. Esters react with amines to form acid amide

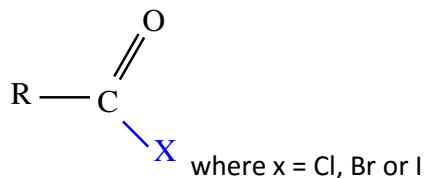


Uses of esters

In formation of perfumes

## Acid halides

These have a general formula



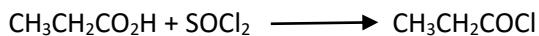
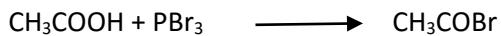
Examples



## Preparation

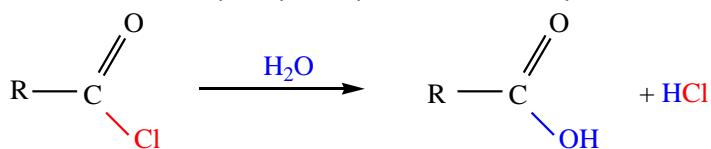
By reacting carboxylic acid with phosphorus halide or thionylchloride

Examples

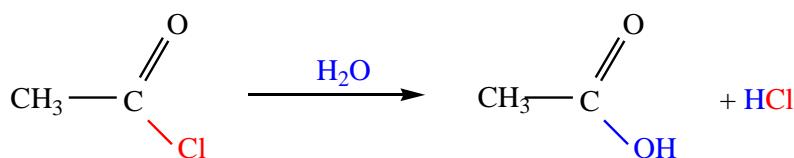


## Chemical properties

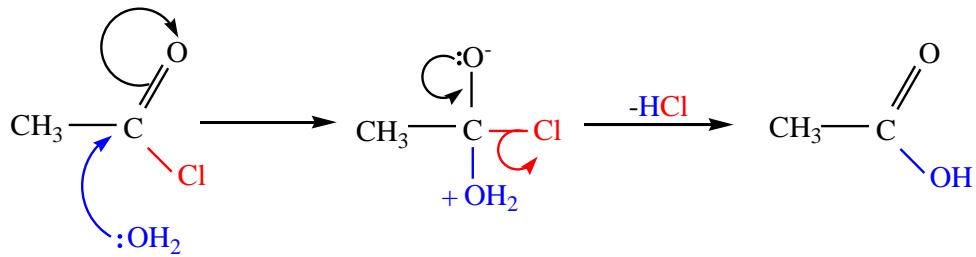
1. Acid halides are hydrolyzed by water to carboxylic acids



Example



## Mechanism

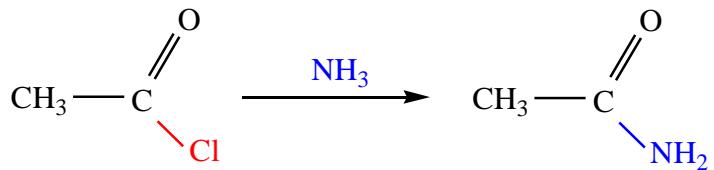


When ethanoyl chloride is exposed to moist air white fumes are seen due to the production of HCl.

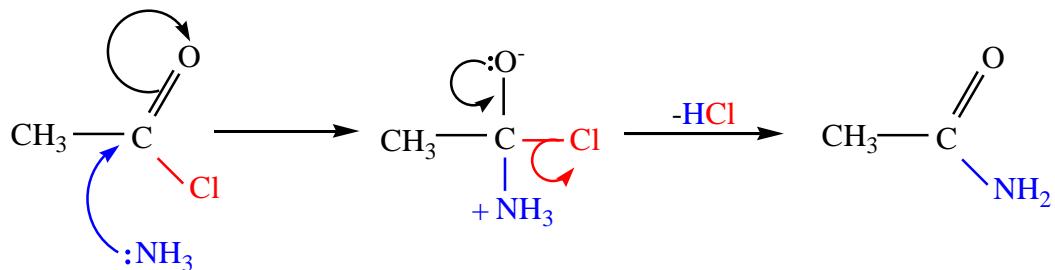


2. Acid halides react with ammonia and amines to produce amides

Example

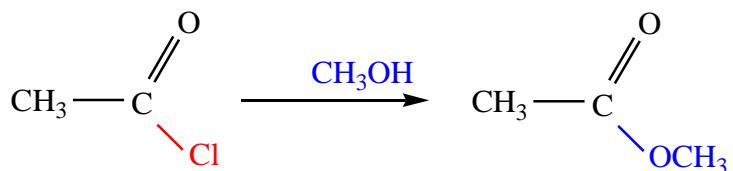


## Mechanism

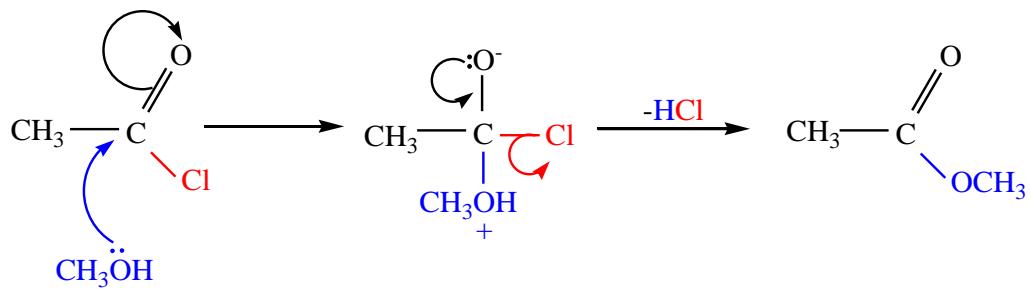


3. Acid halides react with alcohols to form esters

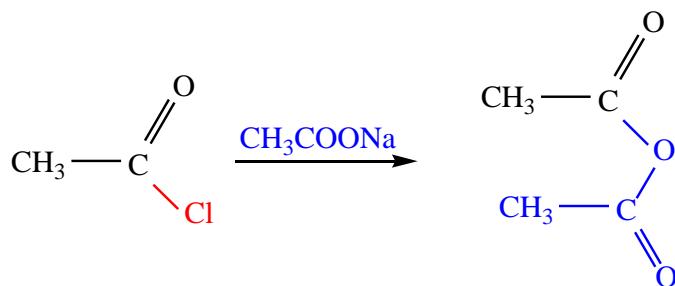
Example



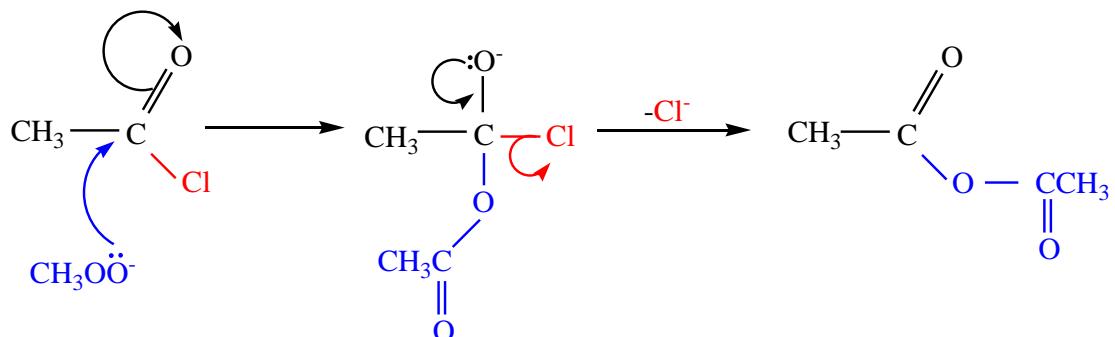
## Mechanism



4. Acid halides react with anhydrous sodium salt of carboxylic acid to form acid anhydride  
Example

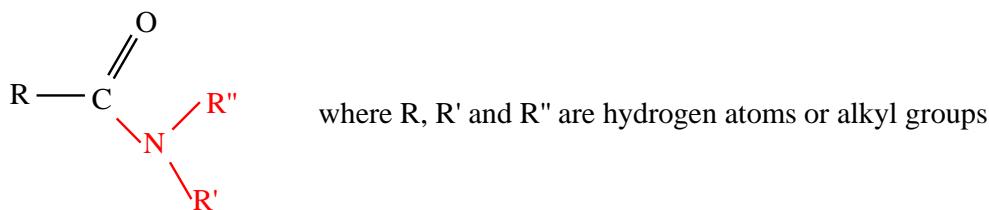


## Mechanism



## Acid amide

These have a general formula



Examples



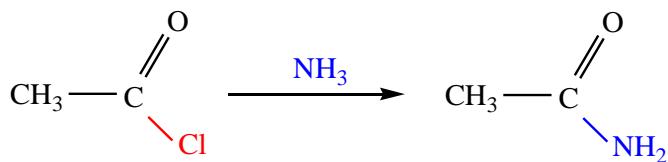
Physical properties

- They are white crystalline salts except methanamide
- Lower members are soluble in water but the solubility decreases with increasing molecular mass.
- They have relatively high boiling points due to formation of intermolecular hydrogen bonds

Preparation

1. By reaction of ammonia with ester, acid anhydride or acid halides

Examples

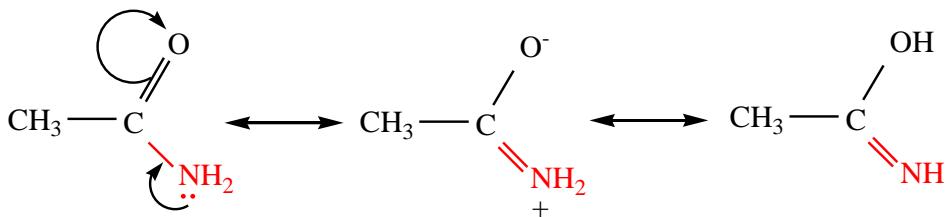


2. Dehydration of carboxylic acids with ammonium carbonate

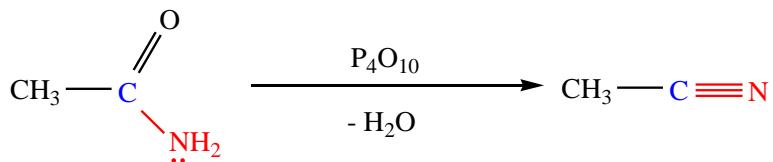


## Chemical properties

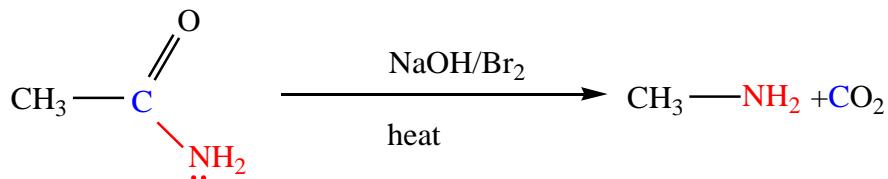
- They are weaker bases compared to amines and are neutral to litmus. They do not form salts with acids as amines do because their lone pair of electron on the nitrogen atom is delocalized.



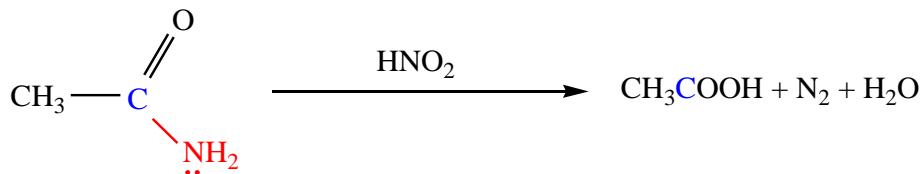
- Amides form nitriles when distilled over phosphorus pentoxide,  $\text{P}_4\text{O}_{10}$ .



- Amides react with hot alkaline bromine solution to give amines

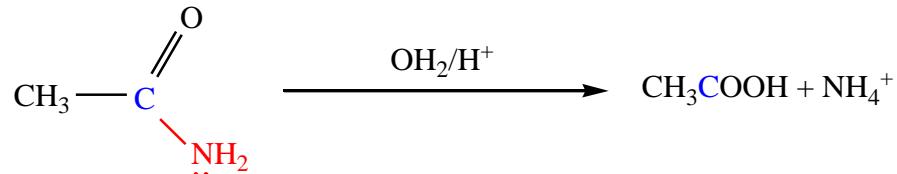


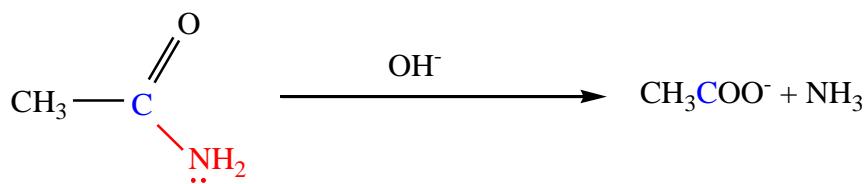
- Like amines, amides react with nitrous acid liberating nitrogen



- Amides are hydrolyzed with mineral acid or alkalis

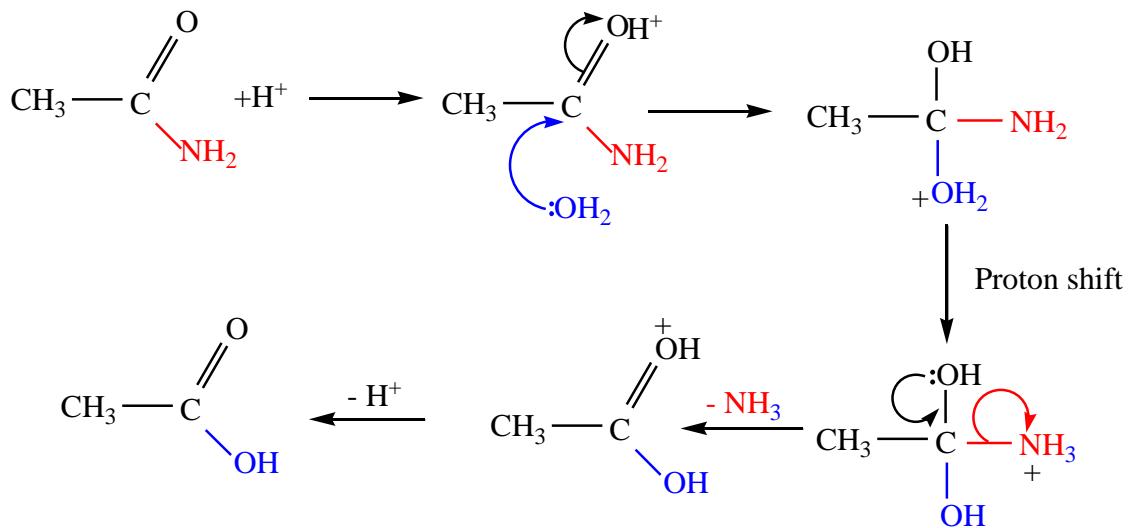
Example





### Mechanism

(a) Acid catalyzed



Thank you

# Aromatic compounds

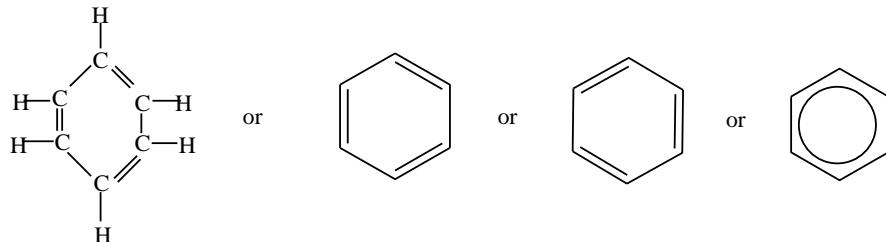
These include benzene and compounds that resemble benzene in chemical behavior.

## Benzene

Chemical formula: C<sub>6</sub>H<sub>6</sub>.

### Structure

Benzene is a cyclic compound with delocalized conjugated double bonds, i.e. the double bond is free to shift from one place to another through the whole molecule.



Effect of delocalization of double bond in to the structure of benzene.

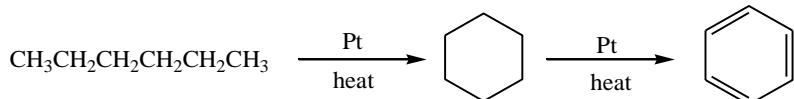
- (i) Benzene ring is very stable that it is preserved in most chemical reaction, that is, it's is generally unreactive towards electrophilic reagents.
- (ii) The six carbon-carbon bonds in the benzene are equal in length (i.e. 1.39 Å) intermediate between the carbon-carbon double bond (1.34 Å) and carbon-carbon single bond (1.54 Å)

## Physical properties

- a. It is a colorless with a characteristic aromatic smell.
- b. It is insoluble in water but soluble in organic solvents and its self is a good solvent.
- c. It burns with a smoky and luminous flame

## Industrial preparation

Benzene is obtained by catalytic dehydration of hexane (from petroleum)



## Chemical properties

Benzene is not easily attacked by electrophilic reagents. In its reactions, benzene undergoes mostly electrophilic substitution reaction in an electrophile substitutes a hydrogen atom, rather than addition reactions in which the benzene ring system would be destroyed.

## Reactions

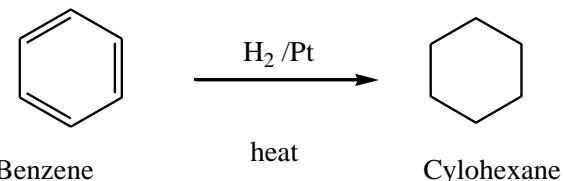
### 1. Combustion

Benzene reacts with oxygen to form carbon dioxide and water only.



### 2. Catalytic hydrogenation

Benzene undergoes catalytic hydrogenation to cyclohexane

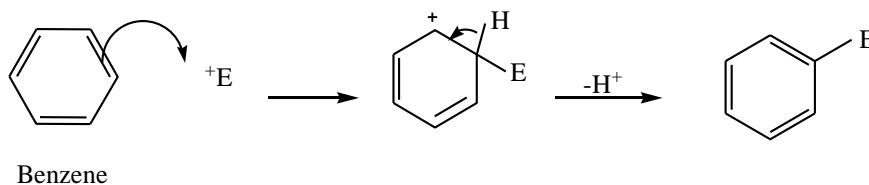


The heats of hydrogenation and combustion of benzene are lower (by 36kcal/mole) than expected. In other words, benzene is more stable by 30kCal than we would expect cyclohexatriene to be. The 36kCal is the benzene stabilization energy or resonance energy.

### 3. Aromatic electrophilic substitution reaction

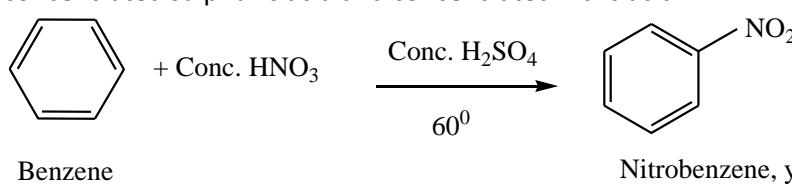
Here an electrophile substitutes a hydrogen atom on a benzene ring.

General mechanism



#### a. Nitration

This is the introduction of the nitro group on the benzene ring using a hot mixture of concentrated sulphuric acid and concentrated nitric acid.

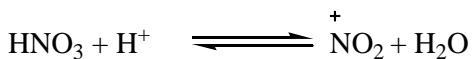


Benzene

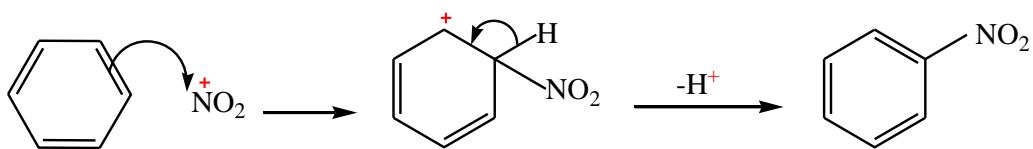
Nitrobenzene, yellow liquid

The formation of a yellow liquid of nitrobenzene when benzene is reacted with a mixture of concentrated nitric acid and concentrated sulphuric acid distinguishes benzene from cyclohexane,

Mechanism



then,



### Uses

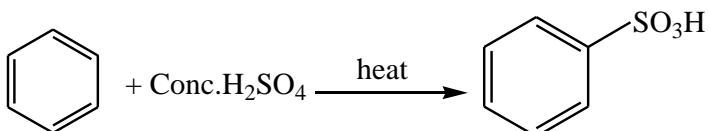
Approximately 95% of nitrobenzene is consumed in the production of aniline,[3] which is a precursor to rubber chemicals, pesticides, dyes (particularly azo dyes), explosives, and pharmaceuticals.

### Specialized applications

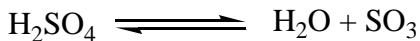
Nitrobenzene is also used to mask unpleasant odors in shoe and floor polishes, leather dressings, paint solvents, and other materials. Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps. A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol (also known as acetaminophen) (Mannsville 1991).[4] Nitrobenzene is also used in Kerr cells, as it has an unusually large Kerr constant.

### b. Sulphonation

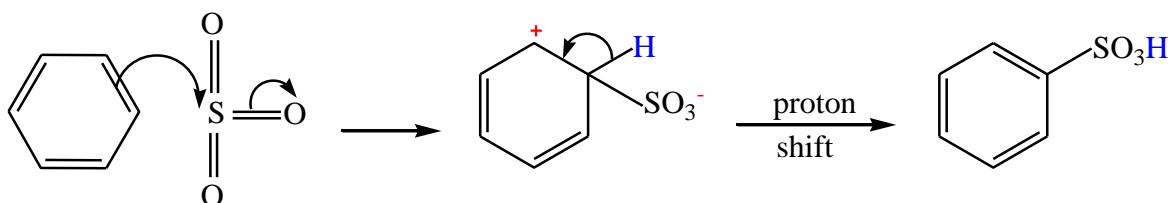
This is the introduction of the sulphonic group ( $-\text{SO}_3\text{H}$ ) on to the benzene ring. It's done by heating benzene with concentrated sulphuric acid. A process for the sulphonation of benzene comprises passing benzene vapor into sulphuric acid, the initial temperature of which is between about 95 and about  $110^\circ\text{C}$ .



### Mechanism



then,



Benzene sulphonic acid is a colorless crystalline compound that is soluble in water.

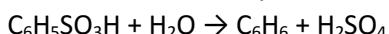
### Uses

Benzensulfonic acid is commonly used as the active ingredient in laundry detergent used in clothes washing machines.[6]

A variety of pharmaceutical drugs are prepared as benzenesulfonate salts and are known as besilates (INN) or besylates(USAN).

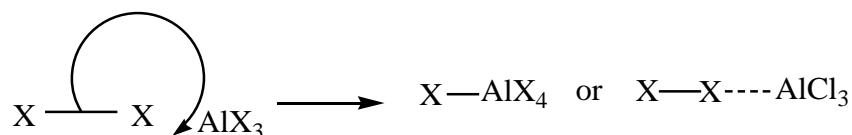
In a diluted form, it is also used as a polymer remover stripping agent.

Benzenesulfonic acid and related compounds undergo desulfonation when heated in water near 200 °C. The temperature of desulfonation correlates with the ease of the sulfonation:

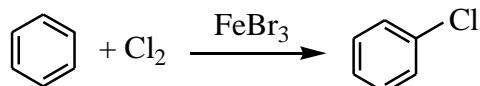


### c. Halogenation

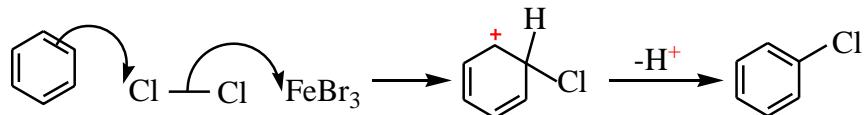
This requires the use of electron carriers ( $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ) as catalysts. The electron carrier is usually a halide of iron or aluminium, the electron carriers' function is to polarize the halogen molecule by withdrawing the electrons from the bond between the two halogen atoms.



#### Example



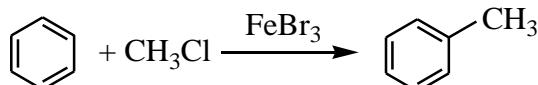
### Mechanism



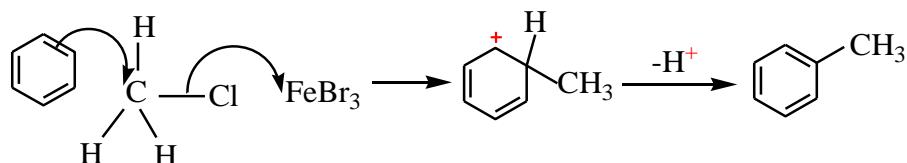
Chlorobenzene was historically important in the manufacture of chlorinated pesticides, especially DDT, and in the production of phenol and aniline. Monochlorobenzene's principal current use is as a chemical intermediate in the production of chemicals such as nitrochlorobenzenes and diphenyl oxide. These chemicals are subsequently used in the production of herbicides, dyestuffs, and rubber chemicals. Additionally, monochlorobenzene is used as a solvent in degreasing processes (e.g., in metal cleaning operations), paints, adhesives, waxes and polishes.

d. Friedel –Craft alkylation

This is a reaction of benzene with an alkyl halide to give an alkyl benzene  
Example



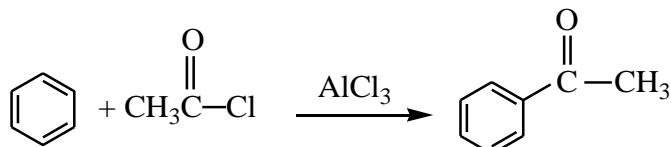
mechanism



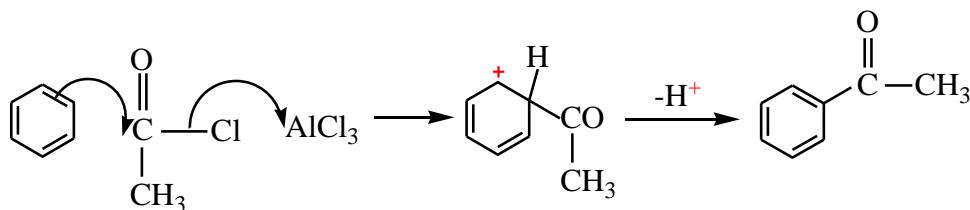
The majority of toluene/methylbenzene is used as a component of petrol. It is also used in paints, lacquers, inks, adhesives, rubber, and cleaning agents. It is used to manufacture benzene, urethane raw materials, and other organic chemicals. It is used in the production of pharmaceuticals, dyes, and cosmetic nail products.

e. This is the introduction of an acylo group (-OCR) to the benzene ring. The reaction is carried out by reacting benzene with an acid halide in presence of a halogen carrier.

Example

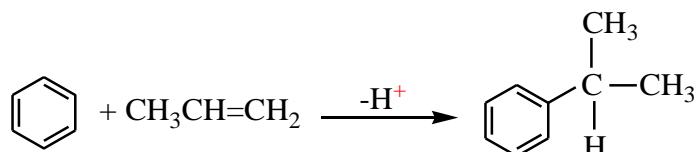


Mechanism

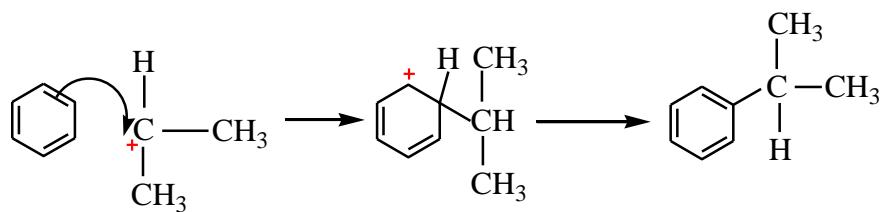


f. Reaction with alkene

In the presence of an acid benzene react with alkenes to form alkylbenzenes.



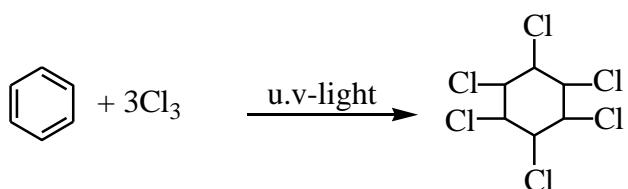
## MECHANISM



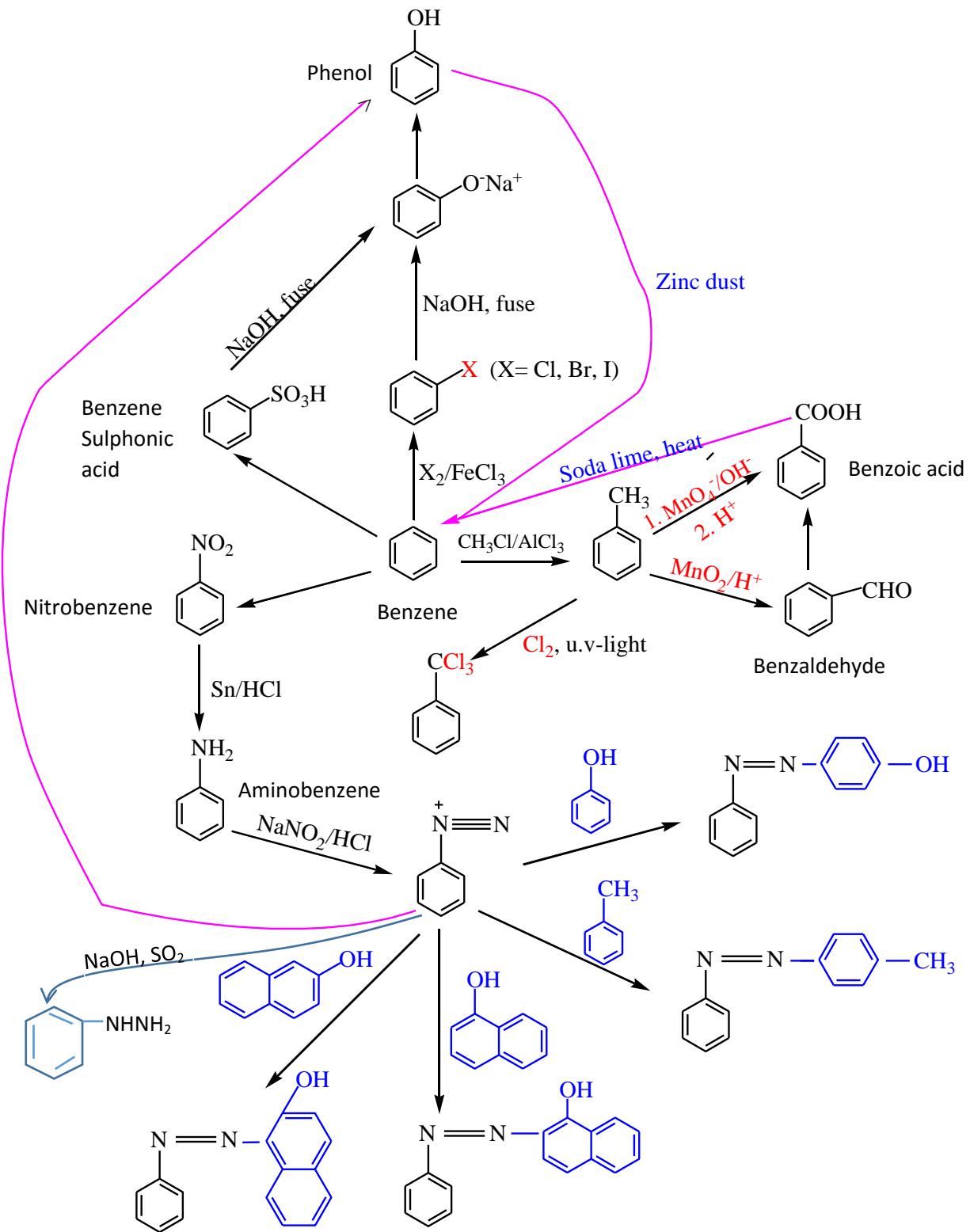
### 4. Other reactions

#### a. Halogenation in the presence of u.v-light

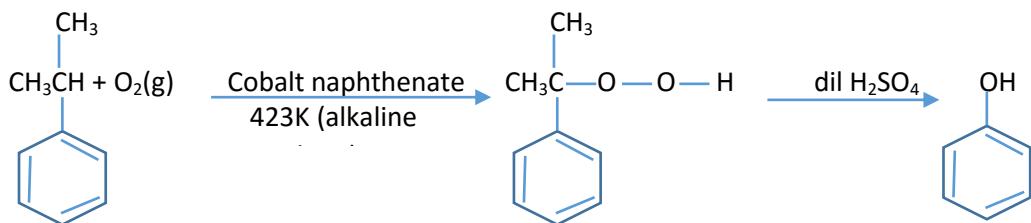
Benzene reacts with chlorine by addition reaction to form saturated product;  
1,2,3,4,5,6-hexachlorohexane



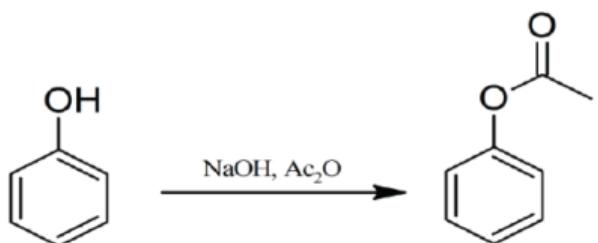
## Derivatives of benzene



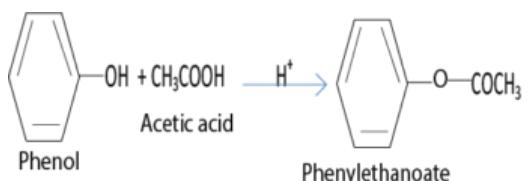
## Preparation of phenol from cumene or 2-phenylpropane



- By reacting phenol and acetic anhydride in presence of sodium hydroxide



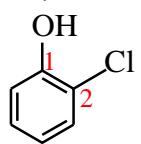
- By reacting phenol with ethanoic/acetic acid in acidic medium



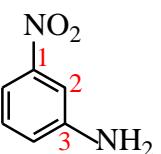
## Nomenclature of derivatives of benzene with more than one substituent.

Number the carbon atoms on the ring and include the position(s) of the groups in the name.

Examples



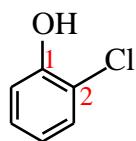
2-Chlorophenol



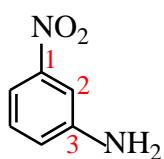
3-aminonitrobenzene

The prefixes; ortho, meta and para- usually abbreviated as o-, m-, and p- may be used for describing the relative positions of substituents in a di-substituted benzene.

Example



2-Chlorophenol  
Or o-chlorophenol



3-aminonitrobenzene  
Or m-aminonitrobenzene

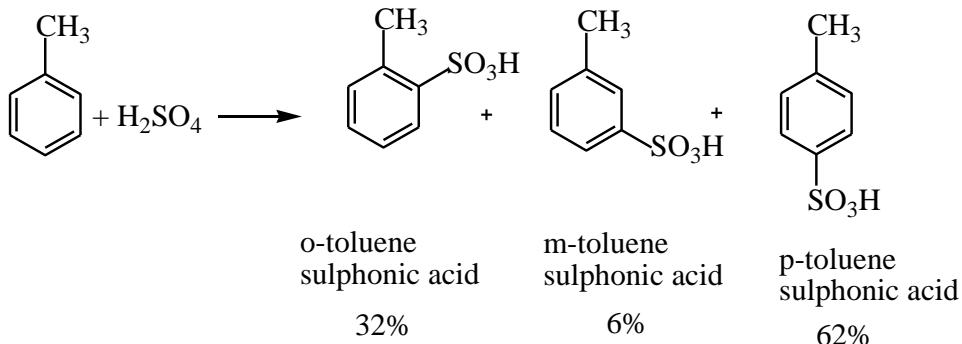
### Effects of substituent group on the reactivity of the ring

A group attached to the benzene ring may have either of the two effects:

- (i) Groups that donate electrons to the benzene ring make the ring more reactive towards electrophilic substitution reaction
- (ii) Groups that donate electrons to the benzene ring like alkyl group that those with at least one lone pair of electron (-NH<sub>2</sub>, -OH) direct the incoming groups to position 2 or position 4. For this reason they are described as 2, 4-directional groups

Example

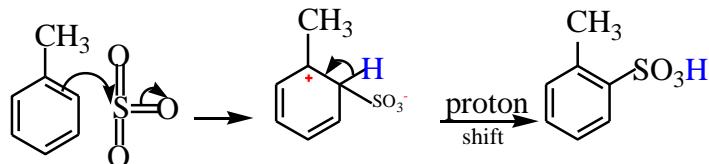
e.g. sulphonation of methylbenzene.



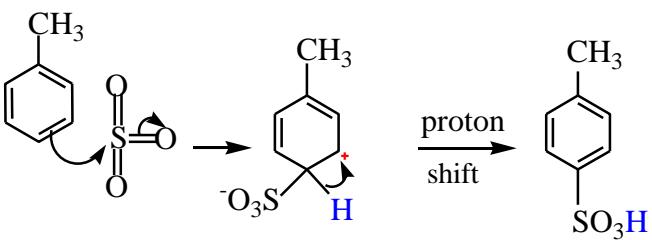
### Mechanism



Then,

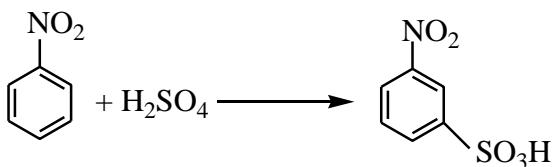


Or



- (iii) Groups that withdraw electron from benzene ring such as nitro or carboxylic groups, make the ring less reactive towards electrophilic reagent. They direct the incoming group to position 3 and are called meta directing groups.

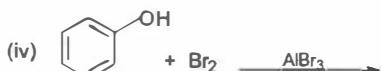
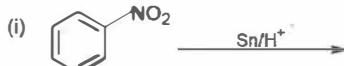
Example



## Exercise

1. (a) What property of benzene and its derivatives are classified as "aromatic".
- (b) Write a formula of benzene suggested by F.A Kekulé. what advantage and disadvantage of this formula.
- (c) Give explanation to "aromatic" properties of benzene in light of modern concepts of its structure.

- (d) Complete the following equations and give the mechanisms for the reactions.



2. (a) Compare the mechanism of electrophilic addition to alkenes with that of electrophilic substitution in the aromatic series, using the reaction of ethene and benzene with bromine. At what stages do the differences show and why?

- (b) Explain why the groups -NO<sub>2</sub> and -CHO should be meta-directors and have deactivating properties.

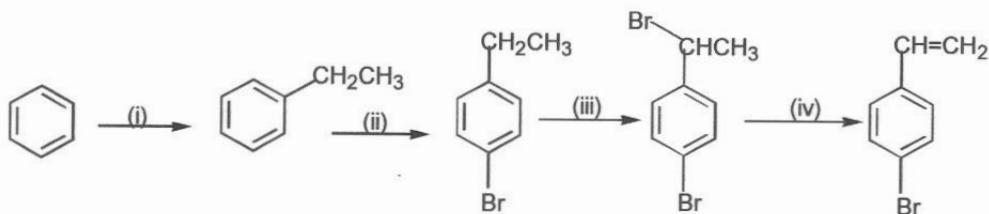
© Why are ortho and para isomers formed in the ratio of 7:9 in chlorination of chlorobenzene and 1:2 in bromination of chlorobenzene.

### Answers

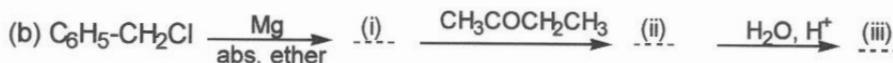
2a) The first stage , consisting in the action of electrophilic reagent Br<sup>+</sup>, is similar to ethene and benzene. The corresponding carbonium ion is formed in each case. The main difference between aromatic substitution and electrophilic addition to alkenes consist in the cause of the second stage. σ-complex is stabilized by ejection of H<sup>+</sup> since an aromatic compound is thus formed, which is advantageous from the energy view point. The carbonium ion formed from ethene reacts with the nucleophilic reagent since this evolves deprotonization-the process that is less advantageous from the energy point of view.

2 (c) The ratio of ortho to para isomers depends on the volume of the entering substituent. the bulky bromine atom makes the ortho substitution difficult.

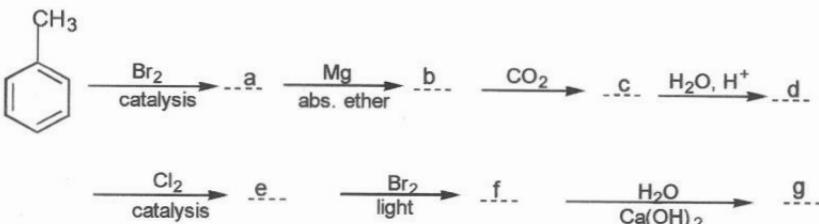
3. What reagents can be used to accomplish the following conversions.



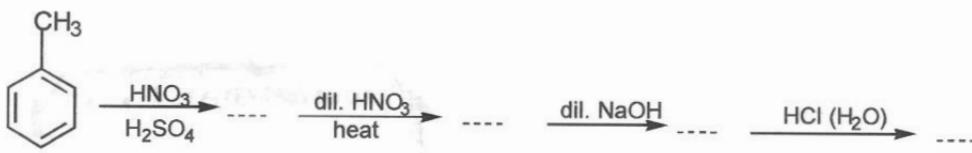
4. Complete the following:



5. What compounds are formed by the following conversion.



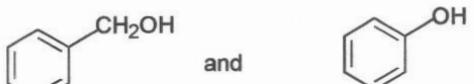
6. Complete the following.



7. Write structural formulas of the intermediate and products in the following



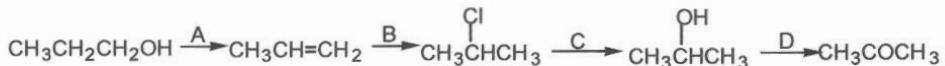
8. Name one reagent that can be used to distinguish between each of the following pair of compounds. In each case state what would be observed if each member of the pair is treated with the reagent and write the equation for the reaction.



9. A compound P,  $\text{C}_4\text{H}_8\text{Br}_2$ , can be converted to Q,  $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_3$ .

- write the structural formula and the IUPAC name of P.
- (i) State the reagent(s) and conditions that can be used to convert P to Q.  
(ii) Write a mechanism for the reaction in b(i) above.

10. Propanone can be prepared from propan-1-ol according to the following scheme:



Identify the reagents A, B, C, and D and state the conditions and write the mechanism for each stage of reaction.

11. The structural formula of a compound Q is shown below:



a. Name the functional groups present in Q.

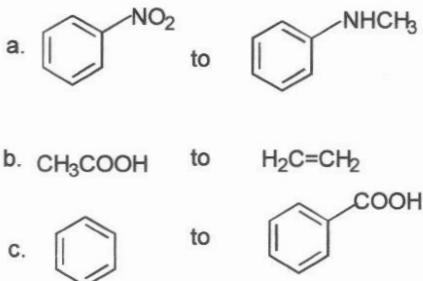
b(i). State what would be observed and write an equation for the reaction between Q and

\* bromine water.

\*\* Nitrous acid

\*\*\* Brady's reagent (2,4-dinitrophenylhydrazine).

12.(a) Write equations to show how the following conversion can be carried out, indicate the reagents and the conditions for the reaction.



(b) write equations, state the conditions and indicate a mechanism for a reaction in which ethanol react differently from phenol.

(c) Write equations to show how phenol can be prepared from benzene and chlorine on industrial scale.

13. Write equations to show how sulfuric acid reacts with each of the following compounds. In each case indicate the conditions for the reaction.

- (a) Ethene
- (b) Benzene
- (c) Ethane-1,2-dioic acid.

14. A compound X,  $\text{C}_4\text{H}_{10}\text{O}$ , forms two layers after 5 minutes when reacted with Conc.  $\text{HCl}$  in presence of anhydrous  $\text{ZnCl}_2$ . X changes the color of acidified potassium dichromate (vi) from orange to green.

- (a) write the structural formula and the IUPAC name of X
- (b) Write equation for the reaction between X and acidified potassium dichromate (vi) solution.
- (c) Write equations to show how you would prepare X using an alkene as one of the starting material. Indicate the conditions for the reaction.

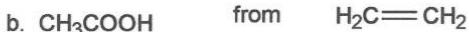
15. Propanone was used as one of the starting materials in manufacture of polypropene.

- (a) write equation to show how propanone can be converted to propene and indicate the conditions for the reactions.
- (b) Outline a mechanism for the reaction that lead to the formation of propene in (a)
- (c) Write an equation for conversion of propene to polypropene.
- (d) Name the type of polymerization in (c)
- (e) State one structural feature that is essential for a molecule to undergo polymerization you have named in (d).

16. Both ethanol and phenol(hydroxybenzene) contain a common functional group.
- Name one reagent that can be used to distinguish the two compound.
  - state what would be observed if each of the compounds is treated with the reagent you have named.
- b. An aqueous solution of phenol is acidic to litmus whereas that of ethanol is neutral. Explain the observation.

- c. Phenol and ethanol react with ethanoyl chloride to give a similar product.
- Write equation for the reaction and name the organic product in each case.
  - outline the mechanism for the reaction between phenol and ethanoyl chloride .

17. Write equations to show how each of the following compounds, can be synthesized from the reagents on the left. Indicate the reagents and conditions for the reactions.



- 18 (a) A compound Y contains carbon, 66.7% and hydrogen, 11.1%, the rest being oxygen. Determine the empirical formula of Y.

- (b) The vapor density of Y is 36, determine the molecular formula. (Hint. Molecular mass is twice the vapor density)

- (c) Y reacts with 2,4-dinitrophenylhydrazine to form a yellow precipitate. Write the formulae and systematic names of all isomers of Y.

- (d) When Y is reacted with iodine in the presence of NaOH, a yellow precipitate is formed.

(I) which one of the structures you gave in (c) is the structure of Y

(ii) Name the yellow precipitate formed.

(iii) write the equation for the reaction.



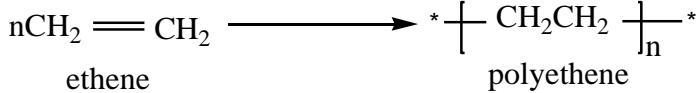
# Polymerization

A polymer is a high molecular mass species consisting of a regular repeating units or chemically similar units, linked by primary covalent bonds.

Polymerization is the process by which high molecular mass species are formed many chemically similar units called monomers.

## Types of polymerization.

1. Addition polymerization: monomers add one to each other to form polymers without loss of any molecule.
    - a. Alkenes undergo addition polymerization to form polyalkenes

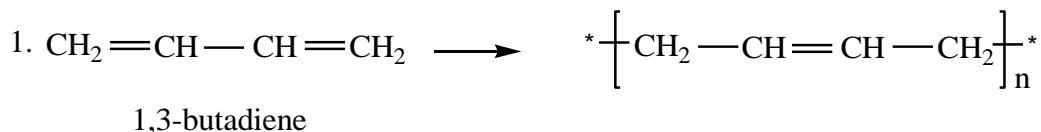


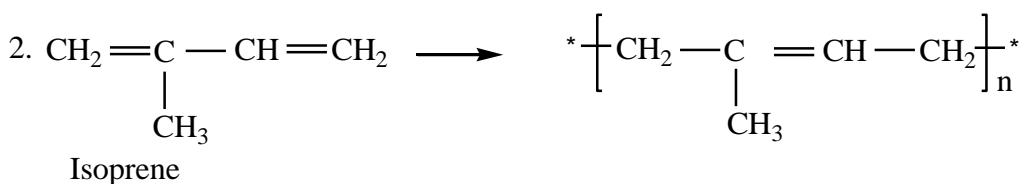
Other common polyalkenes are:

Monomer	Structure	Name of the polymer
<b>Vinyl monomers</b>		
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	Polypropene
Vinylchloride	$\text{CH}_2=\text{CHCl}$	Polyvinylchloride (PVC)
Vinylacetate	$\text{CH}_2=\text{CHCOCH}_3$	Polyvinylacetate
Styrene	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	Polystyrene
acrylonitrile	$\text{CH}_2=\text{CHCN}$	Polyacrylonitrile
Acrylic monomers		
Acrylic acid	$\text{CH}_2=\text{CHCOOH}$	Polyacrylic acid
Methylacrylate	$\text{CH}_2=\text{CHCOOCH}_3$	Polymethylacrylate
butylacrylate	$\text{CH}_2=\text{CHCOOC}_4\text{H}_9$	Polybutylacrylate
Methacrylic acid	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	Polymethacrylic acid
Methylmethacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	Polymethylmethacrylate
Ethylmethacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$	Polyethylmethacrylate
Acrylamide	$\text{CH}_2=\text{CHCONH}_2$	Polyacrylamide

- b. Conjugated dienes undergo addition polymerization to form polydienes.

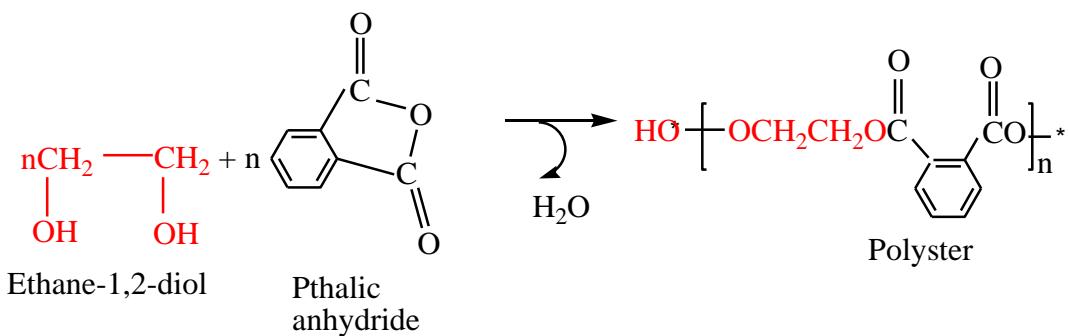
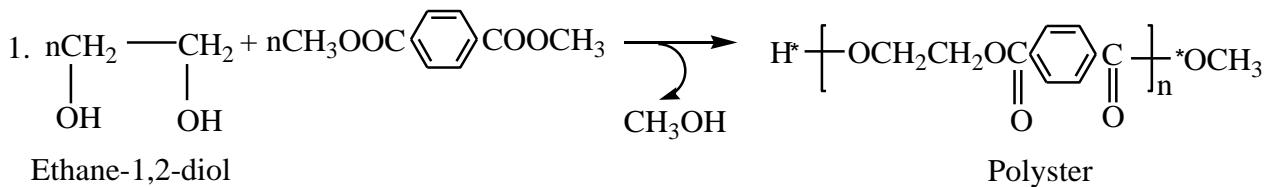
## Examples



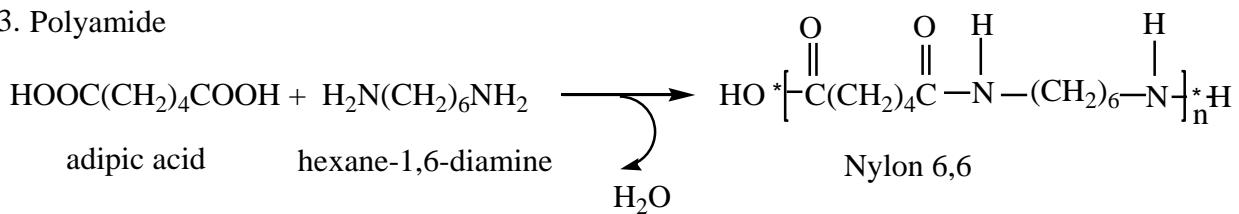


- Condensation polymerization is formation of big molecules called polymers from small molecules called monomers accompanied by loss of small molecules such as water, ammonia e.t.c

## Examples



- ### 3. Polyamide



# Thermoplastic and thermosetting polymers

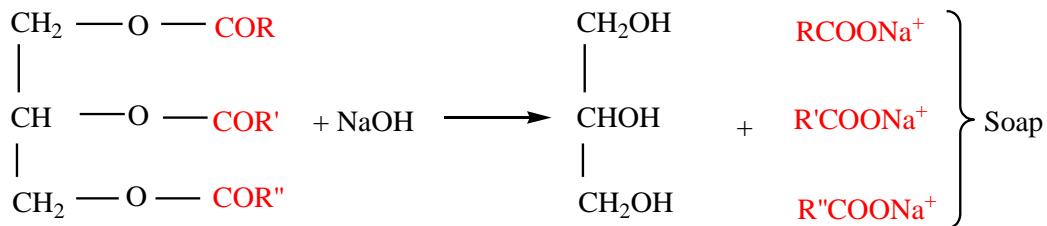
Thermoplastic polymers are polymers that soften and can be remolded on heating, e.g. polyethene.

Thermosetting polymers are polymers that cannot be remolded on heating. E.g. phenolic and epoxy resins.

## Soap and detergents

Soap is a mixture of sodium salt of long chain fatty acids. Fatty acids are straight chain carboxylic acid

Saponification: is the process of making soap; soap is prepared by alkaline hydrolysis of glycerides.



### Sources of vegetable oils

Sun flower seed

Coconut oil seeds

Sim sim

Castor oil seed

### Extraction of oil

Ripe seeds are dried and the oil extracted by application of pressure or by solvent extraction. The residues / husks after extraction of oil are used as fuel, animal feeds or fertilizers.

### Process of making soap

Vegetable oil is boiled with sodium hydroxide until all the oil is hydrolyzed; then saturated solution of sodium chloride is added to precipitate soap. Finally, after cooling soap is skimmed off. When potassium hydroxide is used instead of sodium hydroxide, soft soap (usually used as bathing soap) is obtained.

Glycerin the byproduct of making soap is used in cosmetics and pharmaceutics as a humectant.

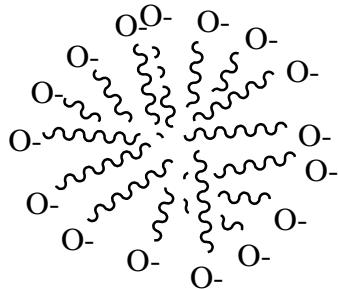
Soaps vary in composition and method of processing, if made from olive oil, it's castile soap, alcohol can be added to it to make it transparent, air can be beaten in it to make it float; perfumes, dyes and germicide can be added. If a potassium salt instead of sodium salt, it is soft soap. Chemically, however, soaps remain pretty the same, and does its job the same way. Other additives include antiseptics, color, perfumes, chelating agents such as polyphosphates, bleaching agents such as peroxides and perborates and fillers such as titanium dioxide.

## Mechanism of soap

A soap molecule has a polar end,  $\text{-COO}^-\text{Na}^+$  and the non-polar end, the long carbon chain of 12 to 18 carbon atoms. The polar end is water soluble and is thus hydrophilic. The non-polar end is water insoluble, thus hydrophobic (or lipophilic, it is soluble in non-polar solvents). Molecules like this are called amphipathic; they have both polar and non-polar end.

When soap is ‘dissolved’ in water, soap is dispersed in spherical cluster called micelles. The non-polar ends bundle together in the center while the polar ends project outwards in the polar solvent – water.

## Soap micelle in water



Negatively charged carboxylate ions stud the surface of the micelle, repulsion between similar charges keeps the micelles dispersed. During the washing fat soluble dirt is removed from the cloth and stabilized inside the micelle while water soluble dirt dissolve in water.

## Detergents

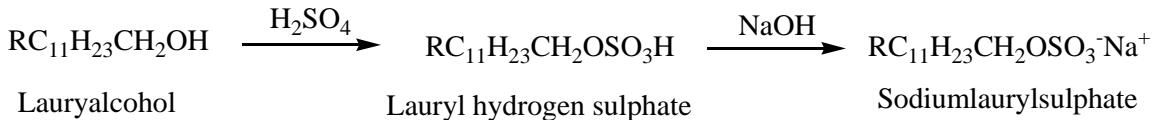
These are synthetic cleansing agent other than sodium and potassium salts of carboxylic acids. Although the synthetic detergents vary considerably in their chemical structures, the molecules of all of them are amphipathic, i.e. have a large non-polar hydrocarbon end that is oil soluble and a polar end that is water soluble.

## Types of detergents

1. Ionic detergents: e.g. salts of alkyl hydrogen sulphates.

## Preparations

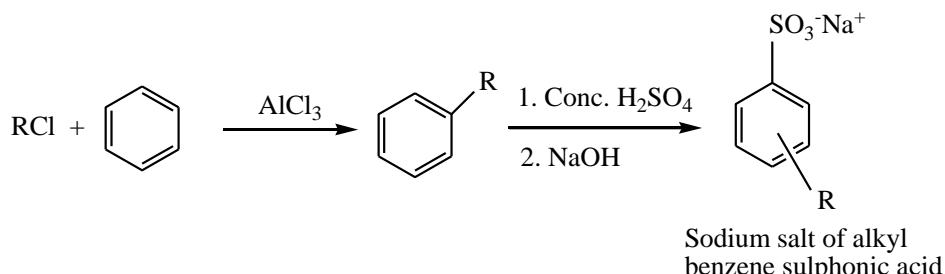
The C12 to C18 alcohols are converted into the salts of alkyl hydrogen sulphates.



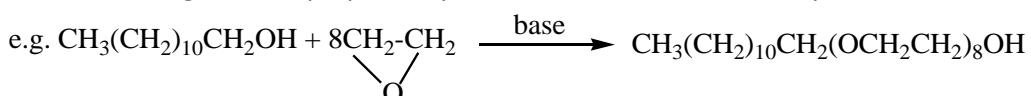
For this, the non-polar end is the long carbon chain and the polar end is  $\text{OSO}_3^- \text{Na}^+$ .

2. Sodium salts of alkyl benzene sulphonlic acids.

These are the most widely detergent; a long chain alkyl group is attached to benzene ring by the action of Friedels-Crafts catalyst and alkyl halide, alkene or alcohol. Sulphonation and neutralization yields the detergent.



3. Nonionic detergents: are prepared by treatment of alcohol with ethylene oxide



Hydrogen bonding to the numerous oxygen atoms makes the polyether end water soluble.

Advantages of detergents over soap

1. The sulphates and sulphonates retain their efficiencies in hard water, since the corresponding calcium and magnesium salts are soluble.
2. They form neutral solutions.

Disadvantages

1. They are non-biodegradable.

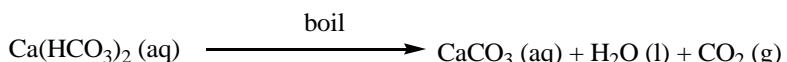
## Hard water

This is water that does not form lather easily with soap. Hardness of water is caused by soluble salt of calcium and magnesium. In presence of magnesium or calcium salts soap react to form

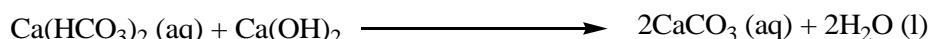
Insoluble salts forming white precipitates called scum.

Types of water hardness.

1. Temporary hardness is a type of hardness that is removed by boiling. It is caused by calcium or magnesium hydrogen carbonates. On boiling, the soluble calcium or magnesium hydrogen carbonates are converted into insoluble carbonates.



It can also be removed by adding slaked lime,  $\text{Ca}(\text{OH})_2$ .



2. Permanent hardness is the type of hardness that cannot be removed by boiling. It is caused by sulphates of calcium and magnesium. It may be removed by:
- (a) Addition of sodium carbonate to precipitate calcium or magnesium ions as carbonates  
$$\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \longrightarrow \text{CaCO}_3(\text{s})$$
  - (b) By ion exchange process using permutit process.
  - (c) By complexation of calcium and magnesium ions with sodium salts of polyphosphates to prevent them from reacting with soap to form scum.

End