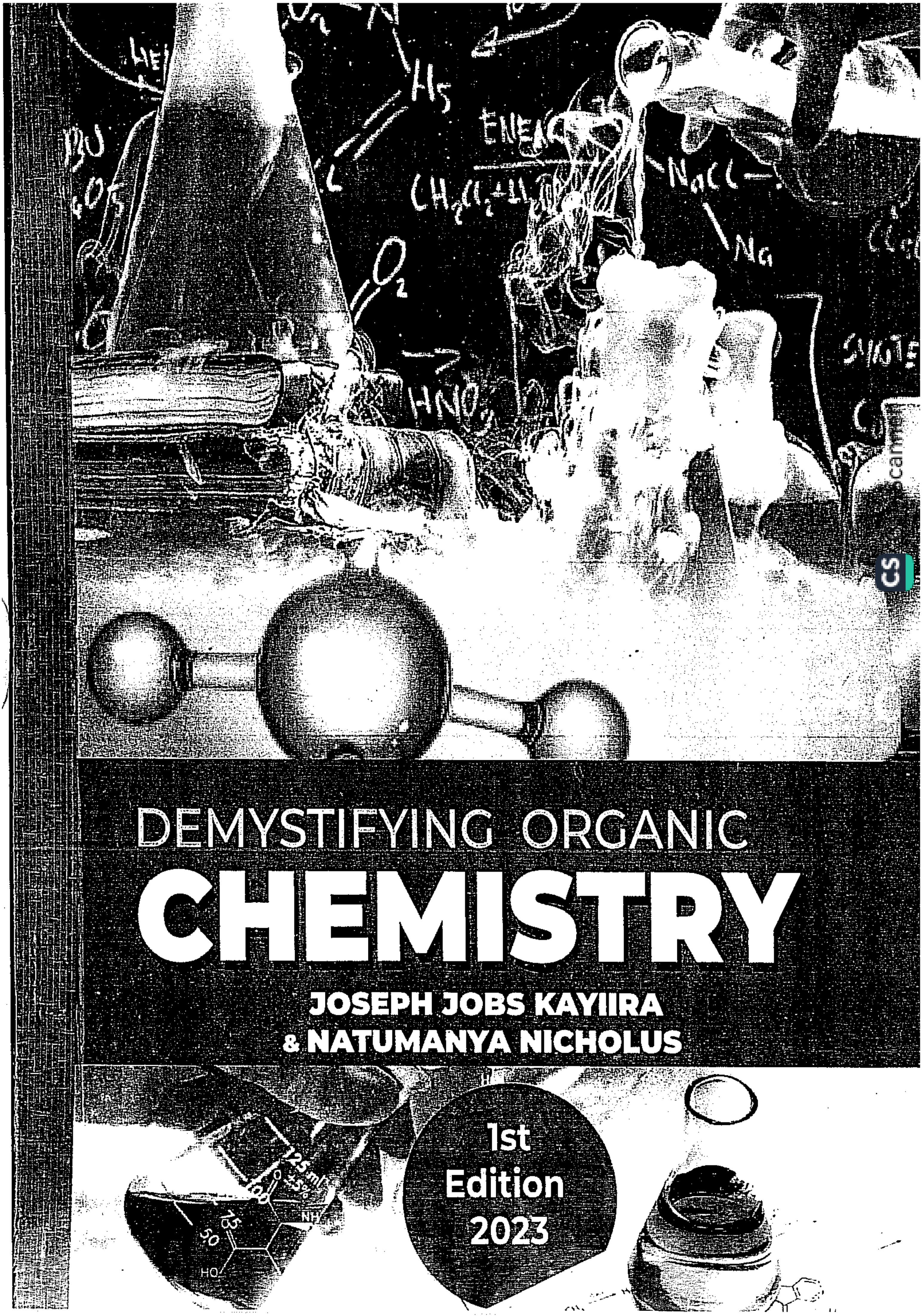

DEMYSTIFYING ORGANIC
CHEMISTRY

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& NATUMANYA NICHOLUS

1st
Edition
2023

DEMYSTIFYING

ORGANIC CHEMISTRY

A simplified, well elaborated and illustrative approach to Advanced level Organic chemistry

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Preface

The authors have an inexorable curiosity in streamlining the chemistry concepts that majority of the students in Uganda consider a nut to crack.

They have taught Chemistry and Mathematics in various schools in Entebbe, Kampala, Wakiso, Mbarara, Bushenyi, Mukono, Buikwe and Butambala. This means that they have analysed the problems students at A' level face in Chemistry.

This organic chemistry collation has been substantially organised and fully compatible with the NCDC Chemistry syllabus-2013.

The authors are contented that this edition contains more than enough material as regards A' level organic chemistry and the subject matter has been arranged and structured so that it can be tackled by students of different abilities. We have tried our best using our versatile experience to make book quite informative as well as simple and lucid.

The concepts are illustrated with a good number of examples involving the synthesis and reaction mechanisms of the organic compounds.

A large number of worked out examples and exercises have been given at the end of each topic. We are sure that this book will be equally useful to teachers and students and quite sure that the book will cater for the exact requirements of students as they prepare to sit for UACE examinations.

Indeed, this book is vital for a student to teach him/herself even in absence of a teacher. However, the teacher is as well vital in cases where you may not well interpret the content. The authors have tried to link organic chemistry with inorganic and physical chemistry concepts where they felt it was necessary.

Variety of examples are given, more than one method of solving a problem illustrated and a diversity of typical examinable revision questions in each subtopic but no answers such that research and consultation is enhanced.

Also feel free to contact the authors using contacts or social media platforms at the back cover of the book for clarity, recommendations, guidance or advice.

This is the only organic chemistry book that you will not regret to have come across.

Table of Contents

Chapter 1

Introduction to Organic Chemistry

Organic chemistry is a branch of chemistry which deals with the study of the chemistry of carbon and it compounds except its oxides, carbonates and hydrogen carbonates. Most carbon containing compounds also contain hydrogen and make the majority of the compounds known to exist than the compounds formed by any other element. Most foods, fuels, clothes and many other things we use in daily life are mainly made of carbon.

1.1 Occurrence of carbon

Carbon, the sixth most abundant element in the universe has been known since ancient times. Carbon is an allotropic element forming both amorphous and crystalline allotropes. In its amorphous form, it mainly exists as coal and wood charcoal. Other amorphous forms include sugar charcoal, coke, animal charcoal and many others.

1. Coal

Coal is mainly made up of carbon with variable amounts of other elements such as hydrogen, oxygen, sulphur and oxygen. The first stage in formation of coal is peat formation.

Peat is a black spongy material formed by partial decomposition of plant material. Peat naturally occurs in bogs, mires, muskegs or moors.

Peat is mainly used for stimulation of plant growth and root development, as a fuel when dried and in making coal.

Coal is in turn used as a fuel, generation of electricity, metal production like aluminium and copper after conversion into coke, cement production and many other applications.

2. Wood charcoal

This is the form of carbon formed by heating wood in a limited amount of oxygen to remove water and other volatile constituents.

It is also used as a fuel, to adsorb gases and purifying liquids.

1.2 Uniqueness of carbon

Carbon is a unique element both in Group IV: where it belongs in the Periodic Table, and in comparison to many other elements.

The uniqueness is because of;

- *the very small atomic radius of carbon atom*
- *the very high electronegativity of carbon*
- *a maximum covalency of four*
- *the high bond energies of the* $C-C$ *and* $C-H$ *bonds*

The last particular reason explains why carbon forms so many more compounds than any other element.

The following are some of the ways in which carbon behaves uniquely as compared to many other elements:

(i) **Carbon has the ability to form long chains of carbon atoms.**

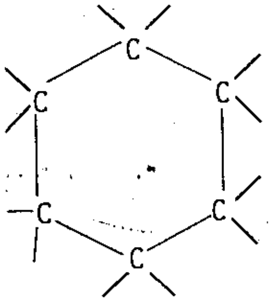
This is called **catenation.** The chains of carbon atoms may exist as short or long chain open systems and with several modes of branching. For catenation to occur for any element, it should have a **valency of at least two** and must be able to form **fairly strong covalent bonds** with its own atoms.

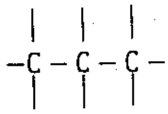
Since carbon has a valency of four, catenation occurs for the element.

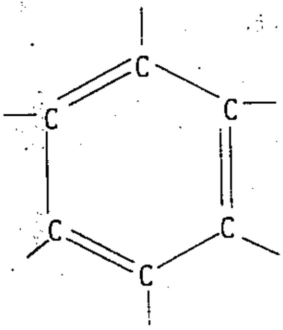
(ii) **The element can also form multiple bonds between itself and atoms of other elements.**

These include carbon-carbon double bonds; (C = C) and carbon-carbon triple bonds (C ≡ C) or bonds between itself and other elements such as oxygen (C = O), sulphur (C = S) and nitrogen (C ≡ N).

Carbon can also form rings of carbon atoms and branched chains of carbon atoms.



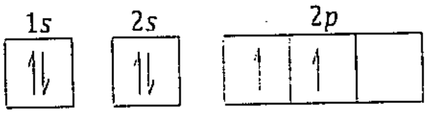




1.3 Hybridisation of carbon

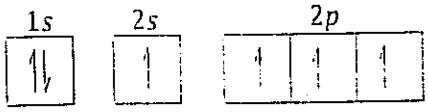
Hybridisation of carbon is the mixing of 2s and 2p-orbitals through promoting a 2s-electron to a 2p-suborbital of carbon, when it is combining with other elements.

In the ground state, carbon with electronic configuration $1s^2 2s^2 2p^2$ seems to have a covalency of two since the atom has only two unpaired electrons.



Carbon atom in ground state

However, when carbon combines with another atom, sufficient energy is acquired for the unpairing of the 2s electrons. The atom then gets unpaired electrons and shows a covalency of four.

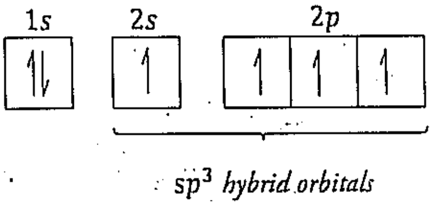


Carbon atom in excited state

1. sp^3 hybridisation

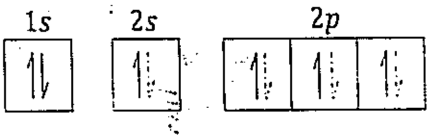
All carbon-carbon single bonds are **sigma (σ) bonds** formed by sp^3hybridisation.

A sigma (σ) bond is a single covalent bond formed by overlap of s and p-orbitals. This occurs after blending of the 2s **electrons** with the three **2p electrons** to form **four exactly similar orbitals**. Since these orbitals are formed from the hybridisation of **one** s and three p **orbitals**, they are called sp^3 hybrid orbitals.



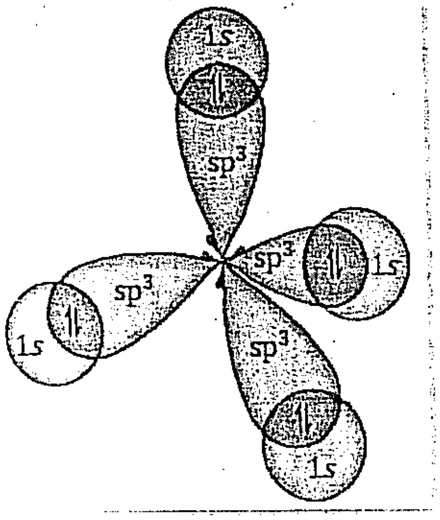
Carbon atom in excited state

In methane (CH_4), the carbon atom is sp^3 hybridised and each hybrid orbitals overlaps with the s-orbital of each of the four hydrogen atoms.



Excited Carbon atom in CH_4

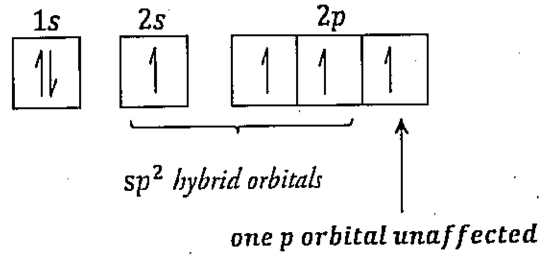
Where ⁝ represents the electrons contributed by each of the four hydrogen atoms



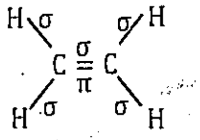
2. sp^2 hybridisation

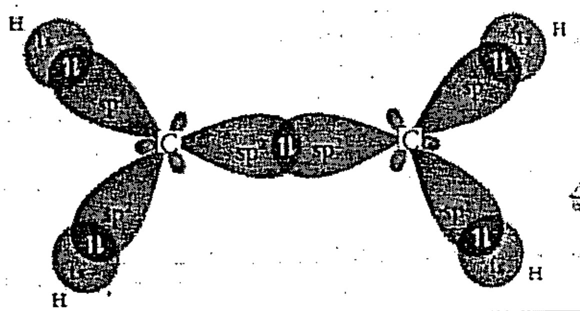
All carbon-carbon double bonds for example in ethene consist of one sigma bond and one pi-bond formed by sp^2 hybridisation.

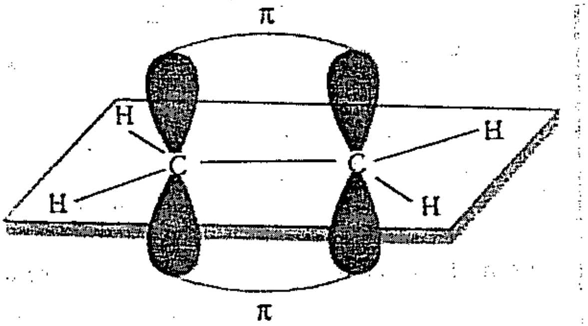
A pi(π) bond is a covalent bond formed by lateral overlap two parallel p-orbitals of adjacent atoms. This involves hybridisation of the **2s** orbital and two **2p**-orbitals, forming three sp^2 hybrid orbitals of equivalent energy leaving a single **2p**-orbital unaffected.



In ethene ($H_2C = CH_2$), two of the sp^2 hybrid orbitals form sigma bonds with the 1s-orbitals of hydrogen. The remaining sp^2 hybrid orbital forms a single bond between the carbon atoms. The unhybridized (unaffected 2p-orbital) forms a pi-bond between the carbon atoms.

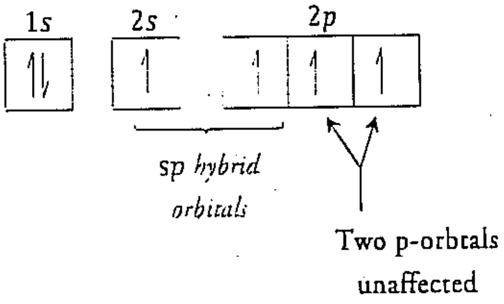


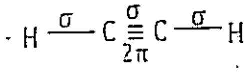


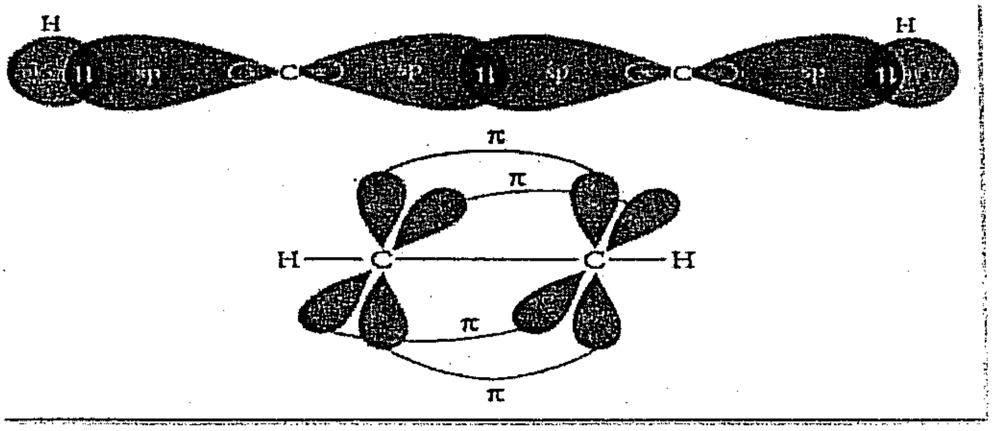


3. *sp* hybridisation

All carbon-carbon triple bonds for example in ethyne consist of one sigma bond and two pi- bond formed by *sp* hybridisation. This involves hybridisation of the $2s$ orbital and one $2p$-orbital, forming two sp hybrid orbitals of equivalent energy leaving two $2p$-orbitals unaffected.




$$H\overset{\sigma}{—}C\underset{2\pi}{\overset{\sigma}{\equiv}}C\overset{\sigma}{—}H$$



Note

The bond lengths and relative bond strengths of carbon-carbon bonds are different. The carbon-carbon single bond in ethane is the longest and weakest followed by the carbon-carbon double bond in ethene and the carbon-carbon triple bond in ethyne is the shortest and strongest.

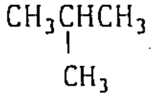
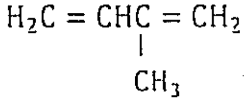
Bond	*Bond length(nm)*	*Bond energy(kJmol^{-1})*
$C-C$	0.154	349
$C=C$	0.134	681
$C\equiv C$	0.120	815

The differences in bond strength are due to the much greater degree of overlap of the atomic orbitals involved in formation of the sigma bond than the pi-bond.

1.4 Aliphatic and aromatic organic compounds

***Aliphatic compounds** are organic compounds possessing open chains of carbon atoms.* The open chains of organic compounds may have the carbon atoms joined in **straight chains** or **branched chains** and may have carbon-carbon **single**, **double** or **triple** bonds.

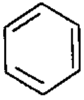
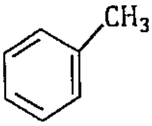
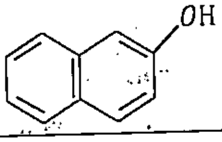
For example:

Aliphatic compound	*Name*
$CH_3CH_2CH_2CH_3$	Butane
 $CH_3\underset{\underset{CH_3}{\mid}}{C}HCH_3$	2-Methylpropane
$CH_3CH=CHCH_3$	But-2-ene
 $H_2C=CH\underset{\underset{CH_3}{\mid}}{C}=CH_2$	2-Methylbuta-1,3-diene
$CH_3C\equiv CCH_3$	But-2-yne

Note: Aliphatic compounds usually burn with a blue or yellow non-sooty flame.

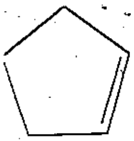
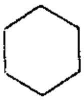
Aromatic compounds are organic compounds possessing a benzene ring. They include benzene itself, benzene derivatives and many others.

Examples include:

Aromatic compound	*Name*
	Benzene
	Methylbenzene
	Naphthalen-2-ol

Note: Aromatic compounds usually burn with a sooty flame because of a high carbon content. However, there are organic compounds that contain **rings of carbon atoms other than the benzene ring**. These are called **alicyclic compounds**. They contain three or more carbon atoms.

For example:

Alicyclic compound	*Name*
	Cyclopropane
	Cyclopentene
	Cyclohexane

1.5 Terms used in organic chemistry

1. *Hydrocarbons*

These are organic compounds containing carbon and hydrogen atoms only. Hydrocarbons are grouped as saturated hydrocarbons and unsaturated hydrocarbons.

Saturated hydrocarbons are compounds containing only carbon-hydrogen and carbon-carbon single bonds. They include all alkanes.

Unsaturated hydrocarbons are compounds containing carbon-carbon multiple bonds. They include alkenes, alkynes and aromatic hydrocarbons.

The saturated hydrocarbons are called so because they contain the maximum number of hydrogen atoms that the carbon compound can possess.

The unsaturated hydrocarbons are called so because they possess fewer than the maximum number of hydrogen atoms, and they are capable of reacting with hydrogen under the proper conditions.

2. *Homologous series*

*A **homologous series** is a set of organic compounds with similar chemical properties and in which one member differs from the next by an additional methylene ($-CH_2-$) group.*

The individual members of a homologous series are called **homologues**.

Considering the series of alkanes, for example, whose general formula is $\mathbf{C_nH_{2n+2}}$, the first four homologues are shown below:

n	*Molecular formula*	*Structural formula*	*Name*
1	CH_4	CH_4	Methane
2	C_2H_6	CH_3CH_3	Ethane
3	C_3H_8	$CH_3CH_2CH_3$	Propane
4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	Butane

Characteristics of a homologous series

- ✓ Members have a general formula. For example, C_nH_{2n+2} for alkanes, C_nH_{2n-2} for alkynes.
- ✓ All members have **similar chemical properties**
- ✓ Each member has **similar methods of preparation** to other members
- ✓ Each member differs from the next by a **methylene group**($-CH_2-$).
- ✓ As each methylene group is added(**as molecular mass increases**) the physical properties like **melting and boiling points of the members change slightly**.
- ✓ Members of the same homologous series have the same **functional group**.

3. *Functional group*

Each homologous series is characterized by a **functional group**.

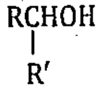
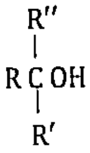
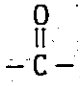
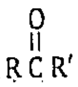
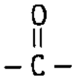
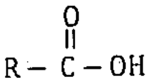
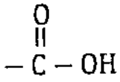
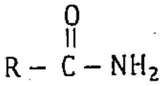
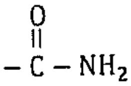
*A **functional group** is a group of atoms or bonds common to a series or a family of compounds and which determine the principal chemical properties of the series.*

The table below shows homologous series, their general structural formulae and functional groups.

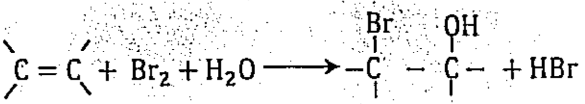
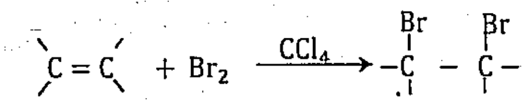
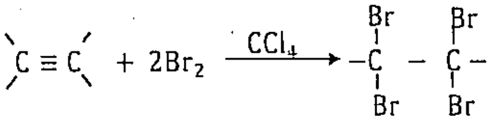
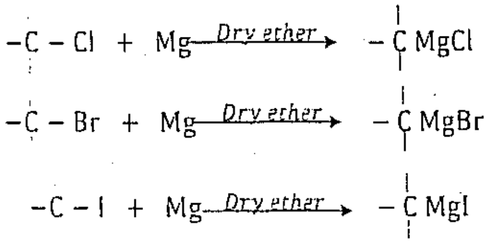
Note: *R* represents an alkyl or group in each case.

R may be the same as *R*′ or *R*″ or all alkyl groups may be different.

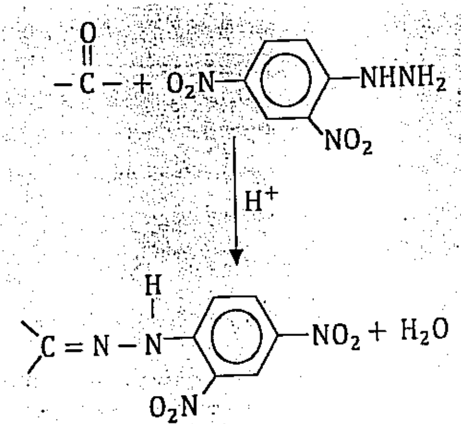
Homologous series	*General formula*	*Structural formula*	*Functional group*	*Name of functional group*
Alkanes	C_nH_{2n+2} where $n \geq 1$	RH	No functional group	
Alkenes	C_nH_{2n} where $n \geq 2$	$RCH = CHR'$	$C = C$	Carbon-carbon double bond
Alkynes	C_nH_{2n-2} where $n \geq 2$	$RC \equiv CR'$	$C \equiv C$	Carbon-carbon triple bond

Alcohols or Alkanols	$C_nH_{2n+1}OH$ where $n \geq 1$	ROH or  $R\underset{R'}{C}HOH$ or  $R\overset{R''}{\underset{R'}{C}}OH$	$-OH$	Hydroxyl group
Alkylhalides	$C_nH_{2n+1}X$ where $n \geq 1$ and $X = Cl, Br$ or I	RX or  $R\underset{R'}{C}HX$ or  $R\overset{R''}{\underset{R'}{C}}X$	$C-X$ Hence $C-Cl$ $C-Br$ $C-I$	Carbon-halogen bond Carbon-chlorine bond Carbon-bromine bond Carbon-iodine bond
Ethers	$C_nH_{2n+1}O$ where $n \geq 2$	$R-O-R'$	$-O-$	Oxygen atom
Aldehydes or Alkanals	$C_nH_{2n+1}CHO$	 $R\overset{O}{\overset{\parallel}{C}}H$	 $-\overset{O}{\overset{\parallel}{C}}-$	Carbonyl group
Ketones or Alkanones	$C_nH_{2n+2}CO$ where $n \geq 2$	 $R\overset{O}{\overset{\parallel}{C}}R'$	 $-\overset{O}{\overset{\parallel}{C}}-$	Carbonyl group
Carboxylic acids	$C_nH_{2n+1}COOH$	RCOOH or  $R-\overset{O}{\overset{\parallel}{C}}-OH$	 $-\overset{O}{\overset{\parallel}{C}}-OH$	Carboxyl group
Primary amines	$C_nH_{2n+1}NH_2$	$R-NH_2$	$-NH_2$	Amino group
Primary amides	$C_nH_{2n+1}CONH_2$	$RCONH_2$ or  $R-\overset{O}{\overset{\parallel}{C}}-NH_2$	 $-\overset{O}{\overset{\parallel}{C}}-NH_2$	Amide group

Specific reagents can be used, in the laboratory, to test for the different functional groups as indicated in the table below:

Functional group	*Reagent(s) and observations*	*Reaction equation(s)*
Carbon-carbon double bond	(i) *Bromine water* Observation *Reddish-brown solution turns colourless* (ii) *Bromine in presence of tetrachloromethane* Observation *Reddish-brown solution turns colourless* Note Other reagents like *alkaline potassium permanganate solution* or *acidified potassium permanganate solution* can also be used to test for the carbon-carbon double bond.	 $>C=C< + Br_2 + H_2O \longrightarrow -\overset{Br}{\underset{\vert}{C}}-\overset{OH}{\underset{\vert}{C}}- + HBr$  $>C=C< + Br_2 \xrightarrow{CCl_4} -\overset{Br}{\underset{\vert}{C}}-\overset{Br}{\underset{\vert}{C}}-$
Carbon-carbon triple bond	Same as for carbon to carbon double bond. For example: (i) *Bromine in presence of tetrachloromethane* Observation *Reddish-brown solution turns colourless*	 $>C\equiv C< + 2Br_2 \xrightarrow{CCl_4} -\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-$
Hydroxyl group	Reagent: *Sodium Metal* Observation *Bubbles of a colourless gas*	$-OH + Na \longrightarrow -\bar{O}Na^+ + \frac{1}{2}H_2$
Carbon-halogen bond	Reagent: *Magnesium turnings in presence of dry ether* Observation *A cloudy solution is formed*	 $-\overset{\vert}{\underset{\vert}{C}}-Cl + Mg \xrightarrow{Dry\ ether} -\overset{\vert}{\underset{\vert}{C}}MgCl$ $-\overset{\vert}{\underset{\vert}{C}}-Br + Mg \xrightarrow{Dry\ ether} -\overset{\vert}{\underset{\vert}{C}}MgBr$ $-C-I + Mg \xrightarrow{Dry\ ether} -\overset{\vert}{\underset{\vert}{C}}MgI$

DEMYSTIFYING Organic Chemistry: K.J. Jobs & N.N. Hyper

Carbonyl group	Reagent: *Brady's reagent* <u>Observation</u> *Yellow precipitate*	 *yellow precipitate*
Carboxyl group	Reagent: *Sodium carbonate solution or sodium hydrogen carbonate solution* <u>Observation</u> *Bubbles of a colourless gas*	$-COOH + NaHCO_3 \longrightarrow -CO\bar{O}Na^+ + CO_2 + H_2O$ or $2(-COOH) + Na_2CO_3 \longrightarrow 2(-CO\bar{O}Na^+) + CO_2 + H_2O$
Primary amine	Reagent: *Concentrated hydrochloric acid* <u>Observation</u>: *Dense white fumes*	$-NH_2 + HCl \longrightarrow \overset{+}{N}H_3Cl^-$

4. Isomerism

Isomerism is the existence of different compounds with the same molecular formula but different structural formulae.

Isomers are compounds that have the same molecular formula but different structural formulae.

There are two main types of isomerism. These include structural isomerism and stereo isomerism.

(a) Structural isomerism

This is the existence of more than one organic compounds with the same molecular formula but different structural formulae due to different arrangement of carbon atoms in the carbon chain.

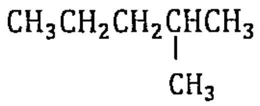
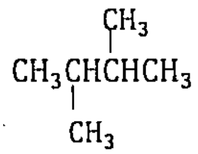
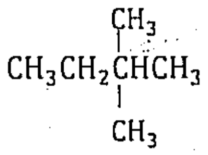
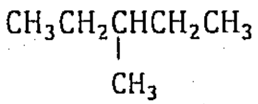
There are three types of structural isomerism. These include:

- Chain isomerism
- Positional isomerism
- Functional group isomerism

(i) Chain isomerism

This is the existence of two or more compounds with the same molecular formula, same functional group and belonging to same homologous series but with different structural formulae due to different arrangement of carbon atoms in the carbon skeleton.

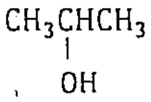
For example, C_6H_{14}, has the following chain isomers:

Structural formula of chain isomer	*Name of isomer*
$CH_3CH_2CH_2CH_2CH_2CH_3$	*n*-Hexane
 $CH_3CH_2CH_2\underset{CH_3}{\underset{\vert}{C}H}CH_3$	2 – Methylpentane
 $CH_3\underset{CH_3}{\underset{\vert}{C}H}\overset{CH_3}{\overset{\vert}{C}H}CH_3$	2,3 – Dimethylbutane
 $CH_3CH_2\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}HCH_3$	2,2 – Dimethylbutane
 $CH_3CH_2\underset{CH_3}{\underset{\vert}{C}H}CH_2CH_3$	3 – Methylpentane

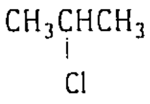
(ii) Positional isomerism

This is the existence of two or more organic compounds with the same molecular formula but differ by the position of the functional group on the same carbon skeleton.

For example C_3H_8O has the following positional isomers:

Structural formula of isomer	*Name of the isomer*
$CH_3CH_2CH_2OH$	Propan-1-ol
 $CH_3\underset{OH}{\underset{\vert}{C}H}CH_3$	Propan-2-ol

C_3H_7Cl has the following positional isomers:

Structural formula of isomer	*Name of the isomer*
$CH_3CH_2CH_2Cl$	1 – Chloropropane
 $CH_3\underset{Cl}{\underset{\vert}{C}H}CH_3$	2 – Chloropropane

C_4H_8 has the following positional isomers:

Structural formula of isomer	*Name of the isomer*
$CH_3CH_2CH = CH_2$	But-1-ene
$CH_3CH = CHCH_3$	But-2-ene

Note: *Positional isomers have similar chemical properties.*

(iii) Functional group isomerism

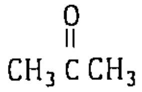
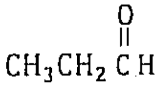
This is the existence of two or more compounds with the same molecular formula but different functional groups.

For example C_2H_6O has the following isomers:

Structural formula of isomer	*Name of the isomer*
CH_3CH_2OH	Ethanol
CH_3OCH_3	Methoxymethane (Dimethylether)

Therefore alcohols are isomeric to ethers.

C_3H_6O has the following isomers:

Structural formula of isomer	*Name of the isomer*
 $CH_3\overset{\overset{O}{\parallel}}{C}CH_3$	Propanone
 $CH_3CH_2\overset{\overset{O}{\parallel}}{C}H$	Propanal

Therefore ketones are isomeric to aldehydes

$C_4H_8O_2$ has the following isomers:

Structural formula of isomer	*Name of the isomer*
$CH_3CH_2CH_2COOH$	Butanoic acid
$CH_3COOCH_2CH_3$	Ethyl ethanoate
$CH_3CH_2COOCH_3$	Methyl propanoate
$HCOOCH_2CH_2CH_3$	Propyl methanoate

Therefore carboxylic acids are isomeric to esters

Alkenes are also isomeric to cycloalkanes. For example, C_3H_6 has the following isomers:

Structural formula of isomer	*Name of the isomer*
$CH_3CH = CH_2$	Propene
	Cyclopropane

(b) Stereoisomerism

This is the existence of compounds with the same molecular formula and the same structural formula but differ by the spatial arrangement of atoms.

There are two types of stereoisomerism which include:

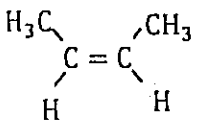
- Geometrical isomerism
- Optical isomerism

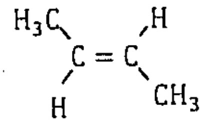
(i) Geometrical isomerism

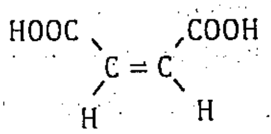
This is the existence of compounds with the same molecular formula and the same structural formula but differ by the prevention of free rotation around at least one double bond in the compound.

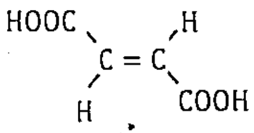
The nomenclature of *cis* is often used when identical substituents are on the same side of the double bond and *trans* when they are on opposite sides.

For example:


cis –But-2-ene


trans –But-2-ene


cis –Butenedioic acid

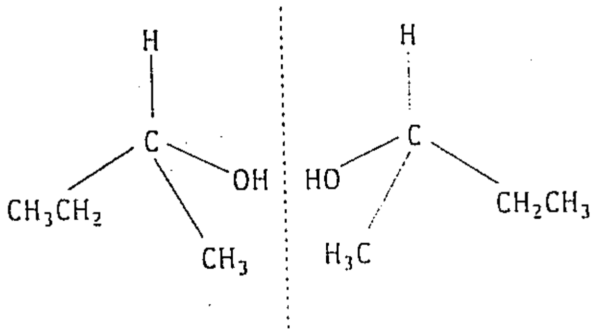

trans – Butenedioic acid

Note: Geometrical isomers have different chemical and physical properties.

(ii) Optical isomerism

This is the existence of compounds with the same molecular and structural formulae but one is not superimposable upon the other.

For example, the optical isomers of butan-2-ol are:



Note: The two mirror images cannot be superimposed upon each other.

1.6 Types of organic reactions

1. Substitution reactions

These are reactions in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms. They are also called *displacement reactions.*

For example, the **hydrolysis of chloroethane.**

$$CH_3CH_2Cl \xrightarrow[\text{heat}]{\bar{O}H(aq)} CH_3CH_2OH + Cl^-$$

There are **two** types of substitution reactions:

- Electrophilic substitution reaction
- Nucleophilic substitution reaction
- Free radical substitution

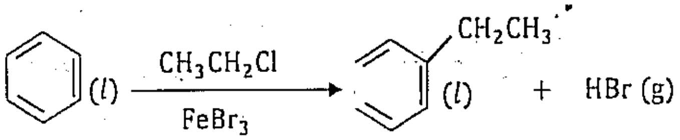
(i) Electrophilic substitution reaction (S_E)

*An **electrophile** is an atom that is positively charged or a species which is electron deficient (lacks lone pairs of electrons).*

*An **electrophilic substitution** reaction is therefore a reaction in which a hydrogen atom of a benzene ring is replaced by an atom or group of atoms which is electron deficient (electrophile).*

All the reactions undergone by benzene, in which a hydrogen atom in the ring is replaced by an electron deficient group are electrophilic substitution reactions.

For example, **alkylation of benzene.**



Such reactions are initiated by the electrophile.

(ii) Nucleophilic substitution reaction (S_N)

*A **nucleophile** is a negatively charged ion or a compound in which an atom has lone pair(s) (electron rich).*

*A **nucleophilic substitution** reaction is therefore a reaction in which an atom in a compound is replaced by an atom or group of atoms which is electron rich (nucleophile).*

The hydrolysis of alkylhalides when heated with aqueous sodium hydroxide is a nucleophilic substitution reaction.

$$(CH_3)_3C-Br \xrightarrow[\text{heat}]{NaOH(aq)} (CH_3)_3C-OH + HBr$$

There are also two types of nucleophilic substitution reactions and these will be described further under halohydrocarbons.

(iii) Free radical substitution

A reaction where a hydrogen atom in a hydrocarbon is replaced by a free radical.

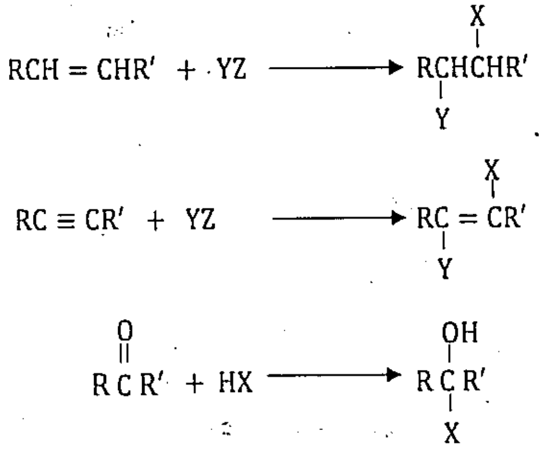
2. Addition reactions

*An **addition reaction** is a reaction in which the attacking reagent adds itself across an unsaturated bond of the reactant to form a saturated product.*

In addition reactions, the unsaturated bonds act as sources of electrons hence are attacked by electron deficient species (electrophiles).

Such reactions are undergone by **alkenes, alkynes** and **carbonyl compounds (aldehydes and ketones)**

Addition reactions for alkenes and alkynes are generally represented as:



$$RCH=CHR' + YZ \longrightarrow R\underset{Y}{C}H\overset{X}{C}HR'$$

$$RC\equiv CR' + YZ \longrightarrow R\underset{Y}{C}=\overset{X}{C}R'$$

$$R\overset{O}{\overset{\|}{C}}R' + HX \longrightarrow R\overset{OH}{\underset{X}{C}}R'$$

There are two types of addition reactions:

- Electrophilic addition reaction
- Nucleophilic addition reaction

(i) Electrophilic addition reaction (A_E)

This is a reaction in which an electron deficient species adds itself across a multiple bond of alkenes or alkynes to form a single product with no loss of any atom. The unsaturated bonds act as a source of electrons. The reaction is initiated by an electrophile.

For example,

- Reaction between ethene with bromine liquid.

$$H_2C=CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

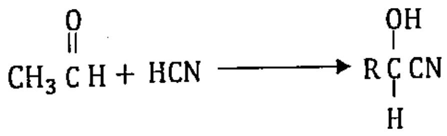
- Reaction between ethyne with excess bromine liquid.

$$HC\equiv CH + Br_2 \longrightarrow CHBr_2CHBr_2$$

(ii) Nucleophilic addition reaction (A_N)

This is a reaction in which an electron rich species simply adds itself across the unsaturated bond to form a single product without loss of any atom. The nucleophile acts as a source of electrons.

For example, reaction between ethanal with hydrogen cyanide.

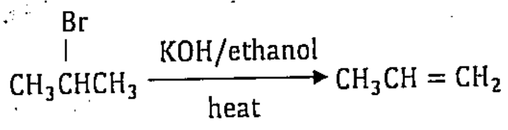


$$CH_3\overset{O}{\overset{\|}{C}}H + HCN \longrightarrow R\overset{OH}{\underset{H}{C}}CN$$

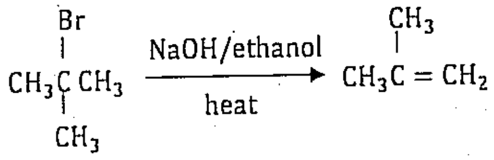
3. Elimination reactions

An elimination reaction is a reaction which involves removal of an atom or group of atoms from two adjacent carbon atoms to form a multiple bond. These reactions are commonly undergone by secondary and tertiary alkylhalides.

For example, the reaction between 2-Bromopropane or 2-Methyl-2-bromopropane and a solution of sodium hydroxide or potassium hydroxide in ethanol on heating.



$$CH_3\overset{Br}{C}HCH_3 \xrightarrow[\text{heat}]{\text{KOH/ethanol}} CH_3CH = CH_2$$



$$CH_3\overset{Br}{\underset{CH_3}{C}}CH_3 \xrightarrow[\text{heat}]{\text{NaOH/ethanol}} CH_3\overset{CH_3}{C} = CH_2$$

In both cases, alkenes are formed as major products.

Note:

Under similar conditions, primary alkylhalides react to form ethers as major products. For example, bromoethane reacts to form an ether (ethoxyethane) as major product. Such a reaction is a nucleophilic substitution reaction.

$$CH_3CH_2Br \xrightarrow[\text{heat}]{\text{KOH/ethanol}} CH_3CH_2OCH_2CH_3$$

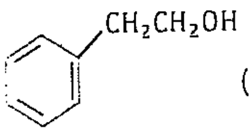
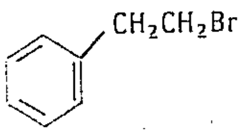
There are also two types of elimination reactions and these will be seen further under alkylhalides.

Note

Alkylhalides and alcohols can be classified as primary, secondary or tertiary.

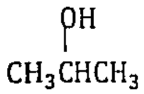
Primary compounds are those in which the carbon atom carrying the functional group is attached to only one alkyl group.

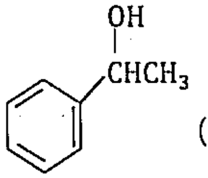
For example

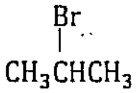
(i) CH_3CH_2OH and  (ii) CH_3CH_2Br and 

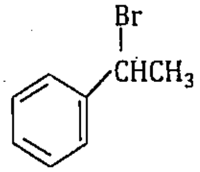
Secondary compounds are those in which the carbon atom carrying the functional group is attached to only two alkyl groups.

For example

(i) 
$CH_3CH(OH)CH_3$

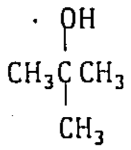
and 

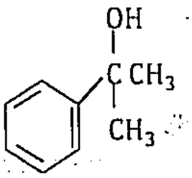
(ii) 
$CH_3CH(Br)CH_3$

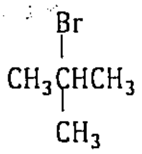
and 

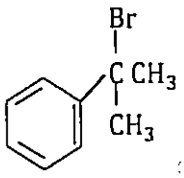
Tertiary compounds are those in which the carbon atom carrying the functional group is attached to three alkyl groups.

For example

(i) 
$CH_3C(OH)(CH_3)CH_3$

and 

(ii) 
$CH_3C(Br)(CH_3)CH_3$

and 

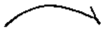
1.7 Organic reaction mechanisms

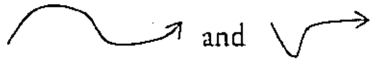
A *mechanism* is a detailed description of a chemical reaction outlining each separate stage.

A reaction mechanism shows the sequence of steps by which a reaction takes place. The reaction mechanism is worked out from a study of kinetics of the reaction.

Such information is not provided by the stoichiometric equation for the organic reaction.

When outlining mechanisms, the following should be noted;

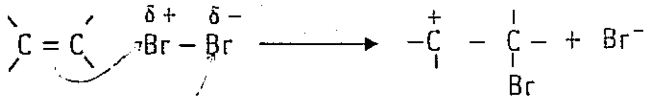
- Curly arrows are used. Such arrows should bend once.
- A double headed curly arrow shows that two electrons are flowing i.e. .
- A single headed arrow implies that one electron is flowing i.e. .
- Arrows of the forms shown below are discouraged for use in mechanism outlines:



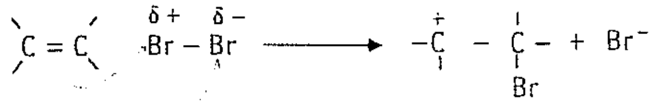
Note

The arrows must begin at the center of double bond where the electrons are and then ends at an electron deficient species (electrophile).

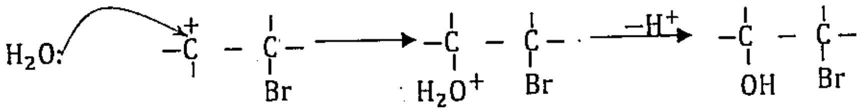
Illustration



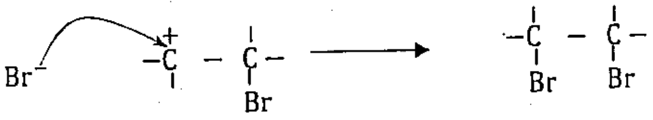
Arrows that have no origin and destination such as those below are discouraged. *The arrows should touch the bonds, electrons or charge.*



Arrows may also begin from a center of a lone pair of electrons or from the negative charge of a nucleophile.



Similarly;



- Electron flow within the mechanism should be consistent.
- In mechanisms where intermediates are involved, they should be clearly written.
- Mechanisms in which reagents are prepared first, the equations for their preparation should be well balanced. Some of the most common equations involved in such mechanisms are written below:

1. $2Fe + 3Br_2 \longrightarrow 2FeBr_3$
2. $2H_2SO_4 \longrightarrow SO_3 + H_3O^+ + HSO_4^-$
3. $H_2SO_4 + HNO_3 \longrightarrow \overset{+}{N}O_2 + HSO_4^- + H_2O$

1.8 Common terms used in organic chemistry reactions

1. Bond polarity

The bonds formed in organic compounds are mainly covalent.

The covalent bonds may be **non-polar** if they are formed between two atoms with similar or almost similar electronegativities which contribute an equal number of electrons to be shared. Such bonds include;

$$Cl-Cl \quad \text{and} \quad Br-Br$$

However, a covalent bond formed between two atoms whose electronegativity values are greatly different becomes a **polar covalent bond**.

The more electronegative atom pulls the bonding electrons towards itself, gaining a partial negative charge and the less electronegative atom gains a partial positive charge. For example in;

$$CH_3\overset{\delta+}{C}H_2-\overset{\delta-}{Br} \quad \text{and} \quad CH_3\overset{\delta+}{C}H_2-\overset{\delta-}{Cl}$$

2. Bond cleavage

During a chemical reaction, chemical bonds have to be broken (cleaved) so that new compounds are formed.

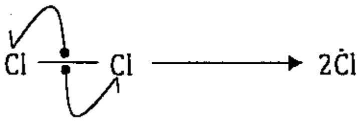
The breaking/ cleavage or fission can be of any of the two types namely:

- Homolytic fission
- Heterolytic fission

(i) Homolytic fission (cleavage)

In this type of cleavage, when the covalent bond breaks, each of the atoms takes one of the bonding electrons forming very reactive free radicals.

The flow of electrons is represented by half arrows as shown below:



$$Cl - Cl \longrightarrow 2\dot{C}l$$

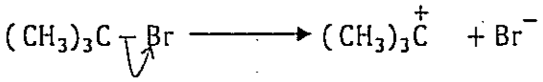
This type of fission usually occurs in covalent bonds where the difference in electronegativity between the bonded atoms is small.

Homolytic fission requires usually requires energy in form sunlight or heat.

(ii) Heterolytic fission (cleavage)

In this type of cleavage, when the covalent bond breaks, one of the atoms that is more electronegative remains with the bonding electrons.

The more electronegative atom gains a negative charge and the less electronegative atom gains a positive charge.



$$(CH_3)_3C - Br \longrightarrow (CH_3)_3\overset{+}{C} + Br^-$$

The ion formed above, which contains a positively charged carbon atom, is called a **carbocation**.

3. A free radical

This is an atom or group of atoms with unpaired electrons.

Free radicals are always formed after homolytic cleavage.

4. Carbocation

A carbocation can also be called a *carbonium ion.*

A *carbocation/ carbonium ion* is an ion containing a positively charged carbon atom.

A carbocation can be **primary**, **secondary** or tertiary depending on the number of alkyl groups surrounding the positively charged carbon atom.

Carbocation	*Example*
Primary carbocation	$CH_3\,CH_2\,\overset{+}{C}H_2$
Secondary carbocation	$CH_3\,\overset{+}{C}H\,CH_3$
Tertiary carbocation	$(CH_3)_3\overset{+}{C}$

The stability of the carbocations increases with the increase in the number of alkyl groups attached to the positively charged carbon atom in order. *Primary* < *Secondary* < *Tertiary*.

6. Nucleophile

A *nucleophile* is an atom that is negatively charged or a compound in which an atom has a lone pair of electrons.

Examples include; $Cl^-, Br^-, I^-, \bar{O}H, CN^-, RO^-, NH_3, H_2O, RNH_2,$ and ROH.

7. Electrophile

An *electrophile* is an atom that is positively charged or a species that is electron deficient.

Examples include $H^+, Cl^+, Br^+, I^+, NO_2^+, RN_2^+, R_3C^+,$ and SO_3.

8. Inductive effect

This is the ability of an atom or group of atoms to donate electrons towards a neighbouring atom or the ability to withdraw electrons from the neighbouring atom.

An atom or group of atoms that donate(s) electrons to a neighbouring atom has/have **positive inductive effect**. These include all **alkyl groups**.

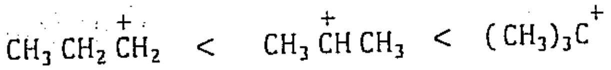
An atom or group of atoms that withdraws electrons from the neighbouring atom has/have **negative inductive effect**. These include all halogen atoms, $-NO_2, -NH_2, -C \equiv N$ and $-SO_3H$.

9. Steric hindrance

Steric hindrance is a condition when the spatial arrangement of atoms or groups in a molecule at or near a reacting site of a molecule hinders or retards a reaction.

The higher the number of alkyl groups surrounding a reaction site in a molecule, the greater the steric hindrance.

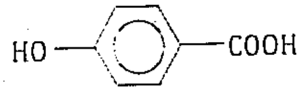
For carbocations, steric hindrance increases in the order, $Primary < Secondary < Tertiary$.



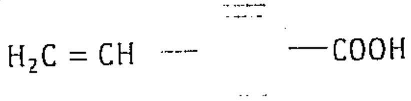
$$CH_3CH_2\overset{+}{C}H_2 < CH_3\overset{+}{C}HCH_3 < (CH_3)_3\overset{+}{C}$$

1.9 End of topic assessment exercise

1. Carbon is a unique element in comparison to so many other elements.
   - (a) State **three** reasons for the uniqueness of carbon compared to many other elements.
   - (b) State any **two** properties that make carbon a unique element.
2. The figure below shows the structure of compound J.



   - (a) Identify the functional groups in J.
   - (b) Name the reagent(s) that can be used to identify each of the functional groups you have identified in (a).
   - (c) State what would be observed when J is treated with the reagent(s) you have named in
3. An organic compound, Q, has the structure:



   - (a) Name the functional groups present in Q.
   - (b) Write the equation for the reaction between Q and;
     - (i) bromine water

(ii) sodium metal

(c) State what would be observed in (b)(i) and (ii) above.

4. Name **one** functional group that can be identified using each of the following reagents. In each case, state what would be observed and write equation for the reaction that would take place.

(a) bromine water
(b) sodium metal
(c) 2,4-dinitrophenylhydrazine
(d) Sodium hydrogencarbonate
(e) Concentrated hydrochloric acid

5. (a) (i) What is meant by the term **structural isomerism?**
(ii) Describe the three types of structural isomerism, giving a suitable example in each case.

(b) Explain what is meant by the following terms;
(i) Nucleophilic addition reaction
(ii) Nucleophilic substitution reaction
(iii) Electrophilic substitution reaction
(iv) Electrophilic addition reaction
(v) An elimination reaction
(vi) Free radical substitution

6. With suitable examples, distinguish between;
(a) homolytic fission and heterolytic fission
(b) Substitution and an addition reaction
(c) an ion and a free radical
(d) a carbocation and a carbanion
(e) a nucleophilic reagent and an electrophilic reagent

Chapter 2

Quantitative Analysis of Organic compounds

Here, determination of empirical formulae and molecular formulae of organic compounds is briefly explained. Details about some of the concepts will be covered in physical chemistry and more about structural formulae will be detailed in further topics.

2.1 Introduction

If the percentage composition by mass of a compound is known, the empirical formula, hence the molecular formula can be determined.

The isomers of the compound can also be predicted.

Any of the methods below can be used;

- Vapour density measurements
- Use of the ideal gas equation
- Use of Graham's law
- Data from colligative properties
- Eudiometry
- Data from steam distillation

Note

The molecular formula is got from the empirical formula using the relationship;

$$\textbf{(Empirical formula)}_n = \textbf{Molecular formula}$$

Where n is a number to be determined.

Molecular formula can be the same as empirical formula if $n = 1$.

The table below shows the empirical formula-molecular formula relationship for some compounds.

Name of compound	*Empirical formula*	*Simplest ratio*	*Molecular formula*	*Value of n*
Water	H_2O	2:1	H_2O	$n = 1$
Ethene	CH_2	1:2	C_2H_4	$n = 2$
Benzene	CH	1:1	C_6H_6	$n = 6$
Ethanoic acid	CH_2O	1:2:1	$C_2H_4O_2$	$n = 2$
Glucose	CH_2O	1:2:1	$C_6H_{12}O_6$	$n = 6$

Note

During the process of obtaining the empirical formula, the simplest ratio is obtained as a decimal fraction. This ratio should have whole numbers only. Therefore figures of the type; 1.1, 1.2, 2.7, 3.8 and 4.9, can be rounded off to 1,1,3,4 and 5 respectively.

However, values of the type; 1.333, 2.4, 1.5, and 3.666 should not be rounded off. Rounding them off creates a very big error. They must be multiplied by a factor to make them whole numbers as summarized below.

Sample calculated ratio	*Factor*	*Correct ratio*
1 : 1.333	3	3 : 4
1.5 : 2	2	3 : 4
2 : 2.499	2	4 : 5
1 : 3.666 : 3	3	3 : 11 : 9
3 : 2.4	2	6 : 5

2.2 Using Vapour density measurements

The relationship **relative molecular mass = Vapour density × 2** is used.

Example

An organic compound Y contains 66.7% carbon, 11.1% hydrogen and the rest being oxygen. If the vapour density of Y is 36, determine its molecular formula.

$$\text{percentage mass of O} = 100 - 66.7 - 11.1 = 22.2$$

Elements	C		H		O
% mass	66.7		11.1		22.2
Moles	$\frac{66.7}{12}$		$\frac{11.1}{1}$		$\frac{22.2}{16}$
Simplest ratio	$\frac{5.5583}{1.3875}$	:	$\frac{11.1}{1.3875}$	:	$\frac{1.3875}{1.3875}$
	4	:	8	:	1

Empirical formula is C_4H_8O.

$$(C_4H_8O)_n = 36 \times 2$$

$$(48 + 8 + 16)n = 36 \times 2$$

$$72n = 72$$

$$\therefore n = 1$$

Molecular formula is C_4H_8O.

2.3 Use of the ideal gas equation

The ideal gas equation states that;

$$\mathbf{pV = nRT}$$

$$\text{since } \mathbf{n} = \frac{\mathbf{m}}{\mathbf{M_r}};$$

$$\text{Then } \mathbf{pV = nRT} \text{ can be written as } \mathbf{pV} = \frac{\mathbf{m}}{\mathbf{M_r}}\mathbf{RT}.$$

M_r can therefore be obtained from the expression;

$$\mathbf{M_r} = \frac{\mathbf{mRT}}{\mathbf{pV}}$$

Where; **p** is the pressure in Pa or Nm^{-2}

V is the volume in m^3

R is the molar gas constant = $8.31JK^{-1}mol^{-1}$

T is the temperature in Kelvin

m is the mass given in the question and ;

M_r is the molecular mass.

Also note that;

$$1\ Nm^{-2} = 1\ Pa$$

$$1\ atm = 101325\ Pa$$

$$\text{therefore} \quad 2\ atm = (2 \times 101325)Pa$$

$$760\ mmHg = 101325Pa$$

$$\text{therefore} \quad 720\ mmHg = \left(\frac{720}{760} \times 101325\right) Pa$$

$$1\ kNm^{-2} = 1\ kPa = 1000\ Nm^{-2}$$

$$\text{therefore } 20.2\ kNm^{-2} = 20.2\ kPa = 20.2 \times 1000\ Nm^{-2}$$

$$1\ cm^3 = 10^{-6}m^3$$

$$56\ cm^3 = (56 \times 10^{-6})m^3$$

$$1\ litre/dm^3 = 1000\ cm^3 = 10^{-3}m^3$$

$$15\ litre/dm^3 = 15000\ cm^3 = 15 \times 10^{-3}m^3$$

Example

A compound Q contains 54.5% carbon, 9.09% hydrogen and the rest being oxygen. Calculate the empirical formula.

0.54g of Q occupies $150.9cm^3$ at a temperature of 19°C and a 740mmHg pressure. Determine the molecular formula of Q.

If Q which produces effervescence with magnesium powder, deduce its structural formula.

$$\text{percentage mass of O} = 100 - 54.5 - 9.09 = 36.41$$

Elements	C		H		O
% mass	54.5		9.09		36.41
Moles	$\frac{54.5}{12}$		$\frac{9.09}{1}$		$\frac{36.41}{16}$
Simplest ratio	$\frac{4.417}{2.2756}$	:	$\frac{9.09}{2.2756}$	:	$\frac{2.2756}{2.2756}$
	2	:	4	:	1

Empirical formula is C_2H_4O.

$$m = 0.54g;\ V = 150.9 \times 10^{-6} m^3$$
$$T = (19 + 273) = 292K;$$
$$P = \left(\frac{740}{760} \times 101325\right) Pa$$
$$PV = nRT$$
$$PV = \frac{m}{M_r} RT$$

$$M_r = \frac{mRT}{PV}$$
$$M_r = \frac{0.54 \times 8.31 \times 292}{\left(\frac{740}{760} \times 101325\right) \times 150.9 \times 10^{-6}}$$
$$M_r = 88$$

$$\text{molar mass of } Q = 88$$
$$(C_2H_4O)_n = 88$$
$$(24 + 4 + 16)n = 88$$
$$44n = 88$$
$$\therefore n = 2$$

∴ Molecular formula is $C_4H_8O_2$

Hint: Its carboxylic acids that form hydrogen when reacted with magnesium.

∴ **Q is $CH_3CH_2CH_2COOH$**

Example

A hydrocarbon Z, on complete combustion gave 0.63g of carbon dioxide and 0.26g of water. Determine the empirical formula of Z.

When 0.716g of Z was vapourised, it occupied a volume of 0.25 litres at s.t.p.

Determine the molecular formula of Z.

$$\text{Molar mass of } CO_2 = 12 + 32 = 44g$$
$$\text{mass of C} = \frac{12}{44} \times 0.63 = 0.1718g$$
$$\text{molar mass of } H_2O = 2 + 16 = 18g$$
$$\text{mass of O} = \frac{2}{18} \times 0.26 = 0.0289g$$

Elements	C		H
mass(g)	0.1718		0.0289
moles	$\frac{0.1718}{12}$		$\frac{0.0289}{1}$
simplest ratio	$\frac{0.014317}{0.014317}$	:	$\frac{0.0289}{0.014317}$
	1	:	2

Empirical formula is CH_2

Standard temperature is 25°C and standard pressure is 101325 Pa or Nm^{-2}.

$$m = 0.72g$$
$$V = 0.25 \times 10^{-3} m^3$$
$$T = (25 + 273) = 298K$$
$$P = 101325\ Pa$$
$$M_r = \frac{mRT}{PV}$$

$$M_r = \frac{0.716 \times 8.31 \times 298}{101325 \times 0.25 \times 10^{-3}}$$
$$M_r = 69.99$$
$$M_r \approx 70$$
$$(CH_2)_n = 70$$
$$(12 + 2)n = 70$$
$$14n = 70$$
$$n = 5$$

Molecular formula of Z is C_5H_{10}

2.4 Using Graham's law.

The concept of diffusion is not a new one to us at this level since you already have an idea from Ordinary level.

The rate at which different gases diffuse is not equal. A lighter gas diffuses more rapidly than a heavier one. After carrying out a number of experiments on the rates at which gases mix together, Graham(1832) came up with *Graham's law of diffusion* which states that; '***at constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density***'.

$$\text{i.e., Rate of diffusion} \propto \frac{1}{\sqrt{\text{density}}}$$

Consider two gases X and Y which diffuse at rates R_X and R_Y respectively. If the densities of the gases are ρ_x and ρ_y respectively;

$$R_X \propto \frac{1}{\sqrt{\rho_x}} \text{ and } R_Y \propto \frac{1}{\sqrt{\rho_y}}$$

$$R_X = k\frac{1}{\sqrt{\rho_x}} \ldots\ldots\ldots\ldots(i) \quad \text{and} \quad R_Y = k\frac{1}{\sqrt{\rho_y}} \ldots\ldots\ldots\ldots(ii)$$

Dividing equation (i) by equation (ii) yields;

$$\frac{R_X}{R_Y} = k\frac{1}{\sqrt{\rho_X}} \Big/ k\frac{1}{\sqrt{\rho_y}}$$

$$\frac{R_X}{R_Y} = \frac{1}{\sqrt{\rho_x}} \times \frac{\sqrt{\rho_y}}{1}$$

$$\therefore \frac{R_X}{R_Y} = \frac{\sqrt{\rho_y}}{\sqrt{\rho_x}}$$

$$\Rightarrow \frac{\textbf{Rate of diffusion of X}}{\textbf{Rate of diffusion of Y}} = \frac{\sqrt{\textbf{density of Y}}}{\sqrt{\textbf{density of X}}}$$

Since density is directly proportional to the relative molecular mass of the gas, we can also have the equation as;

$$\frac{\textbf{Rate of diffusion of X}}{\textbf{Rate of diffusion of Y}} = \frac{\sqrt{\textbf{Molar mass of Y}}}{\sqrt{\textbf{Molar mass of X}}}$$

Graham's law can therefore also be stated as; '*at constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its relative molecular mass*'.

The rate of diffusion of a gas can also be expressed as a reciprocal of the time taken for the gas to diffuse. Therefore;

$$R_X = \frac{1}{t_x} \text{ and } R_Y = \frac{1}{t_y}$$

$$\text{From; } \frac{R_X}{R_Y} = \frac{\sqrt{\rho_y}}{\sqrt{\rho_x}}$$

$$\frac{1/t_x}{1/t_y} = \frac{\sqrt{\rho_y}}{\sqrt{\rho_x}}$$

$$\therefore \frac{t_Y}{t_X} = \frac{\sqrt{\tilde{n}_y}}{\sqrt{\tilde{n}_x}}$$

Similarly,

$$\therefore \frac{t_Y}{t_X} = \frac{\sqrt{M_r \text{ of } Y}}{\sqrt{M_r \text{ of } X}}$$

Rate of diffusion of a gas can also be expressed in terms of volume of the gas and time taken by the gas to diffuse.

$$\text{Rate of diffusion of a gas} = \frac{\text{volume of the gas}}{\text{time taken}}$$

Note: *Most gases are diatomic. This should be observed when calculating molar masses of gases.*

Example

The time taken for $1.76\ cm^3$ of oxygen to diffuse through a porous partition is 103 seconds. Another gaseous alkyne Z at the same conditions of temperature and pressure diffuses through the partition at the rate of $1.3cm^3$ in 101s.

(a) Determine the molecular formula of gas Z.

(b) Write the structural formulae and names of all possible isomers of Z.

(a)

M_r of $O_2 = (16 \times 2) = 32g$ M_r of $Z = ?$

$$R_{O_2} = \left(\frac{1.76}{103}\right) cm^3s^{-1} \qquad R_Z = \left(\frac{1.3}{101}\right) cm^3s^{-1}$$

$$\frac{R_{O_2}}{R_Z} = \frac{\sqrt{M_r \text{ of } Z}}{\sqrt{M_r \text{ of } O_2}}$$

$$\left(\frac{1.76}{103}\right) \div \left(\frac{1.3}{101}\right) = \frac{\sqrt{M_r \text{ of } Z}}{\sqrt{32}}$$

$$\left(\frac{1.76 \times 101}{103 \times 1.3}\right)^2 = \frac{M_r \text{ of } Z}{32}$$

$$\mathbf{M_r \text{ of } Z = 56.4g}$$

The molar mass of Z ≈ 56g

$$C_nH_{2n-2} = 56$$

$$12n + 2n - 2 = 56$$

$$14n = 58$$

$$n = 4.143$$

$$n \approx 4.0$$

Molecular formula of Z is C_4H_6

(b) Isomers

Structural formula	*Name*
$CH_3CH_2C \equiv CH$	But-1-yne
$CH_3C \equiv CCH_3$	But-2-yne

2.5 Using data from colligative properties

The experiments on colligative properties such as depression of freezing point, elevation of boiling point and osmotic pressure measurements can also be used to determine molecular masses of non-volatile organic compounds.

2.5.1 Depression of freezing point

The freezing point of a solution($T_{f\,(solution)}$)containing a non-volatile solute is always lower than the freezing point of pure solvent$\left(T^0_{f\,(solvent)}\right)$. This decrease in boiling point is called the **freezing point depression** (ΔT_f) given by the equation;

$$\Delta T_f = T^0_{f\,(solvent)} - T_{f\,(solution)}$$

The solvent always has a freezing point constant or molal freezing point depression constant or Cryoscopic constant (k_f).

The freezing point constant is the depression in freezing point caused when one mole of a non-ionizing and non-volatile solute is dissolved in 1000g of a solvent.

The units of the cryoscopic constant are **°Cmol⁻¹kg⁻¹** or °Cmol⁻¹ **per 1000g.**

Examples

0.3g of an organic compound Y on complete combustion gave 0.88g of carbon dioxide gas and 0.18g of water. 0.53g of Y in 22g of ethanoic acid lowered the freezing point of ethanoic acid by 0.78K. (k_f for ethanoic acid is $3.89\text{Kmol}^{-1}\text{kg}^{-1}$).

(a) (i) Calculate the empirical formula of Y.

(ii) Determine the molecular mass of Y and its molecular formula Y.

(b) Y burns with a yellow sooty flame and forms a yellow precipitate with 2,4-dinitrophenylhydrazine. Write the structural formulae and the names of the possible isomers of Y.

Hint: *from part (b), Y has a carbonyl group* (C = O) *hence must have elements* C, H *and* O.

(i)

$$\text{Molar mass of } CO_2 = 12 + 32 = 44\text{g}$$

$$\text{mass of C} = \frac{12}{44} \times 0.88 = 0.24\text{g}$$

$$\text{molar mass of } H_2O = 2 + 16 = 18\text{g}$$

$$\text{mass of H} = \frac{2}{18} \times 0.18 = 0.02\text{g}$$

$$\text{mass of O} = 0.3 - 0.24 - 0.02 = 0.04\text{g}$$

Elements	C		H		O
mass	0.24		0.02		0.04
Moles	$\frac{0.24}{12}$		$\frac{0.02}{1}$		$\frac{0.04}{16}$
Simplest ratio	$\frac{0.02}{0.0025}$	:	$\frac{0.02}{0.0025}$	:	$\frac{0.0025}{0.0025}$
	8	:	8	:	1

Empirical formula is C_8H_8O

(ii)

$$\text{Freezing point depression} = 0.78\text{K}$$

$$22\text{g of } CH_3COOH \text{ dissolve } 0.53\text{g of Y}$$

$$1000\text{g of } CH_3COOH \text{ will dissolve } \left(\frac{1000 \times 0.53}{22}\right) \text{g of Y} = 24.09 \text{ g of Y}$$

$$0.78\text{K is depression in freezing point caused by } 24.09\text{g of Y}$$

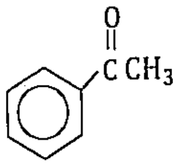
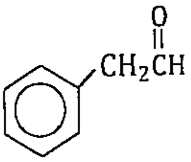
$$3.89\text{K is depression in freezing point caused by } \left(\frac{3.89 \times 24.09}{0.78}\right) = 120\text{g}$$

$$\text{Molecular mass of Y is } 120\text{g}$$

$$\text{Molecular formula of Y is } C_8H_8O$$

Hint: *Y must be an aromatic carbonyl compound since it burns with a sooty flame.*

(b) Isomers

Structural formula	*Name*
	Phenylethanone
	Phenylethanal

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Example

A compound Q contains 60.0% carbon, 13.3% hydrogen and the rest being oxygen. Calculate the simplest formula of Q.

When 0.698g of Q was dissolved in 1000g a solvent, there was a 0.19°C depression in freezing point of solution. (k_f of the solvent = $1.63°Ckg^{-1}mol^{-1}$)

(a) Calculate:

(i) the empirical formula of Q.

(ii) the molecular formula of Q.

(b) Write the names and structural formulae of all possible isomers of Q.

(a) (i)

$$\%\text{ by mass of O} = 100 - 60.0 - 13.3 = 26.9$$

Elements	C		H		O
% mass	60.0		13.3		26.9
Moles	$\frac{60.0}{12}$		$\frac{13.3}{1}$		$\frac{26.9}{16}$
Simplest ratio	$\frac{5.0}{1.68125}$	:	$\frac{13.3}{1.68125}$	:	$\frac{1.68125}{1.68125}$
	3	:	8	:	1

Empirical formula is C_3H_8O

(ii)

100g of solvent dissolve 0.698g of Q

$$1000\text{g of solvent will dissolve} \left(\frac{1000 \times 0.698}{100}\right) \text{g of Q} = 6.98 \text{ g of Q}$$

0.19°C is depression in freezing point caused by 6.98g of Q

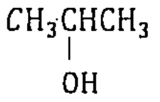
$$1.63°\text{C is depression in freezing point caused by } \left(\frac{1.63 \times 6.98}{0.19}\right) = 59.88\text{g}$$

Molecular mass of Q $\approx$ 60g.

$$(C_3H_8O)_n = 60$$
$$(36 + 8 + 16)n = 60$$
$$60n = 60$$
$$\therefore n = 1$$

Molecular formula of Q is C_3H_8O.

(b)

Structural formula	*Name*
$CH_3CH_2CH_2OH$	Propan-1-ol
 $CH_3\underset{\mid \atop OH}{C}HCH_3$	Propan-2-ol
$CH_3CH_2OCH_3$	Methoxymethane

2.5.2 Elevation in boiling point

The boiling point of a solution($T_{b(solution)}$)containing a non-volatile solute is always higher than the boiling point of pure solvent$\left(T^0_{b\,(solvent)}\right)$. This increase in boiling point is called the elevation in boiling point(ΔT_b) given by the equation;

$$\Delta T_b = T_{b\,(solution)} - T^0_{b\,(solvent)}$$

The solvent always has a **boiling point constant or molal boiling point elevation constant or ebullioscopic constant** (k_b).

The boiling point constant is the elevation in boiling point caused when one mole of a non-ionizing and non-volatile solute is dissolved in 1000g of a solvent.

The units of the cryoscopic constant are °$Cmol^{-1}kg^{-1}$ or °$Cmol^{-1}$ **per 1000g.**

Example

A compound Q contains carbon, hydrogen and oxygen only. When 4.0756g of Q was heated in excess oxygen, 2.03dm³ of carbon dioxide and 0.815g of water were formed at s.t.p.

(a) Determine the empirical formula of Q.

(b) When the same mass of Q as used above was dissolved in 93cm³ of water, the solution boiled at 100.256°C.

  (i) Determine the molecular formula of Q.

  (ii) Deduce the structural formula of Q.

(Ebullioscopic constant for water = 0.52°$Cmol^{-1}kg^{-1}$ and density of water is $1gcm^{-3}$)

(a)

$$\text{Molar mass of } CO_2 = 12 + 32 = 44g$$

$$\text{moles of } CO_2 \text{ formed} = \frac{2.03}{22.4} = 0.090625$$

$$\text{mass of } CO_2 \text{ formed} = (0.090625 \times 44) = 3.9875\text{g}$$

$$\text{mass of C present} = \left(\frac{12}{44} \times 3.9875\right) = 1.0875\text{g}$$

$$\text{molar mass of } H_2O = 2 + 16 = 18\text{g}$$

$$\text{mass of H} = \left(\frac{2}{18} \times 0.815\right) = 0.09056\text{g}$$

$$\text{mass of O} = 0.3 - 0.24 - 0.02 = 0.04\text{g}$$

Elements	C		H		O
mass	1.0875		0.09056		0.04
Moles	$\frac{1.0875}{12}$		$\frac{0.09056}{1}$		$\frac{0.04}{16}$
Simplest ratio	$\frac{0.090625}{0.09056}$	:	$\frac{0.09056}{0.09056}$	:	$\frac{0.18110}{0.09056}$
	1	:	1	:	2

Empirical formula is $\mathbf{CHO_2}$.

(b) (i)

$$\text{Mass of } H_2O \text{ used} = (\text{Volume} \times \text{density}) = (92 \times 1) = 92\text{g}$$

$$92\text{g of } H_2O \text{ dissolve } 4.0756\text{g of Q}$$

$$1000\text{g of } H_2O \text{ will dissolve} \left(\frac{1000 \times 4.0756}{92}\right) \text{g of Q} = 44.3\text{g of Q}$$

$$\text{Elevation in boiling point} = 100.256 - 100 = 0.256°\text{C}$$

$$0.256°\text{C is elevation in boiling point caused by } 44.3\text{g of Q}$$

$$0.52°\text{C is elevation in boiling point caused by} \left(\frac{0.52 \times 44.3}{0.256}\right) = 89.984\text{g}$$

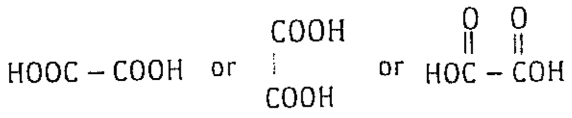
Molecular mass of Q ≈ 90g

(ii)

$$(CHO_2)_n = 90$$
$$(12 + 1 + 32)n = 90$$
$$45n = 90$$
$$n = 2$$

Molecular formula of Q is $\mathbf{C_2H_2O_4}$.

Structural formula of Q is



$$HOOC-COOH \text{ or } \begin{array}{c} COOH \\ | \\ COOH \end{array} \text{ or } HO\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OH$$

2.5.3 Using data from osmotic pressure measurements

Osmotic pressure, ð is a better method to determine the molecular mass of large molecules than ebullioscopic and cryoscopic methods.

If the osmotic pressure of a solution containing $m\ g$ of a solute in $V\ cm^3$ of solution is measured at a temperature, T, the number of moles of solute, n can be determined from the expression;

$$\pi V = nRT$$

Where ð is the osmotic pressure, R is the molar gas constant, T is the absolute temperature.

Since $n = \frac{m}{M_r}$ where M_r is the molar mass of the solute,

Then;

$$\pi V = \frac{m}{M_r} RT$$

$$M_r = \frac{mRT}{\pi V}$$

Example

A 6.3% solution of polyethene in propanone was found to have an osmotic pressure of 0.03667 atm at 25°C.

Calculate the;

(a) molecular mass of polyethene

(b) number of ethene monomers required to make the polymer in (a) above.

Hint: *For osmotic pressure, a 6.3% solution means 6.3g of polyethene in a volume of 100 cm^3 of solution.*

(a)

$$m = 6.3g;\quad V = (100 \times 10^{-6})m^3;\ T = (25 + 273) = 298K$$

$$\pi = (0.03667 \times 101325)Pa$$

$$M_r = \frac{mRT}{\pi V}$$

$$M_r = \frac{6.3 \times 8.31 \times 298}{(0.03667 \times 101325) \times 100 \times 10^{-6}}$$

$$M_r = 41988.496$$

Molar mass of polyethene $\approx$ **41989g**

(b)

$$\text{Molar mass of monomer}, H_2C = CH_2 = (24 + 4) = 28g$$

$$\text{Number of monomers}, \quad n = \frac{41989}{28} = 1499.6 \approx 1500$$

$$\therefore n = 1500$$

2.6 Eudiometry.

In this process, a given volume of a gaseous hydrocarbon is exploded with excess oxygen. The hydrocarbon completely burns to form carbon dioxide and water as the only products.

The vapour is then cooled and contraction in volume occurs due to condensation of water vapour. The resultant volume (residual gas) left is due to carbon dioxide formed and the unreacted oxygen. The volume of carbon dioxide is determined by adding **aqueous sodium hydroxide or potassium hydroxide.** All the carbon dioxide formed is **absorbed** and the **diminution (reduction)** in the volume of the gases is due to carbon dioxide. The volume of gas that remains at this point is the **unreacted oxygen.** The volume of water formed is regarded as negligible.

General equation;

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \longrightarrow x\,CO_2(g) + \frac{y}{2}H_2O(l)$$

Examples

15 dm³ of gaseous hydrocarbon X was exploded with 105dm³ of excess oxygen. The residual gas occupied 75dm³. On addition of concentrated potassium hydroxide, the volume reduced by 45dm³. Determine the molecular formula of X.

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \longrightarrow x\,CO_2(g) + \frac{y}{2}H_2O(l)$$

Volume of carbon dioxide formed = 45 dm³

Volume of unreacted oxygen = (75 − 45) = 30 dm³

Volume of oxygen that reacted = (105 − 30) = 75 dm³

From the above equation, 1 volume of C_xH_y forms x volumes of CO_2.

$$15\ dm^3\ of\ C_xH_y\ forms\ 45\ dm^3 of\ CO_2$$

$$15x = 45$$

$$x = 3$$

Similarly; 1 volume of C_xH_y reacts with $\left(x + \frac{y}{4}\right)$ volumes of O_2.

$$15\ dm^3\ of\ C_xH_y\ reacts\ with\ 75\ dm^3 of\ O_2$$

$$15\left(x + \frac{y}{4}\right) = 75$$

$$15\left(3 + \frac{y}{4}\right) = 75$$

$$y = \left(\frac{75}{15} - 3\right)4$$

$$y = 8$$

Molecular formula of X is C_3H_8.

Example

When 142cm³ of a hydrocarbon Y, of formula, C_aH_b and molecular mass 58g was exploded with excess oxygen and cooled to room temperature, the volume of the residual gas was 694cm³. On treatment with concentrated potassium hydroxide solution, the volume decreased to 126cm³.

(a) Determine the molecular formula of Y.

(b) Write the structural formula and IUPAC name of all possible isomers of Y.

(a)

$$C_aH_b(g) + \left(a + \frac{b}{4}\right)O_2(g) \longrightarrow a\,CO_2(g) + \frac{b}{2}H_2O(l)$$

Volume of carbon dioxide formed is $(694 - 126) = 568\ cm^3$

From the above equation, 1 volume of C_aH_b forms a volumes of CO_2.

$142\ cm^3$ of C_aH_b forms $568\ cm^3$ of CO_2

$$142a = 568$$

$$a = 4$$

$$C_aH_b = 58$$

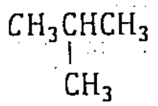
$$C_4H_b = 58$$

$$(4 \times 12) + b = 58$$

$$b = 10$$

Molecular formula of Y is C_4H_{10}.

(b)

Structural formula	*Name*
$CH_3CH_2CH_2CH_3$	Butane
 $\underset{\displaystyle CH_3}{\overset{}{CH_3\underset{\vert}{C}HCH_3}}$	2 – Methylpropane

2.7 Use of data from steam distillation

Steam distillation is the technique of separating a volatile substance, immiscible with water, at a temperature below its boiling point from another substance by bubbling steam through the hot mixture. The volatile substance to be separated vapourises off with steam leaving behind the non-volatile substance.

The expression below is used for calculation purposes;

$$\frac{p_w}{p_L} = \frac{n_w}{n_L}$$

The above equation gives the relative amounts of water and the volatile liquid substance in the distillate where;

- p_w is the vapour pressure of water at the distillation temperature
- p_L is the vapour pressure of the liquid at the distillation temperature
- n_w is the number of moles of water
- n_L is the number of moles of the liquid

Since number of moles , $n = \frac{m}{M_r}$; the above expression can also be written as;

$$\frac{p_w}{p_L} = \frac{n_w/M_{rw}}{n_L/M_{rL}}$$

$$\therefore \frac{p_W}{p_L} = \frac{n_W . M_{r_L}}{n_L . M_{r_W}}$$

Where; M_{r_W} and M_{r_L} are the molar masses of water and the liquid respectively.

The vapour pressure of liquid is normally got from the expression for the total vapour pressure

$$p_{Total} = p_W + p_L$$

$$\therefore p_L = p_{Total} - p_W$$

Examples

A compound Y contains 62.1% carbon, 10.3% hydrogen and the rest being oxygen.

(a) Calculate the empirical formula of Y.

(b) Y distills in steam at 98°C and $1.01 \times 10^5 Nm^{-2}$. Calculate the molecular mass hence deduce the molecular formula of Y if the distillate contained 16.96% by mass of Y.

(a)

$$\text{percentage mass of O} = 100 - 62.1 - 10.3 = 27.6$$

Elements	C		H		O
% mass	62.1		10.3		27.6
Moles	$\frac{62.1}{12}$		$\frac{10.3}{1}$		$\frac{27.6}{16}$
Simplest ratio	$\frac{5.125}{1.725}$	:	$\frac{10.3}{1.725}$	:	$\frac{1.725}{1.725}$
	3	:	6	:	1

Empirical formula is C_3H_6O.

(b)

$$p_{H_2O} = 9.5 \times 10^4 Nm^{-2}$$

$$p_Y = (1.01 \times 10^5) - (9.5 \times 10^4) = 6000Nm^{-2}$$

$$\text{molar mass of } H_2O = 2 + 16 = 18g$$

$$\frac{p_{H_2O}}{p_Y} = \frac{n_{H_2O}}{n_Y}$$

$$\frac{9.5 \times 10^4}{6000} = \frac{83.33}{18} \times \frac{M_{rY}}{16.96}$$

$$M_{rY} = \frac{9.5 \times 10^4 \times 18 \times 16.96}{83.33 \times 6000}$$

$$M_{rY} = 58$$

$$\text{molar mass of Y} = 58$$

$$(C_3H_6O)_n = 58$$

$$(36 + 6 + 16)n = 58$$

$$58n = 58$$

$$n = 1$$

Molecular formula is C_3H_6O.

Example

A compound Z contains 26.09% carbon, 4.89% hydrogen and the rest being iodine.

(a) Calculate the empirical formula of Z.

(b) When a mixture containing compound Z was steam distilled 98°C and 760mmHg, the distillate contained 2.215g of Z and 16.25g of water. If the vapour pressure of water is 750mmHg at 98°C,

(i) determine the molecular formula of Z. ($C = 12$; $H = 1$; $I = 127$)

(ii) write the structural formulae and names of all the possible isomers of Z.

(a)

$$\text{percentage mass of I} = 100 - 26.09 - 4.89 = 69.02$$

Elements	C		H		I
% mass	26.09		4.89		69.02
Moles	$\frac{26.09}{12}$		$\frac{4.89}{1}$		$\frac{69.02}{127}$
Simplest ratio	$\frac{2.17417}{0.54346}$	:	$\frac{4.89}{0.54346}$	:	$\frac{0.54346}{0.54346}$
	4	:	9	:	1

Empirical formula is C_4H_9I.

(b) (i)

$$p_{H_2O} = 750\text{mmHg}$$

$$p_z = 760 - 750 = 10\text{mmHg}$$

$$\text{molar mass of } H_2O = 2 + 16 = 18\text{g}$$

$$\frac{p_{H_2O}}{p_z} = \frac{n_{H_2O}}{n_z}$$

$$\frac{750}{10} = \frac{m_{H_2O}}{M_{rH_2O}} \div \frac{m_Z}{M_{rz}}$$

$$\frac{750}{10} = \frac{16.25}{18} \times \frac{2.215}{M_{rz}}$$

$$M_{rz} = \frac{750 \times 18 \times 2.215}{10 \times 16.25}$$

$$M_{rz} = 184$$

$$\text{molar mass of } Y = 184\text{g}$$

$$(C_4H_9I)_n = 184$$

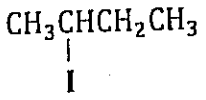
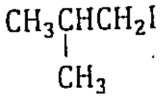
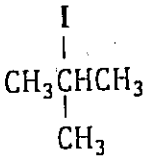
$$(48 + 9 + 127)n = 184$$

$$184n = 184$$

$$n = 1$$

Molecular formula is C_4H_9I.

(ii)

Structural formula of isomer	*Name of isomer*
$CH_3CH_2CH_2CH_2I$	1-Iodobutane
 $CH_3\underset{\underset{\displaystyle I}{|}}{C}HCH_2CH_3$	2-Iodobutane
 $CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2I$	1-Iodo-2-methylpropane
 $CH_3\overset{\overset{\displaystyle I}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}HCH_3$	2-Iodo-2-methylpropane

2.8 Other problems

A gaseous hydrocarbon Q contains 90% carbon. The density of Q is $1.785 \times 10^{-3}\,gcm^{-3}$ at stp. Determine;

(i) the empirical formula of Q

(ii) the molecular formula of Q.

(i)

percentage mass of H = 100 − 90 = 10

Elements	C		H
% mass	90		10
Moles	$\frac{90}{12}$		$\frac{10}{1}$
Simple ratio	$\frac{7.5}{7.5}$	:	$\frac{10}{7.5}$
	3	:	4

Empirical formula Q is C_3H_4.

(ii)

At s. t. p; $1\ cm^3$ contains 1.785×10^{-3}g of Q

$$22400cm^3 \text{ contain} \left(\frac{22400 \times 1.785 \times 10^{-3}}{1}\right)g = 39.984\ g \approx 40g$$

$$\text{Molar mass of Q} = 40g$$

$$(C_3H_4)_n = 40$$

$$(36+4)n = 40$$

$$40n = 40$$

$$n = 1$$

Molecular formula of Q is C_3H_4.

A saturated aliphatic bromocompound X with a general formula of $C_nH_{2n-1}Br$ contains 49.08% by mass of bromine.

(i) Determine the molecular formula of X. ($C = 12;\ H = 1;\ Br = 79.9$)

(ii) Draw the structural formulae of any four possible isomers of X.

(i)

$$\text{Molar mass of } C_nH_{2n-1}Br = 12n + 2n - 1 + 79.9 = (14n + 79.9)\text{g}$$

$$\%\text{ by mass of Br} = \left(\frac{79.9}{4n + 79.9} \times 100\right) = 49.08$$

$$\frac{79.9}{4n + 79.9} = \frac{49.08}{100}$$

$$49.08(14n + 79.9) = 7990$$

$$14n + 79.9 = 162.795$$

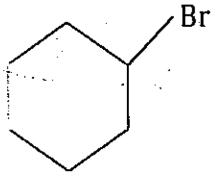
$$\frac{14n}{14} = \frac{82.895}{14}$$

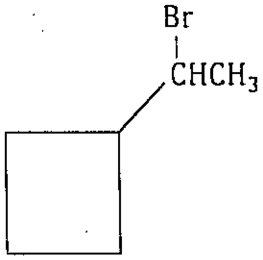
$$n = 5.9 \approx 6$$

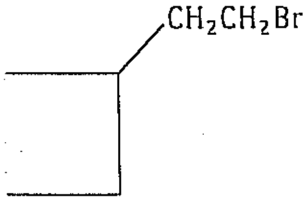
$$n = 6$$

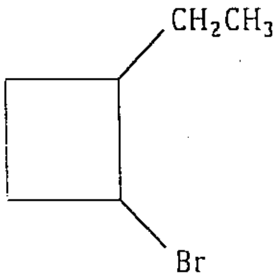
Molecular formula of X is $C_6H_{11}Br$.

(ii)









2.9 End of topic assessment exercise

1. 0.464g of an organic compound Q when burnt gave 1.32g of carbon dioxide and 0.315g of water. When 0.2325g of Q was separately burnt, 7.08 cm^3 of nitrogen gas at s.t.p was produced. Determine the molecular formula and structural formula of Q if its relative density is 46.5.

2. An organic compound, T, on complete combustion yielded 13.2g of carbon dioxide and 2.7g of water. When 4.7g of T was vapourised at standard temperature and pressure, it occupied a volume of $2.7 \times 10^{-3} m^3$.
   (i) Calculate the empirical formula of T.
   (ii) Determine the molecular formula of T.
   (iii) T burns with a sooty flame. Identify T.

3. (a) An organic compound A contains carbon, hydrogen and oxygen only. On combustion, 0.463g of A gave 1.1g carbon dioxide and 0.563g of water. Determine the empirical formula of A.
   (b) When vapourised, 0.1g of A occupies $54.5 cm^3$ at 208°C and 98.3 kPa. Determine the molecular formula of A.
   (c) A reacts with sodium metal with evolution of a gas. Write the structural formula of all possible isomers of A.

4. 1.363g of compound Y containing carbon, hydrogen and bromine on complete combustion gave 1.10g of carbon dioxide and 0.45g of water. When 0.35g of Y was vapourised, it occupied $39.5 cm^3$ at 20°C and 750mmHg. Calculate;
   (a) the simplest formula of Y
   (b) the molecular formula of Y.

5. Oxygen diffuses 1.19 times faster than an amine, $C_nH_{2n+1}NH_2$.
   (a) Determine the molecular formula of the amine.
   (b) Deduce the structural formulae and names of all possible isomers of the amine.

6. 250 cm^3 of an alkene diffuse through a porous medium in 10 seconds and 716 cm^3 of oxygen diffuse through the same medium in 25 seconds under the same conditions. Calculate the molecular mass of the alkene and deduce its structural formula.

7. 25 cm^3 of gas Q diffuse through a small aperture in 48 seconds while 25 cm^3 of an alkane diffuse through the same aperture in 40 seconds. Deduce the molecular formula of the alkane.

8. (a) An aqueous solution containing 7.2g of a non-cyclic substance Z in 250g of water freezes at $-0.744\ °C$. Calculate the molecular mass of Z.
   (the freezing point constant, k_f, for water is $1.86°C mol^{-1} kg^{-1}$)
   (b) If Z contains carbon, 66.7%, hydrogen, 11.1% and the rest being oxygen
      (i) Calculate the simplest formula of Z
      (ii) Determine the molecular formula of Z
      (iii) Write the structures of all possible isomers of Z

(c) *Z* forms a yellow precipitate with Brady's reagent. Write the structures of possible isomers of *Z*.

9. (a) A compound *Y* contains 80% carbon, 6.7% hydrogen, and the rest being oxygen. Calculate the empirical formula of *Y*.

(b) 0.48g of *Y* was dissolved in 50.0g of benzene and caused a freezing point depression of $0.44°C$. Determine the molecular formula of *Y*.
$(k_f\,for\ benzene\ is\ 5.5°C mol^{-1} kg^{-1})$

10. A gaseous hydrocarbon *Q* after complete combustion produced 2.025g of water and $6.72dm^3$ of carbon dioxide at standard temperature and pressure.

(a) Determine the empirical formula of *Q*.

(b) *Q* steam distills at a given temperature under a pressure of 750mmHg. The vapour pressure of water at the same temperature is 726mmHg and the percentage of water in the distillate was found to be 84.22%. Determine the molecular formula of *Q*.

11. 4.7g of compound *Z* contains carbon, hydrogen and oxygen only. *Z* on combustion gave 13.2g of carbon dioxide and 2.7g of water.

(a) Calculate the empirical formula of *Z*.

(b) When a mixture containing compound *Z* was steam distilled at 760mmHg and 98°C, the distillate contained 12.75g of water and 3.7g of *Z*. If the vapour pressure of water is 720mmHg at 98°C, determine the molecular formula of *Z*.

12. $30cm^3$ of a gaseous hydrocarbon *Z* was mixed with $140cm^3$ of oxygen and exploded. After cooling to room temperature and pressure, the residual gas occupied $95cm^3$. On absorption with concentrated potassium hydroxide solution there was a fall in volume by $60cm^3$. Determine the molecular formula of *Z*.

13. 15 cm^3 of a gaseous hydrocarbon were exploded with 105 cm^3 of oxygen in a sealed vessel after cooling, the residual volume occupies $75cm^3$. On addition of caustic potash, there was a diminution of volume to $30cm^3$. Determine the molecular mass of a hydrocarbon.

Note: ***Check further topics for questions involving quantitative and qualitative analysis of organic compounds.***

Chapter 3

Hydrocarbons

(Alkanes, Alkenes & Alkynes)

An introduction to hydrocarbons has already been given in the previous chapter.

Hydrocarbons are organic compounds containing carbon and hydrogen atoms only. They are grouped as saturated hydrocarbons and unsaturated hydrocarbons.

Alkanes are saturated hydrocarbons whereas *alkenes* and *alkynes* are unsaturated hydrocarbons.

3.1 Alkanes

3.1.1 Introduction

Alkanes are hydrocarbons that do not have multiple bonds between carbon atoms.

They form a homologous series of saturated hydrocarbons that conform to the general formula, C_nH_{2n+2} for the aliphatic ones.

The alicyclic alkanes, like cyclopropane, however conform to the general formula, C_nH_{2n}.

The non-cyclic alkanes differ successively by a methylene group($-CH_2-$).

Alkanes are relatively unreactive as compared to the unsaturated hydrocarbons.

3.1.2 Occurrence and sources

The major sources of alkanes are natural gas and petroleum.

(a) Natural gas

Natural gas consists of approximately 90-95% methane,5-10% ethane and smaller quantities of propane, butane and 2-methylpropane.

(b) Petroleum

Petroleum is a thick, viscous, dark-brown or sometimes green liquid containing thousands of hydrocarbons including mainly straight chain, branched and cyclic alkanes.

It is formed from decomposition of marine plants and animals.

Petroleum contains a wide range of alkanes, from the low molecular weight gases to the high molecular weight solids.

In a petroleum refinery, petroleum is converted into useful products by a process called fractional distillation.

During fractional distillation, all the crude oil is introduced into distillation units, where it is heated to high temperatures and separated into fractions.

The fractions are collected over a range of boiling points.

The simpler more volatile alkanes distill off first during the process.

The different fractions obtained during fractional distillation of petroleum, their distillation temperature, approximate carbon content and uses are outlined below;

(i) Refinery gas

This fraction is obtained at 20°C at the top of the distillation column and is mainly constituted of low molecular weight alkanes containing 1-4 carbon atoms.

It is used as a domestic fuel for heating using gas cookers.

(ii) Light petroleum

This is obtained at a temperature range of 20-60°C and contains alkanes with 5-6 carbon atoms.

It is used as an organic solvent.

(iii) Light naphtha or ligroin

Light naphtha distills at a temperature range of 60-100°C .It contains alkanes with 6-7 carbon atoms and is also used as an organic solvent.

(iv) Petrol or Gasoline

Petrol is obtained at a temperature range of 40-205°C .This fraction contains alkanes with 5-12 carbon atoms, including cycloalkanes. It is used as a fuel for internal combustion engines requiring volatile liquids.

(v) Kerosene or Paraffin

This fraction distills at a temperature range of 175-325°C .It contains hydrocarbons with 12-18 carbon atoms, including aromatics. Paraffin is used as a heating fuel and for engines requiring less volatile liquids such as jet engines and tractors.

(vi) Gas oil

This distills at a temperature range of 275-400°C .It contains hydrocarbons with 18-25 carbon atoms and is used in diesel engines.

(vii) Lubricating oil

This fraction contains non-volatile liquid alkanes when hot, with 20-34 carbon atoms and may form solid waxes when cold. The solid waxes are filtered off as paraffin wax. Lubricating oil is used as a lubricant.

(viii) Paraffin wax

This solidifies from lubricating oil. It has alkanes with 25-40 carbon atoms and is as polishing waxes and making petroleum jelly (Vaseline).

(ix) Bitumen (asphalt)

Bitumen is a black residue that remains after removal of all other fractions. It contains hydrocarbons with greater than 30 carbon atoms. It is used for road surfacing and roofing.

3.1.3 Nomenclature of alkanes

The IUPAC SYSTEM is used when naming alkanes. The principles involved in this system are used in naming compounds in other homologous series as well.

The first four homologues retain their original names as shown in the table below.

The other unbranched alkanes all have their names ending with for "-ane".

The stems of the names of most of the alkanes with more than 4 carbon atoms are of Greek and Latin origin.

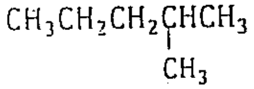
Below are the names of the first 20 unbranched alkanes

No of carbon atoms	*Molecular formula*	*Name*	*Structure*
1	CH_4	Methane	CH_4
2	C_2H_6	Ethane	CH_3CH_3
3	C_3H_8	Propane	$CH_3CH_2CH_3$
4	C_4H_{10}	Butane	$CH_3CH_2CH_2CH_3$
5	C_5H_{12}	Pentane	$CH_3CH_2CH_2CH_2CH_3$
6	C_6H_{14}	Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	C_7H_{16}	Heptane	$CH_3(CH_2)_5CH_3$
8	C_8H_{18}	Octane	$CH_3(CH_2)_6CH_3$
9	C_9H_{20}	Nonane	$CH_3(CH_2)_7CH_3$
10	$C_{10}H_{22}$	Decane	$CH_3(CH_2)_8CH_3$
11	$C_{11}H_{24}$	Undecane	$CH_3(CH_2)_9CH_3$
12	$C_{12}H_{26}$	Dodecane	$CH_3(CH_2)_{10}CH_3$
13	$C_{13}H_{28}$	Tridecane	$CH_3(CH_2)_{11}CH_3$
14	$C_{14}H_{30}$	Tetradecane	$CH_3(CH_2)_{12}CH_3$
15	$C_{15}H_{32}$	Pentadecane	$CH_3(CH_2)_{13}CH_3$
16	$C_{16}H_{34}$	Hexadecane	$CH_3(CH_2)_{14}CH_3$
17	$C_{17}H_{36}$	Heptadecane	$CH_3(CH_2)_{15}CH_3$
18	$C_{18}H_{38}$	Octadecane	$CH_3(CH_2)_{16}CH_3$
19	$C_{19}H_{40}$	Nonadecane	$CH_3(CH_2)_{17}CH_3$
20	$C_{20}H_{42}$	Eicosane	$CH_3(CH_2)_{18}CH_3$

The branched alkanes are named following the rules as shown below:

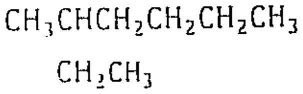
1. The longest continuous chain of carbon atoms is selected and named accordingly. This chain determines the parent name for the alkane.

The following compound, for example is given the parent name pentane because the longest continuous chain contains five carbon atoms:



$$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$$

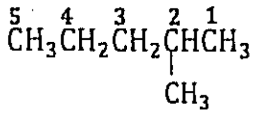
Note that the longest continuous chain may not always be obvious from the way the formula is written. For example, that the following alkane is given the parent name heptane because the longest chain contains seven carbon atoms:



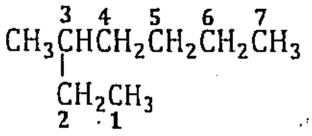
$$CH_3\underset{\displaystyle CH_2CH_3}{C}HCH_2CH_2CH_2CH_3$$

2. **The longest chain is then numbered beginning with the end of the chain nearer the substituent.**

For example the alkanes in (1) above are numbered in the following way:



$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\underset{\overset{|}{CH_3}}{\overset{2}{C}}H\overset{1}{C}H_3$$



$$CH_3\underset{\overset{|}{\underset{2}{C}H_2\underset{1}{C}H_3}}{\overset{3}{C}}H\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_3$$

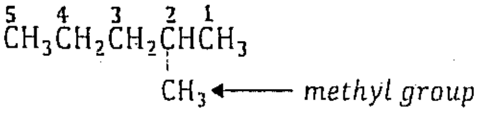
The names of the alkyl group substituents are identified and these prefix the name of the main chain.

Alkyl groups are obtained when one hydrogen atom is removed from an alkane. The alkyl groups have names that end in "-yl".

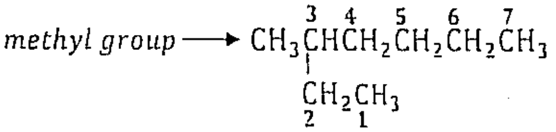
The table below shows some alkyl group substituents.

Alkyl group	*Name of the alkyl group*
$-CH_3$	methyl
$-CH_2CH_3$	ethyl
$-CH_2CH_2CH_3$	propyl
$-CH_2CH_2CH_2CH_3$	butyl
$-CH_2CH_2CH_2CH_2CH_3$	pentyl

In the particular examples in (1) above, both alkanes have a **methyl group** attached to the longest carbon chain.



$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\underset{\overset{|}{CH_3 \longleftarrow \textit{methyl group}}}{\overset{2}{C}}H\overset{1}{C}H_3$$

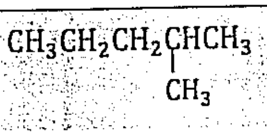
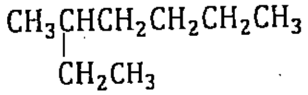


$$\textit{methyl group} \longrightarrow CH_3\underset{\overset{|}{\underset{2}{C}H_2\underset{1}{C}H_3}}{\overset{3}{C}}H\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_3$$

4. The numbers obtained by application of rule 2 are used to indicate the position of the substituent group.

The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. Numbers are separated from words by a hyphen.

The IUPAC names of the two examples above therefore are written as shown in the table below;

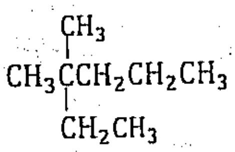
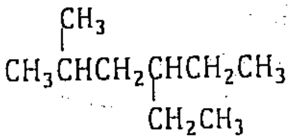
Branched alkane	*IUPAC name*
 $CH_3CH_2CH_2\underset{\underset{CH_3}{\mid}}{CH}CH_3$	2-Methylpentane
 $CH_3\underset{\underset{CH_2CH_3}{\mid}}{CH}CH_2CH_2CH_2CH_3$	3-Methylheptane

5. In cases where two or more substituents are present, each substituent is given a number corresponding to its position on the longest chain.

The substituent groups must be listed alphabetically (i.e., ethyl before methyl).

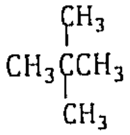
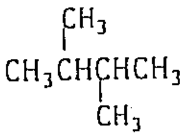
6. When two substituents are present on the same carbon atom, that number is used twice.

The multiplying prefixes such as "di" and "tri" are disregarded when deciding the alphabetical order. Some examples are shown in the table below to apply rules 5 and 6:

Branched alkane	*IUPAC name*
 $CH_3\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_2CH_3}{\mid}}{C}}CH_2CH_2CH_3$	2-Ethyl-2-methylpentane
 $CH_3\overset{\overset{CH_3}{\mid}}{CH}CH_2\underset{\underset{CH_2CH_3}{\mid}}{CH}CH_2CH_3$	4-Ethyl-2-methylhexane

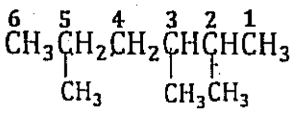
7. In cases where two or more substituents are identical, they are indicated by the use of the prefixes di-, tri-, tetra-, and so on.

Commas must be used to separate the numbers from each other. For example:

Branched alkane	*IUPAC name*
 $CH_3\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}CH_3$	2,2-Dimethylpropane
 $CH_3\overset{\overset{CH_3}{\mid}}{CH}\underset{\underset{CH_3}{\mid}}{CH}CH_3$	2,3-Dimethylbutane

8. **When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.**

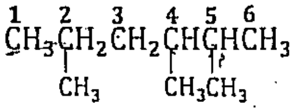
For example:



$$\overset{6}{CH_3}\underset{CH_3}{\overset{5}{C}H_2}\overset{4}{C}H_2\underset{CH_3}{\overset{3}{C}H}\underset{CH_3}{\overset{2}{C}H}\overset{1}{C}H_3$$

2,3,5 – *Trimethylhexane*

NOT



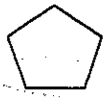
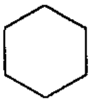
$$\overset{1}{CH_3}\underset{CH_3}{\overset{2}{C}H_2}\overset{3}{C}H_2\underset{CH_3}{\overset{4}{C}H}\underset{CH_3}{\overset{5}{C}H}\overset{6}{C}H_3$$

2, 4, 5 – *Trimethylhexane*

The cycloalkanes are named as shown below:

1. Cycloalkanes with one ring and no substituents are named by counting the number of carbon atoms in the ring a prefix "cyclo" is added to the name of the alkane with that number of carbons.

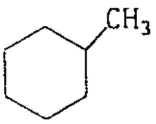
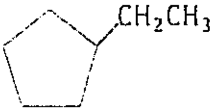
Some examples are shown in the table below:

Structure of cycloalkane	*IUPAC name*
	Cyclopropane
	Cyclobutane
	Cyclopentane
	Cyclohexane

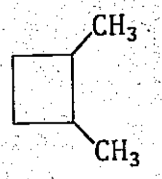
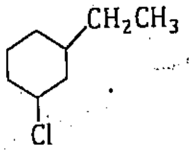
Note: In cycloalkanes, each carbon atom corner indicates a carbon atom and each line represents a bond between any two carbon atoms. Each carbon atom is therefore bonded to two other carbon atom and two hydrogen atoms which are not usually shown.

2. For cycloalkanes with one ring and one substituent, the name of the substituent is added to the beginning of the parent name.

For example;

Structure of cycloalkane	*IUPAC name*
	Methylcyclohexane
	Ethylcyclopentane

3. **For cycloalkanes with one ring and two or more substituents, begin by numbering the carbons in the ring, starting at the carbon with the substituent that is first in the alphabet and number in the direction that gives the next substituent the lower number possible. The substituents are then listed in alphabetical order, not according to the number of their carbon atom.**

Structure of cycloalkane	*IUPAC name*
	2,3-Dimethylbutane
	1-Chloro-3-ethylcyclohexane

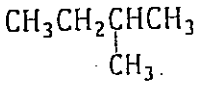
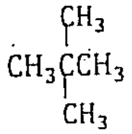
3.1.4 Isomerism in alkanes

Methane, ethane and propane do not exhibit structural isomerism.

Butane and higher alkanes exhibit chain isomerism i.e. all the isomers are due branching of the hydrocarbon chain hence referred to as **chain isomers** or **branched chain isomers**.

Butane has **two isomers** i.e. n-butane and 2-Methylpropane

There are three **isomeric pentanes** as shown in the table below:

Structural formula	*Name of the isomer*
$CH_3CH_2CH_2CH_2CH_3$	Pentane or n-pentane
 $CH_3CH_2\underset{\underset{CH_3}{\vert}}{C}HCH_3$	2-Methylbutane
 $CH_3\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}CH_3$	2,2-Dimethylpropane

The number of isomers progressively increases with increase in number of carbon atoms.

3.1.5 Physical properties of alkanes

(a) Physical state

The first four members of the homologous series of unbranched alkanes (methane, ethane, propane and butane) are gases at room temperature (25°C) and 1 atm pressure

The $C_5 - C_{17}$ unbranched alkanes (pentane to heptadecane) are **liquids**, and the unbranched alkanes with 18 and more carbon atoms are all **solids** at room temperature.

(b) **Boiling points**

The boiling points of the unbranched alkanes show a regular increase with increase in molecular weight.

Qn. The table below shows the boiling points some straight chain alkanes

Alkane	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}
Boiling point(°C)	−162	−89	−42	−0.5	36	69	98

(i) Plot a graph of boiling point against molecular mass of alkane

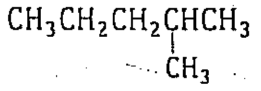
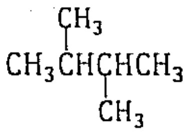
(ii) From your graph in (i) above, determine the boiling point of octane

(iii) Explain the trend in boiling points of the alkanes.

Boiling point increases from methane to heptane.

This is because molecules of the alkanes are held by weak van der Waals' forces of attraction whose strength increases with increase in molecular weight and molecular size. Therefore, an increasing amount of energy is required to separate molecules from one another for boiling to occur.

Note: Branching of the alkanes lowers the boiling point. For example, the some of the isomers of hexane show the variation in melting point as shown below;

Isomer	*Name of the isomer*	*Boiling point(°C)*
$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane	68.7
 $CH_3CH_2CH_2\underset{CH_3}{CH}CH_3$	2-Methylpentane	60.3
 $CH_3\overset{CH_3}{CH}\underset{CH_3}{CH}CH_3$	2,3-Dimethylbutane	58

The boiling points decrease from hexane to 2-Methylpentane to 2,3-dimethylbutane as branching increases.

This is because increased branching makes molecules of the branched isomers to have a nearly spherical shape (more compact) which reduces their surface area hence weaker Vander Waal's forces of attraction will exist between the adjacent molecules.

Hexane is a straight chain molecule which gives the molecule an extended structure resulting into relatively stronger Vander Waal's forces.

(c) Melting points

The straight chain alkanes do not show the same smooth increase in melting points with increasing molecular weight as they do in their boiling points.

There is an alternation from an unbranched alkane with an even number of carbon atoms to the next one with an odd number of carbon atoms.

$$CH_3CH_2CH_2COONa \xrightarrow[\text{heat}]{\text{Sodalime}} CH_3CH_2CH_3 + Na_2CO_3$$

The reaction is called decarboxylation because elements of carbon dioxide are removed from the molecules.

The reaction therefore results into formation of an alkane with one carbon atom less than the original compound.

Instead of a sodium salt of a carboxylic acid, the carboxylic acid itself can be used as shown below;

$$CH_3COOH \xrightarrow[\text{heat}]{\text{Sodalime}} CH_4 + Na_2CO_3$$

$$CH_3CH_2CH_2COOH \xrightarrow[\text{heat}]{\text{Sodalime}} CH_3CH_2CH_3 + Na_2CO_3$$

(e) Grignard reaction

During the Grignard reaction, the Grignard reagent is prepared first by adding an ethereal (ethoxyethane) solution of an alkylhalide (RX) to magnesium turnings or granules and the mixture allowed to stand.

The magnesium dissolves to form a cloudy solution and heat is liberated.

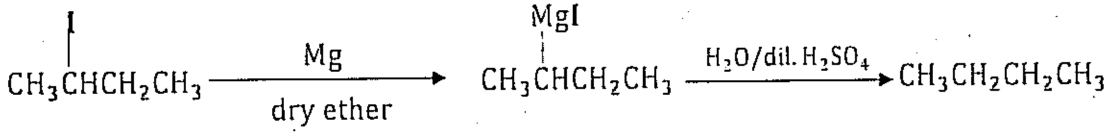
The cloudy solution is a solution of an alkylmagnesium halide (RMgX) that is called the Grignard reagent.

The Grignard reagent forms an alkane on treatment with aqueous hydrochloric acid or sulphuric acid.

$$RX \xrightarrow[\text{dry ether}]{Mg} RMgX \xrightarrow[\text{or } H_2O/\text{dil. } H_2SO_4]{H_2O/\text{dil. HCl}} RH$$

Examples,

$$CH_3CH_2CH_2Br \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2CH_2MgBr \xrightarrow{H_2O/\text{dil. HCl}} CH_3CH_2CH_3$$



$$CH_3\overset{I}{C}HCH_2CH_3 \xrightarrow[\text{dry ether}]{Mg} CH_3\overset{MgI}{C}HCH_2CH_3 \xrightarrow{H_2O/\text{dil. }H_2SO_4} CH_3CH_2CH_2CH_3$$

(f) Clemmensen reaction

Alkanes can be formed by reduction of carbonyl compounds (aldehydes and ketones).

This is done by treating the carbonyl compounds with amalgamated zinc and concentrated hydrochloric acid and this reaction is called the Clemmensen reaction.

Examples;

$$CH_3CHO \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3CH_3$$

$$CH_3CH_2CHO \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3CH_2CH_3$$

$$CH_3COCH_2CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3CH_2CH_2CH_3$$

(g) Kolbe synthesis

This method involves electrolysis of a sodium salt of a monocarboxylic acid in aqueous methanolic solution using platinum electrodes. The alkane is obtained at the anode and hydrogen is evolved at the cathode.

This method is only suitable for preparing symmetrical alkanes.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

At Platinum anode;

$$2CH_3COO^- \longrightarrow CH_3CH_3 + 2CO_2 + 2e$$

(h) Hydrolysis of aluminium carbide or beryllium carbide

This method can only be used to prepare methane.

When aluminium carbide is treated with warm water, methane is formed.

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

Beryllium carbide undergoes a similar reaction.

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$

Aluminium carbide can also be treated with dilute hydrochloric acid.

$$Al_4C_3 + 12HCl \longrightarrow 3CH_4 + 4AlCl_3$$

3.1.7 Chemical properties of alkanes

Alkanes are generally inert to many chemical reagents as compared to alkenes and alkynes.

They are resistant to attack by mineral acids and known oxidising agents

For their reactions to occur, a fairly high temperature, a photochemical or peroxide initiator may be required.

The following are the reasons why alkanes are characterized by inertness;

(i) The carbon–carbon and carbon–hydrogen bonds are quite strong (have very high bond energies) hence not easily broken unless alkanes are heated to very high temperatures.

(ii) The carbon–hydrogen bonds of alkanes are only slightly polar because the carbon and hydrogen atoms have nearly the same electronegativity. Therefore alkanes are generally unaffected by most bases.

(iii) Molecules of alkanes have no unshared electrons to offer as sites for attack by acids.

Some of the reactions undergone by alkanes are shown below;

(a) Combustion

Alkanes burn in **excess oxygen** with a non-smoky flame producing carbon dioxide and steam. The reaction is **exothermic** (produces heat) and proceeds via a high temperature free-radical mechanism.

General equation;

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O \quad \Delta H = -x\ kJmol^{-1}$$

For methane;

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890\ kJmol^{-1}$$

Liquid alkanes such as octane must be vapourised before they burn;

$$C_8H_{18}(g) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l) \quad \Delta H = -5510\ kJmol^{-1}$$

However the **incomplete combustion** of alkanes due to limited oxygen yields **carbon monoxide, a poisonous gas leading to air pollution**.

(b) Cracking

Cracking is the cleavage/breaking of alkanes, particularly in petroleum by heat (pyrolysis).
Alkanes from kerosene are passed through a metal chamber in the vapour phase and heated to 400-700°C in presence of aluminium oxide and silicon(IV) oxide as catalysts.
The alkanes are broken down to form smaller alkanes, alkenes and some hydrogen.

$$\begin{matrix}\text{Alkanes with} \\ \text{large molecules}\end{matrix} \xrightarrow[400-700°C]{Al_2O_3/SiO_2} \begin{matrix}\text{Alkane with} \\ \text{smaller molecules}\end{matrix} + \text{alkene(s)} + \text{Hydrogen}$$

Example

$$2CH_3CH_2CH_3(g) \xrightarrow[400-700°C]{Al_2O_3/SiO_2} CH_4(g) + CH_3CH = CH_2(g) + H_2C = CH_2(g) + H_2(g)$$

(c) Chlorination

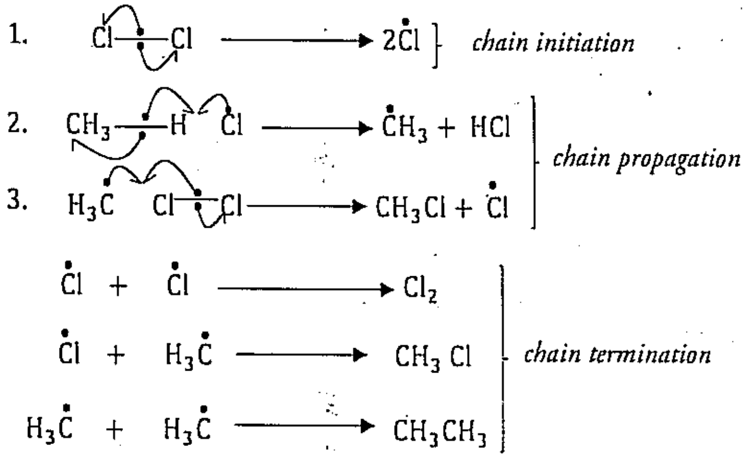
Alkanes react with chlorine in presence of **ultra-violet light** or at a temperature of 250-400°C to form a mixture of products.
Methane, for example, reacts vigorously under the above conditions to form chloromethane (CH_3Cl), dichloromethane(CH_2Cl_2), trichloromethane ($CHCl_3$) and tetrachloromethane (CCl_4).
Hydrogen chloride is also formed and the reaction is a substitution reaction.
When an excess of methane is used, chloromethane is the predominant product.

$$CH_4 \xrightarrow[u.v.\ light]{Cl_2} CH_3Cl + HCl$$

Explanation of mechanism for the reaction;

- The reaction is initiated by homolytic fission of chlorine molecules to form chlorine free radicals which are highly reactive.
- The chlorine radicals then react with methane molecules, abstracting a hydrogen atom from each to form hydrogen chloride molecules and methyl radicals.
- The methyl radicals then react with other chlorine molecules to form chloromethane and more chlorine radicals.

Illustration of the mechanism



Steps (2) and (3) are repeated to form the further products named earlier.

Methane undergoes bromination (but not iodination) by a similar mechanism. Fluorination is violent and dangerously exothermic.

Higher alkanes react with halogens by a similar chain mechanism but the reactions are slower than that of methane.

Note: Alkanes can also be chlorinated by refluxing them with sulphur dichloride dioxide (sulphuryl chloride) at 40-80°C using di(benzoyl)peroxide as a catalyst. This is a better synthetic reaction since it doesn't form a mixture of products.

$$RH \xrightarrow[40-80^\circ C]{SO_2Cl_2/di(benzoyl)peroxide} RCl + HCl + SO_2$$

For example:

$$CH_4 \xrightarrow[40-80^\circ C]{SO_2Cl_2/di(benzoyl)peroxide} CH_3Cl$$

$$CH_3CH_2CH_3 \xrightarrow[40-80^\circ C]{SO_2Cl_2/di(benzoyl)peroxide} CH_3CH_2CH_2Cl$$

(d) Nitration of alkanes

Alkanes react with nitric acid vapour at 150-400°C to form nitroalkanes.

For example;

$$CH_3CH_3 \xrightarrow[150-400°C]{HNO_3} CH_3CH_2NO_2 + H_2O$$

3.1.8 Uses of alkanes

- Due to the heat produced by the combustion of alkanes in excess oxygen, they are used as fuels in internal combustion engine, gas cookers, aviation fuel, ships and electric generators.
- Methane is used in the formation of a mixture of carbon monoxide and hydrogen (known as synthesis gas). The synthesis gas is in turn used to manufacture methanol.

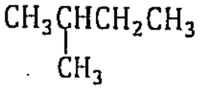
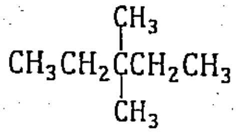
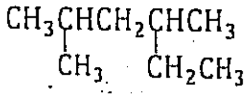
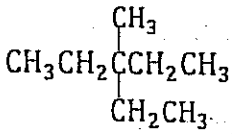
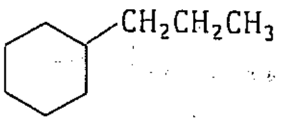
$$CH_4 + H_2O \xrightarrow[900°C, 3atm]{Ni\ catalyst} CO + 3H_2$$

$$CO + 2H_2 \xrightarrow{catalyst} CH_3OH$$

- Methane is also used to make chloromethane (used to make silicones) and dichloromethane (an important solvent) by heating it with chlorine at 400°C.
- Methane is very important in the manufacture of ethyne.
- Methane is also the principal source of hydrogen cyanide.
- Ethane and propane are used to make ethene and propene which are used to make plastics.
- Propane can be used in bottled fuel and to make nitroalkanes when heated with nitric acid vapour at 350 °C. The nitroalkanes are used as solvents.
- Butane is a major source of ethanoic acid.
- Cyclohexane is used to make hexane-1,6-dioic acid, a monomer for manufacture of nylon.

3.1.9 End of subtopic assessment exercise

1. Give the IUPAC name of each of the following;

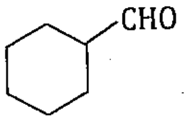
ALKANE	IUPAC NAME
$(CH_3)_2CHCH_2CH_2CH_3$	
 $CH_3\underset{CH_3}{\underset{\vert}{C}}HCH_2CH_3$	
 $CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3$	
 $CH_3\underset{CH_3}{C}HCH_2\underset{CH_2CH_3}{C}HCH_3$	
 $CH_3CH_2\overset{CH_3}{\underset{CH_2CH_3}{C}}CH_2CH_3$	
	

2. Draw the structural formula of each of the following;

Name	*Structural formula*
2,5-Dimethylhexane	
2,3-Dimethylbutane	
2,2,4-Trimethylpentane	
3-Ethyl-2-methylpentane	
4-Ethyl-3,4-dimethylheptane	
2,2,3,3-Trimethylpentane	
3-Bromo-2-chloropentane	

3. Complete the following equations and write the IUPAC name of the main organic product formed in each case.

(a) $(CH_3)_2CHCOOH + NaOH \xrightarrow[\text{heat}]{\text{CaO}}$

(b)  $\xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}}$

(c) $CH_3COCH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}}$

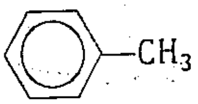
(d) $CH_3CH_2Cl \xrightarrow[\text{ethanol (reflux)}]{\text{Zn} - \text{Cu}}$

(e) $CH_3CH_2CH_2COONa \xrightarrow[\text{heat}]{\text{CaO(s)/NaOH(s)}}$

(f) $CH_3CH_2I \quad + Na \xrightarrow{\text{dry ether}}$

4. Complete the following equations and in each case write a mechanism for the reaction.

(a) $CH_3CH_2CH_3 \xrightarrow[\text{u.v light}]{Br_2}$

(b)  $\xrightarrow[\text{u.v light}]{Br_2}$

5. Write an equation to show how the following conversions can be effected. In each case, indicate the necessary reagents and conditions.

(a) Propane to chloropropane

(b) Ethanoic acid to methane

(c) Propene to propane

(d) Chloroethane to butane

6. (a) Describe any four methods of preparing ethane in the laboratory. In each case, name the reagents and state the conditions required. Include equations in your answer.

(b) Briefly explain the reaction of methane with chlorine. Include a mechanism in your answer.

7. 20cm^3 of a gaseous s hydrocarbon *W* were exploded with 120cm^3 of Oxygen. After the explosion, the volume of gases remaining was 90cm^3 and this decreased to 50cm^3 on treatment with aqueous potassium hydroxide.

(a) Determine the molecular formula and structural formula of the hydrocarbon.

(b) Write equation to show how *W* can be;

  (i) synthesized from ethyne

  (ii) converted to chloroethane.

8. 15 cm^3 of a gaseous hydrocarbon were exploded with 105 cm^3 of oxygen in a sealed vessel after cooling, the residual volume occupies 75cm^3. On addition of caustic potash, there was a diminution of volume to 30cm^3. Determine the molecular formula of the hydrocarbon.

  (i) Write equation for the complete combustion of the hydrocarbon.

  (ii) Briefly explain how the hydrocarbon above can be obtained from 2 - bromopropane. (No equation is required)

9. A mixture of 10 cm^3 of a gaseous hydrocarbon 100 cm^3 of excess oxygen were exploded. The volume after explosion was 75cm^3 and this was reduced to 35cm^3 on treatment with potassium hydroxide solution.

  (i) Deduce the molecular formula of the hydrocarbon.

  (ii) Write the structural formulae of all the possible isomers of the hydrocarbon.

10. (a) When 8.8g of a hydrocarbon, *Z* was burnt in excess air, 14.4g of water and 13.44 dm^3 of carbon dioxide were obtained at stp. Determine the empirical formula of *Z*.

  (b) The vapour density of *Z* is 22. Determine the molecular formula and name of *Z*.

  (c) Write an equation to show how *Z* can be prepared from a Grignard reagent.

11. Explain each of the following observations.

  (a) Hexane boils at 68°C whereas 2-methylpentane boils at 60.3°C yet the two compounds have the same molecular mass.

  (b) Butane has a higher boiling point than ethane.

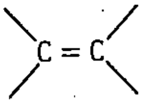
3.2 Alkenes

3.2.1 Introduction

Alkenes form a homologous series of unsaturated hydrocarbons containing at least one carbon-carbon double bond with the general formula C_nH_{2n} for the aliphatic ones; where $n \geq 2$.

The cyclic alkenes for example cyclohexene and alkadienes (alkenes with two double bonds), have a general formula; C_nH_{2n-2}.

The functional group possessed by alkenes is the carbon-carbon double bond i.e



3.2.2 Nomenclature of alkenes

The IUPAC SYSTEM is used when naming alkenes just as it is for alkanes.

The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes:

1. *The parent name is determined by selecting the longest chain that contains the double bond and changing the ending of the name of the alkane of identical length from -ane to -ene.*

Therefore if the longest chain contains four carbon atoms, the parent name for the alkene is butene; if it contains five carbon atoms, the parent name is pentene, and so on.

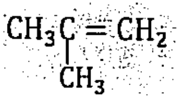
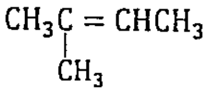
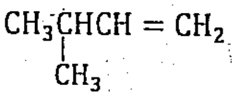
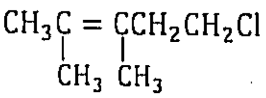
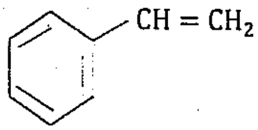
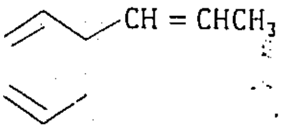
2. *The parent chain is then numbered so as to include both carbon atoms of the double bond, and the numbering should begin at the end of the chain nearer the double bond.*

The position of the double bond is specified by appropriate number between the stem name and the ending -ene except for ethene and propene without positional isomers. Examples;

Structural formula	*IUPAC name*
$H_2C = CH_2$	Ethene
$CH_3CH = CH_2$	Propene
$CH_3CH_2CH = CH_2$	But-1-ene
$CH_3CH = CHCH_3$	But-2-ene
$CH_3CH = CHCH_2CH_2CH_3$	Hex-2-ene
$CH_3CH_2CH_2CH_2CH = CH_2$	Hex-1-ene

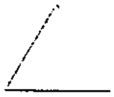
3. *The locations of the substituent groups are indicated by the numbers of the carbon atoms to which they are attached.*

The substituent groups must be listed alphabetically (i.e., *chloro* before *methyl*).

Structural formula	*IUPAC name*
 $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CH_2$	2-Methylpropene
 $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CHCH_3$	2-Methylbut-2-ene
 $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH=CH_2$	3-Methylbut-1-ene
 $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}=\underset{\displaystyle CH_3}{\underset{\vert}{C}}CH_2CH_2Cl$	5-Chloro-2, 3-dimethylpent-2-ene
	Phenylethene
	1-Phenylpropene

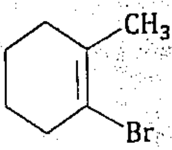
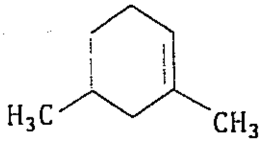
4. *The cycloalkenes are named by counting the number of carbon atoms in the ring and a prefix "cyclo" is added to the name of the alkene with that number of carbons.*

Examples are shown in the table below:

Structural formula of cycloalkene	*IUPAC name*
	Cyclopropene
	Cyclobutene
	Cyclohexene

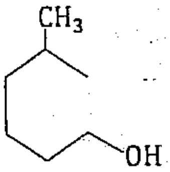
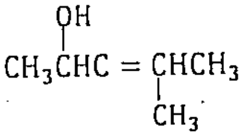
5. ***The substituted cycloalkenes are numbered in the way that gives the carbon atoms of the double bond the 1 and 2 positions and that also gives the substituent groups the lower numbers at the first point of difference.***

With substituted cycloalkenes it is not necessary to specify the position of the double bond since it will always begin with C1 and C2. Some examples are shown in the table below:

Structural formula	*IUPAC name*
	1-Bromo-2-methylcyclohexene
	2,4-Dimethylcyclohexane (not 1,5-Dimethylcyclohexane) (not 1,3-Dimethylcyclohexane)

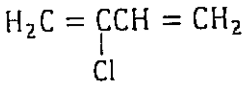
6. ***Compounds containing both a carbon-carbon double bond and a hydroxyl group are named as alkenols (or cycloalkenols).***

For example;

Structural formula	*IUPAC name*
	3-Methylcyclohexene-1-ol
 $CH_3\underset{}{\overset{OH}{C}}HC=\underset{CH_3}{C}HCH_3$	4-Methylpent-3-ene-2-ol

7. ***When an alkene has more than one double bond, each double bond is given a position.***

For example;

 $H_2C=\underset{Cl}{C}CH=CH_2$	2-Chlorobuta-1,3-diene

3.2.3 Isomerism in alkenes

Alkenes exhibit ***structural isomerism***.

They also show ***geometrical isomerism*** (***cis*** and ***trans*** isomers) due to prevention of free rotation about the double bond.

However, we shall deal with structural isomerism for this specific homologous series.

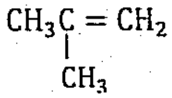
Under structural isomerism, alkenes other than ***ethene*** and ***propene***, show both chain and positional isomers.

Positional isomers differ by position of the carbon-carbon double bond.

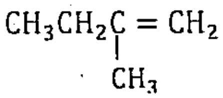
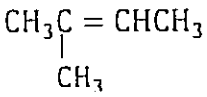
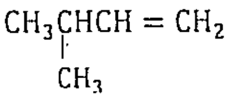
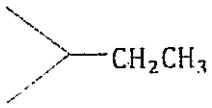
Alkenes with ***3 and more carbon atoms*** are ***isomeric to cycloalkanes***.

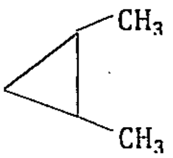
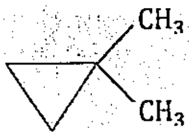
Examples:

C_4H_8 has three structural isomers. Their structural formulae and IUPAC names are shown below:

Structural formula	*IUPAC name*
$CH_3CH_2CH = CH_2$	But-1-ene
$CH_3CH = CHCH_3$	But-2-ene
 $CH_3C(CH_3) = CH_2$	2-methylpropene

C_5H_{10} has the following structural isomers.

Structural formula	*IUPAC name*
$CH_3CH_2CH_2CH = CH_2$	Pent-1-ene
$CH_3CH_2CH = CHCH_3$	Pent-2-ene
 $CH_3CH_2C(CH_3) = CH_2$	2-Methylbut-1-ene
 $CH_3C(CH_3) = CHCH_3$	2-Methylbut-2-ene
 $CH_3CH(CH_3)CH = CH_2$	3-Methylbut-1-ene
	Cyclopentane
	Ethylcyclopropane

	1,2-Dimethylcyclopropane
	1,1-Dimethylcyclopropane

3.2.4 Physical properties of alkenes

As a class, the alkenes possess physical properties that are essentially the same as those of the corresponding alkanes.

(a) Physical state

Alkenes up to four carbon atoms (ethene, propene and butenes) are gases at room temperature. Those with 5-8 carbon atoms are liquids. Higher members with more than 15 carbon atoms are solids at room temperature.

(b) Boiling points

The boiling points of alkenes increase with increasing number of carbon atoms as with the alkanes. The boiling point rise is about 20-30°C for each added carbon atom, except for the very small homologues.

Qn. The table below shows the boiling points some alkenes

Alkenes	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}
Boiling point(°C)	−102	−48	−6.5	30

Explain the trend in boiling points of the alkenes.

Boiling point increases from ethene to propene to butene to pentene.

This is because molecules of the alkenes are held by weak van der Waals' forces of attraction whose strength increases with increase in molecular weight and molecular size.

As for alkanes, branching lowers the boiling point.

This is because increased branching makes molecules of the branched isomers to have a nearly spherical shape (more compact) which reduces their size (surface area) hence weaker Vander Waal's forces of attraction will exist between their molecules.

However, the straight chain molecules have an extended structure resulting into relatively stronger Vander Waal's forces.

The boiling point of an alkene is very nearly the same as that of the alkane with the same number of carbon atoms.

(c) Density

Alkenes are less dense than water.

(d) Solubility

Alkenes are ***virtually insoluble*** in water but ***soluble in non-polar organic solvents*** such as trichloromethane (chloroform), ethoxyethane (ether) and benzene.

3.2.5 Preparation of alkenes by cracking

Alkenes are obtained in the petroleum industry by ***catalytic cracking.***

The part of the light gas-oil fraction obtained by fractional distillation of crude oil, which is not needed as a fuel, is heated in ***presence of a catalyst at high temperature.***

The large molecules are broken down to form smaller molecules.

The gas oil vapour is passed through a fine powder made of ***aluminium oxide*** and ***silicon(IV) oxide*** (sometimes containing small quantities of nickel or tungsten) and heated to 400-700°C.

One of the products of this catalytic cracking is a gas known as ***refinery gas*** which contains the alkenes; ***ethene*** and ***propene*** as major constituents.

Example

$$2CH_3CH_2CH_3(g) \xrightarrow[400-700^\circ C]{Al_2O_3/SiO_2} CH_4(g) + CH_3CH=CH_2(g) + H_2C=CH_2(g) + H_2(g)$$

3.2.6 Laboratory preparation of alkenes

Alkenes are generally prepared by elimination of one atom or groups from two adjacent carbon atoms mainly from alcohols and haloalkanes.

(a) From acid catalyzed dehydration of alcohols.

The alcohols are heated with **excess concentrated sulphuric acid** or **phosphoric acid** at **360°C.**

The reaction involves removal of water molecules hence known as **dehydration reaction.**

The **temperature** and **concentration** of acid required to dehydrate an alcohol depend on the structure of the alcohol.

Primary alcohols are the most difficult to dehydrate. For example dehydration of ethanol requires concentrated sulphuric acid and a temperature of 180°C.

Secondary alcohols usually dehydrate under milder conditions. Cyclohexanol, for example, dehydrates in 85% phosphoric acid at 165–170°C.

Tertiary alcohols are usually so easily dehydrated that relatively mild conditions can be used. 2-methylpropan-2-ol, for example, dehydrates in 20% aqueous sulphuric acid at a temperature of 85°C.

The ease of dehydration of alcohols is therefore:

Tertiary alcohol > Secondary alcohol > Primary alcohol

Note

Since any class of alcohols will be dehydrated at 180°C, this temperature can be used in all cases involving concentrated sulphuric acid.

Similarly, 360°C can be used for all cases involving concentrated phosphoric acid.

The mechanism for the reaction occurs in the order;

(i) protonation of alcohol

(ii) loss of water molecules by protonated alcohol to form a carbocation

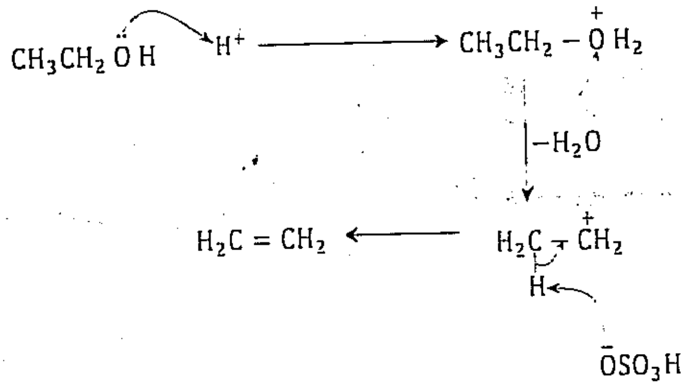
(iii) loss of a proton by the carbocation to form the alkene.

Examples

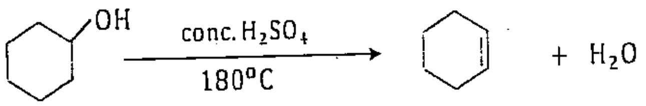
1. $$CH_3CH_2OH \xrightarrow[180^\circ C]{conc.\ H_2SO_4} H_2C=CH_2 + H_2O$$

Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

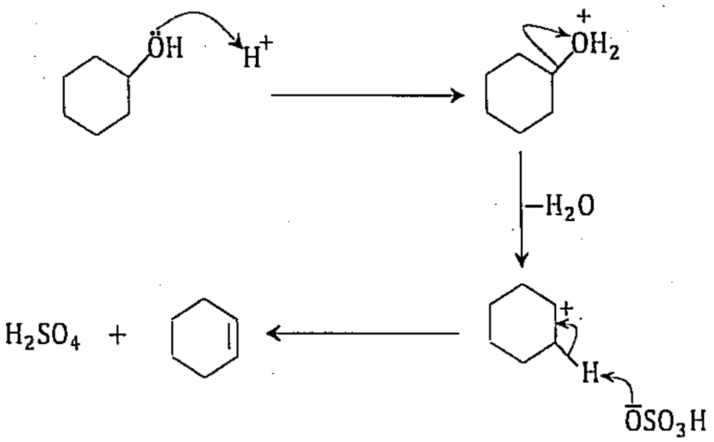


2.



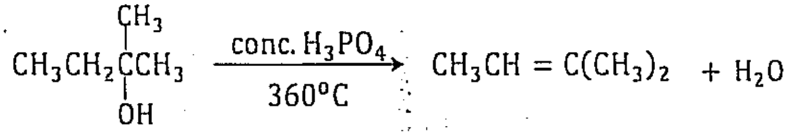
Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$



Note: As seen in the mechanisms above;

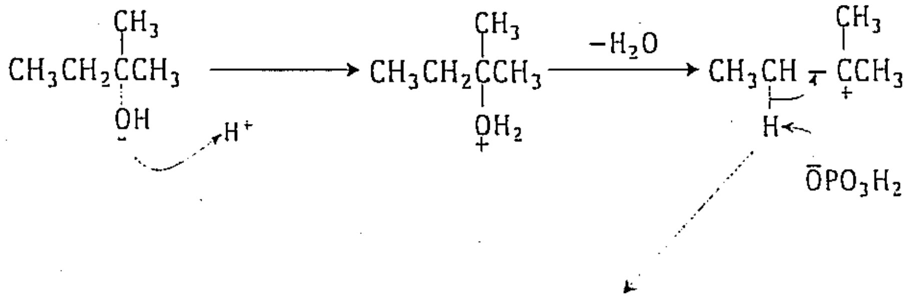
- A carbocation is formed during the mechanism.
- The stability of the carbocation formed depends on the number of alkyl groups attached to it.
- The stability of the carbocations formed therefore increases in the order: Primary carbocation < secondary carbocation < tertiary carbocation
- A hydride shift or a methyl shift may occur if a mechanism involves a primary carbocation so as a more stable secondary or tertiary carbocation is formed.

3. 

$$CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CH_3 \xrightarrow[360°C]{conc.\ H_3PO_4} CH_3CH = C(CH_3)_2 + H_2O$$

Mechanism

$$H_3PO_4 \rightleftharpoons H^+ + \bar{O}PO_3H_2$$



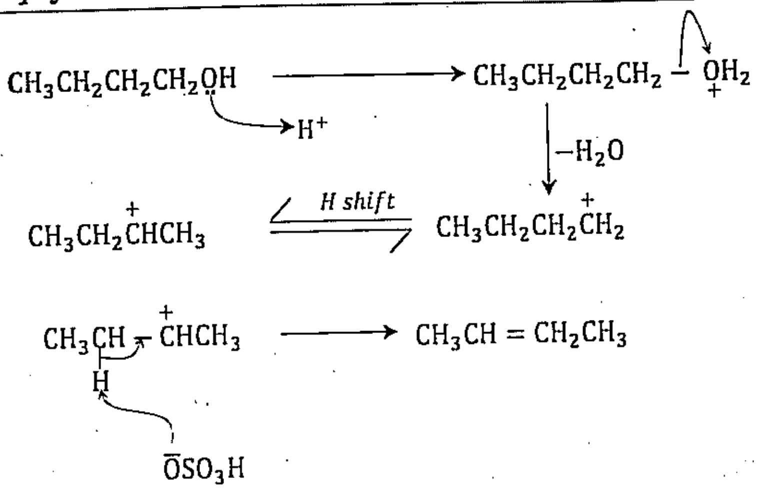
$CH_3CH = C(CH_3)_2$

2 – Methylpent – 2 – ene

4. $CH_3CH_2CH_2CH_2OH \xrightarrow[180°C]{conc.\ H_2SO_4} CH_3CH = CHCH_3 + H_2O$

Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + \bar{O}SO_3H$$



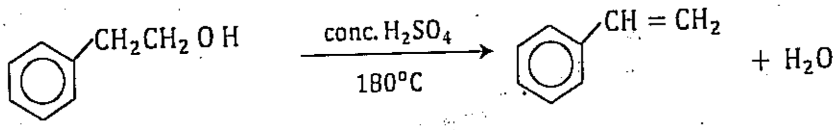
$$CH_3CH_2CH_2CH_2\ddot{O}H \xrightarrow{H^+} CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}H_2$$

$$CH_3CH_2CH_2CH_2-\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3CH_2CH_2\overset{+}{C}H_2$$

$$CH_3CH_2\overset{+}{C}HCH_3 \xrightleftharpoons{H\ shift} CH_3CH_2CH_2\overset{+}{C}H_2$$

$$CH_3\underset{H}{C}H-\overset{+}{C}HCH_3 \xrightarrow{\bar{O}SO_3H} CH_3CH = CH_2CH_3$$

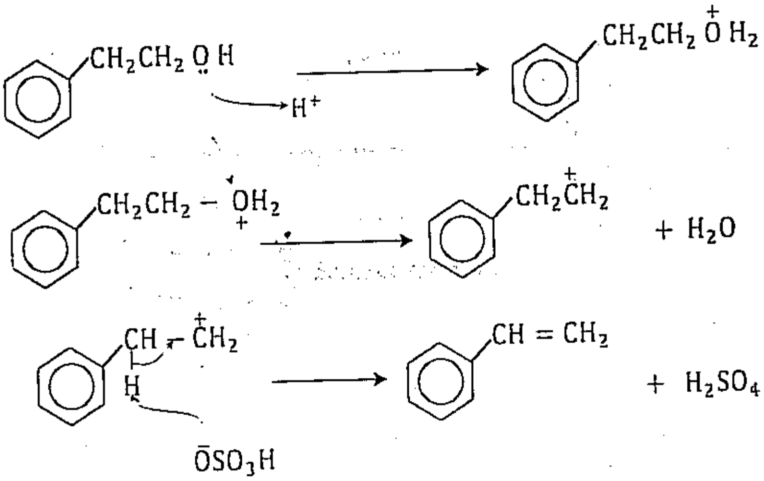
5.



conc. H_2SO_4, 180°C

Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + \bar{O}SO_3H$$



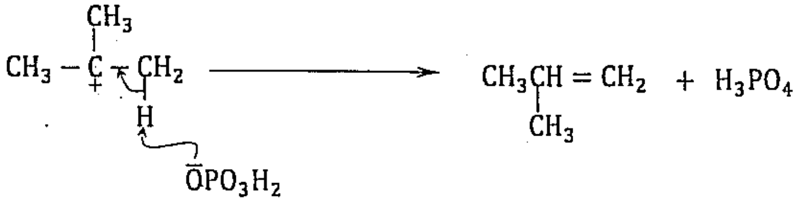
6. Easy dehydration of alcohols follows the order, 3⁰ alcohol > 2⁰ alcohol > 1⁰ alcohol.

$$(CH_3)_3C-OH \xrightarrow[heat]{excess\ conc.\ H_3PO_4} CH_3\underset{CH_3}{C}H = CH_2 + H_2O$$

Mechanism

$$(CH_3)_3C-\ddot{O}H \xrightarrow{\overset{\delta+}{H}-\overset{\delta-}{O}PO_3H_2} (CH_3)_3C-\overset{+}{O}H_2 + \bar{O}PO_3H_2$$

$$(CH_3)_3C-\overset{+}{O}H_2 \rightleftharpoons (CH_3)_3\overset{+}{C} + H_2O$$



$$CH_3-\underset{+}{\overset{CH_3}{C}}-\underset{H}{CH_2} \quad \bar{O}PO_3H_2 \longrightarrow CH_3\underset{CH_3}{CH}=CH_2 + H_3PO_4$$

N.B. The dehydration of alcohols can also be done by passing alcohol vapour over aluminium oxide catalyst heated to 360°C.

$$CH_3CH_2OH \xrightarrow[360^\circ C]{Al_2O_3} H_2C=CH_2$$

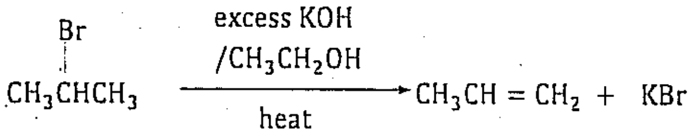
(b) From dehydrohalogenation of halohydrocarbons

Dehydrohalogenation of haloalkanes is carried out by heating them with an alcoholic solution of potassium hydroxide or an alcoholic solution of sodium hydroxide.

The reaction is usually done with secondary and tertiary alkylhalides for a good yield of the alkene. If a primary alkylhalide is used, then it should have more than two carbon atoms.

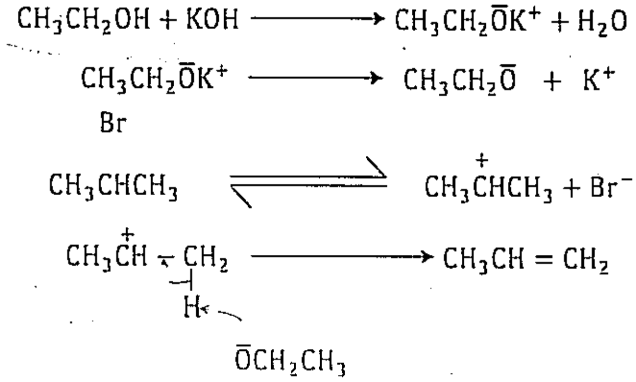
Examples

1.



$$CH_3\overset{Br}{C}HCH_3 \xrightarrow[heat]{excess\ KOH\ /CH_3CH_2OH} CH_3CH=CH_2 + KBr$$

Mechanism



$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$$

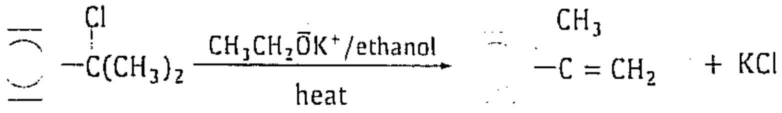
$$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$

$$CH_3\overset{Br}{C}HCH_3 \rightleftharpoons CH_3\overset{+}{C}HCH_3 + Br^-$$

$$CH_3\overset{+}{C}H-\underset{H}{CH_2} \quad \bar{O}CH_2CH_3 \longrightarrow CH_3CH=CH_2$$

$$K^+ + Br^- \longrightarrow KBr$$

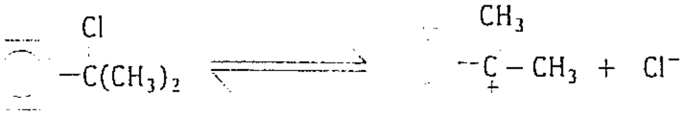
2.



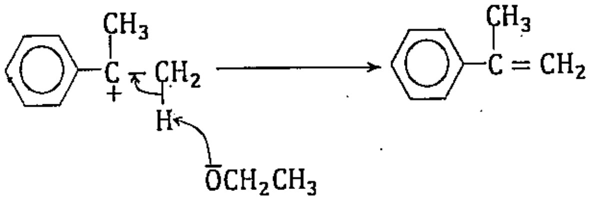
$$-\overset{Cl}{C}(CH_3)_2 \xrightarrow[heat]{CH_3CH_2\bar{O}K^+/ethanol} -\overset{CH_3}{C}=CH_2 + KCl$$

Mechanism

$$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$



$$-\overset{Cl}{C}(CH_3)_2 \rightleftharpoons -\underset{+}{\overset{CH_3}{C}}-CH_3 + Cl^-$$

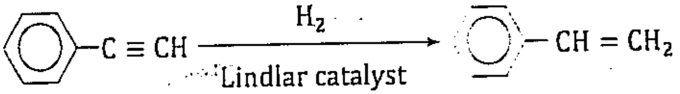


$$K^+ + Cl^- \longrightarrow KCl$$

(c) From alkynes

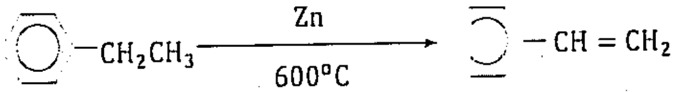
Alkynes react with hydrogen in the presence of Lindlar catalyst to form alkenes.

$$CH_3C \equiv CH \xrightarrow[\text{Lindlar catalyst}]{H_2} CH_3CH = CH_2$$



Note

Industrially, phenylethene is formed by dehydrogenation of phenylethane at 600°C in presence of zinc catalyst.



However, instead of zinc, iron(III) oxide or magnesium oxide can be used at the same temperature.

(d) Dehalogenation of Vicinal dihalides

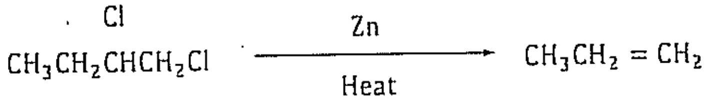
Vicinal dihalides are alkylhalides in which the halogen atoms are attached to the adjacent carbon atoms.

When vicinal dihalides are heated with zinc, alkenes are formed.

However this method is severely limited by the fact that these dihalides are themselves generally prepared from alkenes.

Example

$$CH_2BrCH_2Br \xrightarrow[\text{Heat}]{Zn} CH_2 = CH_2$$



$$CH_3CH_2\overset{Cl}{C}HCH_2Cl \xrightarrow[\text{Heat}]{Zn} CH_3CH_2 = CH_2$$

3.2.7 Chemical properties of alkenes

Alkenes are highly reactive compounds. They undergo electrophillic addition reactions.

This is because alkenes have carbon-carbon double bonds which are a source of π-electrons. The double bonds are therefore a center of high electron density and therefore readily attacked by electron deficient species (electrophiles)

In the addition reactions, the double bond is converted to a single bond and atoms or groups of atoms are added to each of the two carbon atoms.

The additions may proceed through free radical mechanism or ionic mechanism.

(a) Halogenation

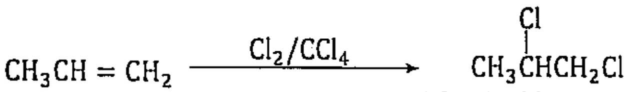
Alkenes react with bromine or chlorine in presence of tetrachloromethane (carbon tetrachloride) to form vicinal dihalides at room temperature in the absence of light.

In the presence of light, free radical addition takes place.

Ethanoic acid can be used instead of tetrachloromethane.

Examples

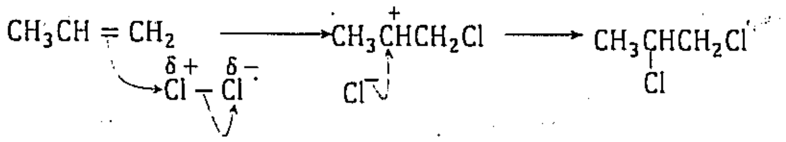
(i)



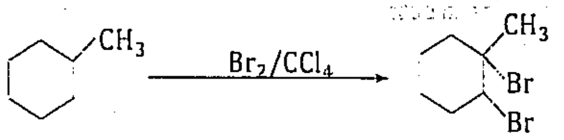
$$CH_3CH = CH_2 \xrightarrow{Cl_2/CCl_4} CH_3\overset{Cl}{C}HCH_2Cl$$

1,2 – *Dichloropropane*

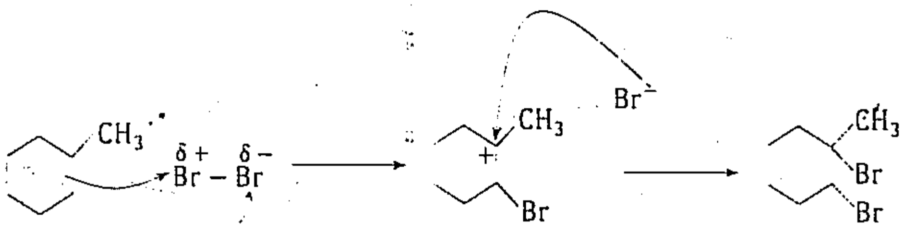
Mechanism



(ii)

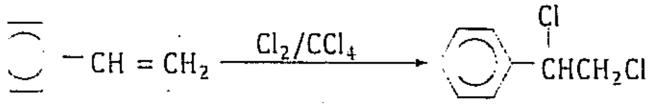


Mechanism



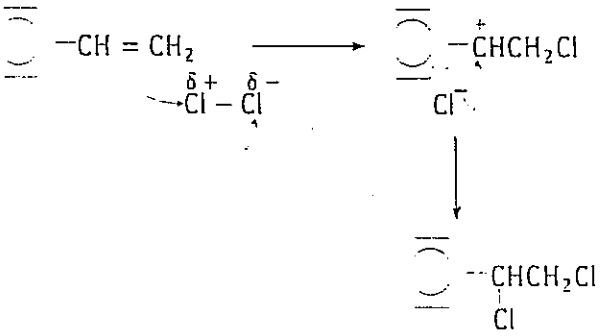
The name of the product is *1,2-Dibromo-1-methylcylcohexane.*

(iii)



1,2 – *Dichloro* – 2 – *phenylethane*

Mechanism



N.B. The above reaction with bromine is a useful test for unsaturation.

Observation: The reddish-brown solution turns colourless.

(b) Addition of bromine water/ chlorine water.

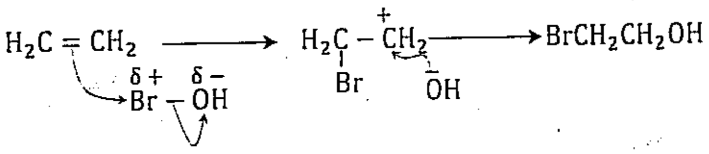
Alkenes react with bromine water or chlorine water to form corresponding bromoalcohols or chloroalcohols.

Examples

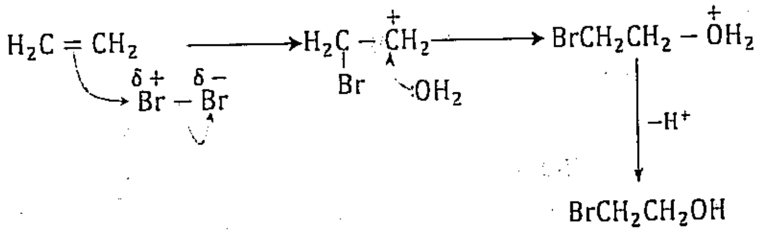
(i) $$CH_2 = CH_2 \xrightarrow{Br_2/H_2O} BrCH_2CH_2OH + HBr$$

Mechanism

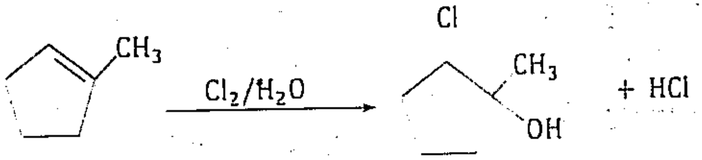
$$Br_2 + H_2O \rightleftharpoons HOBr + HBr$$



Alternatively,

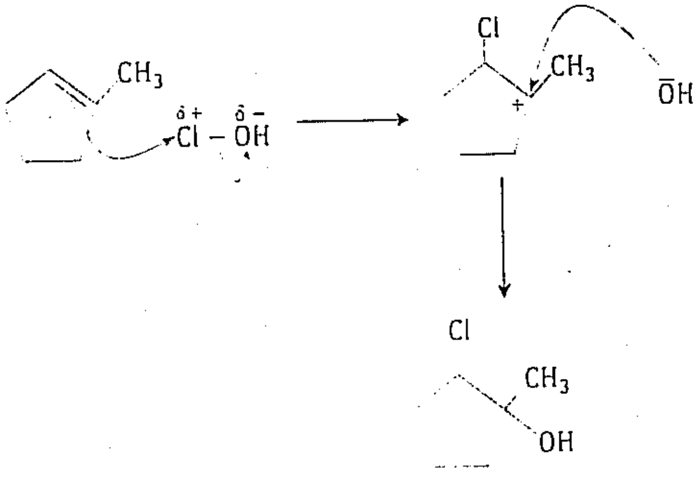


(ii)

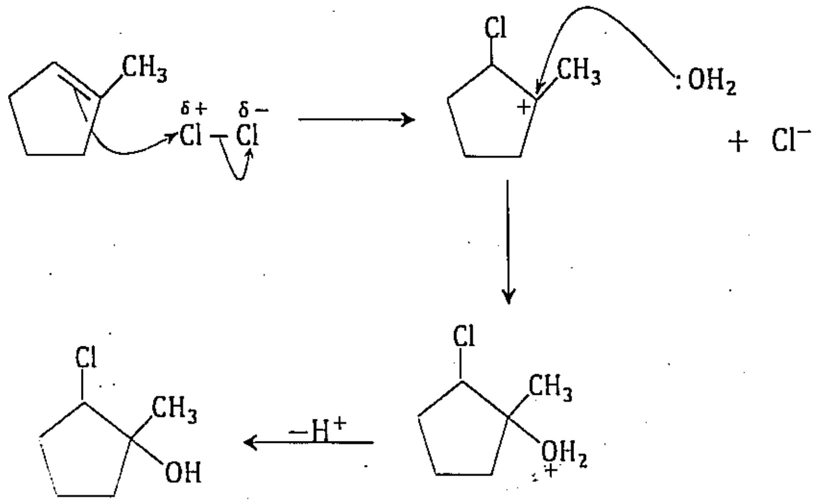


Mechanism

$$Cl_2(g) + H_2O(l) \rightleftharpoons HOCl + HCl$$



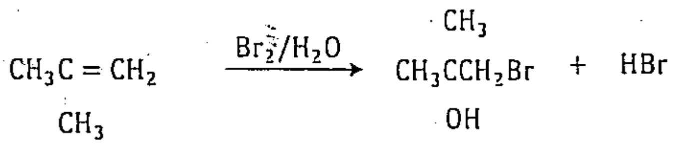
Alternatively



Sample question

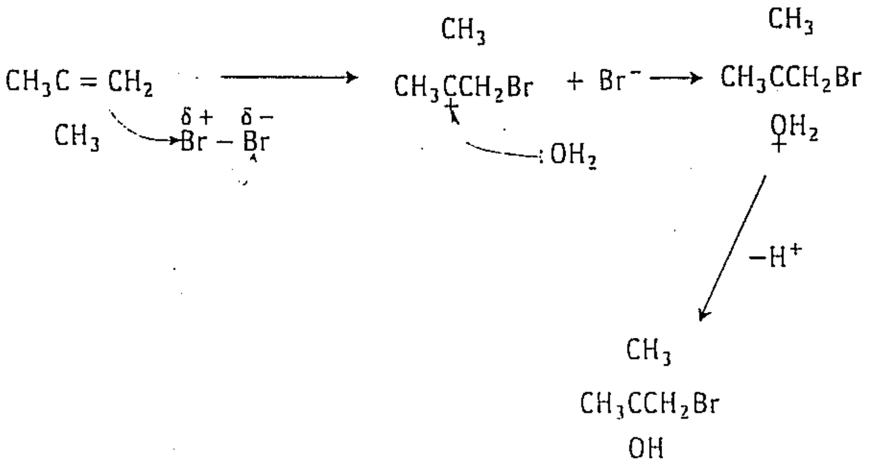
Methylpropene reacts with bromine water to form 1-bromo-2-methylpropan-2-ol as the major product but not 1,2-dibromo-2-methylpropane. Explain this observation.

2-Methylpropene reacts with bromine to form a **carbocation/carbonium ion** and a **bromide ion**. Since **water is present in excess** and is a **better nucleophile** than the **bromide ion**, it attacks the carbocation to form an **unstable intermediate** which loses a **proton** to form **1-bromo-2-methylpropan-2-ol** as shown below:



$$\underset{CH_3}{CH_3C}=CH_2 \xrightarrow{Br_2/H_2O} CH_3\overset{CH_3}{\underset{OH}{C}}CH_2Br + HBr$$

Mechanism

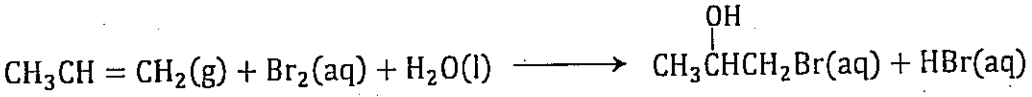


$$H^+ + Br^- \longrightarrow HBr$$

Note

The reaction of alkenes with bromine water is also a useful test for unsaturation.

In case a well-balanced equation is required it can be written as one for propene shown below:



$$CH_3CH = CH_2(g) + Br_2(aq) + H_2O(l) \longrightarrow CH_3\overset{OH}{C}HCH_2Br(aq) + HBr(aq)$$

Observation: The reddish brown solution turns colourless.

(c) Reaction with hydrogen halides.

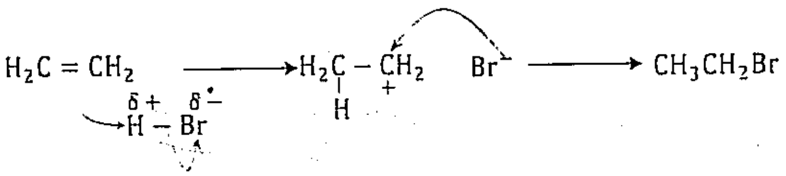
Alkenes react with dry hydrogen bromide, dry hydrogen chloride and dry hydrogen iodide to form corresponding alkylhalides.

The major product is in accordance with Markownikoff's rule which states that:

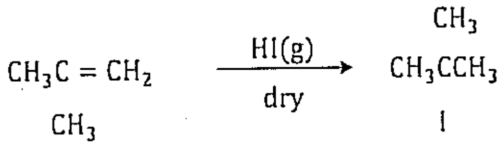
In addition of an unsymmetrical reagent to an unsymmetrical alkene, the more electronegative atom or group becomes attached to the more carbon atom containing fewer hydrogen atoms.

(i) $CH_2 = CH_2 \xrightarrow[\text{dry}]{HBr(g)} CH_3CH_2Br$

Mechanism

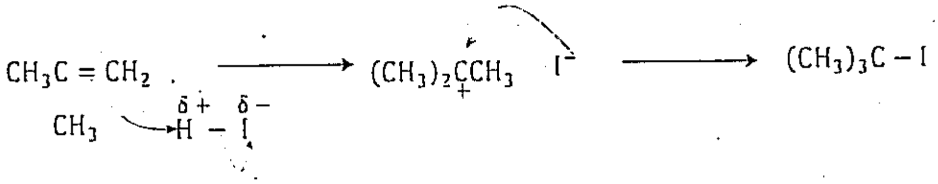


(ii)

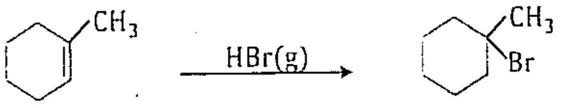


$$CH_3\underset{CH_3}{C} = CH_2 \xrightarrow[\text{dry}]{HI(g)} CH_3\overset{CH_3}{\underset{I}{C}}CH_3$$

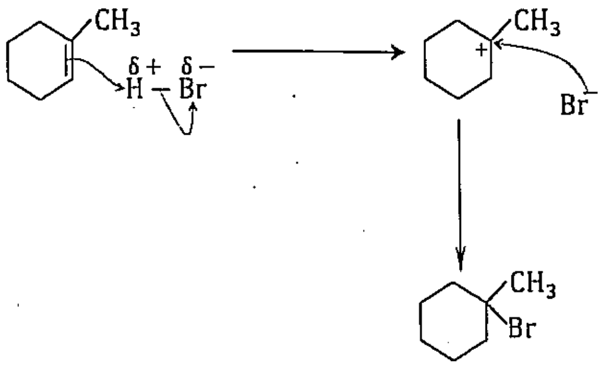
Mechanism



(iii)



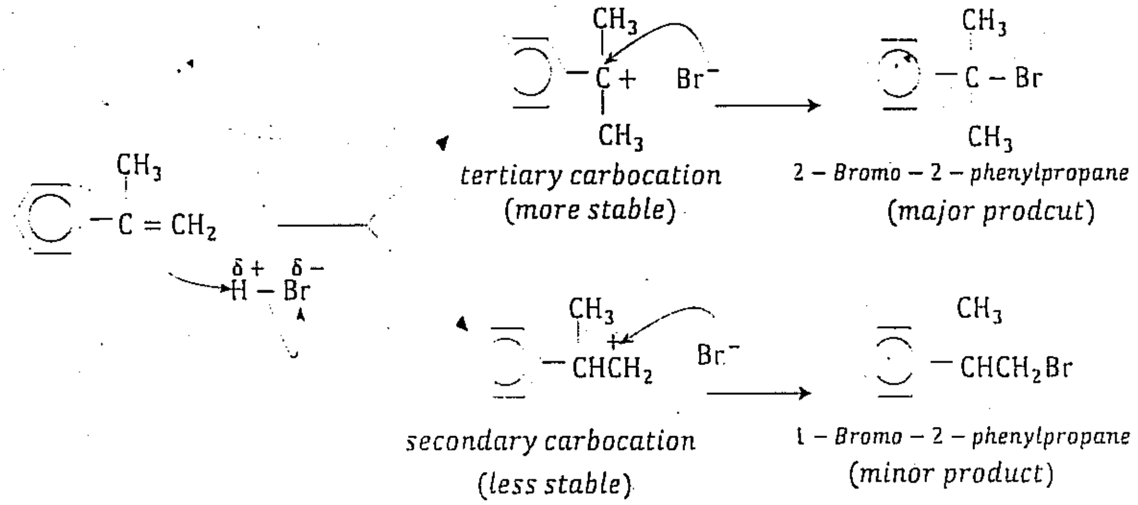
Mechanism



Sample question

When 2-Phenylpropene is reacted with hydrogen bromide, the major product is 2-Bromo-2-phenylpropane but not 1-Bromo-1-phenylpropane. Explain.

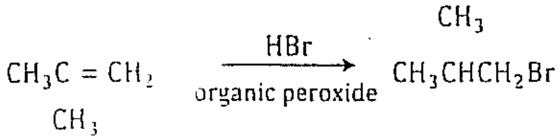
2-Phenylpropene combines with hydrogen bromide to form **bromide ions**, a **tertiary carbocation** and a **primary carbocation**. The tertiary carbocation is **more stable** than the primary carbocation. Therefore, the **concentration** of the **tertiary carbocation** is **higher** than that of the primary carbocation. The **most of the bromide ions combine with** the **tertiary carbocation** to form **2-bromo-2-phenylpropane** while a few **bromide ions combine with the primary carbocation** to form **1-Bromo-1-phenylpropane** as **minor product**.



Note

If for hydrogen bromide, an organic peroxide is used, the reactions proceed via Anti-Markownikoff addition for unsymmetrical alkenes, i.e.,

$$CH_3CH = CH_2 \xrightarrow[\text{organic peroxide}]{HBr} \underset{1-\text{Bromopropane}}{CH_3CH_2CH_2Br}$$



$$\underset{CH_3}{CH_3C} = CH_2 \xrightarrow[\text{organic peroxide}]{HBr} CH_3\overset{CH_3}{CH}CH_2Br$$

Hydrogen chloride and hydrogen iodide even in the presence of an organic peroxide will add onto the alkene by the Markownikoff mechanism.

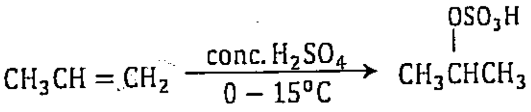
Note

The mechanism for this reaction is free radical but is not required in the limits of the A' level syllabus. However, it is an important reaction, applicable in organic synthesis.

(iv) **Reaction with concentrated sulphuric acid (sulphonation)**

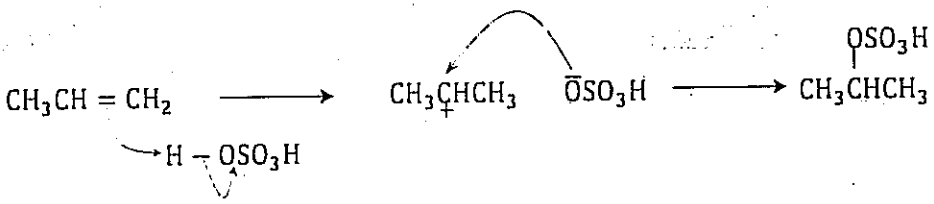
Lower alkenes react with cold concentrated sulphuric acid to form alkylhydrogen sulphates. The mechanism also follows Markownikoff's rule.

Example

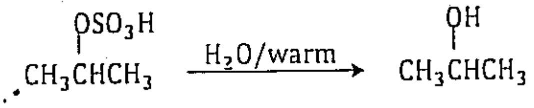


$$CH_3CH=CH_2 \xrightarrow[0-15^\circ C]{conc.\ H_2SO_4} CH_3\overset{OSO_3H}{\overset{|}{C}}HCH_3$$

Mechanism

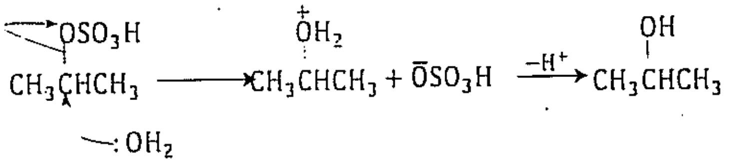


When the mixture above is diluted and warmed, an alcohol is formed.

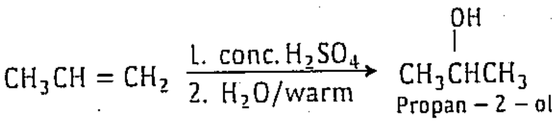


$$CH_3\overset{OSO_3H}{\overset{|}{C}}HCH_3 \xrightarrow{H_2O/warm} CH_3\overset{OH}{\overset{|}{C}}HCH_3$$

Mechanism



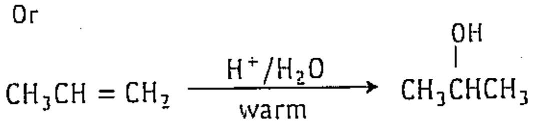
The two reactions can be summarised as the reaction of alkenes with acidified water to form alcohols as shown below:



$$CH_3CH=CH_2 \xrightarrow[2.\ H_2O/warm]{1.\ conc.\ H_2SO_4} CH_3\overset{OH}{\overset{|}{C}}HCH_3$$

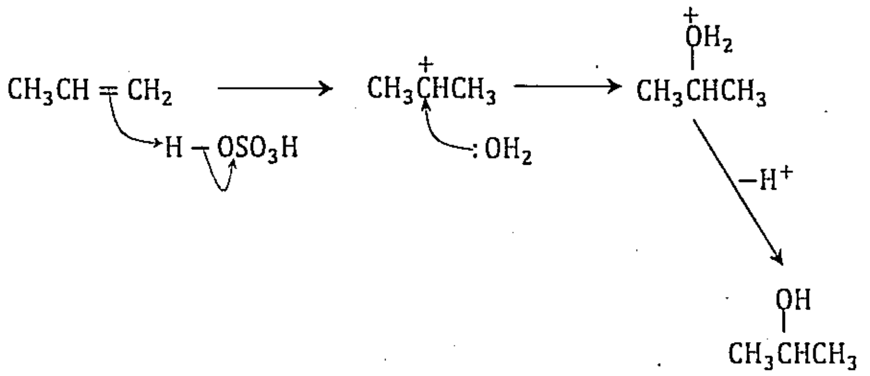
Propan – 2 – ol

Or

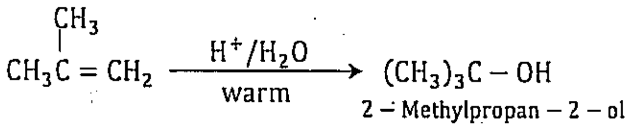


$$CH_3CH=CH_2 \xrightarrow[warm]{H^+/H_2O} CH_3\overset{OH}{\overset{|}{C}}HCH_3$$

Mechanism



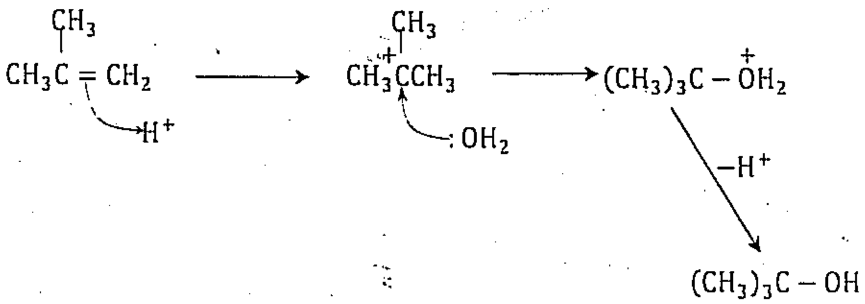
(ii)



$$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[\text{warm}]{H^+/H_2O} (CH_3)_3C-OH$$

2 – Methylpropan – 2 – ol

<u>Mechanism</u>



(v) **Reaction with alkaline potassium manganate(VII) solution**

Alkenes react with dilute alkaline potassium manganate(VII) solution to form diols.

The reaction does not require heating.

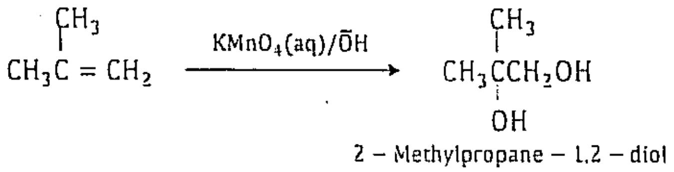
The purple solution turns colourless and a brown solid is deposited.

The brown solid is manganese(IV) oxide.

Examples

$$H_2C=CH_2 \xrightarrow{KMnO_4(aq)/\bar{O}H} HOCH_2CH_2OH$$

Ethane – 1,2 – diol



$$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{KMnO_4(aq)/\bar{O}H} CH_3\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2OH$$

2 – Methylpropane – 1,2 – diol

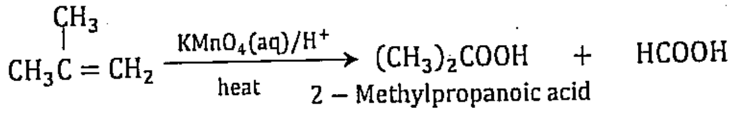
(vi) Reaction with acidified potassium manganate(VII) solution

If the alkene is reacted with potassium manganate(VII) solution that is acidified with sulphuric acid, a carboxylic acid or carboxylic acids are formed.

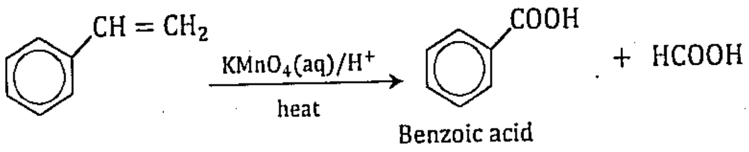
If more than one carboxylic acid is formed, the carboxylic acids may be similar or different.

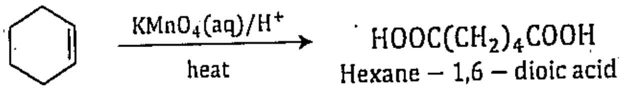
Examples

$$H_2C = CH_2 \xrightarrow[\text{heat}]{KMnO_4(aq)/H^+} \underset{\text{methanoic acid}}{2HCOOH}$$



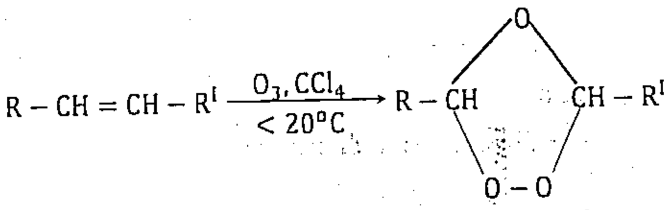
$$\overset{\displaystyle CH_3}{\overset{|}{CH_3C}} = CH_2 \xrightarrow[\text{heat}]{KMnO_4(aq)/H^+} \underset{\text{2 – Methylpropanoic acid}}{(CH_3)_2COOH} + HCOOH$$





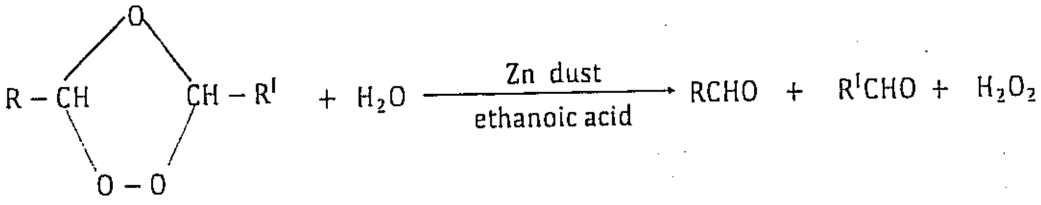
(vii) Ozonolysis

Ozone reacts with a solution of an alkene in tetrachloromethane at a temperature below **20°C** to form an ozonide.



An Ozonide

Subsequent hydrolysis of the ozonide using zinc and ethanoic acid forms one carbonyl compound if R and R' are the same or two different carbonyl compounds if R and R' are different.
The carbonyl compound can be an aldehyde or a ketone or both at the same time depending on the nature of the alkene used.



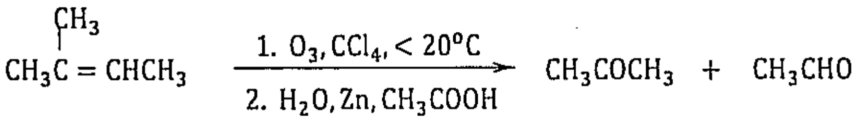
Analysis of the products after hydrolysis of the ozonide can aid in prediction of the structure of the alkene, by determining the position of the double bond.
The two reactions can be summarised as shown below:

$$R - CH = CH - R^I \xrightarrow[2.\ H_2O,\, Zn,\, CH_3COOH]{1.\ O_3,\, CCl_4,\, < 20^\circ C} RCHO + R^ICHO$$

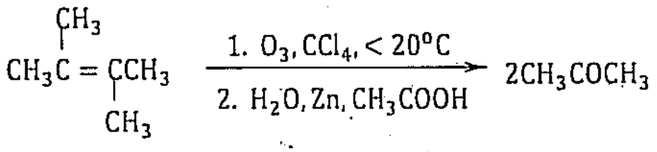
Examples

$$CH_3CH = CH_2 \xrightarrow[2.\ H_2O,\ Zn,\ CH_3COOH]{1.\ O_3,\ CCl_4,\ < 20°C} CH_3CHO + HCHO$$

$$CH_3CH = CHCH_3 \xrightarrow[2.\ H_2O,\ Zn,\ CH_3COOH]{1.\ O_3,\ CCl_4,\ < 20°C} 2CH_3CHO$$



$$CH_3\overset{CH_3}{\overset{|}{C}} = CHCH_3 \xrightarrow[2.\ H_2O,\ Zn,\ CH_3COOH]{1.\ O_3,\ CCl_4,\ < 20°C} CH_3COCH_3 + CH_3CHO$$



$$CH_3\overset{CH_3}{\overset{|}{C}} = \underset{CH_3}{\underset{|}{C}}CH_3 \xrightarrow[2.\ H_2O,\ Zn,\ CH_3COOH]{1.\ O_3,\ CCl_4,\ < 20°C} 2CH_3COCH_3$$

This reaction is not recommendable for organic synthesis since a mixture of products is formed. It should only be used to synthesise carbonyl compounds formed from symmetrical alkenes.

(viii) Hydrogenation

Alkenes react with hydrogen in presence of nickel catalyst at 150°C to form alkanes.

The reaction can also be done using finely divided platinum or palladium catalyst and when any of these is used, the reaction occurs at room temperature.

$$RCH = CHR^I \xrightarrow[or\ H_2/Pt\ or\ Pd]{H_2/Ni,\ 150°C} RCH_2 - CH_2R^I$$

Examples

$$CH_3CH = CH_2 \xrightarrow[150°C]{H_2/Ni} CH_3CH_2CH_3$$

$$H_2C = C(CH_3)_2 \xrightarrow[\text{Room temperature}]{H_2/Pd} CH_3CH(CH_3)_2$$

(ix) Combustion

Alkenes undergo complete combustion in oxygen to form carbon dioxide and water with evolution of heat.

$$C_nH_{2n}(g/l/s) + \frac{3n}{2}O_2(g) \longrightarrow nCO_2(g) + nH_2O(l)$$

Example

$$CH_3CH = CH_2(g) + \frac{9}{2}O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l)$$

They also undergo incomplete combustion in limited oxygen to form carbon monoxide and water.

$$C_nH_{2n}(g/l/s) + nO_2(g) \longrightarrow nCO(g) + nH_2O(l)$$

Example

$$CH_3CH = CH_2(g) + 3O_2(g) \longrightarrow 3CO(g) + 3H_2O(l)$$

(x) Polymerisation

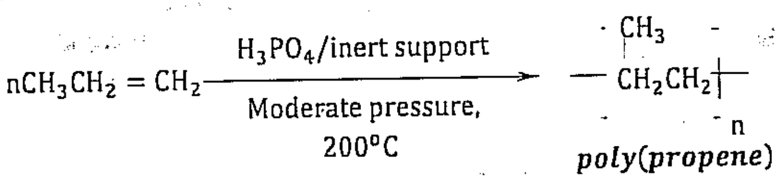
Simple alkenes polymerise to form addition polymers.

Ethene forms polyethene.

$$nCH_2 = CH_2 \xrightarrow[1500\text{atm}, 200^\circ C]{O_2 \text{ initiator}} \left[CH_2 - CH_2 \right]_n$$

poly(ethene)

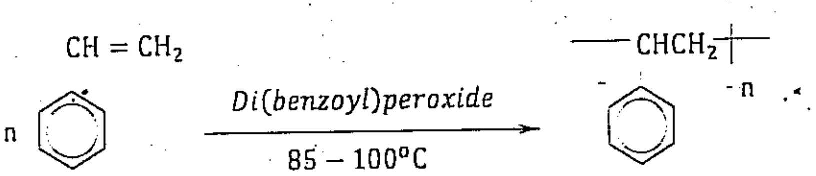
Propene forms poly(propene)



$$nCH_3CH_2 = CH_2 \xrightarrow[\text{Moderate pressure, } 200^\circ C]{H_3PO_4/\text{inert support}} \left[\overset{CH_3}{CH_2CH_2} \right]_n$$

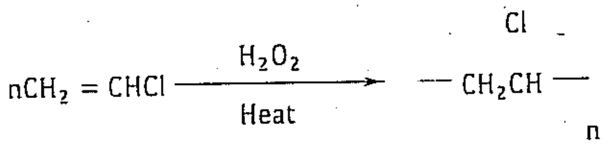
poly(propene)

Phenylethene forms poly(phenylethene)(IUPAC); also known as *polystyrene.*



poly(phenylethene)

Chloroethene forms poly(chloroethene)(IUPAC); also known as *polyvinylchloride*(PVC). The chloroethene is suspended under water and heated with hydrogen peroxide.



$$nCH_2 = CHCl \xrightarrow[\text{Heat}]{H_2O_2} \left[CH_2\overset{Cl}{CH} \right]_n$$

poly(chloroethene)

Tetrafluoroethene forms poly(tetrafluoroethene); also known as PTFE or Teflon or Fluon.

$$nF_2C = CF_2 \xrightarrow[50\text{atm, heat}]{(NH_4)_2S_2O_8} \left[CF_2 - CF_2 \right]_n$$

poly(tetrafluoroethene)

More about polymers will be covered in applied organic chemistry (Chapter 11, section 11.3).

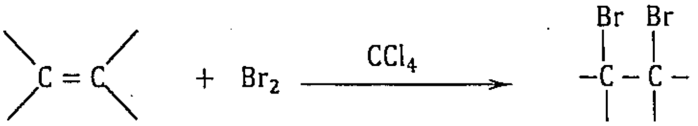
Practical Identification of the Functional Group

The functional group in alkenes is the carbon-carbon double bond. It is identified by bubbling a gaseous alkene or adding the liquid/ solid alkene into any of the following reagents:

Reagent: **Bromine in tetrachloromethane solution**

Observation: **Reddish-brown solution turns colourless**

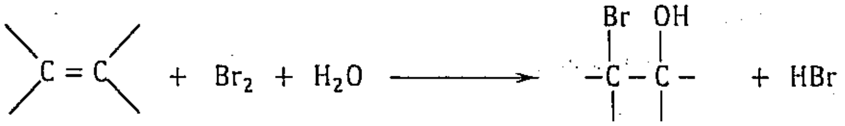
Equation



Reagent: **Bromine water**

Observation: **Reddish- brown solution turns colourless**

Equation



USES OF ALKENES

- Ethene is used in making plastics like poly(ethene) and poly(chloroethene)
- Ethene can also be used to make ethanol
- Propene is also used as a raw material in making plastics, like poly(propene) and poly(propenenitrile), Perspex and gyptal resins.
- Propene is also used to manufacture propanone, propan-2-ol and phenol

3.2.8 Some Synthetic Problems

1. Show how each of the following conversions can be effected

(a) Ethanol to ethane-1,2-diol

(b) $(CH_3)_2CHC \equiv CH$ to $(CH_3)_2CHCH_2CH_2Br$

(c) 1-Chlorohexane from propene

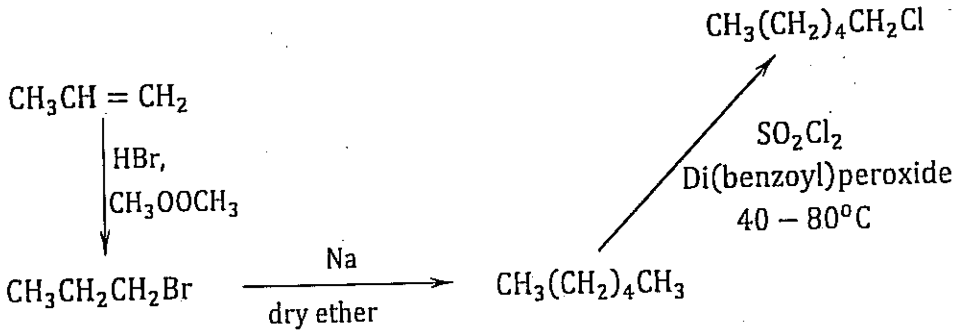
(a) Ethanol to ethane-1,2-diol

$$CH_3CH_2OH \xrightarrow[180^\circ C]{\text{cocnc. } H_2SO_4} H_2C = CH_2 \xrightarrow{MnO_4^-(aq)/\bar{O}H} HOCH_2CH_2OH$$

(b) $(CH_3)_2CHC \equiv CH$ to $(CH_3)_2CHCH_2CH_2Br$

$$\begin{tikzcd}(CH_3)_2CHC \equiv CH \arrow[r, "H_2", "\text{Lindlar catalyst}"'] & (CH_3)_2CHCH = CH_2 \arrow[d, "HBr, CH_3OOCH_3"] \\ & (CH_3)_2CHCH_2CH_2Br\end{tikzcd}$$

(c) **1-Chlorohexane from propene**



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2. *Describe how the following conversions can be effected. No equations required.*
   (a) *Butan-1-ol to ethanol*
   (b) *Chlorocyclohexanol from cyclohexanol*

(a) **Butan-1-ol to ethanol**

Butan-1-ol is heated with concentrated sulphuric acid at 180°C to form but-2-ene.

But-2-ene is then bubbled through tetrachloromethane and ozone bubbled through the mixture at a temperature below 20°C to form an ozonide.

The ozonide is hydrolysed using zinc and ethanoic acid to form ethanol.

(b) **Chlorocyclohexanol from cyclohexanol**

Cyclohexanol is heated with concentrated sulphuric acid at 180°C to form cyclohexene.

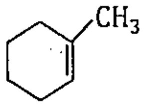
Cyclohexene is then reacted with chlorine water to form chlorocyclohexanol.

3.2.9 End of subtopic assessment exercise

1. Complete the following equations and give the IUPAC name of the major product formed in each case.

(a) $CH_3CH = CH_2 + HI \longrightarrow$

(b)



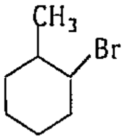
$+ \ HBr \longrightarrow$

(c) $CH_3CH = CHCH_3 \xrightarrow{KMnO_4(aq)/\bar{O}H}$

(d) $(CH_3)_2C = CH_2 + HCl \xrightarrow{\text{peroxide initiator}}$

(e) $CH_3CH = CH_2 \xrightarrow{\text{conc. } H_2SO_4}$

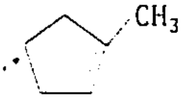
(f)



$\xrightarrow[\text{heat}]{CH_3CH_2\bar{O}K^+/CH_3CH_2OH}$

(g) $(CH_3)_2CBrCH_3 \xrightarrow[\text{heat}]{CH_3CH_2\bar{O}K^+/CH_3CH_2OH}$

(h)



$\xrightarrow[\text{heat}]{\text{conc. } H_2SO_4/H_2O}$

(i) $(CH_3)_2C = CH_2 \xrightarrow[\text{Organic peroxide}]{HBr}$

(j)

$\xrightarrow[\text{dry}]{HBr(g)}$

(k) $CH_3C \equiv CH \xrightarrow[\text{Lindlar catalyst}]{H_2}$

(l) $CH_3CH = CH_2 \xrightarrow{MnO_4^-/\bar{O}H}$

(m) $CH_3CH = CH_2 \xrightarrow{MnO_4^-/\bar{O}H}$

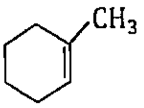
(n) $CH_3CH = CH_2 \xrightarrow{Br_2/H_2O}$

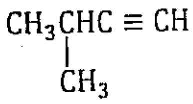
(o) $CH_3CH_2CH_2Cl \xrightarrow[\text{heat}]{NaOH/CH_3CH_2OH}$

(p) $(CH_3)_3CI \xrightarrow[\text{heat}]{CH_3\bar{O}Na^+/CH_3OH}$

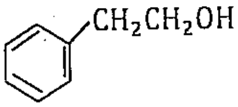
(q) $nCH_3CH = CH_2 \xrightarrow{\text{Catalyst}}$

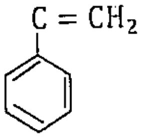
(q) $CH_3CH = C(CH_3)_2 \xrightarrow[\text{heat}]{H^+/H_2O}$

(r)  $\xrightarrow{MnO_4^-/\bar{O}H(aq)}$

(s) 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HC \equiv CH \xrightarrow[\text{Lindlar catalyst}]{H_2}$

(t) $CH_3CH = CH_2 \xrightarrow[CH_3OOCH_3]{HBr}$

(u)  $\xrightarrow[180°C]{\text{conc. } H_2SO_4}$

(v) n  $\xrightarrow[\text{heat}]{\text{Catalyst}}$

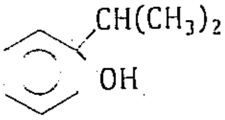
(w) $CH_3CH = CH_2 \xrightarrow{Br_2(aq)}$

2. Complete the following equations and write the mechanisms for the reactions leading to formation of the major organic products.

(a) $(CH_3)_3CCl \xrightarrow[\text{Heat}]{NaOH/CH_3CH_2OH}$

(b) $H_3CH = C(CH_3)_2 \xrightarrow{Br_2/NaCl(aq)}$

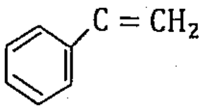
(c) $(CH_3)_2C = CHCH_3 \xrightarrow{HBr}$

(d)  $\xrightarrow[360°C]{\text{Conc. } H_3PO_4}$

(e) $CH_3CH = CH_2 \xrightarrow[CCl_4]{Br_2}$

(f) $(CH_3)_2C = CHCH_3 \xrightarrow{Cl_2/H_2O}$

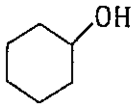
(g)  $\xrightarrow{Br_2/H_2O}$

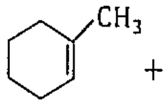
(h)  $+ Br_2 \xrightarrow{CCl_4}$

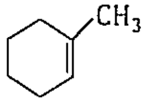
(i) $CH_3CH_2CH_2OH \xrightarrow[\text{Heat}]{\text{Conc. } H_3PO_4}$

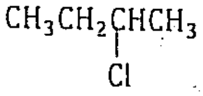
(j) $CH_3CH = CH_2 + \text{Conc. } H_2SO_4 \xrightarrow[\text{Heat}]{H_2O}$

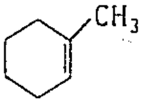
(k) $CH_3CH = CHCH_3 \xrightarrow[\text{Warm}]{H^+/H_2O}$

(l)  $\xrightarrow[350°C]{\text{Conc. } H_3PO_4}$

(m)  $+ HI \longrightarrow$

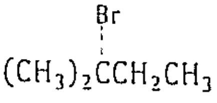
(n)  $\xrightarrow[\text{warm}]{\text{Conc. } H_3PO_4/NaBr}$

(o)  $CH_3CH_2CH(Cl)CH_3 \xrightarrow[CH_3CH_2OH,\ \text{heat}]{CH_3CH_2\bar{O}Na^+}$

(p)  $\xrightarrow[\text{heat}]{H^+/\ H_2O}$

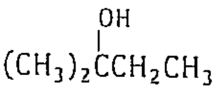
(q)  $\xrightarrow{HBr}$

3. Write a **mechanism** to show how the following conversions can be effected.

(a)  $(CH_3)_2C(Br)CH_2CH_3 \longrightarrow (CH_3)_2C = CHCH_3$

(b) 2 – Iodobutane to but – 2 – ene.

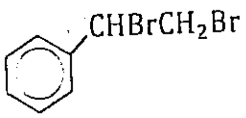
(c) Ethene to ethanol.

(d) $(CH_3)_2C = CHCH_3$ to  $(CH_3)_2C(OH)CH_2CH_3$

(e) $CH_3CH_2CH_2CH_2OH$ to $CH_3CH = CHCH_3$

4. State would be observed and write equation for the reaction that would take place when each of the following compounds are mixed.
   (a) Bromine water and but-1-ene
   (b) Propene and alkaline potassium permanganate solution
   (c) But-1-ene and acidified potassium manganate(VII) solution
   (d) Cyclohexene and alkaline potassium permanganate solution
   (e) Phenylethene is added to a solution of bromine in tetrachloromethane
   (f) Ethene is bubbled through bromine water.

5. Write equations to show how the following synthesises can be carried out. In each case, indicate the necessary reagents and conditions.
   (a) Ethanol to 1,2-dibromoethane
   (b) Propan-2-ol from propan-1-ol
   (c) Cyclohexanol to Bromocyclohexanol
   (d) Butan-1-ol to butan-2-ol
   (e)



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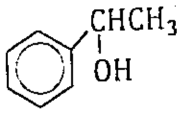
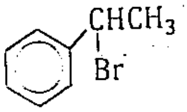


   (f)



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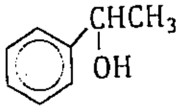
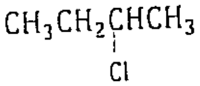


   (g) Cyclohexanol to cyclohexane-1,2-diol.
   (h) Butane from ethene
   (i) Propyne to 1-Bromopropane
   (j) $CH_3C \equiv CH$ to $CH_3CH_2OHCH_3$
   (k) $CH_3CH_2C \equiv CH$ to

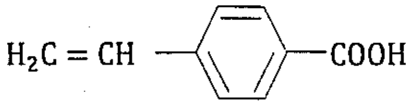


$$CH_3CH_2\underset{\mathrm{Cl}}{\underset{|}{C}}HCH_3$$

6. Desribe how the following conversions can be effected. (No equations are required)
   (a) Propan-2-ol to $CH_3CH_2CH_2Br$
   (b) Ethyne to ethanol
   (c) Calcium carbide to ethane-1,2-diol
   (d) Propan-1-ol to propane

7. Name the reagent that can be used to distinguish between the following pairs of compounds. In each case, state what would be observed if each member is separately treated with the reagent and write equation for the reaction.
   (a) Methane and ethene.
   (b) Benzene and ethene
   (c) Propanoic acid to chloropropane
   (d) Ethanoic acid to Chloromethane.
   (e) $HOOCCH_2CH_2COOH$ and $HOOCCH = CHCOOH$

8. An organic compound *Y* has the structure:



(a) Name the functional groups present in the structure of *Y*

(b) State what is observed and write equation for the reaction in each case that takes place when *Y* is:

(i) treated with a cold aqueous alkaline solution of potassium permanganate.

(ii) heated strongly with sodalime.

9. 250 cm^3 of an alkene diffuse through a porous medium in 10 seconds and 716 cm^3 of oxygen diffuse through the same medium in 25 seconds under the same conditions. Calculate the molecular mass of the alkene and deduce its structural formula.

10. Oxygen diffused through a porous partition in 1.87 minutes. Under similar conditions, the same volume of an alkene, *T* diffused in 2.15 minutes.

(a) Determine the formula of *T*

(b) Write equation and outline mechanism for the reaction between *T* and benzene. Indicate the conditions for the reaction.

11. 100 cm^3 of a gaseous alkene weighed 0.250g at 0^{o}c and 1 atm. If 25.0cm^3 of the alkene reacted with 25.0cm^3 of hydrogen gas;

(i) Determine the molecular formula of the alkene.

(ii) Write the names and structural formulae of all possible isomers of the alkene.

12. 20.0 cm^3 of a gaseous hydrocarbon *G*, were exploded with 150 cm^3 of excess oxygen. After complete combustion, the residual gas was found to be 110 cm^3. When concentrated potassium hydroxide solution was added to residual gas, the volume reduced to 30 cm^3.

(a) Determine the molecular formula of *G*.

(b) Write the structural formulae and names of all possible isomers of *G*

(c) Ozonolysis of *G* yields only one product. Write the mechanism for the reaction between *G* and bromine water.

13. 20.0 cm^3 of a gaseous unsaturated hydrocarbon, *R*, were exploded with 200 cm^3 of oxygen and after cooling to room temperature, 140 cm^3 of gas remained. This volume reduced to 20.0 cm^3 on shaking the gas with potassium hydroxide solution.

(a) Deduce the molecular formula of *R*.

(b) Ozonolysis of *R* and subsequent hydrolysis yielded two different products, one of which was propanone and the other one was *T*. Identify *R* and *T*.

14. When an alkene , *Q* was ozonolysed and then hydrolysed, the products formed were propanone and 2-Methylpropanal. Write the structural formula the IUPAC name of *Q*.

15. The molecular formula of compound *W* is C_4H_8.

(i) Write the structural formula and name of all possible isomers of *W*.

(ii) *W* gives only one product on ozonolysis. Identify *W*.

16. (a) A hydrocarbon, *P* consists of 85.71% carbon. In an experiment, 32g of bromine required 11.2 g of *P* for complete decolourisation. Determine the:

(i) empirical formula of *P*.

(ii) molecular formula of *P*.

(Bromine reacts with P in a ratio of 1: 1)

(b) Write the structural formulae and IUPAC names of the isomers of *P*.

(c) Ozonolysis of *P* produced a single product. Identify *P*.

(i) Identify *P*.

(ii) Write equation for the ozonolysis of *P*. Include the conditions for the reactions.

(d) Outline a mechanism for the reaction between *P* and:

(i) bromine.

(ii) warm dilute sulphuric acid.

(e) Write equations to show how *P* can be obtained from an alkyl halide.

17. An organic compound, *P*, on complete combustion yielded 8.8g of carbon dioxide and 1.8g of water. 0.1g of *P* when vapourised at 273°C and 734 mmHg occupied a volume of $4.46 \times 10^{-2} dm^3$.

(a) Calculate:

(i) the empirical formula of *P*.

(ii) molecular formula of *P*.

(b) When *P* was ozonolysed followed by hydrolysis, compound *Q*, a ketone was formed. Write the structure and IUPAC name of *P*.

(c) Discuss the reactions of *P* with:

(i) sulphuric acid

(ii) bromine

18. Zinc and aluminium oxide are normally employed as reagents in organic reaction(s). For each reagent, write equation to show how it is used in organic reactions. Include reaction condition(s).

(a) Zinc

(b) Aluminium oxide.

19. Explain each of the following observations.

(a) When 2-methylbut-2-ene is reacted with hydrogen iodide, the major product is 2-Iodo-2-methybutane but not 2-Iodo-3-methylbutane.

(b) Propene is more useful as a starting compound for formation of propan-2-ol than propane.

(c) Propan-1-ol is a liquid at room temperature whereas propene is a gas at the same temperature.

3.3 Alkynes

3.3.1 Introduction

Alkynes form a homologous series of unsaturated hydrocarbons containing a carbon-carbon triple bond and corresponding to the general formula, C_nH_{2n-2}.

The unsaturated carbon atoms are sp hybridized and are attached to each other by a **sigma (σ)** bond and two **pi (π)** bonds. The **sigma (σ)** bond results from the overlapping of two hybrid orbitals, and the two **pi (π)** bonds are formed from separate overlapping of two p-orbitals from two adjacent carbon atoms. The other sp hybrid orbital of each unsaturated carbon atoms forms a sigma (σ) bond with another carbon or hydrogen atom. The simplest molecule is ethyne and is linear, allowing orbitals to be as far apart as possible. The availability of electrons in the multiple bonds makes them prone to addition reaction, which, like those of alkenes, characterize the reactions of alkynes.

3.3.2 Nomenclature of alkynes

The IUPAC SYSTEM is used when naming alkynes just as it used is for alkenes.

The unbranched alkynes are named by replacing the –ane of the name of the corresponding alkane with the ending –yne.

The chain must be numbered in such a way that the **carbon atoms of the triple bond have the lowest possible numbers.**

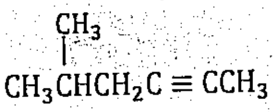
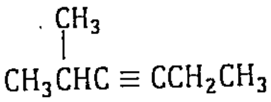
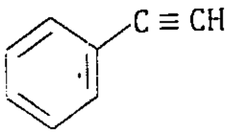
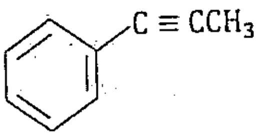
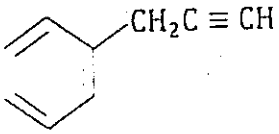
The lowest number of the two carbon atoms of the triple bond is used to designate the location of the triple bond.

Examples;

Structural formula	*IUPAC name*
$HC \equiv CH$	Ethyne
$CH_3C \equiv CH$	Propyne
$CH_3CH_2C \equiv CH$	But-1-yne
$CH_3C \equiv CCH_3$	But-2-yne
$CH_3CH_2CH_2C \equiv CH$	Pent-1-yne
$CH_3C \equiv CCH_2CH_3$	Pent-2-yne

- The locations of the substituent groups of branched alkynes and substituted alkynes are indicated with numbers.
- In case an – OH group is present, its given priority over the triple bond.

Examples;

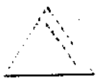
Structural formula	*IUPAC name*
$HC \equiv CCH_2Br$	3-Bromopropyne
$CH_3C \equiv CCH_2I$	1-Iodobut-2-yne
 $CH_3\overset{\overset{CH_3}{\vert}}{C}HCH_2C \equiv CCH_3$	5-Methylhex-2-yne
 $CH_3\overset{\overset{CH_3}{\vert}}{C}HC \equiv CCH_2CH_3$	2-Methylhex-3-yne
$HC \equiv CCH_2CH_2OH$	But-3-yn-1-ol
	Phenylethyne
	1-Phenylpropyne
	3-Phenylpropyne

3.3.3 Isomerism in alkynes

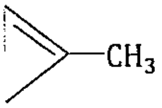
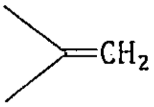
Ethyne has only one structure and therefore non-isomeric.

Propyne and higher homologues exhibit structural isomerism.

C_3H_4 has three structural isomers as shown below:

Structural Formula	*IUPAC name*
$CH_3C \equiv CH$	Propyne
$H_2C = C = CH_2$	Propadiene
	Cyclopropane

C_4H_6 has the following **isomers.**

Structural Formula	*IUPAC name*
$CH_3CH_2C \equiv CH$	But-1-yne
$CH_3C \equiv CCH_3$	But-2-yne
$H_2C = CHCH = CH_2$	Buta-1,3-diene
$CH_3CH = C = CH_2$	Buta-1,2-diene
	Cyclobutene
	1-Methylcyclopropene
	3-Methylcyclopropene
	Methylenecyclopropane

Therefore alkynes with 3 or more carbon atoms are isomeric with dienes and cycloalkenes.

Those with 5 or more carbon atoms show chain isomers in addition to positional isomers and functional group isomers.

3.3.4 Physical properties of alkynes

Alkynes have physical properties that are similar those of the corresponding alkanes.

(a) Physical state

Alkynes with **1-4 carbon atoms** are all **gases** at room temperature with the exception of but-2-yne. Most of those with **5-8 carbon atoms** are **liquids** at room temperature.

(b) Boiling points

The boiling points of alkynes **increase with increase in molecular mass** as explained for alkenes earlier.

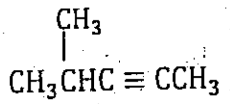
The boiling point rise is about 20-30°C for each added carbon atom, except for the very small homologues.

They are nearly the same as those for alkanes and alkenes with the same number of carbon atoms.

As for alkanes, **chain branching lowers the boiling point.**

Symmetrical alkynes have higher boiling points than non-symmetrical alkynes due to increased stability.

Some alkynes and corresponding boiling points are shown in the table below.

Name	*Structural formula*	*Boiling point(°C)*
Ethyne	$HC \equiv CH$	−75
Propyne	$CH_3C \equiv CH$	−23
But-1-yne	$CH_3CH_2C \equiv CH$	9
But-2-yne	$CH_3C \equiv CCH_3$	27
Pent-1-yne	$CH_3CH_2CH_2C \equiv CH$	40
Pent-2-yne	$CH_3CH_2C \equiv CCH_3$	55
4-methylpent-2-yne	 $CH_3\underset{}{\overset{CH_3}{\overset{\vert}{C}}}HC \equiv CCH_3$	29

(c) Density

Alkynes are less dense than water.

(d) Solubility

Alkynes are virtually insoluble in water but soluble in non-polar organic solvents or solvents of low polarity such as ether, benzene, etc.

3.3.5 Laboratory preparation of alkynes.

A carbon-carbon triple bond is formed by elimination of one atom or groups from two adjacent carbon atoms in the same way as the carbon-carbon double bond in alkenes is formed.

(a) From vicinal dihalides.

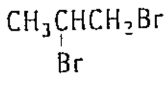
A vicinal dihalide(vic-dihalide) is a compound in which the halogen atoms are on adjacent carbon atoms.

They are also called 1,2-dihalides and are formed by halogenation of alkenes.

The vicinal dihalide is reacted with excess alcoholic potassium hydroxide solution to form an alkyne on heating.

Examples

(i) $$CH_2BrCH_2Br \xrightarrow[\text{heat}]{\text{excess KOH/}CH_3CH_2OH} HC \equiv CH + KBr + H_2O$$

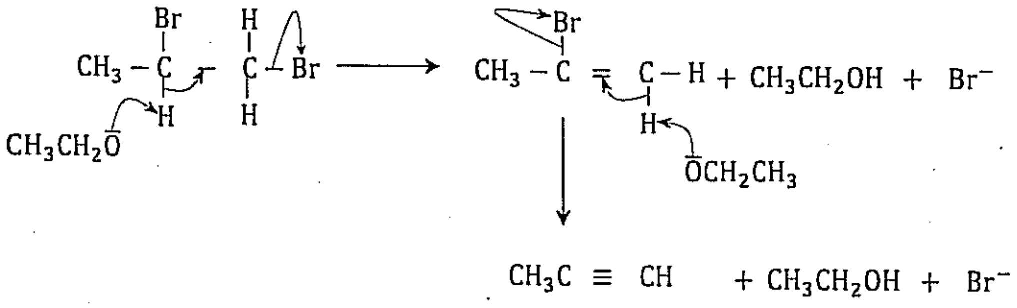
(ii) 

$$CH_3\underset{\underset{Br}{\vert}}{C}HCH_2Br \xrightarrow[\text{heat}]{\text{excess KOH/}CH_3CH_2OH} CH_3C \equiv CH + KBr + H_2O$$

Mechanism

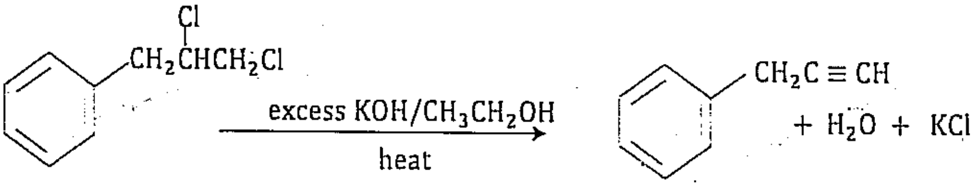
$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$$

$$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$



$K^+ + Br^- \longrightarrow KBr$

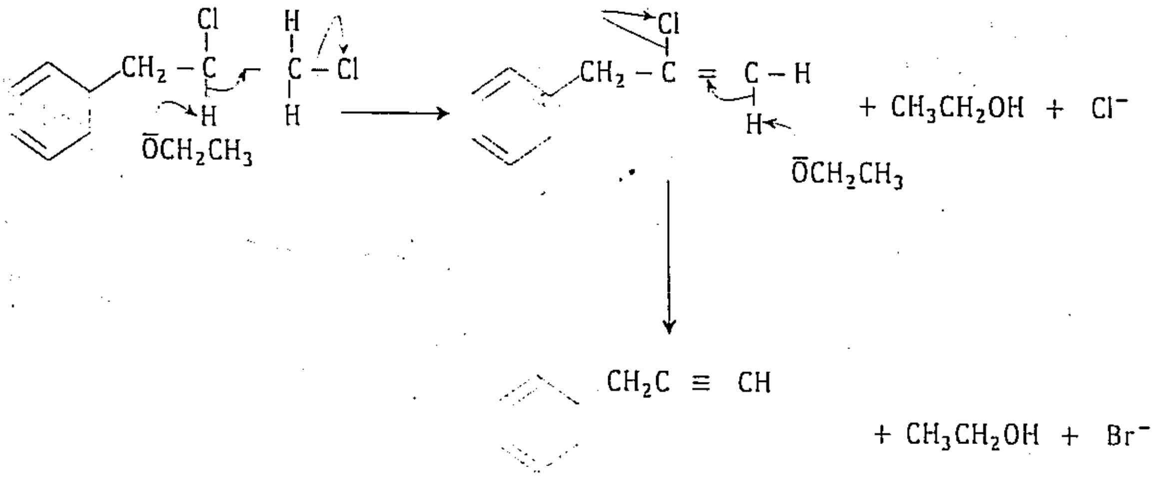
(iii)



Mechanism

$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$

$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$



$K^+ + Cl^- \longrightarrow KCl$

The above reactions are called **dehydrohalogenation** of vicinal dihalides and as shown, occur in two steps; first yielding a **haloalkene** and then an **alkyne**.

Similary, sodium amide, a very strong base can be used. For example;

$$CH_2BrCH_2Br \xrightarrow{NaNH_2/liq.\,NH_3} HC \equiv CH \quad + KCl$$

Mechanism

$$NaNH_2 \longrightarrow Na^+ + \bar{N}H_2$$

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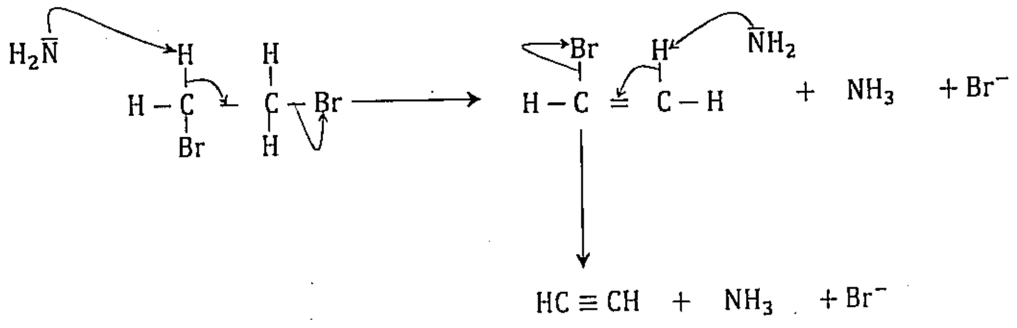


$$Na^+ + Br^- \longrightarrow NaBr$$

Note

Germinal dihalides (which have two halogen atoms on the same carbon atom) can also be converted to alkynes by dehydrohalogenation.

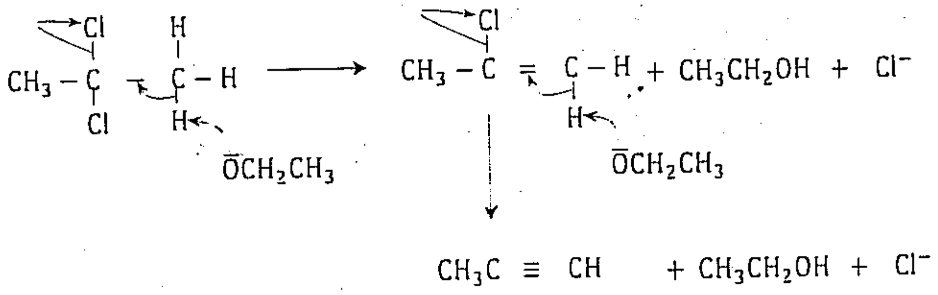
Examples

$$CH_3CCl_2CH_3 \xrightarrow[\text{heat}]{\text{excess } KOH/CH_3CH_2OH} CH_3C\equiv CH$$

Mechanism

$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$$

$$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$



$$K^+ + Cl^- \longrightarrow KCl$$

The germinal dihalides are often got by the reaction of ketones or aldehydes with phosphorus(V) chloride. The exact one above can for example be got by the reaction;

$$CH_3COCH_3 \xrightarrow{PCl_5} CH_3CCl_2CH_3$$

(b) From the reaction of sodium acetylides with primary alkylhalides.

Smaller terminal alkynes are converted to larger alkynes by reacting them first with sodium in liquid ammonia and then with primary alkylhalides.

$$RC\equiv CH \xrightarrow{Na/liq.\,NH_3} RC\equiv \bar{C}Na^+ \xrightarrow{R^IX} RC\equiv CR^I$$

In summary,

$$RC\equiv CH \xrightarrow[2.\ R^IX]{1.\ Na/liq.\,NH_3} RC\equiv CR^I$$

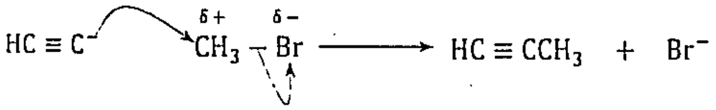
Examples

(i) $$HC \equiv CH \xrightarrow[2.\ CH_3Br]{1.\ Na/liq.NH_3} CH_3C \equiv CH + NaBr$$

Mechanism

$$HC \equiv CH + Na \longrightarrow HC \equiv \bar{C}Na^+ + \tfrac{1}{2}H_2$$

$$HC \equiv C^-Na^+ \longrightarrow HC \equiv C^- + Na^+$$



$$HC \equiv C^- \quad \overset{\delta+}{CH_3} - \overset{\delta-}{Br} \longrightarrow HC \equiv CCH_3 + Br^-$$

$$Na^+ + Br^- \longrightarrow NaBr$$

(ii)
$$\begin{tikzcd}
HC \equiv CH \arrow[r, "1.\ Na/liq.NH_3", "2.\ CH_3CH_2Br\ \ A"'] & CH_3CH_2C \equiv CH \arrow[d, "B", "1.\ Na/liq.NH_3\ \ 2.\ CH_3CH_2Br"'] \\
& CH_3CH_2C \equiv CCH_2CH_3
\end{tikzcd}$$

Mechanism for step B

$$CH_3CH_2C \equiv CH + Na \longrightarrow CH_3CH_2C \equiv \bar{C}Na^+ + \tfrac{1}{2}H_2$$

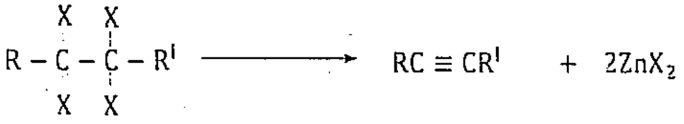
$$CH_3CH_2C \equiv C^-Na^+ \longrightarrow CH_3CH_2C \equiv C^- + Na^+$$

$$CH_3CH_2C \equiv C^- \quad \overset{\delta+}{CH_3CH_2} - \overset{\delta-}{Br} \longrightarrow CH_3CH_2C \equiv CCH_2CH_3 + Br^-$$

$$Na^+ + Br^- \longrightarrow NaBr$$

(c) **From dehalogenation of tetrahalides.**

Tetrahalides can be converted to alkynes by treatment with zinc.



$$R - \underset{X}{\overset{X}{C}} - \underset{X}{\overset{X}{C}} - R^I \longrightarrow RC \equiv CR^I + 2ZnX_2$$

Example

$$CH_3 - \underset{Br}{\overset{Br}{C}} - \underset{Br}{\overset{Br}{C}} - H \longrightarrow CH_3C \equiv CH$$

However, this method is limited for use because the tetrahalides themselves are prepared from alkynes.

Note

Industrially, ethyne can be prepared by the action of water on calcium carbide. The calcium carbide is itself being formed by the reaction of calcium oxide and coke in an electric furnace at 2000-3000°C.

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

$$CaO(s) + 3C(s) \xrightarrow{2000-3000^\circ C} CaC_2(s) + CO(g)$$

$$CaC_2(s) + H_2O(l) \longrightarrow HC\equiv CH + Ca(OH)_2$$

It can also be formed industrially by controlled high-temperature partial oxidation of methane.

$$2CH_4 \xrightarrow{1500^\circ C} HC\equiv CH + 3H_2$$

3.3.6 Chemical properties of alkynes.

Like alkenes, alkynes also undergo electrophilic addition reactions due to loosely held π –electrons. They are however less reactive than alkenes towards electrophilic reagents.

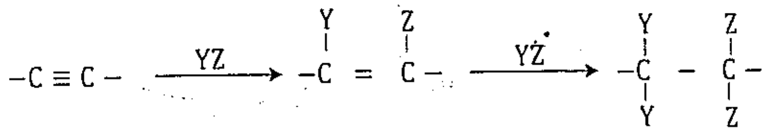
The addition of unsymmetrical reagents across unsymmetrical alkynes also follows Markovnikoff's rule just as for alkenes.

Alkynes also tend to undergo nucleophilic addition reactions.

(a) Electrophilic addition reactions of alkynes.

Alkynes undergo electrophilic addition reactions with hydrogen, halogens and hydrogen halides in a similar way like alkenes.

The only difference with alkynes is that, two molecules of the electrophilic reagent are consumed for each triple bond.



$$-C\equiv C- \xrightarrow{YZ} -\overset{Y}{\overset{|}{C}} = \overset{Z}{\overset{|}{C}}- \xrightarrow{YZ} -\underset{Y}{\underset{|}{\overset{Y}{\overset{|}{C}}}} - \underset{Z}{\underset{|}{\overset{Z}{\overset{|}{C}}}}-$$

(i) Hydrogenation of alkynes

Alkynes form alkanes when heated with hydrogen in presence of nickel catalyst. For example;

$$CH_3C\equiv CH \xrightarrow[150^\circ C]{H_2/Ni} CH_3CH_2CH_3$$

Instead of nickel, finely divided platinum or palladium catalyst can be used but the reaction occurs at ordinary temperatures.

$$CH_3C\equiv CHCH_3 \xrightarrow{H_2/Pd} CH_3CH_2CH_2CH_3$$

$$HC\equiv CH \xrightarrow{H_2/Pd} CH_3CH_3$$

Note

For every one mole of the alkyne, 2 moles of hydrogen gas are used for hydrogenation to form the alkane.

Reduction of certain higher alkynes can occur yielding alkenes only if a special catalyst made of metallic palladium deposited on calcium carbonate and poisoned with quinoline is used. This special catalyst is called Lindlar's catalyst. For example;

Either

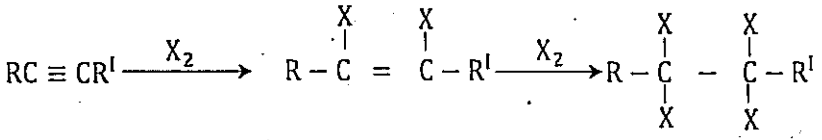
$$CH_3CH_2C \equiv CH \xrightarrow[quinoline]{H_2/Pd/CaCO_3} CH_3CH_2CH = CH_2$$

Or

$$CH_3CH_2C \equiv CH \xrightarrow[Lindlar's\ catalyst]{H_2} CH_3CH_2CH = CH_2$$

(ii) Halogenation

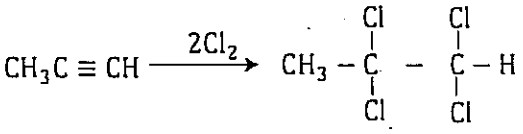
Alkynes react with chlorine and bromine in the same way alkenes do. Dihaloalkanes are formed first and then tetrahaloalkanes. The intermediate dihaloalkene can be isolated under controlled conditions.



$$RC \equiv CR^I \xrightarrow{X_2} R-\overset{X}{C} = \overset{X}{C}-R^I \xrightarrow{X_2} R-\underset{X}{\overset{X}{C}} - \underset{X}{\overset{X}{C}}-R^I$$

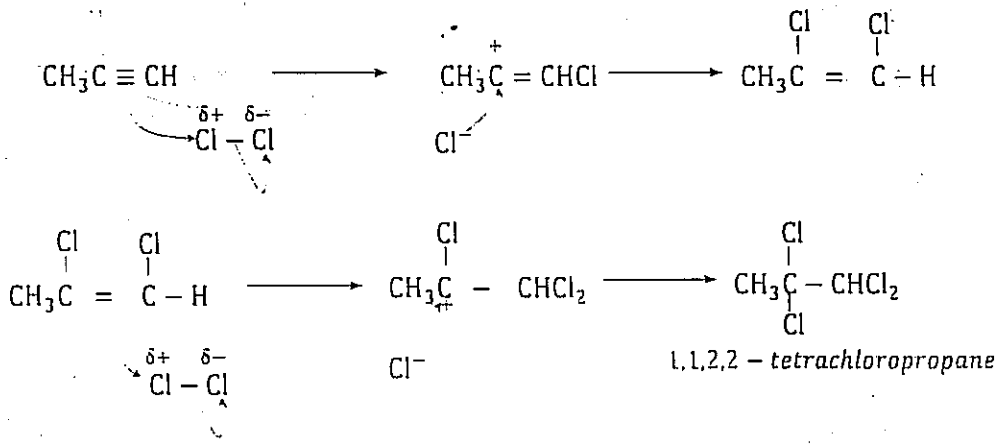
$X = Cl$ or Br

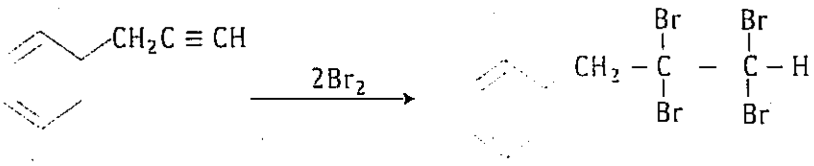
Examples

(i) 

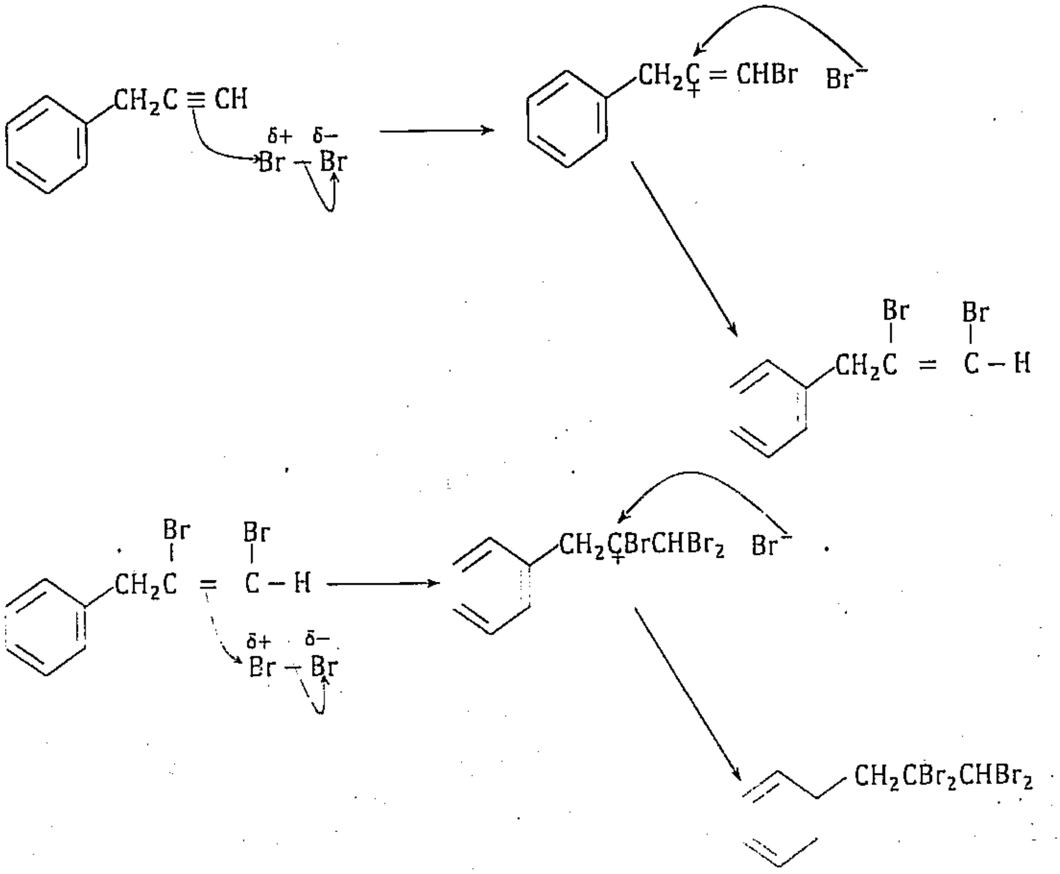
$$CH_3C \equiv CH \xrightarrow{2Cl_2} CH_3-\underset{Cl}{\overset{Cl}{C}} - \underset{Cl}{\overset{Cl}{C}}-H$$

<u>Mechanism</u>



(ii) 

Mechanism



1,1,2,2 – Tetrabromophenylpropane

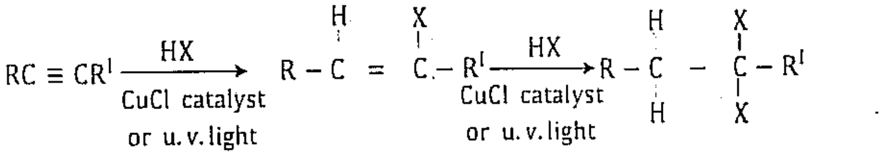
For ethyne to undergo similar reactions, a **metal halide catalyst** is used or **Kieselguhr** (**silicon(IV) oxide**) **catalyst** and **iron fillings** to absorb heat of the reaction. This prevents explosions especially with chlorine. Bromine reacts less violently with ethyne.

$$HC \equiv CH \xrightarrow[\textit{Kieselguhr catalyst}]{Cl_2} CHCl_2CHCl_2$$

1,1,2,2 – Tetrachloroethane

(iii) Reaction with hydrogen halides

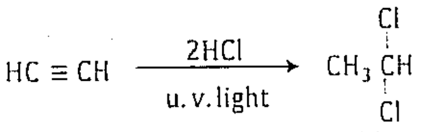
Alkynes react with hydrogen halides in presence of **u.v light** or a **copper(I) chloride catalyst** to form haloalkenes first and then germinal dihalides.



$$RC \equiv CR^{I} \xrightarrow[\text{CuCl catalyst or u.v. light}]{HX} R-\overset{H}{C}=\overset{X}{C}-R^{I} \xrightarrow[\text{CuCl catalyst or u.v. light}]{HX} R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-R^{I}$$

HX = HCl, HBr or HI

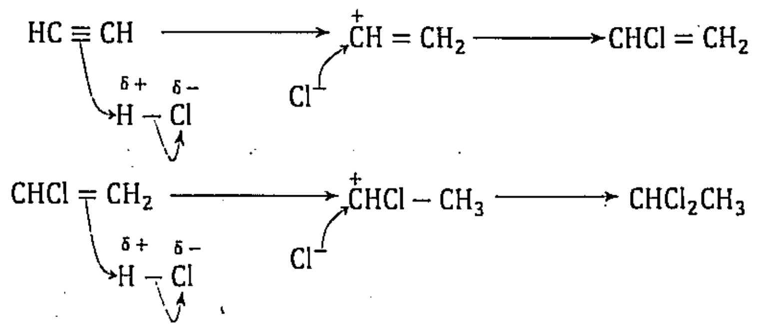
Examples

(i) 

$$HC \equiv CH \xrightarrow[\text{u.v. light}]{2HCl} CH_3\underset{Cl}{\overset{Cl}{C}H}$$

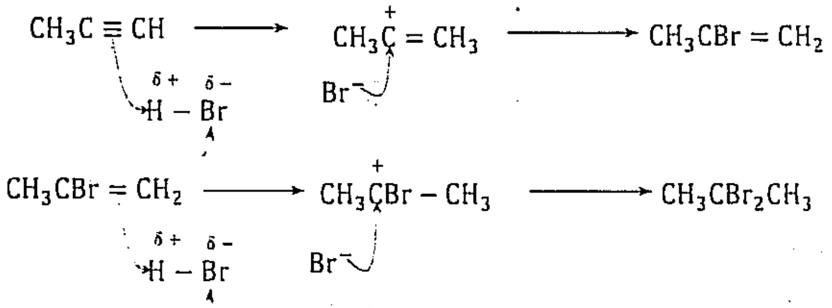
1,1 – Dichloroethane

Mechanism



(ii) $CH_3C \equiv CH \xrightarrow[\text{CuCl Cat.}]{\text{excess HBr}} CH_3CBr_2CH_3$ *2,2 – Dibromopropane*

Mechanism



The two reactions above proceed via Markownikoff's addition. However, addition of hydrogen bromide in presence of an organic peroxide forms an anti-Markownikoff product.

$$CH_3C \equiv CH \xrightarrow[\text{ROOR}]{\text{excess HBr}} CH_3CH_2CHBr_2$$

1,1 – Dibromopropane

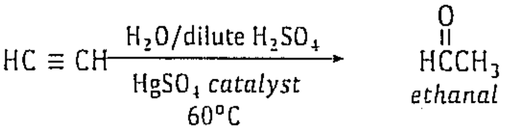
(b) **Nucleophilic addition reactions of alkynes**

One reaction shall be considered here.

Hydration of alkynes (reaction with water)

Ethyne reacts with water in presence of dilute sulphuric acid and mercury(II) sulphate catalyst at 60°C to form ethanal.

The reaction is initiated by nucleophilic attack.

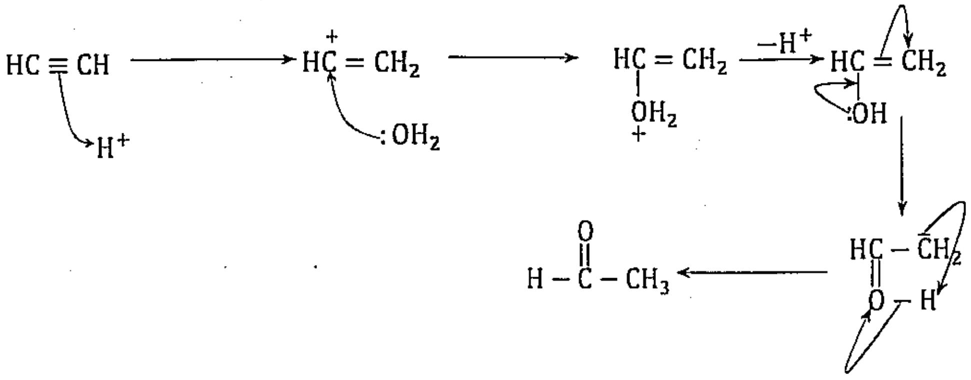


$$HC \equiv CH \xrightarrow[\text{HgSO}_4\text{ catalyst, }60^\circ C]{H_2O/\text{dilute }H_2SO_4} H\overset{O}{\overset{\|}{C}}CH_3$$

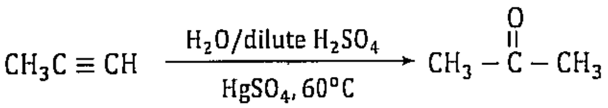
ethanal

Mechanism

$$H_2SO_4(aq) \longrightarrow H^+(aq) + \bar{O}SO_3H(aq)$$



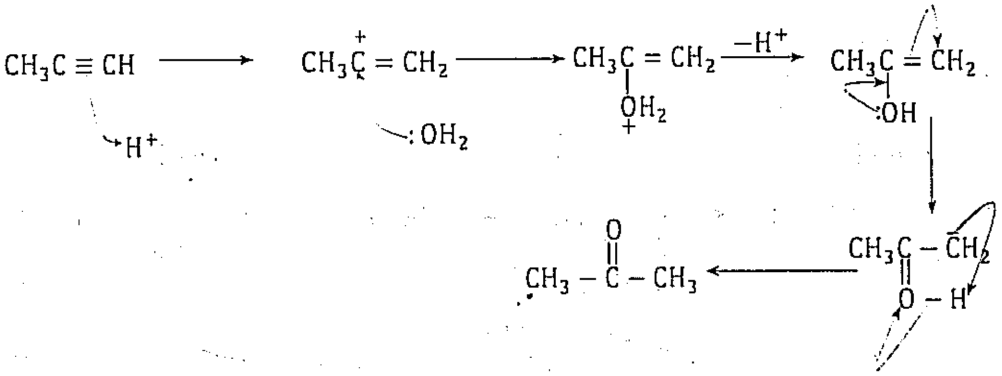
Propyne forms propanone under similar conditions.



$$CH_3C \equiv CH \xrightarrow[HgSO_4,\ 60^\circ C]{H_2O/\text{dilute } H_2SO_4} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Mechanism

$$H_2SO_4(aq) \longrightarrow H^+(aq) + \bar{O}SO_3H(aq)$$



(c) Substitution reactions

(i) Formation of heavy metal dicarbides

Alkynes which have a triple bond at the end of the carbon chain (terminal alkynes) react with;

1. Ammoniacal copper(I) chloride solution to form insoluble copper carbides (acetylides).

Observation; A red precipitate is formed

Examples

$$HC \equiv CH(g) + Cu_2Cl_2(aq) + 2NH_3(aq) \longrightarrow \underset{Copper(I)dicarbide}{CuC \equiv CCu(s)} + 2NH_4Cl$$

$$CH_3CH_2C \equiv CH(g) + Cu_2Cl_2(aq) + 2NH_3(aq) \longrightarrow \underset{red\ precipitate}{2CH_3CH_2C \equiv CCu(s)} + 2NH_4Cl$$

2. Ammoniacal silver nitrate solution.

Terminal alkynes also react with ammoniacal silver nitrate solution to form insoluble silver acetylides.

Observation; A white precipitate is formed.

Examples

$$HC \equiv CH(g) + 2AgNO_3(aq) + 2NH_3(aq) \longrightarrow \underset{Silver(I)dicarbide}{AgC \equiv CAg(s)} + 2NH_4NO_3$$

$$CH_3C \equiv CH(g) + AgNO_3(aq) + NH_3(aq) \longrightarrow \underset{white\ precipitate}{2CH_3C \equiv CAg(s)} + NH_4NO_3$$

Note

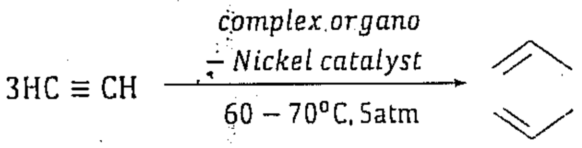
The two reagents above distinguish terminal alkynes from non-terminal alkynes and also terminal alkynes from alkenes.

(ii) Formation of sodium acetylides

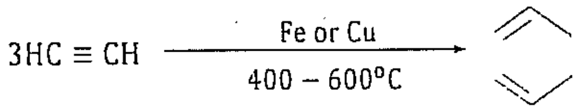
Already discussed under laboratory preparation of alkynes.

(d) Polymerisation of ethyne

Ethyne forms benzene when passed through a heated tube containing complex organo-nickel catalyst.



Similarly,



(e) Combustion

Alkynes burn in excess oxygen to form carbon dioxide and water

$$C_nH_{2n-2} + \left(\frac{3n-1}{2}\right)O_2(g) \longrightarrow nCO_2(g) + (n-1)H_2O(l)$$

Example

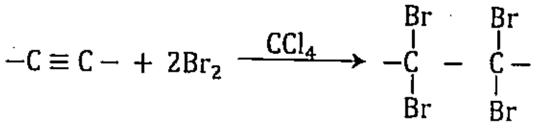
$$C_3H_4(g) + 4O_2(g) \longrightarrow 3CO_2(g) + 2H_2O(l)$$

3.3.7 Test for unsaturation in alkynes

The unsaturation in alkynes is tested the same way as done for alkenes using any of the following reagents;

Reagent; Bromine in tetrachloromethane.

Observation; Reddish-brown solution turns colourless



$$-C\equiv C- + 2Br_2 \xrightarrow{CCl_4} -\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-$$

Reagent; Alkaline potassium manganate(VII) solution.
Observation; Purple solution turns colourless

$$RC\equiv CR^I \xrightarrow[\text{2. dil. HCl}]{\text{1. KMnO}_4\text{(aq)}/\bar{O}H} RCOOH + R^ICOOH$$

The dilute hydrochloric acid converts carboxylate ions that would be formed to carboxylic acids.

Uses of alkynes

Uses of ethyne

- ✓ Used in the manufacture of benzene.
- ✓ Used in manufacturing of polyvinylchloride (PVC).
- ✓ Used in making acrylic fibres to make woolen garments.
- ✓ Used in welding because it burns with an extremely hot flame.

3.3.8 End of subtopic assessment exercise

1. Complete the following equations and give the IUPAC name of the major product formed in each case.

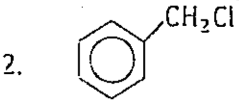
(a) $CH_3CH_2C\equiv CH \xrightarrow[\text{room temp.}]{\text{excess }H_2/Pd}$

(b) $CH_3C\equiv CH \xrightarrow[\text{quinoline}]{H_2/Pd/CO_3}$

(c) $HC\equiv CH \xrightarrow[\text{2. }CH_3CH_2Br]{\text{1. Na/liq. }NH_3}$

(d) $CH_3C\equiv CCH_3 \xrightarrow[\text{2. }H^+]{\text{1. KMnO}_4/\bar{O}H}$

(e) $CH_3C\equiv CH \xrightarrow{\text{1. NaNH}_2\text{/liq. }NH_3}$

2. 

(f) $CH_3CH_2C\equiv CH \xrightarrow{\text{excess }Br_2}$

(g) $CH_3C\equiv CCH_3 \xrightarrow{\text{excess HBr}}$

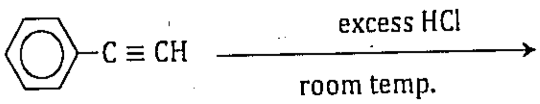
(h) $CH_3CH_2C\equiv CH \xrightarrow[Hg^{2+}/60°C]{H_2O/H^+}$

2. Complete the following equations and write the mechanisms for the reactions leading to formation of the major organic products.

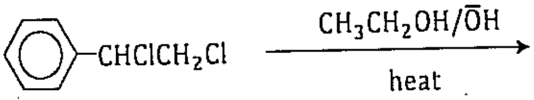
(a) $CH_3CH_2CHBr_2 \xrightarrow[\text{heat}]{KOH/CH_3CH_2OH}$

(b) $CH_3C \equiv CH \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. Na/liq. } NH_3}$

(c) $CH_3CH_2C \equiv CH \xrightarrow{\text{excess HCl}}$

(d) 

(e) $CH_3C \equiv CH + H_2O \xrightarrow[HgSO_4/60^\circ C]{\text{dil. } H_2SO_4}$

(f) 

(g) $CH_3CH_2C \equiv CNa + CH_3Br \xrightarrow{\text{liq. } NH_3}$

(h) $CH_3CBr_2CH_2CH_3 \xrightarrow[\text{heat}]{KOH/CH_3CH_2OH}$

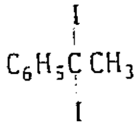
3. Write a mechanism to show how the following conversions can be effected.

(a) 1,2-Dibromopropane to propyne

(b) Ethyne to propyne

(c) $CH_3C \equiv \bar{C}Na^+$ to $CH_3CH_2C \equiv CCH_3$

(d) $CH_3C \equiv CH \xrightarrow{A} CH_3C \equiv CCu \xrightarrow{CH_3CH_2Cl} B$

(e) $C_6H_5C \equiv CH$ to 

$C_6H_5CI_2CH_3$

4. State would be observed and write equation for the reaction that would take place when each of the following compounds are mixed.

(a) Phenylethyne and ammoniacal silver nitrate solution
(b) But-1-yne and ammoniacal copper(I) chloride solution
(c) Ethyne is bubbled through ammoniacal copper(I) chloride solution
(d) 2-3 drops of ammoniacal copper(I) chloride and phenyethyne.

5. Write equations to show how the following synthesises can be carried out. In each case, indicate the necessary reagents and conditions.

(a) Ethanol to propyne

(b) Ethyne to Pent-2-yne

(c) Ethene to but-1-yne

(d) Pent-1-yne from ethene

(e) Ethyne to ethanol

(f) Calcium carbide to ethanol

(g) Magnesium carbide to propan-2-ol

(h) Propane to propyne

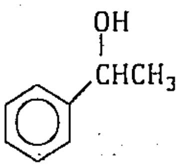
(i) $CH_2 = CH_2$ to $CH_3C \equiv CH$

(j) $CH_2 = CH_2$ to CH_3CHBr_2

(k) Ethanol from CH_2ClCH_2Cl

(l) Ethanol to benzene

(m) Butanone from 2-bromobutane

(n)

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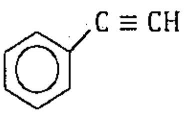
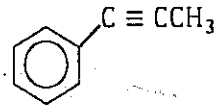
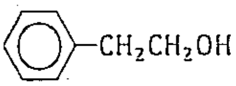


(o)

from $CH_3C \equiv CH$

(p)

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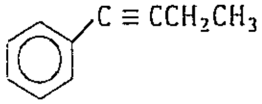
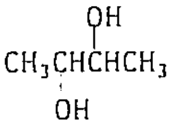
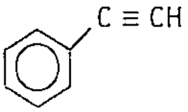


(q) $HC \equiv CH$ to

$CH_3\overset{OH}{C}H\underset{OH}{C}HCH_3$

(r) $CH_3C \equiv CCH_3$ to $CH_3CH_2CH_2CH_3$

(s) 2-Chloropropane to propyne

(t)

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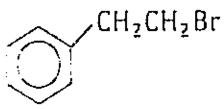
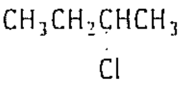


(u) 1,2-Dibromopropane from ethene

(v) Butan-2-ol from ethene

(w) $CH_3CH_2C \equiv CH$ to

$CH_3CH_2\underset{Cl}{C}HCH_3$

6. Desribe how the following conversions can be effected in the laboratory. **(No equations are required)**
   - (a) Ethyne to ethanal
   - (b) Propan-2-ol to propyne
   - (c) But-1-ene to but-1-yne
   - (d) Ethyne to 1,2-dichloroethane
   - (e) Ethyne to but-2-yne
   - (f) But-2-yne from butan-2-ol
   - (g) Ethyne to ethane-1,2-diol
   - (h) Ethanol to butanone
   - (i) Chloroethene from ethene
   - (j) Propene from ethyne

7. Name the reagent(s) that can be used to distinguish between the following pairs of compounds. In each case, state what would be observed if each member is separately treated with the reagent and write equation for the reaction.
   - (a) Ethyne and ethane
   - (b) Propane and propyne
   - (c) Pent-2-yne and pentane
   - (d) Pent-1-yne and pent-1-ene
   - (e) But-2-yne and but-1-yne
   - (f) Pent-2-yne and pent-2-ene

8. (a) Write an equation for the reaction of calcium carbide with water.
   - (b) The organic product, Q, produced by the reaction in (a) above can also be prepared from a haloalkane.
     - (i) Write the structure and name of the haloalkane.
     - (ii) Stating the conditions applicable, write an equation and indicate the mechanism for the reaction that takes place when the haloalkane is converted to Q.

9. A hyrocarbon, G, with a molecular formula, C_4H_6, formed a white precipitate with silver nitrate solution in ammonia.
   - (a) Write the structural formula of G.
   - (b) G reacts with water in presence of sulphuric acid and mercury(II) sulphate to form compound J.
     - (i) Identify J.
     - (ii) Outline the mechanism for the reaction in (b) above.
   - (c) Write equation for the reaction between G and excess hydrogen bromide.
   - (d) Write equation(s) to show how G can be synthesised from but-1-ene.

10. A compound Z, has the formula C_6H_{10}. When reacted with excess hydrogen in the presence of a platinum catalyst, Z yields only hexane as a product.
    (a) Write all the structural formulae of all the possible isomers of Z and their IUPAC names.
    (b) On treatment with hot alkaline potassium permanganate solution followed by acid, Z produces ethanoic acid and butanoic acid. Identify Z.

11. A gaseous hydrocarbon, L, contains 10% hydrogen and has a density of $1.79 \times 10^{-3} gcm^{-3}$ at 273K and $101325Nm^{-2}$.
    (a) Deduce the molecular formula of L.
        (i) L forms a red precipitate with ammoniacal copper(I) chloride solution. Name L.
        (ii) Write an equation for the reaction in (b)(i) above.
    (b) Using equations, show how L can be synthesized from any suitable alcohol.

12. (a) 1.363g of compound Y containing carbon, hydrogen and bromine on complete combustion gave 1.10g of carbon dioxide and 0.45g of water. When 0.35g of Y was vapourised, it occupied 39.5cm³ at 20°C and 750mmHg. Calculate;
        (i) the simplest formula of Y
        (ii) the molecular formula of Y
    (b) Y forms a compound Z when treated with a mixture of potassium hydroxide and an alcohol under reflux. Z reacts with ammoniacal silver nitrate to form a white precipitate Q. Identify:
        (i) Y
        (ii) Z
        (iii) Q
    (c) Write;
        (i) equation for the reaction between Z and ammoniacal silver nitrate solution.
        (ii) the mechanism for the reaction leading to formation of Z.

13. 20 cm³ of a gaseous hydrocarbon, E, with general formula C_nH_{2n-2} were exploded with 100 cm³ of oxygen and cooled to room temperature. When the residual gas mixture was bubbled through concentrated potassium hydroxide solution, the final volume was found to be 20 cm³.
    (a) Calculate the value of **n** and hence deduce the molecular formula of E.
    (b) (i) Write the structural formulae and IUPAC names of the possible isomers of E.
        (ii) One of the isomers in (b)(i) above reacts with a solution of copper(I) chloride in aqueous ammonia to form a red precipitate. Identify the isomer and write equation for the reaction leading to formation of the red precipitate.

14. When 20 cm³ of a gaseous alkyne, J, C_nH_{2n-2} were exploded with 135 cm³ of excess oxygen and cooled to room temperature, the residual gases occupied a volume of 105 cm³. When the residual gases were passed through concentrated sodium hydroxide solution, the volume decreased by 80 cm³.

(a) (i) Write equation for the combustion of J.

(ii) Determine the molecular formula of J.

(b) Write the structural formulae and names of the possible isomers of J.

(c) J reacts with sodium metal in presence of liquid ammonia to form compound M. Identify;

(i) J

(ii) M

(c) Write equation and suggest a mechanism for the reaction between;

(i) J and excess bromine

(ii) M and 1-bromopropane

(d) J was bubbled through ammoniacal silver nitrate solution.

(i) State what was observed.

(ii) Write equation for the reaction

(e) With the aid of an equation, describe how J reacts with water.

15. 30cm^3 of a gaseous hydrocarbon Q was exploded with 200cm^3 of oxygen, which was in excess. The residual gas volume was found to be 155cm^{3}on cooling to room temperature. The volume of the residual gas reduced to 35cm^3 on treatment with concentrated potassium hydroxide solution.

(a) (i) Write the general equation for the reaction between Q and oxygen

(ii) Calculate the molecular formula of Q.

(iii) Write structural formulae of all possible open chain isomers of Q.

(b) When Q was treated with ammoniacal copper(I) chloride solution, a red precipitate was formed.

(i) Identify Q

(ii) Write equation for the formation of the red precipitate.

(c) Q was reacted with water in the presence of dilute sulphuric acid and mercury(II) sulphate at 60°C. Write equation for the reaction and the accepted mechanism.

(d) Write equations to show how Q can be synthesized from but-1-ene.

Chapter 4

Benzene

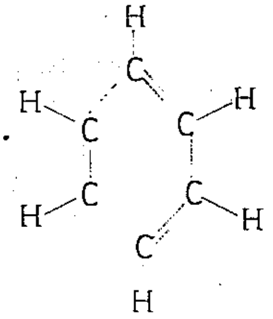
and its derivatives

Benzene is the simplest member of the **aromatic class of hydrocarbons**.
It is a **colourless liquid** and has a molecular formula; C_6H_6.

4.1 The structure of benzene

For so many years, benzene was known as a cyclic compound with a six-membered ring of six carbon atoms and one hydrogen atom.

The carbon atoms were predicted to have **alternating double** and **single bonds** joining them within the ring.

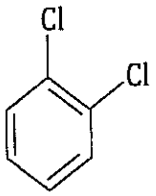


This structure was proposed by Kekule (1865) and is more conveniently written as;

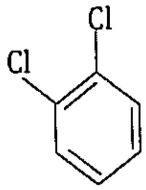
The Kekule structure was however not accepted by all chemists because it would imply that benzene undergoes addition reactions just like alkenes.

Note

(i) If the structure was correct, then it would be possible to have two different disubstituted isomers of benzene that can be isolated such that the two substituent atoms can be either attached to adjacent carbon atoms joined by a single bond or to two carbon atoms joined by a double bond as shown below:

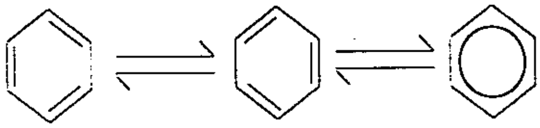


and



However, in no case was more than one isomer of any such compound obtained.

Kekule modified his structure therefore by proposing that benzene rapidly alternated between the structures;



The above structures are called resonance structures.

(ii) Benzene does not easily undergo electrophilic addition reactions like ethene and other compounds containing carbon-carbon double bonds.

This is because the pi-electrons in benzene are not fixed to any two carbon atoms but are delocalized over the entire structure making benzene very stable and not easily attacked by electrophiles. Therefore, benzene does not undergo addition reactions due to resonance stabilization.

However, the carbon-carbon double bond in alkenes has localized pi-electrons hence a centre of high electron density thus readily attacked by electrophiles.

(iii) The carbon-carbon single bonds and carbon-carbon double bonds in benzene have equal length (0.139 nm). This in intermediate between the carbon-carbon single bond length (0.154 nm) and the carbon-carbon double bond length in alkenes (0.133 nm).

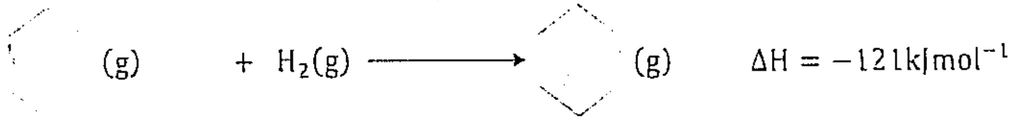
4.2 Stability of the benzene ring

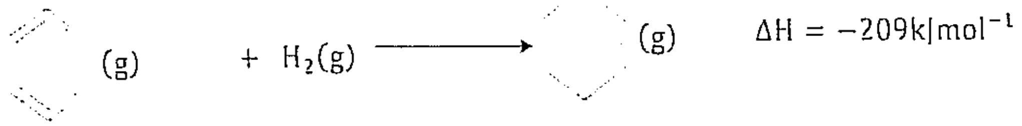
Benzene is more stable than would be expected by comparison to an alkene (the hypothetical cyclohexa-1,3,5-triene)

This can be confirmed from thermochemical measurements.

For example:

The enthalpy of hydrogenation of cyclohexene to cyclohexane is $-121\ \text{kJmol}^{-1}$ and enthalpy of hydrogenation of benzene to cyclohexane is $-209\ \text{kJmol}^{-1}$.





Explanation:

Cyclohexene contains an **alkene carbon-carbon double bond** in which the **pi-electrons** are **localized in the region of unsaturated carbon atoms** hence **only 121 kJ of heat are evolved** per mole of cyclohexene hydrogenated.

If the three carbon-carbon double bonds in benzene had localized pi-electrons, $(3 \times 121) = 363$ kJ of **heat would be evolved per mole** of benzene hydrogenated. However, there is a **difference of $(363 - 209) = 154$kJ** of heat. This implies that the **carbon-carbon double bonds in benzene have delocalized pi-electrons** making the structure **very stable.**

The value of 154kJ is called the **delocalization energy** or **resonance energy** or **stabilization energy** of benzene.

(ii) *Similarly, the theoretical/ calculated enthalpy of formation of gaseous benzene is* $+252\ kJmol^{-1}$ *but the experimental value is* $+82\ kJmol^{-1}$.

This implies that benzene is more stable by $(252 - 82) = +170$ kJmol^{-1} of energy. This also further shows the increased stability of benzene due to delocalized pi-bonds in its ring.

4.3 Physical properties of benzene

- Benzene is a colourless liquid with a boiling point of 80°C and a melting point of 5.5°C.
- It is insoluble/ immiscible with water but soluble in all organic solvents. It is therefore a very good solvent for organic compounds.
- It has a characteristic odour of aromatic compounds.
- Benzene burns with a luminous smoky flame due to its relatively high carbon content.

Note

Both the liquid and benzene vapour are highly poisonous/ toxic hence must be used with care. Its inhalation over a period of time can induce anaemia and leukemia.

4.4 Preparation of benzene

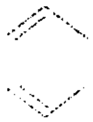
(i) Polymerization of ethyne.

When ethyne is heated at temperature of 60-70°C under a pressure of 5 atm, in the presence of a complex organo-nickel catalyst, benzene is formed.

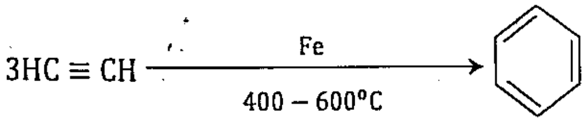
$$3HC \equiv CH \xrightarrow[60 - 70°C,\ 5atm]{\text{complex organo} - \text{nickel catalyst}}$$

Similarly, copper or iron can be used at a temperature of 400-600°C.

$$3HC \equiv CH \xrightarrow[400 - 600°C]{Cu}$$

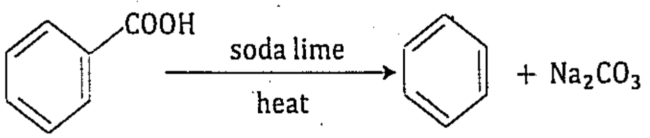


Or

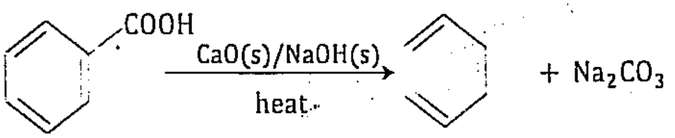


(ii) By decarboxylation of benzoic acid.

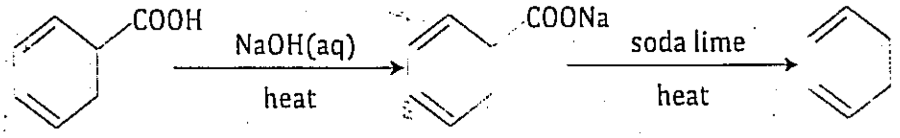
When benzoic acid is heated with sodalime, benzene is formed.



Sodalime is a mixture of solid calcium oxide and solid sodium hydroxide. The equation can therefore similarly be written as;

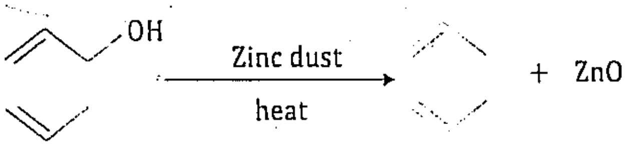


The reaction may also be done in two steps by reacting benzoic acid with sodium hydroxide solution first to form sodium benzoate. The sodium benzoate is then fused with sodalime.



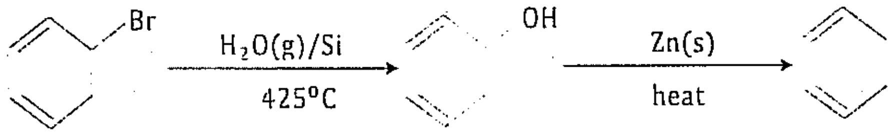
(iii) From phenol (Reduction of phenol)

Benzene can be formed by passing phenol vapour over heated zinc dust.



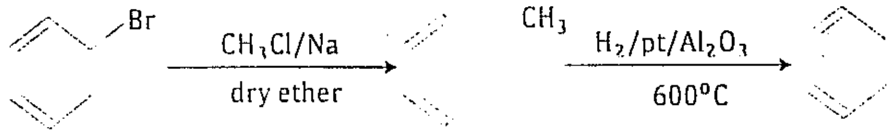
(iv) From bromobenzene

Bromobenzene is first converted to phenol and then phenol is then reduced to benzene by the reaction already shown above.



Note that the water is in the form of steam at the temperature used.

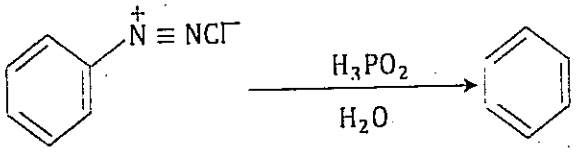
Similarly, the bromobenzene can be converted to methylbenzene which is then converted to benzene under the conditions shown below;



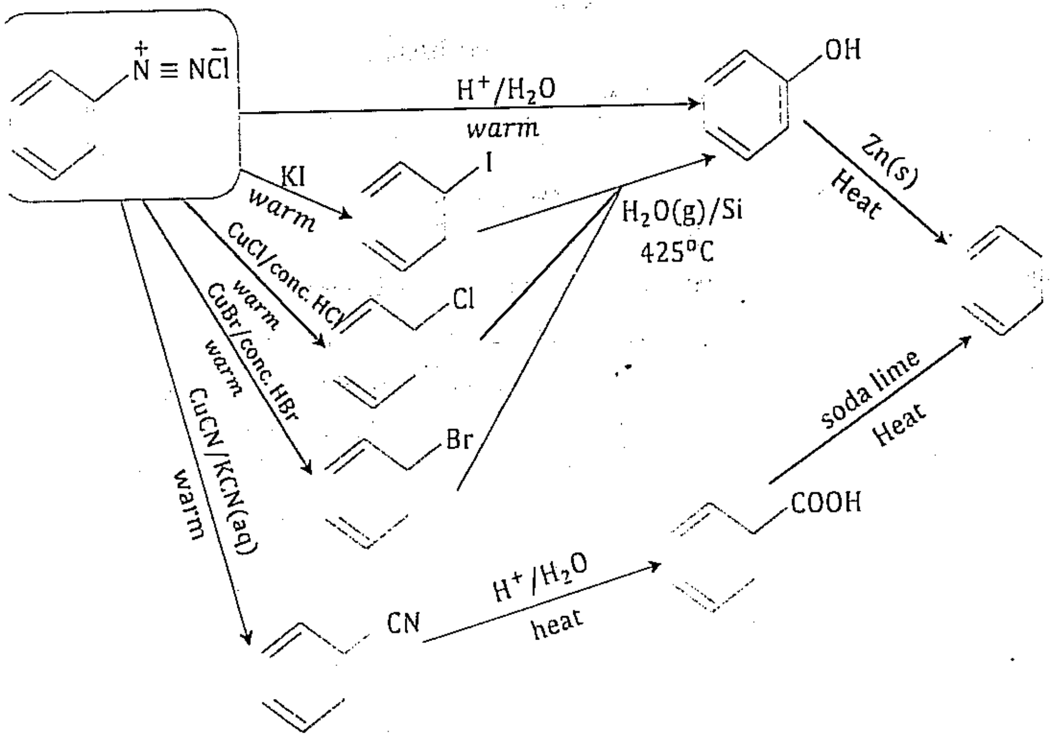
N.B. Chlorobenzene or iodobenzene may be used instead of bromobenzene.

(v) From benzene diazonium chloride

Benzene can be formed by reducing benzenediazonium chloride solution using hypophosphorus acid.

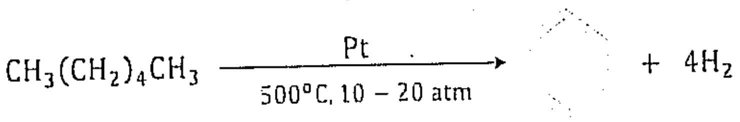


Other longer routes by which benzene can be formed from benzene diazonium chloride are shown below;



(vi) Industrially from petroleum.

Petroleum vapour, containing hexane and other hydrocarbons is passed over a finely divided platinum catalyst at 500°C under 10-20 atmospheres to form benzene.



This process is known as reforming.

4.5 Chemical properties of benzene

Benzene does not easily undergo addition reactions, like alkenes but mainly undergoes **electrophilic substitution** in the ring.

The reasons are already explained before.

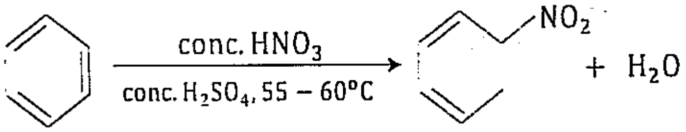
The pi-electrons in the benzene ring serves as a source of electrons.

(i) Nitration

A nitrating mixture containing **equal molar quantities of concentrated nitric acid and sulphuric acid** is mixed together and added to benzene. The mixture is then **refluxed in a water bath at 50-60°C.**

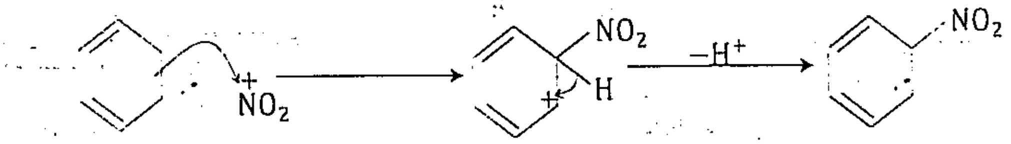
Nitrobenzene is formed as a pale yellow liquid.

Equation;



<u>Mechanism;</u>

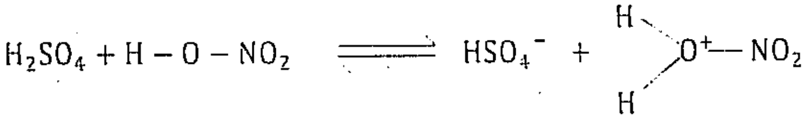
$$HNO_3 + 2H_2SO_4 \rightleftharpoons \overset{+}{N}O_2 + H_3O^+ + 2HSO_4^-$$



$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

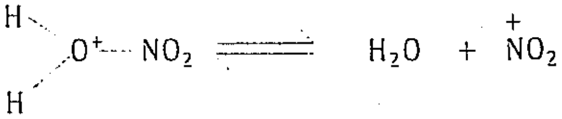
Note

The weaker nitric acid acts as a base in the highly acidic sulphuric acid hence accepts a proton from sulphuric acid.



$$H_2SO_4 + H-O-NO_2 \rightleftharpoons HSO_4^- + H_2O^+-NO_2$$

The protonated nitric acid splits up to form water and a nitryl (nitronium) cation.



$$H_2O^+-NO_2 \rightleftharpoons H_2O + \overset{+}{N}O_2$$

The nitronium ion is an electrophilic reagent which then is attracted to the delocalised pi-electrons of benzene.

The molecule of water formed above is then protonated by a second molecule of sulphuric acid.

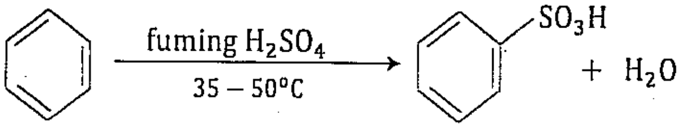
$$H_2O + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^-$$

Combining the three equations above gives the equation given above as the mechanism starts.

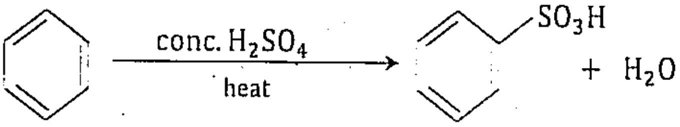
The reaction involves substitution of –H in the benzene ring by a $-NO_2$ group.

(ii) Sulphonation

This reaction occurs when benzene is **gently warmed** with **fuming sulphuric acid** to **35 – 50°C** for 20 – 30 minutes.



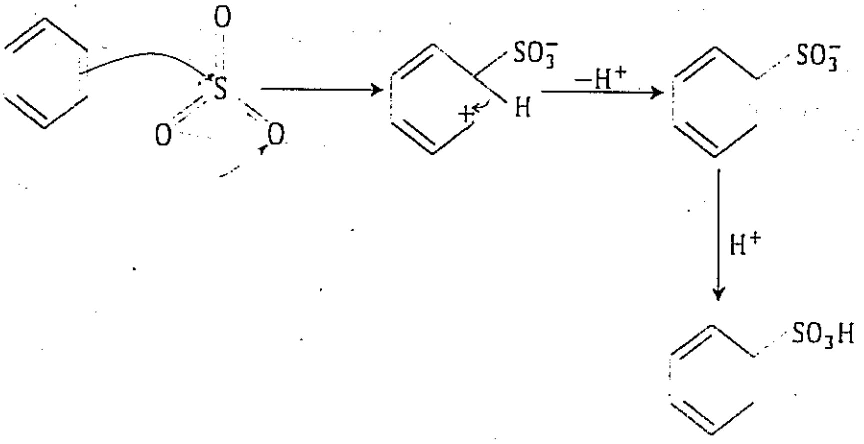
Alternatively, ordinary **concentrated sulphuric acid** can be used but the mixture requires **refluxing** for several hours (about 8 hours).



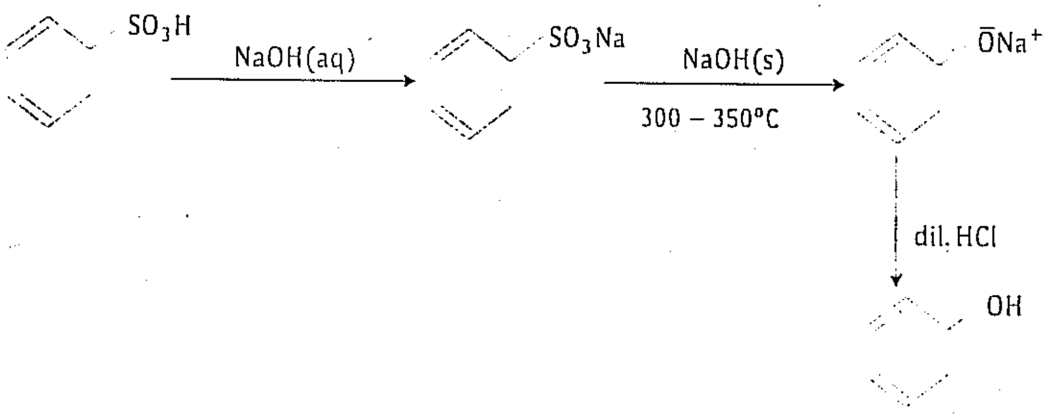
In both cases, the H atom in benzene is substituted by the electrophilic SO_3 to form **benzenesulphonic acid.**

Mechanism

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$



Benzenesulphonic acid is very useful for **preparation of phenol** in the laboratory as shown by the synthetic scheme below;



Sulphonation is also a useful process in the **manufacture of detergents, dyes and drugs.**

(iii) Friedel-Crafts alkylation.

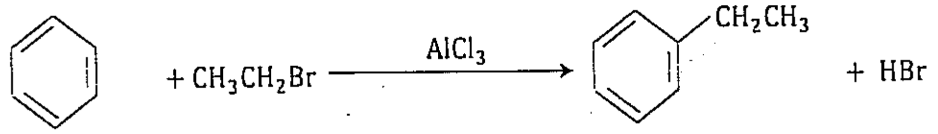
Benzene reacts with an **alkylhalide** in presence of **anhydrous aluminium chloride** catalyst to form an **alkylbenzene.**

Anhydrous aluminium bromide, anhydrous iron(III) chloride or anhydrous iron(III) bromide may similarly be used as catalysts.

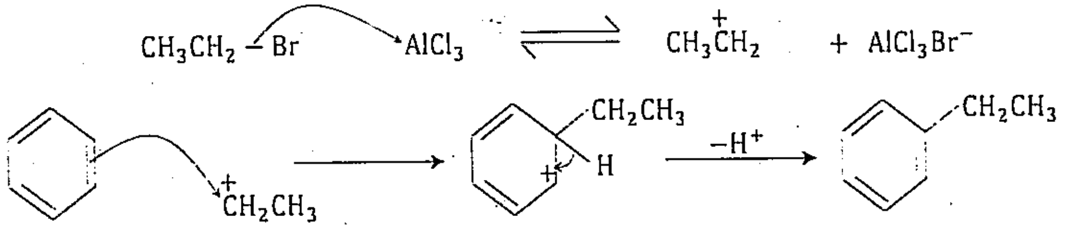
Examples;

Benzene reacts with **bromoethane** in presence of **anhydrous aluminium chloride** catalyst to form **ethylbenzene.**

(a)

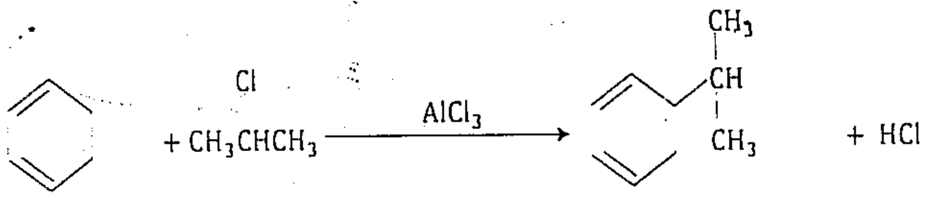


Mechanism;

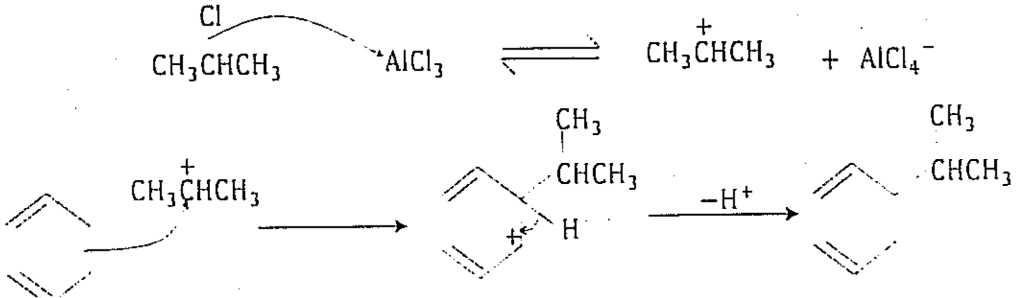


Benzene reacts with **2-chloropropane** in presence of **anhydrous aluminium chloride** catalyst to form 2-phenylpropane.

(b)



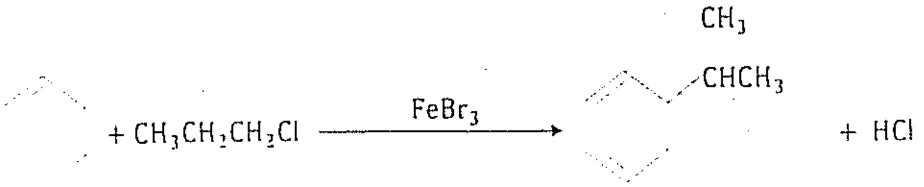
Mechanism;



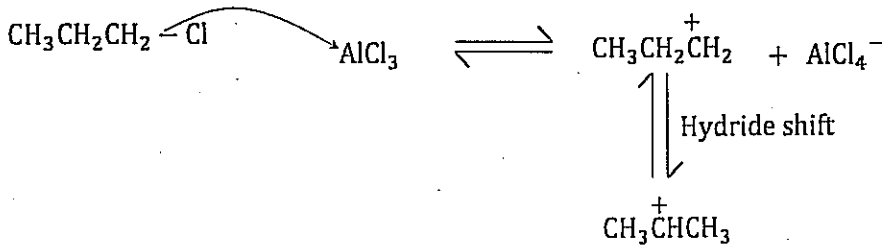
Isopropylbenzene

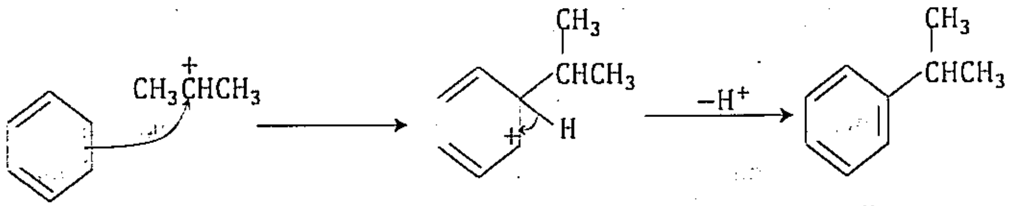
Benzene reacts with 1-chloropropane in presence of anhydrous iron(III) bromide catalyst to form 2-phenylpropane.

(c)



Mechanism:





Isopropylbenzene

$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

Note

In (c), a hydride shift occurs such that a more stable secondary carbocation is formed.

(iv) Friedel-Crafts acylation.

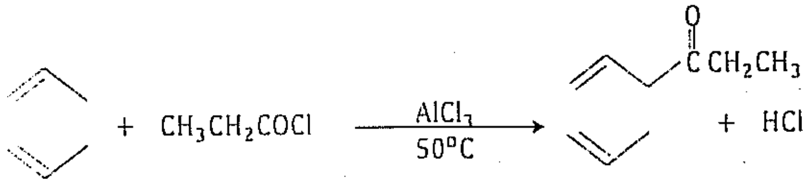
Benzene reacts with **acylchorides** in presence of **anhydrous aluminium chloride catalyst** to form aromatic ketones.

The mixture is **refluxed on a water bath** at 50°C.

Similary, anhydrous iron(III) chloride, anhydrous iron(III) bromide or anhydrous aluminium bromide may be used as catalysts.

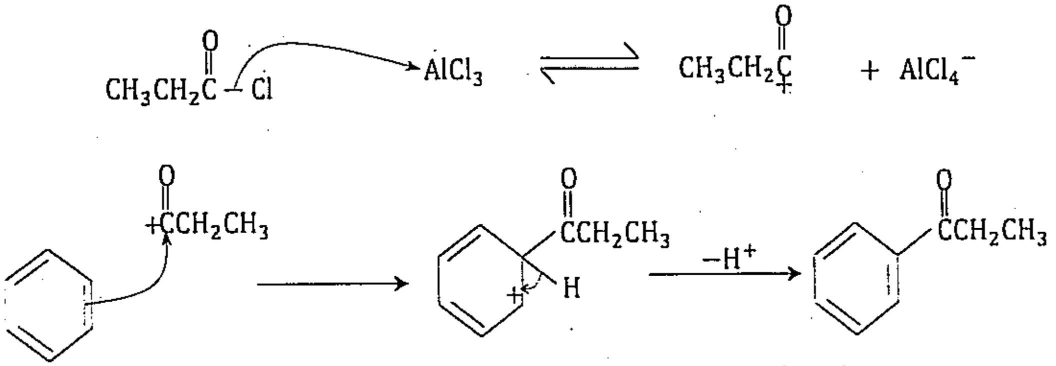
Examples:

(i) Benzene reacts with **propanoylchloride** in presence of **anhydrous aluminium chloride** catalyst to form **phenylpropanone**.



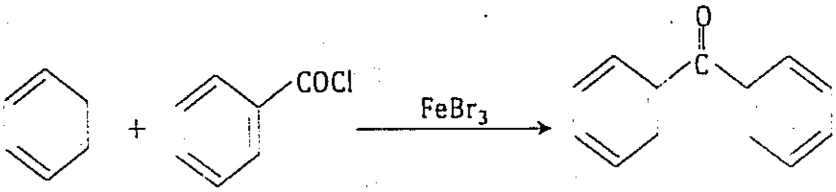
Phenylpropanone

Mechanism;

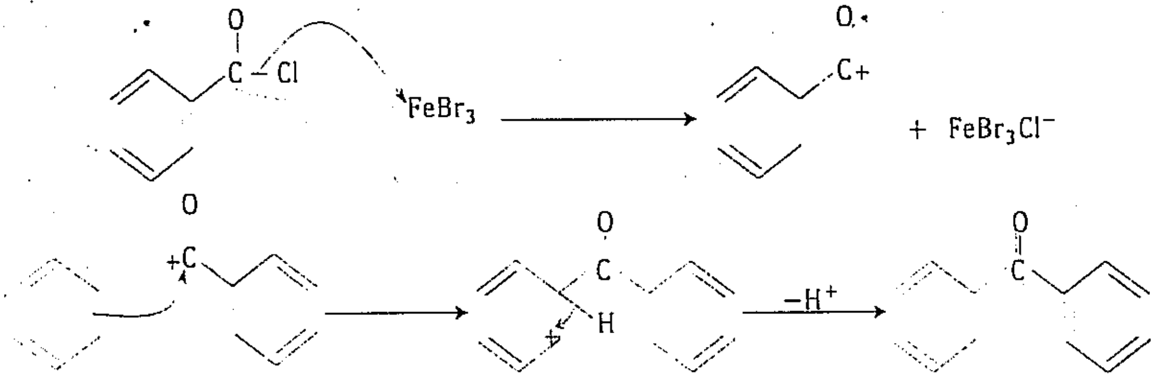


Phenylpropanone

(ii) Benzene reacts with benzoylchloride in presence of anhydrous iron(III) bromide catalyst to form diphenylmethanone(IUPAC name) (Other names; diphenylketone or benzophenone)



Mechanism;

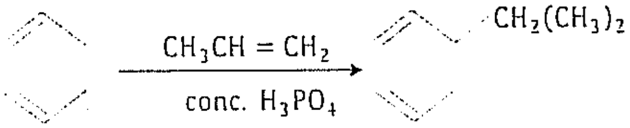


(v) Reaction with alkenes

Instead of using alkylhalides, benzene can also be alkylated using an alkene and a Friedel-Crafts catalyst together with an acid such as hydrochloric acid or phosphoric acid.

Examples;

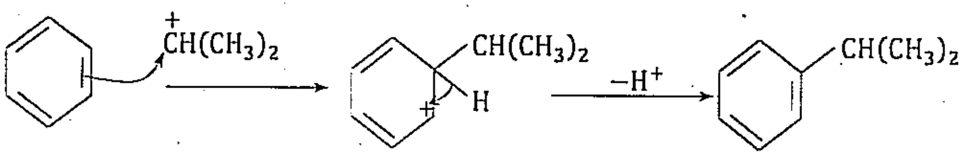
(a)



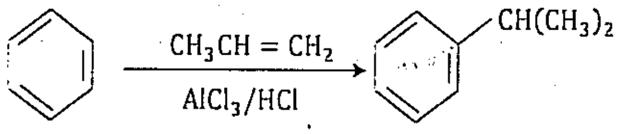
Mechanism;

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$\underset{\curvearrowright H^+}{CH_3CH=CH_2} \longrightarrow \overset{+}{C}H(CH_3)_2$$



(b)



Mechanism;

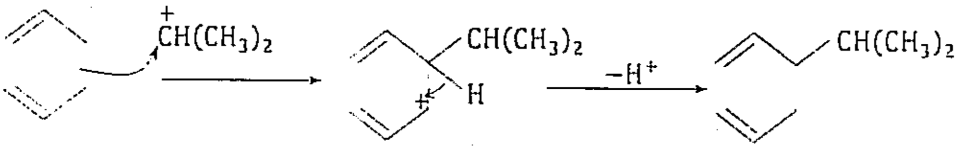
$$HCl \longrightarrow H^+ + Cl^-$$

$$\underset{\curvearrowright H^+}{CH_3CH=CH_2} \longrightarrow \overset{+}{C}H(CH_3)_2 \quad Cl^-$$

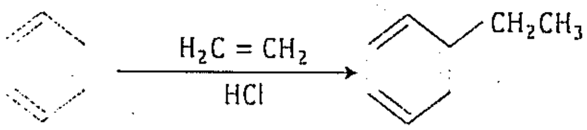
$$\downarrow$$

$$(CH_3)_2CH-Cl$$

$$(CH_3)_2CH-Cl \quad AlCl_3 \longrightarrow (CH_3)_2\overset{+}{C}H + AlCl_4^-$$



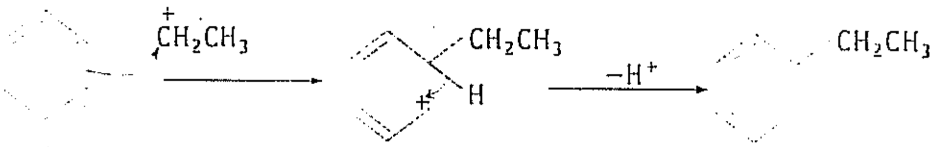
(c)



Mechanism;

$$HCl \longrightarrow H^+ + Cl^-$$

$$\underset{\curvearrowright H^+}{H_2C=CH_2} \longrightarrow \overset{+}{C}H_2CH_3$$



Similarly, instead of an alkene, an alcohol can be used with a suitable Friedel-Crafts catalyst or phosphoric/ hydrochloric acid.

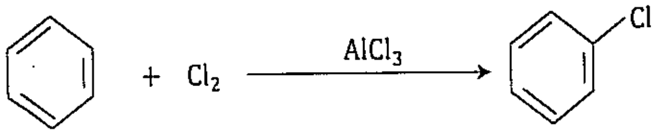
(vi) Halogenation

Benzene reacts with **chlorine** or **bromine** at room temperature in the presence of **iron(III) bromide, aluminium chloride** or **iron(III) chloride catalyst.**

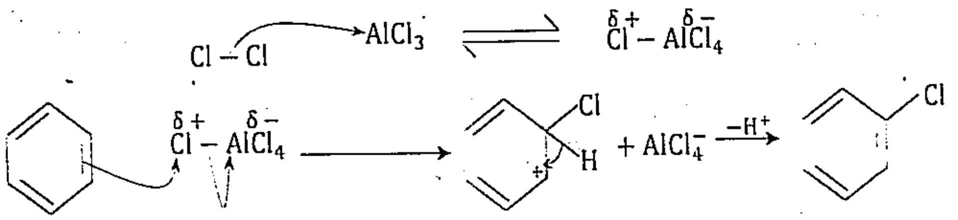
These catalysts are called **halogen carriers** and act as **Lewis acids, inducing a degree of polarity in the halogen molecules.**

Examples;

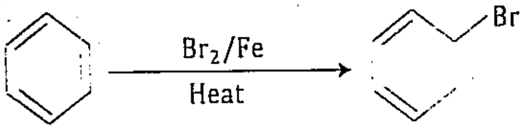
(a)



Mechanism;

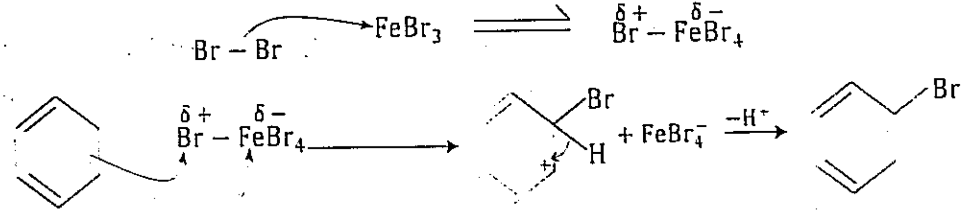


(b)

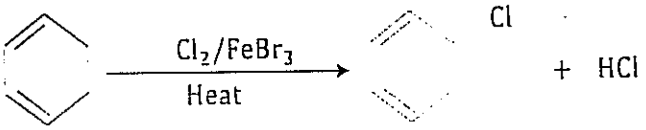


Mechanism;

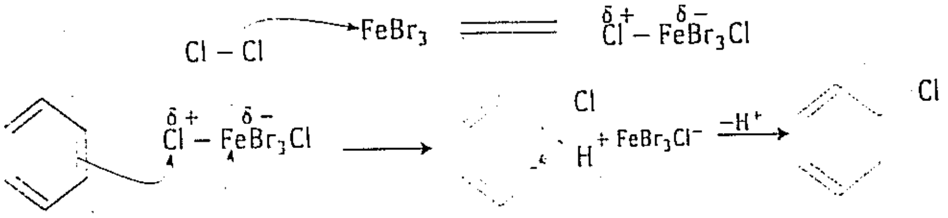
$$2Fe + 3Br_2 \longrightarrow 2FeBr_3$$



(c)

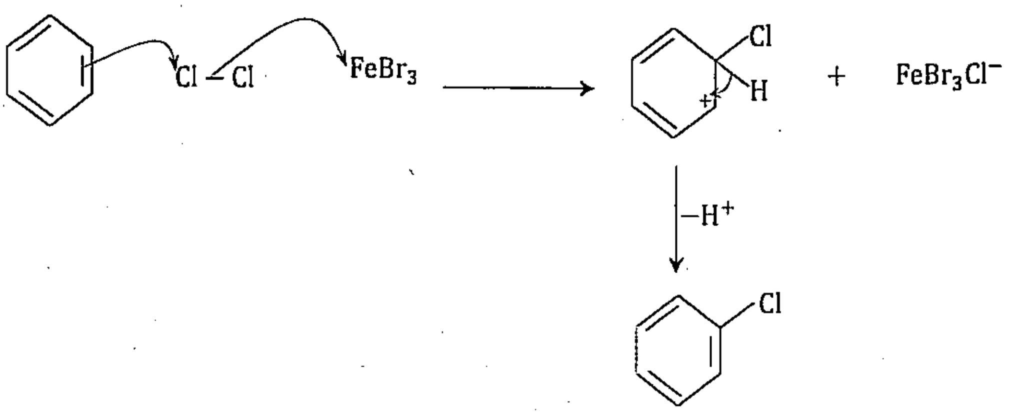


Mechanism



Note

The mechanism above can also be represented as shown in the example below;



$$FeBr_3Cl^- + H^+ \longrightarrow FeBr_3 + HCl$$

The product of chlorination of benzene is **chlorobenzene** while that of bromination is **bromobenzene.**

The bromination test can be used to distinguish benzene and cyclohexane.

Reagent: Bromine in the presence of anhydrous aluminium bromide.

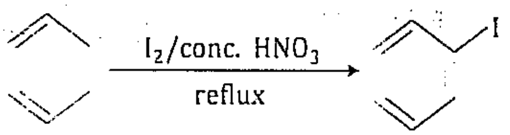
Observations:

With benzene, reddish brown solution turns colourless.

With cyclohexane, no observable change.

Note

Iodine does not easily substitute benzene in the same way. The electrophilic substitution in benzene is rather done by refluxing benzene, iodine and concentrated nitric acid.



Other reactions of benzene include;

(i) Combustion

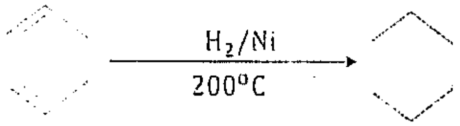
Just like any other hydrocarbons, benzene completely burns in excess air to form carbon dioxide and water, giving off a lot of heat.

Since the reaction is exothermic, benzene can be used as a fuel.

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

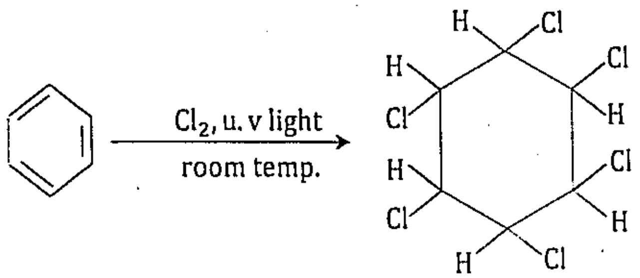
(ii) Hydrogenation

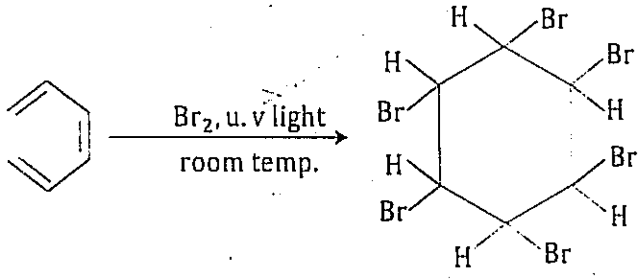
When a mixture of hydrogen and benzene vapour is passed over Raney nickel at 150°C, cyclohexane is formed.



(iii) Halogenation in direct sunlight/u.v light.

Benzene reacts with chlorine or bromine at room temperature and in the presence of direct sunlight or ultra-violet light to form white crystals of 1,2,3,4,5,6-hexachlorocyclohexane and 1,2,3,4,5,6-hexabromocyclohexane respectively.





Both 1,2,3,4,5,6-hexachlorocyclohexane and 1,2,3,4,5,6-hexabromocyclohexane are useful in making insecticides.

Hydrogenation and halogenation in presence of sunlight or u.v light are the only addition reactions undergone by benzene.

4.6 Identification of functional group in benzene

The functional group in benzene is the phenyl group (C_6H_5-).

It can be identified by testing benzene with bromine in presence of aluminium chloride.

Observation

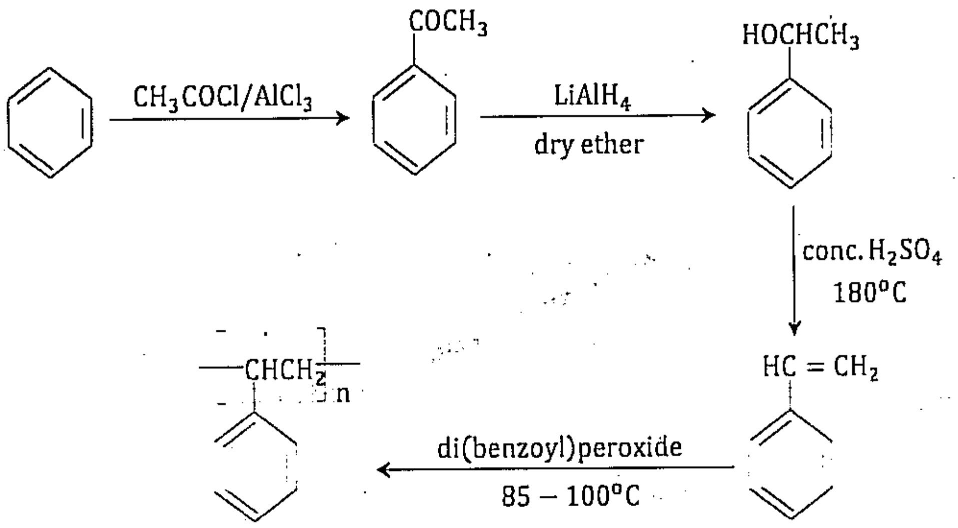
- The reddish-brown solution turns colourless.

4.7 Uses of benzene

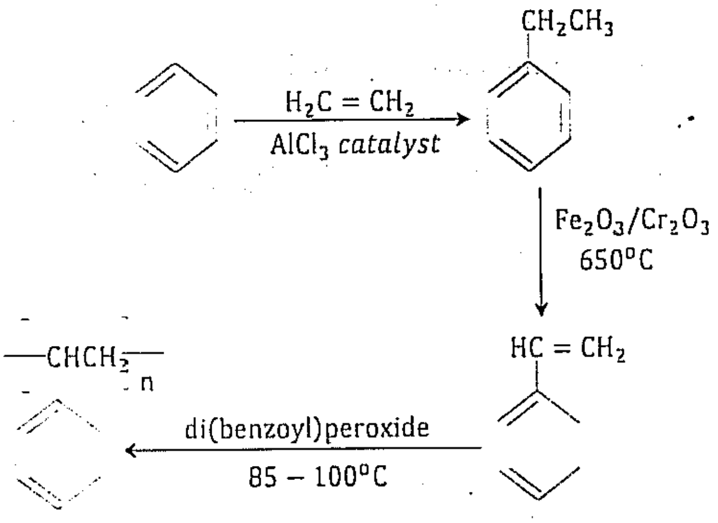
(a) Benzene is used to make materials needed for the plastic industry, for example;

It is converted to phenylethene which is used to make the polymer; poly(phenylethene) (also called polystyrene)

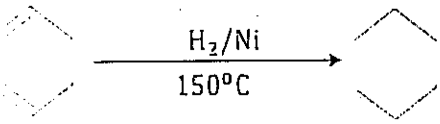
The reaction schemes for formation of polystyrene are shown below;



Similarly,



Benzene can also be converted to cyclohexane, a useful intermediate in the manufacture of nylon.

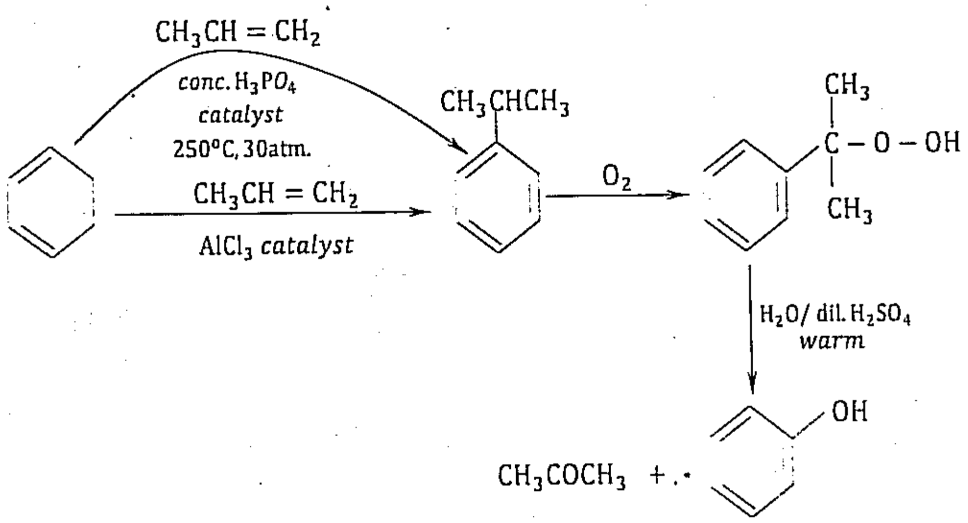


(b) Benzene is also used to make phenol via the cumene process.

During the process, benzene in the vapour phase is compressed with propene at 30 atm in presence of phosphoric acid catalyst at 250 °C to form (1-methylethyl)benzene (also called cumene)

Instead of the vapour phase, benzene may also be alkylated with propene in the liquid phase but in this case aluminium chloride is used as catalyst.

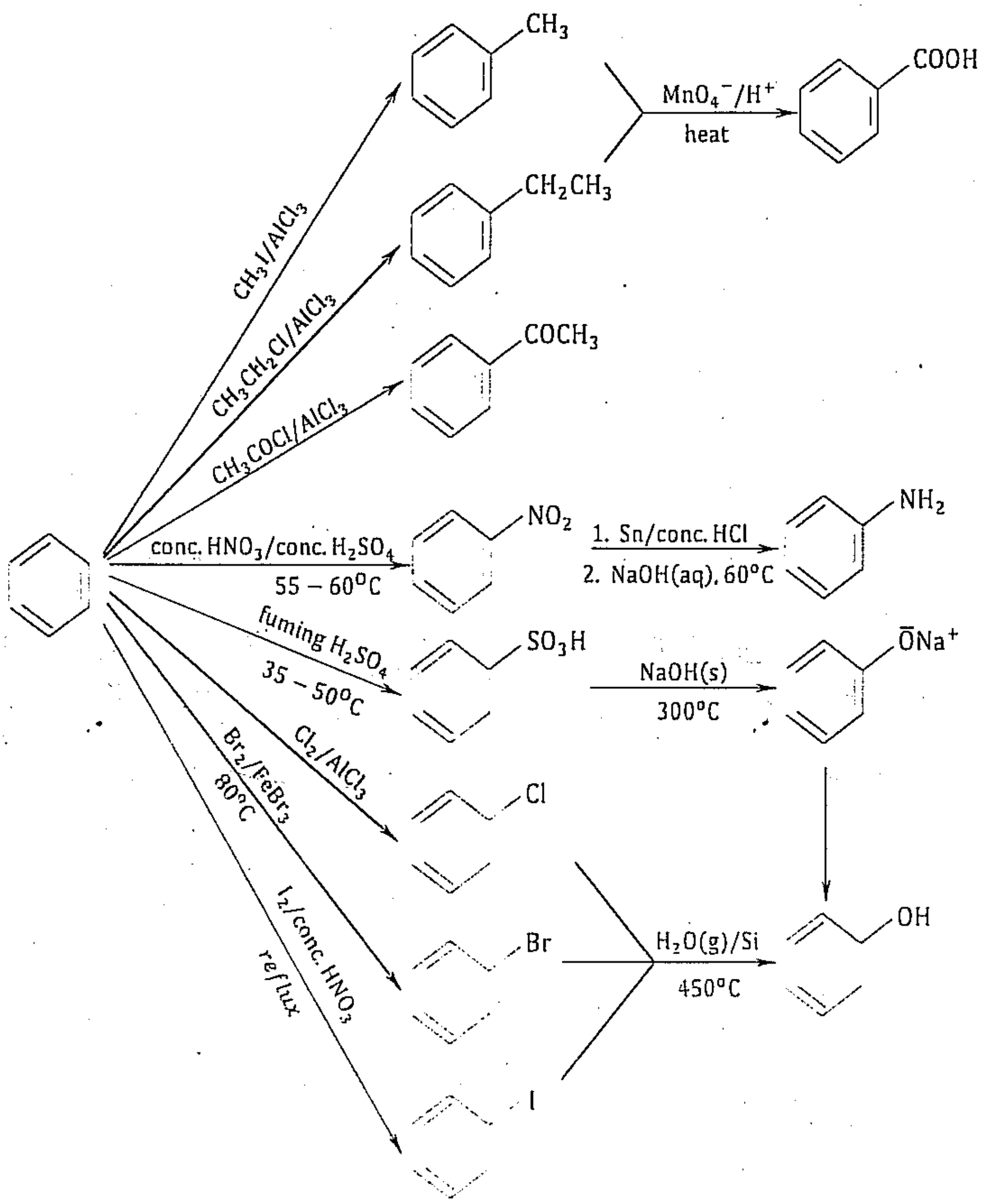
The cumene formed in either case is oxidised by air to form cumene hydroperoxide which when treated with warm dilute sulphuric acid forms phenol as the major product and propanone as a by-product.



4.8 Derivatives of benzene

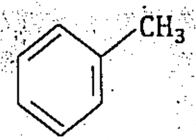
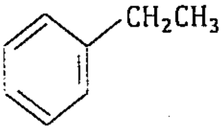
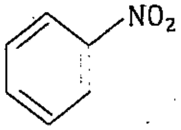
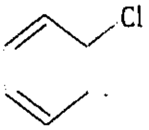
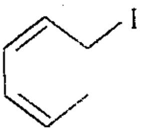
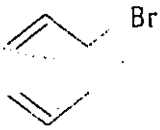
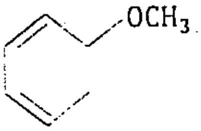
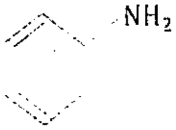
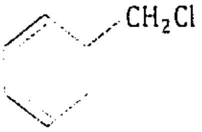
Benzene derivatives are compounds in which one or more of the hydrogen atoms of the benzene ring have been replaced by another atom or group of atoms.

The scheme below shows a summary of the common benzene derivatives.

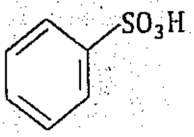
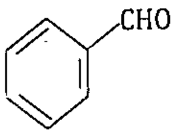
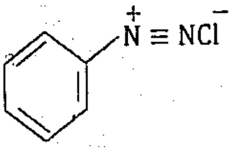


4.8.1 Nomenclature of the common benzene derivatives

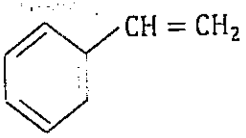
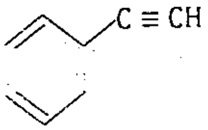
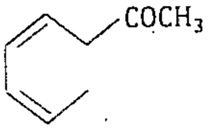
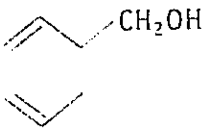
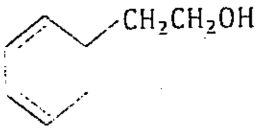
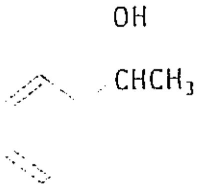
For monosubstituted benzene derivatives, most of them are named by writing the name of the substituent followed by the word benzene.

Benzene derivative	*IUPAC name*
	Methylbenzene
	Ethylbenzene
	Nitrobenzene
	Chlorobenzene
	Iodobenzene
	Bromobenzene
	Methoxybenzene
	Phenylamine
	Chloromethylbenzene
	Phenoxybenzene

Some monosubstituted derivatives are named beginning with the word benzene. For example;

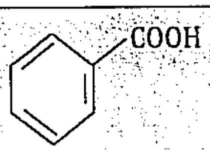
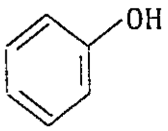
Benzene derivative	*IUPAC name*
	Benzenesulphonic acid
	Benzenecarbaldehyde or Benzaldehyde
	Benzenediazonium chloride

When the benzene ring is attached to a carbon chain having another functional group, the benzene ring is named as a substituent called phenyl- . For example;

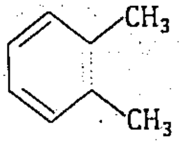
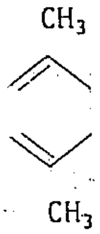
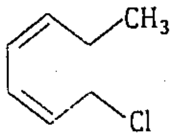
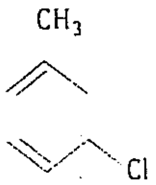
Benzene Derivative	*IUPAC name*
	Phenylethene
	Phenylethyne
	Phenylethanone
	Phenylmethanol
	2-Phenylethanol
	1-Phenylethanol

Note that the position of the phenyl group must be given relative to the functional group in the carbon chain.

Some monosubstituted derivatives have special names. For example;

Benzene derivative	*IUPAC name*
	Benzoic acid
	Phenol

For derivatives of methylbenzene, the positions of the substituents are indicated by numbers with the methyl group given position one. For example;

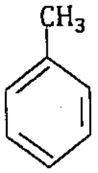
Derivative of methylbenzene	*IUPAC name*
	1,2-Dimethylbenzene
	1,4-Dimethylbenzene
	2-Chloromethylbenzene
	3-Chloromethylbenzene

The main benzene derivative we may consider further in this topic is methylbenzene.

4.8.2 Methylbenzene

Methylbenzene is also called Toluene and resembles benzene in many properties.

Its molecular formula is C_7H_8 and the structural formula is;



4.8.2.1 Physical properties of methylbenzene

Below are physical properties of methylbenzene in comparison to benzene.

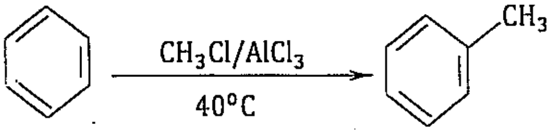
Benzene	*Methylbenzene*
Colourless liquid	Also a colourless liquid closely resembling benzene
Insoluble in water but soluble in organic solvents and itself a good organic solvent	Also insoluble in water but soluble in organic solvents and is itself a good organic solvent.
Has a higher melting point(5.5°C)	Has a lower melting point than benzene (-95°C)
Has a lower boiling point than methylbenzene (80°C)	Has a higher boiling point than benzene(111°C)
Highly toxic	Considerably less toxic compared to benzene hence more preferably used as a solvent than benzene.

Methylbenzene has a higher melting point than benzene because both molecules are held by van der Waal's forces of attraction whose strength increases with molecular mass. Since methylbenzene has a higher molecular mass than benzene, its molecules are held by stronger van der Waal's forces than benzene that require a higher amount of energy to break. However, the melting point of benzene is higher than that of methylbenzene because the planar symmetrical benzene molecules can pack closely together in the crystal hence having stronger cohesive forces than methylbenzene molecules, in which the methyl group makes the methylbenzene molecules not to have such close packing.

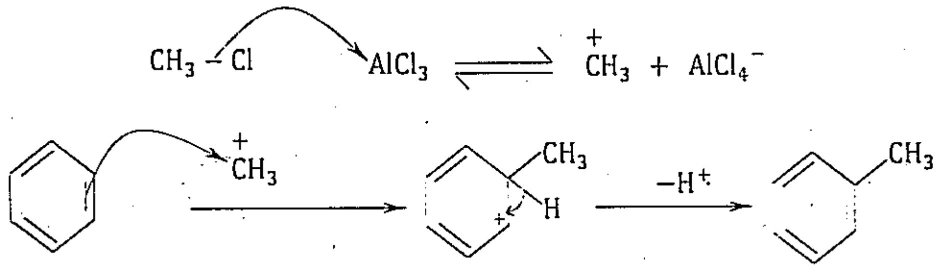
4.8.2.2 Preparation of methylbenzene

(i) From benzene

Methylbenzene is formed by bubbling chloromethane through dry benzene in the presence of anhydrous aluminium chloride catalyst at a temperature of 40°C.

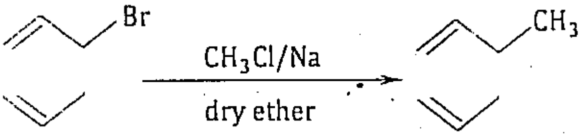


Mechanism;



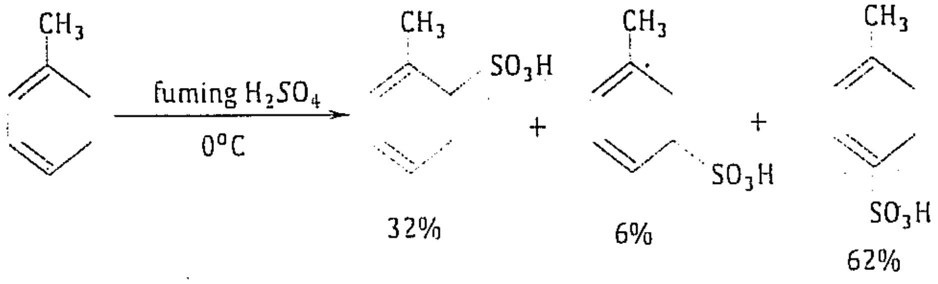
(ii) From bromobenzene (Fittig's reaction)

Methylbenzene can also be formed by adding sodium slowly to a solution of bromobenzene, iodomethane and dry ether.



4.8.2.3 Inductive orientation on benzene ring in relation to methyl group

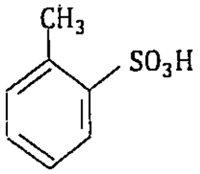
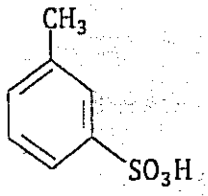
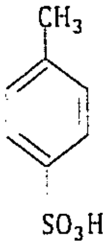
Just like benzene, methylbenzene also undergoes electrophilic aromatic substitution reactions. For example, sulphonation of methylbenzene yields three isomeric products in different amounts.



The isomeric products are named using the prefixes *ortho-*, *meta-* and *para-* which are usually abbreviated as *o*, *m* and *p* respectively.

Each prefix matches a number 2, 3 and 4 respectively to describe the relative positions of the substituent $-SO_3H$ group in relation to the methyl group which is assigned position 1.

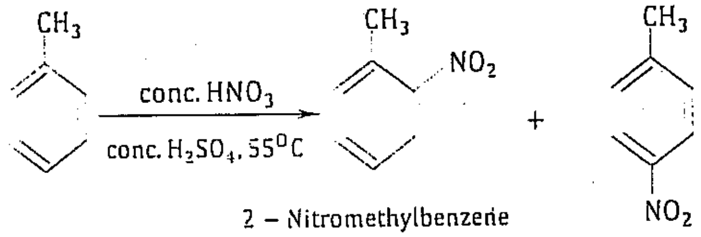
Below are the names of the isomeric products above in o, m , p notation.

	2-substituted isomer	*ortho*-Methylbenzenesulphonic acid (*o*-Methylbenzenesulphonic acid)
	3-substituted isomer	*meta*-Methylbenzenesulphonic acid (*m*-Methylbenzenesulphonic acid)
	4-substituted isomer	*para*-Methylbenzenesulphonic acid (*p*-Methylbenzenesulphonic acid)

From the equations shown above, the *ortho-* and *para-* isomers are formed in larger amounts than the *meta-* isomer.

Similarly, nitration, Friedel-Crafts alkylation or acylation and halogenation of methylbenzene gives mainly the *ortho-* and *para-* isomers and the reactions are faster than would be for benzene.

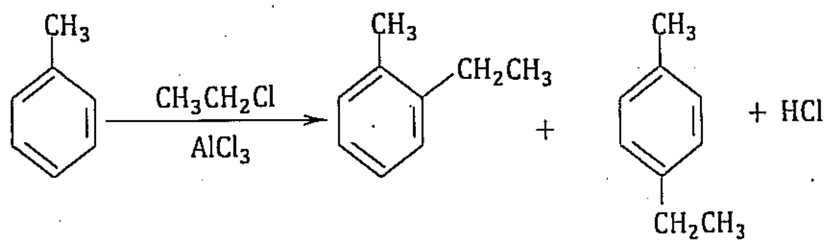
(i)



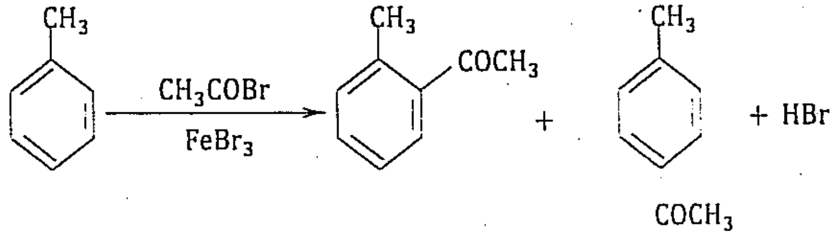
2 – Nitromethylbenzene
(*O – Nitromethylbenzene*)

4 – Nitromethylbenzene
(*p – Nitromethylbenzene*)

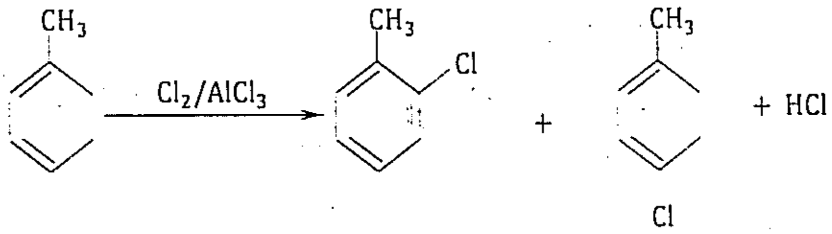
(ii)



(iii)



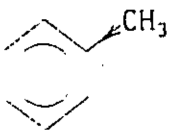
(iv)



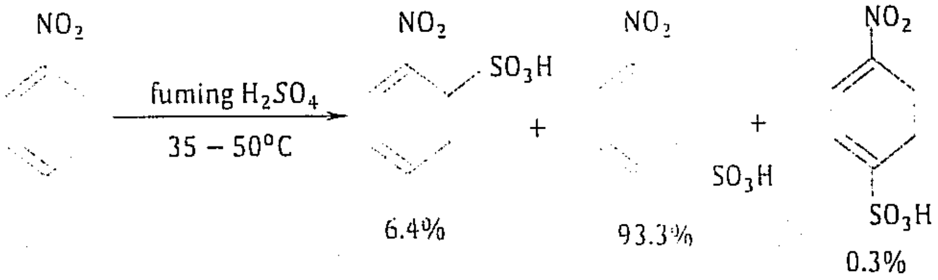
Note;

All the reactions above imply that the methyl group is an *ortho-*, *para-* directing group (2, 4-directing group).

Methylbenzene is more reactive than benzene because the methyl group donates electrons towards the benzene ring hence increasing its electron density making it more reactive towards electron deficient species (electrophiles).



On the other hand, if the sulphonation of methylbenzene shown earlier is instead done with nitrobenzene, the reaction is slower than for benzene and mainly the meta isomer (3-substituted isomer) is formed.



This implies that the nitro group is a *meta-* directing group (3- directing group).

Nitrobenzene is less reactive than benzene because the nitro group withdraws electrons from the benzene ring reducing its electron density hence making it less reactive towards electrophiles.

Therefore, any group atom or group of atoms attached to the benzene ring affects the reactivity of the benzene ring and determines the orientation of the substitution. When an electrophile attacks the benzene ring, it is the atom/ group of atoms attached to the ring that determine how fast and on what position the attack occurs.

A group that makes the benzene ring more reactive than benzene is an **activating group**.

A group that makes the benzene ring less reactive than benzene is a **deactivating group**.

Activating groups are mainly ortho- and para- directing and deactivating groups are mainly meta-directing.

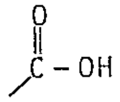
However, halogens, although withdraw electrons from the ring, are ortho- and para- directing.

More examples are given in the table below

Ortho- and para-directing groups (2- and 4- positions)	Meta-directing groups (3- position)
$-NH_2$ $-OH$ $-OCH_3, -OR$ $-NHR$ – Activating $-NR_2$ $-CH_2CH_3$ $-CH_3$	$-NO_2$ $-CN$ $-COOH$ $-SO_3H$ – Deactivating $-CHO$ $-COR$ $-COOR$
$-F$ $-Cl$ $-Br$ – Deactivating $-I$	

Note

For most of the groups deactivating the ring, the atom directly attached to the benzene ring usually has a double bond attached to it, i.e.,



$$-\overset{\overset{O}{\|}}{C}-OH$$

4.8.2.4 Some chemical properties of methylbenzene

Methylbenzene undergoes three types of reaction;

(a) Electrophilic substitution reactions

(b) Substitution in the methyl group

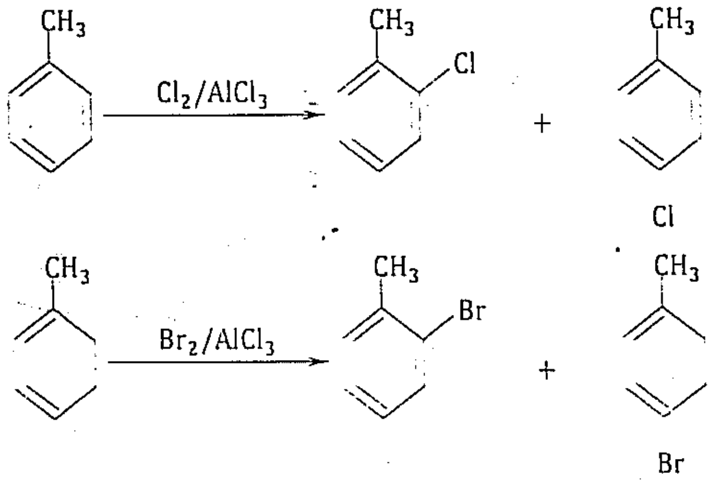
(c) Additional reactions

(a) Electrophilic substitution reactions

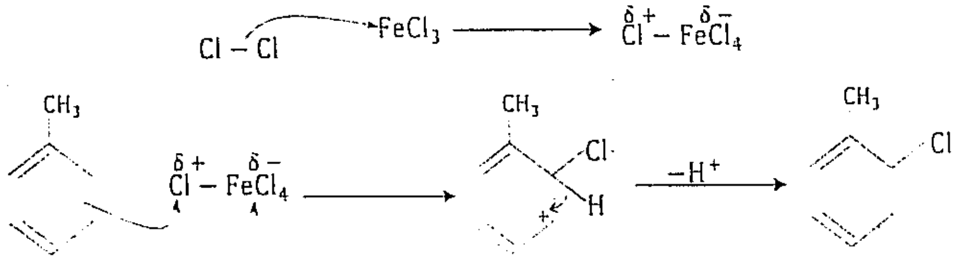
These reactions occur in the benzene ring. Methylbenzene reacts with all electrophilic reagents and in each reaction, it is more reactive than benzene. The substitution in the ring is easier than for benzene because the saturated methyl group is electron donating, activating the benzene ring and making the attack to occur in the 2 - and 4 – position.

(i) Halogenations in the ring

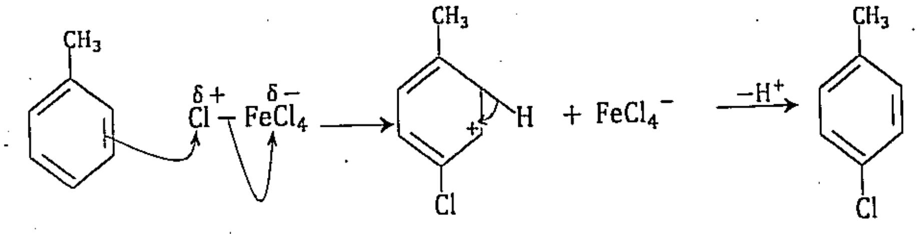
Methylbenzene reacts with chlorine or bromine in presence of iron(III) chloride or aluminium chloride catalyst at room temperature to form 2-chloromethylbenzene and 4-chloromethylbenzene for chlorine and analogous product for bromine



Mechanism



To form 4-chloromethylbenzene, the mechanism proceeds as follows:



$$FeCl_4^- + H^+ \longrightarrow FeCl_3 + HCl$$

(iii) *Nitration, sulphonation* and *Friedel-Crafts acylation* or *alkylation* of the ring occurs by similar mechanisms as for benzene, forming analogous products as for halogenation.

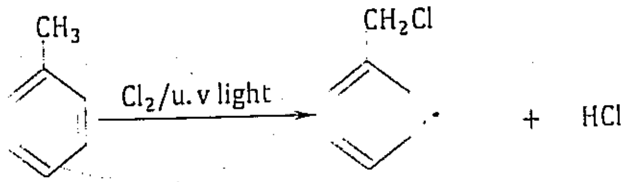
In all the reactions the 4-derivative tends to be yielded in a greater quantity because it is sterically the more favored product.

(b) Substitution in the methyl group

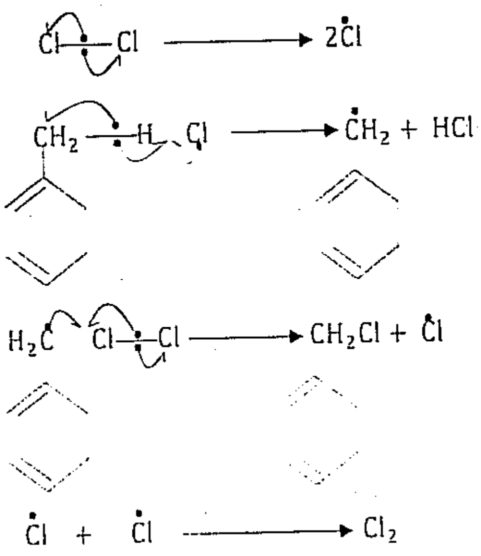
This proceeds via a free radical mechanism and is similar to the substitution in alkanes.

(i) Halogenations in the methyl group

When chlorine is bubbled through boiling methylbenzene in the presence of u.v light or strong sunlight, chloromethylbenzene is formed.

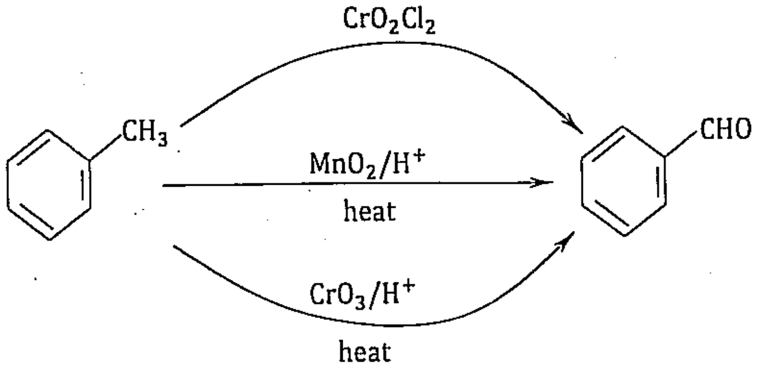


Mechanism

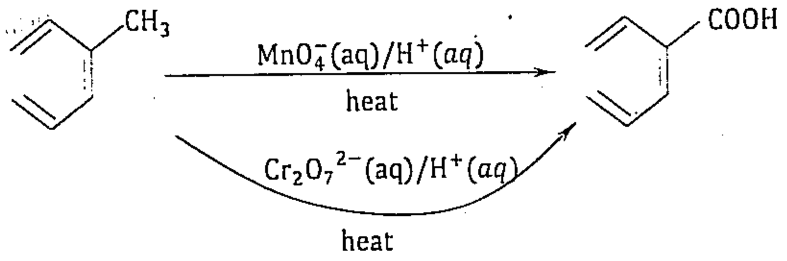


(ii) Oxidation of the methyl group

The methylbenzene can be oxidized to benzaldehyde using a mild oxidizing agent such as manganese(IV) oxide, chromium(VI) oxide or chromium(VI) dichloride dioxide (chromyl chloride).

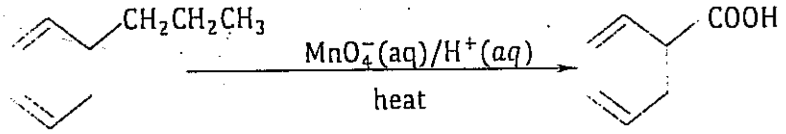


When a strong oxidizing agent is used, for example acidified potassium manganate(VII) solution, acidified potassium dichromate(VI) solution or dilute nitric acid for several hours then benzoic acid is formed.



Note

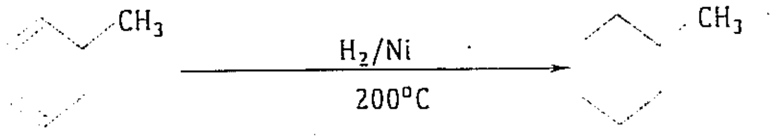
Any alkyl chain on the benzene ring other than methyl group on oxidation forms benzoic acid as well when acidified potassium manganate(VII) solution is used.



This reaction is used to distinguish benzene from methylbenzene. The purple solution turns colorless with methylbenzene and no observable change for benzene

(c) *Addition reactions*

Methylbenzene vapour reacts with hydrogen in presence of nickel catalyst at 200°C to form methyl cyclohexane.



4.9 Some synthesis problems

Write equations to show how the following conversions can be affected

(a) ethene to benzoic acid

(b) Ethyne to methylcyclohexane

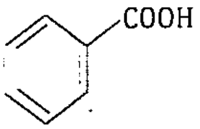
(c) Benzenediazonium chloride to methybenzene

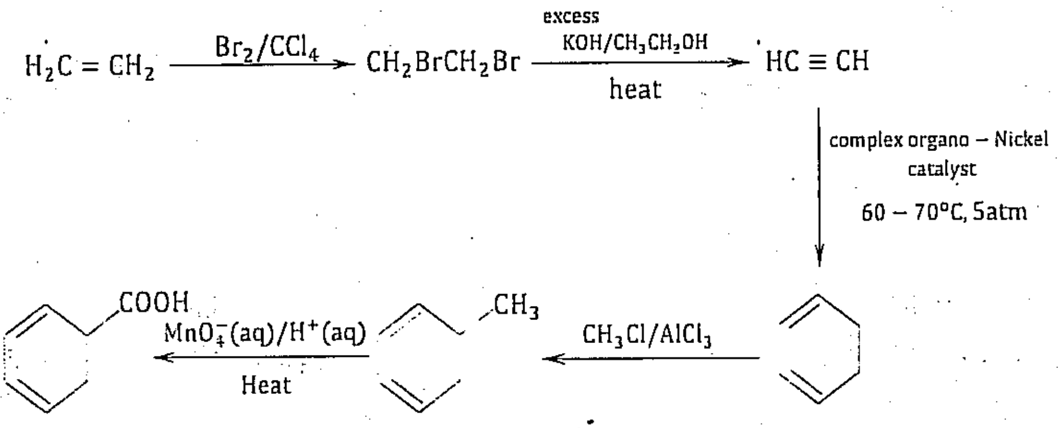
(d) Bromobenzene to phenylethanone

(e) Methylbenzene to benzenesuphonic acid.

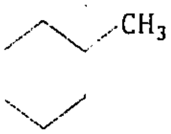
Answers

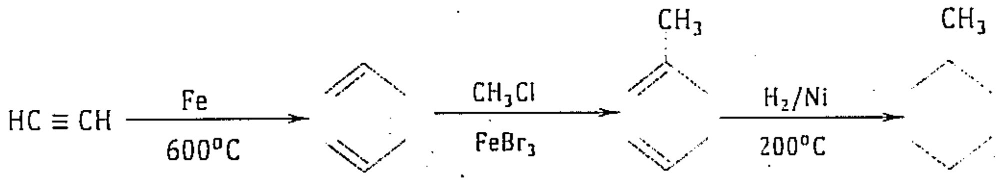
(a) $H_2C = CH_2$ to



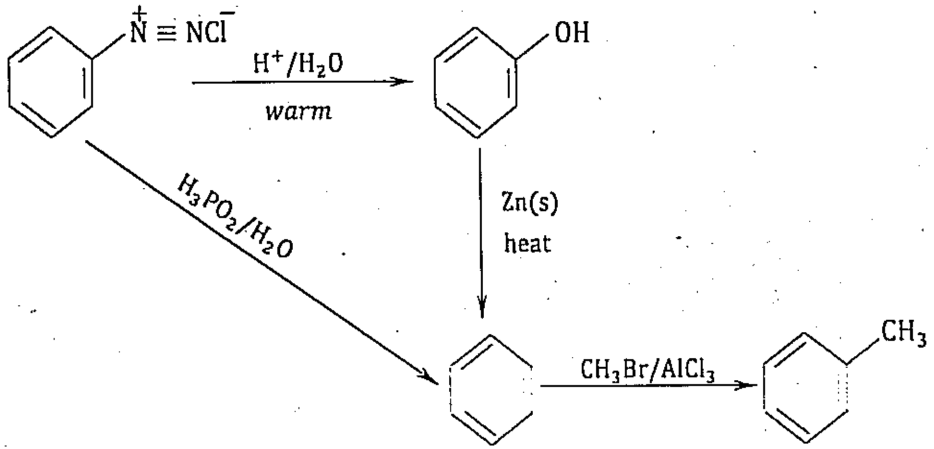


(b) $HC \equiv CH$ to

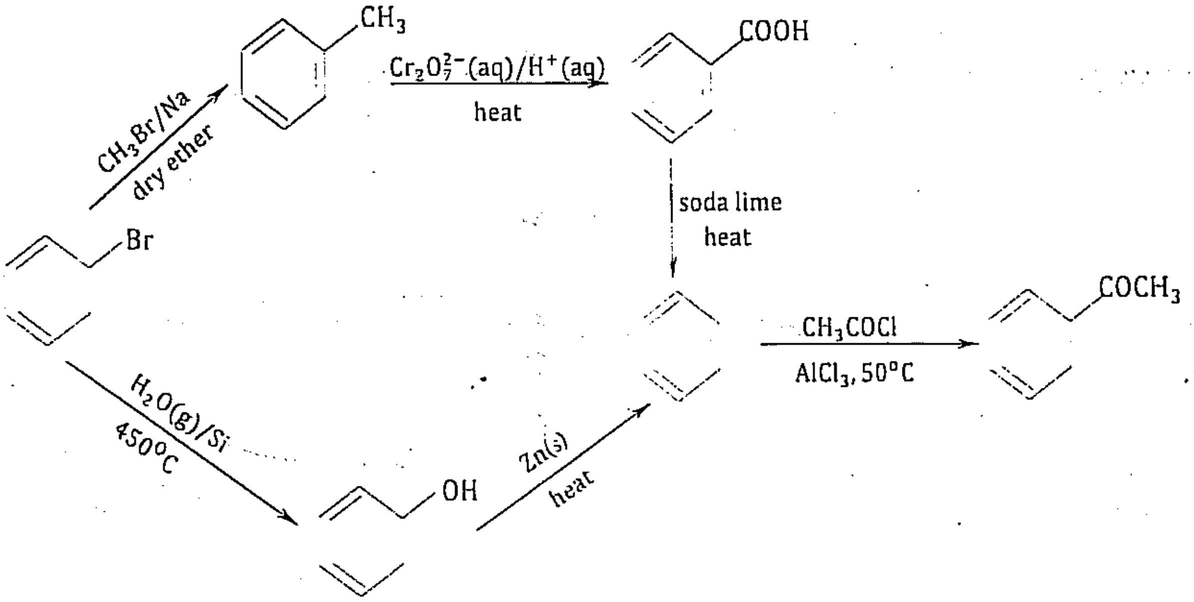




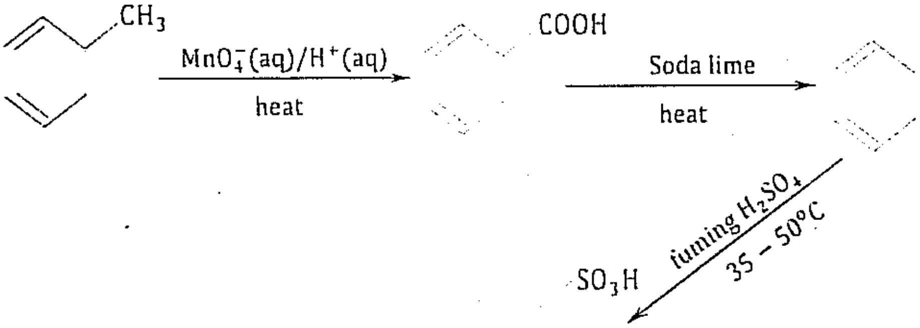
(c)


$\overset{+}{N} \equiv NCl^-$
H^+/H_2O
warm
OH
H_3PO_2/H_2O
Zn(s)
heat
$CH_3Br/AlCl_3$
CH_3

(d)


CH_3
$Cr_2O_7^{2-}(aq)/H^+(aq)$
heat
COOH
CH_3Br/Na
dry ether
Br
soda lime
heat
CH_3COCl
$AlCl_3, 50°C$
$COCH_3$
$H_2O(g)/Si$
450°C
OH
Zn(s)
heat

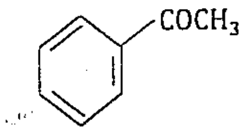
(e)

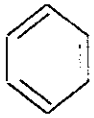

CH_3
$MnO_4^-(aq)/H^+(aq)$
heat
COOH
Soda lime
heat
fuming H_2SO_4
35 – 50°C
SO_3H

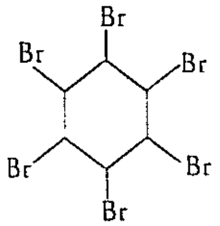
4.10 End of topic assessment exercise

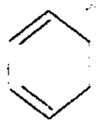
1. Write the accepted mechanisms for each of the following
   - (a) Light catalyzed chlorination of methylbenzene
   - (b) Sulphonation of benzene
   - (c) Nitration of benzene
   - (d) the iron(III) chloride catalyzed chlorination of benzene

2. Name the reagent(s) and condition(s) that can be used to effect the following changes.

(i)


from


(ii)


from


(iii)


from

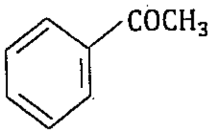

3. Explain each of the following observations
   - (a) Bromination of methylbenzene yields predominantly 2 - and 4 - products whereas bromination of benzaldehyde yields the 3-compound as major product.
   - (b) When liquid bromine was added to benzene there was no observable change. However, on addition of a small amount of anhydrous aluminium chloride, the reddish brown liquid turned colourless.
   - (c) Benzene does not easily undergo addition reactions but ethene easily does.

4. Describe how the following conversions can be effected (No equations are required)
   - (a) Propene to nitrobenzene
   - (b) Benzene to poly(phenylethene)
   - (c) Benzoic acid to chlorobenzene
   - (d) Ethyne to benzaldehyde
   - (e) Benzenesulphonic acid to benzene carbaldehyde
   - (f) Ethene to phenylethanone
   - (g) Phenol to benzoic acid
   - (h) Methylbenzene from benzene sulphonic acid.

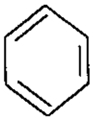
5. Write equations to show how the following conversions can be effected.

(a) Benzene from chlorobenzene

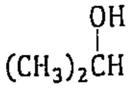
(b)



from



(c)



$(CH_3)_2\overset{\overset{OH}{|}}{C}H$ to phenol.

(d) Methylbenzene from chlorobenzene

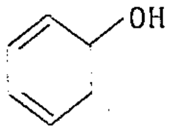
(e) Benzene from ethene

(f) Bromobenzene to benzoic acid

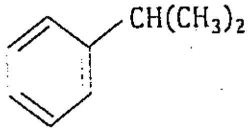
(g) Phenhylpropane to phenol

(i) Hydroxybenzene from bromobenzene

(j)



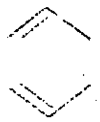
from



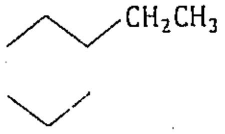
(k) Bromobenzene from phenol

(l) Nitrobenzene from Methylbenzene

(l)

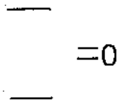


to



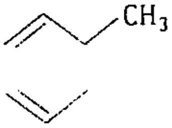
(m)

to

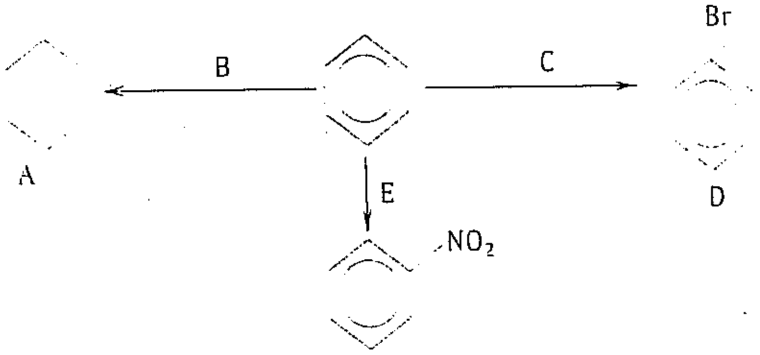


(n)

from



6. Below are some important reactions of benzene summarized

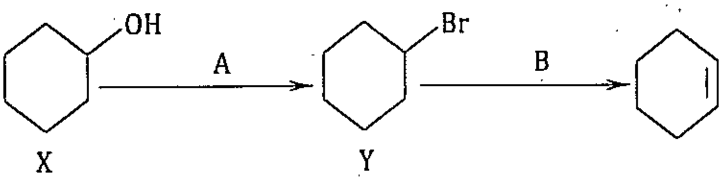


(a) Name the reagents /substances A to E

(b) Suggest the conditions used to form

(i) A (ii) D (iii) Nitrobenzene

(c) Cyclohexene can be prepared by the following



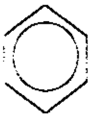
(i) Name the reagents A and B.

(ii) State the IUPAC names of X and Y.

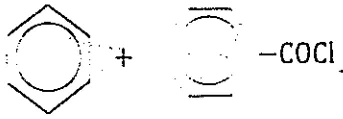
7. (a) Compare and contrast the reactions of propane and benzene with;
   - (i) bromine
   - (ii) suhlphuric acid

(b) Compare and contrast the reactions of cyclohexene and benzene with
   - (i) potassium manganate(VII)
   - (ii) Ethanoyl chloride

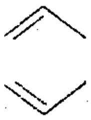
8. Complete each of the following equations and in each case, outline a mechanism for the reaction.

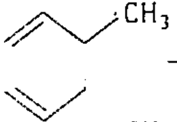
(a)  $\xrightarrow[\text{warm}]{\text{fuming } H_2SO_4}$

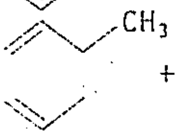
(b)  $+ \; CH_3COCl \xrightarrow{AlCl_3}$

(c)  $\xrightarrow{AlCl_3}$

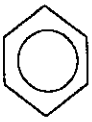
(d)  $+ \; CH_3COCl \xrightarrow{FeCl_3}$

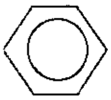
(e)  $\xrightarrow{CH_3I/AlCl_3}$

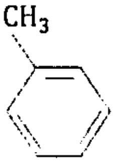
(f)  $\xrightarrow{Cl_2/\text{u.v light}}$

(g)  $+ \; CH_3CH = CH_2 \xrightarrow[AlCl_3]{HCl}$

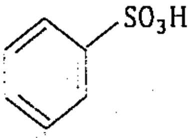
(h)  $\xrightarrow[\text{heat}]{Br_2/Fe}$

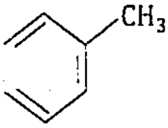
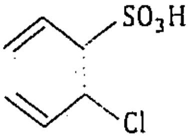
(i)  $\xrightarrow[\text{heat}]{Cl_2/Al}$

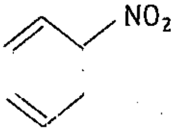
(j)  + Cl_2 $\xrightarrow{FeCl_3}$

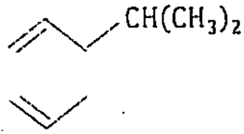
(k)  $\xrightarrow[60^\circ C]{\text{conc. } HNO_3/\text{conc. } H_2SO_4}$

9. Write a mechanism to show how each of the following conversions can be effected.

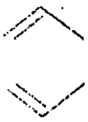
(a)  to 

(b)  to 

(c)  to 

(d)  to 

10. Name a reagent that can be used to distinguish the following pairs of compounds. In each case, state what is observed when each member is separately treated with the reagent and write equations for the reaction

(a)  and 

(b) Benzene and cyclohexene.

11. (a) Methylbenzene can react with chlorine under two different conditions to give different products. State the two conditions and write equation for the reaction between methyl benzene and chlorine under each condition.

(b) Suggest a mechanism for ashy one of the reactions above.

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12. (a) Methylbenzene reacts with chlorine to form 2-chloromethylbenzene. State the conditions for the reaction.

    (b) Under a different condition, the product is phenylchloromethane instead of 2 – chloromethylbenzene.

    (i) State the condition for the reaction

    (ii) Write the accepted mechanism for the reaction

13. The enthalpies of combustion of some substances are given below

Substance	$\Delta H_c(kJmol^{-1})$
Hydrogen	−242
Benzene	−3302
Cyclohexane	−3746
Cyclohexene	−3940

(a) Calculate the enthalpy of hydrogenation

(i) Cyclohexene (ii) Benzene

(b) Comment on the difference in the enthalpies of hydrogenation of cyclohexene and benzene you have calculated in(a) with reference to the structure of the two compounds.

14. $20cm^3$ of a hydrocarbon Z was exploded with $200cm^3$ of oxygen. On cooling to room temperature, the residual gases occupied $160cm^3$ when the residual gases were passed through sodium hydroxide solution, the volume reduced to $20cm^3$

(a) Write equation for the reaction between Z and oxygen

(b) Determine the molecular formula of Z.

(c) Compound Z burns with a sooty flame. When Z was treated with hot alkaline potassium manganese(VII) solution followed by dilute hydrochloride acid, compound T was formed. T reacts with magnesium ribbon liberating hydrogen gas

(i) Identify Z and T.

(d) Write equation to show how T can be obtained from an alkyne.

15. An organic compound T, on complete combustion yielded 13.2g of carbon dioxide and 2.7g of water. When 4.7g of T was vaporized at standard temperature and pressure, it occupier a volume of $2.7x10^{-3} m^3$.

(a) (i) Calculate the empirical formula of T.

(ii) Determine the molecular formula of T.

(b) T burns with a sooty flame. Identify T.

(c) Discuss the reactions of T with;

(i) Bromine

(ii) Propene

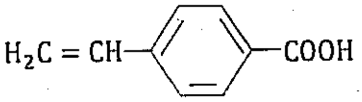
(iii) Ethanoylchloride

(iv) Nitric acid

(Your answer should include conditions for the reactions and mechanisms for the reactions where applicable)

(d) Write equation to show how T can be synthesized from benzaldehyde.

16. An organic compound, R has the structure



(a) Name the functional groups in R.

(b) State what is observed and write equation of reaction in each case that takes place when R is

  (i) treated with a cold aqueous solution of potassium manganate(VII).

  (ii) heated strongly with sodium

Chapter 5

Halohydrocarbons

5.1 Introduction

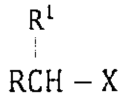
Halohydrocarbons are halogen derivatives of organic compounds. They can be alkyl halides or aryl halides.

Alkyl halides are all compounds with the general formula $R-X$, if they are monohalo-substituted, where R is an alkyl group and $X = (F, Cl, Br \text{ or } I)$. However, the general formula of monohalo-substituted alkyl halides may be written as $C_nH_{2n+1}X$. In all alkyl halides, the halogen atom is attached to a saturated carbon atom.

Alkyl halides can be classified as primary, secondary or tertiary, depending on the number of alkyl groups attached to the carbon atom bonded to the halogen atom.

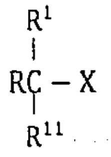
RCH_2-X

Primary alkylhalide



$\begin{array}{c} R^1 \\ | \\ RCH-X \end{array}$

Secondary alkylhalide



$\begin{array}{c} R^1 \\ | \\ RC-X \\ | \\ R^{11} \end{array}$

Tertiary alkylhalide

Alkyl halides can be unsaturated alkyl halides when the halogen atom is attached to a carbon atom which forms a double or triple bond or attached to a carbon atom which forms part of an alkyl chain having a double or triple bond. For example,

$$RCH=CHCl, \quad RC\equiv CCl, \quad \text{and} \quad RCH=CHCH_2Cl$$

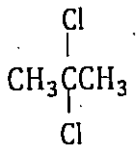
There are also polyhalides, in which more than one halogen atom is attached to the carbon chain. Examples include, trichloromethane ($CHCl_3$), $CH_2BrCH_2CH_2Cl$, $CH_3CHBrCH_2CH_2Cl$, etc.

Polyhalides with two halogen atoms (dihalides) can be *vicinal dihalides* or *germinal dihalides*. Vicinal dihalides are those in which the halogen atoms are attached to adjacent carbon atoms. For example,

CH_2BrCH_2Br (1,2 – Dibromoethane)

$CH_3CHBrCH_2Br$ (1,2 – Dibromopropane)

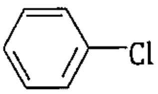
Germinal dihalides are those in which the halogen atoms are attached to the same carbon atom. For example,

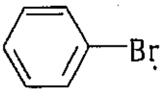


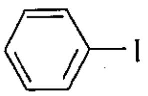
$CH_3C(Cl)_2CH_3$ 2,2 – Dichloropropane

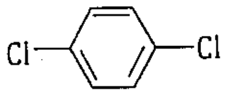
CH_3CHCl_2 1,1 – Dichloroethane

Aryl halides are compounds in which the halogen atom is directly attached to an aromatic ring. Their general formula is ArX where 'Ar' is an aryl group. Examples include

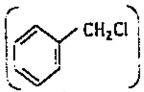






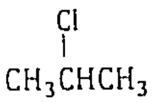
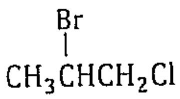
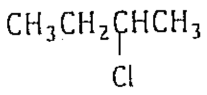


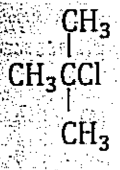
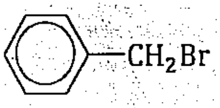
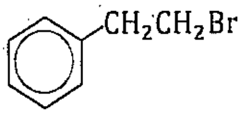
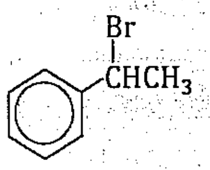
Note

Haloalkanes like chroromethylbenzene  and similar compounds in which the halogen atom is not attached directly to the ring are phenyl substituted haloalkanes but not aryl halides.

5.2 Nomenclature

The names of alkyl halides are derived from the corresponding alkanes and a number is used to indicate the position of halogen atom in the carbon chain. For example

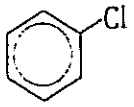
Chemical Formula	*IUPAC name*
CH_3Cl	Chloromethane
CH_3CH_2Br	Bromoethane
$CH_3CH_2CH_2I$	1-Iodopropane
 $CH_3CH(Cl)CH_3$	2-Chloropropane
 $CH_3CH(Br)CH_2Cl$	2-Bromo-1-chloropropane
 $CH_3CH_2CH(Cl)CH_3$	2-Chlorobutane

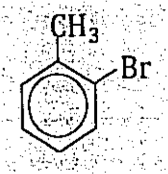
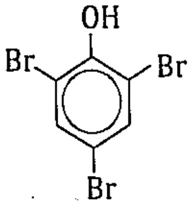
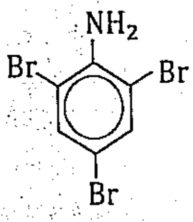
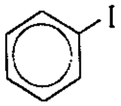
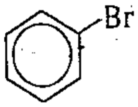
$(CH_3)_3CCl$ or  $CH_3\overset{CH_3}{\underset{CH_3}{CCl}}$	2-Chloro-2-methylpropane
CHI_3	Tri-iodomethane
	Bromomethylbenzene
	2-Phenylbromoethane
	1-Bromo-1-phenylethane

Unsaturated alkyl halides are generally named as derivatives of the corresponding alkenes or alkynes. For example,

Chemical Formula	*IUPAC name*
$H_2C = CHCl$	Chloroethene
$H_2C = CHCH_2CH_2Br$	4-Bromobut-1-ene

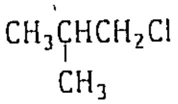
Aryl halides are named as halogen derivatives of the aromatic compound.

Chemical Formula	*IUPAC Name*
	Chlorobenzene
	4-Chloromethylbenzene

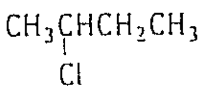
	2-Bromomethylbenzene
	2,4,6-Tribromophenol
	2,4,6-Tribromophenylamine
	Iodobenzene
	Bromobenzene

5.3 Isomerism of halohydrocarbons

Alkyl halides exhibit two types of isomerism. These include **chain isomerism** and **positional isomerism**. The chain isomers differ by arrangement of carbon atoms but have the same position of the halogen atom. The position isomers differ by the position of the halogen atom on the carbon chain. For example C_4H_9Cl has the following isomers

$CH_3CH_2CH_2CH_2Cl$	1 – Chlorobutane
 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2Cl$	1 – Chloro – 2 – methylpropane

The two above are chain isomers.

$CH_3CH_2CH_2CH_2Cl$	1 – Chlorobutane
 $CH_3\underset{\underset{Cl}{\vert}}{C}HCH_2CH_3$	2 – Chlorobutane

The three above are position isomers.

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5.4 Physical properties

(a) Solubility

Alkyl halides are insoluble in water but very soluble in the typical organic solvents. Although their carbon-halogen bonds are polar, they cannot form hydrogen bonds with water.

(b) Density

Alkyl halides are less dense than water. This is due to the closer packing of their relatively smaller molecules in liquid phase. However, alkyl bromides and alkyl iodides are all denser than water.

(c) Boiling points

(i) Haloalkanes have relatively higher boiling points than alkanes of comparable relative molecular mass. This is because, in the haloalkanes, the halogen atom is **more electronegative** than the carbon atom. This makes the **carbon-hydrogen bond polar**, enhancing **dipole-dipole interaction in the liquid phase.** However, the **carbon-hydrogen bonds in alkanes are non-polar.**

(ii) Haloalkanes also have higher boiling points than alkanes with the same number of carbon atoms. For example, Bromoethane (CH_3CH_2Br) boils at 38°C whereas ethane (CH_3GH_3) boils at −89°C. This is because bromoethane has a larger molecular size and larger molecular mass than ethane hence stronger van der waals forces of attraction that require higher amount of energy to break.

(iii) For a given halogen atom, attached to different alkyl groups, boiling point increases as the length of the alkyl group increases. For example,

Compound	CH_3Cl	CH_3CH_2Cl	$CH_3CH_2CH_2Cl$	$CH_3CH_2CH_2CH_2Cl$
Boiling point (°C)	−24.0	12.5	47.0	78.5

Boiling point **increases from Chloromethane to Chloroethane to Chloropropane** to Chlorobutane. This is because the Chloroalkanes are held by **van der waal's forces of attraction whose strength increases with the increase in molecular weight** and molecular size.

(iv) For a given alkyl group, the boiling point increases with increase in atomic mass of the halogen atom. For example,

Compound	CH_3F	CH_3Cl	CH_3Br	CH_3I
Boiling point (°C)	−78.4	−24.0	5.0	43.0

Boiling point **increases from fluoromethane to chloromethane to bromomethane to iodomethane.** This is because the **atomic radius of the halogen atoms increases** in the order F < Cl < Br < I. Molecular size and **molecular mass of alkyl halides increases** hence magnitude of van der waal's forces of attraction holding the **molecules increases.**

(v) The boiling points of aryl halides correspond closely with haloalkanes of comparable relative molecular mass.

(d) Physical state

Chloromethane (CH_3Cl), chloroethane(CH_3CH_2Cl) and bromoethane(CH_3CH_2Br) are colourless gases at room temperature. The other members are colourless liquids with a sweet smell.

5.5 Methods of preparation

(i) From alkanes

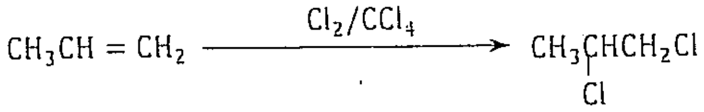
Alkylchlorides can be formed by refluxing alkanes with sulphur dichloride dioxide (sulphuryl chloride) at 40 – 80C using di(benzoyl) peroxide catalyst. For example,

$$CH_3CH_3 \xrightarrow[40-80^\circ C]{SO_2Cl_2/\text{di(benzoyl)peroxide}} CH_3CH_2Cl$$

$$CH_3CH_2CH_3 \xrightarrow[40-80^\circ C]{SO_2Cl_2/\text{di(benzoyl)peroxide}} CH_3CH_2CH_2Cl$$

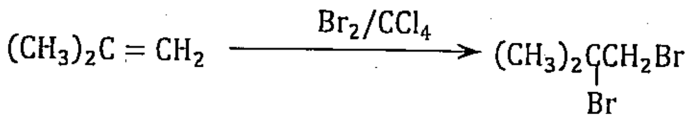
(ii) From alkenes

(a) Chlorine reacts with alkenes in presence of tetrachloromethane to form vicinal dichlorides. For example,

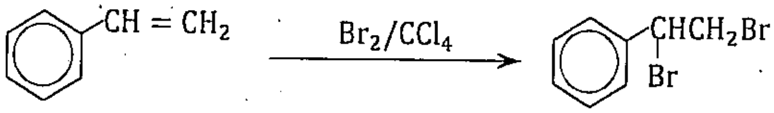


$$CH_3CH=CH_2 \xrightarrow{Cl_2/CCl_4} CH_3\underset{Cl}{C}HCH_2Cl$$

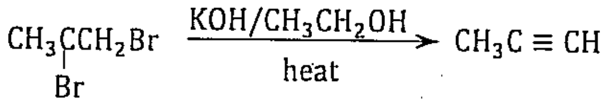
(b) Bromine also reacts with alkenes in a similar way.



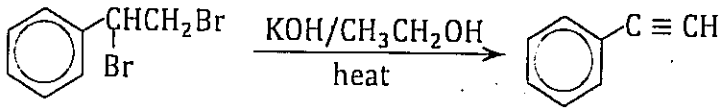
$$(CH_3)_2C = CH_2 \xrightarrow{Br_2/CCl_4} (CH_3)_2\underset{\underset{Br}{|}}{C}CH_2Br$$



The vicinal dihalides formed are useful to synthesize alkynes as shown below.

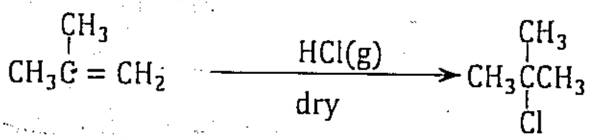


$$CH_3\underset{\underset{Br}{|}}{C}CH_2Br \xrightarrow[\text{heat}]{KOH/CH_3CH_2OH} CH_3C \equiv CH$$



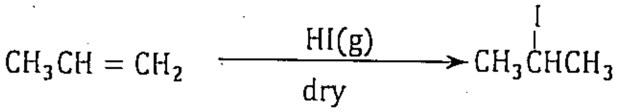
(c) Alkenes can also be converted to alkylhalides by passing dry gaseous hydrogen halides into them. Sometimes a moderately polar solvent, ethanoic acid can be used.

Examples include



$$CH_3\overset{\overset{CH_3}{|}}{C} = CH_2 \xrightarrow[\text{dry}]{HCl(g)} CH_3\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$$

$$H_2C = CH_2 \xrightarrow[\text{dry}]{HBr(g)} CH_3CH_2Br$$



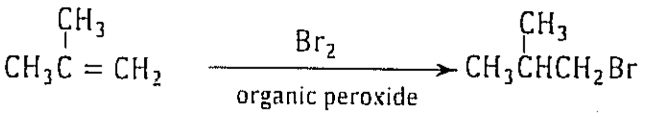
$$CH_3CH = CH_2 \xrightarrow[\text{dry}]{HI(g)} CH_3\overset{\overset{I}{|}}{C}HCH_3$$

Note

All the above three reactions are in accordance to Markownikoff's rule.

If for hydrogen bromide, an organic peroxide is used, the reactions proceed via Anti-Markownikoff addition for unsymmetrical alkenes, i.e.

$$CH_3C = CH_2 \xrightarrow[\text{organic peroxide}]{Br_2} CH_3CH_2CH_2Br$$



$$CH_3\overset{\overset{CH_3}{|}}{C} = CH_2 \xrightarrow[\text{organic peroxide}]{Br_2} CH_3\overset{\overset{CH_3}{|}}{C}HCH_2Br$$

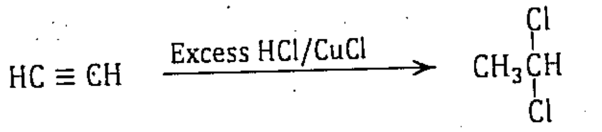
(iii) From alkynes

(a) Ethyne can be converted to 1,1,2,2 – Tetrahaloethanes in presence of Kieselguhr (Silicon(IV) oxide) catalyst and iron filings at ordinary temperatures.

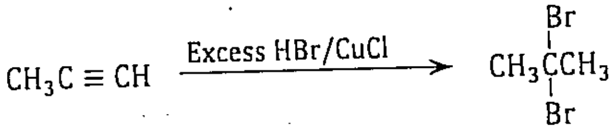
$$HC \equiv CH \xrightarrow{\text{Excess } Cl_2/SiO_2/Fe} CHCl_2CHCl_2$$

$$HC \equiv CH \xrightarrow{\text{Excess } Br_2/SiO_2/Fe} CHBr_2CHBr_2$$

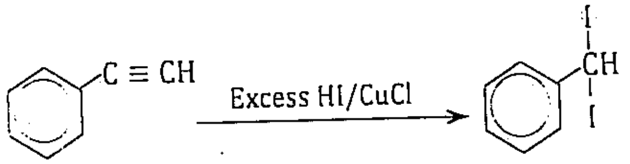
(b) Germinal dihalides can also be formed by reacting alkynes with hydrogen halides in presence of light or metal halide catalysts (HgCl or CuCl) in gaseous phase.



$$HC \equiv CH \xrightarrow{\text{Excess HCl/CuCl}} CH_3\overset{\overset{\large Cl}{|}}{\underset{\underset{\large Cl}{|}}{C}}H$$



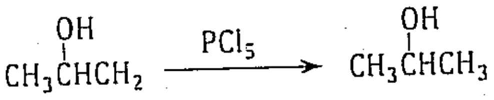
$$CH_3C \equiv CH \xrightarrow{\text{Excess HBr/CuCl}} CH_3\overset{\overset{\large Br}{|}}{\underset{\underset{\large Br}{|}}{C}}CH_3$$



(iv) From alcohols

(a) Chloroalkanes can be formed by reacting alcohols with phosphorus(V) chloride.

$$CH_3CH_2CH_2OH + PCl_5 \longrightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl$$



$$CH_3\overset{\overset{\large OH}{|}}{C}HCH_2 \xrightarrow{PCl_5} CH_3\overset{\overset{\large OH}{|}}{C}HCH_3$$

In both cases, dense white fumes of hydrogen chloride are observed.

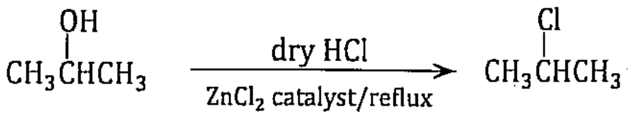
Chloroalkanes can also be formed by refluxing alcohols with sulphur dichloride oxide (thionyl chloride) in the presence of pyridine in small amounts to absorb hydrogen chloride formed.

$$CH_3CH_2CH_2OH \xrightarrow[\text{Pyridine/reflux}]{SOCl_2} CH_3CH_2Cl$$

$$(CH_3)_3C-OH \xrightarrow[\text{Pyridine/reflux}]{SOCl_2} (CH_3)_3C-Cl + SO_2 + HCl$$

Similarly, chloroalkanes can be formed by reacting alcohols with dry hydrogen chloride in the presence of anhydrous zinc chloride.

$$CH_3CH_2OH \xrightarrow[\text{ZnCl}_2\text{ catalyst/reflux}]{\text{dry HCl}} CH_3CH_2Cl$$



$$CH_3CH(OH)CH_3 \xrightarrow[\text{ZnCl}_2\text{ catalyst/reflux}]{\text{dry HCl}} CH_3CH(Cl)CH_3$$

For tertiary alcohols, the reaction occurs readily in presence of water and concentrated hydrochloric acid can be used.

$$(CH_3)_3C-OH \xrightarrow{\text{conc. HCl}} (CH_3)_3C-Cl$$

(b) Alkylbromides can be formed by treating tertiary alcohols with a mixture of red phosphorus and bromine.

$$2P + 3Br_2 \xrightarrow{\text{heat}} 2PBr_3$$

$$(CH_3)_3C-OH \xrightarrow{PBr_3} (CH_3)_3C-Br$$

Similarly, the tertiary alcohols may be treated with hydrogen bromide (which is prepared in situ from sodium bromide and concentrated phosphonic acid).

$$(CH_3)_3C-OH \xrightarrow[\text{heat}]{\text{NaBr/conc. }H_3PO_4} (CH_3)_3C-Br$$

Note

For primary alcohols, the two reactions do not occur easily and require refluxing.

$$CH_3CH_2OH \xrightarrow[\text{reflux}]{PBr_3} CH_3CH_2Br$$

$$CH_3CH_2OH \xrightarrow[\text{reflux}]{\text{NaBr/conc. }H_3PO_4} CH_3CH_2Br$$

(c) **Alkyliodides**

Alkyliodides can be formed by adding iodine to a mixture of an alcohol and red phosphorus and then refluxing on a water bath.

$$2P + 3I_2 \xrightarrow{\text{heat}} 2PI_3$$

$$CH_3CH_2OH \xrightarrow[\text{reflux}]{PI_3} CH_3CH_2I$$

Alkyliodides can also be prepared by treating an alcohol with concentrated hydrogen iodide. The hydrogen iodide is prepared in situ from phosphoric acid and potassium iodide.

$$3KI + H_3PO_4 \xrightarrow{\text{heat}} 3HI + K_3PO_4$$

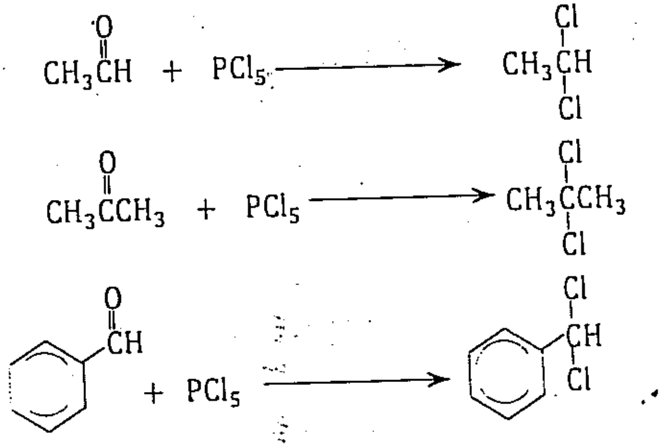
$$CH_3CH_2OH \xrightarrow{HI} CH_3CH_2I$$

Note

Sulphuric acid cannot be used with the potassium iodide because the hydrogen iodide formed is a powerful reducing agent hence would be oxidised to iodine.

(v) From aldehydes and ketones

Under anhydrous conditions, aliphatic and simple aromatic carbonyl conpounds react with phosphorus pentachloride to form germinal dichlorides.



$$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2$$

$$CH_3COCH_3 + PCl_5 \longrightarrow CH_3CCl_2CH_3$$

(vi) Using the halide exchange reaction.

Iodoalkanes can suitably be prepared using this method.

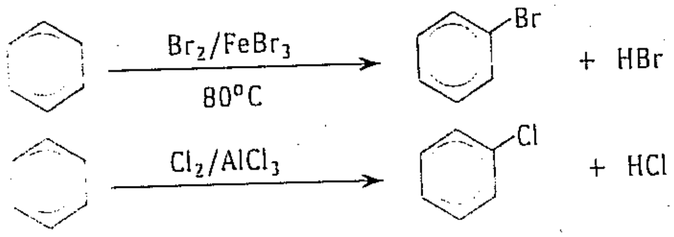
A bromoalkane is heated with a solution of sodium iodide in propanone.

$$CH_3CH_2Br \xrightarrow[CH_3COCH_3]{NaI} CH_3CH_2I$$

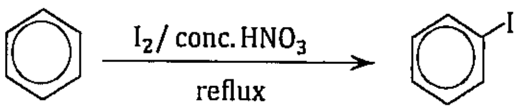
Aryl halides can also be formed by the following methods:

(a) Direct halogenation of benzene

Chlorobenzene and bromobenzene are prepared by reaction of benzene with chlorine and bromine respectively.

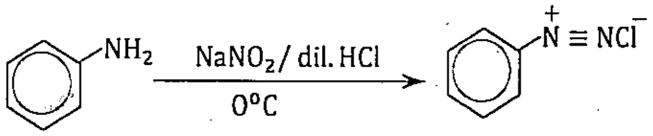


Iodination of benzene is done by refluxing benzene with iodine and concentrated nitric acid.

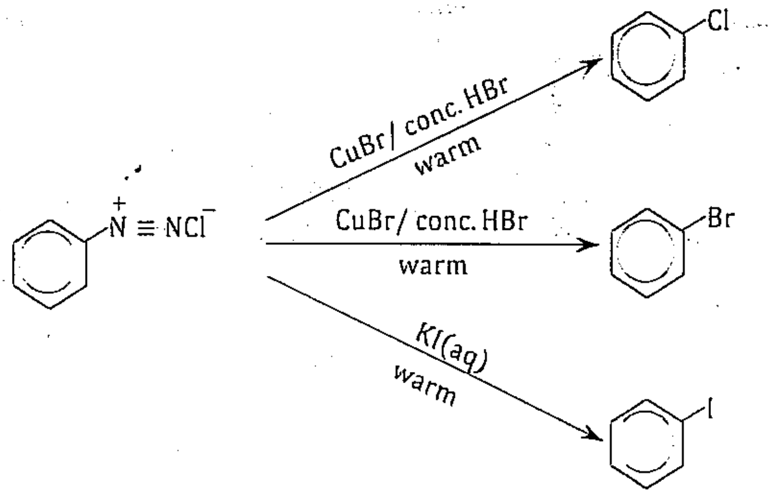


(b) Replacement of a diazonium salt (Sandmeyer reaction)

The diazonium salt is formed by reacting a primary aromatic amine with nitrous acid is prepared in situ from sodium nitrite and dilute hydrochloric acid and the reaction is carried out at 0°C,



Chlorobenzene and bromobenzene are then obtained from benzenediazonium chloride when it is warmed with copper(I) chloride and copper(I) bromide dissolved in the appropriate concentrated hydrochloric acid and hydrobromic acid respectively.
Iodobenzene is obtained when the diazonium salt is warmed with an aqueous solution of potassium iodide.



5.6 Chemical properties of halohydrocarbons

5.6.1 Nucleophilic substitution reactions (S_N)

Haloalkanes are fairly reactive due to the polarity of the carbon-halogen bond.

$$(\overset{\delta+}{R} - \overset{\delta-}{X})$$

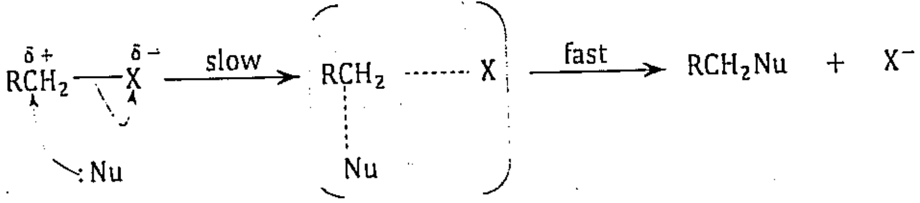
In most of their reactions, they act as electrophilic reagents with the electron deficient carbon in them susceptible to attack by nucleophiles. Therefore, they mostly undergo nucleophilic substitution reactions.

A nucleophilic substitution reaction is therefore a reaction in which an atom in a compound is replaced by an atom or group of atoms which is electron rich (nucleophilic).

Haloalkanes easily undergo nucleophilic substitution reactions because the halogen atom in the haloalkane is more electronegative than the carbon atom. The halogen atom therefore attracts the bonding electrons more towards itself, gaining a partial negative charge and the carbon atom gains a partial positive charge. This makes the carbon – halogen bond polar. The nucleophile is attracted to the carbon atom with a partial positive charge, eventually replacing the halogen atom.

$$RCH_2X + Nu \longrightarrow RCH_2Nu + X^-$$

Where *Nu* is a nucleophile.



Arylhalides do not easily undergo nucleophilic substitution reaction as we shall explain later.

Alkylhalides can undergo two types of nucleophilic substitution reactions namely:

(i) Substitution nucleophilic bimolecular (S_{N2})

(ii) Substitution nucleophilic unimolecular (S_{N1})

(i) Substitution nucleophilic bimolecular (S_{N2}) reaction

The stage of a reaction that involves formation of intermediates before the final product is called the *rate determining step*.

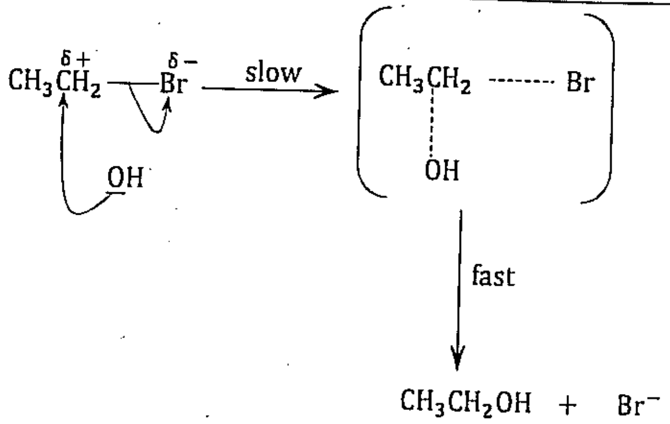
A substitution nucleophilic bimolecular reaction in which the halogen atom in an alkylhalide is replaced by a nucleophile and both the nucleophile and the alkylhalide are involved in the rate determining step. This type of reaction is undergone by primary alkylhalides.

Consider the reaction for alkaline hydrolysis of bromoethane.

$$CH_3CH_2Br \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2OH + NaBr$$

Mechanism

$$NaOH(aq) \longrightarrow Na^+(aq) + \bar{O}H(aq)$$



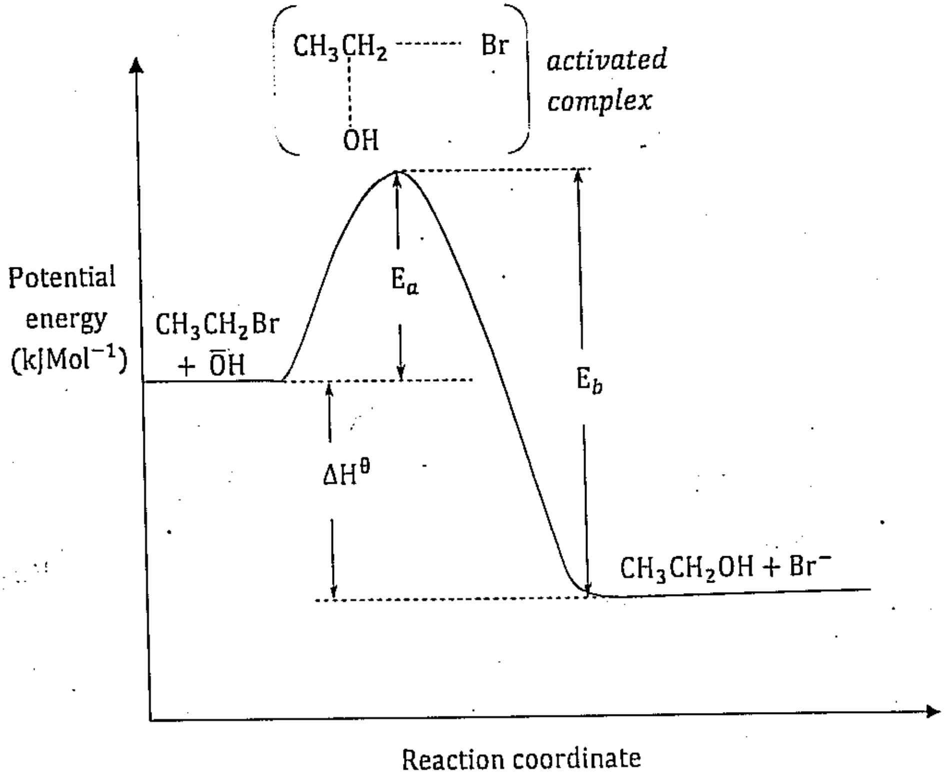
$$Na^+ + Br^- \longrightarrow NaBr$$

Explanation

The nucleophile (hydroxide ion) approaches the partial positive carbon atom of the C – Br bond from the opposite side of the halogen atom. As this happens, the nucleophile begins to form a bond with the carbon atom while the bond between the carbon atom and the bromine atom begins to break. The pair of electrons which forms the new bond is supplied by the hydroxide ion and the pair of electrons in the C – Br bond is gradually acquired completely by the bromine atom. Eventually the new bond is fully formed and C – Br bond is completely broken.

The changes in energy during the SN$_2$ reaction can be represented on an energy profile/enthalpy profile/reaction profile or potential energy diagram. This is usually a sketch of potential energy against reaction coordinate/reaction pathway.

Reaction profile for substitution nucleophilic bimolecular reaction



- This reaction is exothermic.
- Ea is the activation energy for the reaction (also called the energy barrier).
- Eb is the activation energy for the backward reaction.
- ΔH^θ is the enthalpy of reaction.
- Activation energy is the minimum energy which is required to be possessed by reactants in order to react to form products.
- Activation complex is the intermediate unstable compound formed immediately once the reactants have absorbed the activation energy available. This unstable compound undergoes bond re-organisation by releasing some of the energy to form the final stable product. The activated complex can also be called a transition state.

Other nucleophilic reagents which possess at least one unshared pair of electrons can replace the hydroxide ion in this reaction.

In general, the rate of the above S_N2 reaction depends on both the concentration of the alkylhalide and the concentration of the hydroxide ions.

$$\text{Rate} = k[CH_3CH_2Br][\bar{O}H]$$

Since two species CH_3CH_2Br and $\bar{O}H$ are involved in the rate determining step, the reaction is bimolecular (has molecularity of two) hence the name substitution nucleophilic bimolecular. It follows second order kinetics.

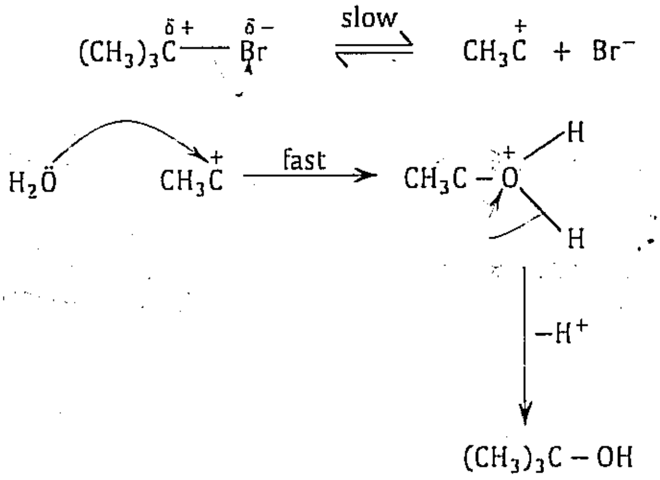
(i) Substitution nucleophilic unimolecular (S_{N1}) reaction

A substitution nucleophilic unimolecular reaction is a reaction in which the halogen atom in a teratiary alkylhalide is replaced by a nucleophile and only the tertiary alkylhalide is involved in the rate determining step. Only tertiary alkylhalides undergo this type of reaction.

Consider the reaction for hydrolysis of tertiary alkylhalides.

$$(CH_3)_3C-Br \xrightarrow[\text{boil}]{H_2O} (CH_3)_3C-OH + HBr$$

Mechanism



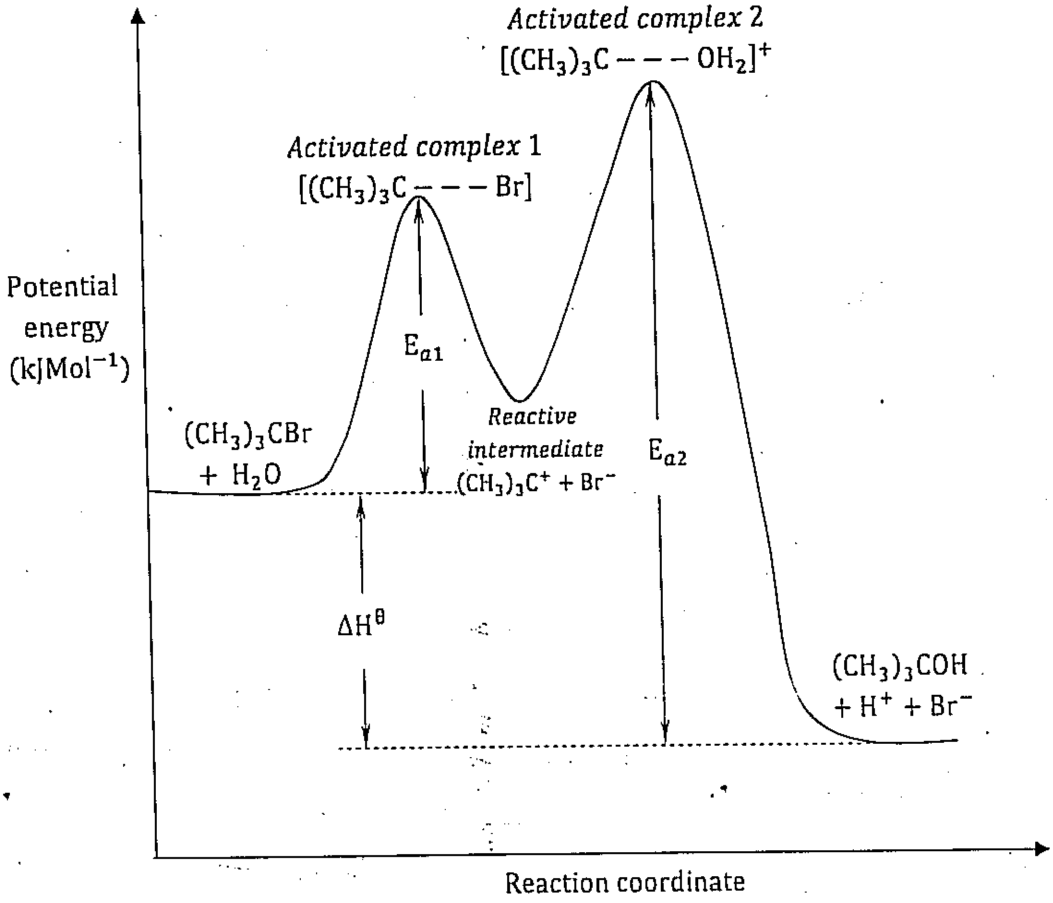
Explanation

The tertiary alkylhalide (2-Bromo-2-methylpropane) ionises spontaneously in solution to form a carbonium ion (carbocation) and a bromide ion. This is the slow rate determining step and involve only the alkylhalide. The carbocation formed is very reactive and is attacked by the nucleophile (water) to form an alcohol. The carbocation can either revert to the reactants by recombining with the bromide ion or form the alcohol by reacting with the nucleophile. Both the two steps are fast and although the recombination with bromine ion has lower activation energy (see reaction profile below), the nucleophile is present in a much higher concentration than bromide ion.

The changes in energy during the S_{N1} reaction can be represented on an energy profile/enthalpy profile/reaction profile or potential energy diagram shown below.

Reaction profile for substitution nucleophilic unimolecular reaction

This reaction proceeds via a reactive intermediate. The reactive intermediate is preceded and also followed by a transition state.



- This reaction is also exothermic.
- Ea_1 is the activation energy for the first step.
- Ea_2 is the activation energy for the second step.
- ΔH^θ is the enthalpy of reaction.

In general, the rate of the above S_{N1} reaction depends only on the concentration of the alkylhalide.

$$\text{Rate} = k[(CH_3)_3CBr]$$

Since only the alkylhalide is involved in the rate determining step, the reaction is unimolecular (has molecularity of one) hence the name substitution nucleophilic unimolecular.

It follows first order kinetics.

This difference in substitution reaction mechanisms of tertiary and primary alkylhalides arises because the tertiary carbonium ion is relatively more stable than a primary carbonium ion.

Secondary alkylhalides like 2-bromopropane are intermediate in behaviour between primary and tertiary alkylhalides. They react partly by S_{N2} reaction and partly by the S_{N1} reaction. However, the second order kinetics (S_{N2} mechanism) predominates.

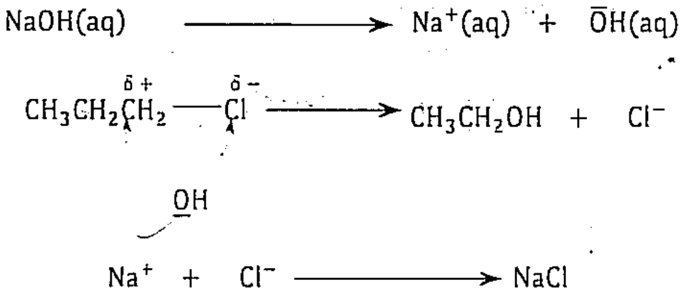
5.6.2 Nucleophilic substitution reactions of alkylhalides

(a) Alcohol formation

On heating, alkylhalides react with sodium hydroxide to form alcohols.
Primary alkylhalides form primary alcohols and the reaction is S_{N2}.
For example,

$$CH_3CH_2CH_2Cl \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2CH_2OH + NaCl$$

<u>Mechanism</u>



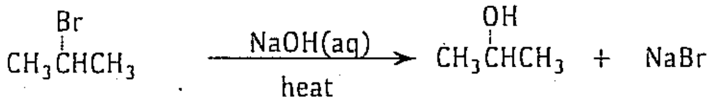
$$NaOH(aq) \longrightarrow Na^+(aq) + \bar{O}H(aq)$$

$$CH_3CH_2\overset{\delta+}{C}H_2 - \overset{\delta-}{Cl} \longrightarrow CH_3CH_2OH + Cl^-$$

$$\bar{O}H$$

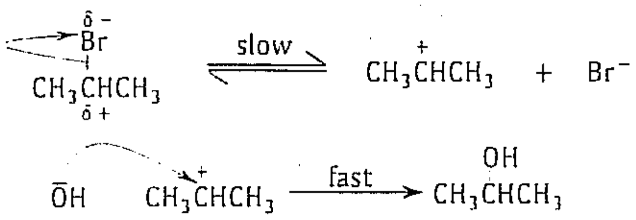
$$Na^+ + Cl^- \longrightarrow NaCl$$

Secondary alkylhalides under similar conditions form secondary alcohols.



$$CH_3\overset{Br}{C}HCH_3 \xrightarrow[\text{heat}]{NaOH(aq)} CH_3\overset{OH}{C}HCH_3 + NaBr$$

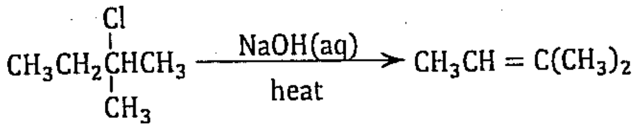
The reaction is mainly S_{N1}.



$$CH_3\underset{\delta+}{\overset{\overset{\delta-}{Br}}{C}}HCH_3 \underset{}{\overset{\text{slow}}{\rightleftharpoons}} CH_3\overset{+}{C}HCH_3 + Br^-$$

$$\bar{O}H \quad CH_3\overset{+}{C}HCH_3 \xrightarrow{\text{fast}} CH_3\overset{OH}{C}HCH_3$$

N.B. Tertiary alkylhalides form alkenes instead of alcohols.



$$CH_3CH_2\overset{Cl}{\underset{CH_3}{C}}HCH_3 \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH=C(CH_3)_2$$

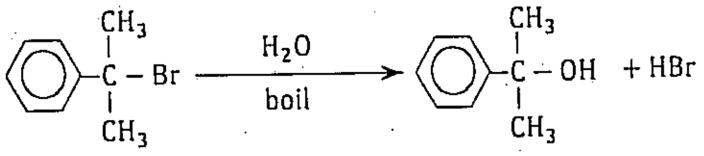
Arylhalides cannot react with sodium hydroxide under the same conditions to form phenols (check under reactions of arylhalides).

(b) Reaction with water

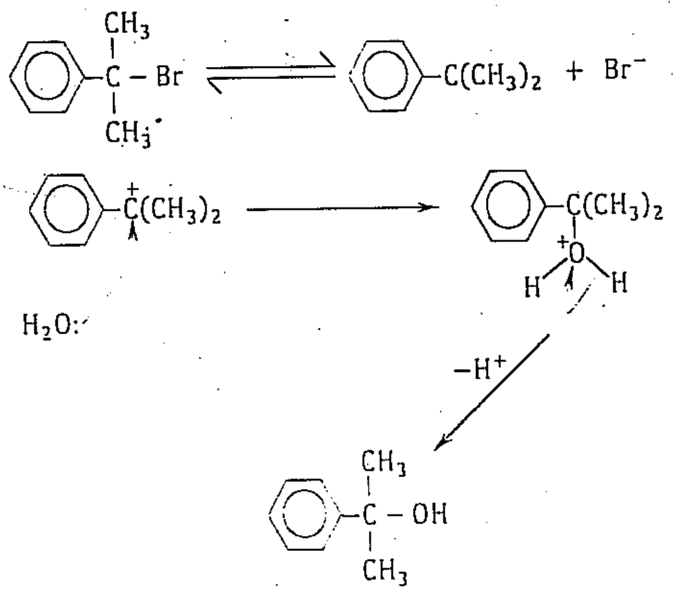
Primary and secondary alkylhalides react very slowly with water alone at ordinary temperatures.

Tertiary alkylhalides rapidly hydrolyse with water on boiling to form tertiary alcohols. The reaction proceeds via S_{N1} mechanism.

For example,



Mechanism



$$H^+ + Br^- \longrightarrow HBr$$

Rapid hydrolysis of the primary or secondary alkylhalides using water can be effected by reacting them with a suspension of silver oxide in moist ether.

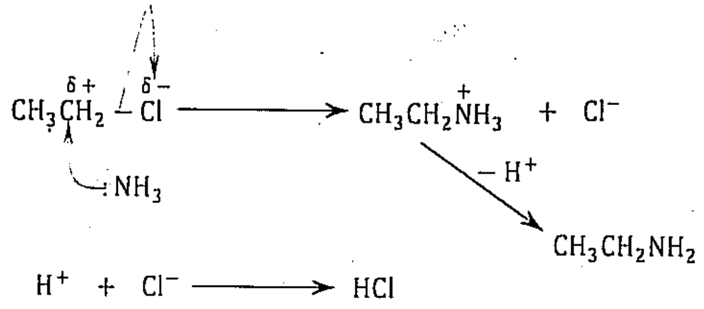
$$CH_3CH_2Br \xrightarrow[\text{moist ether}]{Ag_2O/H_2O} CH_3CH_2OH + AgBr$$

(c) Amine formation

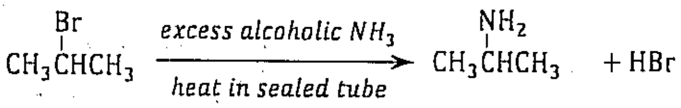
Primary alkylhalides form primary amines when heated with excess alcoholic ammonia solution in a sealed tube. If the ammonia used is not in excess, the yield of the primary amine is low and a mixture of different classes of amines is formed instead which is a disadvantage of this reaction in synthesis.

$$CH_3CH_2Cl \xrightarrow[\text{heat in sealed tube}]{\text{excess alcoholic } NH_3} \underset{\text{aminoethane}}{CH_3CH_2NH_2} + HCl$$

Mechanism (the reaction proceeds via S_{N2})

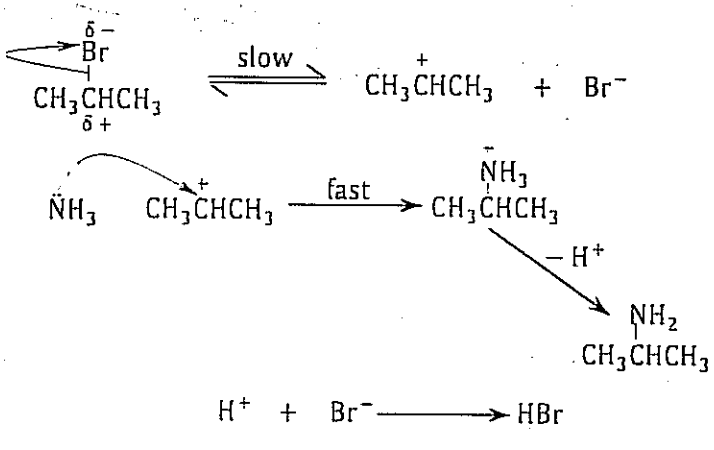


Secondary alkylhalides under similar conditions form secondary amines.



$$CH_3\overset{Br}{C}HCH_3 \xrightarrow[\text{heat in sealed tube}]{\text{excess alcoholic } NH_3} CH_3\overset{NH_2}{C}HCH_3 + HBr$$

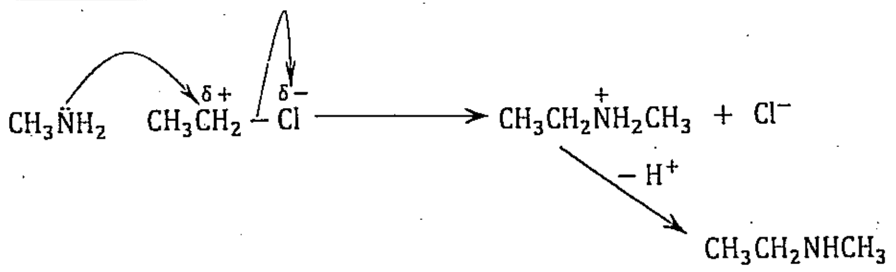
Mechanism (the reaction proceeds via S_{N1})



Secondary amines can also be formed by reacting a primary alkylhalide and a primary amine.

$$CH_3CH_2Cl + \underset{\text{excess}}{CH_3NH_2} \longrightarrow CH_3CH_2NHCH_3 + HCl$$

Mechanism

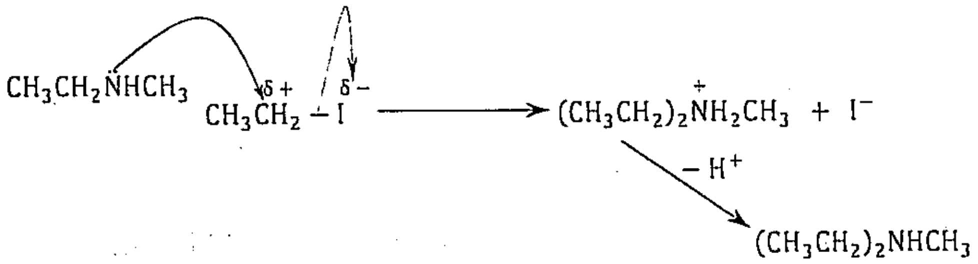


$$H^+ + Cl^- \longrightarrow HCl$$

Tertiary amines can be formed by reacting a primary alkylhalide with a secondary amine.

$$CH_3CH_2NHCH_3 + \underset{excess}{CH_3CH_2I} \longrightarrow (CH_3CH_2)_2NCH_3 + HI$$

Mechanism



$$H^+ + I^- \longrightarrow HI$$

(d) Ether formation (Willamson's synthesis)

Alkylhalides react with a solution of sodium alkoxide or potassium alkoxide in the corresponding alcohol to form ethers. The alkoxide is prepared by dissolving the alkali metal in the excess appropriate alcohol.

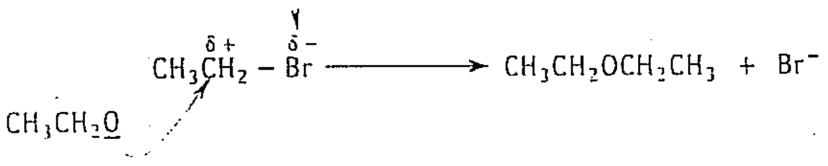
Examples

(i) $$CH_3CH_2Br \xrightarrow[heat]{Na/CH_3CH_2OH} \underset{Diethylether}{CH_3CH_2OCH_2CH_3} + NaBr$$

Mechanism

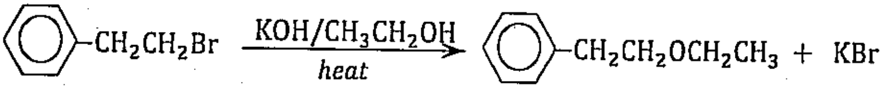
$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2\bar{O}Na^+ + \tfrac{1}{2}H_2$$

$$CH_3CH_2\bar{O}Na^+ \longrightarrow CH_3CH_2\bar{O} + Na^+$$



$$Na^+ + Br^- \longrightarrow NaBr$$

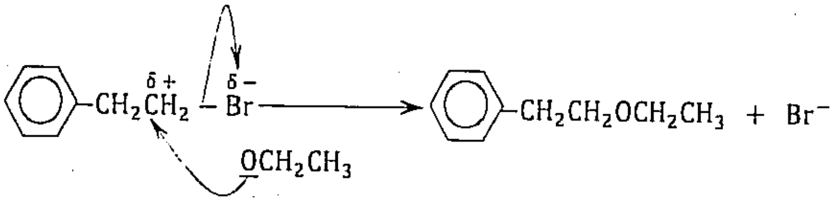
(ii)



Mechanism

$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$

$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$



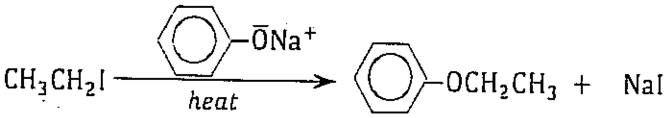
$K^+ + Br^- \longrightarrow KBr$

Note

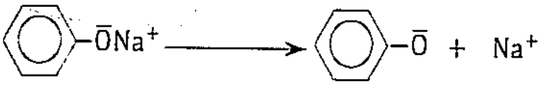
(a) Secondary alklylhalides and tertiary alkylhalides under similar conditions form alkenes via elimination reactions (see later).

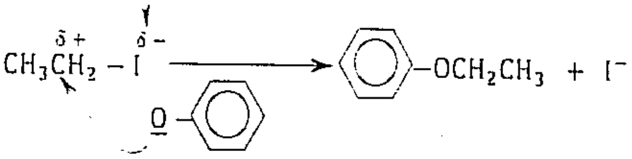
(b) The reaction may be done using a phenoxide or phenol and sodium hydroxide as shown below.

(i)



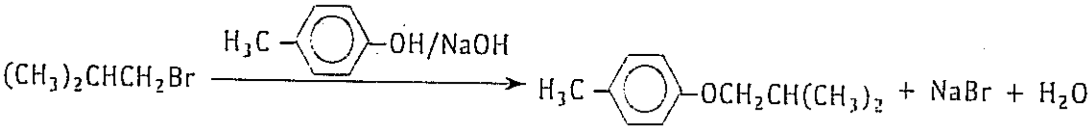
Mechanism



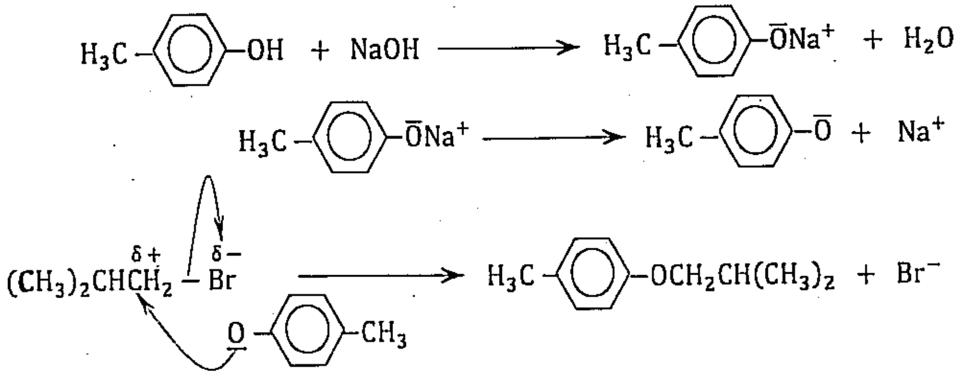


$Na^+ + I^- \longrightarrow NaI$

(ii)



Mechanism



$$Na^+ + Br^- \longrightarrow NaBr$$

(e) Ester formation

When a primary alkylhalide is warmed with an alcoholic solution of a silver salt of a carboxylic acid, an ester if formed. A silver halide is precipitated too.

(i) $$CH_3CH_2Br \xrightarrow[\text{warm}]{CH_3CO\bar{O}Ag^+/\text{Ethanol}} CH_3COOCH_2CH_3 + AgBr$$

Mechanism

$$CH_3CO\bar{O}Ag^+ \longrightarrow CH_3CO\bar{O} + Ag^+$$

$$CH_3CO\bar{O} \quad \overset{\delta+}{CH_3CH_2} - \overset{\delta-}{Br} \longrightarrow CH_3COOCH_2CH_3 + Br^-$$

(f) **Nitrile formation**

This is also called cyanide formation. When an alkylhalide is heated with sodium cyanide or potassium cyanide in aqueous ethanol, a nitrile is formed.

For example

$$CH_3CH_2Br \xrightarrow[\text{heat}]{\text{KCN/aqueous ethanol}} \underset{\textit{propanenitrile}}{CH_3CH_2CN}$$

Mechanism

$$KCN \longrightarrow K^+ + \bar{C}N$$

$$\bar{C}N \quad \overset{\delta+}{CH_3CH_2} - \overset{\delta-}{Br} \longrightarrow CH_3CH_2CN + Br^-$$

$$K^+ + Br^- \longrightarrow KBr$$

Note

The reaction is useful in organic synthesis to increase a carbon chain by a single carbon atom.

The nitrile formed can be converted to carboxylic acid by heating with acidified water.

$$CH_3CH_2CN \xrightarrow[\text{heat}]{H^+/H_2O} CH_3CH_2COOH$$

Aromatic nitriles cannot be prepared by this reaction.

(g) Reaction with sodium acetylides

Primary alkylhalides react with sodium acetylides to form higher alkynes.

(i) $HC \equiv \bar{C}Na^+ \xrightarrow{CH_3CH_2Br} CH_3CH_2C \equiv CH + NaBr$

<u>Mechanism</u>

$$HC \equiv \bar{C}Na^+ \longrightarrow Na^+ + HC \equiv \bar{C}$$

$$HC \equiv \bar{C} \quad \overset{\delta+}{CH_3CH_2} - \overset{\delta-}{Br} \longrightarrow CH_3CH_2C \equiv CH + Br^-$$

$$Na^+ + Br^- \longrightarrow NaBr$$

(ii) $CH_3CH_2C \equiv \bar{C}Na^+ \xrightarrow{CH_3CH_2Br} CH_3CH_2C \equiv CCH_2CH_3 + NaBr$

<u>Mechanism</u>

$$CH_3CH_2C \equiv \bar{C}Na^+ \longrightarrow Na^+ + CH_3CH_2C \equiv \bar{C}$$

$$CH_3CH_2C \equiv \bar{C} \quad \overset{\delta+}{CH_3CH_2} - \overset{\delta-}{Br} \longrightarrow CH_3CH_2C \equiv CCH_2CH_3 + Br^-$$

$$Na^+ + Br^- \longrightarrow NaBr$$

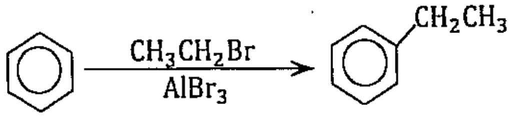
The sodium acetylides are prepared by reacting the corresponding terminal alkyne with sodium in liquid ammonia.

$$RC \equiv CH \xrightarrow{Na(s)/liq.NH_3} RC \equiv \bar{C}Na^+$$

The reaction is very useful in synthesis of higher alkynes from lower ones.

(h) Preparation of alkylaromatic compounds

Alkylhalides react with aromatic compounds in presence of anhydrous aluminium halide catalyst.



This reaction can be regarded as either electrophilic substitution in the benzene ring or nucleophilic substitution by the aromatic compound in the alkylhalide. For mechanism, check benzene and its derivatives.

(i) Halide exchange reaction

(*Check under methods of preparation of alkylhalides*)

5.6.3 Elimination reactions

Alkylhalides also undergo elimination reactions.

An elimination reaction is a reaction which involves removal of an atom or group of atoms from two adjacent carbon atoms to form a multiple bond.

For alkylhalides, hydrogen and halogen atoms from adjacent carbon atoms are eliminated to form either a double bond for monohalohenated alkylhalides or a triple bond for vicinal dihalides.

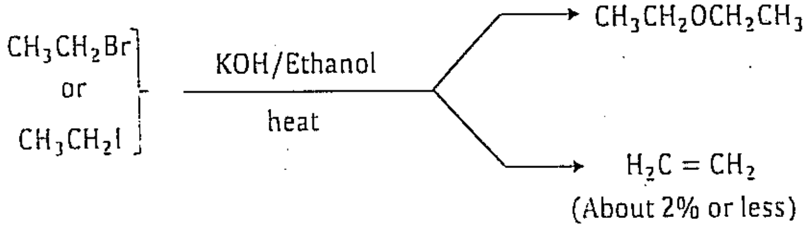
Like nucleophilic substitution, there are two types of elimination reactions.

(i) Bimolecular elimination (E2)

(ii) Unimolecular elimination (E1)

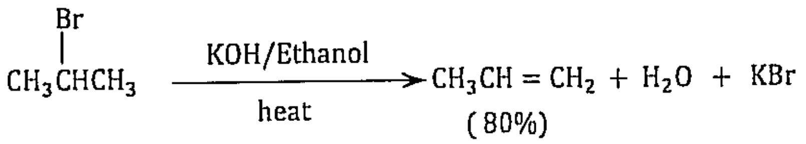
(i) Bimolecular elimination (E2)

When bromoethane or iodoethane is heated with a concentrated solution of sodium hydroxide or potassium hydroxide, ethene can be formed together with ethoxyethane.



The yield of the alkene is so low (about 2% or less). A much better yield can be obtained by higher primary alkylhalides.

The same reaction can occur for 2-bromopropane under the same conditions, yielding a higher percentage of propene (80%) via E₂ mechanism.

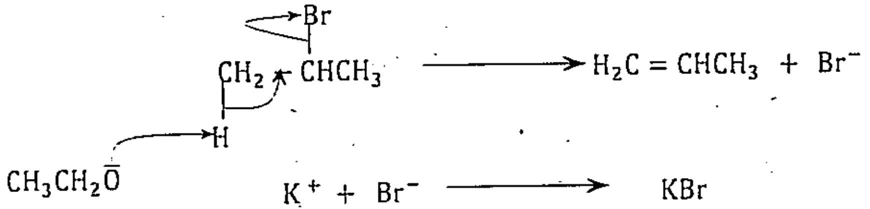


$$CH_3\overset{Br}{\overset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{\text{KOH/Ethanol}} \underset{(80\%)}{CH_3CH = CH_2} + H_2O + KBr$$

Mechanism

$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$$

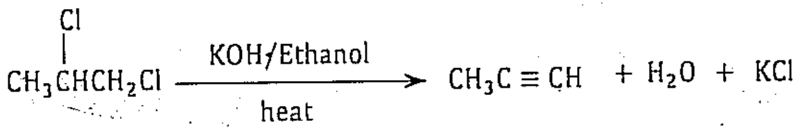
$$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$



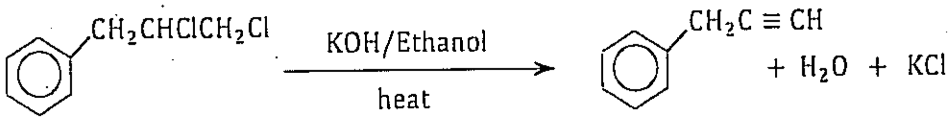
$$K^+ + Br^- \longrightarrow KBr$$

Vicinal dihalides undergo E₂ reaction mechanism too, forming alkynes under similar conditions.

$$CH_2BrCH_2Br \xrightarrow[\text{heat}]{\text{KOH/Ethanol}} HC \equiv CH + H_2O + KBr$$



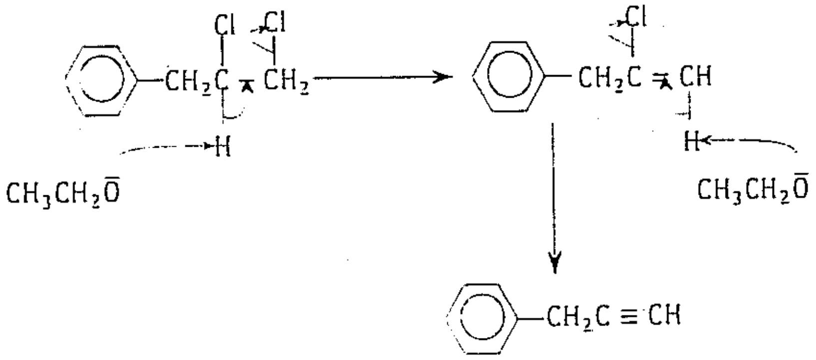
$$CH_3\overset{Cl}{\overset{|}{C}}HCH_2Cl \xrightarrow[\text{heat}]{\text{KOH/Ethanol}} CH_3C \equiv CH + H_2O + KCl$$



Mechanism

$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$$

$$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$



$$K^+ + Cl^- \longrightarrow KCl$$

(ii) Unimolecular elimination (E_1)

Tertiary alkylhalides and to some extent, secondary alkylhalides undergo elimination by a different mechanism, involving formation of a carbocation intermediate.

$$(CH_3)_3C-Br \rightleftharpoons (CH_3)_3\overset{+}{C} + Br^-$$

Considering their reaction with an alcoholic solution of sodium or potassium hydroxide, we have:

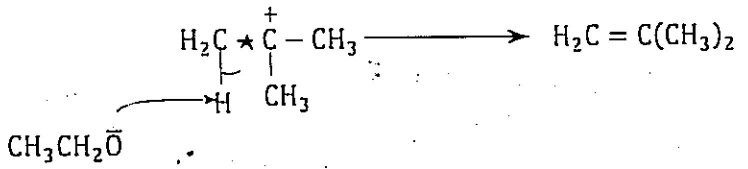
$$(CH_3)_3C-Br \xrightarrow[\text{heat}]{\text{KOH/Ethanol}} (CH_3)_2C=CH_2 + H_2O + KBr$$

<u>Mechanism</u>

$$(CH_3)_3C-Br \rightleftharpoons (CH_3)_3\overset{+}{C} + Br^-$$

$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$$

$$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$



$$H_2C-\overset{+}{C}(CH_3)-CH_3 \longrightarrow H_2C=C(CH_3)_2$$

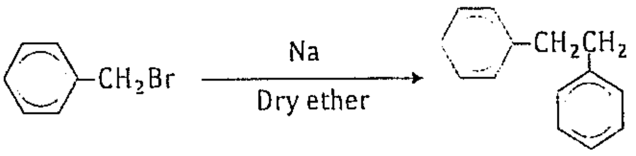
Since only the alkylhalide is involved in the rate determining step the reaction is described as unimolecular.

5.6.3 Reaction with metals

(a) Wurtz reaction

Alkylhalides react with sodium metal in a dry ethereal solution to form alkanes.

$$CH_3CH_2I \xrightarrow[\text{Dry ether}]{\text{Na}} CH_3CH_2CH_2CH_3$$



$$CH_3CH_2CH_2Cl \xrightarrow[\text{Dry ether}]{\text{Na}} CH_3(CH_2)_4CH_3$$

This reaction gives low yields with alkylhalides of low molecular mass but better yields are obtained using alkylhalides of higher relative molecular mass.

(b) With magnesium (Formation of Grignard reagents)

Magnesium turnings or granules are treated with a dry ethereal solution of an alkylhalide and left to stand. A cloudy solution is formed.

$$CH_3CH_2Br \xrightarrow[\text{Dry ether}]{Mg} \underset{\textit{Ethylmagnesium bromide}}{CH_3CH_2MgBr}$$

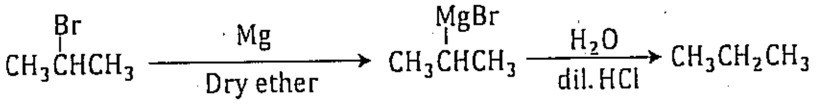
The Grignard reagent is highly reactive and can be used to prepare alkanes, alkenes, alkynes, alcohols, aldehydes, ketones and carboxylic acids.

(i) Preparation of alkanes

On treatment with aqueous hydrochloric acid or sulphuric acid, Grignard reagent forms an alkane.

Examples

$$CH_3CH_2I \xrightarrow[\text{Dry ether}]{Mg} CH_3CH_2MgI \xrightarrow[\text{dil. HCl or dil. } H_2SO_4]{H_2O} CH_3CH_3$$



$$\overset{\overset{Br}{|}}{CH_3CHCH_3} \xrightarrow[\text{Dry ether}]{Mg} \overset{\overset{MgBr}{|}}{CH_3CHCH_3} \xrightarrow[\text{dil. HCl}]{H_2O} CH_3CH_2CH_3$$

(ii) Preparation of alcohols

The Grignard reagent reacts with carbonyl compounds to form alcohols. The alcohol formed depends on the type of carbonyl compound used, i.e. Methanal yields primary alcohols. The intermediate alkylmagnesium halide formed is hydrolysed using a dilute acid to form the primary alcohol.

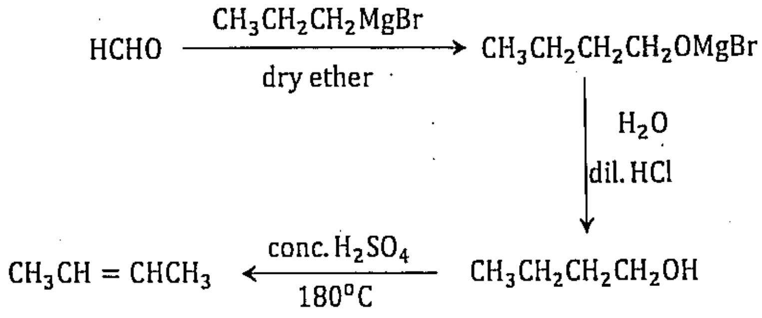
$$HCHO + RMgX \xrightarrow{\text{Dry ether}} RCH_2OMgX \xrightarrow[\text{dil. HCl}]{H_2O} RCH_2OH$$

Examples

(a) Synthesize propa-1-ol from bromomethane

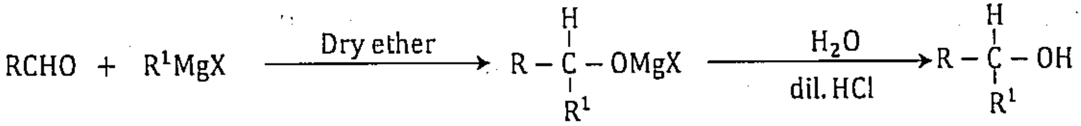
$$\begin{tikzcd}
CH_3Br \arrow[r, "NaOH(aq)", "heat"'] & CH_3OH \arrow[r, "MnO_2(s)/H^+", "heat"'] & HCHO \arrow[d, "CH_3CH_2MgBr", "dry\ ether"'] \\
& CH_3CH_2CH_2OH & CH_3CH_2CH_2OMgBr \arrow[l, "H_2O"', "dil.\ HCl"]
\end{tikzcd}$$

(b) Convert methanal to but-2-ene



$$HCHO \xrightarrow[\text{dry ether}]{CH_3CH_2CH_2MgBr} CH_3CH_2CH_2CH_2OMgBr \xrightarrow[\text{dil. HCl}]{H_2O} CH_3CH_2CH_2CH_2OH \xrightarrow[180^\circ C]{\text{conc. } H_2SO_4} CH_3CH=CHCH_3$$

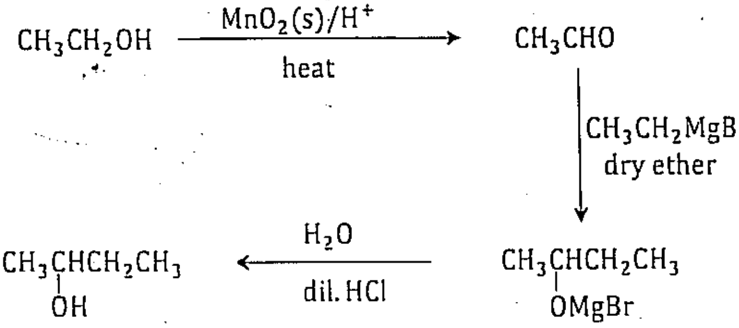
When a higher aldehyde is used instead of methanal, a secondary alcohol is formed.



$$RCHO + R^1MgX \xrightarrow{\text{Dry ether}} R-\underset{R^1}{\overset{H}{C}}-OMgX \xrightarrow[\text{dil. HCl}]{H_2O} R-\underset{R^1}{\overset{H}{C}}-OH$$

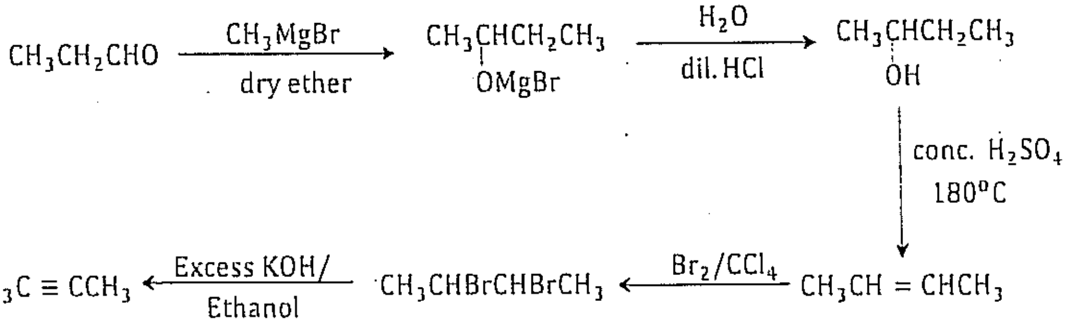
Examples

(a) Convert ethanol to butan-2-ol



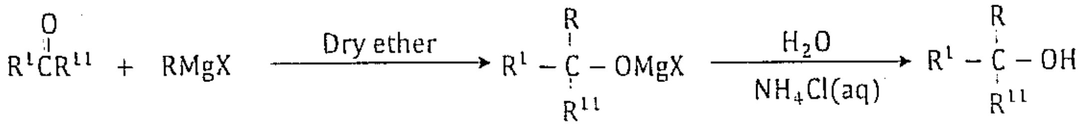
$$CH_3CH_2OH \xrightarrow[\text{heat}]{MnO_2(s)/H^+} CH_3CHO \xrightarrow[\text{dry ether}]{CH_3CH_2MgBr} CH_3\underset{OMgBr}{CH}CH_2CH_3 \xrightarrow[\text{dil. HCl}]{H_2O} CH_3\underset{OH}{CH}CH_2CH_3$$

(b) Synthesize but-2-yne from propanal



$$CH_3CH_2CHO \xrightarrow[\text{dry ether}]{CH_3MgBr} CH_3\underset{OMgBr}{CH}CH_2CH_3 \xrightarrow[\text{dil. HCl}]{H_2O} CH_3\underset{OH}{CH}CH_2CH_3 \xrightarrow[180^\circ C]{\text{conc. } H_2SO_4} CH_3CH=CHCH_3 \xrightarrow{Br_2/CCl_4} CH_3CHBrCHBrCH_3 \xrightarrow[\text{Ethanol}]{\text{Excess KOH/}} CH_3C\equiv CCH_3$$

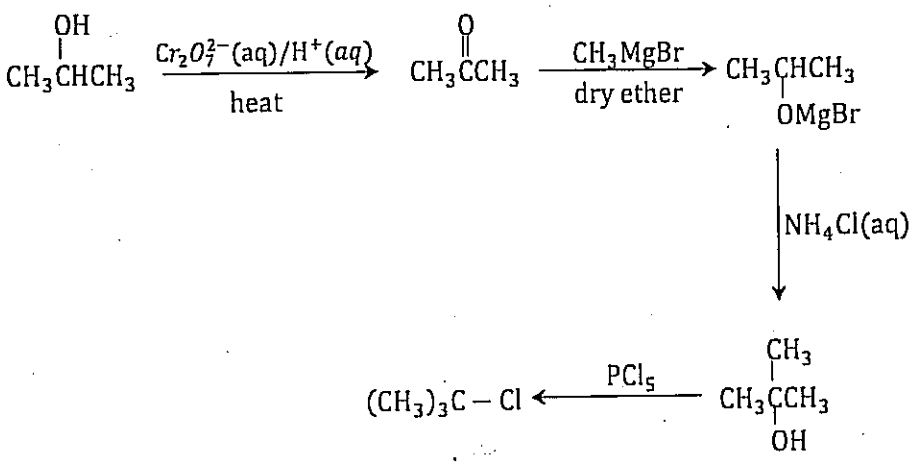
When Grignard reagent is reacted with a ketone, a tertiary alcohol is formed.



$$R^1\overset{O}{\overset{\|}{C}}R^{11} + RMgX \xrightarrow{\text{Dry ether}} R^1-\underset{R^{11}}{\overset{R}{C}}-OMgX \xrightarrow[NH_4Cl(aq)]{H_2O} R^1-\underset{R^{11}}{\overset{R}{C}}-OH$$

Example

(a) Convert propan-2-ol to 2-Chloro-2-methylpropane

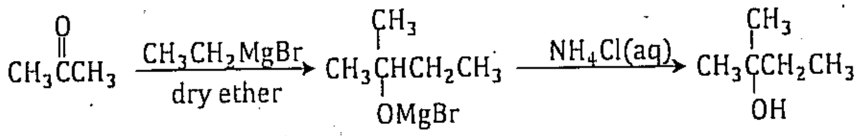


$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{Cr_2O_7^{2-}(aq)/H^+(aq)} CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[\text{dry ether}]{CH_3MgBr} CH_3\underset{OMgBr}{\underset{|}{C}}HCH_3$$

$$CH_3\underset{OMgBr}{\underset{|}{C}}HCH_3 \xrightarrow{NH_4Cl(aq)} CH_3\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_3$$

$$(CH_3)_3C-Cl \xleftarrow{PCl_5} CH_3\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_3$$

(b) Convert propanone to 2-Methylbutan-2-ol



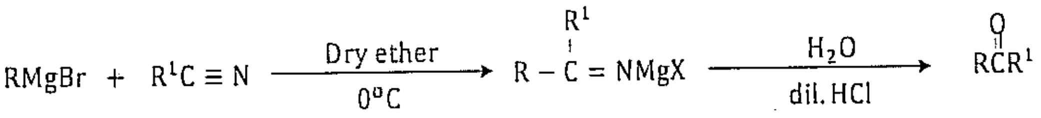
$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[\text{dry ether}]{CH_3CH_2MgBr} CH_3\overset{CH_3}{\overset{|}{\underset{OMgBr}{\underset{|}{C}}}}HCH_2CH_3 \xrightarrow{NH_4Cl(aq)} CH_3\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_2CH_3$$

Note

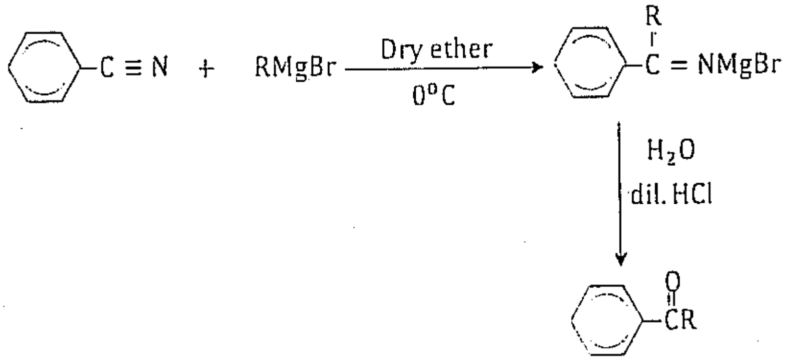
During the preparation of tertiary alcohols, hydrolysis of the alkylmagnesium halide is done using aqueous ammonium chloride instead of dilute acid. This is because the dilute acid brings about dehydration of the alcohol to form an alkene.

(iii) Preparation of ketones

When a Grignard reagent is added to an alkyl or arylnitrile, and the product hydrolysed with a dilute acid, a ketone is formed. CH_3CN cannot be used.

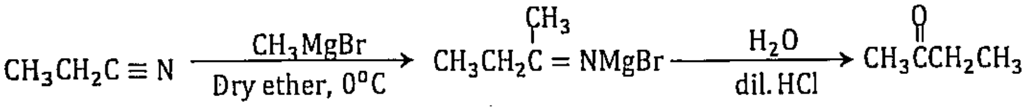


$$RMgBr + R^1C\equiv N \xrightarrow[0^oC]{\text{Dry ether}} R-\overset{R^1}{\overset{|}{C}}=NMgX \xrightarrow[\text{dil. HCl}]{H_2O} R\overset{O}{\overset{\|}{C}}R^1$$

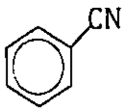
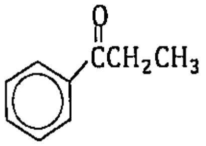


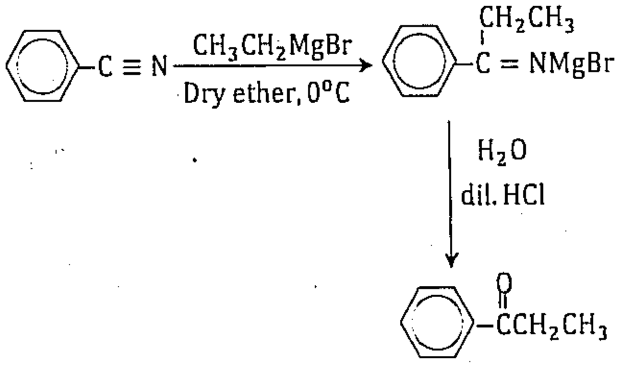
Examples

(a) Synthesise butanone from propanenitrile



$$CH_3CH_2C \equiv N \xrightarrow[\text{Dry ether, } 0^\circ C]{CH_3MgBr} CH_3CH_2\overset{CH_3}{\overset{|}{C}} = NMgBr \xrightarrow[\text{dil. HCl}]{H_2O} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

(b) Convert  to 



(iv) Preparation of carboxylic acids

Aliphatic carboxylic acids can be formed by bubbling carbon dioxide into the Grignard reagent and the product treated with a dilute acid.

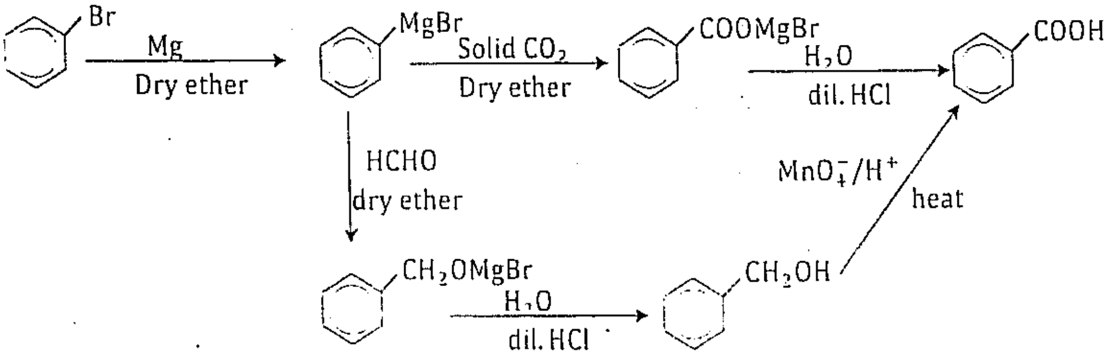
$$RMgBr \xrightarrow[\text{Dry ether}]{CO_2} RCOOMgBr \xrightarrow[\text{dil. HCl}]{H_2O} RCOOH$$

R can be primary, secondary, tertaiary or aromatic.

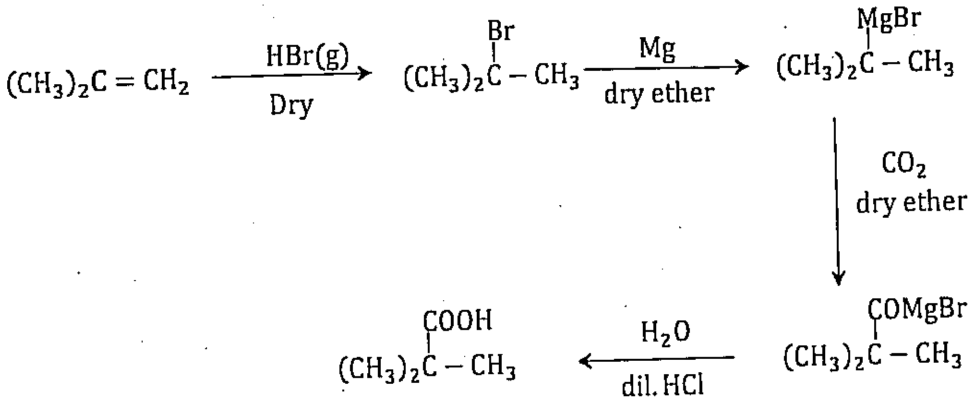
For preparation of benzoic acid, solid carbon dioxide (dry ice) is used.

Examples

(a)



(b) 2-Methylpropene to 2,2-dimethylpropanoic acid



$$(CH_3)_2C=CH_2 \xrightarrow[\text{Dry}]{HBr(g)} (CH_3)_2\overset{Br}{\overset{|}{C}}-CH_3 \xrightarrow[\text{dry ether}]{Mg} (CH_3)_2\overset{MgBr}{\overset{|}{C}}-CH_3 \xrightarrow[\text{dry ether}]{CO_2} (CH_3)_2\overset{COMgBr}{\overset{|}{C}}-CH_3 \xrightarrow[\text{dil. HCl}]{H_2O} (CH_3)_2\overset{COOH}{\overset{|}{C}}-CH_3$$

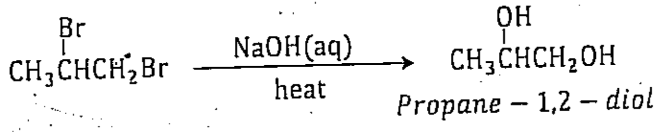
5.6.4 Reactions of vicinal and Germinal dihalides

(a) Hydrolysis

Vicinal dihalides undergo hydrolysis when heated with aqueous sodium hydroxide to form diols.

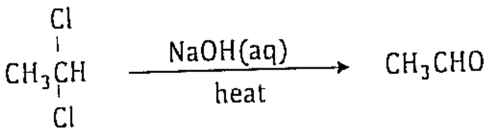
For example

$$CH_2ClCH_2Cl \xrightarrow[\text{heat}]{NaOH(aq)} \underset{\textit{Ethane}-1,2-\textit{diol}}{HOCH_2CH_2OH}$$

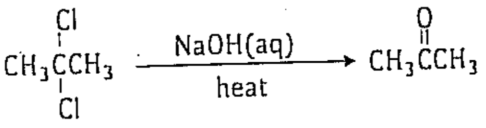


$$CH_3\overset{Br}{\overset{|}{C}}HCH_2Br \xrightarrow[\text{heat}]{NaOH(aq)} \underset{\textit{Propane}-1,2-\textit{diol}}{CH_3\overset{OH}{\overset{|}{C}}HCH_2OH}$$

However, Germinal dihalides on hydrolysis with aqueous sodium hydroxide form ketones or aldehydes.



$$CH_3\underset{Cl}{\overset{Cl}{C}}H \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CHO$$



$$CH_3\underset{Cl}{\overset{Cl}{C}}CH_3 \xrightarrow[\text{heat}]{NaOH(aq)} CH_3\overset{O}{\overset{\|}{C}}CH_3$$

(b) Reaction with alcoholic potassium hydroxide solution

Both vicinal and germinal dihalides form alkynes by elimination reaction.

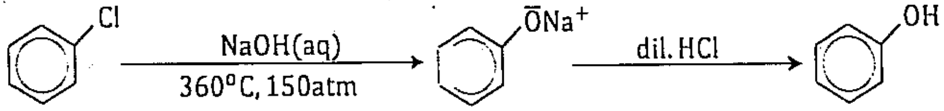
Example

Synthesise Ethane-1,2-dioic acid from Ethene

$$\begin{tikzcd}
H_2C = CH_2 \arrow[r, "Cl_2/CCl_4"] \arrow[d, "MnO_4^-(aq) \\ /\bar{O}H(aq)"] & CH_2ClCH_2Cl \arrow[r, "Cl_2/CCl_4"] & HOCH_2CH_2OH \arrow[dl, "Cr_2O_7^{2-}(aq)/H^+(aq)", "heat"'] \\
HOCH_2CH_2OH \arrow[r, "Cr_2O_7^{2-}(aq)/H^+(aq)", "heat"'] & HOOC - COOH &
\end{tikzcd}$$

5.6.5 Reactions of arylhalides

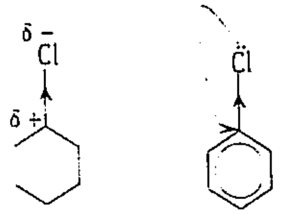
Arylhalides do not easily undergo nucleophilic substitution reaction as for alkylhalides. Their reactions with nucleophiles can only be effected under very vigorous conditions like the industrial preparation of phenol from chromobenzene.



Question

Chlorocyclohexane easily undergoes nuclephilic substitution reaction but chlorobenzene does not. Explain

Answer



In chlrorocyclohexane, the clorine atom is **more electronegative** than the carbon atom. It therefore attracts the bonding electrons more towards itself, gaining a **partial negative charge**. The carbon atom gains a **partial positive charge** and this makes the **carbon – chlorine bond polar**. The partial positive **carbon attracts a nucleophile** which replaces the chlorine atom.

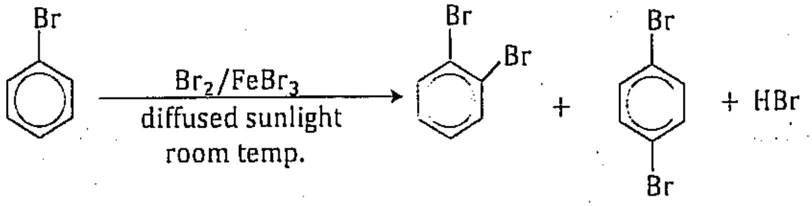
In chlorobenzene, the **lone pair of electrons on the chlorine atom interact with the delocalised pi-electrons of the benzene ring**. This strengthens the carbon – chlorine bond making it very **difficult** to break.

Arylhalides, just like benzene and methylbenzene (covered earlier) undergo electrophilic substitution reactions on the ring. Although the halogen atoms have negative inductive effect on the benzene ring, they make the benzene ring on which they are attached **more reactive**. This is because the **lone pair of electrons of the halogen atom interact with the pi-electrons of the benzene ring**. This **increases the electron density on the benzene ring**, making it **more reactive towards electron deficient species** (electrophiles). The halogen atoms are ortho- and para-directing, hence 2- and 4-derivatives are the major products formed during electrophilic substitution.

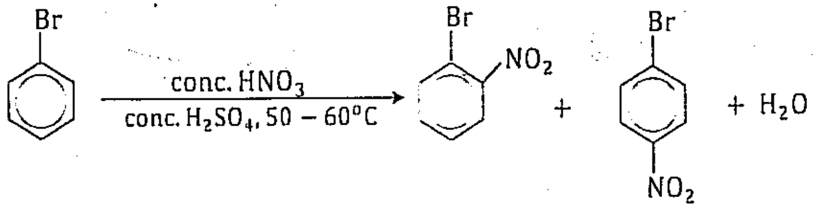
We shall consider chlorobenzene as an example.

(a) Halogenation

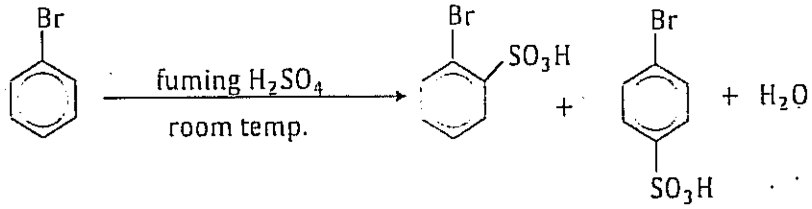
Bromobenzene reacts with bromine in presence of iron(III) bromide at room temperature to form 1,2-dibromobenzene and 1,4-dibromobenzene.



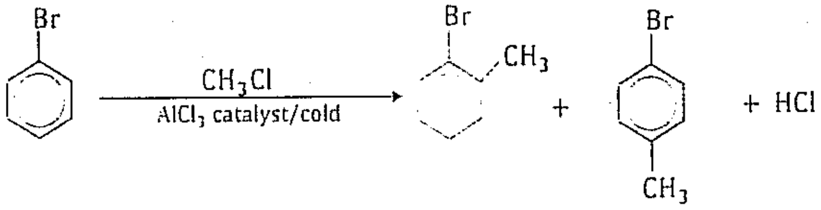
(b) Niration



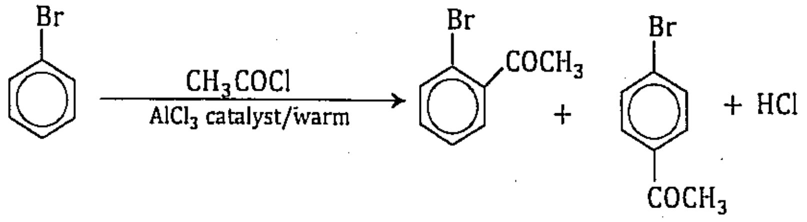
(c) Sulphonation



(d) Friedel-crafts alkylation



(e) Friedel-crafts acylation



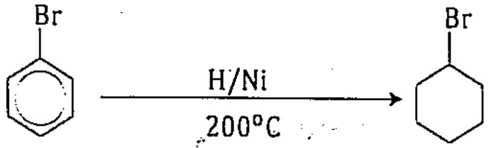
Note

(i) In all the above reactions, similar mechanisms as for benzene occur.

(ii) Steric hindrance in the 2-position favours formation of the 4-product in greater quantity.

Other important reactions of arylhalides include:

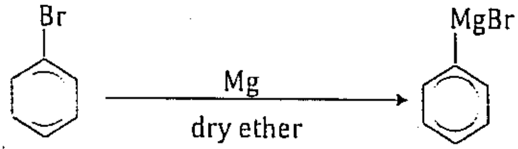
(a) Hydrogenation



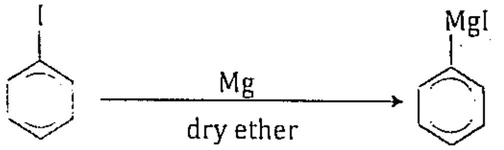
Bromocyclohexane is formed and can be converted to many other compounds using suitable reagents.

(b) Formation of Grignard reagents

Bromobenzene and iodobenzene can form Grignard reagents.



phenylmagnesium bromide

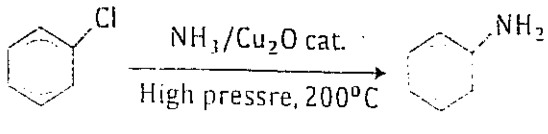


phenylmagnesium iodide

The products can be converted to benzoic acid as seen under section 5.6.3.

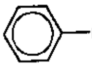
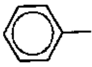
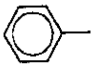
(c) Converting chlorobenzene to aminobenzene

Chlorobenzene reacts with ammonia at high temperature and high pressure in presence of copper(I) oxide catalyst to form aminobenzene.



5.7 Distinguishing alkylhalides and arylhalides

(a) *Using hot silver nitrate solution ethanol*

Alkylhalide	Observation
CH_3CH_2Cl or  $-CH_2Cl$	White precipitate
CH_3CH_2Br or  $-CH_2Br$	Pale yellow precipitate
CH_3CH_2I or  $-CH_2I$	Yellow precipitate

Explanation

The alkylhalides react with silver ions to form silver halides that are insoluble in dilute nitric acid.

$$CH_3CH_2Cl + Ag^+ \longrightarrow CH_3\overset{+}{C}H_2 + AgCl$$
$$CH_3CH_2Br + Ag^+ \longrightarrow CH_3\overset{+}{C}H_2 + AgBr$$
$$CH_3CH_2I + Ag^+ \longrightarrow CH_3\overset{+}{C}H_2 + AgI$$

Silver chloride is white, silver bromide is pale yellow and silver iodide is yellow.

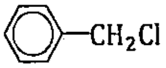
(b) Using hot sodium hydroxide solution followed by dilute nitric acid and silver nitrate solution

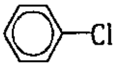
This reagent can be used to distinguish alkylhalides themselves or an alkylhalides and an arylhalide.

For alkylhalides, the same observations as seen above are made. For example,

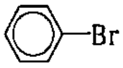
CH_3CH_2Cl – White precipitate
CH_3CH_2Br – Pale yellow precipitate
CH_3CH_2I – Yellow precipitate

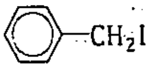
For distinguishing arylhalides and alkylhalides, observations are as shown in the table below

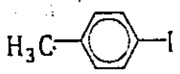
 — *White precipitate*

 — *No observable change*

CH_3CH_2Br — *Pale yellow precipitate*

 — *No observable change*

 — *Yellow precipitate*

 — *No observable change*

Note

(i) The role of nitric acid is to react with the excess hydroxyl ions from sodium hydroxide that would precipitate with silver nitrate to form silver oxide.

(ii) Simply using hot sodium hydroxide solution and silver nitrate solution will give similar observations.

5.8 Sample Questions

Explain the following observations.

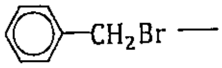
(a) *When treated with hot sodium hydroxide solution followed by dilute nitric acid and silver nitrate solution, 1-Iodobutane formed a yellow precipitate almost immediately while 1-Bromobutane formed a pale yellow precipitate after some time and 1-Chlorobutane formed a white precipitate in the longest time.*

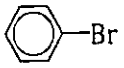
Answer

Iodine has a **larger atomic radius** than bromine which also has a **larger atomic radius** than chlorine. The carbon – iodine bond is therefore **longer and weaker** than the carbon – bromine bond which is also **weaker than the carbon – chlorine bond.** Therefore, the iodine atom is **more easily substituted** than the bromine atom which is also **more easily substituted than the chlorine atom** by the hydroxide ion from sodium hydroxide. Therefore, **more time is taken by the chloride ions to form insoluble silver chloride** than it takes bromide ions to form **insoluble silver bromide.** Iodine ions take the shortest time to form insoluble silver iodide.

(b) *Bromomethylbenzene forms a pale yellow precipitate when warmed with sodium hydroxide solution and acidified silver nitrate solution but bromobenzene shows no observable change.*

Answer


— *Pale yellow precipitate*


— *No observable change*

In bromomethylbenzene, the bromine atom is **more electronegative** than the carbon atom. This makes the bromine atom gain a **partial negative charge and the carbon atom** gains a **partial positive charge**. Therefore, the **carbon – bromine bond is polar**. The partial positive carbon atom is **easily attacked by the hydroxyl ion** and **substituted**, **releasing bromide ions in solution**. The **bromide ions react with silver ions forming insoluble silver bromide**.

In bromobenzene, the **lone pair of electrons on the bromine atom interacts** with the **delocalised pi-electrons of the benzene ring**. This makes the **carbon – bromine bond very strong and difficult to break**.

5.9 Uses of halohydrocarbons

(i) Chlorobenzene is used in manufacture of phenol and DDT (an important insecticide).

(ii) Tetrafluoroethane is used to make Teflon, an important polymer.

(iii) Fluorochloro derivatives of methane and ethane are used as aerosol propellants in dispensers to kill flies, as shaving creams, e.t.c.

(iv) Hydrofluorocarbons are used in air conditioners and refrigerators.

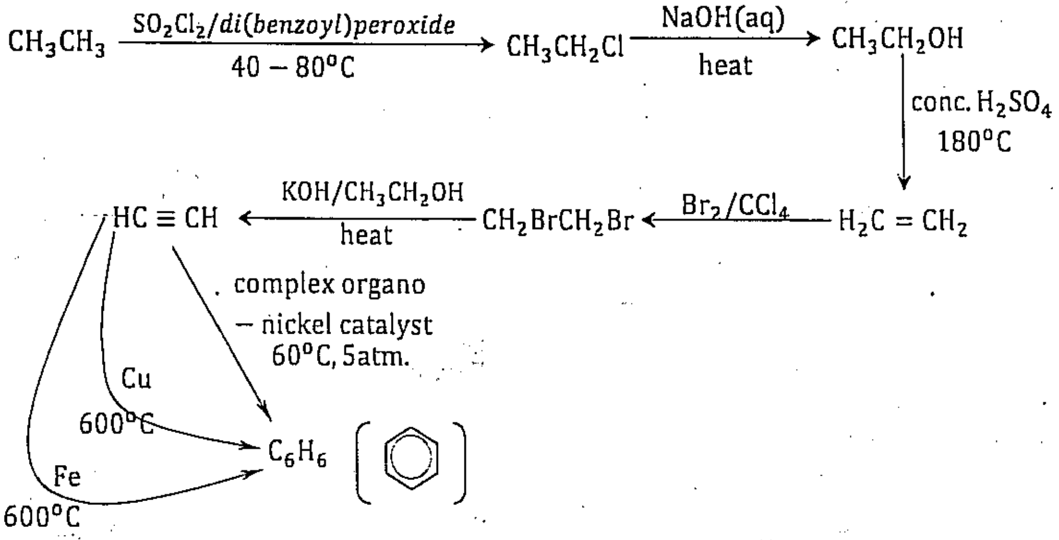
5.10 Some synthetic problems

1. Write equations to show the following conversions can be effected.

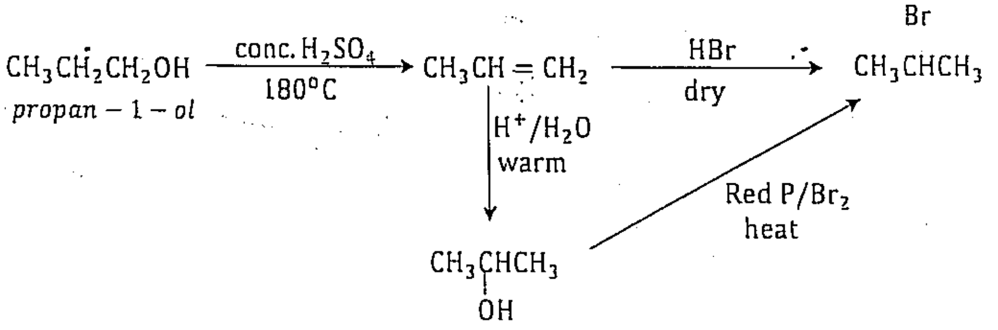
(i) Propan-1-ol from propyne.

$$\begin{tikzcd} \underset{\text{propyne}}{CH_3C\equiv CH} \arrow[r, "H_2", "\text{Lindlar catalyst}"'] & CH_3CH=CH_2 \arrow[r, "HBr", "CH_3OOCH_3"'] & CH_3CH_2CH_2Br \arrow[d, "\begin{array}{c}\text{NaOH(aq)}\\ \text{heat}\end{array}"] \\ & & \underset{\text{propan} - 1 - \text{ol}}{CH_3CH_2CH_2OH} \end{tikzcd}$$

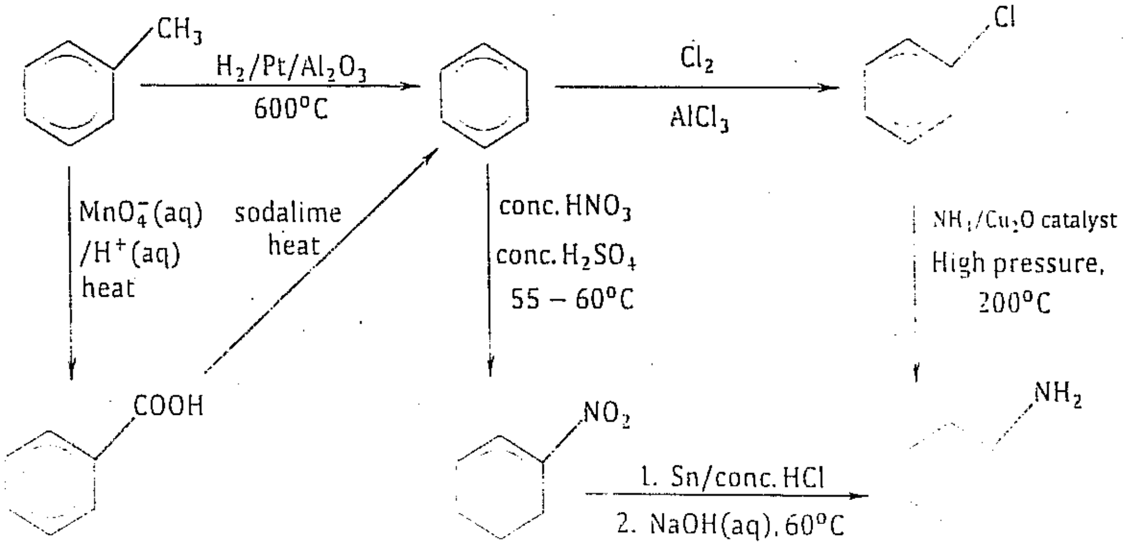
(ii) C_6H_6 from CH_3CH_3



(iii) $(CH_3)_2CHBr$ from propan-1-ol.



(iv) Phenylamine from methylbenzene



2. Describe how the following conversions can be effected.

(i) *Phenol from chlorobenzene*

Either Chlorobenzene is heated with silicon and steam at 425°C to form phenol.

Or Chlorobenzene is reacted with sodium hydroxide solution at a temperature of 360°C and a pressure of 150 atmosphere to form sodium phenoxide. The sodium phenoxide is then reacted with dilute hydrochloric acid to form phenol.

(ii) $CH_3CH_2CH = CH_2$ *from Bromoethane*

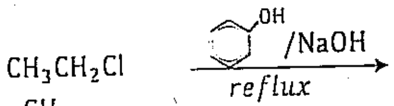
Bromoethane is heated with sodium hydroxide solution to form ethanol which is then dehydrated by excess concentrated sulphuric acid at 180°C to form ethene. Ethene is reacted with chlorine in tetrachloromethane to form 1,2-dichloroethane which is then heated with ethanolic potassium hydroxide solution to form ethyne. Ethyne is reacted with sodium in liquid ammonia to form sodium acetylide that is reacted with chloroethane to form but-1-yne. But-1-yne is reacted with hydrogen in presence of Lindlar catalyst to form but-1-ene.

5.11 End of topic assessment exercise

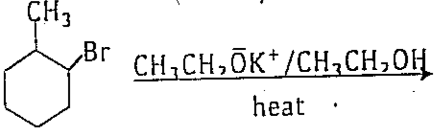
1. Complete the following questions and write the IUPAC names of the main organic product in each case.

(a) $CH_3Br \xrightarrow{CH_3CO\bar{O}Ag^+}$

(b)



(c)

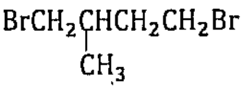


(d) $(CH_3)_3COH \xrightarrow{\text{conc. HCl}}$

(e) $CH_3CH_2CH_2I \xrightarrow[\text{heat}]{NaOH/CH_3CH_2OH}$

(f) $(CH_3)_2CBrCH_3 \xrightarrow[\text{heat}]{C_2H_5\bar{O}K^+/C_2H_5OH}$

(g) $(CH_3)_3CCl \xrightarrow[heat]{CH_3\bar{O}Na^+/CH_3OH}$

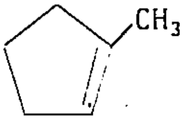
(h) 

$BrCH_2CH(CH_3)CH_2CH_2Br \xrightarrow[heat]{Et\bar{O}K^+/EtOH}$

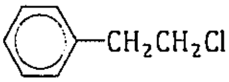
(i) $HC \equiv CH \xrightarrow[\text{Na in liq. } NH_3]{CH_3Br}$

(j) $CH_3CH_2CH_2Cl \xrightarrow[\text{ethanol reflux}]{Cu-Zn}$

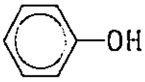
(k) $CH_3CH = CH_2 \xrightarrow[CH_3OOCH_3]{HBr}$

(l) 

$\xrightarrow[\text{2. } PCl_5]{\text{1. } H_2O/\text{conc. } H_2SO_4}$

(m) 

$\xrightarrow[heat]{CH_3CH_2OH/\bar{O}H}$

(n) 

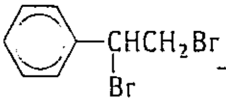
$\xrightarrow[heat]{NaOH/CH_3CH_2OH}$

(o) $(CH_3)_2C = CH_2 \xrightarrow[\text{organic peroxide}]{HBr}$

(p) $C_6H_5Br + CH_3I \xrightarrow[\text{dry ether}]{Na(s)}$

2. Complete the following equations and write the mechanisms for the reaction leading to formation of the major organic products.

(a) $(CH_3)_3CCl \xrightarrow[heat]{NaOH/CH_3CH_2OH}$

(b) 

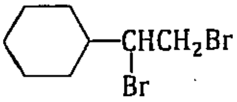
$\xrightarrow[heat]{Et\bar{O}K^+/EtOH}$

(c) $CH_3CH_2Br + CH_3C \equiv CH \xrightarrow{Na/liq. NH_3}$

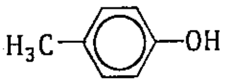
(d) $(CH_3)_3C-Br + \bar{O}H(aq) \longrightarrow$

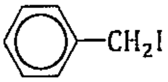
(e) $H_3C-(C_6H_4)-OH + CH_3CH_2Br \longrightarrow$

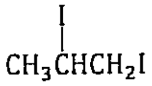
(f) $CH_3CH_2I + KOH(aq) \longrightarrow$

(g)  $\xrightarrow[heat]{CH_3CH_2\bar{O}/Ethanol}$

(h) $CH_3CH_2Cl + HC \equiv CNa \xrightarrow{liq. NH_3}$

(i)  $\xrightarrow[NaOH(aq), heat]{CH_3CH_2I}$

(j)  $+ \bar{O}H(aq) \xrightarrow{heat}$

(k)  $CH_3CH(I)CH_2I \xrightarrow{Et\bar{O}K^+/EtOH}$

(l) $CH_3CH_2CH_2Br \xrightarrow{CH_3CO\bar{O}Ag^+}$

(m) $(CH_3)_3C-Br \xrightarrow[heat]{KOH}$

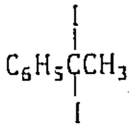
(n) $CH_3CH_2NH_2 + CH_3Cl \xrightarrow{heat}$

(o) $CH_3C \equiv CH \xrightarrow{A} CH_3C \equiv CCu \xrightarrow{(CH_3)_2CHCl} B$

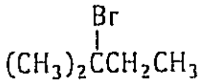
(p) $CH_3CH = C(CH_3)_2 \xrightarrow{Br_2/NaCl(aq)}$

3. Write a mechanism to show how each of the following conversions can be effected.

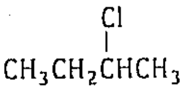
(a) $(CH_3)_3CCl \longrightarrow (CH_3)_2C = CH_2$

(b) $C_6H_5C \equiv CH \longrightarrow$  $C_6H_5CI_2CH_3$

(c) $CH_3CH_2Cl \longrightarrow CH_3CH_2OH$

(d)  $(CH_3)_2CBrCH_2CH_3 \longrightarrow (CH_3)_2C = CHCH_3$

(e) $CH_3CH_2CH_2Cl \longrightarrow CH_3CH_2CH_2NHCH_3$

(f)  $CH_3CH_2CHClCH_3 \longrightarrow CH_3CH = CHCH_3$

(g) $(C_2H_5)_2NH \longrightarrow (CH_3CH_2)_3N$

4. Write equations to show how the following conversions can be effected.

(a) Bromocyclohexane from hydroxybenzene.

(b) $(CH_3)_3COH$ from CH_3COCH_3

(c) $H_2C_2O_4$ from $CH_2 = CH_2$

(d) $(CH_3)_3COH$ from $(CH_3)_2CHOH$

(e) C_6H_5MgCl to C_6H_5OH

(f) 1,2-Dibromopropane from ethene.

(g) Iodomethane to iodoethane.

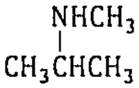
(h) Hydroxybenzene from bromobenzene.

(i) Hexane from propene.

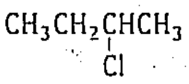
(j) CH_3CH_2OH to $CH_3CH_2CH_2OH$

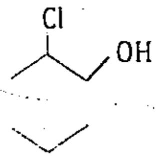
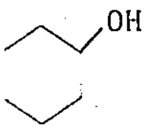
(k) 2,2-Dibromopropane from propan-1-ol.

(l) Chlorobenzene to benzene.

(m) $CH_3CH_2CH_2Br$ to  $CH_3\underset{}{\overset{NHCH_3}{\overset{|}{C}}}HCH_3$

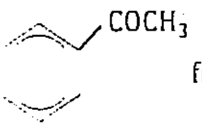
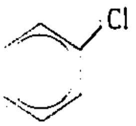
(n) $CH_3CH_2CH_2Br$ from CH_3CH_2Br

(o) $CH_3CH_2C \equiv CH$ to  $CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_3$

(p)  from 

(q) 2 – Bromopropane from propan – 1 – ol

(r) 2 – Bromopropane from ethane

(s)  from 

5. Describe how the following conversions can be effected. (No equations are required)

(a) 1,2-Dibromoethane to ethanol.

(b) But-1-yne from CH_3CH_2OH.

(c) $CH_3CH_2CH_2CH_2I$ to butan-2-ol.

(d) 2-Chloropropane to $CH_3C \equiv CCH_3$.

(e) CH_3CH_2Cl from $CH_3CH_2CH_2Cl$.

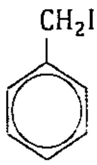
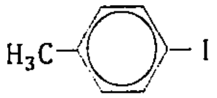
(f) 1-phenylpropanone from chlorobenzene.

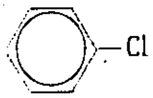
(g) $H_2C = CH_2$ to $(CH_3CH_2)_2O$.

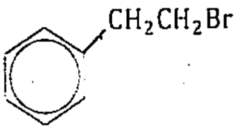
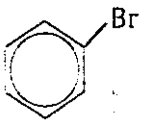
(h) 2-Bromopropane from ethanol.

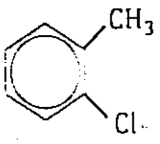
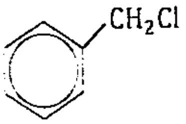
(i) Propan-1-ol from 2-Bromopropane.

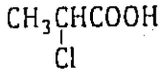
6. Name the reagents that can be used to distinguish between the following pairs of compounds. In each case, state what would be observed if each member of the pair is separately treated with the reagent.

(i)  and 

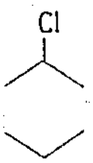
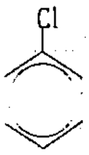
(ii) CH_3CH_2Cl and 

(iii)  and 

(iv)  and 

(v) CH_3COOH and 

$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH$

(vi)  and 

7. (a) Briefly describe how bromoethane can be prepared from ethanol.
   (b) Describe the reactions of bromoethane with:
      (i) sodium hydroxide.
      (ii) potassium cyanide.
      (iii) silver oxide.
   (c) Outline the reactions by which bromoethane can be used to form:
      (i) ethylbenzene.
      (ii) propanonitrile.
      (iii) ethane.

8. 2-Bromo-2-methylpropane reacts with aqueous sodium hydroxide.
   (i) Write an equation for the reaction.
   (ii) Write the rate equation for the reaction.
   (iii) State the molecularity of the reaction.
   (iv) Draw the energy diagram for the reaction.

9. (a) An organic compound X has a molecular formula C_4H_9Br.
   - (i) Name the functional group in X.
   - (ii) Write the structural formulae and names of all isomers of X.
   - (iii) Identify two isomers in (a)(ii) that when reacted with ethanoic acid potassium hydroxide solution give the same product.
   - (iv) Write the structural formula and name of the product in (a)(iii).

   (b) Outline the mechanism for the reaction between the product in (a)(iii) and benzene in presence of an acid.

10. (a) Write an equation for the reaction between calcium carbide and water.

    (b) The organic compound Q, produced by the reaction in (a) above, can also be prepared from a haloalkane.
   - (i) Write the structure and IUPAC name of the haloalkane.
   - (ii) Stating the conditions applicable, write an equation and indicate the mechanism for the reaction when the haloalkane is converted to Q.

11. (a) An organic compound W, consists of 51.92% Carbon, 4.87% hydrogen and the rest being bromine. Determine the simplest formula of W.

    (b) The vapour density of W is 6.6 times that of nitrogen. Calculate the molecular formula of W.

    (c) W, which burns with a sooty flame, formed another compound Z when reacted with sodium hydroxide solution. W also reacts with alcoholic potassium hydroxide on heating to form Y as the major product. Y decolourises bromine water.
   - (i) Write equation(s) leading to formation of Z and Y.
   - (ii) Outline a mechanism leading to formation of Z from W.

    (d) Name the type of reaction between:
   - (i) W and alcoholic potassium hydroxide.
   - (ii) Y and bromine water.

    (e) Write equation and mechanism for the reaction in (d) (ii) above.

    (f) (i) Name a reagent that can be used to distinguish between W and bromobenzene.
   - (ii) Explain the difference in the reactivity of the two substances in (f)(i) when reacted with the reagent named above.

12. (a) An organic compound Q, has a molecular formula C_3H_6Br. Write down the structural formulae and IUPAC names of all isomers of Q.

(b) When Q was heated with sodium metal in ethanol, a compound Y was formed. Y reacts with water in presence of sulphuric acid and mercurous sulphate at 60°C to form compound X. X does not react with Fehling's solution but forms an orange precipitate with Brady's reagent. Identify Q, Y and X.

(c) Write the equation and suggest the mechanism for the reaction between:

(i) Q and sodium metal in ethanol.

(ii) X and Brady's reagent.

13. (a) 1.363g of compound Y containing carbon, hydrogen and bromine on complete combustion gave 1.10g of carbon dioxide and 0.45g of water. When 0.35g of Y was vapourised, it occupied 39.5cm^3 at 20°C and 750mmHg. Calculate:

(i) the simplest formula of Y.

(ii) the molecular formula of Y.

(b) Y forms a compound Z when treated with a mixture of potassium hydroxide and ammonical silver nitrate to form a white precipitate Q. Identify:

(i) Y (ii) Z (iii) Q

(c) Write;

(i) equation for the reaction between Z and ammonical silver nitrate.

(ii) the mechanism for the reaction leading to formation of Z.

14. An organic compound, molecular formula C_7H_7Br burns with a sooty flame and has two isomers P and Q.

(a) P and Q were separately treated with hot aqueous sodium hydroxide solution followed by dilute nitric acid and then silver nitrate solution. P formed a pale yellow precipitate while with Q, there was no observable change. Identify:

(i) P (ii) Q

(b) Explain why P and Q showed differences in the reactivity with the reagent.

(c) State the role of nitric acid in the reagent that distinguishes between P and Q.

(d) Write equations to show how:

(i) P can be converted to phenylethene.

(ii) Q can be converted to benzoic acid.

15. (a) 6.85g of a bromoalkane, E, was reacted with excess sodium hydroxide solution.

The resulting solution was neutralised with nitric acid and diluted to 250cm^3. 25cm^3 of this solution required 12.5cm^3 of 0.4M silver nitrate solution for complete precipitation of silver bromide.

(i) Calculate the relative formula mass of E.

(ii) Determine the molecular formula of E.

(iii) Write the structural formula and IUPAC names of all the possible isomers of E.

(b) E undergoes a nucleophilic substitution bimolecular reaction when reacted with warm sodium hydroxide solution.

(i) Identify E.

(ii) Write the equation for the reaction between E and warm sodium hydroxide solution.

(iii) Write the rate equation for the reaction between E and warm sodium hydroxide solution.

(iv) Draw a well labelled potential energy diagram for the reaction, given that the reaction is exothermic.

(c) Outline a mechanism for the reaction between E and hot sodium hydroxide in methanol.

16. 3.4g of a primary monohalosubstituted alkyhalide Y was reacted with excess hot sodium hydroxide solution and then with dilute nitric acid. The resultant solution was reacted completely with silver nitrate solution and 4.7g of a yellow precipitate was formed.

(a) Write a general equation for the reaction,

(i) between Y and sodium hydroxide.

(ii) for formation of the yellow precipitate.

(b) (i) State the role of nitric acid in the reaction.

(ii) Name the type of reaction between Y and sodium hydroxide shown above.

(c) Calculate the:

(i) molar mass of Y.

(ii) hence deduce the molecular and structural formulae of Y.

(d) Write equations to show how Y can be converted to 2-Iodobutane.

17. 4.1g of a bromoalkane, M, was reacted with excess sodium hydroxide solution. The resulting solution was acidified with excess nitric acid and diluted to exactly 250cm^3 in a volumetric flask. 25.0cm^3 of this solution required 33.25cm^3 of 0.1M silver nitrate solution for complete reaction.

(a) Determine the molecular formula of M.

(b) Write the structural formulae and name of all the possible isomers of M.

(c) P and Q are the isomers of M shown in (b) above. When each of them was reacted separately with sodium ethoxide in ethanol and heated, P formed a colourless gas, R, that decolourised bromine water while Q forms an ether.

(i) Identify P, Q and R.

(d) Name the type of reaction leading to formation of:

(i) R (ii) the ether

Chapter 6

Alcohols and Phenols

6.1 Alcohols

6.1.1 Introduction

Alcohols are compounds containing one or more hydroxyl groups attached to saturated carbon atom(s). They contain the **hydroxyl group** (–OH) as a functional group.

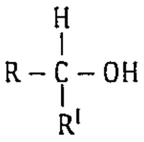
Alcohols with one hydroxyl group are called **monohydric alcohols** and the aliphatic monohydric alcohols have the general formula $C_nH_{2n+1}OH$ or ROH, where R is an alkyl group or substituted alkyl group.

Alcohols with more than one hydroxyl group are called **polyhydric alcohols**, among which we have: **dihyric alcohols** (diols), **trihydric alcohols** (triols), to mention some.

Alcohols can also be classified as **primary**, **secondary** or **tertiary alcohols** depending on the number of carbon atoms bonded on the alcohol carbon.

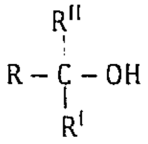
ROH

Primary alcohol



$R-\overset{H}{\underset{R^{I}}{C}}-OH$

Secondary alcohol



$R-\overset{R^{II}}{\underset{R^{I}}{C}}-OH$

Tertiary alcohol

Also, alcohols may be cyclic or open chain, may contain a double bond, a halogen atom or an aromatic ring.

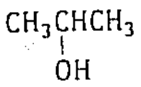
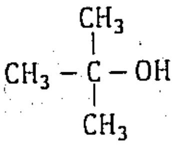
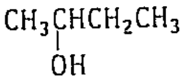
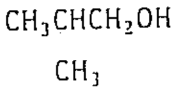
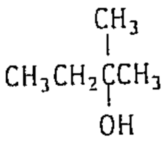
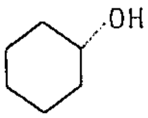
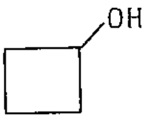
6.1.2 Nomenclature of alcohols

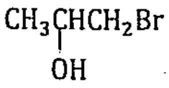
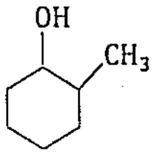
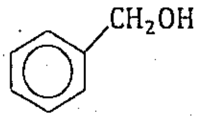
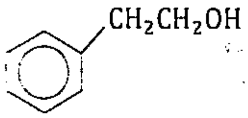
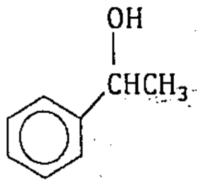
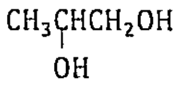
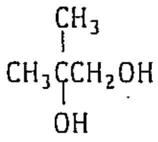
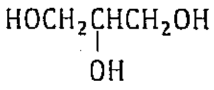
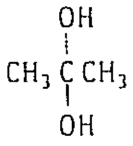
Alcohols are named following the IUPAC system as shown below:

1. The longest continuous carbon chain to which the hydroxyl group is directly attached is selected.
2. The name of the alkane corresponding to the longest continuous carbon chain is then changed to an alcohol by dropping the final '-e' and replacing it with '-ol'. Note that for polyhydric alcohols, the '-e' is maintained.
3. The longest continuous carbon chain is numbered so as to give the lowest possible number to the carbon atom bearing the hydroxyl group. Indicate the

position of the hydroxyl group by using this number as the locant. Then indicate the positions of the other substitutes by using the numbers corresponding to their positions along the carbon chain as locants.

Examples

Structural formula	IUPAC name	Classification
CH_3OH	Methanol	Primary alcohol
CH_3CH_2OH	Ethanol	Primary alcohol
$CH_3CH_2CH_2OH$	Propan-1-ol	Primary alcohol
 $CH_3\underset{\underset{OH}{\mid}}{C}HCH_3$	Propan-2-ol	Secondary alcohol
 $CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-OH$	2-Methylpropan-2-ol	Tertiary alcohol
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol	Primary alcohol
 $CH_3\underset{\underset{OH}{\mid}}{C}HCH_2CH_3$	Butan-2-ol	Secondary alcohol
 $CH_3\underset{CH_3}{CH}CH_2OH$	2-Methylpropan-1-ol	Primary alcohol
 $CH_3CH_2\overset{\overset{CH_3}{\mid}}{\underset{\underset{OH}{\mid}}{C}}CH_3$	2-Methylpropan-2-ol	Tertiary alcohol
	Cyclohexanol	Secondary alcohol
	Cyclobutanol	Secondary alcohol

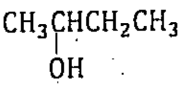
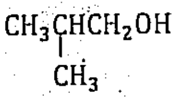
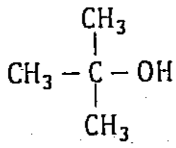
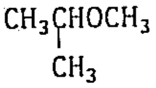
 $CH_3\underset{OH}{\underset{\vert}{C}}HCH_2Br$	1-Bromopropan-2-ol	Secondary alcohol
$ClCH_2CH_2CH_2OH$	3-Chloropropan-1-ol	Primary alcohol
	2-Methylcyclohexanol	Secondary alcohol
	Phenylmethanol	Primary alcohol
	2-Phenylethanol	Primary alcohol
	1-Phenylethanol	Secondary alcohol
$HOCH_2CH_2OH$	Ethane-1,2-diol	Dihydric primary alcohol
 $CH_3\underset{OH}{\underset{\vert}{C}}HCH_2OH$	Propane-1,2-diol	Dihydric with primary and secondary character
 $CH_3\overset{CH_3}{\overset{\vert}{\underset{OH}{\underset{\vert}{C}}}}CH_2OH$	2-Methylpropane-1,2-diol	Dihydric with primary and tertiary character
 $HOCH_2\underset{OH}{\underset{\vert}{C}}HCH_2OH$	Propane-1,2,3-triol	Trihydric with both primary and secondary character
 $CH_3\overset{OH}{\overset{\vert}{\underset{OH}{\underset{\vert}{C}}}}CH_3$	Propane-2,2-diol	Germinal diol

6.1.3 Isomerism of alcohols

Alcohols exhibit **chain** and **positional isomerism**. They are also isomeric to ethers.

Example

The organic compound $C_4H_{10}O$ has the following isomers as illustrated in the table below.

Structural formula of isomer	IUPAC name of isomer
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol
 $CH_3\underset{\substack{\mid\\ OH}}{C}HCH_2CH_3$	Butan-2-ol
 $CH_3\underset{\substack{\mid\\ CH_3}}{C}HCH_2OH$	2-Methylpropan-1-ol
 $CH_3-\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}-OH$	2-Methylpropan-2-ol
$CH_3CH_2OCH_2CH_3$	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	1-Methoxypropane
 $CH_3\underset{\substack{\mid\\ CH_3}}{C}HOCH_3$	2-Methoxypropane

Note

Tests can be carried out to distinguish the isomeric alcohols and also distinguish alcohols from ethers as we shall see later.

6.1.4 Physical properties of alcohols

(a) Physical state

Aliphatic alcohols with less than 12 carbon atoms and the lower aryl alcohols are liquids at room temperature. Aliphatic alcohols containing more than 12 carbon atoms and higher aryl alcohols are waxy solids.

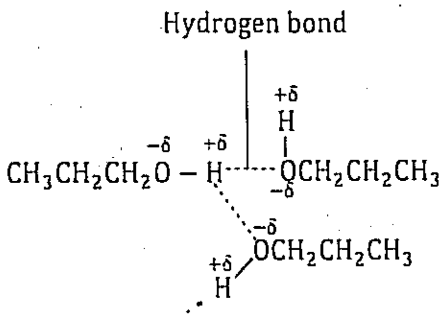
(b) Boiling points

Boiling points of alcohols increase with increasing relative molecular mass. For the same reasons as for alkanes, increased branching of the carbon chain leads to a decrease in boiling point. Alcohols also have higher boiling points than alkanes or ethers of approximately the same molecular weight.

For example, butane (Mr=58) boils at -0.5^{0}C whereas propan-1-ol (Mr=60) boils at 98^{0}C.

Explanation

In propan-1-ol, the oxygen atom is **more electronegative** than the hydrogen atom of the hydroxyl group and therefore **attracts the bonding electrons more towards itself than the hydrogen atom does**. The oxygen atom gains a partial negative charge while the hydrogen gains a **partial positive charge**. This makes the O – H bond polar and therefore propan-1-ol molecules **interact more strongly by intermolecular hydrogen bonding** that would require **higher amount of energy to break** in liquid phase.



In butane, the carbon-hydrogen bonds are **non-polar** since carbon and hydrogen nearly have the **same electronegativity**. Butane molecules are only weakly held by the weak Van der Waal's forces that require a **lower amount of energy to break.**

Polyhydric alcohols have higher boiling points than monohydric alcohols containing the same number of carbon atoms. For example, ethane-1,2-diol boils at 197^{0}C while ethanol boils at 78.3^{0}C.

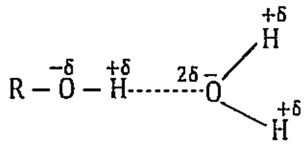
Explanation

Ethane-1,2-diol has two **hydroxyl groups** and forms **more intermolecular hydrogen bonds per molecule** than ethanol which has **only one hydroxyl group**. Hence, ethane-1,2-diol molecules are **more highly associated**, requiring **higher amount of energy** to separate than does the ethanol molecules.

Note: For the same reason, ethane-1,2-diol is used as an antifreeze coupled with its very high solubility in water.

(c) Solubility

Methanol, ethanol, propan-1-ol, propan-2-ol and 2-methylpropan-2-ol are all completely miscible with water. This is due to their ability to form intermolecular hydrogen bonds with water molecules.



The solubility of alcohols in water decreases as the hydrocarbon chain of the molecule lengthens. All alcohols are soluble in organic (non-polar) solvents and the simpler ones are themselves useful organic solvents.

6.1.5 Preparation methods of alcohols

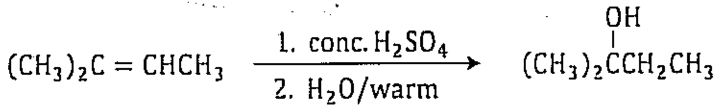
(a) Ethanol by fermentation (REFER TO THE CHAPTER: APPLIED ORGANIC CHEMISTRY).

(b) Acid-catalysed hydration of alkenes

Alkenes react with concentrated sulphuric acid at room temperature to form an alkyhydrogensulphate intermediate which when added to water and warmed is hydrolysed to an alcohol.

For example

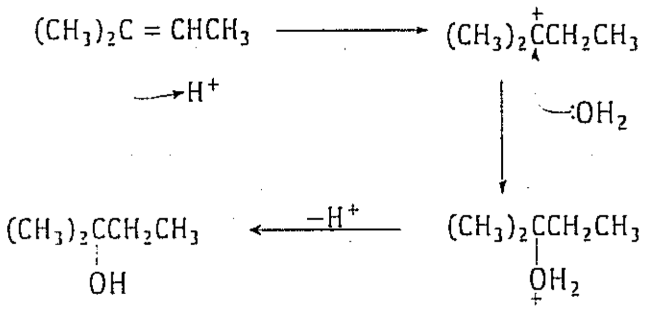
(i)



$$(CH_3)_2C=CHCH_3 \xrightarrow[2.\ H_2O/warm]{1.\ conc.\ H_2SO_4} (CH_3)_2\overset{OH}{C}CH_2CH_3$$

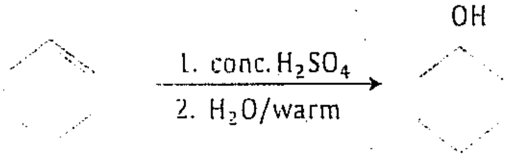
Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$



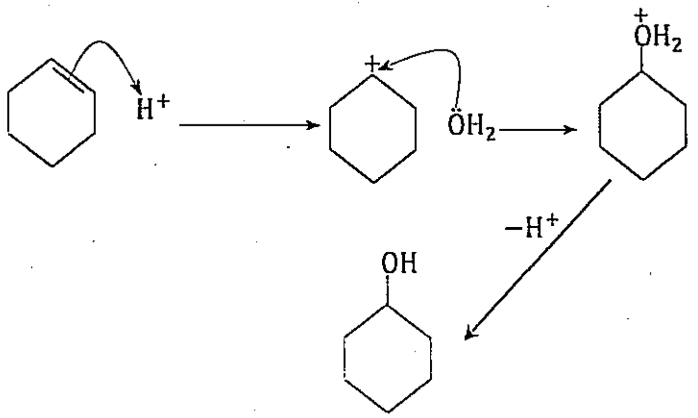
$$(CH_3)_2C=CHCH_3 \xrightarrow{H^+} (CH_3)_2\overset{+}{C}CH_2CH_3 \xrightarrow{:OH_2} (CH_3)_2\underset{\overset{+}{O}H_2}{C}CH_2CH_3 \xrightarrow{-H^+} (CH_3)_2\underset{OH}{C}CH_2CH_3$$

(ii)



Mechanism

$$H_2O \rightleftharpoons H^+ + HSO_4^-$$



(c) Hydrolysis of halohydrocarbons

- Alcohols can be formed by reacting alkylhalides with an aqueous solution of sodium hydroxide or potassium hydroxide.

For example

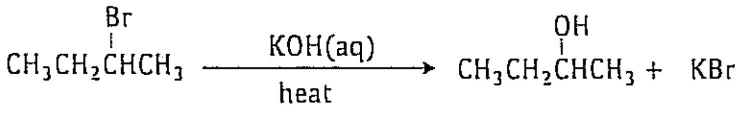
(i) $$CH_3CH_2CH_2I \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2CH_2OH + NaI$$

<u>Mechanism</u>

$$NaOH(aq) \longrightarrow Na^+(aq) + \bar{O}H(aq)$$

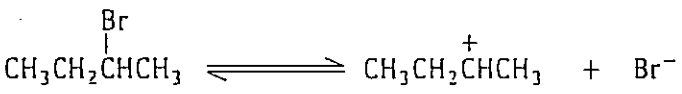
$$H\bar{O} \quad CH_3CH_2CH_2 - I \longrightarrow CH_3CH_2CH_2OH + I^-$$

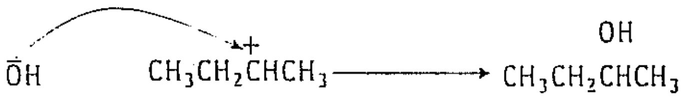
$$Na^+ + I^- \longrightarrow NaI$$

(ii)

$$CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3 \xrightarrow[\text{heat}]{KOH(aq)} CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3 + KBr$$

<u>Mechanism</u>

$$KOH(aq) \longrightarrow K^+(aq) + \bar{O}H(aq)$$


$$CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3 \rightleftharpoons CH_3CH_2\overset{+}{C}HCH_3 + Br^-$$


$$\bar{O}H \quad CH_3CH_2\overset{+}{C}HCH_3 \longrightarrow CH_3CH_2\overset{OH}{C}HCH_3$$

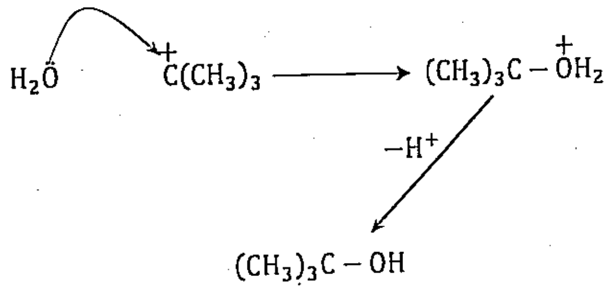
$$K^+ + Br^- \longrightarrow KBr$$

(iii) For tertiary alkylhalides, water alone can rapidly hydrolyse them to tertiary alcohols on boiling.

$$(CH_3)_3C-Br \xrightarrow[boil]{H_2O} (CH_3)_3C-OH \quad + \quad HBr$$

Mechanism

$$(CH_3)_3C-Br \rightleftharpoons (CH_3)_3C^+ \quad + \quad Br^-$$



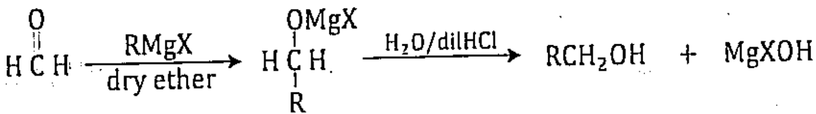
$$H_2\ddot{O} \quad \overset{+}{C}(CH_3)_3 \longrightarrow (CH_3)_3C-\overset{+}{O}H_2 \xrightarrow{-H^+} (CH_3)_3C-OH$$

$$H^+ \quad + \quad Br^- \longrightarrow HBr$$

(d) Using Grignard's reagents

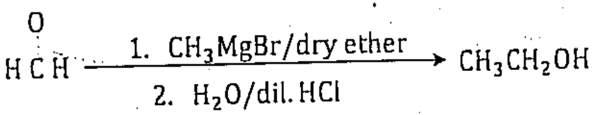
Carbonyl compounds can be reduced to alcohols by Grignard synthesis.

(i) With methanol, a primary alcohol is formed.

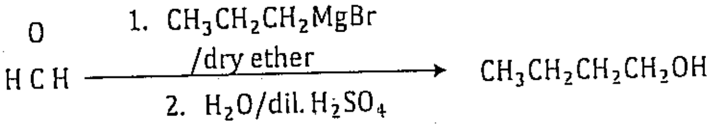


$$H\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{dry ether}]{RMgX} H\underset{R}{\overset{OMgX}{C}}H \xrightarrow{H_2O/dilHCl} RCH_2OH \quad + \quad MgXOH$$

For example

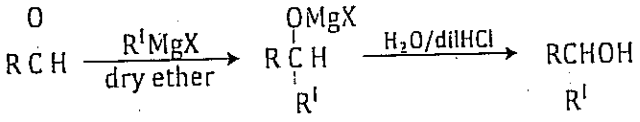


$$H\overset{O}{C}H \xrightarrow[\text{2. } H_2O/dil.HCl]{\text{1. } CH_3MgBr/\text{dry ether}} CH_3CH_2OH$$



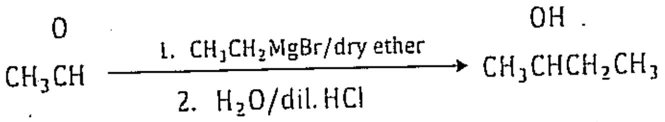
$$H\overset{O}{C}H \xrightarrow[\text{2. } H_2O/dil.H_2SO_4]{\text{1. } CH_3CH_2CH_2MgBr\ /\text{dry ether}} CH_3CH_2CH_2CH_2OH$$

(ii) With any other aldehydes other than methanol, secondary alcohols are formed.

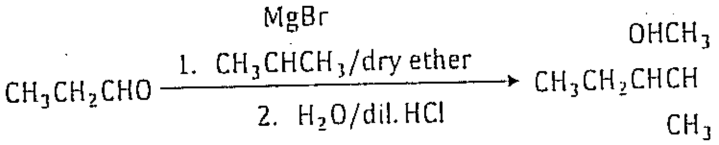


$$R\overset{O}{C}H \xrightarrow[\text{dry ether}]{R^IMgX} R\underset{R^I}{\overset{OMgX}{C}}H \xrightarrow{H_2O/dilHCl} R\underset{R^I}{C}HOH$$

For example

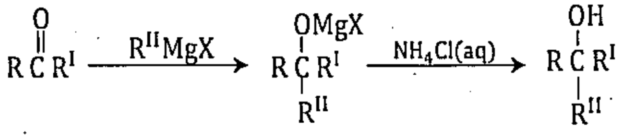


$$CH_3\overset{O}{C}H \xrightarrow[\text{2. } H_2O/dil.HCl]{\text{1. } CH_3CH_2MgBr/\text{dry ether}} CH_3\overset{OH}{C}HCH_2CH_3$$



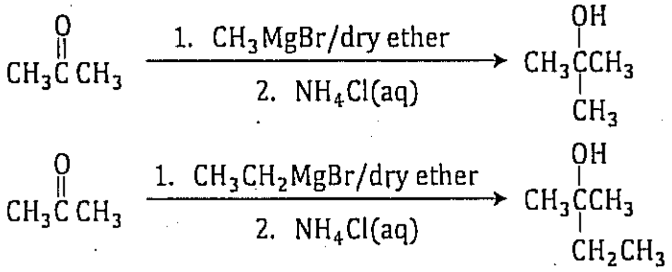
$$CH_3CH_2CHO \xrightarrow[\text{2. } H_2O/dil.HCl]{\text{1. } CH_3\overset{MgBr}{C}HCH_3/\text{dry ether}} CH_3CH_2\overset{OH}{C}H\underset{CH_3}{\overset{CH_3}{C}H}$$

(iii) Tertiary alcohols are formed from ketones but the hydrolysis is done using aqueous ammonium chloride because the dilute acid tends to dehydrate the alcohol forming an alkene.



$$R\overset{\overset{O}{\|}}{C}R^{I} \xrightarrow{R^{II}MgX} R\overset{OMgX}{\underset{R^{II}}{C}}R^{I} \xrightarrow{NH_4Cl(aq)} R\overset{OH}{\underset{R^{II}}{C}}R^{I}$$

For example



$$CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[2.\ NH_4Cl(aq)]{1.\ CH_3MgBr/dry\ ether} CH_3\overset{OH}{\underset{CH_3}{C}}CH_3$$

$$CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[2.\ NH_4Cl(aq)]{1.\ CH_3CH_2MgBr/dry\ ether} CH_3\overset{OH}{\underset{CH_2CH_3}{C}}CH_3$$

Note

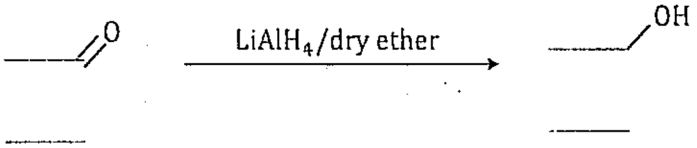
Grignard synthesis is a very important method in synthesis of organic compounds since it increases the carbon chain to any required number of carbon atoms and can also introduce branches in a given compound.

(e) Reduction of carbonyl compounds using lithium tetrahydridoaluminate(III)

Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols. Dry ether is used as a solvent in this method.

Examples

$$CH_3CH_2CHO \xrightarrow{LiAlH_4/dry\ ether} CH_3CH_2CH_2OH$$

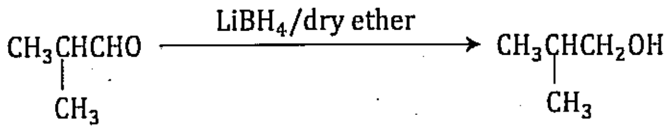


Other reducing agents that can be used include:

- Lithium tetrahydridoborate(III) in presence of dry ether.
- Sodium tetrahydridoborate(III) in water or methanol.
- Hydrogen in presence of nickel catalyst on heating.
- Sodium and ethanol.
- Zinc and ethanol acid.

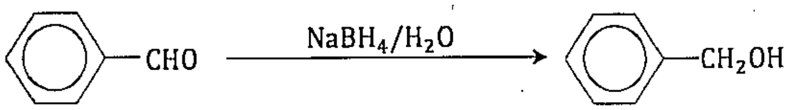
Examples

(i)

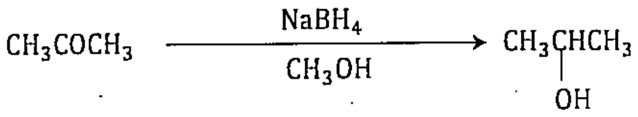


$$CH_3\underset{\displaystyle CH_3}{CH}CHO \xrightarrow{LiBH_4/\text{dry ether}} CH_3\underset{\displaystyle CH_3}{CH}CH_2OH$$

(ii)

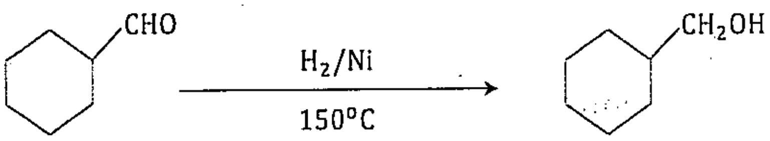


(iii)

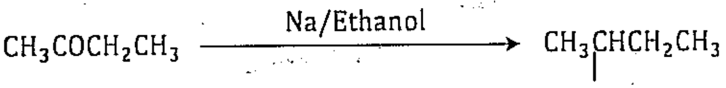


$$CH_3COCH_3 \xrightarrow[CH_3OH]{NaBH_4} CH_3\underset{\displaystyle OH}{CH}CH_3$$

(iv)

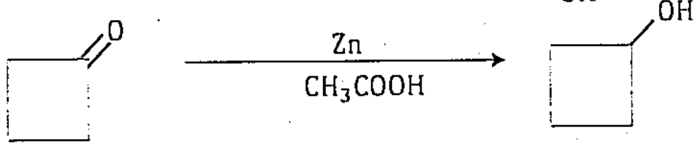


(v)



$$CH_3COCH_2CH_3 \xrightarrow{Na/\text{Ethanol}} CH_3\underset{\displaystyle OH}{CH}CH_2CH_3$$

(vi)



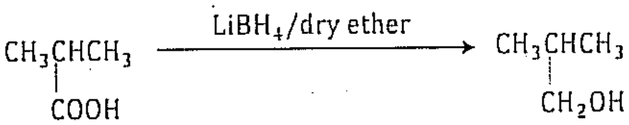
(f) Clemmensen reduction

(CHECK alkanes and carbonyl compounds)

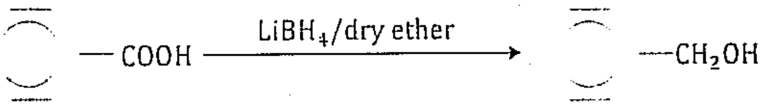
(g) Reduction of carboxylic acids

Primary alcohols can be formed by reduction of carboxylic acids using lithium tetrahydridoaluminate(III) in dry ether.

Examples



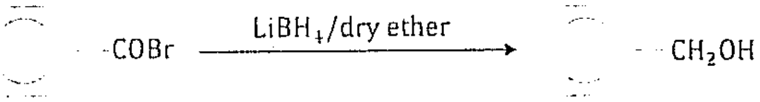
$$CH_3\underset{\displaystyle COOH}{CH}CH_3 \xrightarrow{LiBH_4/\text{dry ether}} CH_3\underset{\displaystyle CH_2OH}{CH}CH_3$$



(h) Reduction of acid halides

Acid halides are reduced by lithium tetrahydridoaluminate(III) to alcohols.

$$CH_3CH_2COCl \xrightarrow{LiBH_4/\text{dry ether}} CH_3CH_2CH_2OH$$



The reduction can also be achieved by bubbling hydrogen through the acid halide as shown in the example below:

$$CH_3COCl \xrightarrow[1,2-\text{dimethylbenzene}]{H_2/\text{colloidal Pt catalyst}} CH_3CH_2OH$$

(i) Reduction of esters

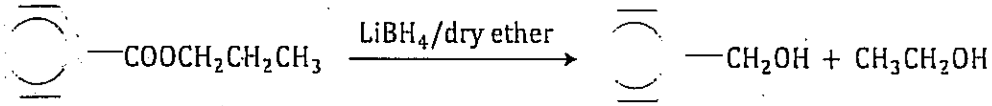
Alcohols can be formed by reduction of esters using either lithium tetrahydridoaluminate(III) or sodium in ethanol.

For example,

$$CH_3COOCH_3 \xrightarrow{LiBH_4/\text{dry ether}} CH_3CHOH + CH_3OH$$

$$HCOOCH_2CH_3 \xrightarrow{Na/\text{Ethanol}} CH_3OH + CH_3CH_2OH$$

$$CH_3CH_2COOCH_2CH_2CH_3 \xrightarrow{LiBH_4/\text{dry ether}} 2CH_3CH_2CH_2OH$$

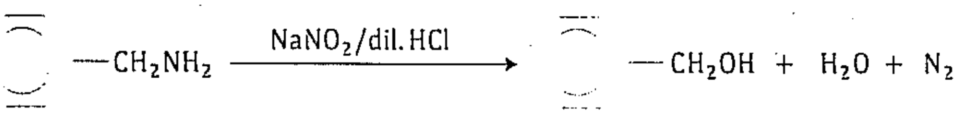


(j) From primary amines

Primary amines react with nitrous acid which is formed in situ from sodium nitrite and dilute hydrochloric acid to form primary alcohols.

For example,

$$CH_3CH_2NH_2 \xrightarrow{NaNO_2/\text{dil. HCl}} CH_3CH_2OH + H_2O + N_2$$



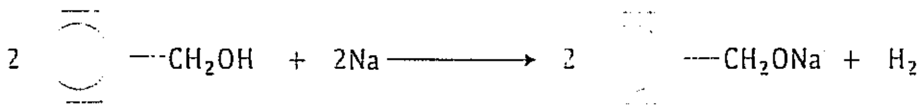
6.1.6 Chemical properties of alcohols

(a) Reaction with sodium

Alcohols react with sodium to form hydrogen gas and a sodium alkoxide.

For example, ethanol forms sodium ethoxide and hydrogen gas.

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$$



(b) Reaction with concentrated sulphuric acid

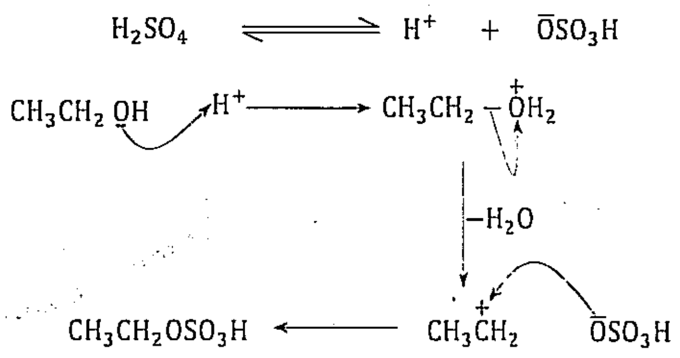
Alcohols react with concentrated sulphuric acid to form different products depending on reaction conditions and the type of alcohol.

(i) At 0°C, an alkylhydrogensulphate is formed.

Ethanol, for example, forms ethlyhydrogensulphate.

$$CH_3CH_2OH \xrightarrow[0^oC]{conc.\ H_2SO_4} CH_3CH_2OSO_3H + H_2O$$

Mechanism



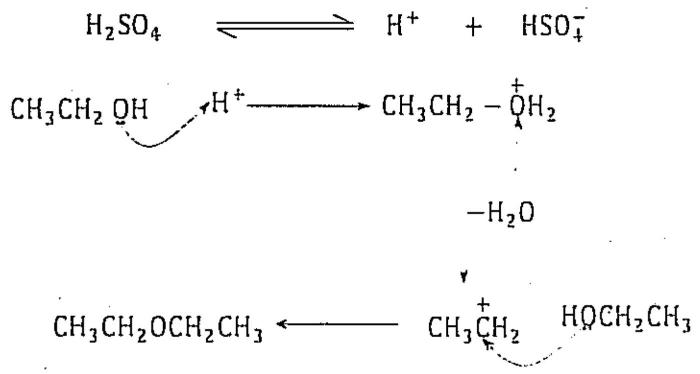
$$CH_3CH_2CH_2OH \xrightarrow[0^oC]{conc.\ H_2SO_4} CH_3CH_2CH_2OSO_3H$$

(ii) When concentrated sulphuric acid is used and an excess of a primary alcohol at 140°C, an ether is formed.

For example, ethanol forms ethoxyethane.

$$CH_3CH_2OH \xrightarrow[140^oC]{conc.\ H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

Mechanism

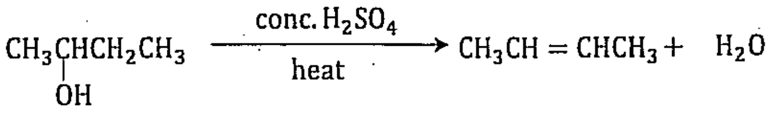


(iii) When an excess of concentrated sulphuric acid is used and the temperature raised to 170–180°C, an alkene is formed.

For example, ethanol forms ethene at 170–180°C.

$$CH_3CH_2OH \xrightarrow[180^oC]{conc.\ H_2SO_4} H_2C=CH_2 + H_2O$$

Secondary and tertiary alcohols too can be dehydrated to form corresponding alkenes.



$$CH_3\underset{OH}{CH}CH_2CH_3 \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} CH_3CH = CHCH_3 + H_2O$$

$$(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} (CH_3)_2C = CH_2 + H_2O$$

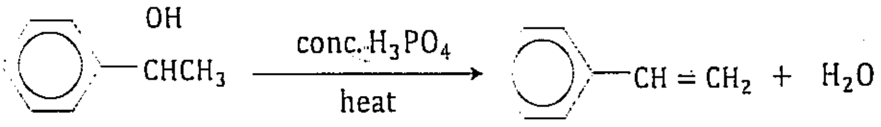
(*Check section 3.2.6 for mechanisms*)

(c) Reaction with concentrated phosphoric acid

Alcohols can also be dehydrated to form alkenes using hot concentrated phosphoric acid.

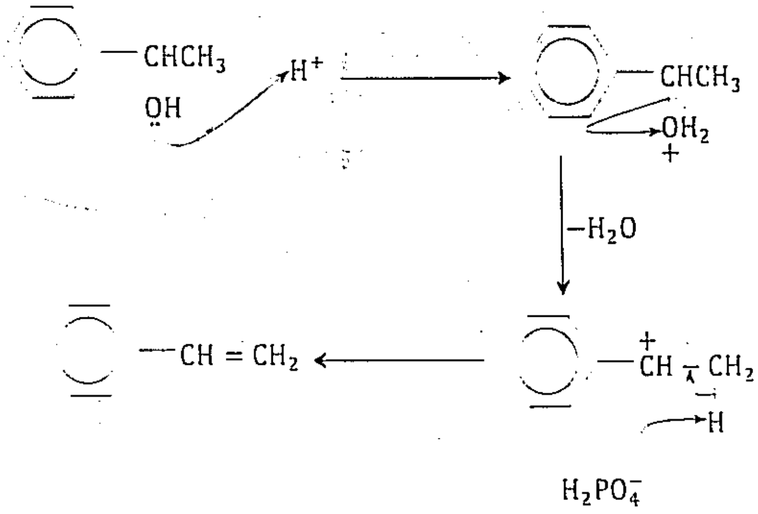
For example

(i)



Mechanism

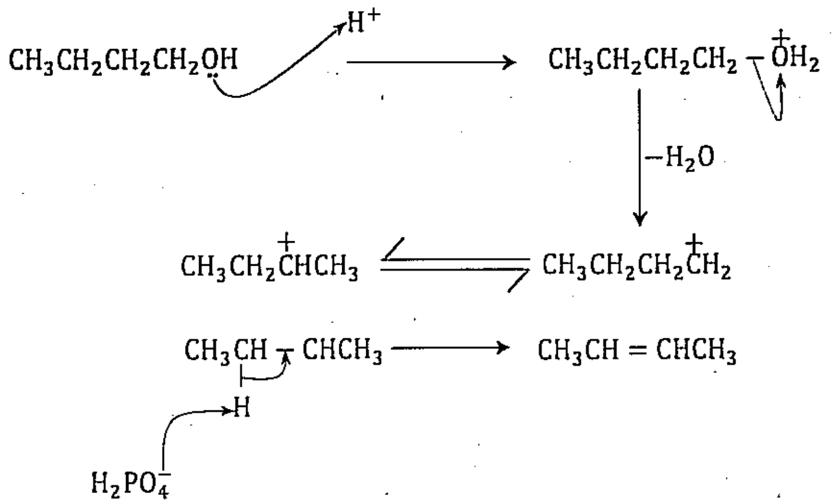
$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$



(ii) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{conc. } H_3PO_4} CH_3CH = CHCH_3 + H_2O$

Mechanism

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$



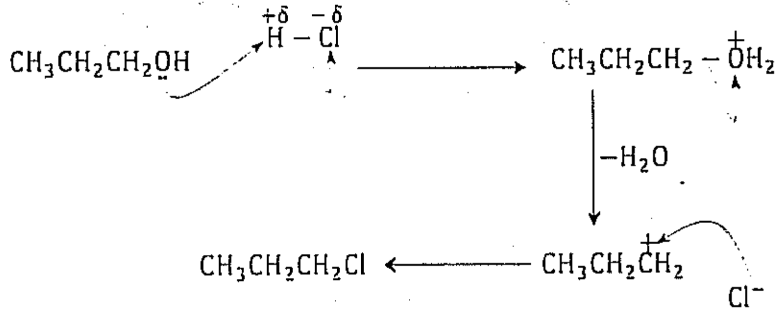
(d) Reaction with hydrogen halides

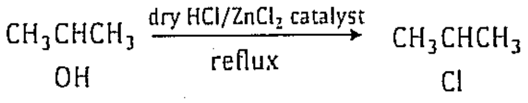
(i) Chlorination

Anhydrous alcohols react with dry hydrogen chloride gas in presence of anhydrous zinc chloride catalyst to form alkylchlorides. The gas is bubbled through the alcohol or concentrated hydrochloric acid can be used until the solution is saturated and refluxed on a water bath.

$$CH_3CH_2CH_2OH \xrightarrow[\text{reflux}]{\text{dry HCl/ZnCl}_2\text{ catalyst}} CH_3CH_2CH_2Cl$$

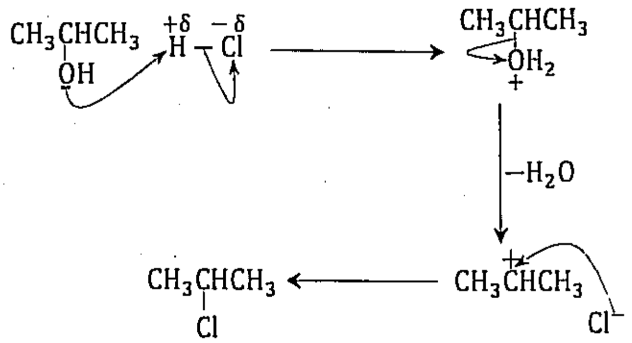
<u>Mechanism</u>





$$\underset{\text{OH}}{CH_3CHCH_3} \xrightarrow[\text{reflux}]{\text{dry HCl/ZnCl}_2\text{ catalyst}} \underset{\text{Cl}}{CH_3CHCH_3}$$

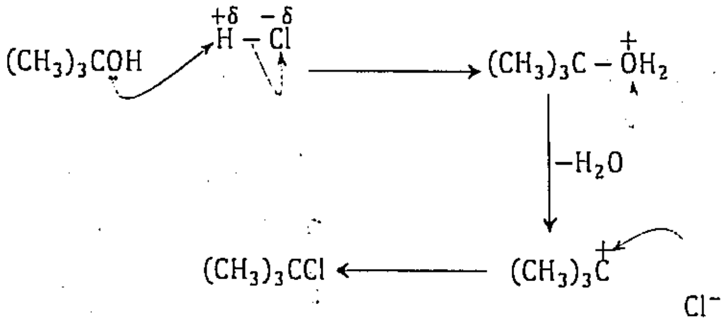
<u>Mechanism</u>



For tertiary alcohols, the catalyst may not be used.

$$(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc. HCl}} (CH_3)_3CCl$$

Mechanism



(ii) Bromination

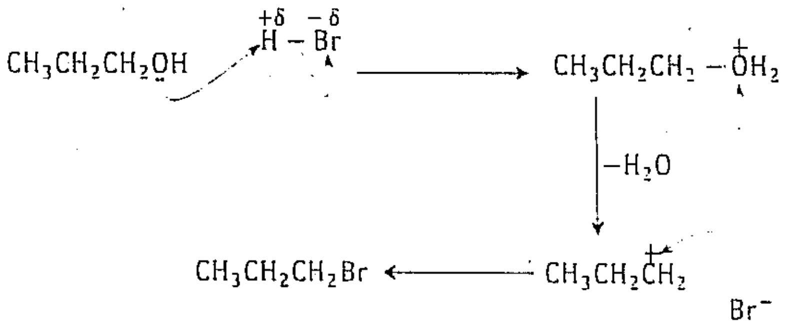
Alcohols react with hydrogen bromide for form alkylbromides.

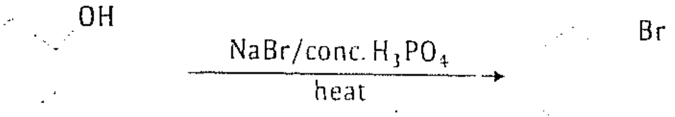
The hydrogen bromide is prepared from sodium bromide and concentrated phosphoric acid.

$$CH_3CH_2CH_2OH \xrightarrow[\text{reflux}]{\text{NaBr/conc. } H_3PO_4} CH_3CH_2CH_2Br$$

Mechanism

$$H_3PO_4 + 2NaBr \longrightarrow 2HBr + Na_2HPO_4$$

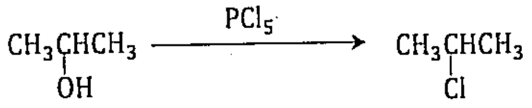




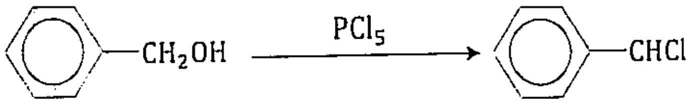
(e) **Reaction with phosphorus halides**

(i) Alcohols react with phosphorus(V) chloride to form alkylchlorides.

For example



$$\underset{OH}{CH_3CHCH_3} \xrightarrow{PCl_5} \underset{Cl}{CH_3CHCH_3}$$



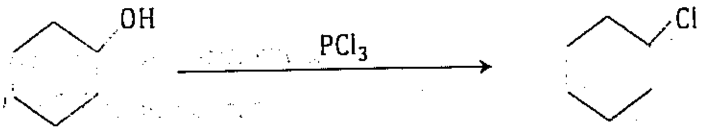
The general equation is:

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

Sulphur dichloride oxide (thionyl chloride) can similarly be used in presence of pyridine on reflux.

$$CH_3CH_2OH \xrightarrow[\text{pyridine/ reflux}]{SOCl_2} CH_3CH_2Cl$$

Phosphorus(III) chloride can also be used although the reaction is slow.



(ii) Alcohols also react with phosphorus(III) bromide or phosphorus(III) iodide to form alkyl bromides and alkyl iodides respectively.

Bromine or iodine is added to the alcohol and red phosphorus and the mixture refluxed on a water bath.

$$CH_3CH_2OH \xrightarrow[\text{reflux}]{I_2 + \text{Red } P_4} CH_3CH_2I$$

$$CH_3CH_2OH \xrightarrow[\text{reflux}]{Br_2 + \text{Red } P_4} CH_3CH_2Br$$

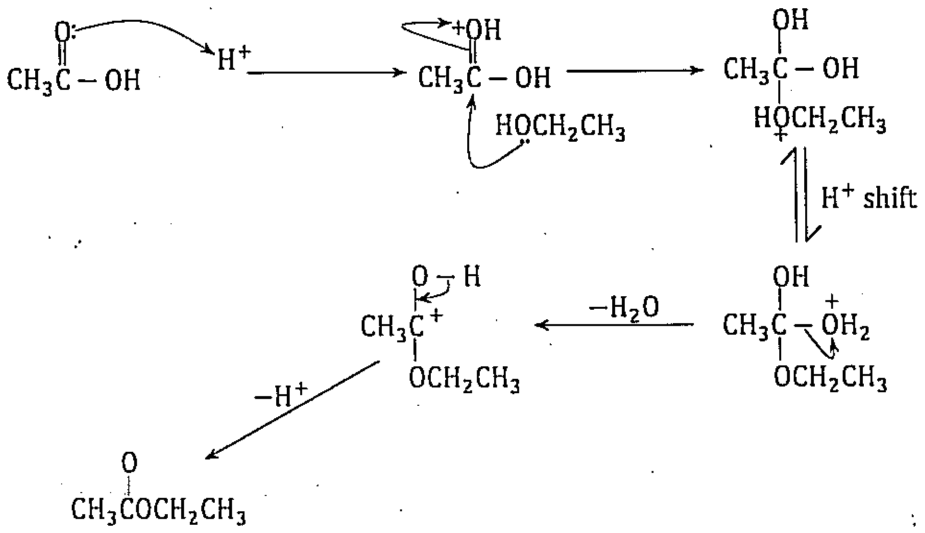
(f) **Esterification using carboxylic acids**

Alcohols react with carboxylic acids in presence of concentrated sulphuric acid catalyst to form esters on heating.

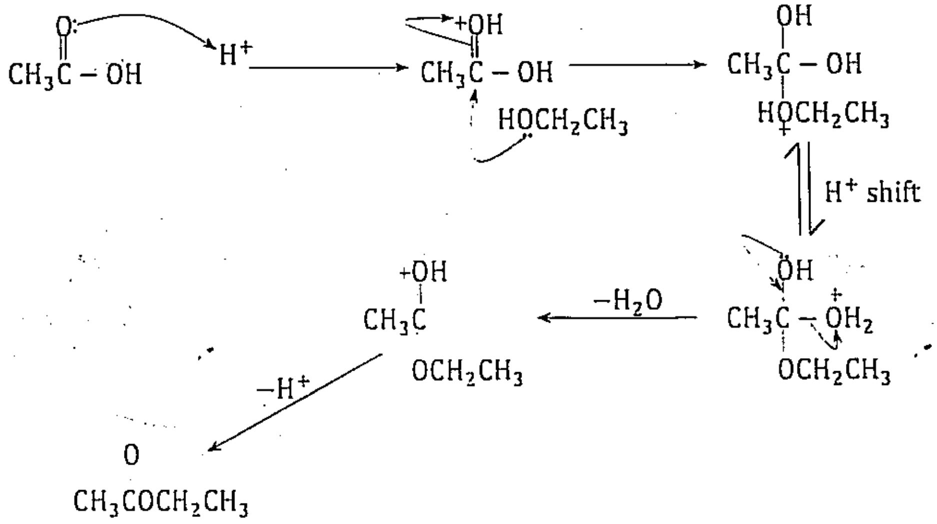
For example

$$CH_3CH_2OH + CH_3COOH \xrightarrow[\text{Heat}]{\text{conc. } H_2SO_4} CH_3COOCH_2CH_3 + H_2O$$

<u>Mechanism</u>



Alternatively



Note

For more explanation of this kind of esterification check under carboxylic acids and esters.

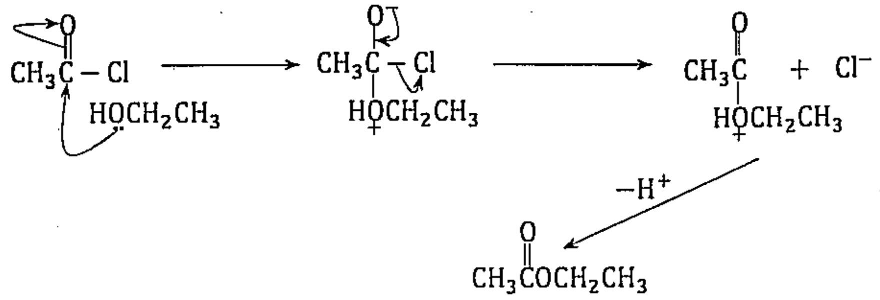
(g) Reaction with acid halides

Alcohols react with acid halides to form esters.

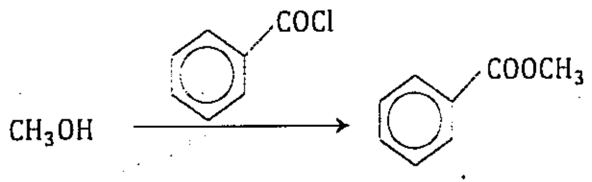
For example

(i) $CH_3CH_2OH + CH_3COCl \longrightarrow CH_3COOCH_2CH_3 + HCl$

<u>Mechanism</u>

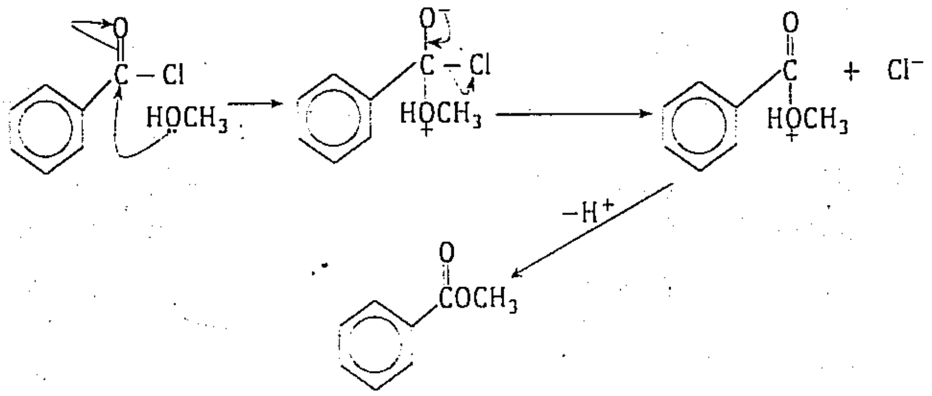


$H^+ + Cl^- \longrightarrow HCl$

(ii) 

methylbenzoate

Mechanism



$H^+ + Cl^- \longrightarrow HCl$

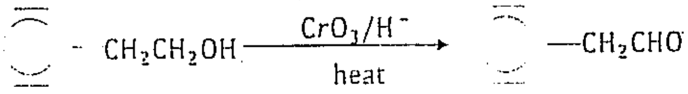
(h) Oxidation of primary and secondary alcohols

1. Primary alcohols can be oxidized to aldehydes using acidified potassium dichromate(VI) solution, acidified manganese(IV) oxide or acidified chromium(VI) oxide on heating.

Examples

(i) $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{K_2Cr_2O_7(aq)/H^+(aq)} CH_3CH_2CHO$

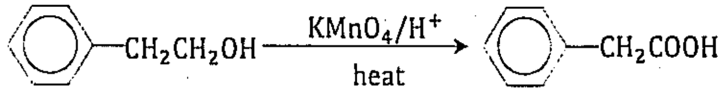
(ii) $CH_3CH_2OH \xrightarrow[\text{heat}]{MnO_2/H^+} CH_3CHO$

(iii) 

Note

When excess of the acidified dichromate solution is used, a carboxylic acid is formed. Acidified potassium manganate(VII) solution is a very powerful an oxidizing agent and will oxidise the primary alcohols to carboxylic acids.

(i) $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{K_2Cr_2O_7(aq)/H^+(aq)} CH_3CH_2COOH$

(ii) 

General balanced equations,

$$3RCH_2OH(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \longrightarrow 3RCHO(l) + 2Cr^{3+}(aq) + 7H_2O(l)$$

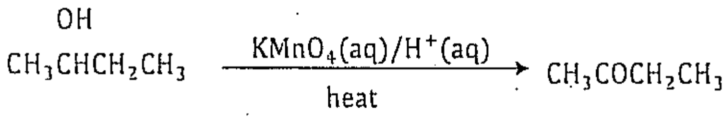
$$3RCH_2OH(l) + CrO_3(s) + 6H^+(aq) \longrightarrow 3RCHO(l) + 2Cr^{3+}(aq) + 6H_2O(l)$$

$$3RCH_2OH(l) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \longrightarrow 3RCOOH(l) + 4Cr^{3+}(aq) + 11H_2O(l)$$

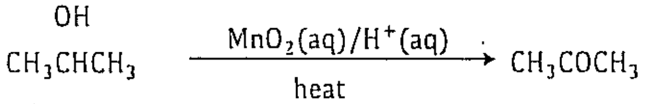
Observation for each reagent

Reagent used	Observation
Acidified potassium dichromate(VI) solution	Orange solution turns green
Acidified chromium(VI) oxide	Red solution turns green
Acidified potassium manganate(VII) solution	Purple solution turns colourless

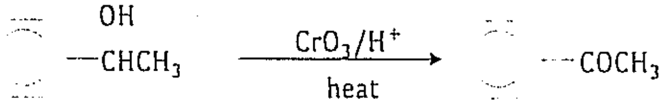
2. Secondary alcohols are oxidized to ketones by any suitable oxidizing agent.

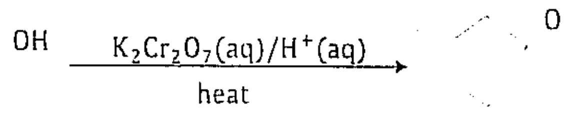
(i) 

$$CH_3\overset{OH}{C}HCH_2CH_3 \xrightarrow[\text{heat}]{KMnO_4(aq)/H^+(aq)} CH_3COCH_2CH_3$$

(ii) 

$$CH_3\overset{OH}{C}HCH_3 \xrightarrow[\text{heat}]{MnO_2(aq)/H^+(aq)} CH_3COCH_3$$

(iii) 

(iv) 

Note: Tertiary alcohols are resistant to oxidation.

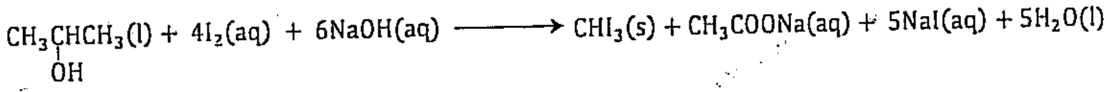
(i) Oxidation of methylalcohols

The only primary alcohol with a methyl group attached to the carbon atom containing a hydroxyl group (ethanol) and all secondary alcohols of the form $CH_3\underset{\substack{|\\OH}}{C}HR$, are oxidized by iodine solution in presence of sodium hydroxide to form a yellow precipitate of triiodomethane (CHI_3).

This test is called the **iodoform test.**

Examples

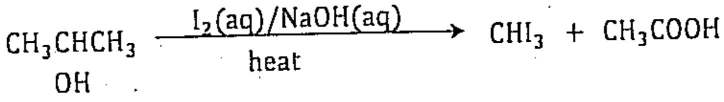
$$CH_3CH_2OH(l) + 4I_2(aq) + 6NaOH(aq) \longrightarrow CHI_3(s) + HCOONa(aq) + 5NaI(aq) + 5H_2O(l)$$



$$CH_3\underset{\substack{|\\OH}}{C}HCH_3(l) + 4I_2(aq) + 6NaOH(aq) \longrightarrow CHI_3(s) + CH_3COONa(aq) + 5NaI(aq) + 5H_2O(l)$$

Similarly, the equations may be written as:

$$CH_3CH_2OH \xrightarrow[\text{heat}]{I_2(aq)/NaOH(aq)} CHI_3 + HCOOH$$



$$\underset{OH}{CH_3CHCH_3} \xrightarrow[\text{heat}]{I_2(aq)/NaOH(aq)} CHI_3 + CH_3COOH$$

6.1.7 Test for alcohols

The functional group in alcohols is the hydroxyl group (–OH). It can be tested using sodium metal.

Observation: Bubbles of a colourless gas produced.

Phosphorus pentachloride or ethanoylchloride can also be used to test for the - OH group.

Observation: Dense white fumes are formed.

Note

All classes of alcohols give positive results for the above tests. However, the three classes of alcohols can be distinguished using ***Lucas reagent.***

Lucas reagent is a mixture of equimolar quantities of concentrated hydrochloric acid and anhydrous zinc chloride at room temperature.

Each of the classes of alcohols forms a corresponding alkyl chloride.

Primary alcohols show no observable change.

Secondary alcohols form a cloudy solution within 5 minutes.

Tertiary alcohols form a cloudy solution immediately.

6.1.8 Uses of ethanol

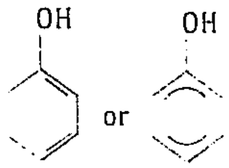
- Ethanol is used in the manufacture of alcoholic beverages.
- As a solvent for pharmaceutical preparations and a constituent for medicines.
- Manufacture of ethanal, ethyl ethanoate, cosmetics, ethanoic acid, chloroform, e.t.c.
- As a solvent for paints, oils, perfumes, dyes, varnishes, gums, etc.
- Used as a preservative for biological specimens.
- As a fuel in spirit lamps and stoves.

6.2 Phenol

Phenol belongs to a group of organic compounds called phenols. Phenols are compounds containing the **hydroxyl group directly attached to an aromatic ring.** Phenols have the general formula **ArOH** where **Ar** is a phenyl (C_6H_5-) group, a substituted phenyl or any other aryl group.

6.2.1 Structure of phenol

Phenol has a molecular formula C_6H_5OH or C_6H_6O. It is sometimes called ***hydroxybenzene***. The structural formula of phenol is

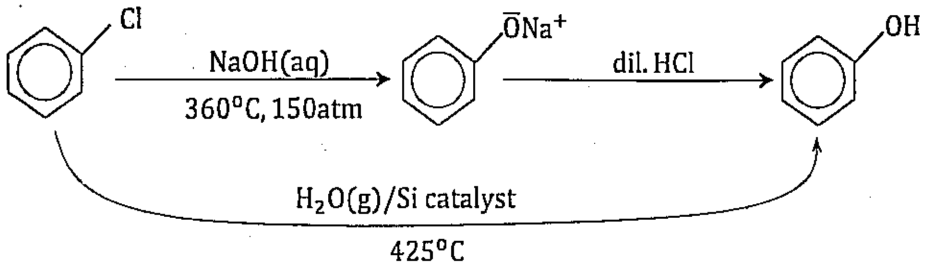


In phenol, the hydroxyl group is attached to sp^2 hybridized carbon atom of the aromatic ring and the oxygen atom of the hydroxyl group has two lone pairs. The C–O bond length in phenol is slightly less than that in methanol due to resonance in the aromatic ring of phenol.

6.2.2 Preparation of phenol

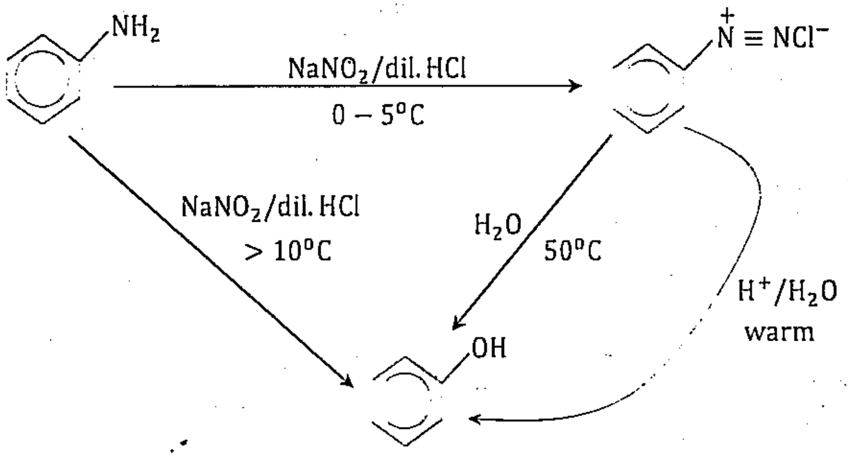
(a) From chlorobenzene

Chlorobenzene is hydrolysed by aqueous sodium hydroxide at 360^0C and 150atm to form sodium phenoxide which is reacted with dilute hydrochloric acid to form phenol. Similarly, chlorobenzene can be catalytically hydrolysed by passing it with steam over silicon catalyst at 425^0C.



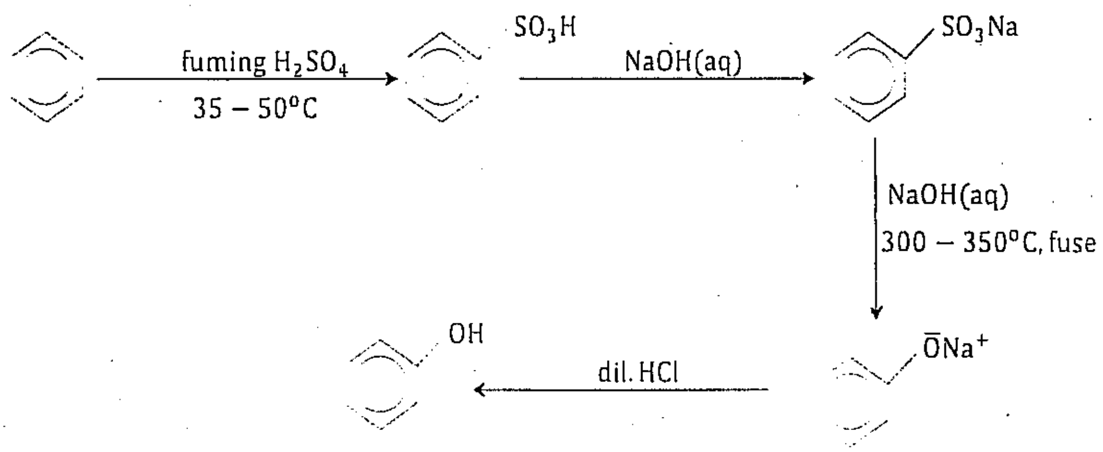
(b) From benzenediazonium salt

Benzenediazonium chloride is first formed by the reaction between phenylamine and sodium nitrite and dilute hydrochloric acid at 0–5°C. It is then warmed with water or dilute acid to form phenol.



(c) From benzenesulphonic acid

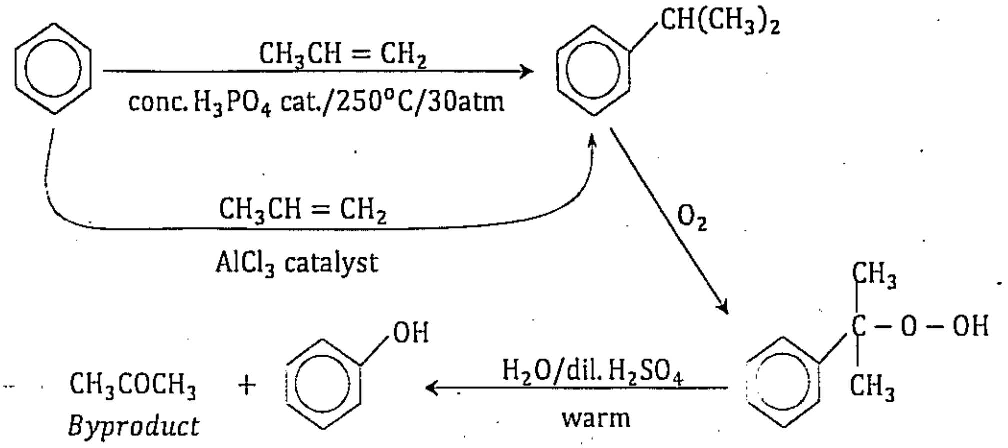
The benzenesulphonic acid is formed from sulphonation of benzene. It is then converted to sodium benzenesulphonate which is then fused with sodium hydroxide to form sodium phenoxide which is finally converted to phenol by reaction with dilute hydrochloric acid.



(d) The cumene process

Benzene is alkylated with propene in the liquid phase with aluminium chloride catalyst or in the gas phase with phosphoric acid catalyst at 250°C and 30atm to form cumene.

The cumene is then oxidized by air to form cumene hydroperoxide which is then decomposed with warm dilute sulphuric acid to form phenol along with propanone.



6.2.3 Physical properties of phenol

(a) Appearance

Phenol is a colourless crystalline hygroscopic solid but becomes pink on exposure to air and light. It has a peculiar characteristic smell and a strong corrosive action on the skin.

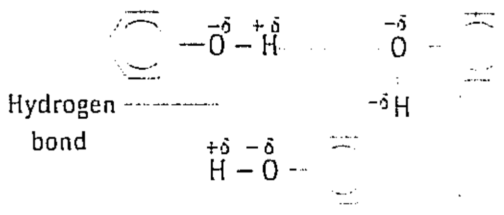
(b) Melting and boiling point

Phenol melts at 42°C and boils at 182°C.

The boiling point of phenol is much higher than corresponding aromatic hydrocarbons. For example, phenol boils at 182°C whereas methylbenzene boils at 110.6°C yet the two compounds have almost the same molecular weight.

Explanation

In phenol, the oxygen atom is **more electronegative** than the hydrogen atom of the hydroxyl group. This makes the **oxygen atom to withdraw the bonding electrons more towards itself** than does the hydrogen atom. This makes the **hydrogen-oxygen bond polar** and therefore phenol molecules interact through **intermolecular hydrogen bonding** which require a **higher amount of energy to break.**



However, molecules of methylbenzene are held by weak Van der Waal's forces that require a **lower amount of energy to break.**

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(c) Solubility

Phenol is only completely miscible with water above 65.5^{0}C. Below this temperature, phenol is only partially miscible with water because of the hydrophobic benzene ring. Its solubility in water above 65.5^{0}C is due to ability to form intermolecular hydrogen bonds with water molecules.

Phenol is however very soluble in organic solvents.

6.2.4 Chemical properties of phenol

6.2.4.1 Acidic nature

A solution of phenol is acidic.

Observation

A solution of phenol turns blue litmus paper red whereas a solution of ethanol has no effect on litmus paper.

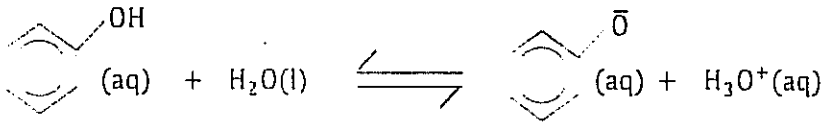
Explanation

A solution of phenol is acidic while that of ethanol is neutral.

In phenol, the **lone pair of electrons on the oxygen atom interacts with and forms part of the delocalized pi-electrons of the benzene ring, increasing the effective electron density** about it. This **strengthens the carbon-oxygen bond but weakens the oxygen-hydrogen bond**. Therefore, in aqueous solution, the oxygen-hydrogen bond easily breaks and phenol **releases protons in solution**, making the solution acidic.

In ethanol, however, the ethyl group **donates electrons towards the oxygen atom, increasing its electron density and strengthening the oxygen-hydrogen bond.** Therefore, ethanol **does not easily release protons** in aqueous solution.

The dissociation of phenol in water to form a stable phenoxide ion and hydrogen ions makes it a weak acid.



The acidic nature of phenol enables it to:

- turn blue litmus to red.
- react with sodium metal to liberate hydrogen gas.
- react with sodium hydroxide solution to form sodium phenoxide and water.

However, phenol is so weak an acid that it cannot liberate carbon dioxide from aqueous solutions of sodium carbonate or sodium hydrogen carbonate. The two reagents can therefore be used to distinguish phenol and any carboxylic acid.

6.2.4.2 Reactions of Phenol

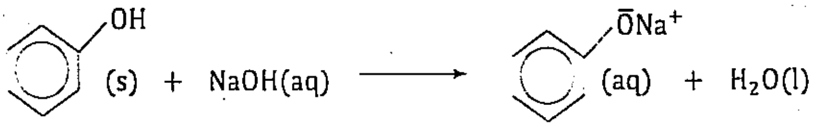
Phenol undergoes two different reactions:

- Reactions of the –OH group.
- Electrophilic substitution in the benzene ring.

1. Reactions of the –OH group

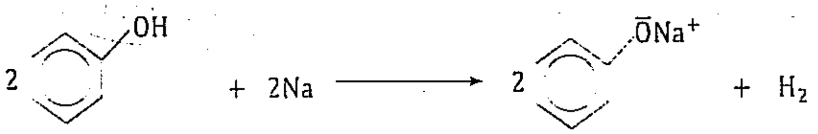
(i) Reaction with sodium hydroxide

By virtue of its acidic nature, phenol reacts with sodium hydroxide (an alkali) to form sodium phenoxide (a salt) and water.



(ii) Reaction with sodium metal

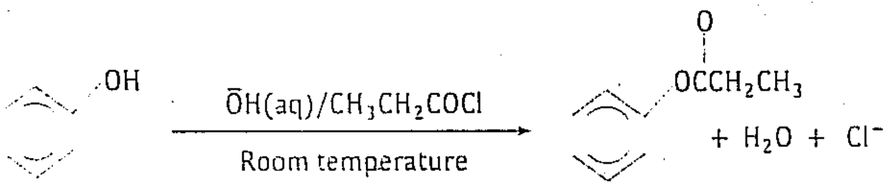
Like all alcohols, phenol reacts with sodium metal to from sodium phenoxide and hydrogen gas.



(iii) Esterification

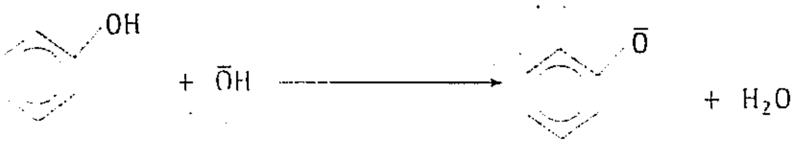
Phenol reacts with acid chlorides to form esters but the reaction occurs in alkaline medium.

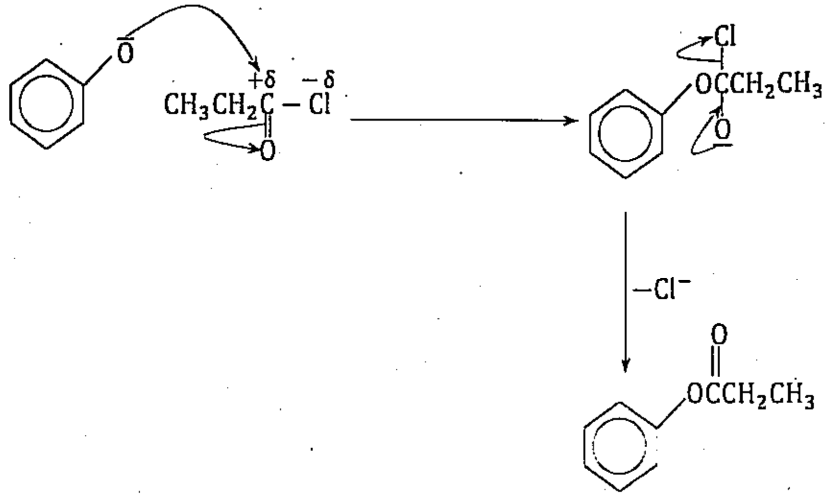
For example,

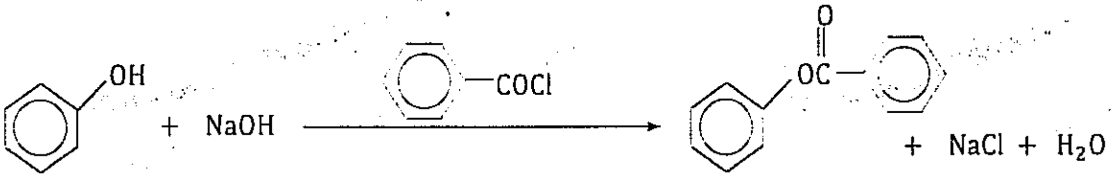


Phenylpropanoate

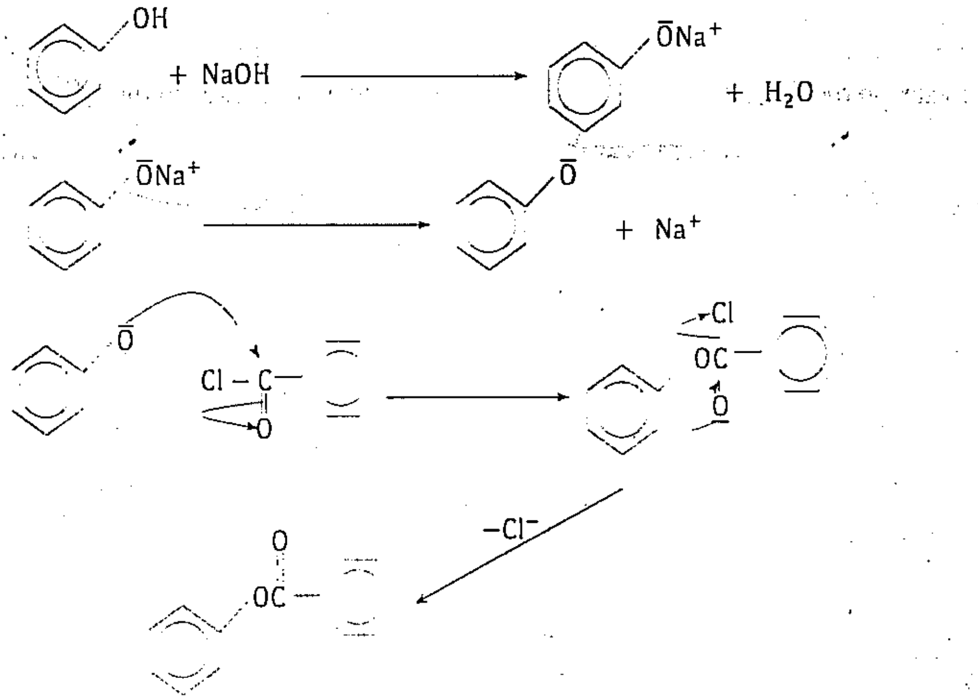
<u>Mechanism</u>







Mechanism



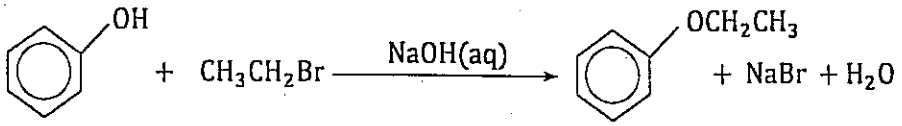
$Na^+ + Cl^- \longrightarrow NaCl$

Note

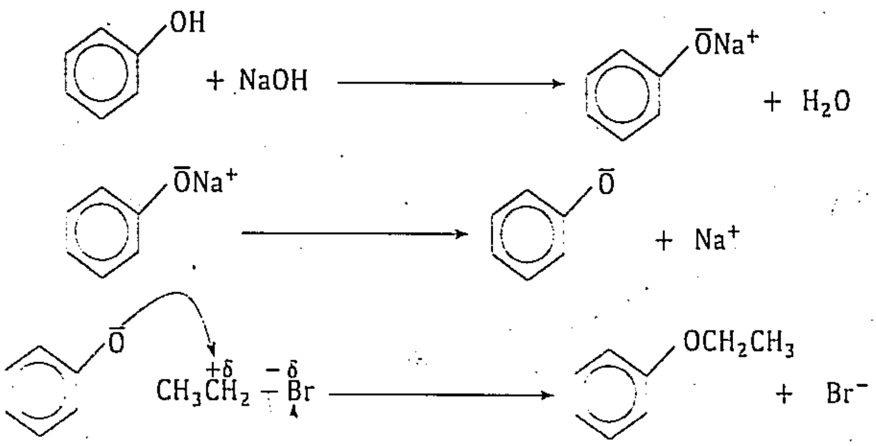
Phenol does not esterify with carboxylic acids.

(iv) Ether formation (Williamson's synthesis)

Phenol reacts with haloalkanes in alkaline solution to form corresponding ethers.



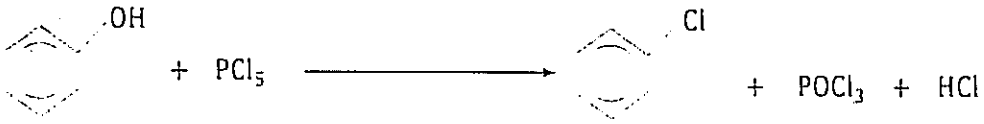
Mechanism



$$Na^+ \; + \; Br^- \longrightarrow NaBr$$

(v) Reaction with phosphorus(V) chloride

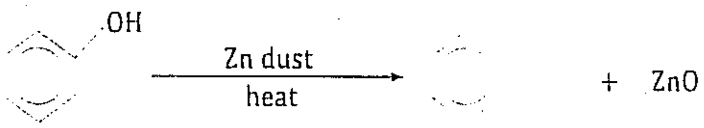
Phenol reacts very slowly with phosphorus pentachloride to form chlorobenzene. The reaction occurs much less readily than it is in alcohols and the yield of chlorobenzene is poor.



Note: Phenol does not react with hydrogen chlorides.

(vi) Reaction with zinc

Phenol vapour reacts with heated zinc dust to form benzene.

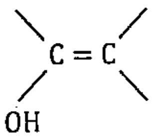


(vii) Reaction with neutral iron(III) chloride solution

Phenol reacts with **neutral iron(III) chloride** solution to form a complex.

Observation: Purple/violet colouration.

This is the chemical test for phenol and also for all compounds containing the enol group.



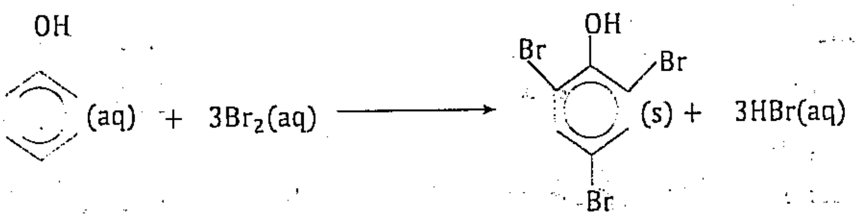
= **enol group**

2. Electrophilic substitution with the benzene ring

This is also called electrophilic aromatic substitution. Phenol is more reactive towards electrophilic aromatic substitution than benzene. The substitution occurs at the ortho- and para- (2- and 4-) positions because the hydroxyl group is ortho- and para-directing. The higher reactivity of phenol than benzene is explained in one of the reactions below:

(i) Reaction with bromine water

Phenol reacts readily with bromine water to form 2,4,6-tribromophenol. No Lewis acid is required as is the case of benzene.



2,4,6 – *tribromophenol*

Observation: A white precipitate is formed.

With chlorine water, a similar reaction occurs and 2,4,6-trichlorophenol is formed.

The reaction is fast with phenol but requires a halogen carrier for benzene. Why?

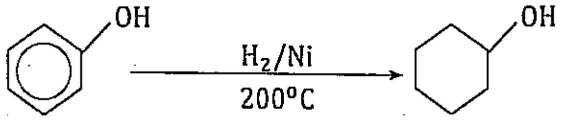
<u>Reason</u>

In phenol, the **lone pair of electrons on the oxygen atom interacts with the delocalized pi-electrons** of the benzene ring, **increasing the electron density of the benzene ring, activating it** and making it **readily attacked by electrophiles**. Phenol therefore easily reacts with bromine water to form **insoluble 2,4,6-tribromophenol.**

For benzene, the **double bonds in benzene are not true double bonds** but rather **contains delocalized pi-electrons.** A catalyst is required **to induce a degree of polarity in the bromine-bromine bond** to produce an **electrophile** that is attacked by benzene to form bromobenzene.

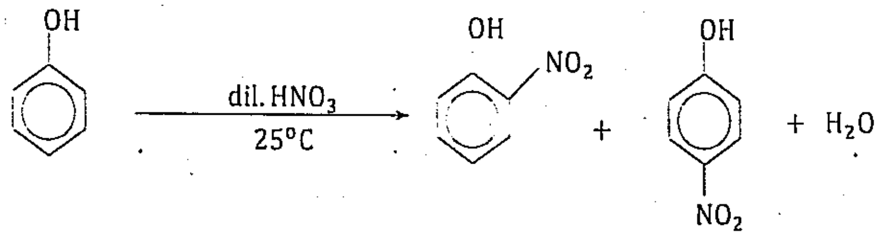
(ii) Hydrogenation

Phenol is reduced to cyclohexanol by hydrogen when passed over nickel at about 200°C.



(iii) Nitration

Phenol reacts with **dilute nitric acid** at **room temperature** to form **2-nitrophenol** (major product) along with **4-nitrophenol.**

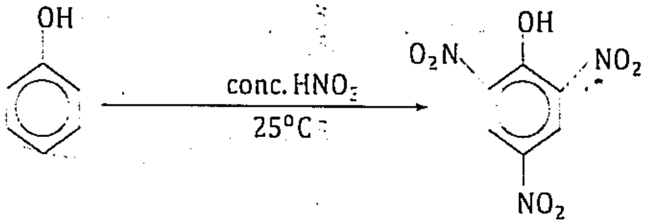


2 – nitrophenol
(major product)

4 – nitrophenol

The two isomers can be separated by steam distillation.

When **concentrated** or **excess nitric acid** is used, **2,4,6-trinitrophenol** is formed.

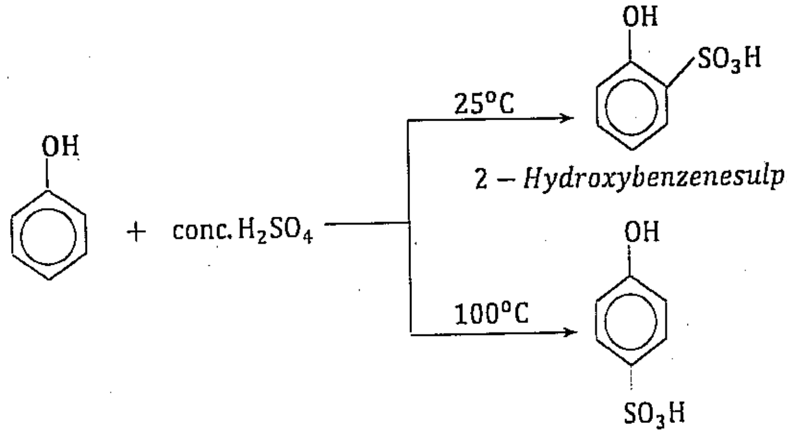


2,4,6 – *trinitrophenol*
(*common name*: ***Picric acid***)

(iv) Sulphonation

Phenol readily reacts with **ordinary concentrated sulphuric acid** at **room temperature** to form **2-hydroxybenzenesulphonic acid.**

If a **temperature of 100°C** is used, **4-hydroxybenzenesulphonic acid** is formed as the major product.



2 – *Hydroxybenzenesulphomic acid*

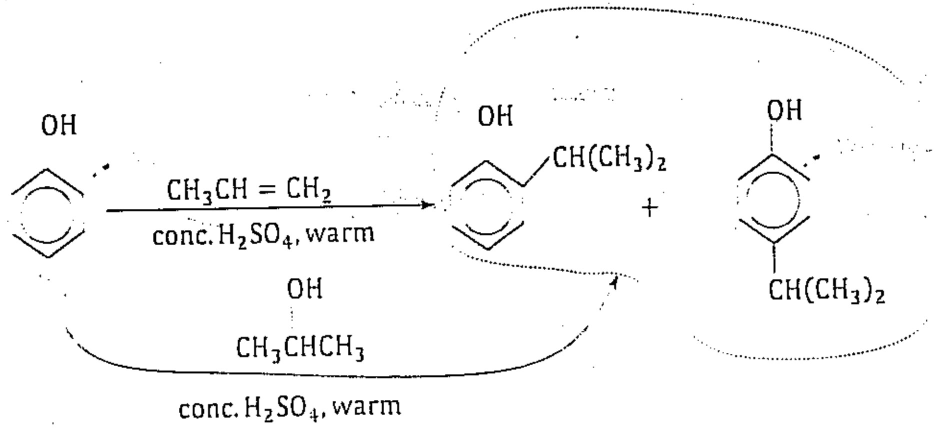
4 – *Hydroxybenzenesulphomic acid*

(v) Alkylation

Alkylation of the benzene ring of phenol requires an alcohol or alkene in presence of concentrated sulphuric acid catalyst on gentle warming.

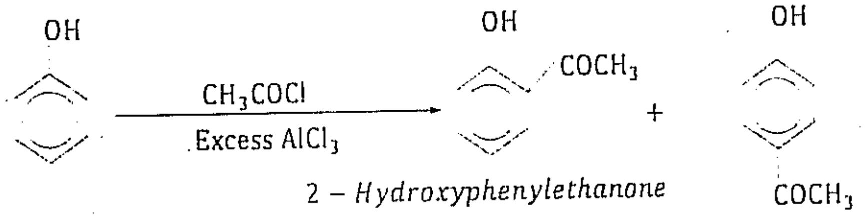
Secondary or tertiary alcohols are preferred because the mechanism involves formation of a stable carbonium ion. The alkylphenol is formed in a low yield.

Examples



(vi) Acylation

Phenol reacts with ethanoychloride in presence of a **large excess of aluminium chloride** to from corresponding 2- and 4-substituted phenolic ketones.

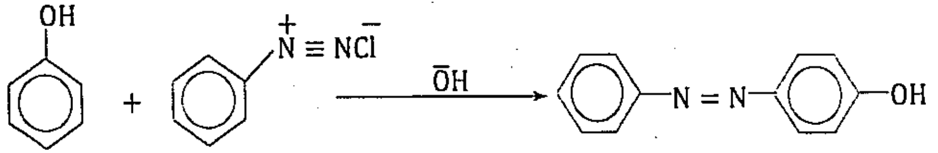


2 – *Hydroxyphenylethanone*

4 – *Hydroxyphenylethanone*

(vii) Coupling reactions

Phenol reacts with benzenediazonium salt in alkaline solution to form an insoluble bright coloured azo compound.



(4 – Hydroxyphenyl)azobenzene

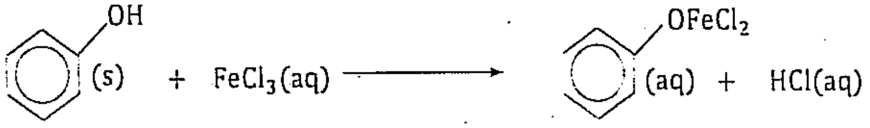
Observation: Bright yellow precipitate formed.

6.2.5 Confirmatory test for phenol

Reagent: Neutral iron(III) chloride solution.

Observation: Purple/violet colouration.

Equation



6.2.6 Comparison between reactions of phenol and ethanol

Reagent	Ethanol	Phenol
Sodium metal	Reacts to form hydrogen gas	Reacts to form hydrogen gas
Phosphorus(V) chloride	Reacts rapidly to form hydrogen chloride	Reacts very slowly giving a poor yield of chlorobenzene
Ethanoylchloride	Reacts readily to form ethyethanoate	Reacts in presence of an alkaline solution to form phenylethanoate
Concentrated sulphuric acid	Readily reacts and is dehydrated to ethene at 180°Cwith excess of the acid	Readily reacts and is sulphonated to form ortho- and para-isomers

Sodium hydroxide solution	No reaction since it is neutral	Reacts o form sodium phenoxide since it is acidic
Neutral iron(III) chloride	No reaction	Phenol reacts to form a violet coloured complex
Halogen acids (HCl, HBr, HI)	Forms corresponding haloalkanes	No reaction
Ethanoic acid	Reacts to form ethyl ethanoate	No reaction
Hydrogen/nickel catalyst	No reaction	Reacts at 200^{0}C to form cyclohexanol
Concentrated nitric acid	No reaction	Forms 2,4,6-trinitrophenol
Bromine water	No reaction	Forms a white precipitate of 2,4,6-tribromophenol
Zinc	No reaction	Reacts on heating to form benzene
Iodine solution and sodium hydroxide solution	Forms a yellow precipitate of triiodoromethane	No reaction
Benzenediazonium chloride	No reaction	Forms a bright yellow precipitate of an azo dye

6.2.7 Uses of phenol

(i) Manufacture of cyclohexanol, which is used for production of nylon and as a solvent for rubber.

(ii) To make Dettol, a powerful antiseptic.

(iii) Manufacture of azo-dyes, phenolphthalein, etc.

(iv) Manufacture of picric acid which is used as an explosive and for dyeing silk and wool.

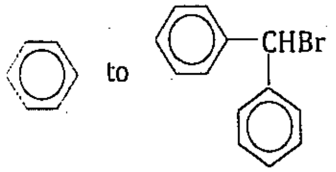
(v) Manufacture of drugs like aspirin.

6.3 Some synthetic problems

1. Write equations to show how the following conversions can be effected.

(a) Ethanoylchloride to ethanol.

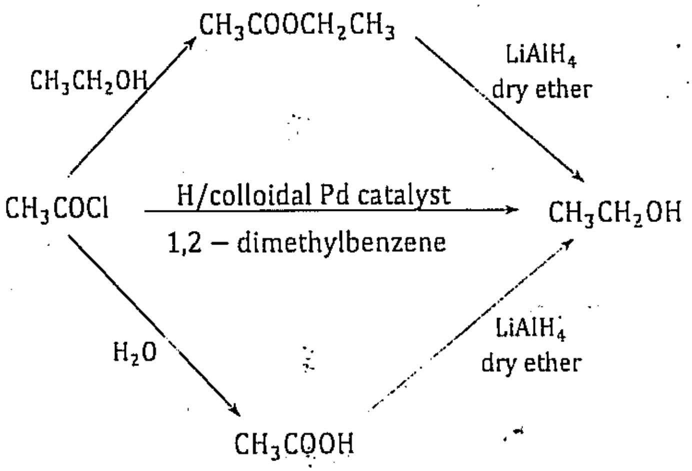
(b)



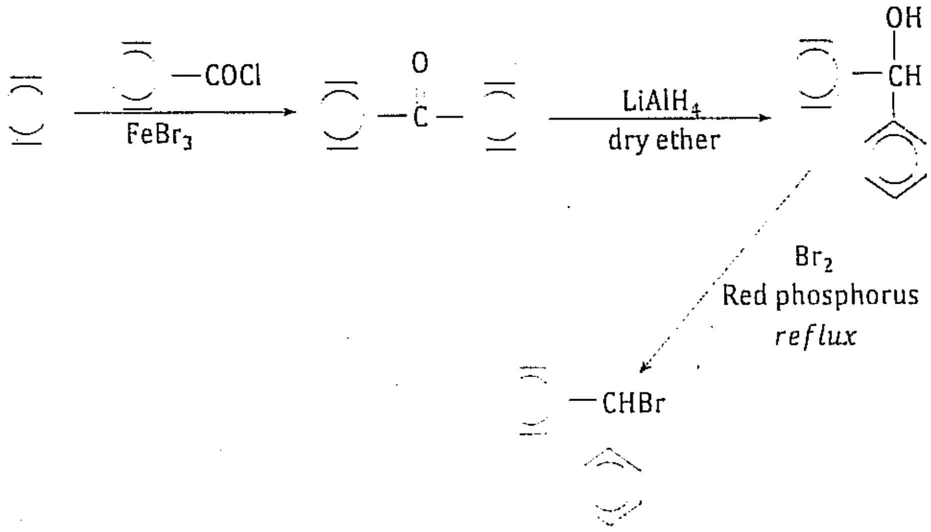
(c) Ethanol to 3 – bromo – 2 – methylbutan – 2 – ol.

Solution

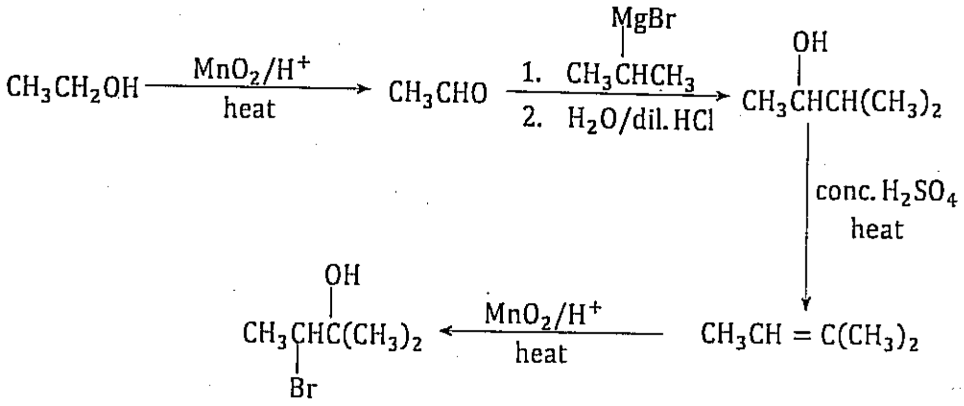
(a)



(b)



(c)



$$CH_3CH_2OH \xrightarrow[\text{heat}]{MnO_2/H^+} CH_3CHO \xrightarrow[2.\ H_2O/\text{dil.}HCl]{1.\ CH_3\overset{MgBr}{C}HCH_3} CH_3\overset{OH}{C}HCH(CH_3)_2 \xrightarrow[\text{heat}]{\text{conc.}\ H_2SO_4} CH_3CH=C(CH_3)_2$$

$$CH_3CH=C(CH_3)_2 \xrightarrow[\text{heat}]{MnO_2/H^+} CH_3\underset{Br}{C}H\overset{OH}{C}(CH_3)_2$$

2. Without using equations, show how the following conversions can be effected.

(a) 2-phenylpropane to hydroxybnzene.

(b) But-2-ene to ethanol.

Solution

(a)

2-phenylpropane is oxidized by air to form cumenehydroperoxide that is decomposed with warm dilute sulphuric acid to yield phenol.

(b)

A solution of but-2-ene in tetrachloromethane is reacted with ozone at a temperature below 20^{0}C to form an ozonide. The ozonide is hydrolysed using zinc and ethanoic acid to form ethanal. Ethanal is reduced using an ethereal solution of lithium tetrahyridoaluminate(III) to form ethanol.

6.4 End of topic assessment exercise

1. Complete the following equations and write the IUPAC name of the main organic product in each case.

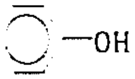
(a) $(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc. } H_3PO_4}$

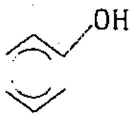
(b) $(CH_3)_3COH \xrightarrow[\text{conc. HCl}]{\text{anhydrous } ZnCl_2}$

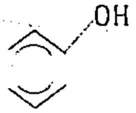
(c) $CH_3COCH_3 \xrightarrow[\text{(ii) aq. } NH_4Cl]{\text{(i) } CH_3MgI}$

(d) $CH_3CH_2COOCH_2CH_3 \xrightarrow[\text{dry ether}]{LiAlH_4}$

(e) $CH_3CO_2H + CH_3CH_2CH_2OH \xrightarrow[\text{reflux}]{\text{dry HCl}}$

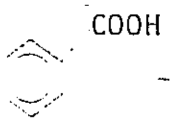
(f)

$\xrightarrow[\text{heat}]{Al_2O_3}$

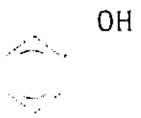
(g)

$\xrightarrow[\text{conc. } H_2SO_4\text{, warm}]{CH_3CH = CH_2}$

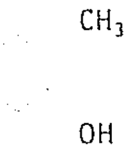
(h)

$\xrightarrow{Cl_2(aq)}$

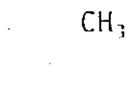
(i)

$\xrightarrow[\text{room temperature}]{\text{conc. } HNO_3}$

(j)

$\xrightarrow[(CH_3CH_2)_2O]{LiAlH_4}$

(k)

$\xrightarrow[200^\circ C]{H_2/Ni}$

(l)

$\xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+}$

(m)

$\xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+}$

2. Complete the following equations and in each case, write a mechanism for the reaction.

(a) $CH_3CH_2CH_2OH \xrightarrow[360°C]{conc.\ H_3PO_4}$

(b) $CH_3(C_6H_5)OH + CH_3CH_2Br \xrightarrow[heat]{NaOH(aq)}$

(c) $(CH_3)_3CBr + \bar{O}H(aq) \longrightarrow$

(d) $(CH_3)_3COH \xrightarrow[180°C]{conc.\ H_2SO_4}$

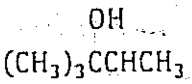
(e) $CH_3CH_2CH_2Cl \xrightarrow[heat]{\bar{O}H(aq)}$

(f) $CH_3CH_2CH_2CH_2OH \xrightarrow[180°C]{conc.\ H_2SO_4}$

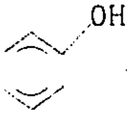
(g) $CH_3CH_2OH \xrightarrow[reflux]{NaBr/conc.\ H_3PO_4}$

(h) $CH_3CH_2OH \xrightarrow[140°C]{conc.\ H_2SO_4}$

(i) $CH_3CH_2CH_2OH \xrightarrow[0°C]{conc.\ H_2SO_4}$

(j) 

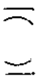
$(CH_3)_3C\overset{OH}{C}HCH_3 \xrightarrow[heat]{conc.\ H_3PO_4}$

(k) 

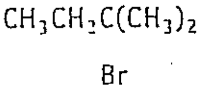
$\xrightarrow[heat]{conc.\ H_3PO_4}$

3. Write a mechanism to show how each of the following conversions can be effected.

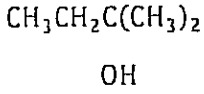
(a)  $-CH_2I \longrightarrow$  $-CH_2OH$

(b)  $-OH \longrightarrow$  $-OCH_2CH_2CH_3$

(c) $CH_3CH_2COBr \longrightarrow$  $-OOCH_3$

(d) 

$CH_3CH_2\underset{Br}{C}(CH_3)_2 \longrightarrow$

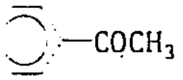
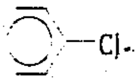


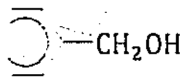
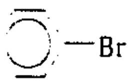
$CH_3CH_2\underset{OH}{C}(CH_3)_2$

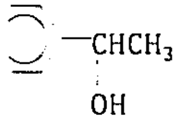
(e) $CH_3CH_2OH \longrightarrow (CH_3CH_2)_2O$

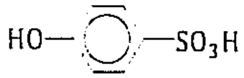
4. State what is observed and write equation(s) for the reaction that occurs when.
   - (a) Neutral iron(III) chloride solution is added to an aqueous solution of hydroxybenzene.
   - (b) Benzenediazonium chloride is added to phenol in aqueous sodium hydroxide.
   - (c) Bromine water is added to phenol.

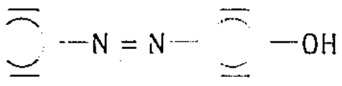
5. Write equations to show how the following conversions can be carried out. In each case, indicate the necessary reagents and conditions.
   - (a) Propan-1-ol from propyne.
   - (b) Bromocyclohexane from hydroxybenzene.
   - (c) $(CH_3)_3COH$ from CH_3COCH_3.
   - (d) Hydroxybenzene from bromobenzene.
   - (e) Propan-1-ol to 2,2-dichloropropane.
   - (f) Ethene to 2-methylbutan-2-ol.
   - (g) Propan-2-ol from ethanol.
   - (h) Ethene to butan-2-ol.

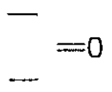
(i)  from 

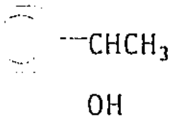
(j)  from 

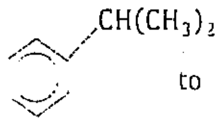
(k)  from 

(l)  from benzene.

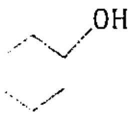
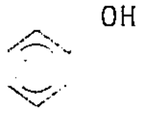
(m)  to 

(n)  to 

(o)  to 

(p)  to Phenol

6. Describe how the following conversions can be effected in the laboratory (No equations are required)
   - (a) Ethylamine from ethanol.
   - (b) Benzene from phenymethanol.
   - (c) 1-methylcyclobutene to 2-methylcyclobutanol.
   - (d) Propan-1-ol to 2-bromopropane.
   - (e) Chlorobenzene to phenol.
   - (f) Benzene to methylbenzoate.
   - (g) 2,2-dibromopropane from propan-1-ol.
   - (h) Ethylbenzoate from phenol.

7. Name the reagent(s) that can be used to distinguish between the following pairs of compounds. In each case, state what would be observed if each member is separately treated with the reagent and write equation for the reaction.
   - (a) 1-phenylethanol and 2-phenylethanol.
   - (b) Phenol and butan-1-ol.
   - (c) Butan-1-ol and 2-methylpropan-2-ol.
   - (d) C_6H_5COOH and C_6H_5OH.
   - (e) Methanol and ethanol.
   - (f) Ethanol and propan-2-ol.
   - (g) Sodium benzoate and hydroxybenzene.
   - (h) Phenylethanol and 2-phenylpropan-2-ol.
   - (i) 2-phenylpropan-2-ol and 3-phenylpropan-1-ol.
   - (j)  and 

8. Compare the reactivity of ethanol and phenol with each of the following reagents. (Include equations for reactions if any)
   - (a) Sodium hydroxide.
   - (b) Sodium metal.
   - (c) Phosphorus(V) chloride.
   - (d) Ethanoyl chloride.
   - (e) Bromine water.
   - (f) Iodine solution and sodium hydroxide solution.
   - (g) Benzenediazonium chloride.
   - (h) Neutral iron(III) chloride.

(i) Concentrated suphuric acid.

9\. (a) An organic compound, Q, contains carbon, hydrogen and oxygen only. On combustion, 0.463g of Q gave 1.1g of carbon dioxide and 0.563g of water. Determine the empirical formula of Q.

(b) When vapourised, 0.1g of Q occupies $54.5cm^3$ at 208^0C and 98.3kPa. Determine the molecular formula of Q.

(c) Q reacts with sodium metal with evolution of a gas. Write the structural formula of all possible isomers of Q.

(d) Q reacts with anhydrous zinc chloride and concentrated hydrochloric acid to form a cloudy solution in about 5 minutes.

(i) Identify Q.

(ii) Show how Q ca be synthesized from but-2-ene.

10\. A compound W contains 52.2% carbon, 13% hydrogen and the rest being oxygen.

(a) Determine the empirical formula of W.

(b) When vapourised, 0.1g of W occupied $78.8cm^3$ at 150^0C and a pressure of 740mmHg.

(i) Calculate the formula mass of W.

(ii) Determine the molecular formula of W.

(iii) Write the structural formula of all possible isomers of W.

(c) W does not react with sodium metal. Identify W.

(d) Write an equation to show how W can be prepared from methanol.

11\. (a) A solution of R containing $2.8gdm^{-3}$ exerts an osmotic pressure of 370mmHg at stp. Calculate the molar mass of R.

(b) An organic compound R contains carbon, hydrogen and oxygen. 3.4g of R burns with a sooty flame producing $5.04dm^3$ of carbon dioxide and 2.70g of water at stp.

(i) Calculate the empirical formula of R.

(ii) Hence determine the molecular formula of R.

(c) R reacts with a mixture of anhydrous zinc chloride and concentrated hydrochloric acid but does not react with acidified potassium dichromate(VI).

(i) Identify R.

(ii) Write equation for the reaction between R and a mixture of anhydrous zinc chloride and concentrated hydrochloric acid.

(d) Write equations to show how **R** can be converted to an alkyne.

12. Identify any pair of alcohols that can be distinguished by the following reagents and in each case, state what is observed when each of the compounds in the pair is reacted with the reagent(s).
    (a) Iodine solution and sodium hydroxide solution.
    (b) Anhydrous zinc chloride and concentrated hydrochloric acid.

13. (a) A compound T contains carbon, hydrogen and oxygen only. On complete combustion, 7.50g of T formed 17.8g of carbon dioxide and 9.27g of water. Determine the empirical formula of T.
    (b) When vapourised at 760mmHg and 400K, 0.225g of T occupied $100cm^3$.
        (i) Determine the molecular formula of T.
        (ii) Write down the structural formulae and IUPAC names of isomers of T.
    (c) T does not react with an acidified solution of potassium dichromate(VI), but reacts readily with a mixture of anhydrous zinc chloride and concentrated hydrochloric acid to form a cloudy solution.
        (i) Identify T.
        (ii) Write equation and indicate mechanism for conversion of T to alkene.

14. $60.0cm^3$ of a gaseous hydrocarbon Y was exploded with $400cm^3$ of oxygen. On cooling to room temperature and pressure, the residual gas occupied a volume of $280cm^3$. On shaking with aqueous potassium hydroxide, the volume left occupied $40cm^3$. When Y was treated with hydrogen chloride gas, compound G was formed. G reacts with sodium hydroxide solution to form compound J. J reacts with ethanoic acid to form compound L. Compound L has an empirical formula of C_3H_6O and J is resistant to oxidation.
    (a) Determine the molecular formula of Y and write the structural formula of the possible isomers of Y.
    (b) Write the names and structural formulae of G, J and L and write equations leading to their formation.
    (c) Write equations to show how you would convert
        (i) G to Y.
        (ii) Y into methanol.
        (iii) J to G.

15. (a) A compound Z conatins 60.0% carbon, 13.3% hydrogen and the rest being oxygen. Calculate the simplest formula of Z.

(b) When 0.698g of Z was dissolved in 100g of a solvent, there was 0.19°C depression in freezing point of the solution (K_f of the solvent = 1.63°C). Calculate

(i) the simplest formula of Z.

(ii) the molecular formula of Z.

(c) Write the names and structural formulae of all possible isomers of Z.

(d) When Z was reacted with iodine in aqueous sodium hydroxide, a yellow precipitate was formed.

(i) Identify Z.

(ii) Write equation for the reaction between Z and iodine in aqueous sodium hydroxide.

(iii) State what would be observed if Z is reacted with acidified potassium dichromate(VI) solution and name the major organic product.

(e) When Z was heated with excess concentrated sulphuric acid, a gas W which turned the purple solution of acidified manganate(VII) to colourless was evolved. Write equation for the reaction:

(i) Z and concentrated sulphuric acid and suggest a mechanism for reaction.

(ii) W and acidified manganate(VII) ions and name the major product.

(f) Suggest a plausible mechanism for the reaction between W and hydrogen iodine.

16. 4.7g of Z containing carbon, hydrogen and oxygen only. Z on combustion give 13.2g of carbon dioxide and 2.7g of water.

(a) Determine the empirical formula of Z.

(b) When a mixture cantaining compound Z was steam distilled at 760mmHg and 98°C, the distillate contained 12.75g of water and 3.7g of Z. If the vapour pressure of water is 720mmHg at 98°C, determine the molecular formula of Z.

(c) Z burns with a sooty flame and the pH of its aqueous solution is less than 7. Write the molecular structure of Z.

(d) Z was reacted with benzenediazonium chloride in presence of sodium hydroxide.

  (i) State what was observed.

  (ii) Write equation for the reaction that took place.

17. A compound X contains 76.32% carbon, 6.38% hydrogen and the rest being oxygen. A solution of X in water turns blue litmus paper pink but does not liberate carbon dioxide from carbonates. A solution of 1.50g of X in 20.90g of benzene freezes at 1.3^{0}C while pure benzene freezes at 5.50^{0}C.

(a) Determine,

  (i) the empirical formula of X.

  (ii) the molecular formula and write the structural formula of X. (K_f of benzene is 5.49^{0}C per 1000gmol^{-1})

(b) Explain why a solution of X turns blue litmus pink.

(c) Describe the reaction between X and bromine water.

(d) Write equation, indicate conditions and outline mechanism for the reaction between X and ethanoyl chloride.

(e) Write equations to show how X can be,

  (i) prepared from benzene and propene.

  (ii) converted to methylcyclohexane.

(f) Name a reagent that when separately treated with X and ethanol.

  (i) gives a similar observation.

  (ii) can be used to distinguish X and ethanol. (In each case, state what would be observed)

18. (a) Both phenol and ethanol contain the same functional group.

  (i) Name one reagent that can be used to distinguish phenol and ethanol.

  (ii) State what would be observed if each of the above compounds is separately treated with the reagent you have named in (a) (i) above and write the equation for the reaction that occurs if any.

  (iii) Describe three chemical properties in which the chemistry of phenol and ethanol is similar.

(b) An aqueous solution of phenol turns blue litmus paper red whereas that of ethanol has no effect. Explain this observation.

(c) Write equation and mechanism for the reaction between:

  (i) phenol and propanoylchloride in alkaline medium.

(ii) ethanol and methanoic acid in presence of dilute sulphuric acid.

(iii) phenol and 2-chlorpropane in alkaline medium.

19. 6.20g of a bromoalkane Q, $C_nH_{2n+1}Br$ contains 65.04% by mass bromine.

(a) Determine the molecular mass of Q.

(b) Write the structural formula and IUPAC names of all possible isomers of Q.

(c) When Q is refluxed with aqueous potassium hydroxide, a compound W is formed which forms two layers after five minutes with a mixture of concentrated hydrochloric acid and anhydrous zinc chloride. Identify

(i) Q.

(ii) W.

(d) Write equation and suggest a mechanism for the reaction between

(i) Q and alcoholic potassium hydroxide solution.

(ii) Q and an alkaline solution of phenol.

(e) State what would be observed and write equation for the reaction between W and acidified chromium(VI) oxide.

20. When 30cm³ of an organic compound Y, of formula $C_nH_{3n}O$ was burnt in excess oxygen and cooled to room temperature, 240cm³ of the residual gas was formed. On addition of concentrated potassium hydroxide solution, the volume reduced 180cm³. Y burns in oxygen according to the equation:

$$C_nH_{3n}O(g) + \left(\frac{7n-2}{4}\right)O_2(g) \longrightarrow nCO_2(g) + \left(\frac{3n}{2}\right)H_2O(g)$$

(a) (i) Determine the molecular formula of Y.

(ii) Write dowm the structural formulae and IUPAC names of the possible isomers of Y.

(b) Y reacts with sodium metal forming bubbles of a colourless gas. Identify Y.

(c) Discuss the reactions of Y with sulphuric acid. Indicate equations and mechanisms for the reactions.

21. Explain each of the following observations

(a) Phenol is a stronger acid than cyclohexanol.

(b) The boiling point of ethanol is higher than that of ethylamine.

(c) Phenol is sparingly soluble in water but very soluble in dilute sodium hydroxide solution.

(d) Phenol reacts readily with bromine water to from a white precipitate but benzene requires a catalyst to reach with bromine.

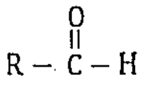
Chapter 7

Carbonyl compounds

7.1 Introduction

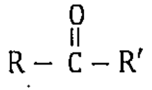
Carbonyl compounds are organic compounds with the carbonyl functional group, $>C = O$.

It is the carbonyl group that largely determines the chemistry of aldehydes and ketones. There are two classes of carbonyl compounds i.e., **aldehydes** and **ketones**.



$R-\overset{O}{\overset{\|}{C}}-H$

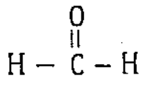
Aldehyde



$R-\overset{O}{\overset{\|}{C}}-R'$

Ketone

Aldehydes (Alkanals) are compounds with the general formula RCHO. They possess a single hydrogen atom attached to the carbonyl carbon (with the exception of methanal, HCHO) that possesses two hydrogen atoms attached to the carbonyl carbon and no hydrocarbon substituent.



$H-\overset{O}{\overset{\|}{C}}-H$

Methanal

This hydrogen atom attached to the carbonyl carbon gives aldehydes certain properties which ketones do not possess enabling the two classes to be distinguished.

Ketones (Alkanones) are compounds with the general formula, RCOR', hence there are two hydrocarbon substituents attached to the carbonyl group of Ketones.

The general formula of **saturated aliphatic aldehydes and ketones** is $C_nH_{2n}O$. The cyclic ketones have a general formula $C_nH_{2n-2}O$.

The difference in structure of aldehydes and ketones affects their properties in two ways:

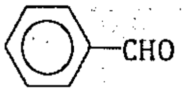
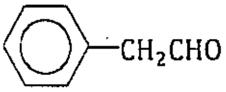
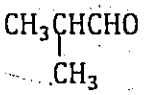
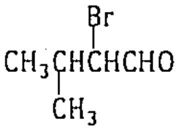
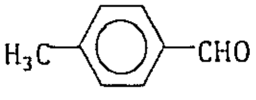
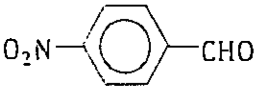
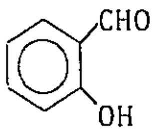
(a) *Aldehydes are quite easily oxidized whereas ketones are oxidized only with difficulty.*

(b) *Aldehydes are usually more reactive than ketones towards nucleophilic addition.*

7.2 Nomenclature

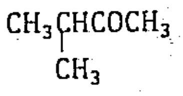
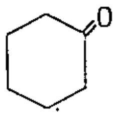
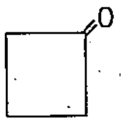
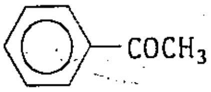
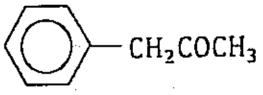
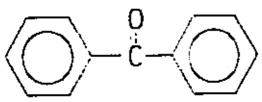
The IUPAC nomenclature of aliphatic aldehydes considers dropping the ending "-e" of the corresponding alkane and replacing it with the suffix "-al". The main carbon chain is named as usual. The *carbonyl carbon* is considered as *carbon number 1.*

Examples

Formula	*IUPAC name*
HCHO	Methanal
CH_3CHO	Ethanal
CH_3CH_2CHO	Propanal
$CH_3CH_2CH_2CHO$	Butanal
	Benzaldehyde
	Phenylethanal
 $CH_3\underset{CH_3}{CH}CHO$	2 – Methylpropanal
 $CH_3\underset{CH_3}{CH}\overset{Br}{CH}CHO$	2 – Bromo – 3 – methylbutanal
	4 – Methylbenzaldehyde
	4 – Nitrobenzaldehyde
	2 – Hydroxybenzaldehyde

For ketones, the IUPAC names are derived by taking the stem of the name of the corresponding alkane and replacing the ending "-e"with a suffix "-one".

The position of the carbonyl group is indicated by a number, the carbonyl carbon being given the lowest possible number.

Formula	*IUPAC name*
CH_3COCH_3	Propanone
$CH_3CH_2COCH_3$	Butanone
$CH_3COCH_2CH_2CH_3$	Pentan – 2 – one
$CH_3CH_2COCH_2CH_3$	Pentan – 3 – one
 $\underset{\displaystyle CH_3}{CH_3\underset{\vert}{C}HCOCH_3}$	3 – Methylbutanone
	Cyclohexanone
	Cyclobutanone
	Phenylethanone
	Phenylpropanone
	Diphenylmethanone

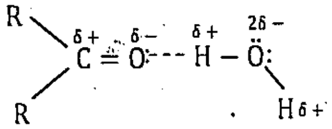
7.3 Physical properties

(a) Physical state

Methanol is a gas, other aliphatic aldehydes and ketones of relatively low molecular weight are colourless liquids at 20°C. Those with high molecular masses are solids.

(b) Solubility

The liquid aldehydes and ketones of low molecular weight are very soluble in water, for example methanol, ethanol and propanone are all miscible with water. This is because they form intermolecular hydrogen bonds with water molecules.



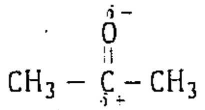
Higher carbonyl compounds with more than five carbon atoms and the aromatic carbonyl compounds are insoluble in water.

Carbonyl compounds are soluble in the usual organic solvents and some of them like propanone themselves useful organic solvents. Solubility in water decrease with increase in size of the molecule because increased molecular size distorts the formation of hydrogen bonds with water.

(c) Boiling points

The polar carbonyl group makes aldehydes and ketones polar compounds hence they have higher boiling points than non-polar compounds of comparable molecular weight.

For example, propanone has a higher boiling point (56°C) than butane (−0.5°C) yet both compounds have the same molecular weight.



$$CH_3-\overset{\overset{\delta-}{O}}{\overset{\|}{\underset{\delta+}{C}}}-CH_3 \qquad CH_3(CH_2)_2CH_3$$

m.p. 56°C *m.p.* −0.5°C

The oxygen atom in propanone is **more electronegative than the carbon atom** to which it is bonded. It therefore pulls the bonding electrons more towards itself gaining a **partial negative charge** and the carbon atom gains a **partial positive charge**.

This makes the **carbon–oxygen double bond** polar and the **whole molecule polar**. Propanone molecules therefore are **held by stronger intermolecular forces of attraction** (permanent dipole-dipole van der waal's forces of attractions) that require a **higher amount of energy to break**. However, butane molecules are **non-polar** hence have **weaker forces of attraction** (temporary dipole-dipole van der waal's forces of attraction) that **require a lower amount of energy to break**.

However, carbonyl compounds have lower boiling points as compared to alcohols or carboxylic acids of comparable molecular mass. This is because of their inability to form hydrogen bonds between their molecules.

For example

Although ethanal and ethanol have almost equal molecular masses ethanal boils at 21°C yet ethanol boils at 78°C.

Ethanal **cannot form intermolecular hydrogen bonds between its molecules**. Its molecules only interact through **weak van der waals forces of attraction** that require a **lower amount of energy to break**. For ethanol however, the **oxygen atom is more electronegative than the hydrogen atom** to which it is bonded. The oxygen atom gains a **partial negative charge** and the hydrogen atom gains a **partial positive charge**. This makes the **oxygen-hydrogen bond polar** and ethanol molecules interact through **intermolecular hydrogen bonds** that require a **higher amount of energy to break**.

7.4 Isomerism

Carbonyl compounds exhibit structural isomerism. They can show chain isomerism and positional isomerism among themselves.
They also show functional group isomerism among themselves (aldehydes and ketones) and with alcohols, alkenes, enols and ethers.

Example

An organic compound Q contains 66.67% carbon, 22.22% oxygen and the rest being hydrogen.

(a) Determine the empirical formula of Q.

(b) Deduce its structural formula if its vapour density is 36.

(c) Write the structure formulae and names of all the possible isomers of Q

(a) percentage mass of H = 100 – (66.67 + 22.22) = 11.11

Elements	C		H		O
% mass	66.7		11.11		22.22
Moles	$\frac{66.67}{12}$		$\frac{11.11}{1}$		$\frac{22.22}{16}$
Simplest ratio	$\frac{5.5558}{1.38875}$	:	$\frac{11.11}{1.38875}$	:	$\frac{1.38875}{1.38875}$
	4	:	8	:	1

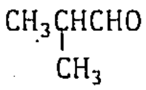
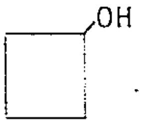
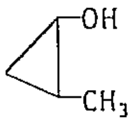
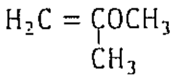
Empirical formula is C_4H_8O.

(b)

$$(C_4H_8O)_n = 36 \times 2$$
$$(48 + 8 + 16)n = 36 \times 2$$
$$72n = 72$$
$$\therefore n = 1$$

Molecular formula is C_4H_8O.

(c)

STRUCTURE OF ISOMER	NAME
$CH_3CH_2CH_2CHO$	Butanal
$CH_3COCH_2CH_3$	Butanone
 $CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCHO$	2 – Methylpropanal
	Cyclobutanol
	2 – methylcyclopropanol
$CH_3CH = CHCH_2OH$	But – 2 – en – 1 – ol
$H_2C = CHCH_2CH_2OH$	But – 3 – en – 1 – ol
$CH_3CH_2OCH = CH_2$	Ethoxyethene
 $H_2C = \underset{\displaystyle CH_3}{\underset{\vert}{C}}OCH_3$	2 - Methoxypropene

7.5 Laboratory Preparation

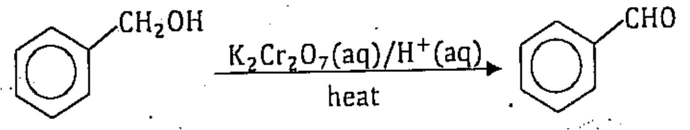
(a) From controlled oxidation of alcohols

(i) Aldehydes can be prepared by controlled oxidation of primary alcohols using an acidified potassium dichromate(VI) solution or acidified potassium permanganate solution. The reactions require heating.

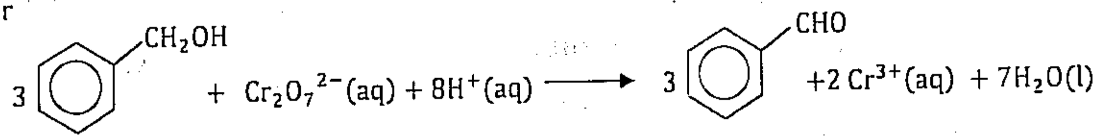
$$CH_3CH_2OH \xrightarrow[\text{warm}]{K_2Cr_2O_7(aq)/H^+(aq)} CH_3CHO$$

Or

$$3CH_3CH_2OH(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \longrightarrow 3CH_3CHO(l) + 2Cr^{3+}(aq) + 7H_2O(l)$$



Or



Note

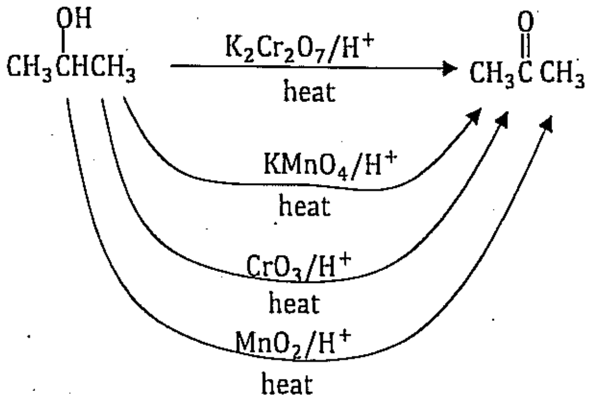
Primary alcohols may undergo secondary oxidation to carboxylic acids. The aldehyde must be distilled from the reaction mixture as it is formed.

Also, in order to avoid the secondary oxidation, it is preferable to use a dichromate(VI) solution rather than manganate(VII) solution since dichromate ions are milder in the oxidizing action. The orange solution turns green in case a dichromate is used.

Acidified chromium(VI) oxide may be used or acidified manganese(II) oxide, on heating in both cases.

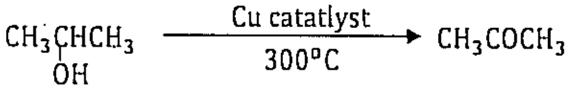
$$\begin{tikzcd} CH_3CH_2OH \arrow[r, "CrO_3/H^+", "\text{heat}"'] \arrow[r, bend right=60, "MnO_2/H^+"', "\text{heat}"] & CH_3CHO \end{tikzcd}$$

(ii) Ketones can be formed by oxidation secondary alcohols using acidified potassium dichromate(VI) solution, acidified potassium manganate(VII) solution, acidified chromium(VI) oxide or acidified manganese(IV) oxide. Heat is required in all cases.



Oxidation can also be achieved by dehydrogenation of the alcohols when passed over copper catalyst heated to about 300°C.

$$CH_3CH_2OH \xrightarrow[300^\circ C]{\text{Cu catalyst}} CH_3CHO$$



$$CH_3\underset{OH}{C}HCH_3 \xrightarrow[300^\circ C]{\text{Cu catatlyst}} CH_3COCH_3$$

Note

Industrially, methanal is formed by oxidation of methanol vapour over heated silver.

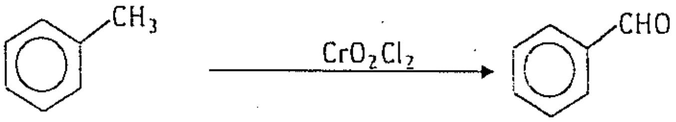
$$CH_3OH \xrightarrow[500^\circ C]{O_2/Ag\ \text{catalyst}} HCHO$$

Ethanal can be formed in a similar way.

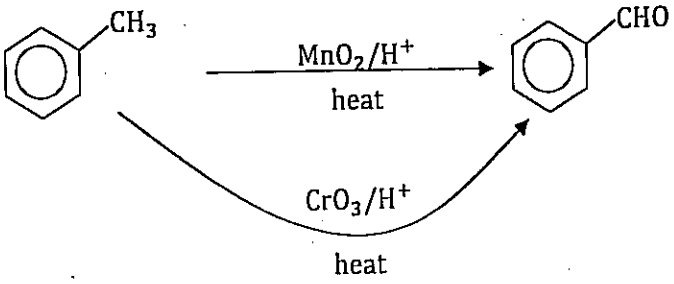
$$CH_3CH_2OH \xrightarrow[500^\circ C]{O_2/Ag\ \text{catalyst}} CH_3CHO$$

(b) Oxidation of methylbenzene

This method is only suitable for preparation of benzenecarbaldehyde (benzaldehyde). The methyl group on the benzene ring is oxidized using chromium(VI) dichloride dioxide (chromyl chloride). No heat required.

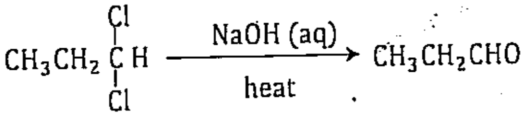


Acidified manganese(IV) oxide or acidified chromium(VI) oxide may be used but the reaction requires heating.

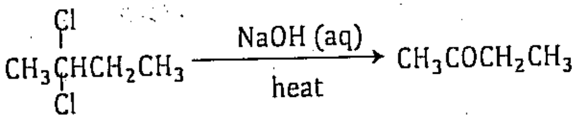


(c) Hydrolysis of germinal dihalides

Germinal dihalides are hydrolysed with aqueous sodium hydroxide to form ketones or aldehydes depending on the position of the halogen atoms.



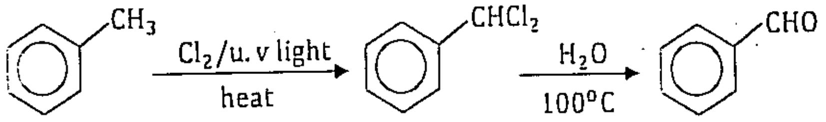
$$CH_3CH_2\overset{Cl}{\underset{Cl}{C}}H \xrightarrow[\text{heat}]{\text{NaOH (aq)}} CH_3CH_2CHO$$



$$CH_3\overset{Cl}{\underset{Cl}{C}}HCH_2CH_3 \xrightarrow[\text{heat}]{\text{NaOH (aq)}} CH_3COCH_2CH_3$$

This preparative method is not commonly used for aliphatic compounds because of the difficulty in obtaining the dichloro compounds.

However, benzaldehyde can be formed using the method because the dichloro compound is easily obtained by free radical chlorination of methylbenzene. Water alone can effect the hydrolysis.

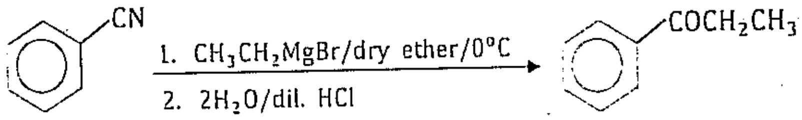


(d) From Grignard reagents

Ketones can be prepared when a Grignard reagent is added to an alkyl or arylnitrile and the product hydrolysed with a dilute acid. CH_3CN cannot be used.

$$RMgBr \xrightarrow[\text{2. } 2H_2O/\text{dil. HCl}]{\text{1. } R'CN/\text{dry ether}/0^\circ C} RCOR'$$

Examples



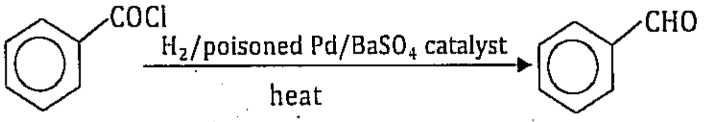
$$CH_3CH_2CN \xrightarrow[\text{2. } 2H_2O/\text{dil. HCl}]{\text{1. } CH_3MgBr/\text{dry ether}/0^\circ C} CH_3CH_2COCH_3$$

(e) From acyl chlorides. (The Rosenmund reaction)

This method is **only suitable for preparation of aldehydes**.

Acyl chlorides are reduced to aldehydes by hydrogen on a poisoned palladium catalyst supported on barium sulphate. The catalyst is poisoned using sulphur and quinoline. This prevents reduction of the aldehyde to a primary alcohol.

$$CH_3CH_2COCl \xrightarrow[\text{heat}]{H_2/\text{poisoned } Pd/BaSO_4 \text{ catalyst}} CH_3CH_2CHO$$



(f) Decarboxylation of calcium salts of carboxylic acids

$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow[400^\circ C]{\text{dry distill}} 2CH_3CH_2CHO + 2CaCO_3$$

$$(CH_3COO)_2Ca \xrightarrow{\text{heat}} CH_3COCH_3 + 2CaCO_3$$

The calcium salts are prepared by reacting a carboxylic acid with calcium carbonate. For example:

$$\begin{tikzcd}
CH_3CH_2COOH \arrow[r, "CaCO_3"] & (CH_3COO)_2Ca \arrow[r, "\text{heat}"] \arrow[d, "(HCOO)_2Ca", "\text{dry distill}/400^\circ C"'] & CH_3COCH_2CH_2CH_3 \\
 & CH_3CH_2CH_2CHO &
\end{tikzcd}$$

Note

Calcium salts of carboxylic acids when heated decompose to form ketones. For example, ethanoates of calcium, magnesium and barium form propanone and corresponding carbonates.

$$(CH_3COO)_2Ba \xrightarrow{\text{heat}} CH_3COCH_3 + BaCO_3$$

$$(CH_3COO)_2Mg \xrightarrow{\text{heat}} CH_3COCH_3 + MgCO_3$$

Ehanoates of nickel, copper and zinc form propanone, corresponding oxide and carbon dioxide.

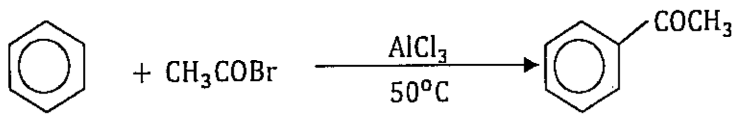
$$(CH_3COO)_2Ni \xrightarrow{\text{heat}} CH_3COCH_3 + NiO + CO_2$$

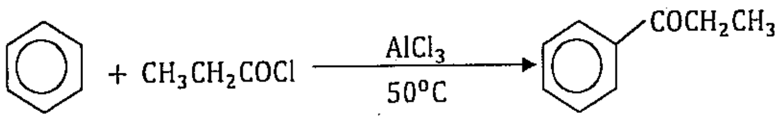
$$(CH_3COO)_2Cu \xrightarrow{\text{heat}} CH_3COCH_3 + CuO + CO_2$$

Propanoates form butanone on heating.

(g) By Friedel Crafts acylation

Aromatic ketones can be formed by reacting benzene with acylchlorides in presence of anhydrous aluminium chloride catalyst.



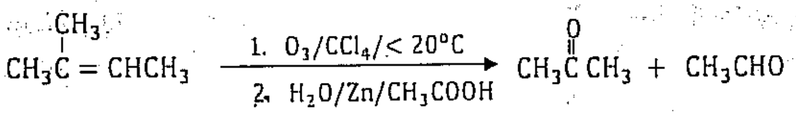


(h) Ozonolysis

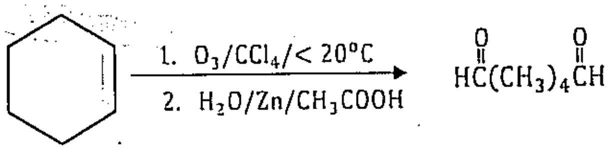
Carbonyl compounds can be formed by bubbling ozone through a solution of an alkene in tetrachloromethane at temperature below 20° C to form an ozonide. The ozonide is then hydrolysed using zinc and ethanoic acid.

$$CH_3CH = CH_2 \xrightarrow[2.\ H_2O/Zn/CH_3COOH]{1.\ O_3/CCl_4/< 20^\circ C} CH_3CHO + HCHO$$

$$CH_3CH = CHCH_3 \xrightarrow[2.\ H_2O/Zn/CH_3COOH]{1.\ O_3/CCl_4/< 20^\circ C} 2CH_3CHO$$



$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C} = CHCH_3 \xrightarrow[2.\ H_2O/Zn/CH_3COOH]{1.\ O_3/CCl_4/< 20^\circ C} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + CH_3CHO$$

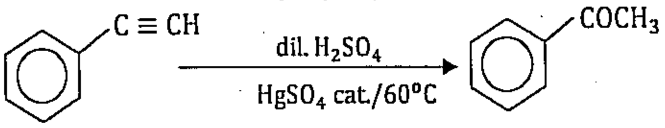


This method is not recommendable for organic synthesis since a mixture of products is formed. It may only be used to synthesize carbonyl compounds formed from symmetrical alkenes.

(i) Hydration of alkynes.

Carbonyl compounds can be formed by reacting alkynes with dilute sulphuric acid in presence of mercury(II) sulphate catalyst at 60°C. Ethyne forms ethanal while other alkynes from ketones.

$$HC \equiv CH \xrightarrow[HgSO_4\ cat./60°C]{dil.\ H_2SO_4} CH_3CHO$$



$$CH_3C \equiv C\,CH_3 \xrightarrow[HgSO_4\ cat./60°C]{dil.\ H_2SO_4} CH_3CO\,CH_2CH_3$$

7.6 Chemical properties of carbonyl compounds

Carbonyl compounds undergo different types of reactions. These include:

(a) **Nucleophilic addition reactions.**

(b) Condensation reactions

(c) Reduction reactions

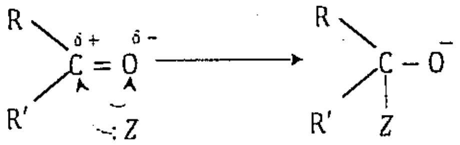
(d) Oxidation reactions

(e) Other reactions.

(a) Nucleophilic addition reactions

The highly polar carbonyl group provides a site for nucleophilic addition in carbonyl compounds. The carbonyl compounds undergo this type because: '*the oxygen atom on the carbonyl carbon is more electronegative than the carbon atom*'. The oxygen atom therefore attracts the bonding electrons more towards itself, gaining a **partial negative charge** whereas the carbon atom gains a **partial positive charge**. This makes the **carbon-oxygen bond polar. The partial positive carbon is therefore readily attacked by the nucleophile which adds itself across the carbonyl group** forming a single product.

Illustration



R' can be H or hydrocarbon group

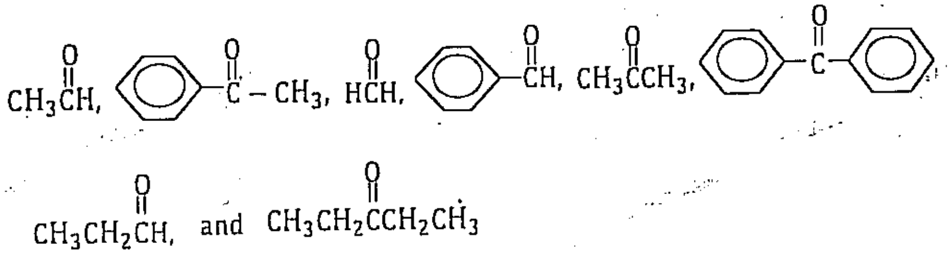
Aldehydes are more reactive than ketones towards nucleophilic addition.

This is because ketones usually have two alkyl (or aryl) groups attached to the carbonyl carbon. These groups are electron-releasing hence reduce the degree of positive charge on the carbonyl carbon, reducing how readily the carbonyl carbon is attacked by the nucleophile. Furthermore, the bulky hydrocarbon groups in

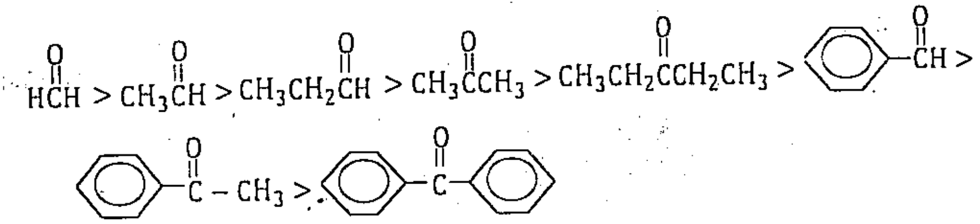
ketones increase steric hindrance about the carbonyl carbon, impeding the approach of the attacking nucleophile, reducing reactivity.

The aldehydes contain one hydrocarbon group and the carbonyl carbon is more positive and less sterically hindered than in ketones. Also, aldehydes with shorter (less bulky) hydrocarbon groups are more reactive than aldehydes with more bulky hydrocarbon groups on the carbonyl carbon. This similarly applies to ketones.

Consider the carbonyl compounds below:



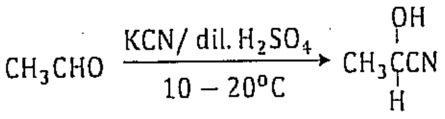
The compounds can be arranged in order of decreasing reactivity towards nucleophilic attack as shown below, for reasons explained above.



Examples of nucleophilic addition reactions

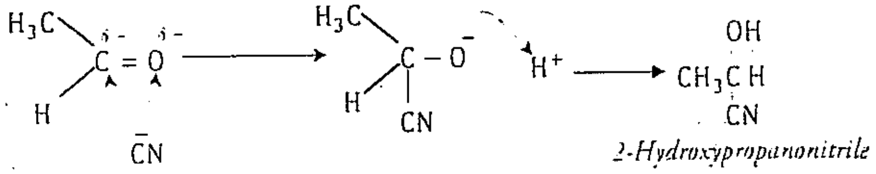
(i) Addition of hydrogen cyanide (Cyanohydrin formation)

Aldehydes and simple ketones react with hydrogencyanide at 10-20°C to form 2-Hydroxyalkanonitriles (Cyanohydrins). The hydrogencyanide is prepared in situ from the reaction between dilute sulphuric acid and potassium cyanide or sodium cyanide. For example;

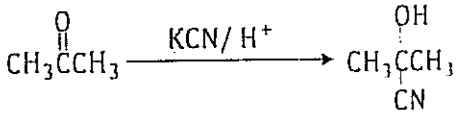


$$CH_3CHO \xrightarrow[10-20^\circ C]{KCN/\text{ dil. }H_2SO_4} CH_3\overset{OH}{\underset{H}{C}}CN$$

<u>Mechanism</u>

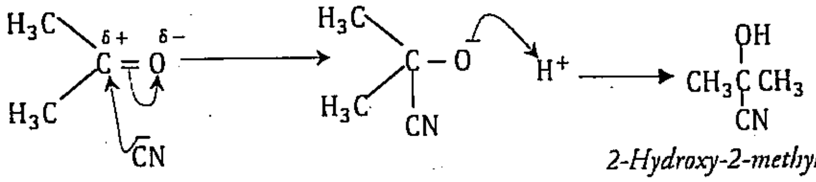


2-Hydroxypropanonitrile



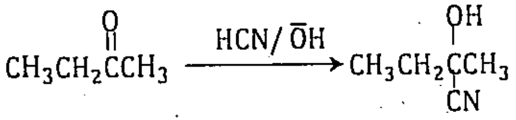
$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{KCN/\,H^+} CH_3\overset{OH}{\underset{CN}{C}}CH_3$$

Mechanism



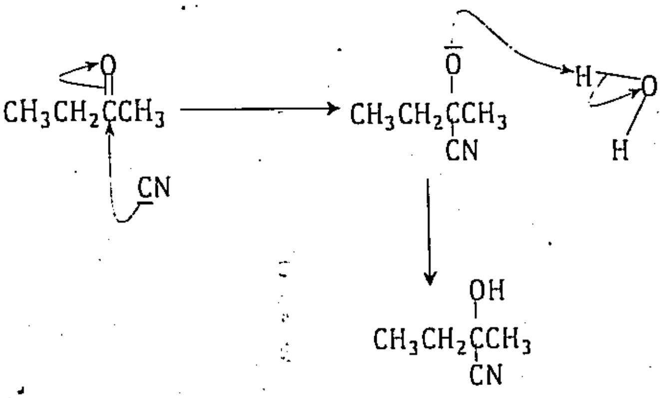
2-Hydroxy-2-methylpropanonitrile

The reaction occurs very slowly but can be made to occur rapidly in presence of an alkali.



$$\mathrm{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{HCN/\bar{O}H} CH_3CH_2\underset{CN}{\overset{OH}{C}}CH_3}$$

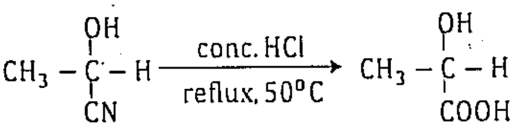
Mechanism



2-Hydroxy-2-methylbutanonitrile

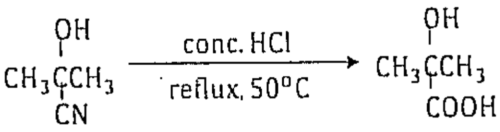
Note

- The cyanohydrins formed can be hydrolysed to form corresponding hydroxycarboxylic acids, i.e.,



$$\mathrm{CH_3-\underset{CN}{\overset{OH}{C}}-H \xrightarrow[\text{reflux, }50^\circ C]{\text{conc. HCl}} CH_3-\underset{COOH}{\overset{OH}{C}}-H}$$

2-Hydroxypropanoic acid



$$\mathrm{CH_3\underset{CN}{\overset{OH}{C}}CH_3 \xrightarrow[\text{reflux, }50^\circ C]{\text{conc. HCl}} CH_3\underset{COOH}{\overset{OH}{C}}CH_3}$$

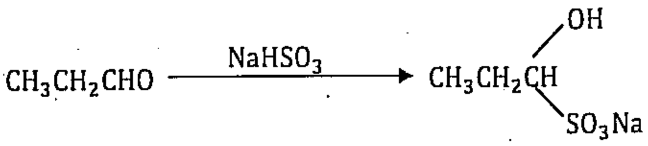
2-Hydroxy-2-methylpropanoic acid

- Benzaldehyde reacts with potassium cyanide in a different manner. It cannot form a cynohydrin.

(ii) Addition of sodium hydrogen sulphite

Most aldehydes and methyl ketones react with excess sodium hydrogen sulphite solution at room temperature to form white crystals which are an addition product.

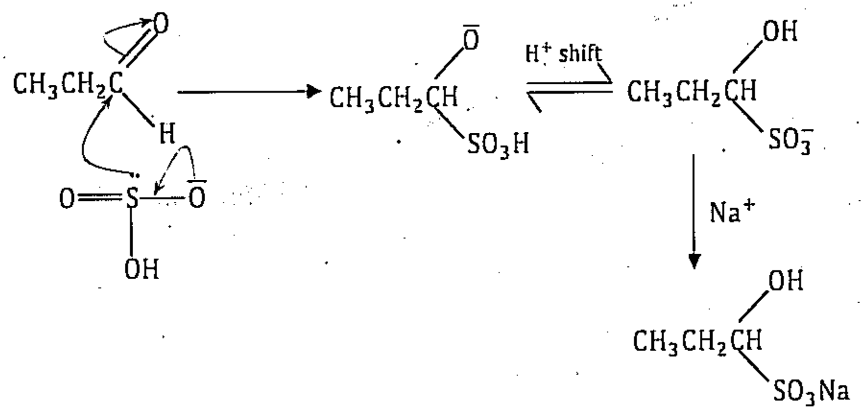
Examples



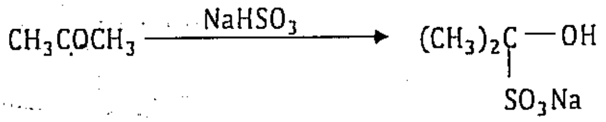
$$CH_3CH_2CHO \xrightarrow{NaHSO_3} CH_3CH_2CH(OH)SO_3Na$$

Mechanism

$$NaHSO_3 \longrightarrow Na^+ + HSO_3^-$$



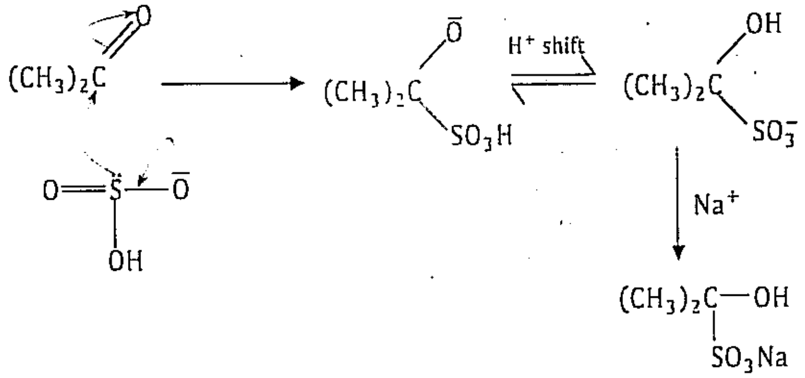
Propanal hydrogensulphite



$$CH_3COCH_3 \xrightarrow{NaHSO_3} (CH_3)_2C(OH)SO_3Na$$

Mechanism

$$NaHSO_3 \longrightarrow Na^+ + HSO_3^-$$



Propanone hydrogensulphite

Note

Aldehydes undergo this reaction more readily than ketones for reasons already explained.

Only methylketones undergo this reaction because the methyl group is the smallest hydrocarbon group that can be attached to the carbonyl carbon.

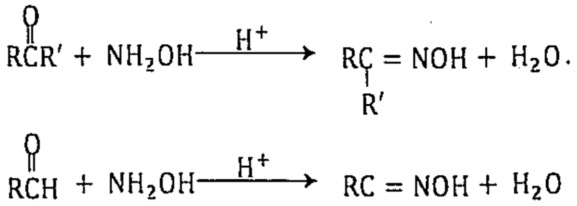
Any two larger groups attached to the carbonyl carbon hinder approach of the nucleophilic sulphite ion to the carbonyl carbon due to steric hinderance.

(b) Condensation reactions

Carbonyl compounds react with compounds containing the amino group ($-NH_2$) to form compounds containing the imine group ($\rangle C = N-$), with elimination of a water molecule. The reactions take place fast in presence of a dilute acid catalyst but very slow in the absence of the acid.

Examples

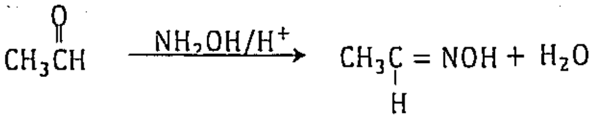
(i) With hydroxylamine (NH_2OH), oximes are formed



$$R\overset{O}{\overset{\|}{C}}R' + NH_2OH \xrightarrow{H^+} R\underset{R'}{\underset{|}{C}} = NOH + H_2O.$$

$$R\overset{O}{\overset{\|}{C}}H + NH_2OH \xrightarrow{H^+} RC = NOH + H_2O$$

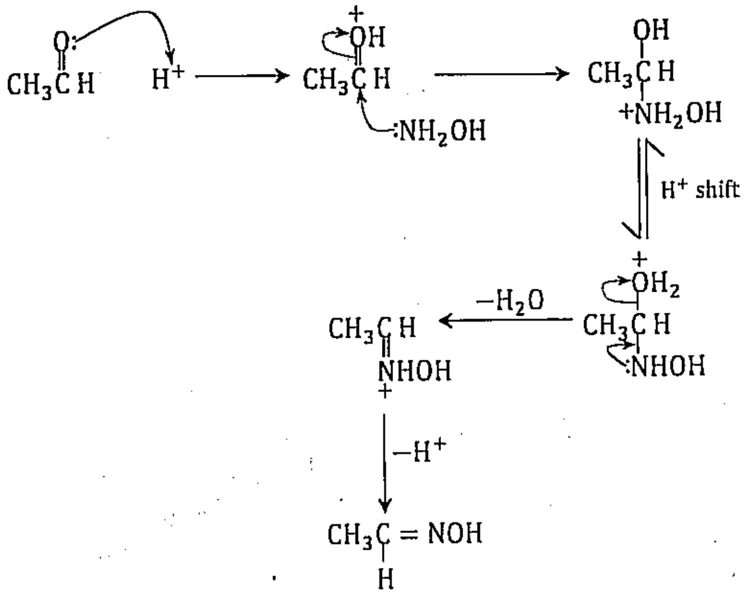
<u>Examples</u>



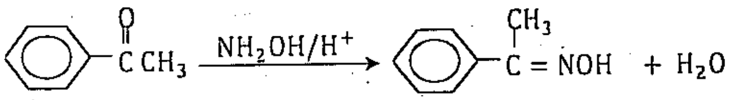
$$CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow{NH_2OH/H^+} CH_3\underset{H}{\underset{|}{C}} = NOH + H_2O$$

Ethanal oxime

<u>Mechanism</u>

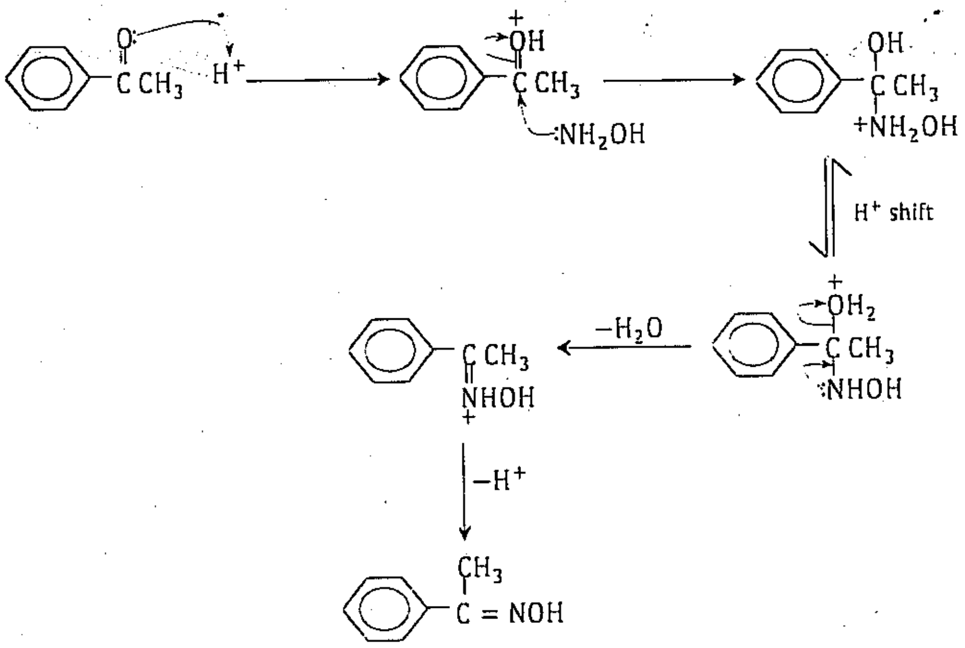


Ethanal oxime



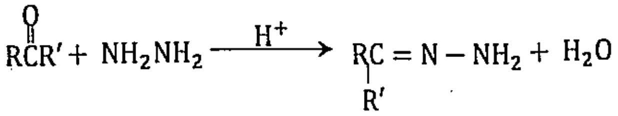
Phenyethanone oxime

Mechanism

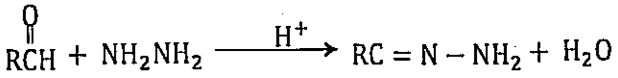


Note: The oximes formed are crystalline solids.

(ii) With hydrazine (NH_2NH_2)

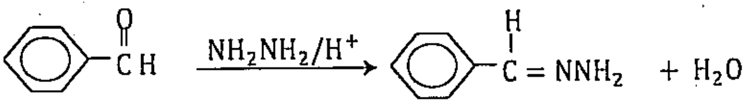


$$R\overset{O}{\overset{\|}{C}}R' + NH_2NH_2 \xrightarrow{H^+} R\underset{R'}{\underset{|}{C}} = N-NH_2 + H_2O$$



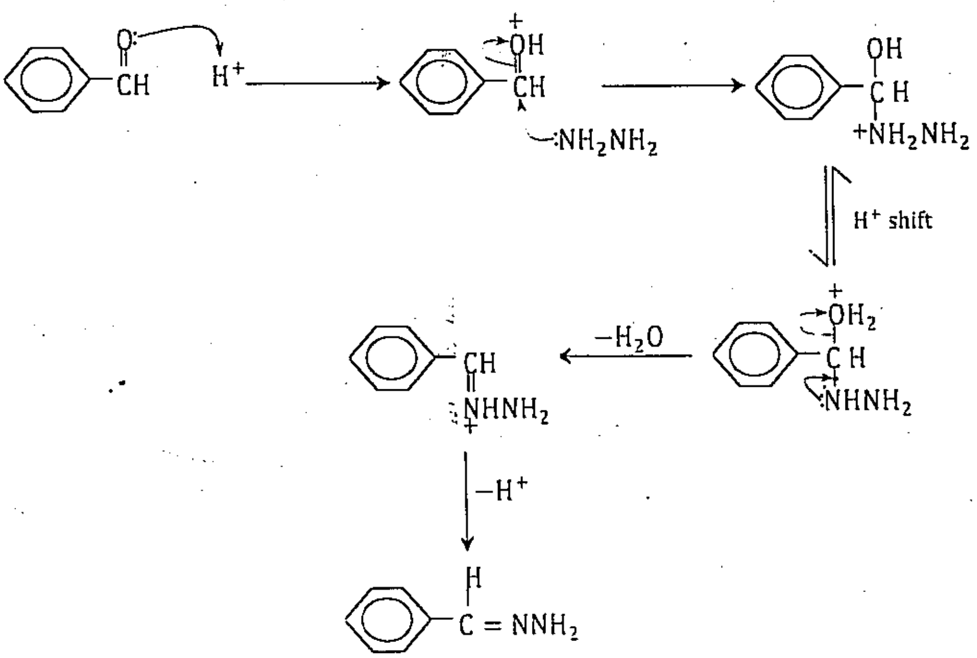
$$R\overset{O}{\overset{\|}{C}}H + NH_2NH_2 \xrightarrow{H^+} RC = N-NH_2 + H_2O$$

Hydrazones are formed. Since hydrazones also have an amino group, they may react further with the carbonyl compound to form an azine.

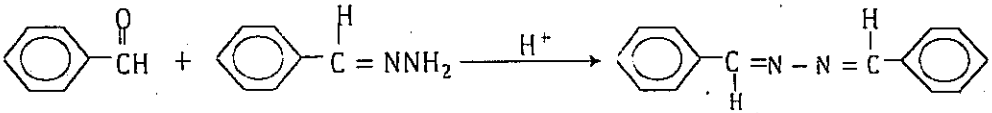


Benzaldehyde hydrazone

Mechanism

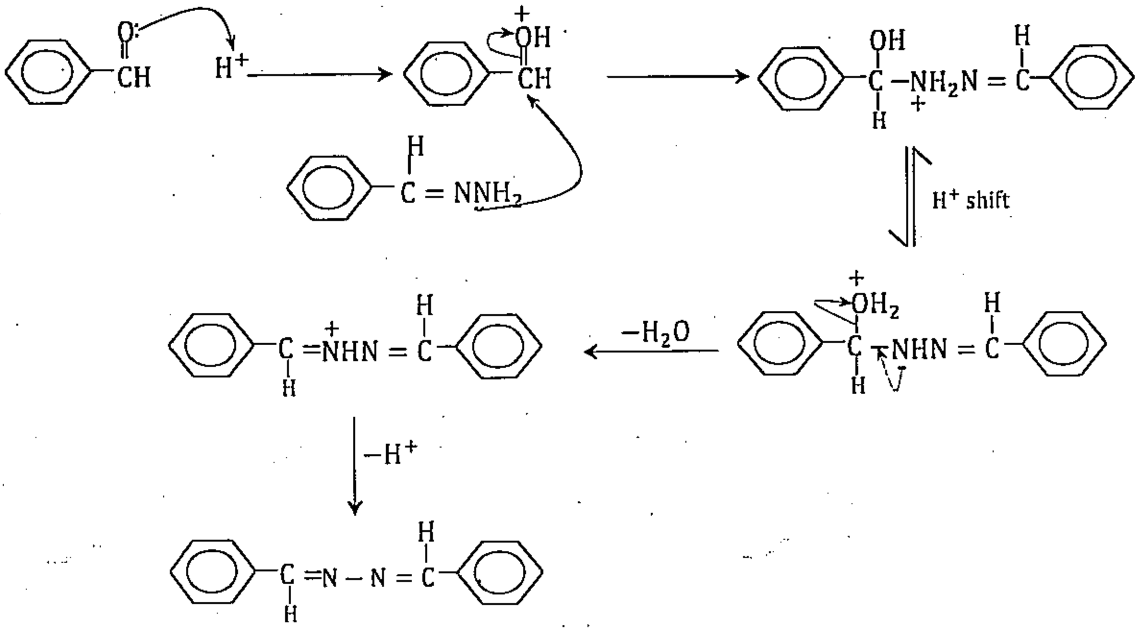


Formation of the azine

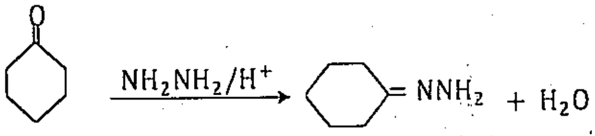


An azine

Mechanism

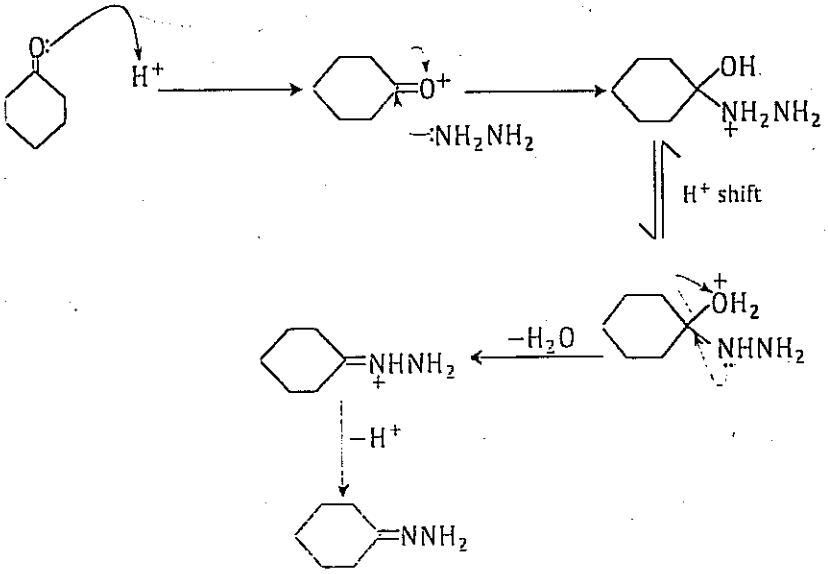


An azine



Cyclohexanone hydrazone

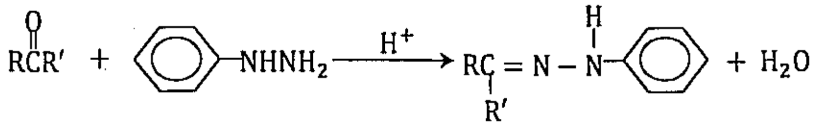
Mechanism

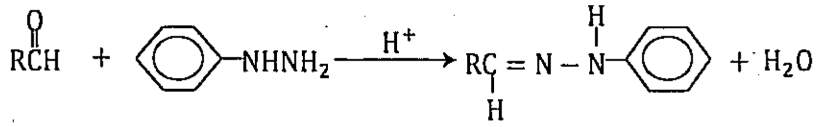


Cyclohexanone hydrazone

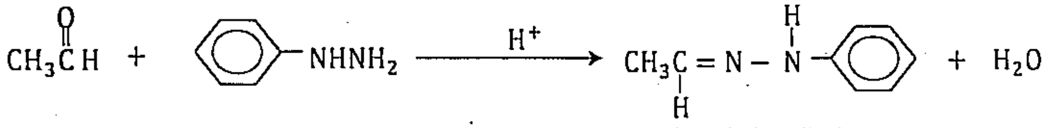
Note Both hydrazones and azines are crystalline solids.

(iii) With phenylhydrazine, phenylhydrazones are formed.



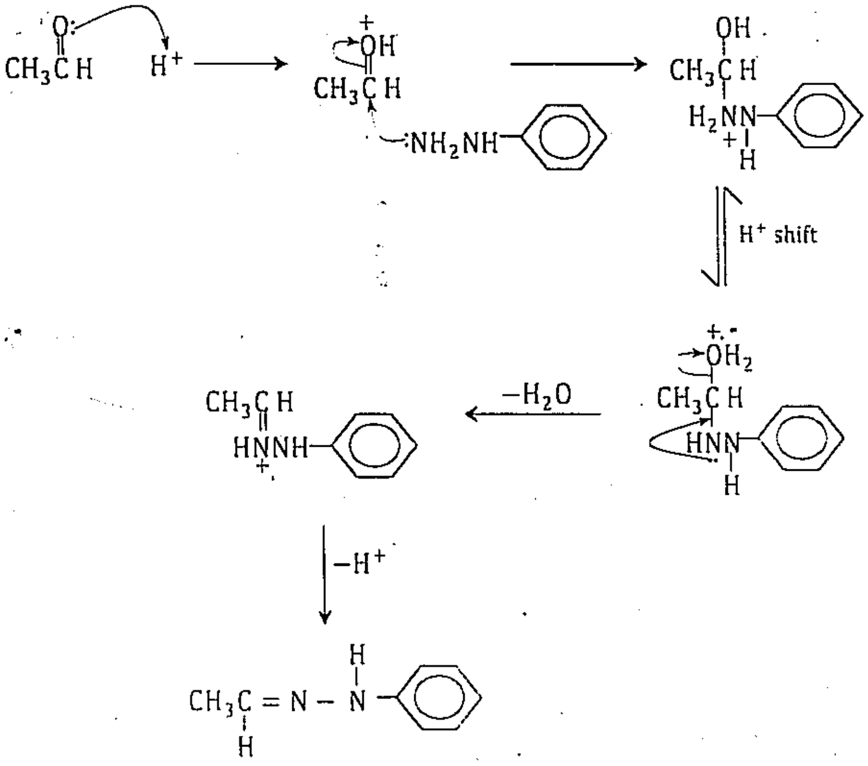


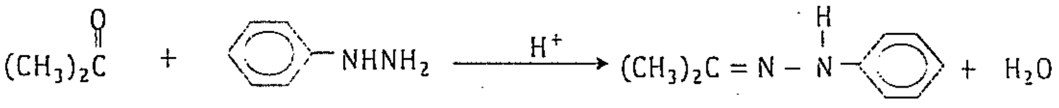
Examples



Ethanal phenylhydrazone

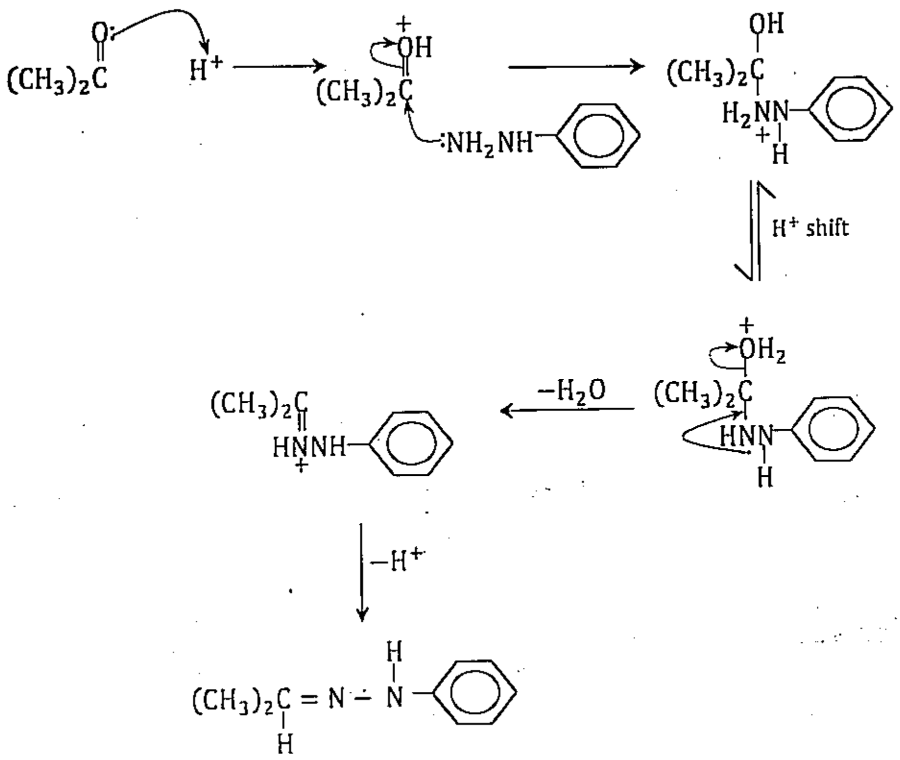
Mechanism





Propanone phenylhydrazone

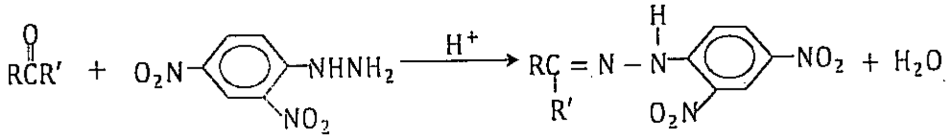
Mechanism

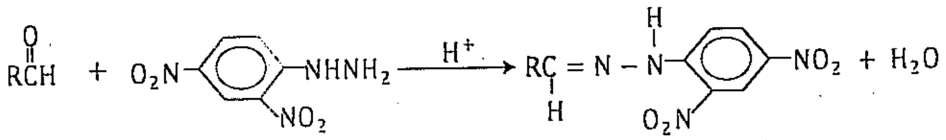


(iv) With Brady's reagent(2,4 – dinitrophenylhydrazine)

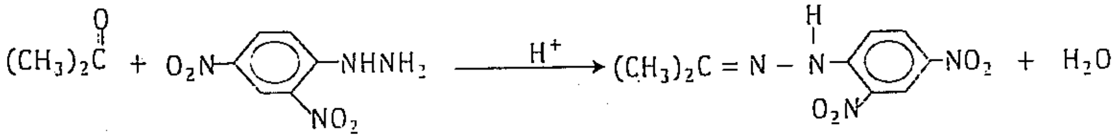
This reagent is used to confirm the carbonyl functional group.

2,4 – dinitrophenylhydrazine is dissolved in methanol and then shaken with a few drops of concentrated sulphuric acid. Yellow precipitates are formed. These are 2, 4 – dinitrophenylhydrazones formed.



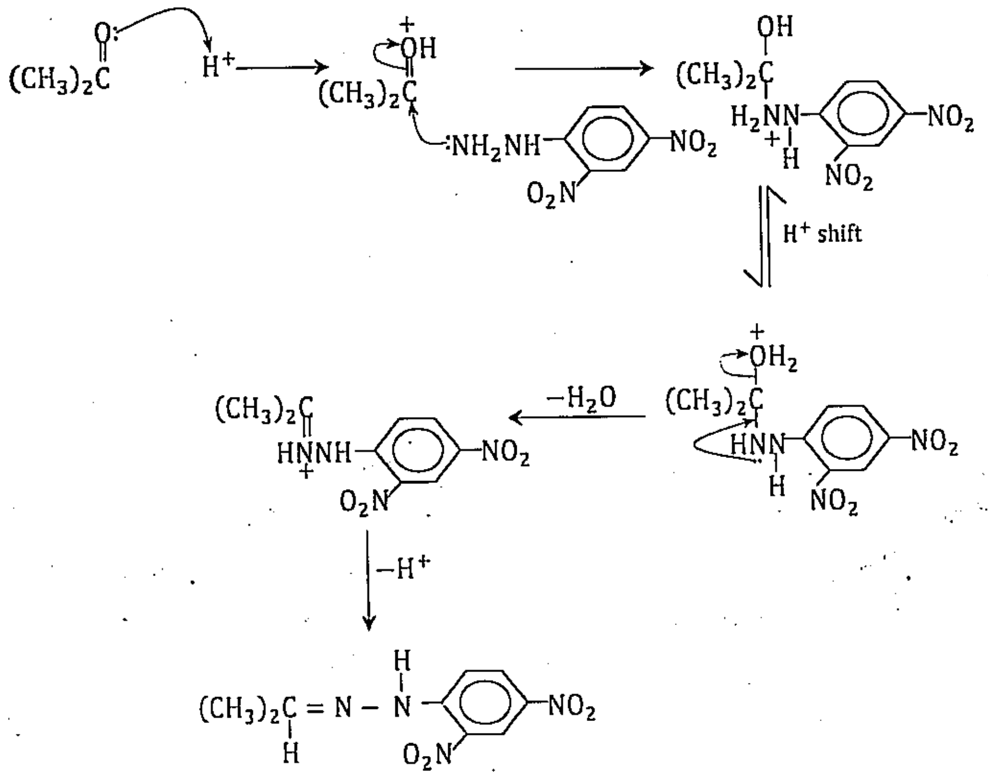


Example

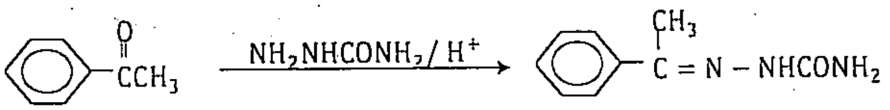


Propanone -2,4-dinitrophenylhydrazone

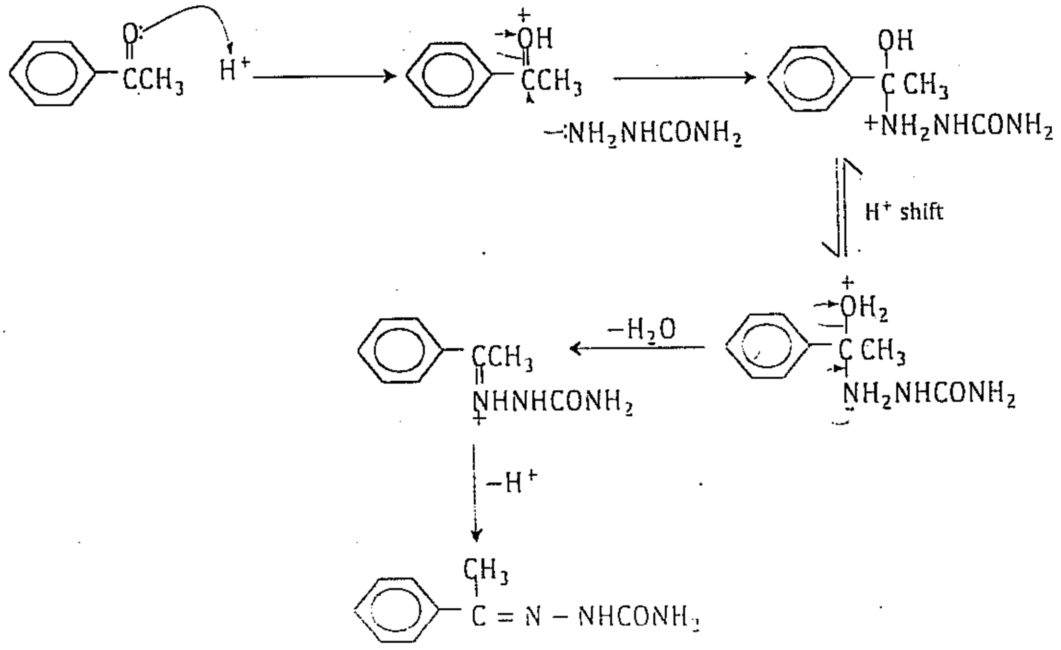
Mechanism



(v) **With semicarbazide,** semicarbazones are formed.



Mechanism



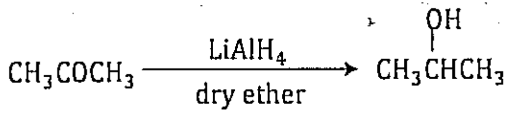
(c) Reduction reactions

Carbonyl compounds can be reduced to primary or secondary alcohols. A number of reducing agents can be used. These include:

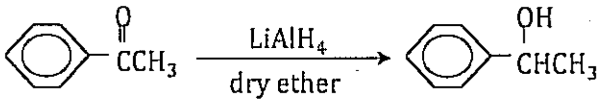
- Lithium tetrahydridoaluminate in presence of dry ether (($LiAlH_4$/dry ether)
- Lithium tetrahydridoborate in presence of dry ether ($LiBH_4$/dry ether)
- Sodium tetrahydridoborate in water or methanol ($NaBH_4/H_2O$ or $NaBH_4/CH_3OH$)
- Hydrogen in presence of nickel catalyst on heating.
- Sodium and ethanol.

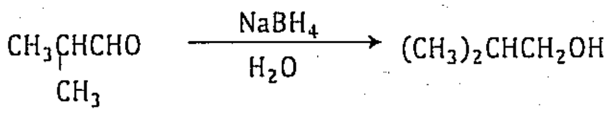
Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols. For example:

(i) $CH_3CHO \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2OH$

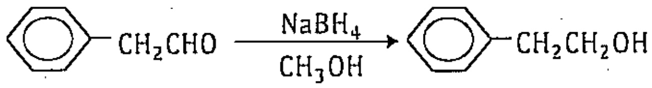
(ii)


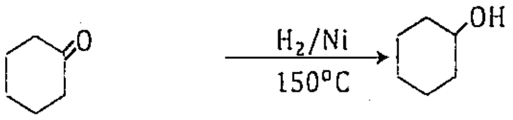
$$CH_3COCH_3 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3\overset{OH}{C}HCH_3$$

(iii)


(iv)


$$CH_3\underset{CH_3}{C}HCHO \xrightarrow[H_2O]{NaBH_4} (CH_3)_2CHCH_2OH$$

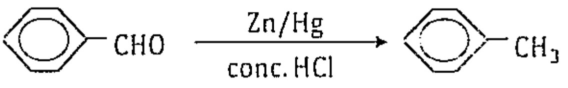
(v)


(vi)


(vii) $CH_3CH_2CHO \xrightarrow[CH_3CH_2OH]{Na} CH_3CH_2CH_2OH$

Carbonyl compounds can also be reduced to corresponding hydrocarbons when treated with amalgamated zinc and concentrated hydrochloric acid. This called the clemmensen reaction.

$$CH_3COCH_3 \xrightarrow[\text{conc. HCl}]{Zn/Hg} CH_3CH_2CH_3$$



(d) Oxidation reactions

Aldehydes are oxidized to carboxylic acids by a number of different oxidizing agents.

Ketones are difficult to oxidize in solution.

Most of these reactions are used to distinguish aldehydes and ketones.

(i) Using acidified potassium dichromate(VI) solution

Aldehydes are oxidized to carboxylic acids using an acidified solution of potassium dichromate(VI) solution. **Orange solution turns green.**

$$CH_3CHO \xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+} CH_3COOH$$

Similarly, acidified potassium manganate(VI) solution may be used or nitric acid or the vapour mixed with oxygen and passed over finely divided heated copper or platinum catalyst.

$$CH_3CHO \xrightarrow[\text{heat}]{KMnO_4/H^+} CH_3COOH$$

$$CH_3CHO \xrightarrow[\text{heat}]{O_2/\text{Cu or Pt catalyst}} CH_3COOH$$

$$CH_3CHO \xrightarrow[\text{heat}]{CrO_3/H^+} CH_3COOH$$

The general equation using acidified dichromate ion is;

$$3RCHO + Cr_2O_7^{2-}(aq) + 8H^+(aq) \longrightarrow 3RCOOH(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$$

Under the same conditions, ketones are not so easily oxidized and more vigorous conditions are required to break the strong carbon-carbon single bond.

(ii) Using ammoniacal silver nitrate solution

This is a solution of silver nitrate in an excess solution of ammonia.

- **Aldehydes** reduce the silver ions to silver which is formed as a deposit on the wall of the test tube.

  Observation: **Silver mirror is formed.**
- Ketones give no observable change.

The reaction with aliphatic aldehydes is almost immediate but **benzaldehyde requires warming**. Similarly, ammonia solution may be added to a solution of silver nitrate in dilute aqueous sodium hydroxide until the brown precipitate just dissolves. This reagent is Tollen's reagent and gives a silver mirror with aldehydes too.

$$RCHO(l) + 2Ag(NH_3)_2OH\,(aq) \longrightarrow RCOONH_4(aq) + 2Ag(aq) + 4H_2O(l) + 3NH_3(aq)$$

Or

$$RCHO(l) + 2Ag(NH_3)_2^{+}(aq) + 2\bar{O}H(aq) \longrightarrow RCOOH(aq) + 2Ag(aq) + H_2O(l) + 4NH_3(aq)$$

Considering ethanal,

$$CH_3CHO(l) + 2Ag(NH_3)_2OH\,(aq) \longrightarrow CH_3COONH_4(aq) + 2Ag(aq) + 4H_2O(l) + 3NH_3(aq)$$

Or

$$CH_3CHO(l) + 2Ag(NH_3)_2^{+}(aq) + 2\bar{O}H(aq) \longrightarrow CH_3COOH(aq) + 2Ag(aq) + H_2O(l) + 4NH_3(aq)$$

(iii) Using Fehling's solution

This is a solution of **copper(II) sulphate in a solution of sodium tartarate** and **excess sodium hydroxide solution**. The whole mixture makes a deep blue solution.

Aliphatic aldehydes form a **reddish-brown precipitate on warming**. This is because the **aliphatic aldehydes reduce the copper(II) ions** to an **insoluble copper(I) oxide** which **deposits as a reddish brown precipitate.**

Equation

$$RCHO(l) + 2Cu^{2+}(aq) + 5\bar{O}H(aq) \longrightarrow RCOO^{-}(aq) + 2Cu_2O(s) + 3H_2O(l)$$

Considering ethanal:

$$CH_3CHO(l) + 2Cu^{2+}(aq) + 5\bar{O}H(aq) \longrightarrow CH_3COO^{-}(aq) + 2Cu_2O(s) + 3H_2O(l)$$

Ketones and benzaldehyde do not react with Fehling's solution hence give no observable change.

(iv) Using the iodoform test

Iodoform test involves a solution of iodine in sodium hydroxide.

Iodine solution followed by sodium hydroxide solution is added drop wise to the carbonyl compound until the solution is pale yellow. The mixture is then warmed and allowed to stand

Any **methyl ketone** and **only one aldehyde (ethanal)** form a **yellow precipitate.**

This test is therefore positive only for carbonyl compounds with a methyl group attached to the carbonyl carbon.

The iodoform reagent contains the iodate(I) ion, which is a strong oxidizing agent.

The yellow precipitate formed is called Triodomethane (CHI_3). The general equation for the reaction is:

$$CH_3COR + 3I_2 + 4NaOH \longrightarrow RCOONa + 3H_2O + CHI_3 + 3NaI$$

This reaction is used to distinguish ethanal and other aldehydes or methylketones and other ketones.

Examples

$$CH_3CHO(l) + 3I_2(aq) + 4NaOH(aq) \longrightarrow CHI_3(s) + HCOONa(aq) + 3H_2O(l) + 3NaI(aq)$$

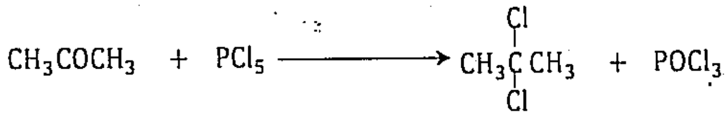
$$(CH_3)_2CO(l) + 3I_2(aq) + 4NaOH(aq) \longrightarrow CHI_3(s) + CH_3COONa(aq) + 3H_2O(l) + 3NaI(aq)$$

$$CH_3COCH_2CH_3(l) + 3I_2(aq) + 4NaOH(aq) \longrightarrow CHI_3(s) + CH_3CH_2COONa(aq) + 3H_2O(l) + 3NaI(aq)$$

(e) Other reactions

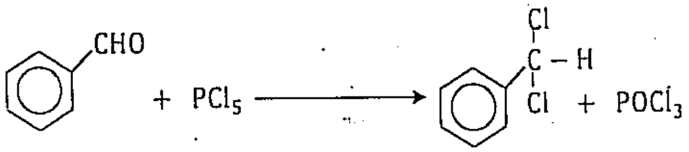
(i) chlorination

Aliphatic and simple aromatic carbonyl compounds react with phosphorus(V) chloride to form germinal dichlorides.



$$CH_3COCH_3 + PCl_5 \longrightarrow CH_3\overset{Cl}{\underset{Cl}{C}}CH_3 + POCl_3$$

$$CH_3CHO + PCl_5 \longrightarrow CH_3\overset{Cl}{\underset{Cl}{C}}H + POCl_3$$

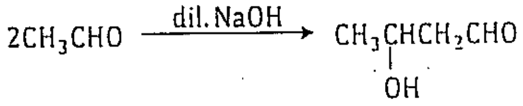


(ii) Aldol condensation

This reaction only occurs for aldehydes and ketones containing at least one hydrogen atom on the carbon atom adjacent to the carbonyl group. The reaction is catalyzed by a base. Methanal (HCHO) and benzaldehyde do not under go this reaction.

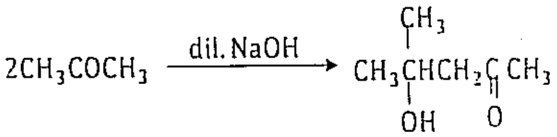
When a cold dilute solution of an alkali is used, an aldol is formed.

An aldol contains both an aldehyde group and an alcohol group.



$$2CH_3CHO \xrightarrow{\text{dil.NaOH}} CH_3\underset{OH}{C}HCH_2CHO$$

3-Hydroxybutanal



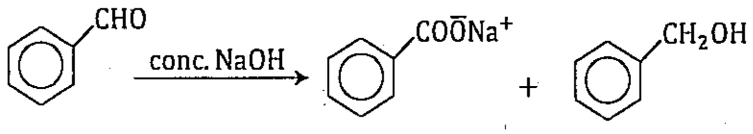
$$2CH_3COCH_3 \xrightarrow{\text{dil.NaOH}} CH_3\overset{CH_3}{\underset{OH}{C}}HCH_2\underset{O}{\overset{\|}{C}}CH_3$$

4-Hydroxy-4-methylpentan-2-one

(iii) Cannizzaro reaction

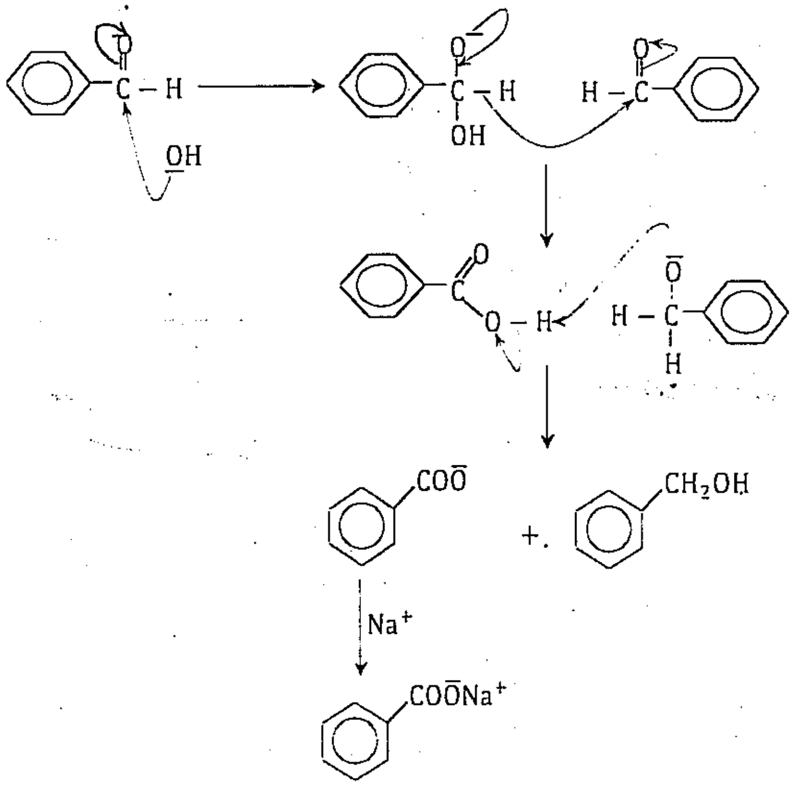
Aldehydes which do not contain at least one hydrogen atom on the carbon atom next to the carbonyl group (e.g. methanal and benzaldehde) do not undergo condensation reactions.

They however undergo the cannizzaro reaction with concentrated alkali at room temperature. One half of the quantity is oxidized and the other half is reduced to form a salt of a carboxylic acid and an alcohol respectively.



Mechanism

$$\text{NaOH} \longrightarrow \text{Na}^+ + \bar{\text{O}}\text{H}$$



7.7 Distinguishing aldehydes and ketones

Both aldehydes and ketones form a yellow precipitate with Brady's reagent. However the two can be distinguished using Tollen's reagent and Fehling's solution as shown below.

Reagent	Carbonyl compound	Observation
	Aldehyde, e.g. CH_3CHO	Silver mirror formed on the wall of the test tube

Ammonical silver nitrate solution or Tollen's reagent	Ketone, e.g., CH_3COCH_3	No observable change
Fehling's solution	Aldehyde, e.g., CH_3CH_2CHO	Reddish brown precipitate
	Benzaldehyde	No observable change
	Ketones, e.g., $CH_3COCH_2CH_3$	No observable change

Ethanal can be distinguished from other aldehydes and methylketones from other ketones using the iodoform test.

Reagent	Examples of compounds distinguished	observation
Iodine solution and sodium hydroxide solution and warm	CH_3CHO	Yellow precipitate
	other aldehydes e.g., CH_3CH_2CHO	No observable change
	CH_3COCH_3 or $CH_3COCH_2CH_3$ or $C_6H_5COCH_3$	Yellow precipitate
	$CH_3CH_2COCH_2CH_3$ or $C_6H_5COCH_2CH_3$	No observable change

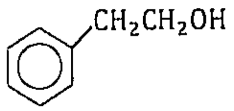
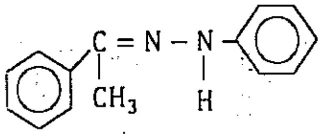
7.8 Uses of carbonyl compounds

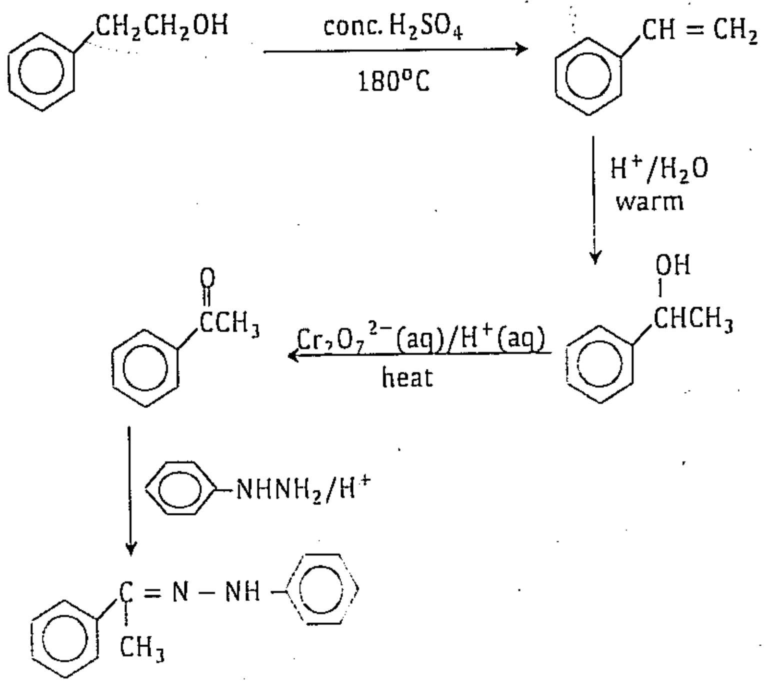
- Methanal is used in manufacture of thermosetting plastics such as a 40% aqueous solution called formalin, to preserve biological specimens
- Ethanal is used in manufacture of ethanoic acid, DDT, dyes and buta-1,3- diene which is in turn used in rubbers.
- propanone is used in manufacturing laloforms, perspex and as a solvent for plastics, vanishes and greases.

- Benzaldehyde is used in scenting soaps, flavouring food (almonds) and manufacturing dyes and antibiotics.

7.9 Some synthetic problems.

(a) Write equations to show how the following conversions can be effected.

(i)  to 



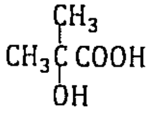
(ii) Ethanoyl chloride to ethanol

$$CH_3COCl \longrightarrow CH_2CH_2OH$$

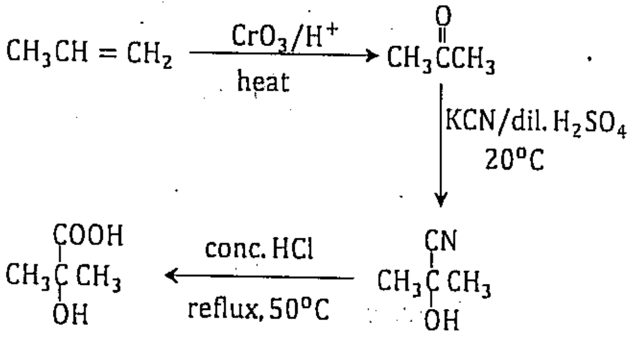
$$\begin{tikzcd}
CH_3COCl \arrow[r, "H_2/\text{poisoned Pd, } BaSO_4 \text{ cat}", "\text{heat}"'] & CH_3CHO \arrow[d, "LiAlH_4", "\text{dry ether}"'] \\
 & CH_3CH_2OH
\end{tikzcd}$$

(iii) Propene to 2-hydroxy-2-methylpropanoic acid.

$CH_3CH = CH_2$ to

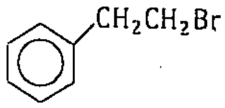


$$CH_3\overset{CH_3}{\underset{OH}{C}}COOH$$

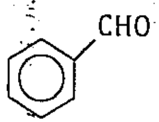


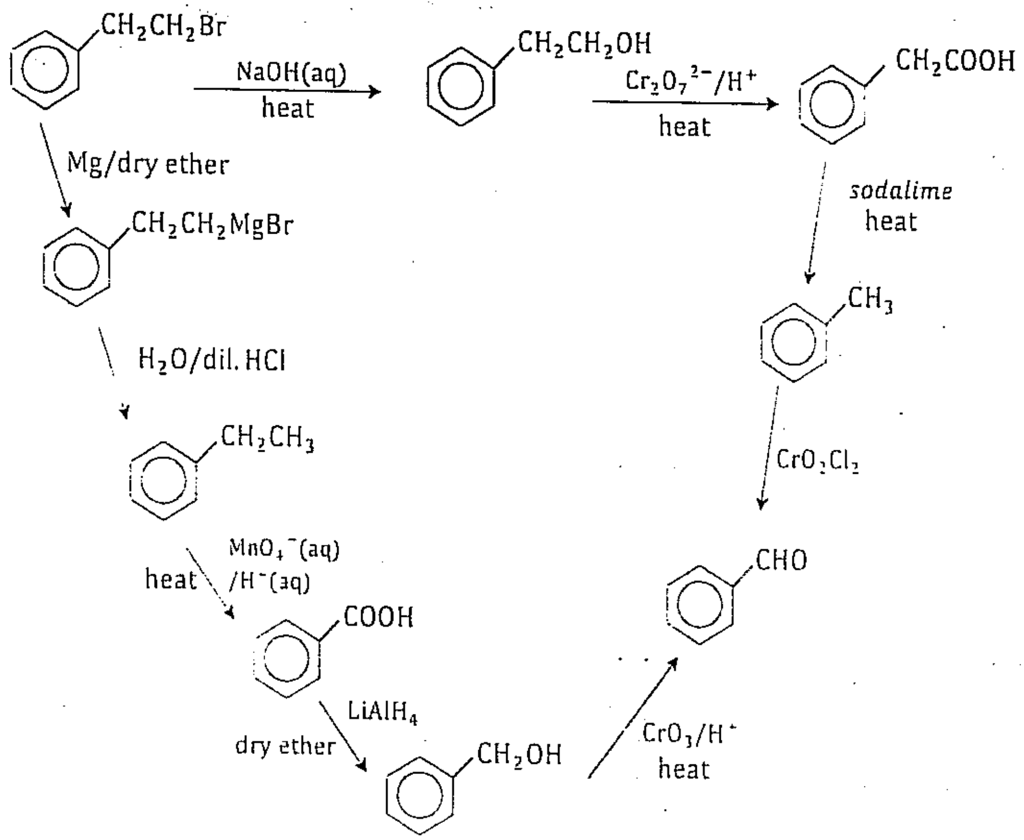
$$\begin{tikzcd}
CH_3CH = CH_2 \arrow[r, "CrO_3/H^+", "\text{heat}"'] & CH_3\overset{O}{\overset{\|}{C}}CH_3 \arrow[d, "KCN/\text{dil. } H_2SO_4", "20^\circ C"'] \\
CH_3\overset{COOH}{\underset{OH}{C}}CH_3 & CH_3\overset{CN}{\underset{OH}{C}}CH_3 \arrow[l, "\text{conc. HCl}", "\text{reflux, } 50^\circ C"']
\end{tikzcd}$$

(iv)



to





(b) Describe how the following conversions can be effected. (NO equations required)

(i) **Propanone from ethanol**

Ethanol is dehydrated by heating it with excess concentrated sulphuric acid at 180°C to form ethene. Ethene is reacted with chlorine in the presence carbontetrachloride to form 1, 2-dichloroethane which is then reacted with excess alcoholic potassium hydroxide solution on heating to form ethyne. Ethyne is reacted with sodium in liquid ammonia to form sodium acetylide. Sodium acetylide is reacted with bromomethane to yield propyne which is then reacted with dilute sulphuric acid in presence of mercury(II) sulphate at 60°C to form propanone.

(ii) **Methylbenzene to 1-phenylethanol**

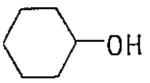
Methylbenzene is heated with acidified potassium manganate(VII) solution to form benzoic acid which is then heated with sodalime to form benzene. Benzene is reacted with ethanoyl chloride in presence of anhydrous aluminium chloride, the mixture being refluxed on a water bath at 50°c to form phenylethanone which is reduced by lithium tetrahydridoaluminate in presence of dry ether to form 1-phenylethanol.

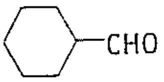
7.10 End of topic assessment exercise

1. Complete the following equations and write the IUPAC name of the main organic product in each case.

(a) $(CH_3COO)_2Pb \xrightarrow{\text{heat}}$

(b) $CH_3COCH_3 \xrightarrow{PCl_5}$

(c)  $\xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+}$

(d)  $\xrightarrow[\text{Zn/Hg}]{\text{conc. HCl}}$

(e) $CH_3CH_2COCH_3 \xrightarrow[\text{Zn/Hg}]{\text{conc. HCl}}$

(f) $CH_3C \equiv CH + H_2O \xrightarrow[H_2SO_4,\ 60°C]{Hg^{2+}(aq)}$

(g) $2(CH_3)_2CO \xrightarrow{\text{dil. NaOH}}$

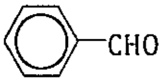
(h) $HC \equiv CH + H_2O \xrightarrow[\text{warm}]{Hg^{2+}(aq)/H^+(aq)}$

(i) $(CH_3COO)_2Ba \xrightarrow{\text{heat}}$

(j) $CH_3COCH_3 \xrightarrow{NaBH_4/CH_3OH}$

(k) $C_6H_5CHO \xrightarrow[\text{dry ether}]{LiAlH_4}$

(l) $CH_3CH_2CHO \xrightarrow{[Ag(NH_3)_2]^+}$

(m)  $\xrightarrow{PCl_5}$

(n) $(CH_3CH_2COO)_2Ca \xrightarrow{\text{heat}}$

(o) $CH_3CHO \xrightarrow{NaHSO_3}$

(p) $CH_3COCH_3 \xrightarrow{\text{dil. }NaOH(aq)}$

(q) $CH_3CH_2COCH_3 \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgI}$

2. Complete the following equations and in each case write a mechanism for the reaction.

(a) $CH_3CHO \xrightarrow{NH_2NH_2}$

(b) $CH_3CH_2CHO \xrightarrow[10-20^\circ C]{KCN/\text{dil. }H_2SO_4}$

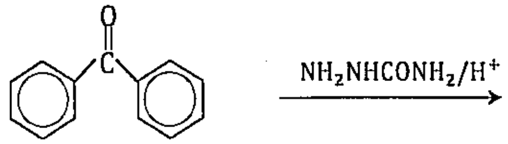
(c) $CH_3COCH_3 \xrightarrow[H^+]{Na_2SO_3}$

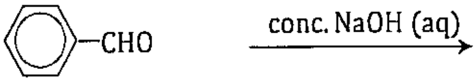
(d)  $+ CH_3COCl \xrightarrow{AlCl_3}$

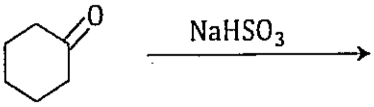
(e) $CH_3COCH_3 \xrightarrow{NaHSO_3}$

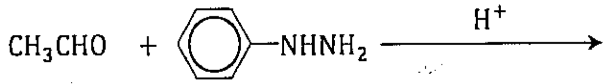
(f) $CH_3COCH_3 \xrightarrow{H_2NOH/H^+}$

(g) $CH_3COCH_3 \xrightarrow{HCN/\bar{O}H}$

(h) 

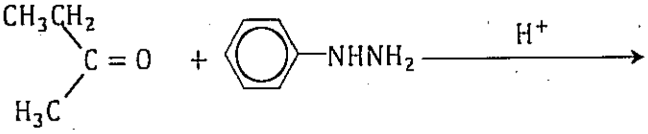
(i) 

(j) 

(k) 

(l) $CH_3CH_2CHO + NaHSO_3 \xrightarrow{H^+}$

(m) $(CH_3)_2C = O \xrightarrow{NH_2NHCONH_2/H^+}$

(n) 

3. State what is observed and write equation for the reaction for the reaction in each when the following compounds are mixed.
   - (a) Propanone and Brady's reagent.
   - (b) Ethanal and a saturated solution of sodium bisulphite.
   - (c) 2,4- dinitrophenylhydrazine and ethanal in acidic medium.
   - (d) To 2- methylpropanal is added $1cm^3$ silver nitrate solution, 3 drops of sodium hydroxide solution and then excess ammonia solution
   - (e) Fehling's solution and ethanal on warming.
   - (f) Propanal and silver nitrate in aqueous ammonia on warming.

4. Describe how the following conversion can be effected.(No equations are required)
   - (a) 2- chloropropane to propanonehydrazine
   - (b) Ethanol to methanol
   - (c) Propyne to propanone.
   - (d) Propene to propanalphenylhydrazine.
   - (e) Cyclohexanone from cyclohexene
   - (f) Ethanoic acid to propanone.
   - (g) Ethene to Hydroxyethanoic acid.
   - (h) Benzaldehyde phenylhyazone from benzene .
   - (i) Propanal to propyne.

(j) But-2-ene to Propyne.

(k) Ethyne to $CH_3CH{=}CHCHO$

(l) Ethyne to benzaldehyde.

5. An organic compound has a molecular formular $C_2H_4Cl_2$.

(a) Write the structural formulae and names of all possible isomers of the compound.

(b) Each of the isomers in (a) above when separately refluxed with concentrated sodium hydroxide solution gives a different product. The product from one isomer forms a yellow precipitate with 2,4- dinitrophenylhydrazine and one from the other isomer gives no observable change.

(i) State which isomer gives a product that forms a yellow precipitate with Brady's reagent.

(ii) Write equations for the reactions that occur between each isomer and concentrated sodium hydroxide solution.

5. A compound Q, has an empirical formula C_3H_6O. Oxygen diffuses 1.345 times faster than Q.

(a) (i) Determine the molecular formula of Q.

(ii) Write the structural formulae of all possible isomers of Q.

(b) (i) Q does not react with Fehling's solution. Using equations, show how Q can be formed from propene

(ii) Write an equation for the reaction between Q and sodium hydrogen sulphite and the mechanism.

6. Compound Y, C_3H_6O reacts with 2,4- dinitrophenylhydrazine to form a yellow solid.

(a) Write the structural formulae and IUPAC names of all isomers of Y.

(b) When Y is heated with Fehling's solution, a red precipitate is formed. Identify Y.

(c) Write a mechanism for the reaction that would take place between Y and hydroxylamine.

(d) Write equations to show how Y can be converted to an alkene.

7. (a) An aqueous solution containing 7.2g of non-cyclic substance Z in 250g of water freezes at $-0.744^\circ C$. Calculate the molecular mas of Z.

(The freezing point constant, Kf for water is $1.86^\circ C mol^{-1} Kg^{-1}$).

(b) If Z contains carbon, 66.7% hydrogen 11.1% and the rest being oxygen.

(i) Calculate the simplest formula of Z.

(ii) Determine the molecular formula of Z

(c) Z reacts with phenylhydrazine to form an addition product and yellow precipitate with iodine solution in presence of sodium hydroxide Name Z.

8. (a) An organic compound F contains 66.4% carbon, 5.53% hydrogen and the rest being chlorine. Determine the empirical formular of F.

(b) When 0.35g of F was vapourised, it occupied 75.43cm^3 at 103°C and 860mmHg. Determine the molecular formular of F.

(c) F burns with a sooty flame. Write the structural formulae and names of all the possible isomers of F.

(d) F reacts with potassium hydroxide solution on heating to form another compound G. G reacts with acidified chromium(VI)oxide on heating to form compound H. H forms a yellow precipitate with silver nitrate solution in excess ammonia.

Identify F, G and H.

(e) Write equation and indicate mechanism for the reaction between:

(i) F and phenol in presence of sodium hydroxide solution.

(ii) H and Brady's reagent.

(f) Write equations to show how F can be synthesized from benzene.

9. (a) A compound H contains 22.86% oxygen, 8.57% hydrogen and the rest being carbon.

(i) Calculate the empirical formula of H.

(ii) When 0.30g of H is vapourised at 80°C and 134.77cm^3. Determine the molecular formula of H.

(b) H forms a yellow precipitate with 2, 4-dinitrohenylhydrazine and does not react with Tollen's reagent. Identify H.

(c) Write equation for the formation of the yellow precipitate in b).

10. (a) An organic compound J has a molecular formula $C_3H_6Br_2$. Write down the structural formulae and IUPAC names of all isomers of J.

(b) When J was heated with sodium metal in ethanol a compound K was formed. K reacts with water in presence of sulphuric acid and mercurous sulphate at 60°C to form a compound L. L does not react with Fehling's solution but forms a yellow precipitate with 2,4-dinitrophenylhydrazine. Name compounds J, K and L.

(c) Write the equation and suggest the mechanism for the reaction between:

(i) J and sodium metal in ethanol.

(ii) L and 2, 4-dinitrophenylhydrazine.

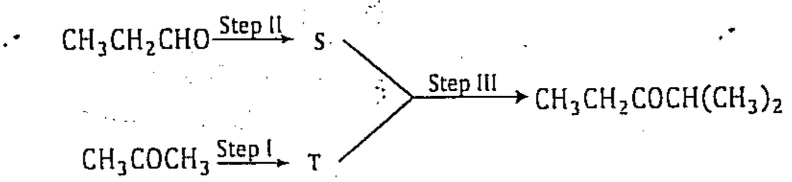
11. (a) Write the structural formulae and names of all possible isomers of organic compound with the molecular formula, C_3H_8O.

(b) One of the isomers in (a) above, M, reacts with acidified potassium clichromate to form a compound N. N reacted with phosphorous pentachloride to form compound P. P forms a compound Q when hydrolysed with aqueos sodium hydroxide on heating. Q forms a yellow precipitate with iodine solution and sodium hydroxide solution. Identify M, N, P and Q.

(c) Write equation and indicate mechanism for the reaction between and concentrated sulphuric acid.

12. (a) Describe a simple chemical test to distinguish between propane and propanal.

(b) Compound R can be synthesized by the reaction between S and T as shown below.



(i) Identify compounds S and T.

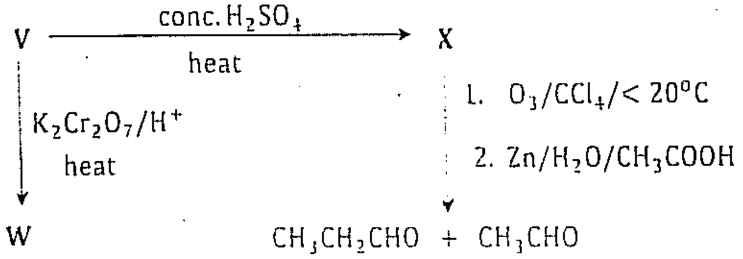
(ii) Name the type of reaction that occurs in steps I and II.

(c) Identify the reagents and state the conditions necessary for the reaction

(i) Step I (ii) Step III

(d) Write the mechanism for the reaction that occurs in step III

13. An organic compound V has a molecular formular $C_5H_{12}O$. V reacts with sodium metal to form hydrogen gas and undergoes other reactions as shown by the scheme below.



W reacts with phenylhydrazine and gives a positive test with iodoform.

(a) Identify V, W and X.

(b) Describe the test that can distinguish the products from ozonolysis of X.

14. A compound Z, whose molecular mass is 142, contains 16.9% oxygen, and the rest being hydrogen.

(a) (i) Determine the empirical formula of Z.

(ii) Workout the molecular formular of Z.

(b) On heating Z decomposes to form a white residue, X and a gas Y that reacts with Brady's reagent in acidic medium to form a yellow precipitate.

(i) Deduce the chemical formula of Z.

(ii) Identify X and Y.

(c) Write equations for the reaction that:

(i) takes place when Z is heated.

(ii) leads to formation of the yellow precipitate.

(d) (i) State what will be observed when dilute sulphuric acid is added to X.

(ii) Write equation for the reaction between dilute sulphuric acid and X.

(e) Write:

(i) the mechanism for the reaction in (c) (iii)

(ii) equation(s) for conversion of Y in ethene.

15. (a) A compound Q contains 63.7% lead, 14.8% carbon, 1.8% hydrogen and the rest being oxygen. When vapourised 0.225g of Q occupies 15.5cm^3 at standard temperature and pressure.

(i) Calculate the empirical formula of Q.

(ii) Deduce the molecular formula of Q.

(b). Compound Q decomposed on heating to form a yellow residue on cooling and a colourless vapour that turned lime water milky and formed a yellow precipitate with Bradys's reagent in presence of sulphuric acid.

(i) Write the name and formula of Q.

(ii) Write equation leading to formation of the yellow precipitate.

16. Compound Q contains 62.1% carbon, 10.3% hydrogen and the rest being oxygen.

(a) Calculate the empirical formula of Q.

(b) Q distills in steam at 98°C and $1.01 \times 10^5 Nm^{-2}$. If the vapour pressure of water at 98°C $9.5 \times 10^4 Nm^{-2}$,

(i) Calculate the molecular mass of Q if the distillate contained 16.67% by mass of Q.

(ii) Determine the molecular formula of Q.

(c) Q formed a grey precipitate when treated with ammoniacal silver nitrate. Write equation and outline a mechanism for the reaction between Q and sodium hydrogen sulphite.

17. (a) An organic compound Z contains by mass 51.90% carbon, 4.86% hydrogen and the rest being bromine. Determine the empirical formula of Z.

(b) When 0.8g of Z was vapourised at 80°C and a pressure of 700mmHg, it occupied a volume of $136cm^3$. Deduce the molecular formula of Z.

(c) When Z was heated with excess sodium hydroxide solution, it formed a compound Y. On heating Y with acidified manganese(IV) oxide, a substance W was formed. W formed a yellow precipitate with 2,4 – dinitrophenylhydrazine in presence of dilute sulphuric acid but gave no observable change with aqueous ammonia in presence of silver nitrate solution.

(i) Write the equations leading to formation of substances Y and W and the yellow precipitate indicating all reagents and conditions.

(ii) Write equations for the reaction between substance W and semicarbazine in presence of dilute sulphuric acid. Outline the mechanism for the reaction.

(iii) Write equation(s) to show how compound Y can be synthesized from benzene. Indicate the necessary conditions and reagents.

18. 0.3g of an organic compound Y, on complete combustion, gave 0.88g of carbondioxide gas and 0.18g of water. 0.53g of Y in 22g of ethanoic acid lower freezing point by 0.78K. (K_f for ethanoic acid is $3.89Kmol^{-1}$)

(a) (i) Calculate the empirical formula of Y.

(ii) Determine the molecular mass of Y and write the possible structural formula of Y.

(b) Y burns with a yellow sooty flame, gives a yellow precipitate with 2,-dinitrophenylhydrazine but does not form silvery deposits with ammoniacal silver nitrate solution.

(i) Identify Y.

(ii) Write an equation and suggest a possible mechanism for the reaction between Y and 2,4-dinitrophenylhydrazine in acidic media

(c) Write equations indicating conditions to show how you would obtain phenylethyne from Y.

19. (a) An organic compound, Q, contains 54.55% carbon, 9.09% hydrogen and the rest being oxygen. The density of Q at 50°C and 2.0 atm pressure is 3.3185gdm^{-3}. Calculate the:

(i) Empirical formular of Q.

(ii) Molecular formular of Q.

(b) (i) Q forms a yellow precipitate with a solution of 2,4-dinitrophenylhrazine in ethanol and concentrated sulphuric acid . Identify Q and state its IUPAC name.

(ii) State what would be tobserved when Q is added to ammoniacal silver nitrate solution and the mixture warmed

(iii) Write an equation for the reaction that occurs in b(ii) above.

(c) Suggest a suitable mechanism for the reaction between Q and acidified hydroxylamine, H_2NOH.

20. When 7.5g of an organic compound Q was burnt completely in excess oxygen, 11.2dm^3 of carbon dioxide and 4.5g of water were formed at s.t.p.

(a) (i) Calculate the empirical formula of Q.

(ii) Determine the molecular formula of Q (Density of Q is 5.357gdm^{-3} at s.t.p).

(b) Q burns with a sooty flame and forms a yellow precipitate with Brady's reagent and also forms a pale yellow precipitate with iodine solution in sodium hydroxide solution. Identify Q.

(c) Write equation and suggest a mechanism for reaction between Q and:

(i) 2, 4-dinitrophenylhydrazine in acidic medium.

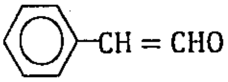
(ii) Sodium hydrogensulphite solution.

(d) Using equations only, show how Q:

(i) can be synthesized from benzaldehyde.

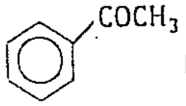
(ii) can be converted to alkene.

21. An organic compound, A has the structure



- (a) Name the functional groups present in A
- (b) Write equation for the reaction between A and:
  - (i) bromine in tetrachloromethane.
  - (ii) Saturated sodium hydrogensulphite solution.
- (c) State what would be observed in (b) (i) above.

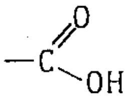
22. (a) Propanone and propanal undergo nucleophilic addition reactions.
  - (i) What is meant by a nucleophilic addition reaction?
  - (ii) Explain why carbonyl compounds undergo nucleophilic addition reactions.
- (b) Name:
  - (i) the functional group in propanone and propanal.
  - (ii) a reagent that can be used to identify the functional group in propanone and propanal. State what would be observed and write equation for the reaction that takes place.
  - (iii) a reagent that can be used to distinguish between propanone and propanal. State what is observed and write equation for the reaction.
- (c) Propanal was added to saturated solution of sodium hydrogen sulphite.
  - (i) State what was observed.
  - (ii) Outline an acceptable mechanism for the reaction.
- (d) Propanone was warmed with a mixture of iodine and sodium hydroxide solution.
  - (i) State what was observed
  - (ii) Write equation for the reaction.

23. (a) Write equation to show how each of the following compounds can be synthesized. In each case, indicate a mechanism for reaction.
  - (i)  from benzene.
  - (ii) $CH_3C = N - OH$ from propanone.
- (b) Name the reagent(s) that can be used to differentiate between the compounds in each of the following pairs. In each case, State what would be observed and write the equation(s) for the reaction if any when each member of the pairs is treated with the reagent(s) used.
  - (i) Phenol and cyclohexanol.
  - (ii) Ethanol and phenylmethanol.
- (c) Using equations while stating conditions for ah step, clearly show how bromopropane can be converted to phenol. 2-

Chapter 8

Carboxylic acids and derivatives

8.1 Introduction

Carboxylic acids are organic compounds with the carboxyl functional group, 

The carboxyl group is so called because it contains both a carbonyl and a hydroxyl group. The carboxyl group can also be written as $-COOH$ or $-CO_2H$. Carboxylic acids derived from alkanes are sometimes called ***alkanoic acids***.

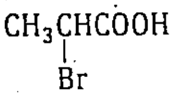
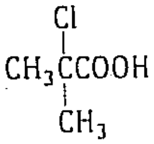
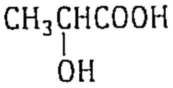
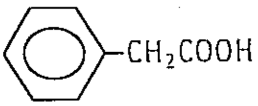
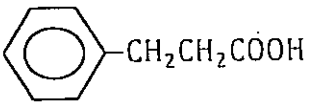
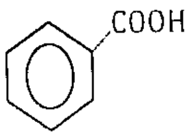
The saturated aliphatic monocarboxylic acids have the general molecular formula $C_nH_{2n+1}COOH$ or RCOOH, R being an alkyl group. Aromatic carboxylic acids have the carboxyl group attached directly to an aryl group.

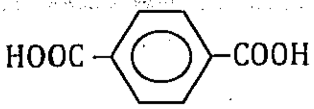
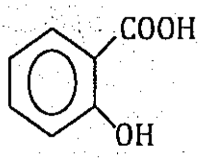
8.2 Nomenclature

The IUPAC nomenclature of monocarboxylic acids considers dropping the ending '**-e**' of the corresponding alkane and replacing it with the suffix '**-oic**' acid. In case of substituents, the carbon atom in the $-COOH$ group is always considered as carbon number 1 and the substituents given locants.

Aromatic carboxylic acids are named by adding the suffix '**-carboxylic acid**' to the name of the parent aromatic hydrocarbon. Alternatively, the suffix '**-oic acid**' can be used.

Examples

FORMULA	IUPAC NAME
$HCOOH$	Methanoic acid
CH_3COOH	Ethanoic acid
CH_3CH_2COOH	Propanoic acid
$CH_3CH_2CH_2COOH$	Butanoic acid
$(CH_3)_2CHCOOH$	2-Methylpropanoic acid
$(CH_3)_2CHCH_2COOH$	3-Methylbutanoic acid
$CH_2ClCOOH$	Chloroethanoic acid
$CHBr_2COOH$	2,2-Dibromoethanoic acid
CCl_3COOH	2,2,2-Trichloroethanoic acid
$CH_3CH = CHCOOH$	But-2-enoic acid
 $CH_3\underset{\mid\atop Br}{C}HCOOH$	2-Bromopropanoic acid
 $CH_3\overset{Cl\atop\mid}{\underset{\mid\atop CH_3}{C}}COOH$	2-Chloro-2-methylpropanoic acid
 $CH_3\underset{\mid\atop OH}{C}HCOOH$	2-Hydroxypropanoic acid
	2-Phenylethanoic acid
	3-Phenylpropanoic acid
	Benzenecarboxylic acid or Benzoic acid

	4-Methylbenzoic acid or 4-Methylbenzenecarboxylic acid
	Benzene-1,4-dicarboxylic acid
	2-Hydroxybenzoic acid or 2-Hydroxybenzenecarboxylic acid
 $\mathrm{COOH}-\mathrm{COOH}$	Ethanedioic acid
$HOOCCH_2COOH$	Propanedioic acid
$HOOCCH_2CH_2COOH$	Butanedioic acid
$HOOC(CH_2)_4COOH$	Hexane-1,6-dioic acid

8.3 Physical properties

(a) Physical state

All the simple aliphatic carboxylic acids with 1 – 10 carbon atoms are liquids at room temperature. Anhydrous ethanoic acid freezes below 17°C to form an ice-like solid called glacial ethanoic acid.

Aromatic carboxylic acids, for example, benzoic acid, 4-Methylbenzoic acid are crystalline solids.

(b) Solubility

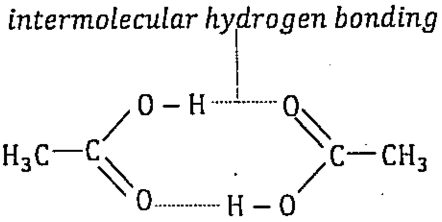
Low molecular weight aliphatic carboxylic acids (1-4 carbon atoms) are appreciably soluble in water. However, solubility decreases as the length of the carbon chain increases. The solubility in water is due to formation of **intermolecular hydrogen bonds** between the carboxylic acid and water molecules.

Benzoic acid is only slightly soluble in cold water but readily dissolves in hot water.

All carboxylic acids are soluble in organic solvents.

Note

The highly polar carboxylic acid molecules exist as dimers in liquid phase, vapour phase and also in solution with organic solvents like benzene and carbon tetrachloride as illustrated for ethanoic acid below.



Similarly, the molecular mass of methanoic acid or ethanoic acid obtained by elevation of boiling point method is usually twice the actual value, using benzene as the solvent.

Question

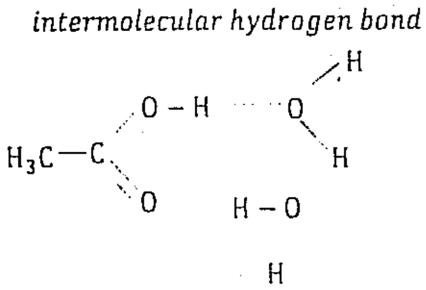
Explain why the molecular mass of ethanoic acid obtained by ebullioscopic method 120g using benzene as the solvent.

$$\text{Actual molecular mass of } CH_3COOH = 12 \times 2 + 1 \times 4 + 16 \times 2 = 60g$$

Therefore, the molecular mass of ethanoic acid obtained by boiling point elevation method is **twice the actual value**. This is because, in benzene, ethanoic acid molecules **associate through intermolecular hydrogen bonding to form dimers**. This reduces the **actual number of particles in solution** and **subsequently lowers the boiling point elevation to half the actual value**. As a result, the molecular mass calculated becomes **twice the actual value**.

However, in aqueous solution, the dimers dissociate to form monomers in order to form hydrogen bonds with water molecules.

Illustration



(c) Boiling points and melting points

Boiling points of carboxylic acids increase with increase in relative molecular mass.

Aromatic carboxylic acids have higher melting points than aliphatic ones of the same relative molecular mass.

Aliphatic monocarboxylic acids have higher boiling points than corresponding alcohols and carbonyl compounds.

Example

Ethanoic acid boils at 118°C whereas ethanol and ethanal boil at 78°C and 21°C respectively. Explain.

Both **ethanoic acid and ethanol molecules** associate through **intermolecular hydrogen bonds**. However, ethanoic acid forms **two hydrogen bonds per molecule,** forming **dimers** whereas ethanol forms **only one hydrogen bond per molecule.** As a result, **more energy is required to break the hydrogen bonds** in ethanoic acid than in ethanol.

Ethanal cannot form intermolecular hydrogen bonds between its molecules. Its molecules therefore interact through **weak Van der Waal's forces** of attraction that require a **lower amount of energy to break.**

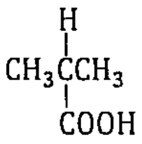
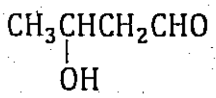
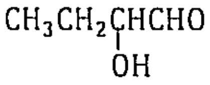
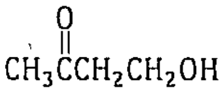
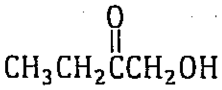
Note

Lower aliphatic carboxylic acids have sharp, pungent, penetrating odours.

8.4 Isomerism

Monocarboxylic acids can show **chain isomerism, position isomerism** and also exhibit **functional group isomerism** with esters and hydroxy-carbonyl compounds. Carboxylic acids can however be distinguished from isomeric esters and hydroxy-carbonyl compounds by chemical reactions in which the carboxyl group is involved. These will be seen later in this chapter.

The table below shows all isomers of the compound with molecular formula $C_4H_8O_2$.

Structure of isomer	**Name**
$CH_3CH_2CH_2COOH$	Butanoic acid
 $CH_3\overset{H}{\underset{COOH}{C}}CH_3$	2-methylpropanoic acid
$CH_3CH_2COOCH_3$	Methyl propanoate
$CH_3COOCH_2CH_3$	Ethyl ethanoate
 $CH_3\underset{OH}{C}HCH_2CHO$	3-Hydroxybutanal
 $CH_3CH_2\underset{OH}{C}HCHO$	2-Hydroxybutanal
$HOCH_2CH_2CH_2CHO$	4-Hydroxybutanal
 $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2OH$	4-hydroxybutanone
 $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2OH$	1-hydroxybutanone

8.5 Laboratory preparation of carboxylic acids

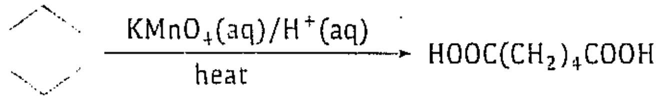
(a) From the reaction between alkenes and acidified potassium manganate(VII) solution.

A carboxylic acid or a mixture of carboxylic acids is formed.

Examples

$$CH_3CH = CHCH_3 \xrightarrow[\text{heat}]{KMnO_4(aq)/H^+(aq)} CH_3COOH$$

$$CH_3CH = CH_2 \xrightarrow[\text{heat}]{KMnO_4(aq)/H^+(aq)} CH_3COOH + HCOOH$$



$$\xrightarrow[\text{heat}]{KMnO_4(aq)/H^+(aq)} HOOC(CH_2)_4COOH$$

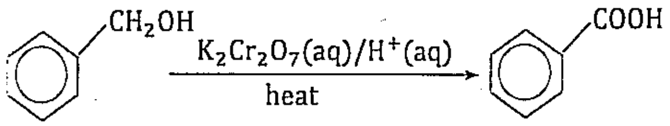
Note

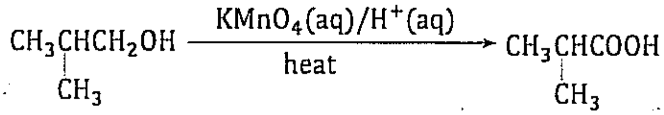
This reaction is not recommended for use in synthesis if a mixture of acids is formed.

(b) From primary alcohols

Primary alcohols are oxidized by excess acidified potassium dichromate(VI) solution to carboxylic acids. Acidified potassium manganate(VII) solution can similarly be used.

Examples





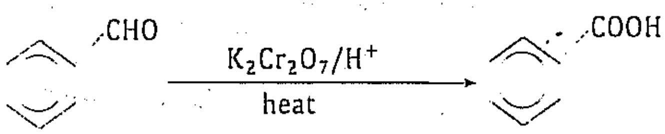
$$CH_3CH(CH_3)CH_2OH \xrightarrow[\text{heat}]{KMnO_4(aq)/H^+(aq)} CH_3CH(CH_3)COOH$$

Note

Check the topic on alcohols for details about general balanced equations and observations.

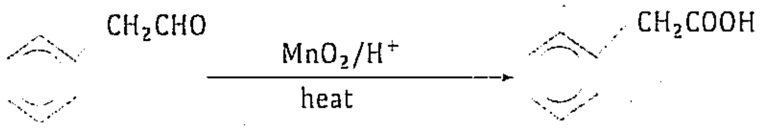
(c) From aldehydes

Carboxylic acids can be formed by oxidation of aldehydes using acidified potassium dichromate(VI) solution, potassium mamganate(VII) solution, acidified chromium(VI) oxide or acidified manganese(IV) oxide. For example



$$HOCH_2CH_2CH_2OH \xrightarrow[\text{heat}]{KMnO_4/H^+} HOOCCH_2COOH$$

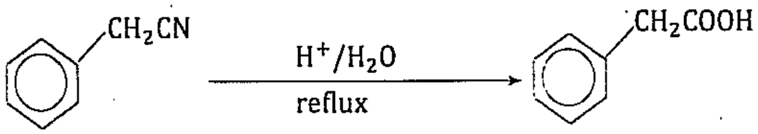
$$CH_3CHO \xrightarrow[\text{heat}]{CrO_3/H^+} CH_3COOH$$

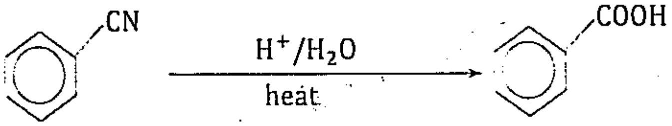


(d) Hydrolysis of nitriles

Nitriles are completely hydrolysed to carboxylic acids when boiled under reflux with an aqueous mineral acid.

$$CH_3CH_2CN \xrightarrow[\text{heat/reflux}]{H^+/H_2O} CH_3CH_2COOH$$





Note

Hydroxycarboxylic acids can be formed from cyanohydrins. Check cyanohydrin formation under the chapter on carbonyl compounds.

(e) From carbonation of Grignard reagents

Aliphatic carboxylic acids can be formed by bubbling carbon dioxide gas into a Grignard reagent followed by hydrolysis using a dilute acid.

For example

General reaction:

$$RMgBr \xrightarrow[\text{dry ether}]{CO_2(g)} RCOOMgBr \xrightarrow{H_2O/H^+} RCOOH$$

Or

$$RMgBr \xrightarrow[\text{2. } H_2O/H^+]{\text{1. } CO_2(g)\text{ /dry ether}} RCOOH$$

R can be primary, secondary or tertiary alkyl group.

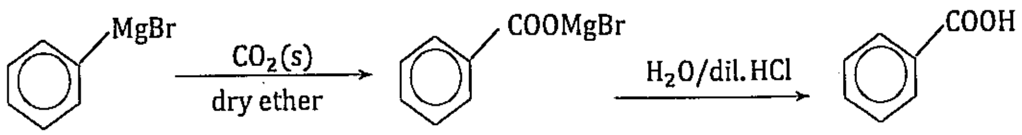
For example

$$CH_3CH_2Br \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2MgBr \xrightarrow[\text{2. } H_2O/H^+]{\text{1. } CO_2(g)} CH_3CH_2COOH$$

$$(CH_3)_3C-Cl \xrightarrow[\text{dry ether}]{Mg} (CH_3)_3CMgCl \xrightarrow[\text{2. } H_2O/H^+]{\text{1. } CO_2(g)} (CH_3)_3CCOOH$$

Note

For preparation of benzoic acid, solid carbon dioxide (dry ice) is used. It aids in cooling the reaction mixture.



(f) From acid amides

Amides are hydrolysed, on heating with a dilute mineral acid, to carboxylic acids. When an aqueous alkali is used, ammonia is evolved together with the carboxylate ions. When nitrous acid is used, nitrogen is evolved together with the carboxylic acid.

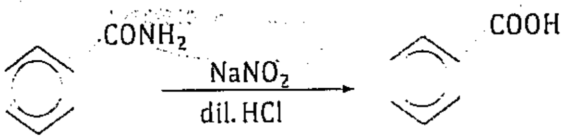
Generally,

$$\begin{tikzcd}
 & RCOOH + NH_4^+ & \\
RCONH_2 \arrow[ur, "H_2O/H^+", "heat"'] \arrow[r, "NaOH(aq)", "heat"'] \arrow[dr, "NaNO_2"', "dil.\ HCl"'] & RCO\bar{O}Na^+ \arrow[r, "dil.\ HCl"] & RCOOH + NH_3 \\
 & RCOOH + N_2 + H_2O &
\end{tikzcd}$$

Examples

$$CH_3CONH_2 \xrightarrow[heat]{H_2O/H^+} CH_3COOH$$

$$CH_3CH_2CONH_2 \xrightarrow[heat]{NaOH(aq)} CH_3CH_2CO\bar{O}Na^+ \xrightarrow{dil.\ HCl} CH_3CH_2COOH$$

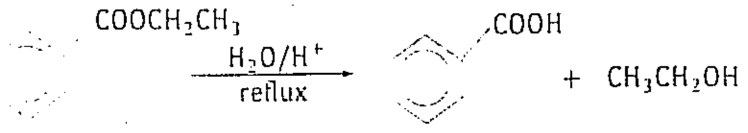


(g) From hydrolysis of esters

The esters can be boiled under reflux with concentrated aqueous sodium hydroxide solution to form a carboxylate salt and an alcohol. The carboxylate salt is then acidified to the carboxylic acid. Acid hydrolysis is also possible.

Examples

$$\begin{tikzcd}
CH_3COOCH_2CH_3 \arrow[r, "NaOH(aq)", "heat"'] & CH_3CO\bar{O}Na^+ \arrow[d, "dil.\ HCl"] + CH_3CH_2OH \\
 & CH_3COOH
\end{tikzcd}$$



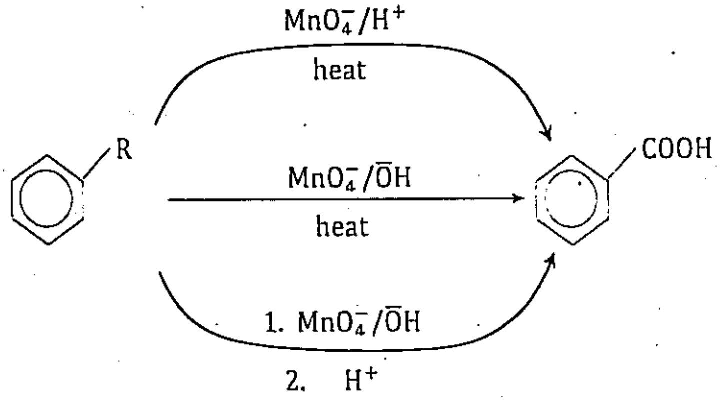
Note

For mechanisms, check under the chapter on esters.

(h) Synthesis of benzoic acid

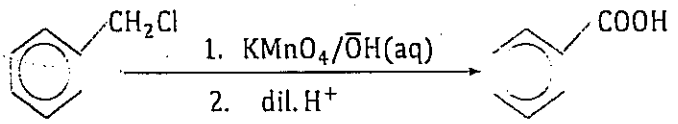
Benzoic acid can be synthesized by the methods in (b), (c), (d), (e) and (f) above. However, more specific ones are shown below:

(1) From alkylbenzene

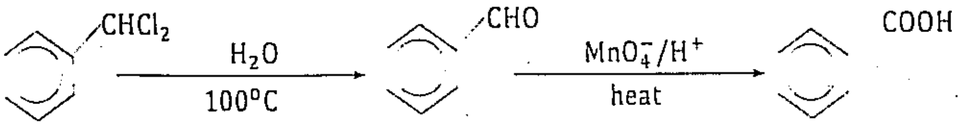


Where R is any alkyl group other than $-C(CH_3)_3$.

(2) From chloromethylbenzene



(3) From dichloromethylbenzene



8.6 Chemical properties

8.6.1 Acidic behaviour

Carboxylic acids are weak acids. They are only partially ionized in aqueous solution.

$$RCOOH(aq) + H_2O(l) \rightleftharpoons RCOO^-(aq) + H_3O^+(aq)$$

They are much weaker than common mineral acids but stronger acids than alcohols. Like the common mineral acids, carboxylic acids:

- turn blue litmus paper red.
- react with alkalis to from a salt and water.
- liberate carbon dioxide from carbonates and hydrogen carbonates.

- react with highly electropositive metals to form hydrogen gas.

Every carboxylic acid has its own Ka (acid dissociation constant) value which indicates its acid strength. The **larger the Ka value,** the **greater the degree of ionization** and the **stronger an acid it is.**

The nature of the groups attached to the carboxyl group has a great effect on the acid strength due to **inductive effect. Electron-withdrawing groups** such as $-F$, $-Cl$, $-Br$ and $-I$ have **negative inductive effect.** They make carboxylic acids **stronger by making the oxygen-hydrogen bond more polar** and **weaker** hence **release of hydrogen ions in solution becomes easier. Electron donating groups such as alkyl groups have a positive inductive effect.** They make carboxylic acids **weaker** by making the **oxygen-hydrogen bond less polar** and **stronger** hence **release of hydrogen ions in solution becomes harder** and few are released in aqueous solution.

Examples

1. *The table below shows acid dissociation constants, Ka, for some acids at a particular temperature.*

Acid	HCOOH	CH_3COOH	CH_3CH_2COOH
Ka(moldm^{-3})	1.77×10^{-4}	1.70×10^{-5}	1.30×10^{-5}

State and explain the trend in strength of the acids.

Acid strength **decreases** in the order **$HCOOH > CH_3COOH > CH_3CH_2COOH$.**

The strength of an acid **depends on how easily it dissociates to release protons in aqueous solution.** The **higher the Ka,** the **greater is the degree of dissociation** of the acid and the **higher is its strength.**

HCOOH is the **strongest** of the acids because the **hydrogen** atom attached to the carboxyl group has **no inductive effect** hence the **oxygen-hydrogen bond** in it is the **weakest, easily breaks to release many hydrogen ions** in aqueous solution.

CH_3COOH and CH_3CH_2COOH have **electron donating alkyl groups** (methyl group and ethyl group respectively) attached to the carboxyl group, **decreasing the polarity of the oxygen-hydrogen bond,** making it **stronger.** Therefore, **fewer hydrogen ions** are released in aqueous solution. However, ethyl group has a higher positive inductive effect than methyl, therefore **fewer hydrogen ions** are released by CH_3CH_2COOH in solution than CH_3COOH. Hence, CH_3COOH is stronger acid than CH_3CH_2COOH.

2. *The table below shows acid dissociation constants, Ka, for some acids at a particular temperature.*

Acid	CH_3COOH	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH
Ka(moldm⁻³)	1.70×10^{-5}	1.40×10^{-3}	5.10×10^{-3}	2.20×10^{-1}

State and explain the trend in strength of the acids.

Acid strength **increases** in the order $CH_3COOH < CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$.

The **strength of an acid depends on how easily it releases protons in aqueous solution.**

CH_3COOH is the **weakest acid** because the methyl group attached to the carboxyl group has **positive inductive effect** hence the oxygen – hydrogen bond in it has the **lowest polarity** making it the **strongest** and **does not easily release protons.**

The chlorine atom is **more electronegative** than the carbon atom. The **increase in number of chlorine atoms** from chloroethanoic acid through dichloroethanoic acid to trichloroethanoic acid **increases the negative inductive effect** and **polarity of the oxygen-hydrogen bond** in the same order. The oxygen-hydrogen bonds become **increasingly weaker** and **easier to break** in order to **release hydrogen ions** in aqueous solution.

8.6.2 Reactions of carboxylic acids

A carboxylic acid can undergo reactions involving removal of a proton (H of the −OH group) or reactions involving the entire – OH group or reactions involving the carboxyl group as a whole. The acids can also undergo reactions involving the alkyl or aryl group.

(a) Reactions involving removal of a proton

(i) Reactions with strongly electropositive metals

Carboxylic acids react with strongly electropositive metals such as sodium, potassium, magnesium and zinc to form bubbles of a colourless gas (hydrogen) and corresponding salts.

Examples

$$HCOOH + Na \longrightarrow HCOONa + \tfrac{1}{2}H_2$$

$$CH_3COOH + K \longrightarrow CH_3COOK + \tfrac{1}{2}H_2$$

$$2CH_3CH_2COOH + Mg \longrightarrow (CH_3CH_2COO)_2Mg + H_2$$

(ii) Reactions with alkalis

Carboxylic acids neutralize hydroxides to form corresponding salts and water.

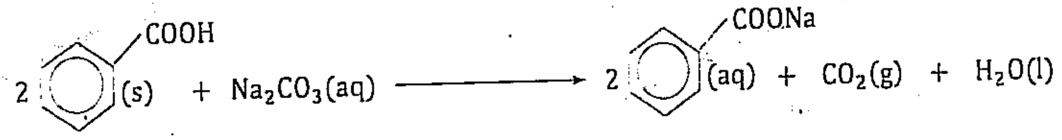
$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$

$$HOOCCH_2COOH(aq) + 2NaOH(aq) \longrightarrow NaOOCCH_2COONa(aq) + 2H_2O(l)$$

(iii) Reaction with carbonates and hydrogen carbonates

Carboxylic acids react with carbonates and hydrogen carbonates to liberate carbon dioxide gas.

$$CH_3COOH(aq) + NaHCO_3(aq) \longrightarrow CH_3COONa(aq) + CO_2(g) + H_2O(l)$$



Note

- *The reaction with carbonates and hydrogen carbonates is a confirmatory test for carboxylic acids.*
- *For each reaction in (i), (ii), and (iii) above, the carboxylic acids can be regenerated by reacting the salts with a dilute mineral acid. For example:*

$$CH_3COONa(aq) + HCl(aq) \longrightarrow CH_3COOH(aq) + NaCl(aq)$$

- *When treating solid carboxylic acids (aromatic ones), aqueous sodium carbonate or aqueous sodium hydrogen carbonate is used.*
- *Sodium carbonate or sodium hydrogen carbonate can be used to distinguish carboxylic acids from other organic compounds.*
- *The reaction with aqueous sodium carbonate distinguishes carboxylic acids from phenols.*

(iv) Reaction with neutral Iron(III) chloride solution

Aliphatic carboxylic acids react with neutral Iron(III) chloride solution to form a red colouration. For example, ethanoic acid forms Iron(III) ethanoate which is a soluble compound.

$$3CH_3COOH(aq) + FeCl_3(aq) \longrightarrow (CH_3COO)_3Fe(aq) + HCl(aq)$$

However, on warming, the Iron(III) ethanoate undergoes hydrolysis to form ethanoic acid and hydroxide ions which reach with Iron(III) ions to form insoluble Iron(III) hydroxide, a brown precipitate.

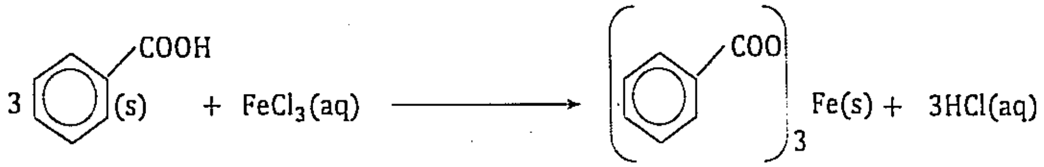
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$$

The general observation and equation therefore are:

Red colouration forms a **brown precipitate on heating.**

$$Fe^{3+}(aq) + 3CH_3COO^-(aq) + 3H_2O(l) \longrightarrow Fe(OH)_3(s) + 3CH_3COOH(aq)$$

Aromatic carboxylic acids form a **reddish brown precipitate** with **neutral Iron(III) chloride solution.** For example, benzoic acid forms **insoluble Iron(III) benzoate.**



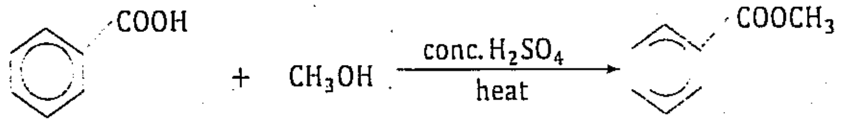
(b) Reactions involving the −OH group.

(i) Esterification

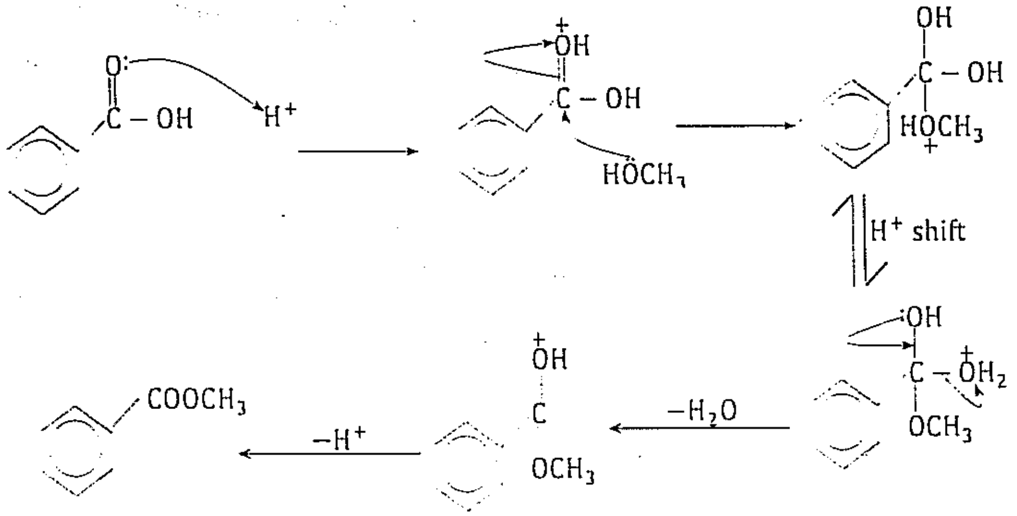
Carboxylic acids react with alcohols in presence of concentrated sulphuric acid to form esters.

Examples

$$HCOOH + CH_3CH_2OH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} HCOOCH_2CH_3$$



Mechanism

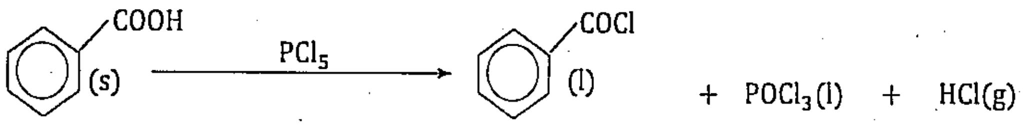


Note

For details of these reactions check the chapter on esters.

(ii) Reaction with phosphorus pentachloride

Carboxylic acids react with phosphorus(V) chloride to form acylchlorides. Similarly, phosphorus(III) chloride or thionyl chloride can be used.



$$CH_3CH_2COOH(l) \xrightarrow{SOCl_2} CH_3CH_2COCl(l) + SO_2(g) + HCl(g)$$

Note

- Thionyl chloride ($SOCl_2$) is preferred because the gaseous products easily escape.
- **Misty fumes are observed in each case.**
- Similar reactions occur with phosphorus bromides.

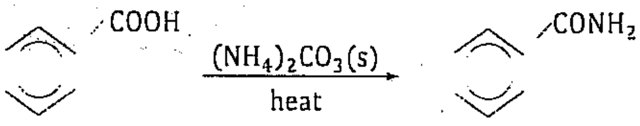
$$CH_3CH_2COOH \xrightarrow[\text{or Red P }/Br_2]{PBr_5} CH_3CH_2COBr + POBr_3 + HBr$$

(iii) Amide formation

Carboxylic acids react with ammonium carbonate in presence of an excess of the free acid when heated to 100 – 200°C to form amides.

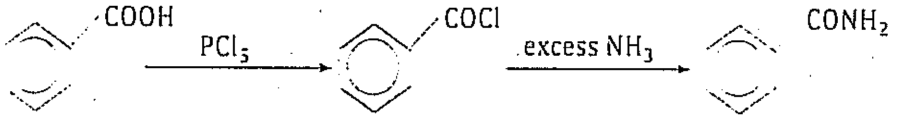
$$CH_3COOH \xrightarrow[\text{heat}]{(NH_4)_2CO_3(s)} CH_3CONH_2$$

Ethanamide



Benzanamide

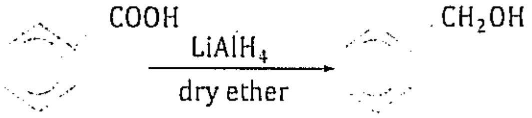
Similarly, amides can be formed from carboxylic acids via acylchorides. The acylchlorides are reacted with ammonia.



$$CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl \xrightarrow{\text{excess }NH_3} CH_3CH_2CONH_2$$

(iv) Reduction

Carboxylic acids are reduced to primary alcohols by lithium tetrahydridoaluminate.



$$CH_3CH_2COOH \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2CH_2OH$$

(c) Reactions involving the carboxyl group as a whole

(i) Decarboxylation

Discussed under section 3.1.6(d) and 4.4(ii).

(d) Reactions involving the alkyl or aryl group

The C – H bond in the alkyl group attached to the carboxyl group is converted to a C – Cl bond when chlorine gas is bubbled into the hot acid in presence of ultraviolet light, in the same way as occurs in alkanes. The aryl group in aromatic carboxylic acids may also undergo reactions similar to those occurring in benzene.

$$(CH_3)_2CHCOOH \xrightarrow[\text{heat}]{Cl_2/u.v.} (CH_3)_2CClCOOH + HCl$$

$$CH_3COOH \xrightarrow[\text{heat}]{Cl_2/u.v.} CH_2ClCOOH + HCl$$

$$CH_2ClCOOH \xrightarrow[\text{heat}]{Cl_2/u.v.} CHCl_2COOH + HCl$$

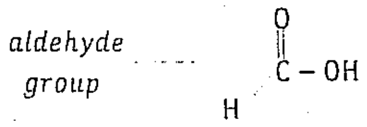
$$CHCl_2COOH \xrightarrow[\text{heat}]{Cl_2/u.v.} CCl_3COOH + HCl$$

8.6.3 Identification of the functional group

The carboxyl group can be identified by adding **solid sodium hydrogen carbonate** to an **aqueous solution of the carboxylic acid**. **Bubbles of a colourless gas** which turns lime water milky are evolved. **Sodium carbonate solution** can also be used.
For **solid carboxylic acids** at room temperature, **aqueous sodium hydrogen carbonate** or **sodium carbonate solution** can be used.

8.6.4 Uniqueness of methanoic acid

Monocarboxylic acids are resistant to oxidation. However, methanoic acid can be oxidized by Tollen's reagent, Fehling's solution or Benedict's solution, acidified **potassium manganite(VII)** solution and **acidified potassium dichromate(VI)** solution. This is due to the presence of an **aldehyde group** that **can be oxidized**.



$$H-\overset{\overset{O}{\|}}{C}-OH$$

Examples

(i) Methanoic acid forms a silver mirror with Tollen's reagent (Ammonical silver nitrate solution) **on warming** whereas ethanoic acid gives no observable change.

This is because methanoic acid has an **aldehyde group** which makes it a **reducing agent.** It reduces **diamminesilver(I) ions** to **silver metal** and is itself **oxidized** to **carbon dioxide.**

Equation

$$HCOOH(aq) + 2Ag(NH_3)_2^+(aq) + 2\bar{O}H(aq) \longrightarrow 2Ag(s) + 2H_2O(l) + CO_2(g) + 4NH_3(g)$$

Or

$$HCOOH(aq) + 2Ag^+(aq) + 2\bar{O}H(aq) \longrightarrow 2Ag(s) + 2H_2O(l) + CO_2(g)$$

(ii) Using Fehling' s or Benedict's solution

The **copper(II) ions** in the solution are reduced to **copper(I) oxide.**

Observation: **Reddish-brown precipitate formed on warming.**

Equation

$$HCOOH(aq) + 2Cu^{2+}(aq) + 4\bar{O}H(aq) \longrightarrow Cu_2O(s) + H_2O(l) + CO_2(g)$$

(iii) Using acidified potassium manganite(VII) solution

Observation: **Purple solution turns colourless on heating.**

Half equations

$$5HCOOH(aq) \longrightarrow 5CO_2(g) + 10H^+(aq) + 10e$$

$$2MnO_4^{2-}(aq) + 16H^+(aq) + 10e \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

General equation

$$5HCOOH(aq) + 6H^+(aq) + 2MnO_4^-(aq) \longrightarrow 5CO_2(g) + 8H_2O(l) + 2Mn^{2+}(aq)$$

(iv) Using acidified potassium dichromate(VI) solution

Observation: **Orange solution turns green on heating.**

Half equations

$$3HCOOH(aq) \longrightarrow 3CO_2(g) + 6H^+(aq) + 6e$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

General equation

$$3HCOOH(aq) + 8H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 3CO_2(g) + 7H_2O(l) + 2Cr^{3+}(aq)$$

Note

The four reagents above can therefore be used to distinguish methanoic acid from the other carboxylic acids.

Heating/warming is required for each of the reagents.

Sodium methanoate (HCOONa) can give similar observations.

Oxalic acid/Ethanedioic acid/ethanedioate ions or sodium ethanedioate give a positive test with the last two reagents.

8.7 Derivatives of carboxylic acids

When the hydroxyl group of a carboxylic acid is replaced with Cl, Br, I, NH_2 or OR, the classes formed are called acid derivatives.

We shall summarize the chemistry of these derivatives and how they are interconverted to other compounds but we shall not demystify all details of their chemistry as this is above the scope of coverage of Advanced Level chemistry.

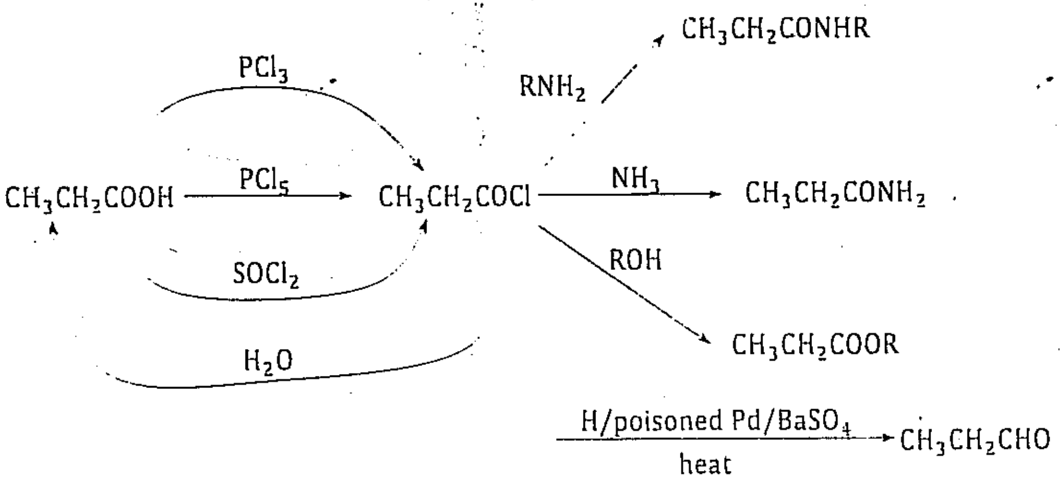
8.7.1 Acid halides

These have the general formula RCOX, where X is F, Cl, Br or I.

Examples include

CH_3COCl	Ethanoyl chloride
CH_3CH_2COBr	Propanoyl bromide
C_6H_5COCl	Benzoyl chloride

The preparation and chemical reactions of acid halides are summarized using the scheme below, using propanoyl chloride as a example.



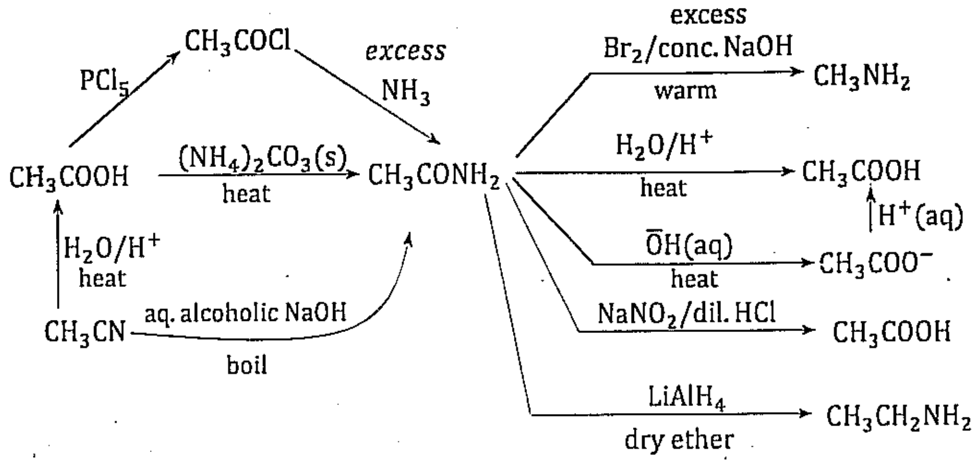
8.7.2 Acid amides

Primary amides have the general formula $RCONH_2$, where R is alkyl or aryl group.

Examples include

$HCONH_2$	Methanamide
CH_3CONH_2	Ethanamide
$CH_3CH_2CONH_2$	Propanamide
$C_6H_5CONH_2$	Benzamide/Benzenecarboxyamide.

The preparation and chemical reactions of amides are summarized in the scheme below using ethanamide as an example.



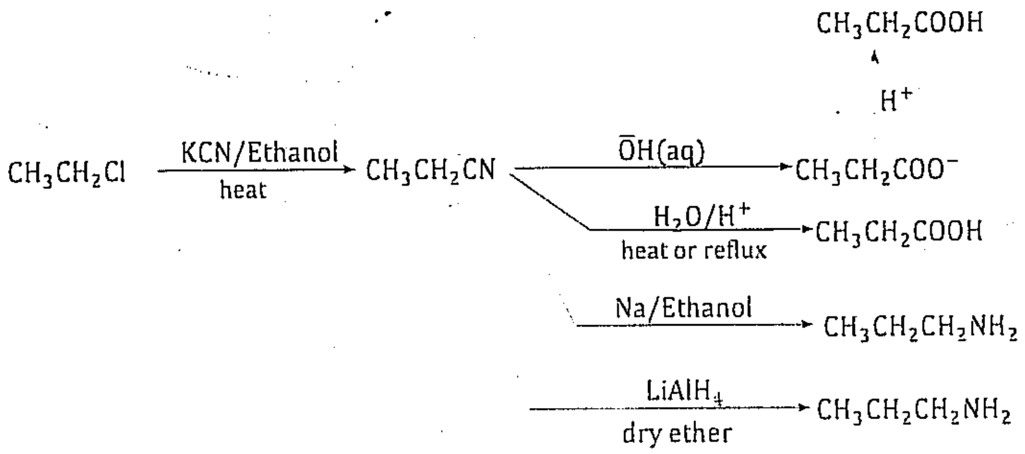
8.7.3 Acid nitriles

These have a general formula RCN, where R can be an alkyl or aryl group.

Examples include

CH_3CN	Ethanenitrile
CH_3CH_2CN	Propanenitrile
C_6H_5CN	Benzonitrile

The preparation and chemical reactions of nitriles are summarized in the scheme below using ethanenitrile as an example.

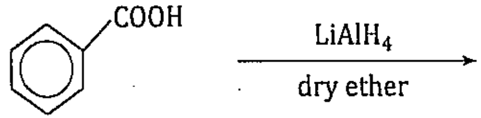


8.7.4 Esters

Check Chapter 9.

8.8 End of topic assessment exercise

1. Complete the following equations and name the main organic product.

(i) 

(ii) $CH_3CH_2CH_2CO\bar{O}Na^+ \xrightarrow[\text{heat}]{CaO}$

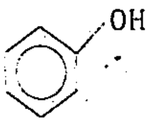
2. An organic compound, Q, has the structure, $RCH = CHCH_2COOH$. Name the functional groups in Q and, for each functional group, name the reagent used to identify it. In each case, state the observation made and write equation for the reaction that takes place.

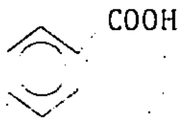
3. Name one reagent that can be used to distinguish the following pairs of compounds. In each case, state what would be observed.

(a) $CH_3CH_2CH_2COOH$ and $CH_3CH_2COOCH_3$

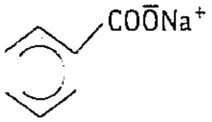
(b) $HCOOH$ and CH_3COOH

(c) $HCO\bar{O}Na^+$ and $CH_3CO\bar{O}Na^+$

(d) 

and 

(e) $HCO\bar{O}$ and $CH_3CO\bar{O}$

(f) 

and $CH_3CO\bar{O}Na$

(g) $H_2C_2O_4$ and $HCOOH$

(h) $CH_3CO\bar{O}$ and $C_2O_4^{2-}$

4. Using equations only, show how the following conversions can be effected.

(a) Propanone from propanoic acid.

(b) 2-hydroxypropanoic acid to but-2-ene.

(c) Methylbenzene to methyl benzoate.

(d) CH_3CH_2COOH fromethanoic acid.

(e) CH_3CH_2I to CH_3CH_2COOH.

(f) $CH_3CH_2CH_2OH$ to CH_3COOH.

(g) CH_3CH_2COOH from ethene.

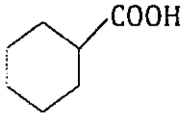
(h) Methylbenzene to benzamide.

(i) CHCOOH from propan-1-ol.

(j) $CH_3CH_2CH_2OH$ to $CH_3CH_2CH_2COOH$.

5. Complete the following equations and write a mechanism for the reaction.

(i) $CH_3COOH + CH_3CH_2OH \xrightarrow[\text{reflux}]{\text{dry HCl}}$

(ii)  $+\ CH_3CH_2OH \xrightarrow[\text{heat}]{H^+}$

6. An organic compound, W, consists of 48.6% carbon, 8.1% hydrogen and the rest being oxygen.

(a) Determine the empirical formula of W.

(b) 0.453g of a vaporized sample of W occupied 200cm^3 at 100^{0}C and 95.0kPa. Deduce the molecular formula of W.

(c) W reacts with magnesium metal with evolution of a gas. Write:

(i) the structural formula of W.

(iii) equation of the reaction between W and magnesium metal.

7. (a) When 6.1g of an organic compound, D, was burnt completely in oxygen, 15.4g of carbon dioxide and 2.7g of water were formed. 0.252g of D when vaporized at 273^{0}C and 2.25atm form 43.04cm^3 of vapour.

(i) Calculate the empirical formula of D.

(ii) Determine the molecular formula of D.

(b) D burns with a sooty flame. Identify D.

(c) When D was treated with an ethereal solution of lithium tetrahydridoaluminate(III), compound E was formed. When E was warmed with an acidified solution of chromium trioxide, compound G was formed.

(i) Identify E and G.

(ii) Write equation leading to formation of E and G.

(d) Write equation and suggest a mechanism for the reaction between:

(i) E and propanoyl chloride.

(ii) G and Brady's reagent.

(e) Without using equations, describe how D can be synthesized from benzene.

8. Explain the following observations:
   (a) When methanoic acid was warmed with Fehling's solution, a red precipitate was formed whereas with ethanoic acid, there was no observable change.
   (b) Sodium methanoate solution forms a silver mirror with Tollen's reagent while ethanoic acid gives no observable change.

9. State what would be observed and write equation for the reaction when:
   (a) neutral iron(III) chloride solution is added to 1cm^3 of propanoic acid.
   (b) a mixture of acidified potassium manganate(VII) and sodium ethanedioate is heated.
   (c) benzoic acid is added, to a saturated solution of sodium hydrogen carbonate.

10. A compound, J, containing 12.8% carbon, 2.2% hydrogen, the rest being bromine is hydrolysed by aqueous potassium hydroxide to form compound L. L is oxidized in several stages by nitric acid, the final product being a carboxylic acid, M, of relative molecular mass 90. On warming, M, decolorizes an acidified solution of potassium manganate(VII).
    (a) Calculate the empirical formula of J.
    (b) Identify compounds L and M.
    (c) Write the equation for the reaction of M with acidified potassium manganate (VII).
    (d) Write the structural formula of a compound isomeric with J.

11. An organic compound, Q, contains 22.8% nitrogen, 28% oxygen, 8.5% hydrogen and the rest being carbon.
    (a) Calculate the empirical formula of Q.
    (b) 0.5g of Q dissolved in 80g of water forming a solution that freezes at -0.197^{0}C. Calculate the molecular formula of Q.
    (Cryoscopic constant for water is 1.86^{0}C per 1000g of water)
    (c) When Q was refluxed with potassium hydroxide, ethanoic acid and ammonia were formed.
        (i) Identify Q.
        (ii) Write equations to show how Q can be obtained from a carbonyl compound.

12. 0.5g of compound, R, at a pressure of 209.94kPa when vapourised at 127^{0}C occupied a volume of 90cm^3.
    - (a) (i) Calculate the relative molecular mass of R.
        - (ii) The empirical formula of R is C_2H_4O. Determine the molecular formula of R.
        - (iii) Write the structures of possible isomers of R.
    - (b) When heated with methanol and a little sulphuric acid, compound R formed a sweet smelling substance T and when reacted with phosphorus pentachloride, R, gave white fumes and another organic substance, W, formed. Identify R, T and W.

13. (a) When 2.3g of a compound, X, containing carbon, oxygen and hydrogen was burnt in excess air, it produced 2.2g of carbon dioxide and 0.9g of water. Calculate the empirical formula of X.
    - (b) The density of X is 2.0536gl^{-1}. Determine the molecular formula of X.
    - (c) X dissolves in sodium hydrogen carbonate solution with effervescence. Write the structural formula of X.
    - (d) State what would be observed and write equation for the reaction that would take place when a solution of X is treated with:
        - (i) acidified potassium manganate(VII) solution.
        - (ii) Fehling's solution.

14. Without using equations, describe how the following conversions can be effected.
    - (a) Bromobenzene to benzoic acid.
    - (b) Propanoic acid to ethylamine.
    - (c) Ethanoic acid to propanone.
    - (d) Ethylamine from ethanoic acid.
    - (e) Ethanoylchloride from ethene.
    - (f) Methylamine from ethanoic acid.
    - (g) Ethanoic acid from methanol.
    - (h) Butanoic acid from propene.

15. When 0.0291g of an organic compound, Y, containing carbon, hydrogen and oxygen only was burnt in excess oxygen, 0.0581g of carbon dioxide and 0.023g of water were formed.
    - (a) Calculate the empirical formula of Y.

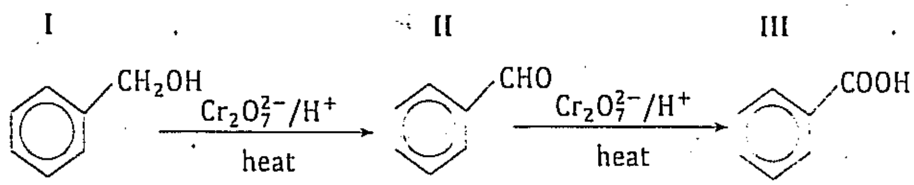
(b) 0.41g of Y when vapourised at 20°C and 740mmHg occupied 39.5cm^3. Determine

- (i) the molecular mass of Y.
- (ii) the molecular formula of Y.

(c) When a saturated solution of sodium hydrogen carbonate was added to Y, effervescence of a colourless gas occurred.

- (i) Write the structural formula of Y.
- (ii) Write equations to show how Y can be converted to 1-aminopropane.

16. Benzyl alcohol can be converted to benzoic acid as shown.



Suggest a test that you would carry out to demonstrate the functional group and state what would be observed on carrying out the test.

- (i) for compound I.
- (ii) for compound II.
- (iii) for compound III.

17. (a) A solid organic compound, Z, contains 41.379% by mass of carbon, 3.448% hydrogen and the rest being oxygen.

- (i) Calculate the empirical formula of Z.
- (ii) Determine the molecular formula of Z (RFM of Z = 116).

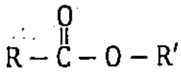
(b) Z reacts with sodium carbonate solution evolving bubbles of a colourless gas and it decolourizes liquid bromine.

- (i) Identify Z by its structural formula and IUPAC name.
- (ii) Write equation for the reaction between Z and liquid bromine.

Chapter 9

Esters

Esters are naturally abundant and contribute to flavours and aromas in many fruits and flowers. They also make up the bulk of animal fats and vegetable oils. Esters have the general formula:

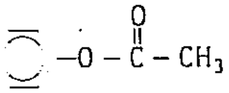
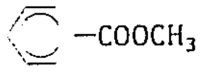
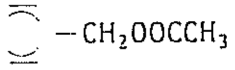
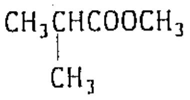
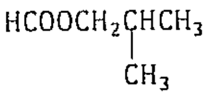


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

Where R and R^1 may be alkyl or aryl groups and may be the same or different.

9.1 Nomenclature of Esters

Esters are named using the IUPAC system by taking the parent name of the carboxylic acid and replacing the ending "-ic" with the suffix "-ate" and preceding this with the name of the alkyl or aryl group of the appropriate alcohol or phenol.

Formula of ester	*IUPAC name*
$HCOOCH_3$	Methyl methanoate
$CH_3COOCH_2CH_3$	Ethyl ethanoate
$CH_3CH_2COOCH_2CH_2CH_3$	Propyl propanoate
$HCOOCH_2CH_3$	Ethyl methanoate
CH_3COOCH_3	Methyl ethanoate
	Phenyl ethanoate
	Methyl benzoate
	Benzyl ethanoate
$CH_3CH_2COOCH_2CH_3$	Ethyl propanoate
 $\underset{\displaystyle CH_3}{CH_3\underset{\mid}{C}HCOOCH_3}$	Methyl 2-methylpropanoate
 $HCOOCH_2\underset{\displaystyle CH_3}{\underset{\mid}{C}H}CH_3$	2-Methylpropyl methanoate

9.2 Physical Properties

(a) Smell

Simple esters are colourless liquids with pleasant fruity smells.

(b) Solubility

Methylmethanoate ($HCOOCH_3$) is very soluble in water. There is a rapidly decreasing solubility in water as relative molecular mass of the esters increases.

Esters of aromatic carboxylic acids are insoluble in water. However, esters are soluble in organic solvents.

(c) Melting points and boiling points

The melting points and boiling points are below those of corresponding carboxylic acids.

For example;

Methylmethanoate has boiling point 32°C whereas methanoic acid boils at 101°C. Ethylethanoate has boiling point 77°C whereas ethanoic acid boils at 118°C. This is because carboxylic acids associate through intermolecular hydrogen bonding but ester molecules cannot associate through hydrogen bonding.

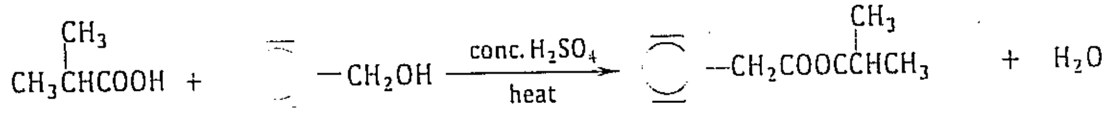
9.3 Laboratory preparation

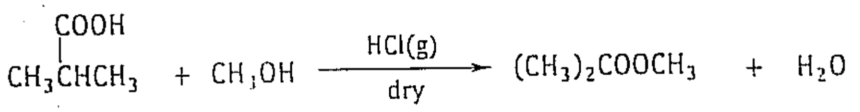
(a) From alcohols

Alcohols react with carboxylic acids in the presence of 5% concentrated sulphuric acid as a catalyst or by bubbling gaseous hydrogen chloride through the reaction mixture.

Examples:

$$CH_3CH_2OH + CH_3COOH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} CH_3COOCH_2CH_3 + H_2O$$



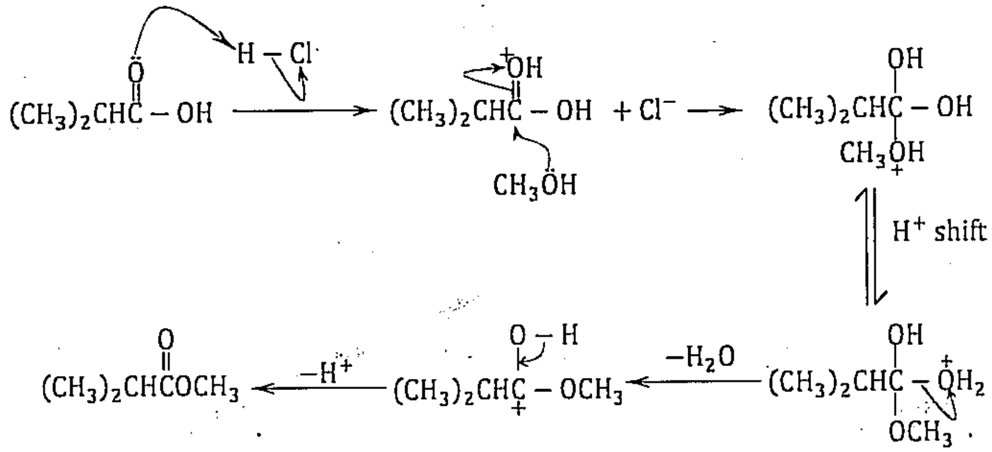


$$CH_3\underset{}{\overset{COOH}{\overset{|}{C}}}HCH_3 + CH_3OH \xrightarrow[\text{dry}]{HCl(g)} (CH_3)_2COOCH_3 + H_2O$$

$$HCOOH + CH_3CH_2OH \xrightarrow{\text{dry HCl}} HCOOCH_2CH_3 + H_2O$$

Mechanism: (The third reaction is considered)

$$(CH_3)_2CHCOOH + CH_3OH \xrightarrow[\text{dry}]{HCl(g)} (CH_3)_2CHCOOCH_3 + H_2O$$



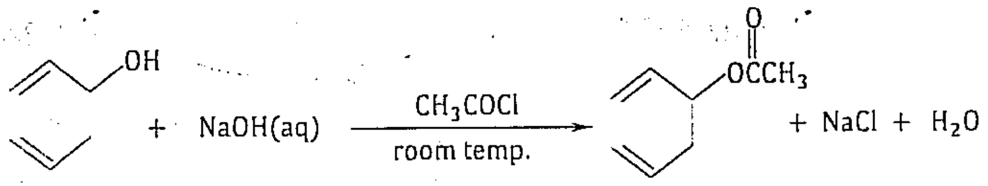
$$H^+ + Cl^- \longrightarrow HCl$$

(b) From Phenol

Esters formed from phenol are phenyl alkanoates. Unlike alcohols, phenol does not esterify with acids but in presence of an alkaline solution, it reacts with acid halides to form esters.

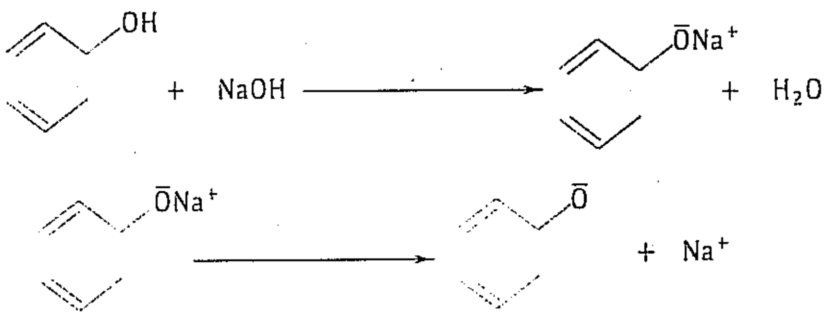
Examples

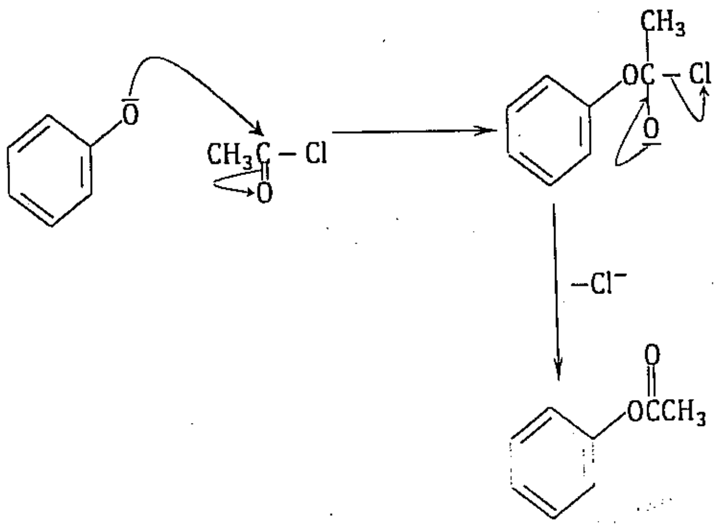
(i)



Phenylethanoate

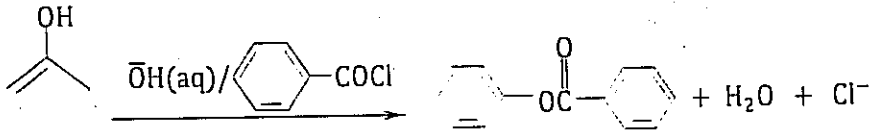
Mechanism





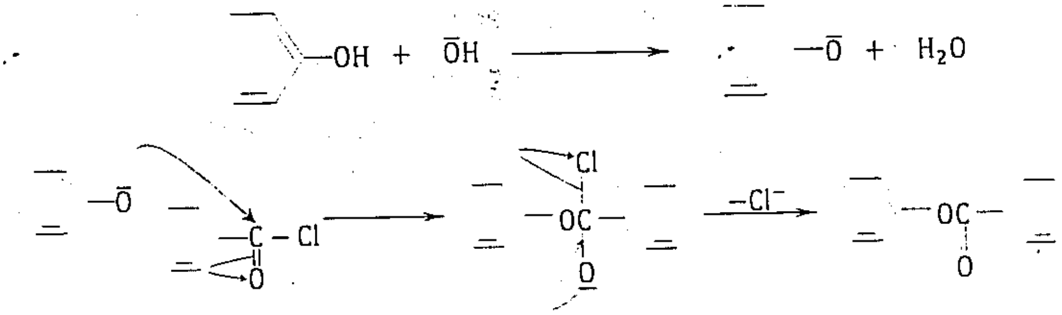
$$H^+ \quad + \quad Cl^- \longrightarrow HCl$$

(ii)



Phenylbenzoate

Mechanism

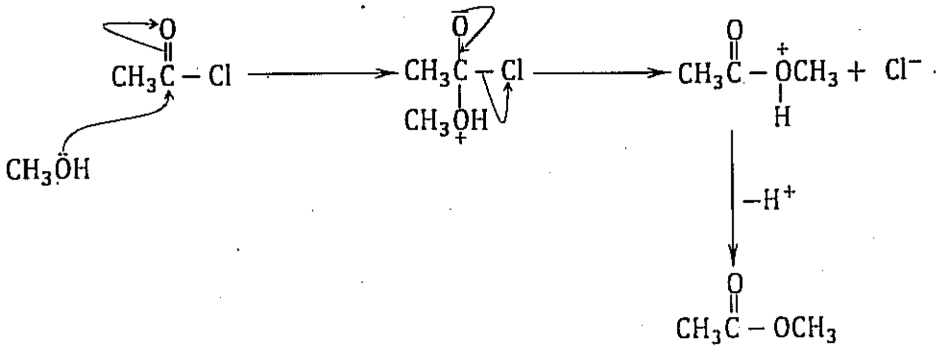


(c) From alcohols and acid chlorides

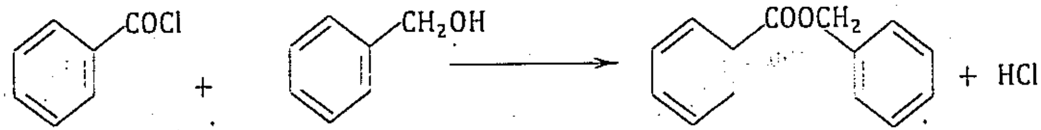
Acid halides react with alcohols to form esters.

(i) $CH_3COCl \quad + \ CH_3OH \longrightarrow CH_3COOCH_3 \quad + \ HCl$

Mechanism



$$H^+ + Cl^- \longrightarrow HCl$$

(ii) 

(d) From silver salts of carboxylic acids

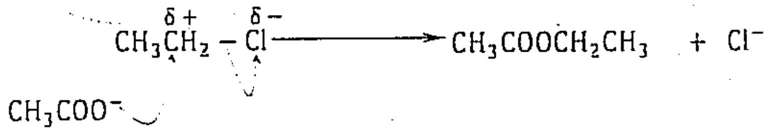
The silver salts of carboxylic acids react on heating with alkylhalides to form esters.

Example

$$CH_3COOAg + CH_3CH_2Cl \xrightarrow{heat} CH_3COOCH_2CH_3 + AgCl$$

<u>Mechanism</u>

$$CH_3COOAg \longrightarrow CH_3COO^- + Ag^+$$



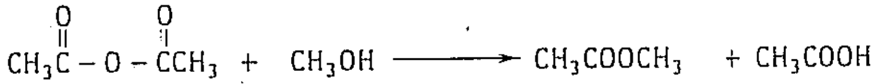
$$\overset{\delta+}{CH_3CH_2}-\overset{\delta-}{Cl} \longrightarrow CH_3COOCH_2CH_3 + Cl^-$$

$$CH_3COO^-$$

$$Ag^+ + Cl^- \longrightarrow AgCl$$

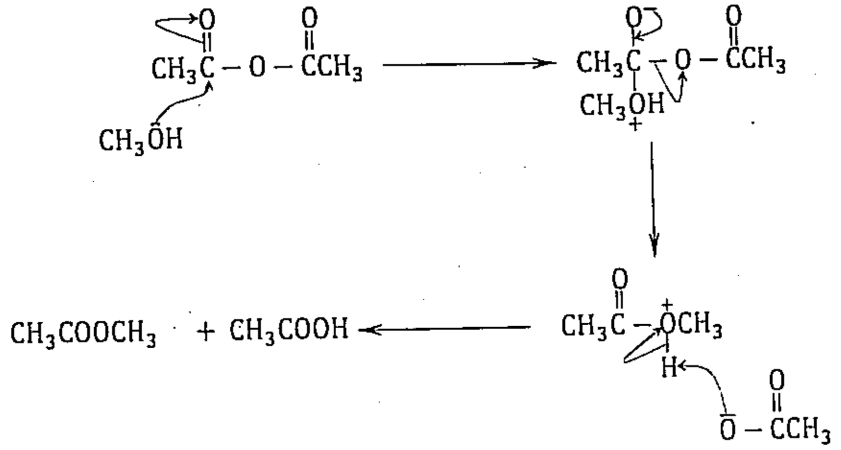
(e) From acid anhydrides

Acid anhydrides react with alcohols to form esters.

(i) 

$$CH_3\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}CH_3 + CH_3OH \longrightarrow CH_3COOCH_3 + CH_3COOH$$

<u>Mechanism</u>



(ii)

$$CH_3\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}CH_3 + CH_3CH_2OH \longrightarrow CH_3COOCH_2CH_3 + CH_3COOH$$

9.4 Chemical properties of esters

Esters undergo nucleophilic substitution like any other carboxylic acid derivatives. Nucleophilic attack occurs at the electron deficient carbonyl carbon, and results into the replacement of $-OR'$ by $-OH$, $-OR''$ or $-NH_2$.

(a) Hydrolysis

Esters can be hydrolysed by heating with dilute mineral acids or dilute alkalis.

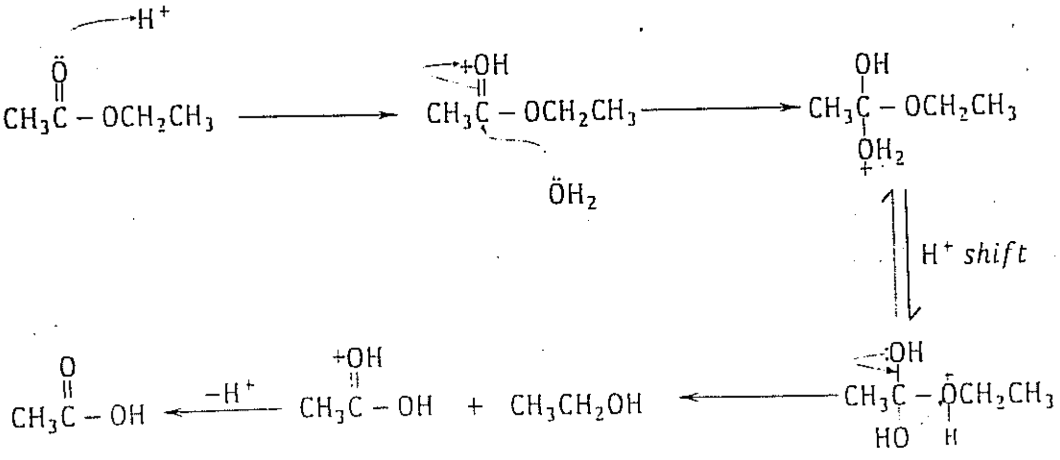
(i) Acid catalyzed hydrolysis

The acid catalyzed hydrolysis of esters forms a carboxylic acid and an alcohol or phenol. The reaction is the exact opposite of esterification and can be reversed back to the ester.

For example

$$CH_3COOCH_2CH_3 \xrightarrow[\text{reflux}]{H_2O/H^+ \text{ catalyst}} CH_3COOH + CH_3CH_2OH$$

Mechanism



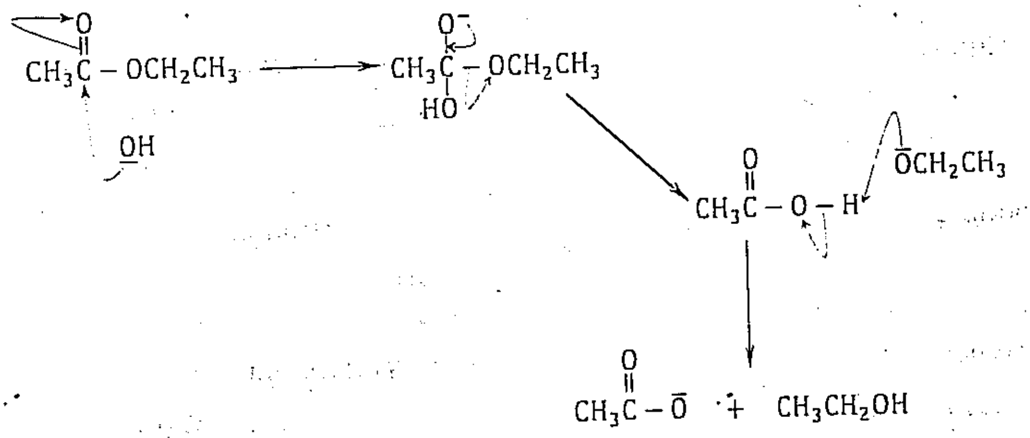
The acid catalysis makes the carbonyl carbon more susceptible to nucleophilic attack.

(ii) Base catalyzed hydrolysis

Ester hydrolysis is more satisfactorily done under alkaline conditions. However, the carboxylic acid formed in this case reacts with hydroxide ions to form a carboxylate ion. The process is referred to as saponification because esters are converted to soaps in a similar way. The process is more efficient than acid hydrolysis because all the ester is converted into hydrolysis products.

$$CH_3COOCH_2CH_3 \xrightarrow[\text{reflux}]{H_2O/\bar{O}H} CH_3CO\bar{O} + CH_3CH_2OH$$

<u>Mechanism</u>



The carboxylic acid may be obtained by adding a dilute acid.

(b) Reduction

Just like carboxylic acids, esters are reduced to alcohols by lithium terahydriodoaluminate in presence of dry ether.

Examples

$$CH_3COOCH_2CH_3 \xrightarrow[\text{dry ether}]{LiAlH_4} 2CH_3CH_2OH$$

$$CH_3CH_2COOCH_3 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2CH_2OH + CH_3OH$$

Reduction can also be achieved using sodium in ethanol.

$$CH_3COOCH_3 \xrightarrow[CH_3CH_2OH]{Na} CH_3CH_2OH + CH_3OH$$

Esters can also be reduced by catalytic hydrogenation using copper(II) oxide or copper(II) chromate catalyst at 250°C.

$$CH_3COOCH_2CH_2CH_3 \xrightarrow[250^\circ C]{H_2/CuO \text{ or } CuCrO_4} CH_3CH_2OH + CH_3CH_2CH_2OH$$

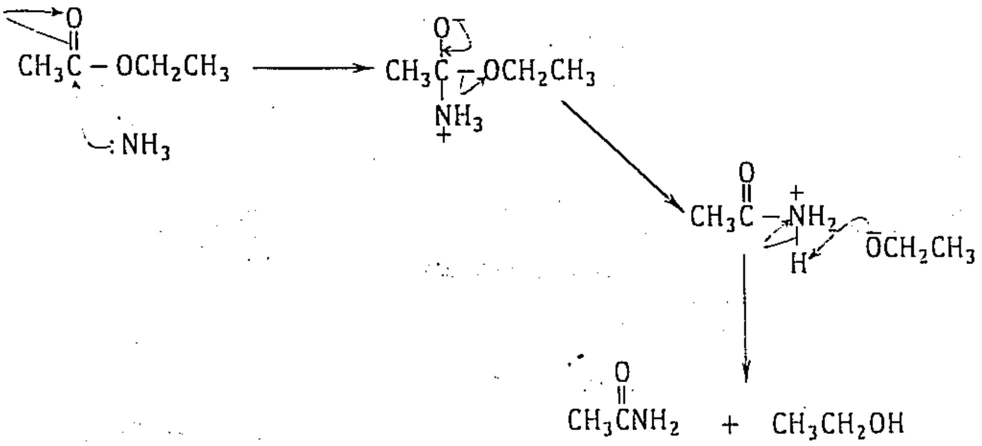
$NaBH_4$ cannot be used to effect the reduction.

(c) Ammonolysis (Amide formation)

Esters react with ammonia dissolved in an alcohol or concentrated aqueous ammonia contained dissolved ammonium salts to form amides.

$$CH_3COOCH_2CH_3 \xrightarrow[\text{conc. } NH_3(aq)/NH_4^+(aq)]{NH_3/\text{ethanol} \text{ or}} CH_3CONH_2 + CH_3CH_2OH$$

Mechanism

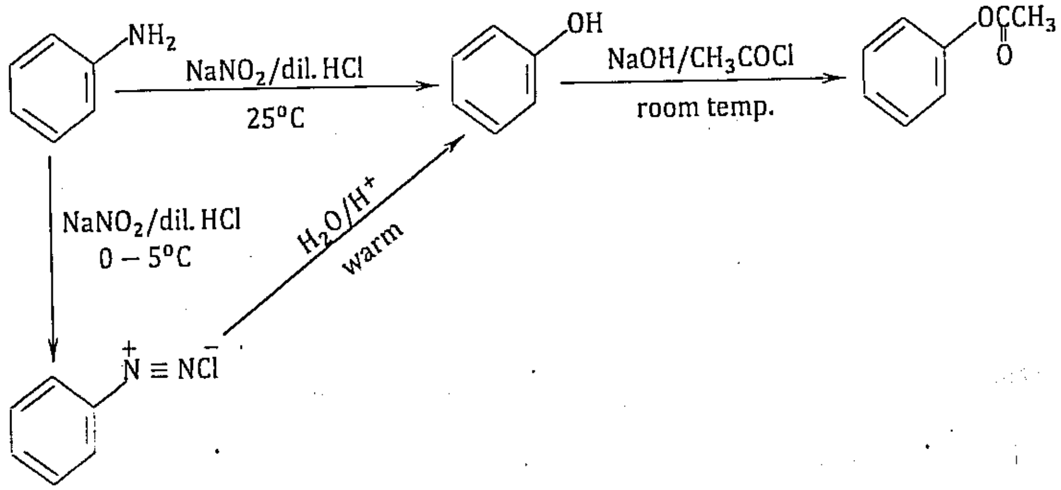


9.5 Uses of esters

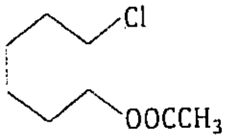
- ✓ Esters are used as solvents in the laboratory and industry.
- ✓ Methyl 2-methylpropenoate is used in making Persex, a polymer used for packaging, making aeroplane windows, lenses, etc.
- ✓ Some long chain esters are used as special lubricants.
- ✓ As food flavourings in the food industry and scenting perfumes.
- ✓ Aspirin and paracetamol are esters used in the medicine industry.

9.6 Some synthetic problems

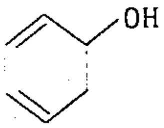
(i) Phenylethanoate from aminobenzene

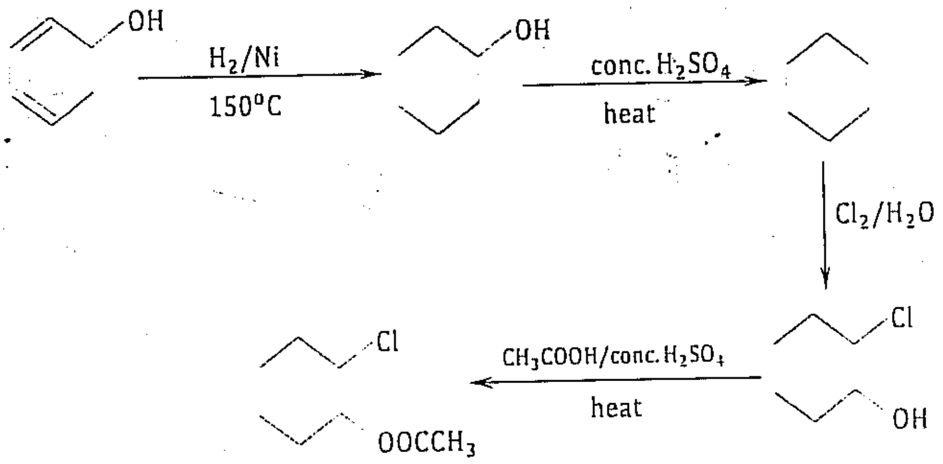


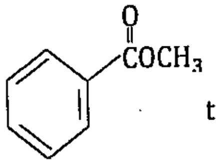
(ii)

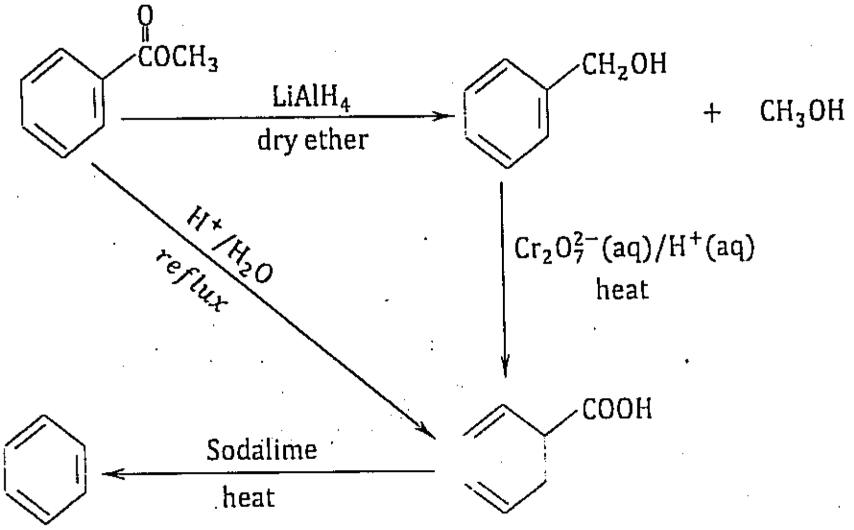


from





(iii)  to benzene



(iv) $CH_3CH_3CO_2CH_3$ from ethanol.

$$\begin{tikzcd}
CH_3CH_2OH \arrow[r, "PCl_5"] & CH_3CH_2Cl \arrow[r, "KCN/Ethanol", "heat"'] & CH_3CH_2CN \arrow[d, "H^+/H_2O", "heat"'] \\
CH_3CH_2COOCH_3 & & CH_3CH_2COOH \arrow[ll, "CH_3OH/conc.\ H_2SO_4"', "heat"]
\end{tikzcd}$$

9.7 End of topic assessment exercise

1. Complete the following equations and write the IUPAC names of the main organic product in each case.

(a)  $—CH_2Br \xrightarrow{CH_3CH_2CO\bar{O}Ag^+}$

(b) $CH_3OH \xrightarrow[\text{conc. } H_2SO_4\text{, warm}]{HCOOH}$

(c) $CH_3CH_2CH_2Br \xrightarrow{CH_3COOAg}$

(d) $CH_3CH_2COOCH_2CH_3 \xrightarrow[\text{dry ether}]{LiAlH_4}$

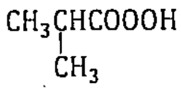
(e) $HCO_2H + CH_3CH_2CH_2OH \xrightarrow[\text{dry ether}]{LiAlH_4}$

2. Complete the following equations and in each case write a mechanism for the reaction.

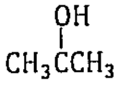
(i) $C_6H_5COOH + CH_3OH \xrightarrow[\text{heat}]{H^+}$

(ii) $CH_3CO_2C_2H_5(l) + \bar{O}H(aq) \xrightarrow[\text{heat}]{H_2O}$

(iii) $CH_3CH_2COOCH_2CH_3 \xrightarrow{\text{Alcoholic } NH_3}$

(iv) 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOOH + CH_3OH \xrightarrow[\text{heat}]{H^+}$

(v) 

$CH_3COCl + CH_3\overset{\displaystyle OH}{\overset{|}{C}}CH_3 \longrightarrow$

3. Name a reagent that can be used to distinguish between the following pairs of compounds and state what is observed in each case when the compounds are separately treated with the reagent.

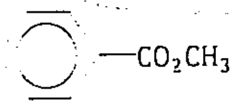
(a) $CH_3CH_2COOCH_3$ and $CH_3CH_2CH_2COOH$

(b) CH_3COOCH_3 and $HCOOCH_2CH_3$

4. Write equations to show how each of the following organic compounds can be synthesized. In each case indicate the reagents and conditions for the reactions.

(a) $CH_3COOC_2H_5$ from ethanol

(b) $CH_3CO_2CH_3$ from ethene

(c)  from benzene

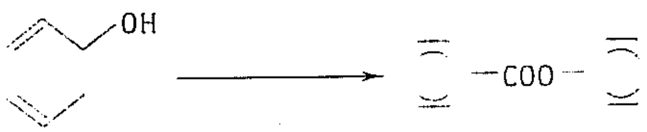
(d) Ethylbenzene from phenol

(e) Chloroethane to phenylethanoate

5. Write a mechanism to show how each of the following conversions can be effected.

(a) $CH_3COOAg \longrightarrow CH_3COOCH_2CH_3$

(b) $CH_3COOCH_3 \longrightarrow CH_3CO\bar{O} + CH_3OH$

(c) 

6. An organic compound E, contains 58.8% Carbon, 9.8% hydrogen and the rest being oxygen.

(a) Calculate the empirical formula of E.

(b) If the vapour density of E is 51, determine its molecular formular

(c) (i) E reacts with aqueous sodium hydroxide under reflux to produce propan-1-ol as one of the products. Identify E.

(ii) Write the equation and mechanism for the reaction in (ii) above.

(d) Write equations to show how E can be synthesized from a suitable carboxylic acid.

7. An organic compound F contains 54.55% Carbon, 36.36% oxygen and the rest being hydrogen.
   (a) Calculate the empirical formular of F.
   (b) When 1.76g of F was hydrolysed, it required 2×10^{-2} moles of sodium hydroxide for complete hydrolysis.
      (i) Determine the molecular formular of F.
      (ii) Write the names and structural formulae of all the possible Isomers of F.
   (c) If one of the products of the reactions in (b) above was methanoic acid after addition of a dilute acid.
      (i) Identify F
      (ii) Write the mechanism for the reaction between F and water in presence of an acid catalyst.

8. An organic compound G has the structural formular; $CH_3CH = CHCH_2COOC_2H_5$. Write equation for the reaction between G and;
   (i) $LiAlH_4$
   (ii) Sodium hydroxide solution and mixure is heated
   (iii) Hydrogen and Nickel at 150°C
   (iv) Bromine liquid
   (v) Ozone followed by Zinc and ethanoic acid.

9. A liquid H of molecular formular $C_5H_{10}O_2$ was reduced by Lithium tetrahydridoaluminate in dry ester to form two alcohols J and K. Both J and K reacted with iodine in alkaline solution to form a pale yellow crystalline solid L. H is insoluble in cold, dilute aqueous sodium hydroxide but on boiling, the mixture gradually becomes one layer. J forms a cloudy solution after 8 minutes with anhydrous zinc chloride in the presence of concentrated hydrochloric acid.
   (a) Identify H, J, K and L.
   (b) Write equation for the reaction between K and:
      (i) Iodine in alkaline.
      (ii) Anhydrous zinc chloride and concentrated hydrochloric acid.

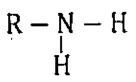
10. (a) Benzylethanoate can be reduced to two alkanols.
      (i) Write the structural formula of benzyl ethanoate.
      (ii) Give one reagent that can be used for the reduction.
      (iii) Write the structural formula of the alkanols.
   (b) Hydrolysis of esters using mineral acids gives alkanols and alkanoic acids gives alkanols and alkanoic acids. Briefly describe a method that can be used to determine whether the oxygen atom in alkanol comes from the ester or water.

Chapter 10

Amines

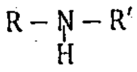
10.1 Introduction

Amines are organic derivatives of ammonia formed by replacing one or more hydrogen atoms in ammonia with a corresponding number of alkyl or aryl groups. Amines are classified as ***primary***, ***secondary*** or ***tertiary*** amines according to the number of alkyl or aryl groups attached to the nitrogen atom.



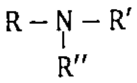
$R-\underset{|}{\overset{}{N}}-H$ with H on N

Primary amine



$R-N(H)-R'$

Secondary amine



$R-N(R'')-R'$

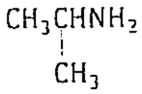
Tertiary amine

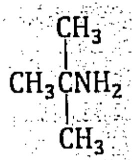
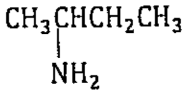
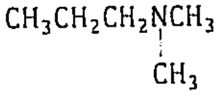
Where R and R^1 may be alkyl or aryl groups and may be the same or different.

Amines with only alkyl groups attached to the nitrogen atom are ***aliphatic amines*** while those with at least one aryl group attached to the nitrogen atom are ***aromatic amines***.

10.2 Nomenclature of Amines

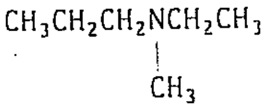
Aliphatic amines are named basing on the name(s) of the alkyl group(s) attached to the nitrogen atom followed by the word ***'amine'*** as shown by the examples in the table below.

Formula of amine	*Name*	*Class of amine*
CH_3NH_2	Methylamine	Primary
$CH_3CH_2NH_2$	Ethylamine or aminoethane	Primary
$CH_3CH_2CH_2NH_2$	Propylamine or aminopropane	Primary
 $CH_3CH(CH_3)NH_2$	1-Methylethylamine	Primary

 $CH_3\overset{CH_3}{\underset{CH_3}{C}}NH_2$	1,1-Dimethylethylamine	Primary
 $CH_3\underset{NH_2}{CH}CH_2CH_3$	2-Aminobutane	Primary
$H_2NCH_2CH_2NH_2$	Ethane-1,2-diamine	Primary
$H_2NCH_2(CH_2)_4CH_2NH_2$	Hexane-1,6-diamine	Primary
CH_3NHCH_3	Dimethylamine	Secondary
$CH_3CH_2NHCH_3$	Ethylmethylamine	secondary
$(CH_3CH_2)_2NH$	Diethylamine	Secondary
$(CH_3)_3N$	Trimethylamine	Tertiary
$(CH_3CH_2)_3N$	Triethylamine	Tertiary
 $CH_3CH_2CH_2\underset{CH_3}{N}CH_3$	Ethyldimethylamine	Tertiary

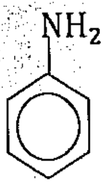
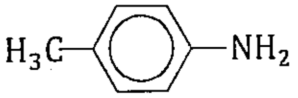
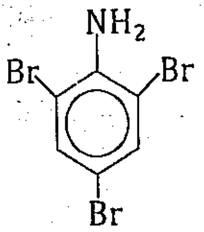
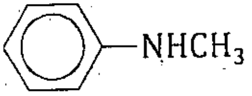
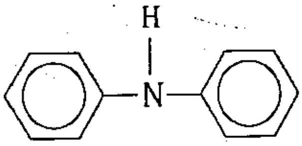
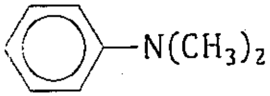
Note

More complex tertiary amines are named as derivatives of the long chain amine with an italicized *N* before the name of each substituent. For example,


$CH_3CH_2CH_2\underset{CH_3}{N}CH_2CH_3$

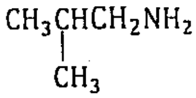
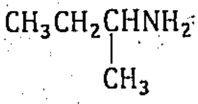
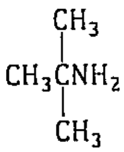
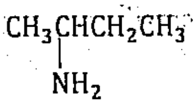
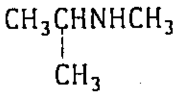
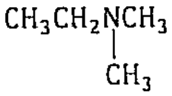
Ethylmethylpropylamine
or
N-ethyl-*N*-methylpropylamine

Aromatic amines are named as derivatives of phenylamine, as shown in the table below.

Formula of amine	*Name*	*Class of amine*
	Phenylamine	Primary aromatic
	4-Methylphenylamine	Primary aromatic
	2,4,6-Tribromophenylamine	Primary aromatic
	*N*-Methylphenylamine	Secondary aromatic
	Diphenylamine	Secondary aromatic
	*N,N*-Dimethylphenylamine	Tertiary aromatic

10.3 Isomerism

Aliphatic straight chain amines are represented by the general formula, $C_nH_{2n+3}N$. They exhibit functional group isomerism, chain isomerism and position isomerism. For example the amine, $C_4H_{11}N$, exhibits the following isomers.

Structure of isomer	*Name*	*Class of amine*
$CH_3CH_2CH_2CH_2NH_2$	Butylamine or aminobutane	Primary
 $CH_3\underset{CH_3}{CH}CH_2NH_2$	2-Methylpropylamine	Primary
 $CH_3CH_2\underset{CH_3}{CH}NH_2$	1-Methylpropylamine	Primary
 $CH_3\overset{CH_3}{\underset{CH_3}{C}}NH_2$	1,1-Dimethylethylamine	Primary
 $CH_3\underset{NH_2}{CH}CH_2CH_3$	2-Aminobutane	Primary
$CH_3CH_2CH_2NHCH_3$	*N*-Methylpropylamine	Primary
$CH_3CH_2NHCH_2CH_3$	Diethylamine	Primary
 $CH_3\underset{CH_3}{CH}NHCH_3$	*N*-Methyl-2-propanamine	Primary
 $CH_3CH_2\underset{CH_3}{N}CH_3$	Ethyldimethylamine	Secondary

10.4 Physical Properties

(a) Physical state

Lower aliphatic amines are gases or low boiling point liquids which have characteristic ammonia-like smell. Higher homologues are liquids with distinctive fishy odour. Very high molecular mass amines are solids.

Aromatic amines can be liquids or solids.

(b) Solubility

All amines are readily soluble in non-polar organic solvents like ether, benzene, etc. lower molecular mass amines dissolve in water because they can from hydrogen bonds with water since they are polar.

Solubility in water however decreases as the hydrocarbon chain of the amines increases especially for amines with more than six carbon atoms.

Phenylamine is soluble in fatty tissue and is a highly toxic liquid, easily absorbed through the skin, hence a dangerous compound.

(c) Boiling points

- **Lower aliphatic amines have low boiling points but their boiling points are lower than those of alcohols with corresponding number of carbon atoms and higher than those of corresponding alkanes.**

Reason

The N-H bond is **more polar** than the C-H bond but **less polar** than the O-H bond. This is because nitrogen is **more electronegative** than carbon but **less electronegative** than oxygen. The lower amines therefore form **stronger intermolecular hydrogen bonds** than corresponding alkanes whose molecules are held by weaker Van der waal's **forces**. The hydrogen bonds formed by the lower amines are **however weaker** than those in corresponding alcohols.

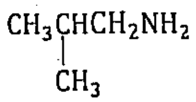
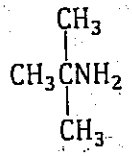
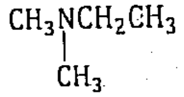
- For isomeric amines, boiling points decrease from primary to secondary to tertiary and among the primary amines, decreases with branching.

Reason

Branching causes **steric hindrance of the hydrogen bonding** and Van der Waal's **interaction between adjacent amine molecules** and therefore reduces intermolecular forces of attraction between them, thereby decreasing boiling point. Primary amines form **more hydrogen bonds** than secondary amines while tertiary amines **do not form hydrogen bonds** and are only **held by weak** Van der Waal's forces.

Example

The table below shows boiling points of some isomeric amines.

Isomer	*Class*	*Boiling point (°C)*
$CH_3CH_2CH_2CH_2NH_2$	Primary	78
 $CH_3\underset{\underset{\displaystyle CH_3}{\vert}}{C}HCH_2NH_2$	Primary	68
 $CH_3\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}NH_2$	Primary	56
$CH_3CH_2NHCH_2CH_3$	Secondary	56
 $CH_3\underset{\underset{\displaystyle CH_3}{\vert}}{N}CH_2CH_3$	Tertiary	36.5

Observations

- For the primary isomers, boiling points **decrease with increase in branching.**

Reason

Molecules of the three primary amines interact through **intermolecular hydrogen bonding** due to presence of **N-H polar bonds**, as well as Van der Waal's forces of **attraction**. Butylamine has straight chain molecules with an **extended structure resulting into stronger** Van der Waal's forces of attraction between the molecules. However, as branching increases in the other two isomers, the molecules become **nearly spherical** (more compact), **reducing the surface area of contact** with neighboring molecules, thereby **weakening** the Van der Waal's forces of attraction between adjacent molecules.

- Also, boiling points decrease in the order **primary > secondary > tertiary amines**.

Reason

Amines are **polar molecules** and their molecules interact through **intermolecular hydrogen bonding** due to **presence of N-H polar bonds**, as well as Van der waal's **forces of attraction**. Primary amines form **more hydrogen bonds per molecule** than the secondary amines and are **therefore held more strongly**. Therefore, butylamine has a higher boiling point than dimethylamine. N,N-dimethylethylamine, a tertiary amine, has the lowest boiling point because its molecules interact only through weak Van der waal's forces and cannot form **hydrogen bonds** because its lacks polar N-H bonds.

10.5 Basicity of amines

Ammonia is a weak base. Its basic nature is attributed to the lone pair of electrons on the nitrogen atom which can be donated to a proton. Just like ammonia, amines are weak bases and their solutions are alkaline. They form salts when reacted with acids. Amines ionize partially in water to form hydroxide ions and alkylammonium ions.

$$RNH_2(aq) + H_2O(l) \rightleftharpoons R\overset{+}{N}H_3(aq) + OH(aq)$$

By the law of mass action:

$$K_b = \frac{[R\overset{+}{N}H_3][\bar{O}H]}{[RNH_2]}$$

Where K_b is the base dissociation constant.

The higher the value of K_b, the stronger is the base and vice versa.

K_b can also be expressed as $K_b = \frac{c\alpha^2}{1-\alpha}$. where α is the degree of dissociation.

However, when α is small compared to 1, then $(1-\alpha) \approx 1$ such that $K_b = c\alpha^2$.

Hence

$$\alpha = \sqrt{\frac{K_b}{c}}$$

The concentration of hydroxide ions; $[\bar{O}H] = c\alpha$, and once known, $[H^+]$ is got by $[H^+] = \frac{K_w}{[\bar{O}H]}$.

Hence the pH of the solution is calculated from:

$$pH = -\log_{10}[H^+]$$

pK_b can also be used to express basic strength of amines. The smaller the pK_b value, the stronger the base and vice versa.

$$pK_b = -\log_{10} K_b$$

Note

For details of derivations and calculations involving the above formulae check the book, 'Demystifying Physical Chemistry by Joseph Jobs Kayiira (Chapter 7)'.

The basic strength of amines in water depends on two factors:

(i) **the availability of electron pairs to donate to a proton.**

(ii) **the ease with which the protonated amine can undergo solvation with water.**

Electron donating groups make bases stronger by makng the lone pair of electrons readily available for protonation. On this basis alone, basic strength would be in the order: Tertiary amine > secondary amine > primary amine > NH_3.

On basis of solvation, amine that form more hydrogen bonds with water become more solvated. Thus, solvation of protonated amines is in the order: NH_3 > Primary amine > Secondary amine > Tertiary amine.

A combination of both solvation and electron donating effect (positive inductive effect) makes basic strength of amines decrease in the order: secondary amine > primary amine > tertiary amine > NH_3.

However, the overcrowding of bulky alkyl groups around the nitrogen atoms (steric hindrance) makes the approach of a proton relatively difficult hence reducing basicity. Although aliphatic amines are stronger bases than ammonia, phenylamine is a much weaker base than ammonia as will be explained later.

Example

The table below shows the base dissociation constants of different bases in aqueous solutions.

Base	Base dissociation constant, Kb ($moldm^{-3}$)	pKb
$C_6H_5NH_2$	3.5×10^{-10}	9.46
NH_3	1.8×10^{-5}	4.75
$(CH_3)_3N$	6.0×10^{-5}	4.22
CH_3NH_2	4.4×10^{-4}	3.36
$CH_3CH_2NH_2$	4.7×10^{-4}	3.33
$(CH_3)_2NH$	5.1×10^{-4}	3.29
$(CH_3CH_2)_3N$	5.5×10^{-4}	3.26
$(CH_3CH_2)_2NH$	9.5×10^{-4}	3.02

(a) Compare and explain the basic strength of NH_3, CH_3NH_2 and $CH_3CH_2NH_2$.

(b) Compare and explain the basic strength of CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$.

(c) Explain why phenylamine is a weaker base thanethylamine.

Solution

(a)

Basic strength increases from NH_3 to CH_3NH_2 to $CH_3CH_2NH_2$.

The **basic strength of the amines depends on the availability of lone pair of electrons on the nitrogen atom.** Ammonia is the **weakest base** because the **hydrogen atoms** attached to the nitrogen atom have **no inductive effect.** The **alkyl groups** attached to the nitrogen atom in methylamine and ethylamine have a **positive inductive effect** which **increases the electron density on the nitrogen atom,** making the **lone pairs of electrons readily available for protonation.** The **positive inductive effect increases with increase in the number of carbon atoms in the alkyl groups** hence ethylamine is a **stronger base** than methylamine.

(b)

Basic strength increases in the order $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$.

The **basic strength of these amines depends on the availability of lone pair electrons on the nitrogen atom** and **the ease of solvation of the protonated amines.** The **three methyl groups** attached to the nitrogen atom in trimethylamine have the **greatest inductive effect** but due to **steric hindrance to the approach of a proton towards the nitrogen atom** and **the poorest solvation of the protonated amine,** trimethylamine is the weakest of the three amines.

The **methyl groups** attached to the nitrogen atom in methyl amine and dimethyl amine have **positive inductive effect** which **increases with electron density on the nitrogen atom** making the **lone pairs of electrons readily available.** Methylamine and dimethyl amine also have **nitrogen-hydrogen bonds** hence **protonated amines are easily solvated.** The **positive inductive effect** and **solvation increase with the number of alkyl groups attached to the nitrogen atom** and **the number of nitrogen-hydrogen bonds respectively.** Hence dimethyl amine is a stronger base than methylamine.

(c)

The **basic strength of amines depends on the availability of lone pair of electrons on the nitrogen atom.**

Phenylamine is a **weaker base** because the lone pair of electrons on the nitrogen atom **interacts with the delocalized pi-electrons** in the benzene ring. This reduces the

electron density on the nitrogen atom making the lone pair of electrons less available for protonation.

For ethylamine, the **ethyl group** attached to the nitrogen atom has **positive inductive effect** which **increases the electron density** on the nitrogen atom, making the lone pair of electrons **readily available for protonation.**

10.6 Preparation of amines

(a) From alkylhalides

Aliphatic amines can be formed by reacting alkyl halides with excess alcoholic ammonia under pressure in a sealed tube.

$$CH_3CH_2CH_2Br \xrightarrow[\text{heat in a sealed tube}]{\text{excess alcoholic } \ddot{N}H_3} CH_3CH_2CH_2NH_2 + HBr$$

However, this reaction gives a mixture of primary, secondary, tertiary and quaternary ammonium salts. The method is therefore of limited synthetic application due to the multiple alkylations.

$$CH_3CH_2CH_2Br + CH_3CH_2CH_2NH_2 \longrightarrow (CH_3CH_2CH_2)_2NH + HBr$$

$$CH_3CH_2CH_2Br + (CH_3CH_2CH_2)_2NH \longrightarrow (CH_3CH_2CH_2)_3N + HBr$$

$$CH_3CH_2CH_2Br + (CH_3CH_2CH_2)_3N \longrightarrow (CH_3CH_2CH_2)_4\overset{+}{N}Br^-$$

Aryl amines cannot be prepared by this method.

(b) Reduction of nitro-compounds

Primary amines can be prepared by reducing nitroalkanes. The reducing agent can be hydrogen in presence of Nickel or Lithium tetrahydridoaluminate.

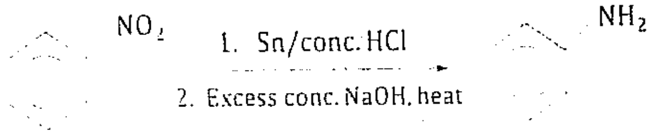
For example,

$$CH_3CH_2NO_2 \xrightarrow{H_2/Ni} CH_3CH_2NH_2$$

$$CH_3CH_2CH_2NO_2 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2CH_2NH_2$$

Note

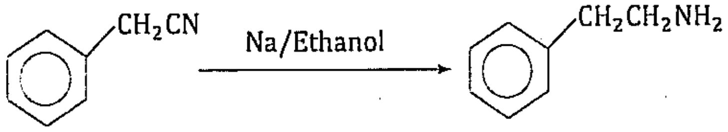
The reduction of nitrobenzene to phenylamine is done using Tin and concentrated hydrochloric acid and excess concentrated sodium hydroxide.



(c) Reduction of nitriles

Nitriles can be reduced to primary amines using sodium and absolute ethanol or Lithium tetrahydridoalimunate in ether or hydrogen and Nickel catalyst.

$$CH_3CN \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2NH_2$$



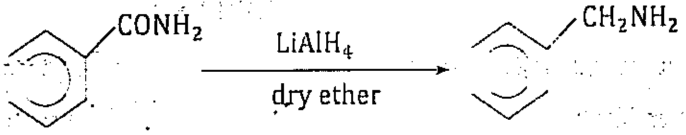
$$NCCH_2CH_2CN \xrightarrow[\text{dry ether}]{LiAlH_4} H_2NCH_2CH_2CH_2CH_2NH_2$$

$$CH_3CH_2CN \xrightarrow{H_2/Ni} CH_3CH_2CH_2NH_2$$

(d) From amides

1. Primary amines can also be formed by reduction of amides.

$$CH_3CONH_2 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2NH_2$$

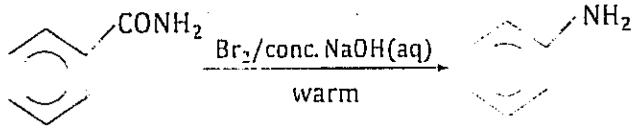


This method yields an amine with the same number of carbon atoms as the amide.

2. Amides can also be converted to primary amines by Hoffmann degradation.

The amide is warmed with bromine and a concentrated aqueous solution of sodium hydroxide. However, this method yields an amine one carbon atom less than the amide.

$$CH_3CH_2CONH_2 \xrightarrow[\text{warm}]{Br_2/\text{conc. NaOH(aq)}} CH_3CH_2NH_2$$



10.7 Chemical properties of amines

The main reactions undergone by amines are due to presence of a lone pair of electrons on the nitrogen atom. This lone pair aids amines to act a nucleophiles and can be donated to electrophiles.

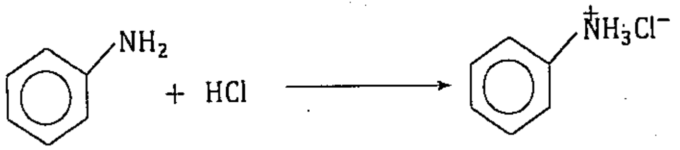
(a) Reaction with acids

All amines react with mineral acids to form stable crystalline salts.

Examples,

$$CH_3CH_2NH_2 + HCl \longrightarrow CH_3CH_2\overset{+}{N}H_3Cl^-$$

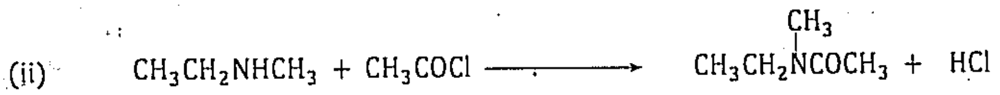
$$CH_3CH_2CH_2NH_2 + HNO_3 \longrightarrow CH_3CH_2\overset{+}{N}H_3NO_3^-$$



(b) Acylation

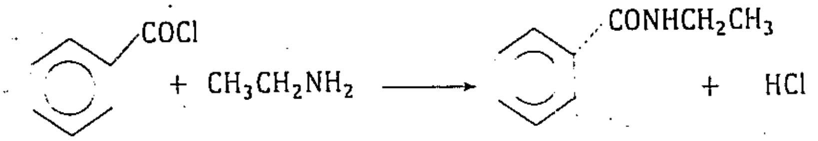
Primary and secondary amines react with acid chlorides in the cold to form amides.

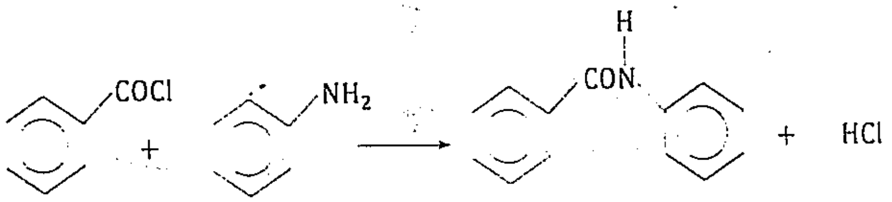
(i) $CH_3CH_2NH_2 + CH_3COCl \longrightarrow CH_3CH_2NHCOCH_3 + HCl$



(ii) $CH_3CH_2NHCH_3 + CH_3COCl \longrightarrow CH_3CH_2\underset{}{\overset{\overset{CH_3}{|}}{N}}COCH_3 + HCl$

Benzoylation can be done using benzoyl chloride in presence of excess aqueous alkali.





(c) Alkylation

Amines react with alkylhalides to form a mixture of primary, secondary, tertiary and quaternary ammonium salts.

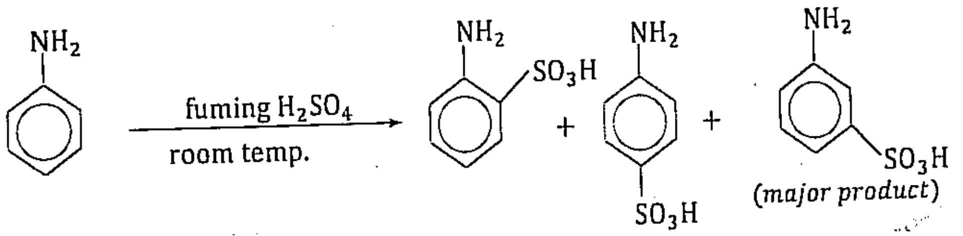
Example

$$\begin{tikzcd}
CH_3CH_2NH_2 \arrow[r, "CH_3CH_2Br"] & (CH_3CH_2)_2NH \arrow[r, "CH_3CH_2Br"] & (CH_3CH_2)_3N \arrow[dl, "CH_3CH_2Br"] \\
& (CH_3CH_2)_4\overset{+}{N}Br^- &
\end{tikzcd}$$

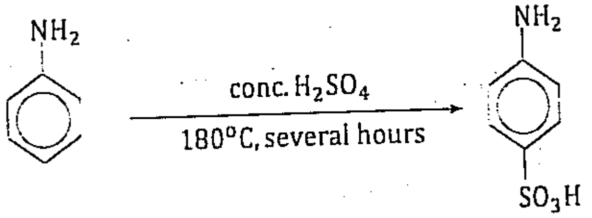
10.7.1 Some chemical reactions of phenylamine

(a) Sulphonation

Phenylamine reacts with fuming sulphuric acid at room temperature to form, 2-, 3- and 4-aminobenzenesulphonic acids. The 3-isomer is the major product.



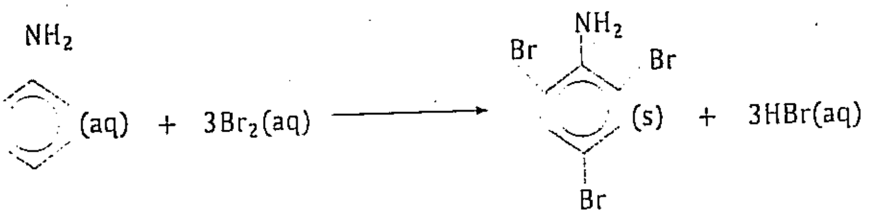
If ordinary concentrated sulphuric acid is used at 180°C for several hours, the 4-isomer only is formed.



(b) Bromination

Phenylamine reacts with bromine water in the cold to form 2,4,6-tribromophenylamine.

Observation: Reddish brown solution turns colourless and a white precipitate formed.



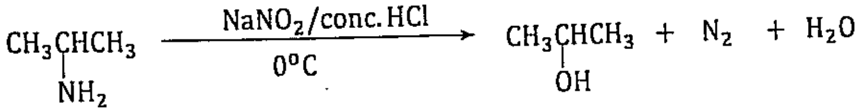
10.7.2 Testing for amines

Amines react with **concentrated hydrochloric acid** to form **dense white fumes** of alkylammonium chlorides. This test can be used for any class of amines.

However, the different classes of amines can be distinguished using ***concentrated hydrochloric acid and sodium nitrite at 0°C***. the actual reacting species is nitrous acid but it is unstable and thus prepared in situ by the two compounds above.

- Aliphatic primary amines react to form alcohols and nitrogen gas.
  Observation: a colourless solution and **bubbles of a colourless gas**.

$$CH_3CH_2NH_2 \xrightarrow[0^\circ C]{NaNO_2/conc.\,HCl} CH_3CH_2OH + N_2 + H_2O$$



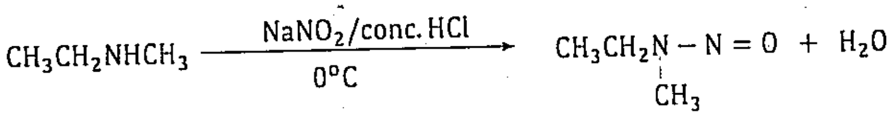
$$CH_3CH(NH_2)CH_3 \xrightarrow[0^\circ C]{NaNO_2/conc.\,HCl} CH_3CH(OH)CH_3 + N_2 + H_2O$$

The reaction of primary aliphatic amines is called ***diazotization*** because it yields highly unstable aliphatic diazonium salts that decompose to form mixtures of alkenes, alcohols and alkylhaides. Since a complex mixture of products is formed, this reaction is rendered of little importance for synthetic purposes.

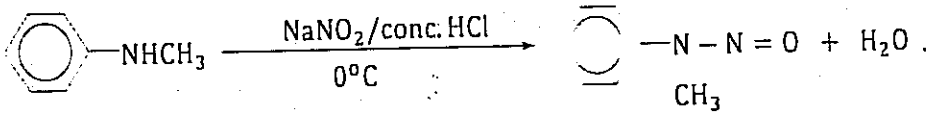
- **Secondary amines** (both alkyl and aryl ones) react with nitrous acid to form **N-nitrosoamines** which are insoluble in water.

  Observation: **yellow oil formed.**

  Examples by equations:



$$CH_3CH_2NHCH_3 \xrightarrow[0^\circ C]{NaNO_2/conc.\,HCl} CH_3CH_2N(CH_3)-N=O + H_2O$$

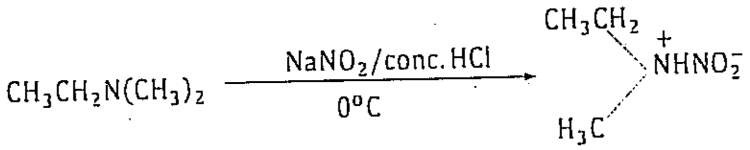


- **Aliphatic tertiary amines** do not undergo diazotization or nitrosation. They instead form **nitrite salts which are soluble in water.**

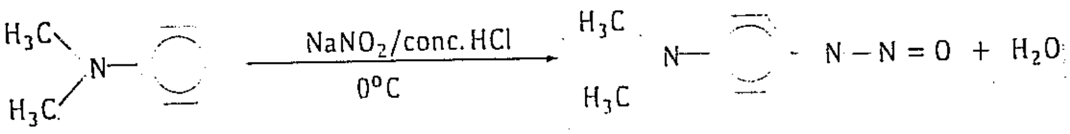
  Observation: a **colourless solution is observed**

  Examples by equations:

$$(CH_3)_3N \xrightarrow[0^\circ C]{NaNO_2/conc.\,HCl} (CH_3)_3\overset{+}{N}HNO_2^-$$



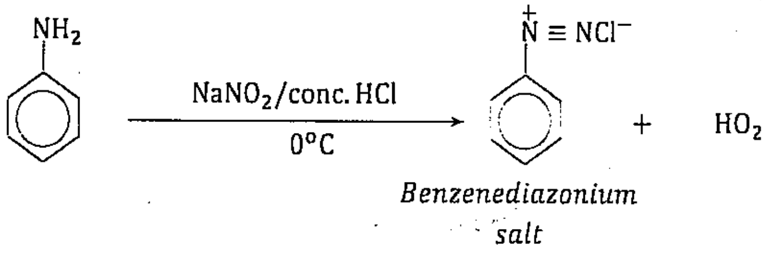
Tertiary aromatic amines react with nitrous acid to form nitrosoaromatic compounds. Nitrosation takes place exclusively at the para position if open and at the ortho position if the para position is not open.



- **Aromatic primary amines** react with nitrous acid to form **diazonium salts** which are more stable than aliphatic ones and do not decompose when the temperature is kept below 5°C.

  Observation: a colourless solution is formed.

  Equation



However, on warming, bubbles of a colourless gas are formed, i.e., nitrogen is formed.

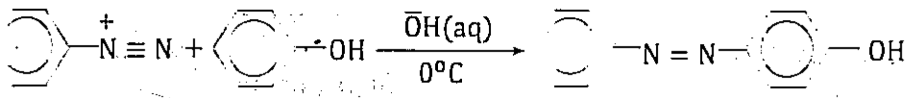
Note

The diazonium salt formed is of great synthetic value due to the reactions it undergoes.

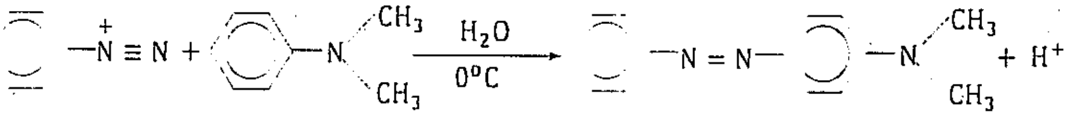
(i) The diazonium salt reacts with an alkaline solution of phenol to form an azodye.

Observation:bright yellow precipitate.

Equation:

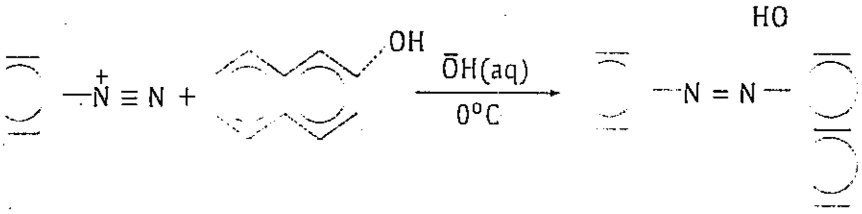


(ii) The diazoium salt reacts with tertiary aromatic amines to form an azodye. The reaction takes place in neutral solution.



(iii) The diazonium salt also reacts with **naphthalene-2-ol (2-naphthol) in alkaline medium.**

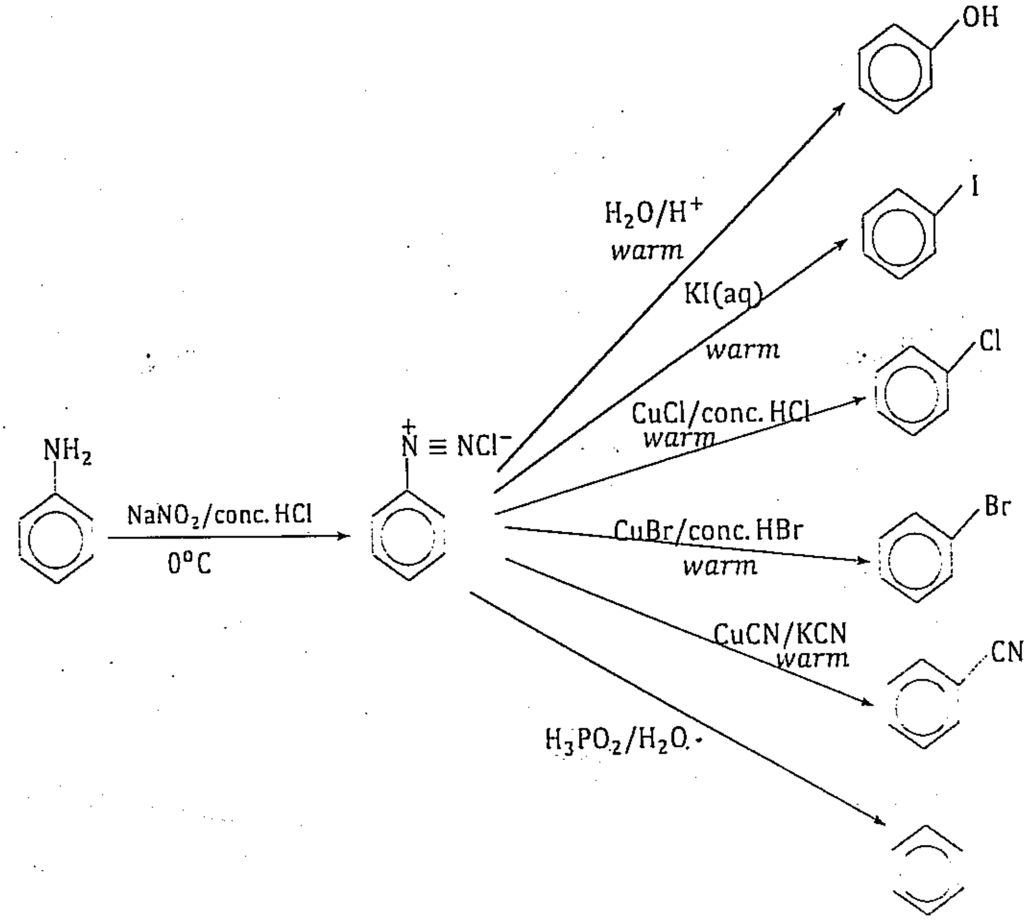
Observation: **bright red precipitate.**



Note: Formation of a red precipitate when an amine is treated with nitrous acid and the resultant solution poured in an alkaline solution of 2-naphthol confirms that the amine is a primary aromatic amine (phenylamine).

The above three reactions are called coupling reactions of benzenediazonium salts.

(iv) Benzenediazonium salt can also be converted to a number of compounds by replacement of the diazonium group by a number of other atoms or groups. A summary is shown below:



In all the six reactions above, nitrogen gas is formed.

10.8 Uses of amines

(i) Phenylamine is used in the manufacture of benzenediazonium chloride, which is a starting material for many azo-dyes; making Schiff bases which act as antioxidants in the rubber industry and in making sulphur drugs.

(ii) Phenylamine is used to make sulphanilic acid; which is then used to make methyl orange indicator.

(iii) Phenylamine is used to make azo-dyes via benzenediazonium salt. The azo-dyes are used as colouring material for food and other substances.

(iv) Lower aliphatic amines are used:

- as reagents in organic synthesis.
- as solvents in laboratory and industry.
- as stabilisers in rubber latex industry.

- in petroleum refining.
- in the manufacture of detergents.

10.9 End of topic assessment exercise

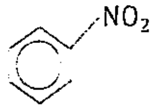
1. Complete each of the following equations and in each case, name the major organic product.

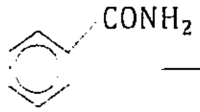
(a) $CH_3CH_2CONH_2 \xrightarrow[\text{warm}]{Br_2(aq)/\text{conc. } NaOH(aq)}$

(b) $(CH_3)_2NH + CH_3CH_2Cl \longrightarrow$

(c) $C_6H_5NH_2 \xrightarrow[\text{dil. } HCl,\ 0^\circ C]{NaNO_2}$

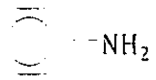
(d) $(CH_3)_2NH \xrightarrow[\text{dil. } HCl,\ 0^\circ C]{NaNO_2}$

(e)  $\xrightarrow[\text{2. NaOH, heat}]{\text{1. Sn/conc. HCl}}$

(f)  $\xrightarrow[\text{warm}]{Br_2(aq)/\text{conc. } NaOH(aq)}$

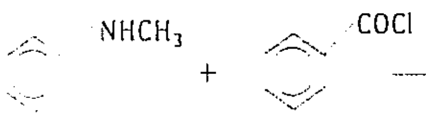
2. Complete each of the following equations and in each case, outline a mechanism for the reaction.

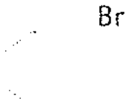
(a) $CH_3CH_2CH_2Cl \xrightarrow[\text{heat}]{CH_3NH_2}$

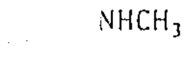
(b)  $+ CH_3COCl \longrightarrow$

(c) $(CH_3)_2NH + CH_3COCl \longrightarrow$

(d) $CH_3CH_2CH_2NH_2 + CH_3COCl \longrightarrow$

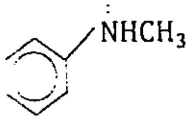
(e)  $\longrightarrow$

(f)  $\xrightarrow[\text{heat}]{CH_3CH_2OH/NH_3}$

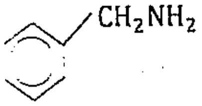
(g)  $+ (CH_3CO)_2O \longrightarrow$

3. Write equations to show how the following synthesises can be carried out. In each case, indicate the necessary reagents and conditions.

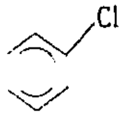
(a) Methanol from ethanamide
(b) $CH_3CONHCH_2CH_3$ from bromomethane
(c) Chloroethane to ethanamide
(d) $(CH_3)_2C = NCH_2CH_2CH_3$ from 2-iodopropane
(e) Phenylamine from methylbenzene
(f) Phenylhydrazine from phenylamine
(g) Bromopropane to propanamide
(h) $CH_3CH = CH_2$ to $CH_3CH_2NH_2$
(i) $CH_3CH_2CH_2NHCH_3$ from propene
(j) Aminocyclohexane from cyclohexene
(k) Phenylethanoate from aminobenzene
(l) Aminobenzene to 2-nitrophenol

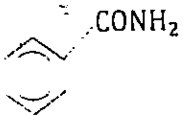
(m) 

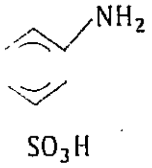
from benzene.

(n) 

from benzene.

(o) 

to 

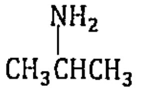
(p) 

from benzene.

4. Describe how the following conversions can be effected. (No equations required)

(a) Benzoic acid to aminobenzene
(b) Ethylamine from ethanol
(c) Ethylamine from methanol
(d) Methylamine from ethanoic acid
(e) Iodoethane to propanamide
(f) Phenylamine from hydroxybenzene
(g) Ethanal to ethylamine

5. (a) For the pair of organic compounds given below,



$CH_3\overset{NH_2}{\overset{|}{C}}HCH_3$ and $(CH_3)_3N$

name the reagent(s) that can be used to:

(i) test for the functional group.

(ii) distinguish between the pair of the organic compounds.
In each case state the observations made.

(b) State what is observed and write equation for the reaction that takes place when sodium nitrite in presence of concentrated hydrochloric acid is added to ethylmethylamine.

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

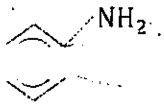
(a) 2-aminopropane and dimethylamine.

(b) $(CH_3)_2NH$ and CH_3CH_3

(c) $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$

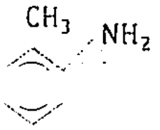
(d) $(CH_3)_3N$ and $(CH_3)_2NH$

(e)



and $CH_3CH_2NHCH_2CH_3$

(f)



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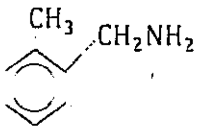
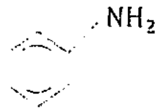


(g)



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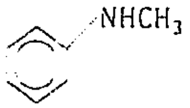
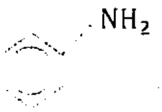


(h)



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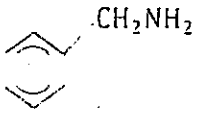
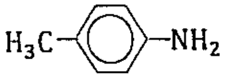
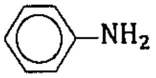
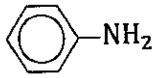
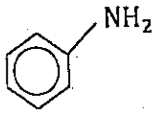
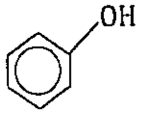
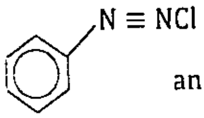


(i)  and 

(j) $CH_3CH_2CH_2CH_2NH_2$ and 

(k)  and 

(l)  and $CH_3CH_2N \equiv NCl$

7. An organic compound Y contains 22.8% nitrogen, 28% oxygen, 8.5% hydrogen and the rest being carbon.

(a) Calculate the empirical formula of Y.

(b) 0.5g of Y dissolved in 80g of water forming a solution that freezes at $-0.197\,°C$. Calculate the molecular formula of Y.

($Cryoscopic\ constant\ for\ water\ is\ 1.86°C mol^{-1} per\ 1000g\ of\ water$).

(c) When Y was refluxed with potassium hydroxide, ethanoic acid and ammonia was produced.

(i) Identify Y.

(ii) Write equations to show how Y is obtained from a carbonyl compound.

8. (a) State Graham's law of gaseous diffusion.

(b) Equimolar amounts of amine, T and oxygen were allowed to diffuse through the same porous partition under the same conditions of temperature and pressure. The amine, T diffuses 1.19 times as fast as the time by oxygen.

(i) Determine the molecular mass of T.

(ii) Determine the molecular formula of T.

(c) (i) Write equation for the reaction when T is dissolved in water.

(ii) Determine the pH of a 0.1M aqueous solution of compound T. The base dissociation constant, K_b of T is $1.85 \times 10^{-5} mol dm^{-3}$ and K_w for water is $1.0 \times 10^{-14} mol^2 dm^{-6}$.

9. (a) An organic compound, Q, contains carbon, hydrogen and nitrogen. On complete combustion, one mole of Q formed one mole of carbon dioxide and 2.5 moles of water. The vapour density of Q is 15.5. Calculate the molecular formula of Q.

(b) Write the structural formula of Q.

(c) *Q* is a liquid at room temperature and dissolves in water to form a solution of pH 9.20. State why;

(i) *Q* is a liquid

(ii) a solution of *Q* in water has a pH of 9.20

(d) An aqueous solution of *Q* was added to nickel(II) sulphate solution dropwise until in excess.

(i) State what was observed.

(ii) Write equation(s) for the reaction(s) that took place.

10. (a) Phenylamine was mixed with concentrated hydrochloric acid and sodium nitrite at a temperature of 0-5 $°C$. The resultant solution , *W* was treated with a mixture of phenol and sodium hydroxide. State what is observed and write equation for the reaction that takes place between;

(i) Phenylamine and a mixture of concentrated hydrochloric acid and sodium nitrite.

(ii) W and phenol in aqueous sodium hydroxide.

11. 20cm^{3}of 0.05M aqueous phenylamine was mixed with 50cm^3 of 1M sodium bromide and electrolyzed at current of 0.2A. The first permanent bromine colour was observed after 48.25 minutes and then electrolysis was stopped. (Faraday's constant = 96500Cmol^{-1}).

(i) Calculate the number of moles of bromine that reacted with 1 mole of phenylamine.

(ii) Hence write equation of the reaction between bromine and phenylamine. Name the product

12. (a) A compound *R*, contains carbon, hydrogen and nitrogen. On combustion, 0.72g of *R* produced 1.615g of carbon dioxide and 0.42g produced 84cm^3 of nitrogen at 15°C and 760mmHg. Calculate the empirical formula of *R*.

(b) When *R* was vapourised, it took 38 seconds to diffuse through the same porous partition under similar conditions whereas oxygen takes 28 seconds. Calculate the molecular formula of R.

(c) *R* reacts with a mixture of concentrated hydrochloric acid and aqueous sodium nitrite to form a yellow oily liquid.

(i) Identify *R*.

(ii) Write equation for the reaction that takes place.

13. An organic compound *T*, $C_4H_{11}N$ when treated with a mixture of concentrated hydrochloric acid and sodium nitrite solution, there was effervescence of a colourless neutral gas *Y* and another organic compound *Z* were formed.

    (a) (i) Identify *Y*

    (ii) Write the structural formulae and IUPAC names of possible isomers of *T*.

    (b) When *Z* was treated with iodine solution and sodium hydroxide solution, a pale yellow precipitate *R* was formed. Identify

    (i) T

    (ii) Z

    (iii) pale yellow precipitate R

    (c) Write equations and suggest a mechanism for the reaction between

    (i) T and ethanoylchloride

    (ii) Z and hot concentrated phosphoric acid.

    (d) Using equations only, show how *T* can be synthesized from propyne.

14. The structural formulae of amines *P*, *Q* and *R* are shown below,

P	Q	R
$(CH_3)_2NH$	$(CH_3)_3N$	$C_6H_5NH_2$

(a) (i) Describe the test that can be used to distinguish *P*, *Q* and *R*. *(Your answer should include observations and equations)*

(ii) State and explain the trend in acid strength of the amines.

(b) (i) Write equation(s) to show how *R* can be prepared from ethyne. *(Your answer should include reagents and conditions)*

(ii) *R* can be used in the manufacture of an azo-dye. Outline the steps you would follow in preparing azo-dye starting from *R*. *(Your answer should include observations and equations).*

15. (a) A compound *G*, relative molecular mass 93, burns with a sooty flame and contains 77.42% carbon, 7.53% hydrogen and the rest being nitrogen. Determine the molecular formula of *G*.

(b) *G* is soluble in hydrochloric acid. Write the structural formula of *G*.

(c) *G* was reacted with nitrous acid and to the product was added 2-naphthol.

(i) State what was observed

(ii) Write the equation for the reaction that took place.

(d) *G* can be prepared from nitrobenzene. Write equation to show how nitrobenzene can be prepared from benzene.

16. Ethylamine, dimethylamine and ammonia are weak bases in aqueous solution.

(a) (i) Arrange the compounds in order of increasing basic strength.

(ii) Suggest why the basic strength is in that order.

(b) (i) Name a reagent that can be used to identify the functional group of the bases.

(ii) State what is observed when each of the bases is separately treated with the named reagent.

(c) Using equations and showing the necessary conditions, show how:

(i) dimethylamine could be prepared from ethanol.

(ii) ethylamine could be converted to propanoic acid.

(d) (i) Name the reagent that could be used to distinguish between the bases.

(ii) State what is observed when each of the bases is separately treated with the named reagent.

(iii) Write the equation for the reaction that took place in each case.

17. Explain each of the following observations.

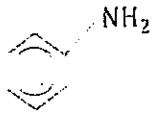
(a) The boiling point of ethanol is higher than that of ethylamine.

(b) Phenylamine is a weaker base than ethylamine.

(c) Ammonia is a weaker base than ethylamine

(d) The basic strength of ammonia, methylamine and aminobenzene is in the order; $C_6H_5NH_2 < NH_3 < CH_3NH_2$

(e) The basic strength of aminobenzene, ammonia and dimethylamine are in the order.



$< NH_3 < (CH_3)_2NH$

Chapter 11

Applied Organic Chemistry

In this topic, we shall consider the following subtopics:

(a) Fermentation

(b) Soaps and soapless detergents

(c) Polymers and polymerization

11.1 Fermentation

Ethanol can be obtained by fermentation of sugars (carbohydrates).

(a) If ethanol is to be prepared from starch;

A source of starch such as maize, rice, potatoes, wheat or sorghum is used.

Any of the above sources of **starch is squeezed with hot water** and filtered to obtain **a solution of starch**. The aqueous starch solution is **heated to about 60°C** with **malt**. Malt is germinated cereal (usually barley but can be any other) that contains an enzyme known as **diastase**. Diastase **hydrolyses starch** to **maltose**.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[60^\circ C]{\text{Diastase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}}$$

The liquid is then **cooled to 35°C** and yeast is added. Yeast contains the **enzyme maltase** which **catalyses the hydrolysis of maltose to glucose**.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6$$

Another enzyme in the yeast called **Zymase, converts glucose to ethanol**.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CH_3CH_2OH + 2CO_2$$

(b) From Sugar

Molasses containing sugar is **mixed with water and yeast** and allowed to **ferment for several days** after which **ethanol** is obtained. One of the enzymes in yeast called **sucrase catalyses the hydrolysis of sucrose** in molasses to **glucose** and **fructose**.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Sucrase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Another enzyme in yeast called **Zymase** then **catalyses the decomposition of glucose to ethanol** and **carbon dioxide.**

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CH_3CH_2OH + 2CO_2$$

When the concentration of ethanol **reaches 12%**, it **kills the yeast** and **fermentation stops.** This obtained liquor is **purified** to obtain **pure ethanol by distillation.** The distillation results into formation of a mixture containing **95% ethanol.** Further distillation forms a **constant boiling mixture** (an azeotropic mixture) whose **composition does not change.** This mixture is known as **rectified spirit.** The rectified spirit is stored over **quick lime** in the laboratory.

Subsequently the mixture is **refluxed over quicklime** for about **6 hours** and then **allowed to stand overnight** to obtain absolute ethanol which is then **distilled off.**

In industry, **benzene is added** to the rectified spirit and then **fractionally distilled.** Pure ethanol is obtained at 78°C.

Uses of ethanol

(i) Manufacture of ethanoic acid.

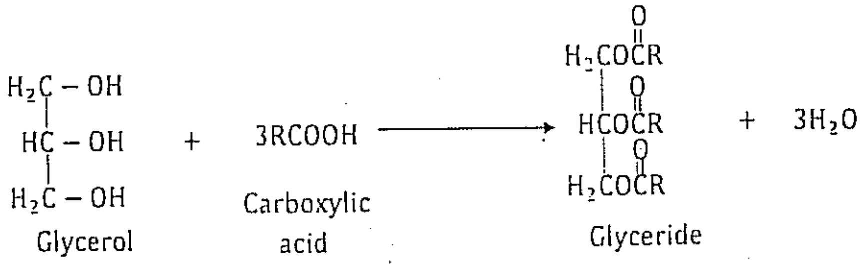
(ii) Manufacture of ethylesters.

(iii) As a solvent for many organic compounds.

11.2 Soaps and soapless detergents

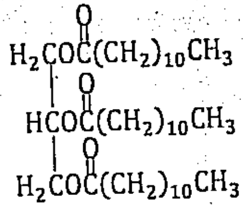
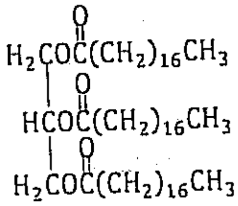
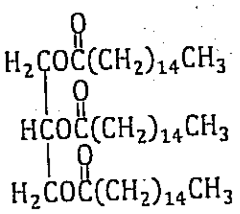
11.2.1 Soap

Soap is a **sodium or potassium salt of a long chain carboxylic acid.** Soaps are obtained from **vegetable oils** or **natural fats** known as **glycerides.** The fats (glycerides) are esters of a **triol** known as **glycerol** or **propane – 1, 2, 3 – triol** and **long chain carboxylic acids** as shown by the general equation below.



The carboxylic acid used to obtain the glycerides are usually saturated and have an even number of carbon atoms in the range (12-20).

Examples are shown below:

Carboxylic acid	*Formula*	*Glyceride (fat used to form soap)*
Dodecanoic acid (lauric acid) (12 carbon atoms)	$CH_3(CH_2)_{10}COOH$	 $H_2CO\overset{\overset{O}{\|}}{C}(CH_2)_{10}CH_3$ $HCO\overset{\overset{O}{\|}}{C}(CH_2)_{10}CH_3$ $H_2CO\overset{\overset{O}{\|}}{C}(CH_2)_{10}CH_3$
Octadecanoic acid (stearic acid) (18 carbon atoms))	$CH_3(CH_2)_{16}COOH$	 $H_2CO\overset{\overset{O}{\|}}{C}(CH_2)_{16}CH_3$ $HCO\overset{\overset{O}{\|}}{C}(CH_2)_{16}CH_3$ $H_2CO\overset{\overset{O}{\|}}{C}(CH_2)_{16}CH_3$
Hexadecanoic acid (palmitic acid) (16 carbon atoms)	$CH_3(CH_2)_{14}COOH$	 $H_2CO\overset{\overset{O}{\|}}{C}(CH_2)_{14}CH_3$ $HCO\overset{\overset{O}{\|}}{C}(CH_2)_{14}CH_3$ $H_2CO\overset{\overset{O}{\|}}{C}(CH_2)_{14}CH_3$

Any of the fat (glyceride) above or others not shown can be used to make soap. Fats **are solids at room temperature** and are **saturated** compounds. They can be obtained from coconut.

However vegetable oils are **liquids at room temperature** and are **highly unsaturated** and are usually obtained from **plants**.

Samples of the oils include **cotton seed** oil, **sim sim** oil, **groundnut** oil, **sunflower** oil, **palm** oil and **cashew nut** oil, e.t.c.

11.2.2 Extraction of Animal Fat and Vegetable Oils

Animal Fat

The animal tissue is **heated with water**. The fat **melts and floats** on the surface of the hot water. The molten fat is then **skimmed off** into a separate container, **allowed to cool** until it solidifies.

Vegetable Oils

Using groundnut seeds;

The **dried seeds** are roasted and then **crushed** to obtain a **paste**. The paste is **added to water** and the mixture **boiled until oil floats on top of the mixture.** The oil is then **decanted off.**

11.2.3 Preparation of Soap

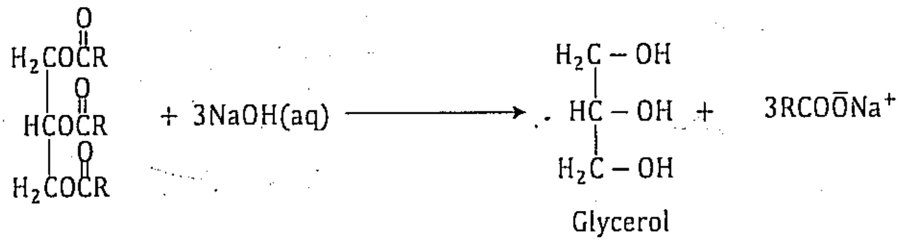
Soap is prepared by the process called saponification.

Procedure

The vegetable oil / animal fat is **boiled** with **concentrated sodium hydroxide solution** while **stirring** until the vegetable oil / fat **completely dissolves**.

The solution is **cooled** and **concentrated sodium chloride** (brine) is added to **precipitate soap**. The **soap floats** and is **skimmed off**. It can then be processed into **bars** or **soap powder**.

General Equation:



$$\begin{array}{l} H_2COCR \; (\overset{O}{\|}) \\ HCOCR \; (\overset{O}{\|}) \\ H_2COCR \; (\overset{O}{\|}) \end{array} + 3NaOH(aq) \longrightarrow \underset{\text{Glycerol}}{\begin{array}{l} H_2C-OH \\ HC-OH \\ H_2C-OH \end{array}} + 3RCO\bar{O}Na^+$$

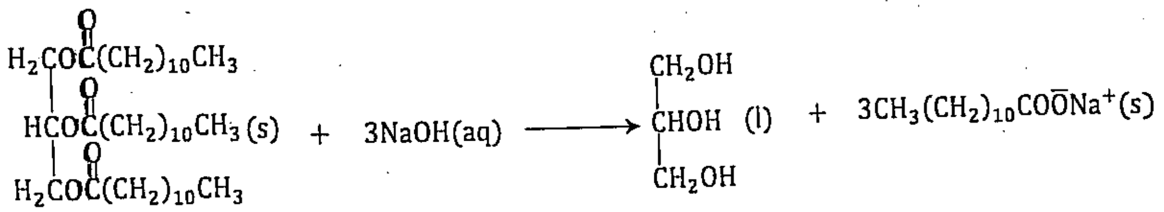
Where R is an alkyl group.

Note:

(a) Glycerol is a valuable bi-product because it is used in the manufacture of nitroglycerin which is a constituent of many explosives. Glycerol is also used in manufacture of glyptal plastics.

(b) Sodium soaps have limited solubility in water and can be obtained as solid cakes. Whereas potassium soaps are more soluble and are used as gels in shampoos and shaving creams.

(c) If the glyceride used is specified then in the equation for the reaction R is specified. For example:



$$\begin{array}{l} H_2C\text{–}O\text{–}\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3 \\ HC\text{–}O\text{–}\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3\,(s) \\ H_2C\text{–}O\text{–}\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3 \end{array} + 3NaOH(aq) \longrightarrow \begin{array}{l} CH_2OH \\ CHOH\ (l) \\ CH_2OH \end{array} + 3CH_3(CH_2)_{10}CO\bar{O}Na^+(s)$$

(d) If the mass of glyceride used is known, then we can calculate the mass of soap formed.

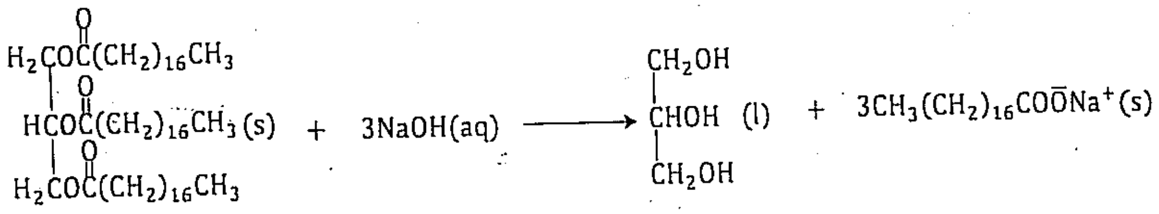
Worked Example

Soap was prepared from 96.95g, of a fat mainly derived from octadecanoic acid,

(a) Write equation for the reaction leading to formation of soap.

(b) Calculate the mass of soap formed after complete reaction.

(a)



$$\begin{array}{l} H_2C\text{–}O\text{–}\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \\ HC\text{–}O\text{–}\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3\,(s) \\ H_2C\text{–}O\text{–}\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \end{array} + 3NaOH(aq) \longrightarrow \begin{array}{l} CH_2OH \\ CHOH\ (l) \\ CH_2OH \end{array} + 3CH_3(CH_2)_{16}CO\bar{O}Na^+(s)$$

(b)

Molar mass of the ester

$$= (12 \times 19 \times 3) + (16 \times 2 \times 3) + (37 \times 2) + (36 \times 1)$$

$$= 890g$$

$$\text{Number of moles of ester used} = \frac{96.95}{890} = 0.108933$$

1 mole of ester form 3 moles of soap.

$$0.108933 \text{ moles of ester form } \left(\frac{0.108933 \times 3}{1}\right) \text{moles of soap}$$

$$= 0.326798 \text{ moles of soap}$$

Molar mass of soap($CH_3(CH_2)_{16}COONa$)

$$= (18 \times 12) + (35 \times 1) + (16 \times 2) + (23 \times 1)$$

$$= 306g$$

$$\text{Mass of soap formed} = 306 \times 0.326798$$

$$= 100g$$

11.2.4 The cleansing action of soap

Soap acts **by lowering the surface tension** between **water** and **oil / grease** or **other insoluble material** and also **emulsifying them.**

The soap molecule has both a **long chain hydrocarbon chain** which is **non-polar** and **hydrophobic** and a **carboxylate group** which is **polar** and **hydrophilic.** When soap is added to water, the **hydrocarbon chain** (alkyl group) **is attracted** to **the oil/grease** and the **carboxylate group is attracted to the water.** This **reduces the surface tension between water and the dirt.** The oil / grease / dirt particles are **removed** and **suspended in water** (emulsified).

Note

(a) Soap is **not effectively used in hard water** because it forms **insoluble calcium** or **magnesium salts** (scum) leading to **soap wastage.**

$$2RCOONa(aq) + Mg^{2+}(aq) \longrightarrow (RCOO)_2Mg(s) + Na^+(aq)$$

$$2RCOONa(aq) + Ca^{2+}(aq) \longrightarrow (RCOO)_2Ca(s) + Na^+(aq)$$

Lather can only be formed when all the magnesium ions or calcium ions are completely precipitated as scum.

(b) Soap is not recommendable for continuous use when washing aluminium utensils. This is because soap is a salt of a **strong base** and a **weak organic acid.** Soap therefore undergoes **hydrolysis** in solution to form **week acid** and **hydroxide** ions.

$$RCOO^-(aq) + H_2O(aq) \rightleftharpoons RCOOH(aq) + \bar{O}H(aq)$$

The **hydroxide ions react with aluminium**, to form **aluminate ions** and **hydrogen.** This causes **wearing** off of aluminum utensils.

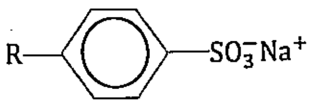
$$2Al(s) + 2\bar{O}H(aq) + 6H_2O(aq) \longrightarrow Al(OH)_4^-(aq) + 3H_2(g)$$

(c) Soaps with longer alkyl chains are **more effective** than those with shorter alkyl chains. For example sodium octadecanoate ($CH_3(CH_2)_{16}COONa$), also called sodium stearate, is more effective than sodium dodecanoate ($CH_3(CH_2)_{10}COONa$). This is because sodium octadecanoate has a **longer non-polar,** hydrophobic alkyl chain, which **congregates more dirt than that in sodium dodecanoate.**

11.2.5 Soapless Detergents

Soapless detergents are sodium salts of alkyl benzene sulphonic acids or sodium salts of long chain alkylhydrogensulphate.

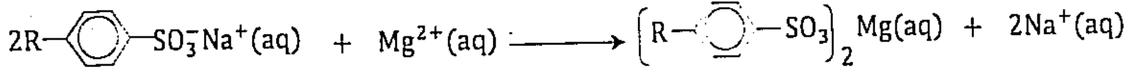
Their general structures are as shown below;



or $RCH_2OSO_3^-Na^+$

Where R is an alkyl group.

Unlike soaps, soapless detergents have the **sulphonate group** (in **alkylbenzenesulphonates**) and **sulphate group** (in alkyl sulphates) instead of the carboxylate group. Therefore detergents are **effective even in hardwater** because the corresponding **magnesium** or **calcium salts formed** are **soluble.**



$$2RCH_2OSO_3^-Na^+(aq) + Mg^{2+}(aq) \longrightarrow (RCH_2OSO_3)_2Mg(aq) + 2Na^+(aq)$$

Examples of common detergents include: Omo, Nomi, surf, etc.

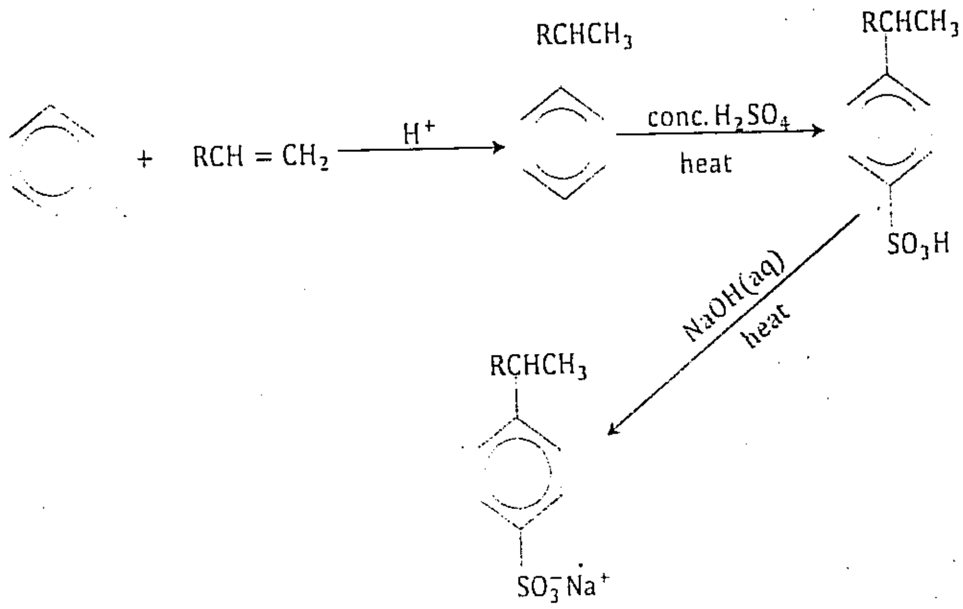
11.2.6 Preparation of Soapless detergents

(a) The most commonly used detergents are sodium salts of alkylbenzene sulphonic acids. These are made from:

(i) Non-branched, alkenes containing 12 – 18 carbon atoms.

Procedure

Benzene is reacted with a **long chain alkene** in presence **of an acid** to form **alkylbenzene**. The alkylbenzene formed is **heated** with **concentrated suplhuric acid** to form an **alkylbenzene sulphonic acid** which is then heated with **sodium hydroxide solution** to form a **detergent** or **alkylbenzenesulphonate**.



(ii) From an alcohol

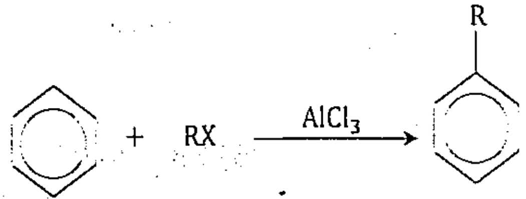
The **long chain alcohol** is **heated** with **excess concentrated sulphuic acid** to form an **alkene.**

$$RCH_2CH_2OH \xrightarrow[180°C]{conc.\ H_2SO_4} RCH = CH_2$$

The **alkene formed** is then **treated as in procedure (a)(i)** above **to obtain** the **detergent.**

(iii) From an alkylhalide

Benzene is reacted with a **long chain alkylhalide** in the presence of **aluminum chloride** to form **alkylbenzene.** The alkylbenzene is then treated as in (a)(i) above until the alkylbenzene sulphonate is obtained.



(b) Detergents in the form of sodium salts of long chain alkylhydrogen sulphates are prepared by the procedure described below:

They are prepared from long straight chain alcohols.

A **long chain alcohol** (for example dodecanol) is reacted with **cold concentrated sulphuric acid** and the mixture **stirred** to form an **alkylhydrogen sulphate** (dodecylhydrogen sulphate for dodecanol). The **alkylhydrogen sulphate** is reacted with **sodium hydroxide solution** to form a **detergent** (a sodium alkylsulphate).

$$CH_3(CH_2)_{10}CH_2OH \xrightarrow{conc.\ H_2SO_4} CH_3(CH_2)_{10}CH_2OSO_3H \xrightarrow{NaOH(aq)} CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$$

Note

Some additives are added to detergents for specific uses. These include:

(i) Sodium sulphate – to increase the bulk of the detergent.

(ii) Inorganic phosphates – react with calcium ions in the dirt to form soluble complex calcium salts.

(iii) Sodium peroxoborate – to act as bleaching agent.

11.2.7 The cleansing action of soapless detergents

Soapless detergents act in essentially the same way as soap does.

The soapless detergent molecule has an **alkylbenzene group** or a long alkyl chain which is **non-polar** and **hydrophobic** and a **sulphonate group** (for alkylbenzenesulphates) that is **polar** and **hydrophilic**. When a **soapless detergent is added to water**, the **alkylbenzene group / alkyl chain** is **attracted to the oil grease/dirt** and the **sulphonate / sulphate group** is **attracted to the water**. This reduces the surface **tension between water and the dirt**. The dirt particles are **removed** and **suspended** in water (emulsified).

Advantage of soaps over detergents

Soaps are biodegradble whereas the alkylbenzenesulphonates are only slowly biodegradable.

Disadvantage of soap

Soap forms scum with hard water leading to soap wastage.

Advantage of soapless detergents over soaps

Detergents can be used even in hard water because their Calcium and magnesium salts are soluble in water.

Disadvantages of detergents over soap

- Alkylbenzene sulpohonates are only slowly biodegradable hence pollute the environment.
- Detergents also contain inorganic phosphates which are nutrients for algae growth which deprives lakes and rivers of oxygen. This leads to suffocation of aquatic organisms hence death.

11.3 Polymers and Polymerization

A polymer is large molecular mass compound formed by repeatedly joining together many smaller molecules called *monomers*.

The monomers are connected by covalent bonds.

Polymerization is the process by which many small molecules are repeatedly joined together to form a large molecular mass compound.

There are fundamentally two types of polymerization. They include:

(i) **Addition polymerization**
(ii) **Condensation polymerization.**

11.3.1 Addition polymerization

This is the type of polymerization in which very many molecules of an unsaturated monomer join together to form a large molecule which has the same empirical formula as the monomer without loss of small molecules.

Examples of addition polymers include:

(i) Poly(ethene)
(ii) Poly(phenylethene); also called polystyrene
(iii) Poly(propene)
(iv) Poly(chloroethene); also called polyvinylchloride (PVC)
(v) Poly(methyl2-methylpropenoate); also called Perspex.
(vi) Poly(tetrafluroethene); also called PTFE or Teflon or Fluon.
(vii) Natural rubber and synthetic rubbers.
(viii) Poly(propenonitrile); also called Orlon.

Details about structure, preparation, properties and uses f each of the addition polymers are described below:

(i) Poly(ethene)

Poly(ethene) is also called Polythene. Its monomer is ethene ($H_2C = CH_2$) and the polymer has the structure $-(CH_2CH_2)_n-$.

There are two types of poly (ethene).

(a) Low density poly(ethene)

This type has a low softening point (about 120°C). It is formed by compressing ethene at a high pressure of 1500 atmospheres and a temperature of 200°C in a very small amount of oxygen. This is called the ICI high pressure process.

Equation

$$nH_2C = CH_2 \xrightarrow[1500atm,\ 200^\circ C]{O_2\ initiator} -CH_2CH_2-_n$$

Low density poly(ethene) is used;

- As a film for packaging and for coating.
- As a covering for cables.
- For making plastic bags.
- For making toys.

(b) High density poly(ethene)

This type has a higher softening point (about 130°C). It is made by passing ethene into an inert solvent (usually an aromatic hydrocarbon) containing a suspension of triethylaluminium and titanium(IV) chloride as catalyst.

A dilute acid is added after polymerization and polyethene filtered off. This is called the **Zeigler process.**

$$nH_2C = CH_2 \xrightarrow[\text{(ii) dilute acid}]{\text{(i) } (CH_3CH_2)_3Al + TiCl \text{ /Aromatic hdrocarbon}} -\!\left[CH_2CH_2\right]\!-_n$$

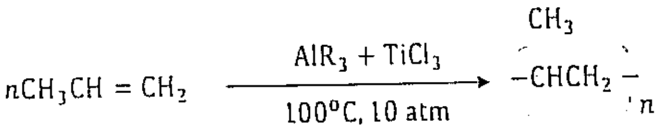
High density poly(ethene) is more rigid than low density poly(ethene) and is used:

- For making kitchen ware, food boxes, bowls and buckets
- Making good quality mouldings including bottles, etc.

(ii) Poly(propene)

Poly(propene) can be used in place of poly(ethene) due to the advantages it has over poly(ethene). It is lighter, tougher and has a higher melting point than poly(ethene). Poly(propene) has a high tensile strength that enables it to be pulled to make tough fibres.

Poly(propene) is made by passing propene under pressure into an inert solvent (heptane) which contains a trialkylaluminium and a titanium compound.



$$nCH_3CH = CH_2 \xrightarrow[100^\circ C,\ 10\ atm]{AlR_3 + TiCl_3} -\!\left[\overset{CH_3}{CH}CH_2\right]\!-_n$$

The polymer is used for:

- Making ropes, carpets and bottles.
- Making packaging materials.

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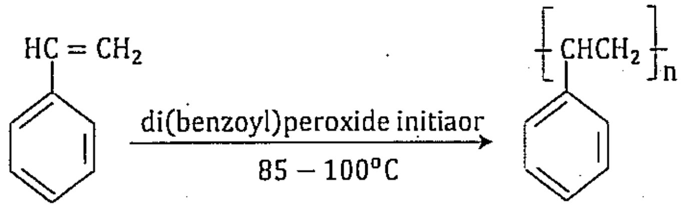
(iii) Poly(phenylethene)

Poly(phenylethene) is also called polystyrene. It's free radical polymerization is done by using di(benzoyl) peroxide as an initiator at a temperature of 85-100°C

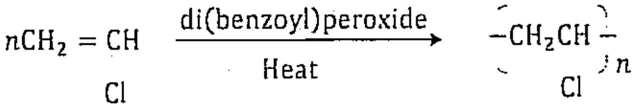


The uses of poly(phenylethene) include:

- Making thermal and electrical insulators
- Making light weight packaging materials
- Making household goods like egg boxes
- Making lining material for refrigerators
- Making theatrical properties
- For decorative purposes etc.

(iv) Poly(chloroethene)

It is also called polyvinyl chloride (PVC). Poly(chloroethene) is formed by heating chloroethene in an inert solvent with di(benzoyl) peroxide to initiate polymerization.



$$nCH_2=\underset{Cl}{CH} \xrightarrow[\text{Heat}]{\text{di(benzoyl)peroxide}} \left[-CH_2\underset{Cl}{CH}-\right]_n$$

PVC is a very tough polymer. A plasticizer is usually added to soften it. The polymer is also easy to colour.

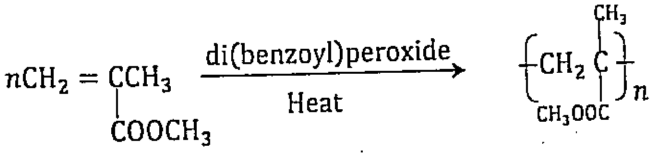
It is also resistant to weathering, fire and chemicals and a good electrical insulator.

Uses of Polyvinyl chloride (PVC)

- Manufacture of plastic raincoats, curtains, furniture coverings, water piping and guttering, and floor coverings.
- As an insulator for cables.
- Manufacture of artificial leather e.g. car upholstery.
- Making gramophone records, etc.

(v) Poly(methyl 2-methylpropenoate)

This polymer is also called Perspex, plexiglass or Diakon (in its powder form). It is formed in the same way as poly(phenylethene).



$$nCH_2 = \underset{\displaystyle COOCH_3}{CCH_3} \xrightarrow[\text{Heat}]{\text{di(benzoyl)peroxide}} \left[CH_2 - \underset{\displaystyle CH_3OOC}{\overset{\displaystyle CH_3}{C}} \right]_n$$

Perspex is a light, strong and transparent plastic.

It has a variety of uses although most frequently used as replacement for glass.

The uses include:

- Packaging
- Making aeroplane windows, lenses and corrugated roof lights.

(vi) Poly(tetrafluoroethene) – (PTFE)

This is also called Teflon or Fluon. It is made by heating tetrafluolroethene under pressure in the presence of ammonium peroxosulphate as a catalyst.

$$nF_2C = CF_2 \xrightarrow{(NH_4)_2S_2O_8 \text{ catalyst}} \left(-CF_2CF_2- \right)_n$$

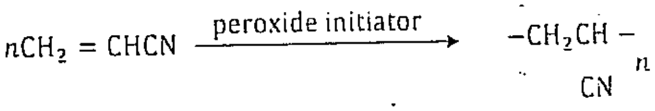
Teflon has a high softening point of 327°C and very stable at temperatures in excess of 400°C. It is also highly resistant to chemicals and has a low coefficient of friction.

Uses of Teflon include:

- Making seals and gaskets.
- Surface coating for cooking equipment.
- Making low friction bearings.

(vii) Poly(propenonitrile)

This is also called Polyacrylonitrile or Orlon. The equation for its formation from the monomer (propenonitrile) is as shown below:



$$nCH_2 = CHCN \xrightarrow{\text{peroxide initiator}} \left(-CH_2\underset{\displaystyle CN}{CH}- \right)_n$$

The polymer is used for making clothes, blankets and carpets.

(viii) Rubber

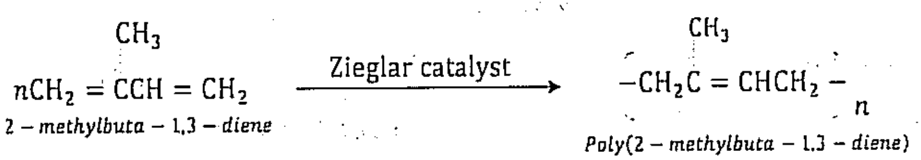
There are two forms of rubber namely;

- Natural rubber.
- Artificial / synthetic rubber

(a) Natural rubber

Raw rubber is obtained from Latex, which is an emulsion of rubber particles in water found in the bark of many tropical and sub-tropical trees.
The Latex extrudes from the bark when the tree is cut. The raw rubber is the coagulated by adding ethanoic acid.

Natural rubber is also called polyisoprene and is a polymer of the monomer whose IUPAC name is 2-methylbuta-1, 3-diene (also called Isoprene).



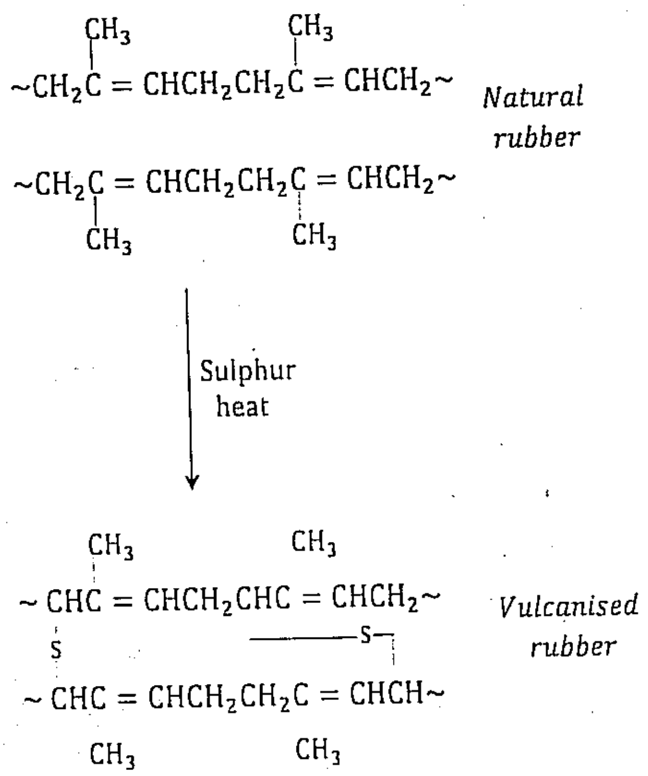
$$\underset{2-methylbuta-1,3-diene}{nCH_2 = \overset{CH_3}{C}CH = CH_2} \xrightarrow{\text{Zieglar catalyst}} \underset{Poly(2-methylbuta-1,3-diene)}{\left[-CH_2\overset{CH_3}{C} = CHCH_2-\right]_n}$$

Natural rubber is not strong enough and not an elastic enough material for use. It softens and becomes sticky on heating. On cooling it becomes hard and brittle. These problems can be largely solved by a process called *vulcanization.*

Vulcanization of rubber

The raw rubber is heated with up to 8% sulphur. The sulphur forms cross-linkages between neighbouring polymeric chains of rubber. Accelerators of vulcanization are used to increase the rate of combination and to allow the process take place at a lower temperature.
The accelerators may be organic or inorganic

Illustration



$$\begin{array}{c}\sim CH_2\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}=CHCH_2\sim \\ \sim CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2\sim\end{array}\xrightarrow[\text{heat}]{\text{Sulphur}}\begin{array}{c}\sim \underset{S}{CH}\overset{CH_3}{C}=CHCH_2CH\overset{CH_3}{C}=CHCH_2\sim \\ \text{—S—} \\ \sim CH\underset{CH_3}{C}=CHCH_2CH_2\underset{CH_3}{C}=CHCH\sim\end{array}$$

Vulcanized rubber is better for use than natural rubber because;

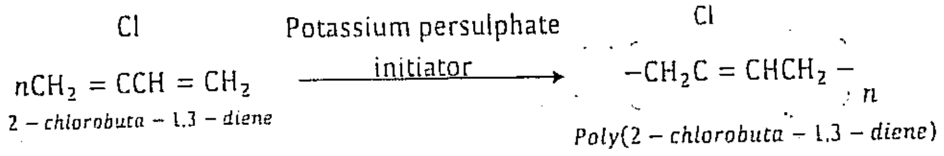
- It has a greater tensile strength.
- It is more durable
- It is more elastic.

(b) Synthetic rubber

Synthetic rubber, also called Neoprene is the polymer whose IUPAC name is poly(2-chlorobuta-1, 3-diene), and is made from the monomer, 2-chlorobuta-1, 3-diene.

Neoprene rubber is resistant to organic solvents and is strong.

However, it is more expensive to produce than natural rubber. During polymerization, potassium persulphate is used as a catalyst.



$$nCH_2=\overset{Cl}{C}CH=CH_2 \xrightarrow[\text{initiator}]{\text{Potassium persulphate}} \left(-CH_2\overset{Cl}{C}=CHCH_2-\right)_n$$

Uses of rubber

- Making coverings for underwater cables.
- Making golf balls.
- Making car tyres.
- Making shoe soles.
- Making waterproof boots.
- Making hoses and gaskets etc.

11.4.2 Condensation Polymerization

This is the type of polymerization in very many **molecules of two different bifunctional monomers** join together to form a large molecule with loss of **small molecules** such as **water, ammonia, methanol, carbon dioxide** and **hydrogen chloride.**

Examples of condensation polymers include:

(i) Terylene; also called Dacron or Fortrel
(ii) Nylon 6, 6
(iii) Nylon 6, 10
(iv) Bakelite
(v) Melamine
(vi) Proteins
(vii) Lipid
(viii) Polyurethanes
(ix) Silicones
(x) Wool

Details about structure, preparation, properties and uses of some of the condensation polymers are described below:

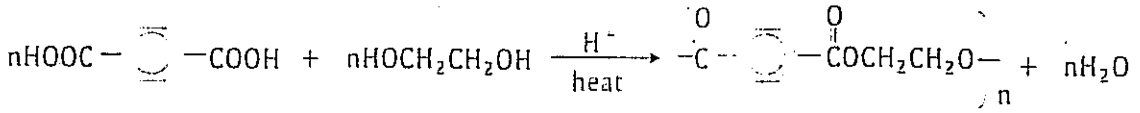
(i) Terylene

Terylene is also known as Dacron or Fortrel. It is polyester formed by the interaction between a dicarboxylic acid and a diol. Terylene is formed from two monomers;

(a) Benzene – 1,4 – dicarboxylic acid, HOOC— —COOH

(b) Ethane – 1,2 – diol, $HOCH_2CH_2OH$

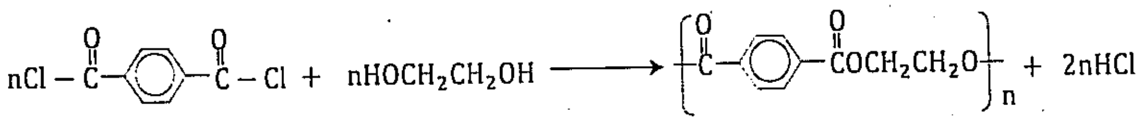
Equation



An acid catalyst is used in the above reaction and water molecules are lost.

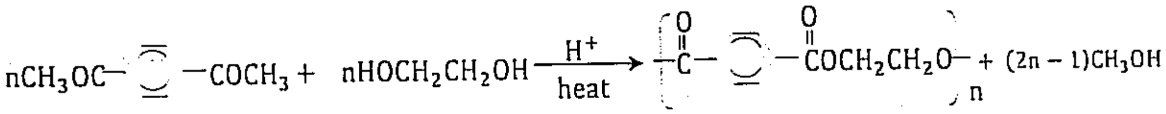
Instead of benzene-1, 4- dicarboxylic acid, Benzene-1, 4-dioyldichloride can be used and ethane-1, 2-diol.

Equation



In this reaction, no catalyst is required. Molecules of hydrogen chloride are lost.

Another method is to use a methyl ester of benzene-1, 4-dicarboxylic acid which is known as Dimethylbenzene -1-4- dicarboxylate and ethane-1, 2-diol. This reaction also requires an acid catalyst.



Methanol molecules are lost.
Polyesters have good thermal and chemical stability although they can be hydrolysed by alkalis. They can make permanent creases in fabrics.

Uses of polyesters e.g. Terylene

- Making clothes
- Making ropes
- Making safety belts

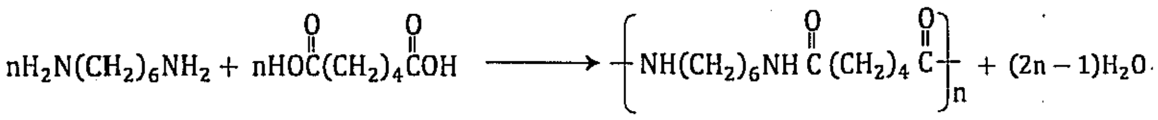
(ii) Nylon 6,6

Nylons belong to a class of polymers called polyamides.
Nylon 6, 6 is called so because it is made from two monomers, each of which has 6 carbon atoms.
The monomers are

(a) Hexane – 1,6 – diamine, $H_2N(CH_2)_6NH_2$

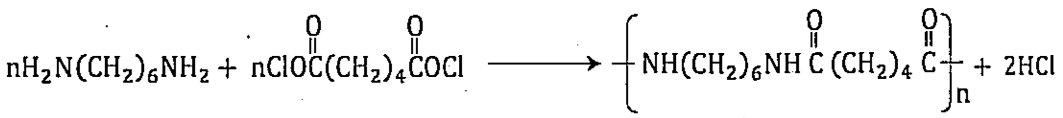
(b) Hexane – 1,6 – dioic acid, $HOOC(CH_2)_4COOH$

Equation



$$nH_2N(CH_2)_6NH_2 + nHO\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OH \longrightarrow \left[NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n + (2n-1)H_2O$$

Similarly, hexane-1, 6-dioyldichloride can be used instead of the dioic acid as monmer.



$$nH_2N(CH_2)_6NH_2 + nClO\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCl \longrightarrow \left[NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n + 2HCl$$

In this case, hydrogen chloride is eliminated instead of water.

Nylon 6, 6 is greatly versatile and its manufacture is done at a low cost. It is also insoluble in common solvents, has a melting point of 263°C, strong, tough, rigid and resistant to chemical attack.

It is used for:

- Making fishing nets, bottles, ropes and clothing.
- Making sutures, gears, unlubricated bearings and tarpaulins.

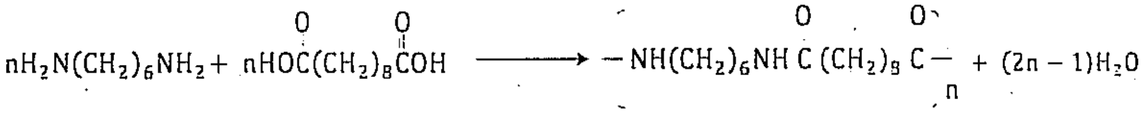
(ii) Nylon 6,10

Nylon 6,10 is called so because it is formed from a diamine with 6 carbon atoms and a dioic acid or a dioyldichloride with 10 carbon atoms. Therefore, the monomers are;

(a) Hexane – 1,6 – diamine, $H_2N(CH_2)_6NH_2$

(b) Decane – 1,10 – dioic acid, $HOOC(CH_2)_8COOH$

<u>Equation</u>



$$nH_2N(CH_2)_6NH_2 + nHO\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OH \longrightarrow -NH(CH_2)_6NH\overset{O}{C}(CH_2)_8\overset{O}{C}-_n + (2n-1)H_2O$$

Similarly, hexane-1, 10-dioyldichloride can be used instead of the dioic acid as monmer.

$$nH_2N(CH_2)_6NH_2 + nClO\overset{O}{\overset{|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OCl \longrightarrow -NH(CH_2)_6NH\overset{O}{C}(CH_2)_8\overset{O}{C}-_n + 2HCl$$

In this case, hydrogen chloride is eliminated instead of water.

Nylon 6,10 has properties similar to Nylon 6,6. Nylon 6,10 is useful in making synthetic bristles.

(iv) Bakelite

This is a condensation polymer formed from phenol and methanol.

It is used for making switches, electrical plugs, radio cases, fuse holders and doors handles.

11.4.3 Differences between addition and condensation polymerization.

Addition polymerization	*Condensation Polymerization*
Involves one type of monomer	Involves two different types of monomers
All atoms of the monomer form part of the polymer	Some atoms of the monomers are lost in form of small molecules
Empirical formula of polymer is the same as that of monomer	Empirical formula is different from the constituent monomers
Monomers usually contain at least a cabon-carbon double bond	Monomers do not have carbon-carbon double bonds.
Molecular weight of polymer is an integral multiple of the molecular weight of monomer	Molecular weight of the polymer is not an integral multiple of molecular weight of any of the monomers.

11.4.4 Classes of Polymers

Polymers can be classified as natural or synthetic.

(a) Natural Polymers

These are naturally occurring polymers not made by man. Examples are summarized in the table below:

Type of natural polymer	*Examples*	*Monomer(s)*	*Uses*
Addition natural polymers	Natural rubber	2-Methylbuta-1, 3-diene	Making car tyres, shoe sols, golf balls, etc.
	Wool	Amino acids	Making clothings, blankets, woolen carpets etc.
Condensation natural polymers	Cotton	Cellulose	making clothes, bed sheets, paper, etc,
	Silk	Amino acids	Making clothes, beddings, etc.

	Starch	Glucose	Manufacture of ethanol, as animal food, etc.

(b) Synthetic polymers

These are man-made polymers. Examples are summarized in the table below:

Type of artificial polymer	*Examples*	*Monomer(s)*	*Uses*
Addition synthetic polymers	Poly(ethene)	Ethene	Packaging, making plastic bags, buckets, etc.
	Poly(phenylethene) (polystyrene)	Phenylethene	Making packaging materials, egg boxes, etc.
	Poly(chloroethene) (PVC)	Chloroethene	Plastic rain coats, curtains, insulator for cables, etc.
	Perspex	Methyl-2-methyl-propenoate	Making lenses, aeroplane windows, corrugated rooflights etc.
	Teflon	Tetrafluroethene	Making seals and gaskets etc
	Synthetic rubber	2-Chlorobuta-1, 3-diene	Making car tyres, shoe soles, golf balls, etc.
Condensation synthetic polymers	Terylene (Dacron)	Ethane-1,2-diol & Benzene-1, 4-dicarboxylic acid	Making clothes, ropes, safety belts, etc
	Nylon 6, 6	Hexane-1, 6-diamine Hexane-1, 6-dioic acid	Making fishing nets, bottles, ropes, clothings, sutures, etc.
	Nylon 6,10	Hexane-1, 6-diamine Decane-1, 10-dioic acid	

	Bakelite	Phenol & methanol	Making switches, electrical plugs, fuse holders etc.
	Melamine	Methanal & melamine	Making table ware, plates, etc

11.4.5 Fibres

Some polymers can be classified as fibres.

Fibres are **polymers which can be made into thin, strong threads that can made into thin, strong threads**.

Fibres can also further be classified as natural or synthetic fibres. Example are summarized below. Their uses, properties and monomers from which they are derived have already been discussed.

Natural fibres	*Synthetic fibres*
Wool	Nylon 6, 6
Cotton	Nylon 6,10
Silk	Poly(propenonitrile)

These fibres are used in the textile industry

11.4.6 Plastics

A plastic is a polymerized organic solid substance of a high molecular mass which at some time in its manufacture can be shaped to flow.

Plastics can be moulded into required shapes and for manufacture of a wide range of substances.

Plastics are widely used to manufacture many substances because of its properties. These include toughness, resistance to water and corrosion, ease of moulding, colour change and insulation to electricity and heat.

The properties of plastics can be modified by the following substances:

(i) Plasticisers

These compounds, for example esters of benzene 1, 2, - dicarboxylic acids with long chain alcohols, are added to PVC to make it softer and a more easily worked material.

(ii) Dyes and pigments

These are added to give plastic colour.

(iii) Filler

This increases the bulk of the plastic, making it less expensive without altering its desirable properties.

There are two types of plastics namely; ***thermosoftening plastics*** and ***thermosetting plastics.***

(a) Thermosoftening plastics

These are also called **thermoplastics.**

These are plastics which become soft when heated hence can be remoulded.

Thermoplastics easily soften on heating because they consist of long polymer chains held by weak intermolecular forces which require only small changes in temperature to overcome. Examples of thermoplastics include:

(i) Poly(ethene)
(ii) Polyvinyl chloride
(iii) Poly(propene)
(iv) Perspex

(b) Thermosetting Plastics

These are also called thermosets.

These are **plastics which contain a three-dimensional network of bonds and are moulded during the polymerization stage of their manufacture and cannot be softened to be remoulded on heating.**

These polymers require very strong heating to bring about any form of chemical change. This is because the three-dimensional structure in them has chains that are cross-linked and held by strong covalent bonds.

Examples of thermosets include:

(i) Bakelite
(ii) Melamine
(iii) Polyurethanes
(iv) Vulcanized rubber
(v) Epoxyresins
(vi) Glyptal resins, etc.

Differences between thermoplastics and thermosets

Thermoplastics	*Thermosets*
Have low melting point	Have high melting
Soften on heating and can be reshaped	Not easily softened on heating hence cannot be reshaped
Polymeric chains held by weak vander waal's forces of attraction	Polymeric chains are held by strong covalent bonds
They have linear polymeric chains	The polymeric chains are cross-linked
Thermoplastics can be recycled	Thermosets cannot be recycled
Are soft and flexible	Are hard and brittle

Effects of Plastics on the environment

Plastics are non-bio degradable hence their poor disposal to the environment leads environmental pollution. When some plastics are burnt, they form toxic gases like hydrogen chloride from PVC, hydrogen cyanide from poly(propenonitrile). These problems can most effectively be overcome by recycling.

11.5 End of topic assessment exercise

1. Ethanol can be formed by fermentation of molasses.

   (a) (i) Name two other raw materials from which ethanol can be produced by fermentation using molasses.

   (ii) Write equations to show how crude ethanol formed in (a) above.

   (b) Describe how 100% (absolute) ethanol can be produced from crude ethanol formed in (a) above.

   (c) Write equation(s) to show each of the following compounds could be obtained from ethanol.

   (i) Polythene

(ii) Ethoxyethane.

2. Vegetable oils have great economic and social importance

(a) (i) Explain what is meant by the term vegetable oils.

(ii) Name two sources of vegetable oils.

(iii) Describe how vegetable oil can be obtained on a large scale from one of the sources you have named in (a) (i) above. (Technical details are not required)

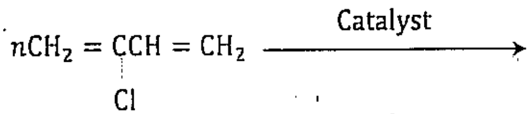
(b) (i) State the name given to the reaction leading to the formation of soap from oil.

(ii) Write a general equation for the formation of soap from oil.

(iii) Outline how soap is manufactured. (Technical details not required).

3. Complete the following equations and give the IUPAC name of the major organic

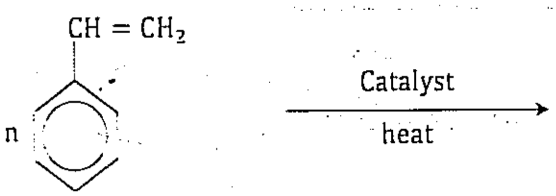
(i)



$$nCH_2 = \underset{Cl}{C}CH = CH_2 \xrightarrow{\text{Catalyst}}$$

(ii) $nCH_3CH = CH_2 \xrightarrow{\text{Catalyst}}$

(iii)



4. (a) (i) State the main difference between fats and vegetable oils.

(ii) Name any one source of vegetable oils.

(b) (i) Define the term soap.

(ii) State a chemical name of any soap you know.

(c) (i) Briefly describe how soap can be prepared from any vegetable oil.

(ii) When 9.5g of an oil derived from $C_{15}H_{31}COOH$ (hexadecanoic acid) was boiled with sodium hydroxide, soap was formed. Calculate the mass of soap formed.

(iii) State two uses of the byproduct formed in (iii) above.

(d) (i) Explain how soap removes dirt from a fabric.

(ii) State the difference between a soap and a soapless detergent.

(iii) State one advantage and one disadvantage of a soapless detergent over soap.

5. (a) Distinguish between soap and soapless detergent.

(b) Using equations only describe how an alkylbenzene sulphonate can be prepared from dodecan-1-ol.

(c) Briefly explain the cleansing action of a soapless detergent.

(d) State one:

(i) advantage of soap over a detergent.

(ii) disadvantage of soap over detergent.

6. Soap was prepared form a fat derived from hexadecanoic acid,

(i) Explain briefly how soap is formed from the fat.

(ii) Write the equation leading to formation of soap.

(iii) Calculate the mass of soap formed.

7. (a) Name any two sources of vegetable oils.

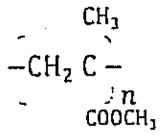
(b) Describe briefly how vegetable oil can be obtained on a large scale from one of the sources you have named in (a).

(c) Soap was prepared from 19.0g of oil formed between hexadecanoic acid, and glycerol.

(i) Write equation for the reaction leading to formation of soap.

(ii) Calculate the mass of soap formed.

8. Perspex is a polymer of structure:



$$\left[-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-\right]_n$$

(a) Name the reaction leading to formation of Perspex.

(b) Write the structure and give the IUPAC name of the monomer used to manufacture Perspex.

(c) A solution containing 5.5g of Perspex in 1dm^3 of benzone has an osmotic pressure of 6.796×10^{-2} atmospheres at 25°C. Calculate the:

(i) Molecular mass of perspex.

(ii) Value of n

(iii) State one application of Perspex

9. (a) Explain what is meant by the term "condensation polymerization".

(b) Nylon-6, 10 can be made by reacting hexane-1, 6-diamine and decane dioyldichloride.

Write the structural formula of:

(i) Hexane-1, 6-diamine

(ii) Decane dioyldichloride

(iii) Nylon-6, 10

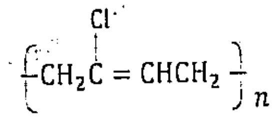
(c) State one use of nylon-6, 10.

10. The osmotic pressure of a solution containing 1.4g of a polymer per 100cm^3 of a solution is 1200Nm^{-2} at 25°C.

(a) Calculate the relative molecular mass of the polymer.

(b) If the molecular mass of the monomer is 28, determine the number of monomers in the polymer.

11. (a) Neoprene, is a synthetic polymer which has the following structure



$$\left[-CH_2\overset{Cl}{\overset{|}{C}}=CHCH_2-\right]_n$$

(i) Name the type of polymerization reaction which leads to formation of neoprene.

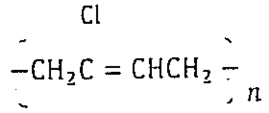
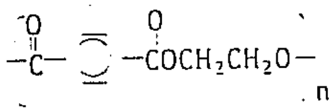
(ii) Name of the monomer from which neoprene is formed.

(b) When 350g of the monomer was polymerized 9.89 x 10^{-2} moles of neoprene was formed. Calculate the relative molecular mass of neoprene.

(c) State one use of neoprene.

12. (a) Distinguish between thermoplastics and thermosetting plastics.

(b) For each of the following polymers write the structure(s) of the monomer(s) from which they were synthesized.

Polymer	Structure of monomer
 $\left[-CH_2\overset{Cl}{C}=CHCH_2-\right]_n$	
 $\left[-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{C}OCH_2CH_2O-\right]_n$	

(c) A solution containing 1.00g of polyphenylethene in 100cm^3 of benzene is found to have an osmotic pressure of 59 Nm^{-2} at 27°C. Calculate the average relative molecular mass of polyphenylethene.

13. Chloroethene, hexane-1, 6-dioic acid and hexane-1, 6-diamine are monomers for two polymers.

(a) Define the term polymer

(b) Write the structural formulae of:

(i) Chloroethene

(ii) Hexane-1, 6-dioic acid

(iii) Hexane-1, 6-diamine

(c) Write the:

(i) Structural formula of the polymer and type of polymerization undergone by chloromethane.

(ii) Name and structural formula of polymer formed from hexane-1, 6-dioic acid and hexane-1, 6-diamine.

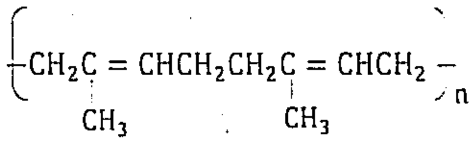
(d) State one use of each of the polymers in (c) above.

(e) Name one natural polymer formed by the same reaction as:

(i) The polymer in (i) above.

(ii) The polymer in (ii) above.

14. Natural rubber has the following structure



$$\left[-CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_2- \right]_n$$

(a) Write the structure and name of the monomer of natural rubber.

(b) (i) Name the type of polymerization by which natural rubber is formed.

(ii) Give a reason for your answer in (b) (i) above.

(c) When 135g of the monomer was polymerized, 584 x 10^{-3} moles of natural rubber was formed. Calculate the relative molecular mass of natural rubber.

15. (a) Explain what is meant by the terms:

(i) Addition polymerization

(ii) Condensation polymerization

(b) Natural rubber is a natural polymer formed by addition polymerization. Write the structural formula and name of the monomer of natural rubber.

(c) One stage involved in the processing of rubber is vulcanization.

(i) Describe how vulcanization is carried out.

(ii) What is the effect of vulcanization on the properties of rubber?

(iii) Give one use of rubber.

(d) Write the structural formula and name of the monomer of synthetic rubber.

(e) Polyphenylethene is another polymer formed by addition polymerization.

Write equations to show how polyphenylethene is prepared starting form benzene.

(f) Nylon 6,6 is also a polymer formed by condensation polymerization.

(i) Write the structural formula(e) and name(s) of the monomers of nylon 6,6.

(ii) Write the equation leading to formation of nylon 6,6.

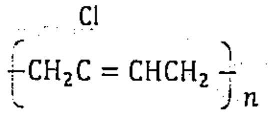
16. (a) Teflon, which is used in making non-stick utensils is an addition polymer whose synthesis is represented by the equation below:

$$nF_2C = CF_2 \xrightarrow[(NH_4)_2S_2O_8\ \text{catalyst}]{H_2O\ \text{under pressure}} \left[CF_2CF_2 \right]_n$$

What is meant by an addition polymer?

(b) 3.0g of Teflon were dissolved in 2 litres of solvent X at 25C. The osmotic pressure of the resultant solution was 247.9Nm^{-2}. Calculate the value of n is the formular of Teflon.

17. (a) Neoprene rubber is a polymer with the structure.



$$\left[CH_2\overset{Cl}{C} = CHCH_2 \right]_n$$

(i) Name the type of reaction by which neoprene is formed.

(ii) Write equation leading to formation of neoprene rubber. (Indicate condition(s) for the reaction)

(b) A solution containing 28.76gdm^{-3} of neoprene rubber had an osmotic pressure of 0.23 atmosphere at 27°C. Determine the,

(i) molecular mass of the polymer.

(ii) number of monomers in the formula of the polymer.

18. (a) Soap can be prepared from a vegetable oil or an animal fat.

Briefly describe how an oil can be extracted form a natural source.

(b) (i) Briefly describe how soap is prepared.

(ii) Write the equation for the reaction leading to formation of soap.

(iii) State one advantage and one disadvantage of using soap.

(iv) Briefly explain the cleansing action of soap.

(c) (i) Distinguish between soap and a non-soapy detergent.

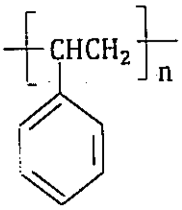
(ii) Starting from duodecan-1-ol, write equations to who how you would prepare a soapless detergent.

(d) (i) Distinguish between addition and condensation polymerization.

(ii) Write equations to show how the polymers, Perspex, Terylene and nylon 6, 6 are formed.

(e) State the difference between thermosetting and themosoftening plastics.

19. The structure of a polymer, G, is,



The osmotic pressure of a solution containing $5.5gdm^{-3}$ of G in benzene is 106.39 Pa at 20°C.

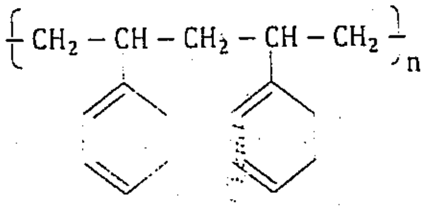
(i) Calculate the relative molecular mass of G.

(ii) Determine the number of monomers that formed polymer G.

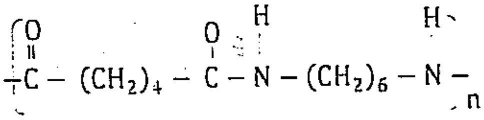
20. (a) Distinguish between addition and condensation polymerization.

(b) The structural formulae of polymers; P, Q, R and S are given below.

P :

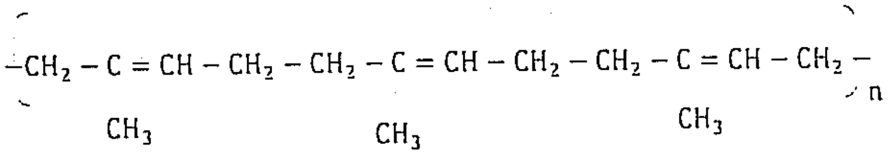


Q :



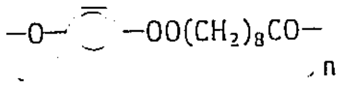
$$\left[\overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \right]_n$$

R :



$$\left[-CH_2 - \underset{CH_3}{C} = CH - CH_2 - CH_2 - \underset{CH_3}{C} = CH - CH_2 - CH_2 - \underset{CH_3}{C} = CH - CH_2 - \right]_n$$

S :



In the table below, write the structural formula of the monomer(s) in each case and name the type of polymerization that lead to the formation of each polymer.

	Structural formula of monomer(s)	Type of polymerization
P		
Q		
R		
S		

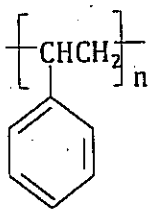
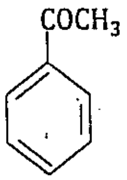
(i) Give use of Q

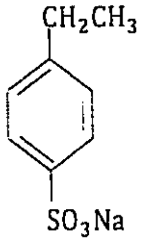
(ii) R exists as natural rubber. State how it is treated before putting it to industrial use.

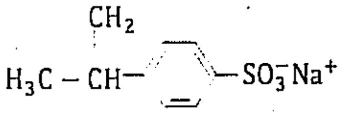
21. Nylon 6,6 is a synthetic polymer made by condensation polymerization.
    (a) Explain the terms:
        (i) Synthetic polymer
        (ii) Condensation polymerization
    (b) (i) Write the structure of nylon 6,6.
        (ii) Give one example of a natural polymer formed by the same type of reaction as Nylon 6,6.
        (iii) State the monomer of the polymer given in b (ii) above.
    (c) (i) Name one soapless detergent.
        (ii) Using available materials, write equations to how how the detergent named in (b) (i) above is prepared.

22. (a) (i) An organic compound Q, consists of 38.7% Carbon, 51.613% oxygen and the rest being hydrogen. The density of Q is 2.7662g per litre at s.t.p. Calculate the empirical formula of Q.
        (ii) Determine the molecular formula of Q.
    (b) (i) Q is oxidized by nitric acid to form a dioic acid and then carbon dioxide and water.
        (ii) Explain why Q boils at 197°C but ethanol boils at 75°C.
    (c) (i) Q reacts with a dioic acid K to form a polyester. Name K and draw the structure of the polyester.
        (ii) Name one use of the polyester in (c) (i) above.

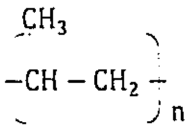
23. Write equations to show how the following conversions can be effected.

(a)  from 

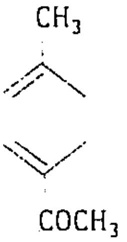
(b)  from ethyne

(c)  from benzene

(d) Nylon 6,6 from Cyclohexanol

(e) Propanol to 

$$\left[-\underset{}{\overset{CH_3}{CH}}-CH_2-\right]_n$$

(f)  to Terylene