ORGANIC CHEMISTRY NOTES

CHAPTER 1

INTRODUCTION

What is Organic chemistry?

Is the branch of chemistry that deals with the study of compounds of carbon

All organic compounds contain carbon together with one or more other elements such as hydrogen, oxygen, chlorine, Nitrogen and sulphur

These organic compounds range from simple molecules such as methane, ethene, ethyne, giant molecules such as Deoxyribonucleic acid (DNA),rubber, cotton, drugs, insecticides, explosives and photographic films- of which all these compounds are of great importance in everyday life

Organic chemistry is also the foundation for basic studies in Botany, nutrition, agriculture, pharmacy, technology, forestry, zoology etc

UNIQUENESS OF CARBON IN ORGANIC COMPOUNDS

Carbon behaves differently from the rest of the group members due:

- Small Atomic radius
- High electronegativity
- Lack of vacant orbital

Some of the properties in which Carbon differs from the rest of the members include:

- It forms a stable multiple bonds with itself and with other non-metals.
- Carbon can form a number of hydrocarbons because it can catenate. Catenation is the ability of the element to form bonds between atoms of the same element.
- It forms gaseous oxides unlike other members
- The halides are stable to hydrolysis.

CHARACTERISTIC PROPERTIES OF ORGANIC COMPOUNDS

Most organic compounds are:

- Covalently bonded and generally gases, volatile liquids and low melting point solids with few elements such as carbon, hydrogen, sulphur, nitrogen and halogens
- Low melting and boiling point compounds
- Generally insoluble in water except those with polar functional groups such as $-OH$, $-COOH$, $-SO_3H$
- The reactions are generally slow although some are explosive and most reactions require catalysts

REACTANTS AND REACTIONS

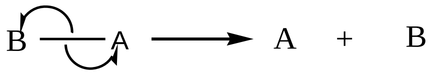
In chemical reactions, the reactants molecules are that are attacked are called SUBSTRATE but the general term given to the attacking substrate is called a REAGENT.

Substrates and Reagents usually interact to yield the products involve redistribution of electrons.

Generally there are two ways in which a covalent bond can be broken include:

(a) Homolytic cleavage

In this type, the bond is broken symmetrically and each atom remains with one electron to form a radical. Example include



These types of reactions are usually catalysed by:

- Ultraviolet light or short wavelength light or sunlight
- High temperatures
- Peroxide

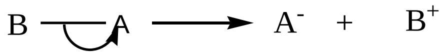
(b) Heterolytic cleavage

In this of the reactions, the bonds are broken unsymmetrically generating cation and anion

If the molecule contains different atoms with different electronegativity, the tendency of ions formation differs.

These breakages usually take place in solvents of high ionizing power which is catalysed by ionic polar catalysts

Example include: If A is more electronegative than B, then



CARBOCATION OR CARBONIUM IONS

These are formed when fragments of a molecule in which a group and the bonding electrons are removed from the carbon chain

Carbocations are divided into 1^0, 2^0 and 3^0

The stability of the Carbocations depend on the number of the electron releasing group e.g. CH_3 and is expressed as $3^0 > 2^0 > 1^0$

ELECTROPHILES AND NUCLEOPHILES

Electrophiles are species which are electron loving since they are electron deficient while Nucleophiles are species which are electron rich

Examples of Electrophiles and Nucleophiles include:

Electrophiles: $\overset{+}{N}O_2$, H+, Cl^+, Br^+,R_3C^+ and RN_2^+

Nucleophiles: H_2O, ROH,RO^- ,^-OH, Br^- CN^- and NH_3

HYDROCARBONS

These compounds that contain carbon and hydrogen as the only elements present.

They are classified as:

(a) Saturated hydrocarbons

These are hydrocarbons that contain a carbon- carbon single bond e.g. in Alkanes

(b) Unsaturated hydrocarbons

These are hydrocarbons that contain multiple bonds between the carbon atoms e.g Alkenes

Further classification includes:

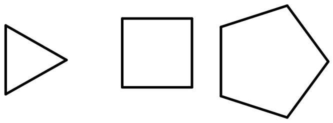
(a) Aliphatic Hydrocarbons

These are hydrocarbons that contain low carbon-hydrogen ratio. Usually on burning, they burn with a non-sooty flame.

(b) Aromatic hydrocarbons

These are hydrocarbons that contain a high carbon- hydrogen ratio. Usually on burning, they burn with a sooty flame. These compounds are usually considered as derivatives of benzene.

N.B Also Alicyclic hydrocarbons which are hydrocarbons in which carbon atoms are arranged in the ring other than benzene ring e.g



FUNCTIONAL GROUPS AND HOMOLOGOUS SERIES

Homologous series is a series in which organic compounds can be placed. The characteristics of homologous series include;

- Member of a homologous series can be represented by a general formula e.g. C_nH_{2n+2} for Alkanes, C_nH_{2n} for Alkenes
- Each member of a series has a similar method of preparation
- Members in a given series has a similar chemical properties to each other
- As a series is ascended down, a methylene group is added to each successive member therefore physical properties such as boiling and melting points change slightly.
- Several homologous series are regarded as alkane derivatives since the hydrogen atom in the alkane is replaced by a functional group

Functional group is atom or group of atoms which impart specific chemical properties to the chemical compounds containing then regardless of the nature of the hydrocarbon part of the molecule.

Generally Organic compounds are classified based upon the functional group because compounds having the same functional groups have the similar chemical properties.

The table below shows some of the examples of functional groups:

Name	Structural formula	Examples
Alkane	RH or C_nH_{2n+2}	$CH_3CH_2CH_3$
Alkenes	$RCH{=}CH_2$ or C_nH_{2n}	$CH_3CH{=}CH_2$
Alkynes	$RC\equiv CR$ or $C_n H_{2n-2}$	$CH_3C\equiv CCH_3$
Halogen compounds	RCH_2X (x=Cl, Br and I)	CH_3CH_2Cl
Alcohols	RCH_2OH or $C_nH_{2n+1}OH$	CH_3CH_2OH
Carbonyl compounds	Aldehydes: RCHO or $C_nH_{2n+1}CHO$ Ketones: RCOR or $C_nH_{2n+2}CO$	CH_3CH_2CHO CH_3COCH_3
Carboxylic acids	RCH_2COOH or $C_nH_{2n+1}COOH$	CH_3COOH
Amines	RCH_2NH_2or $C_nH_{2n+1}COOH$	$CH_3CH_2NH_2$,CH_3NHCH_3
Ethers	ROR or $C_nH_{2n+1}O$	$CH_3CH_2OCH_3$

TYPES OF ORGANIC REACTIONS

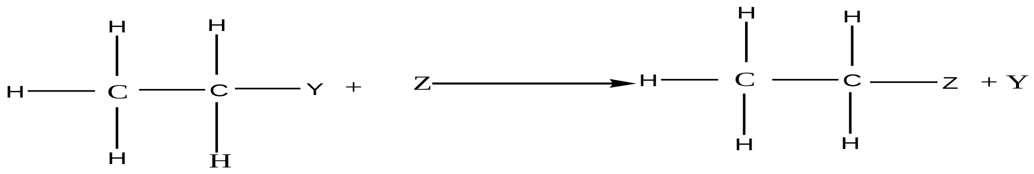
Organic reactions are usually initiated by Electrophiles or Nucleophiles or free radical attack upon the substrate. These reactions include:

(a) Substitution or Displacement reactions

These reactions involve the direct displacement of an atom or group by another atom or group.

The number of atoms displaced depends on the nature of the reactants and conditions under which the reaction is carried out.

Generally they are represented as;



e.g.

$$CH_3CH_2Cl \xrightarrow[\text{Heat}]{\text{NaOH (aq)}} CH_3CH_2OH + NaCl$$

Substitution reactions are divided into two classes:

(i) Nucleophilic substitution reaction (S_N).

These are reactions whereby electron rich species simply displaces an atom or group. These reactions are undergone by Alkyl halides.

(ii) Electrophilic substitution reaction (S_E)

These are reactions where by electron deficient group displaces an atom. These reactions are undergone by Benzene where hydrogen atom is replaced by an electron deficient group

According to the number of species involved in the formation of the activated complex in the rate determining step, Nucleophilic substitution reaction is divided into two:

(i) Nucleophilic substitution unimolecular (S_N1) where a single species is involved.

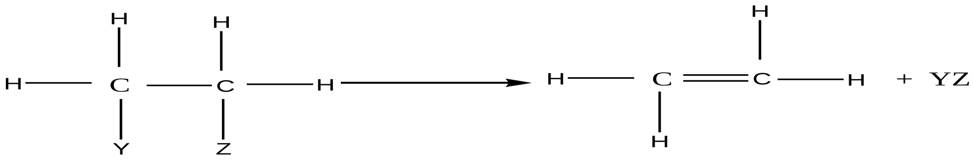
(ii) Nucleophilic substitution Bimolecular (S_N2) where two species are involved.

(b) Elimination reactions

These are reactions involve the removal of atoms or groups of atoms from two adjacent atoms to form a multiple bond or unsaturated compound.

These reactions are usually encountered to yield alkenes and alkynes

Generally they are represented as;



$$H-\overset{H}{\underset{Y}{C}}-\overset{H}{\underset{Z}{C}}-H \longrightarrow H-\underset{H}{C}=\overset{H}{C}-H + YZ$$

e.g.

$$CH_3CH_2OH \xrightarrow[180^oC]{Conc.H_2SO_4} H_2C=CH_2 + H_2O$$

Elimination reaction is also divided into two types based upon the number of species involved in the formation of activated complex in the rate determining step.

(i) Elimination Unimolecular (E_1) e.g dehydrohalogenation and dehydration of 3^0 Alkyl halides and Alcohols respectively

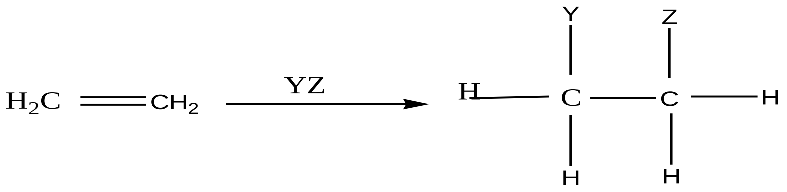
(ii) Elimination Bimolecular (E_2) e.g dehydrohalogenation and dehydration of 2^0 Alkyl halides and Alcohols.

(c) Addition reactions

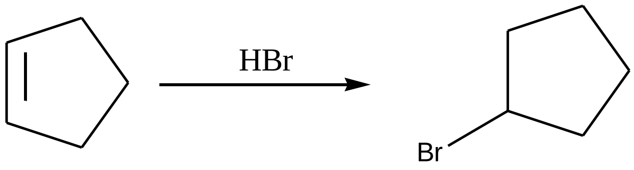
These are reactions wherebythe attacking reagent simply adds across the unsaturated bond of the reactant to saturated product.

These reactions are usually the reverse of the elimination reactions and the unsaturated reactants act as Nucleophiles and consequently more vulnerable to attack by Electrophiles.

These are reactions are generally represented as:



Example include



Addition reactions are divided into classes:

(i) Electrophilic addition reactions (A_E)

These are reactions where the electron loving species simply adds itself to unsaturated compound e.g. addition reactions of alkenes and alkynes.

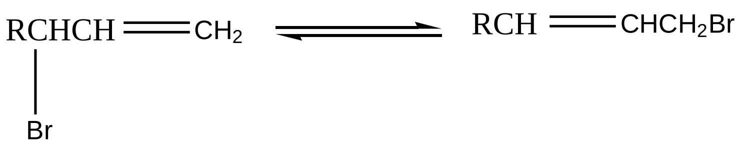
(ii) Nucleophilic addition reactions (A_N)

These are reactions where the electron rich species simply adds itself to the unsaturated bond of the bond e.g. addition reactions of carbonyl compounds

(d) Rearrangement reactions

These are reactions which involve the migration of an atom or group from one site to another within the same molecule. It involve the migration of a functional group from one position to another within the same molecule

Example include



$$RCH(Br)CH{=}CH_2 \rightleftharpoons RCH{=}CHCH_2Br$$

MECHANISM OF ORGANIC REACTIONS

Mechanisms of reaction are sequence steps by which the reactions take place from start to the end. The mechanism is worked out from a study of the kinetics of the reactions. Other method include spectroscopy and use of radioactive isotopes

ISOMERISM

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

Compounds with same molecular formulae but different structural formulae are known as Isomers. Isomerism is divided into two classes:

(a) Structural Isomerism

This is the type of isomerism which shows the sequence in which the atoms in a molecule are bonded or linked.

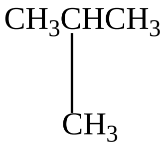
It is divided into three classes:

(i) Chain Isomerism. This is the type of structural isomerism where by the isomers differ in the carbon chain. The isomers usually have the same functional group and belong to the same homologous series.

It can be divided into classes⍰ i.e. Straight chain and branch chain

Example included: *Q has molecular formula C_4H_{10}, write down possible chain structural formula of Q. Since the M.F. is C_4H_{10} isomers are:*

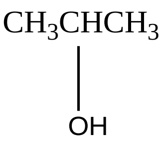
$CH_3CH_2CH_2CH_3$ and



$$CH_3CH(CH_3)CH_3$$

(ii) Positional Isomerism. This is the isomerism where the substituent groups are in different positions in the same carbon skeleton. The isomers are chemically similar because they possess the same functional groups

$CH_3CH_2CH_2OH$ and



$CH_3CH(OH)CH_3$

$CH_3CH_2CH{=}CH_2$ and $CH_3CH{=}CHCH_3$

(iii) Functional Isomerism. This is the isomerism where by the isomers in different homologous series have different functional groups.

Examples include:

(a) A compound Q has Molecular formula C_2H_6O

$\Rightarrow$ *The isomers are* CH_3CH_2OH *(from Alcohol) and* CH_3OCH_3 *(from ether)*

(b) A compound W has molecular formulaC_3H_6O

$\Rightarrow$ *The isomers are* CH_3COCH_3 *(from Ketones) and* CH_3CH_2CHO *(from Aldehydes)*

(c) A compound Z has molecular formula $C_4H_8O_2$

$\Rightarrow$ *The isomers are* $CH_3CH_2CH_2COOH$ *(from Carboxylic acid) and*

$CH_3COOCH_2CH_3$ *(from Esthers)*

(b) Stereoisomerism

This is the type of isomerism where by the compounds have the same molecular formula and same structural formula but differ in the spatial arrangement of the bonds.

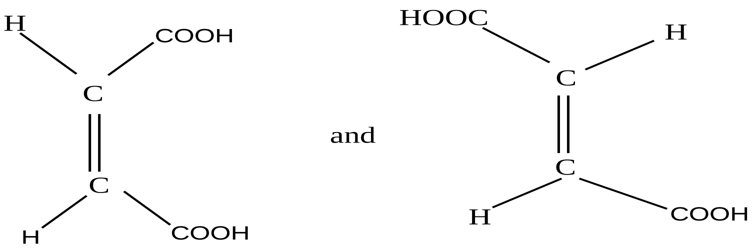
Stereoisomerism is divided into two classes:

(i) Cis-trans Isomerism (Geometrical Isomerism)

This occurs in compounds in which free rotation is prevented by the presence of multiple bonds, a ring or steric factors.

Geometrical Isomers differ in spatial arrangement giving rise to Cis isomers which has identical atoms or groups on the same side of the multiple bond and a Trans isomers which has the atoms or groups in opposite side.

Examples include:



Cis-isomers

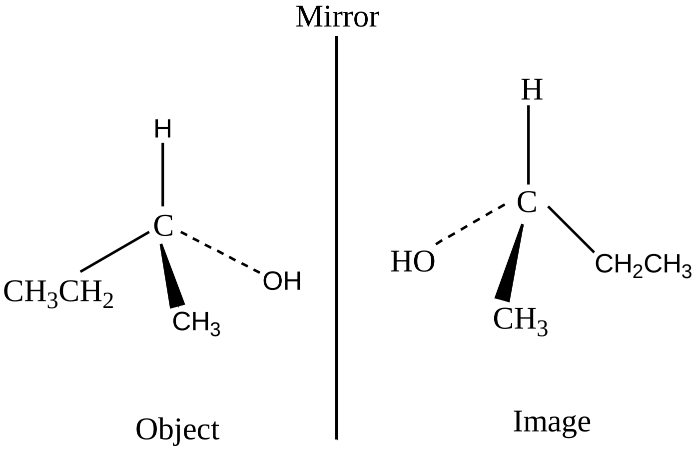
Trans-isomers

(ii) Optical Isomerism

This occurs in compounds with four atoms or groups attached to the same carbon such that the isomers obtained are not super imposable on the mirror images.

These isomers which are not super imposable are referred as to as Enantiomers and the structures are said to be chiral.

Example includes:



Enantiomers have same physical properties but may be distinguished from each other by the ability they rotate polarized light due to optical activity.

If the rotation of the plane is in clockwise direction (to the right), the substance is dextrorotatory (with + sign) while if the rotation is in the anticlockwise (to the left), the substance is laevorotatory (with ⍰ sign)

The degree of rotation is determined by use of a polarimeter.

METHODS OF RELATIVE MOLECULAR MASS DETERMINATION OF ORGANIC COMPOUNDS

The four commonly used methods for determining the relative molar mass of organic compounds include:

(a) Vapour density measurements using gas syringe or Victor Meyer's method

Example

A hydrocarbon Q contains 91.3% carbon and the rest hydrogen.

(a) Determine the empirical formula of Q (C=12, H=1)

(b) The vapour density of Q is 39 at a constant temperature and pressure.

Determine the:

(i) Molecular mass of Q

(ii) Molecular formula of Q

(c) Q burns with a sooty flame, write down the possible isomer(s) of Q

Soln:

(a)

Elements:	*C*		*H*
Masses (%):	*91.3*		*8.7*
Moles:	$\frac{91.3}{12}$		$\frac{8.7}{1}$
=	*7.6083*		*8.7*
Mole ratio:	$\frac{7.6083}{7.6083}$	*:*	$\frac{8.7}{7.6083}$
=	*1*	*:*	*1*

$\Rightarrow$ *E.F. of Q is CH*

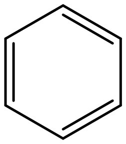
(b) (i) From $\frac{M.mass}{2} = v.density$ $M.mass = 39 \times 2 = 78g$

(ii) From M.F= (E.F)$_n$ *= M .mass*

$(CH)_n = 78$ *Or* *n (12+1) = 78* $\therefore n = 6$

$\Rightarrow M.F$ *Of Q is* C_6H_6

(c) The molecular structure of Q is



Example

When 0.29g of substance Q was burnt in oxygen, 0.66g of carbondioxide and 0.27g of water were formed.

(a) Calculate the empirical formula of Q

(b) Q forms a yellow solid with 2, 4-dintrophenylhydrazine. The vapour density of Q is 29.

(i) Write the structural formulae of the isomers and names of Q

(ii) What type of structural isomerism is exhibited by Q.?

(iii) How can the structural isomers be differentiated

Soln:

(a) *RFM of* $CO_2 = 1(12) + 2(16) = 44$

RFM of $H_2O = 2(1) + 1(16) = 18$

Mass of Carbon in Q = $\frac{1(12)}{44}\times 0.66 = 0.18g$

Mass of Hydrogen in Q = $\frac{2(1)}{18}\times 0.27 = 0.03g$

$\Rightarrow$ *Mass of Oxygen in Q = 0.29- (0.18+ 0.03)*

= 0.08g

Elements:	*C*	*H*	*O*
Masses (g):	*0.18*	*0.03*	*0.08*
moles:	$\frac{0.18}{12}$	$\frac{0.03}{1}$	$\frac{0.08}{16}$
=	*0.015*	*0.03*	*0.005*
Ratio:	$\frac{0.015}{0.005}$	$\frac{0.03}{0.005}$	$\frac{0.005}{0.005}$
	3:	*6 :*	*1*

$\Rightarrow$ *E.F. of Q is* C_3H_6O

(b) (i) M. mass of Q = 29×2 = 58g $\Rightarrow (C_3H_6O)_n = 58$

$\therefore n(3(12) + 6(1) + 1(16)) = 58$ *or* $58n = 58$ *or* $n = 1$

M.F of Q is C_3H_6O with S.F CH_3COCH_3 Propanone and CH_3CH_2CHO- Propanal

(ii) Functional Isomerism

(iii) By using Ammoniacal Silver nitrate solution

Example

(a) Define the hydrocarbon

(b) A compound X, on combustion gave 0.629g of carbondioxide and 0.257g of water. Determine the empirical formula of X

(c) When 0.10g of X was vapourised, it occupied a volume of 40cm3 at s.t.p

(i) Calculate the molecular mass of X

(ii) Determine the molecular mass of X hence write the structural formulae of the possible isomers

Soln:

(a) A compound that contains carbon and hydrogen as the only elements present

(b) Mass of Carbon = $\frac{1(12)}{44}\times 0.629 = 0.1715g$

Mass of Hydrogen = $\frac{2(1)}{18}\times 0.257 = 0.0286g$

Elements:	*C*	*H*
Moles:	$\frac{0.1715}{12}$	$\frac{0.0286}{1}$
=	*0.0143*	*0.0286*

Hence mole ratio = 1:2 $\Rightarrow$ *E.F of X is CH_2*

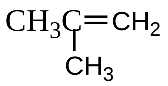
(c) (i) From PV = nRT $\Rightarrow Mr = \frac{mRT}{PV}$

$$= \frac{0.1\times 8.314\times 273}{101325\times 40\times 10^{-6}} = 56g$$

(ii) $(CH_2)_n$ = 56

n (12+2) = 56 $\Rightarrow n = 4$

$\therefore$ *M.F of X is C_4H_8*



$CH_3C(CH_3){=}CH_2$

$CH_3CH_2CH{=}CH_2$

$CH_3CH{=}CHCH_3$

(b) Colligative Properties of dilute solutions containing non-volatile solutes

These include lowering of vapour pressure, cryoscopy, ebullioscopy and osmotic pressure

Cryoscopic method has an advantage over Ebullioscopic method that it is not affected very much by pressure changes of which boiling points depend on the atmospheric pressure

Molecular mass of polymers is determined using Osmotic pressure because they are easily denatured by heat and a amount of polymer changes the osmotic pressure of the solvent significantly.

Example

A compound W contains Carbon, Hydrogen and oxygen. When 1.5g of W was burnt in excess oxygen, 1.467g of carbon dioxide and 0.297g of water were formed.

(a) Determine the empirical formula of W

(b) 7.5g of W was dissolved in 204.4g of water to a solution .The prepared boiled at 100.212^oC.

The boiling point constant of water is 0.52^oC per mole per kg.

Determine the:

(i) Molecular mass of W

(ii) Molecular formula

(iii) Structural formula of w

(c) State the condition(s) employed in order for W to react with following compounds.

In each case write the equation of reaction

(i) Sulphuric acid

(ii) Potassium manganate (VII) solution

(d) Name the reagent that can be used to distinguish between W and Methanoic acid.

Soln:

(a) Mass of hydrogen = $\frac{2}{18}\times 0.297$ *= 0.033g, Mass of Carbon =* $\frac{12}{44}\times 1.467 = 0.40g$

$\therefore$ Mass of oxygen = 1.5- (0.033+0.40) = 1.067g

Elements:	*C*	*H*	*O*		*0.033*	*0.033*	*0.067*
Moles:	$\frac{0.40}{12}$	$\frac{0.033}{1}$	$\frac{1.067}{16}$		*$\Rightarrow$ Mole ratio:*	*1: 1: 2*	

$\therefore$ E.F of W is CHO_2

$\Delta T = 100.212 - 100 = 0.212^oC$

(b) (i) 204.4g of water contains 7.5g of W

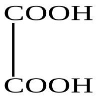
$\Rightarrow$ 1000g of water contains $\frac{7.5}{204.4}\times 1000 = 36.69g$ *of W.*

0.212^oC is the elevation in b.p.t caused by 36.69g of W

$\therefore$ 0.52 ^oC is the elevation in b.p.t caused by $\frac{36.69}{0.212}\times 0.52 = 90g$ *of W*

(ii) $(CHO_2)_n$= 90 $\Rightarrow$ n = $\frac{90}{45} = 2$ *$\therefore$ M.F of W is $C_2H_2O_4$*

(iii)



$$\begin{array}{c}COOH\\ |\\ COOH\end{array}$$

(c) (i) Concentrated acid and heat

$$H_2C_2O_4 \xrightarrow[\text{Heat}]{\text{Conc.}H_2SO_4} H_2O + CO + CO_2$$

(ii) Acidified Potassium permanganate solution and warm the solution to about 70^oC

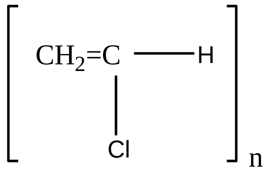
$$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

(d) Ammoniacal Silver nitrate solution

Example

(a) Differentiate between Diffusion and Osmosis

(b) The osmotic pressure of a solution containing $4.00gdm^{-3}$ of polyvinylchloride,



$$\left[\begin{array}{c} CH_2{=}\underset{|}{\overset{}{C}}{-}H \\ Cl \end{array}\right]_n$$

In dioxin is 65Pa at 20^oC. Determine the number of monomers, n, in the polymer.

(c) State two conditions under which the Osmotic laws cannot be obeyed

Soln

(a) Diffusion is the movement of molecules from high concentrated area to a low concentrated area while Osmosis is the movement of solvent molecules from a dilute solution to concentrated solution across a semi-permeable membrane

(b) From $\Pi v = nRT \Rightarrow Mr = \frac{mRT}{\Pi V}$ = $\frac{4\times 8.314\times 293}{65\times 10^{-3}} = 149.91\times 10^{3}$

$\therefore$ *n (24+3 + 35.5)=149.91X10^3* $\Rightarrow n = 2399$

(c) When the solution is concentrated

When the solute associate or dissociate in the solvent

(c) Eudiometry method or Gaseous explosion

This method is suitable for gaseous hydrocarbon only

Example

(a) State Gay-Lussac’s law.

(b) 30cm^3 of a gaseous hydrocarbon Y burnt at constant temperature and pressure produced 120cm^3 of carbon dioxide and 120cm^3 of steam.

(i) Determine the formula of Y.

(ii) Write structures and names of all the isomers of Y.

Soln

(a) When gases combine together at a constant temperature and pressure they do so in volumes which bear a simple ratio to each other and to the volume of gaseous product.

(b) (i)

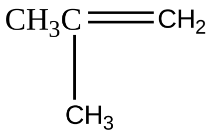
$$\begin{array}{lllll} CxHy & + \ (x+y/_4)\ O_2 & \longrightarrow & xCO_2 & + \ y/_2H_2O \\ 30cm^3 & 30(x+y/4)cm^3 & & 30xcm^3 & 15ycm^3 \end{array}$$

$\Rightarrow$ 15y=120 or y= 8

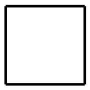
$\Rightarrow$ 30x=120 or x=4 C_4H_8

(ii)

$CH_3CH_2CH{=}CH_2$ $CH_3CH{=}CHCH_3$



$CH_3\underset{CH_3}{C}{=}CH_2$



Example

30cm^3 of gaseous hydrocarbon were mixed with 140cm^3 of excess oxygen and exploded. After cooling to room temperature the residual gases occupied 95cm^3. By absorption with potassium hydroxide solution a diminution of 60cm^3 was produced. Determine the molecular mass of the hydrocarbon

Soln

$$\begin{array}{lllll} C_xH_y & + \ (x+ y/4)\ O_2 & \longrightarrow & xCO_2 & + \ y/2\ H_2O \\ 3ocm^3 & 30(x+y/4)\ cm^3 & 30xcm^3 & 15ycm^3 & \end{array}$$

$\Rightarrow$ *Volume of excess oxygen = 95-60 = 35cm^3*

Volume of Oxygen used = 140-35= 105cm^3

Also Volume of carbondioxide produced= 60cm^3

$\Rightarrow$*30x=60 or x=*$\frac{60}{30} = 2$ *Also* $(x+\frac{y}{4}) = \frac{105}{30} = 3.5$ *or y=6*

M.F of the hydrocarbon is C_2H_6 with molecular mass = 2(12) + 6(1) = 30g

(d) Steam Distillation

This is the technique of separating a volatile substance that is immiscible with water from a non-volatile component at a temperature below its boiling point.

This method helps in separating organic compounds that decompose near their boiling point and distil at a temperature below their boiling points.

It uses the principle of

$\frac{n_1}{n_2} = \frac{p_1}{p_2}$ Where n_1 and n_2 are moles of component 1 and 2 respectively with vapour pressure P_1 and P_2 respectively

$\Rightarrow \frac{m_1}{m_2} = \frac{W_1 p_1}{W_2 p_2}$ Where W_1 and W_2 are the molecular mass of 1 and 2 respectively

Example

(a) When 4.9g of an organic compound X was burnt in excess oxygen, 14.78g of carbondioxide and 5.38g of steam was formed. Calculate the simplest formula of X

(b) X was steam distilled at 80°C and 760mmHg and the distillate was found to contain 90.8% by mass of X. The vapour pressure of water at the same temperature is 240mmHg.

(i) Calculate the formula mass of X

(ii) Deduce the molecular formula of X

(iii) Write down the possible isomers of X

Soln:*Mass of Carbon =* $\frac{12}{44} \times 14.78 = 4.304g$

Mass of Hydrogen= $\frac{2}{18} \times 5.38 = 0.598g$

Elements: C H

Moles: $\frac{4.304}{12}$ $\frac{0.598}{1}$

Ratio 1 : 1.667

$\Rightarrow$ 3 : 5 *hence E.F. of X is* C_3H_5

(b) (i) From $\frac{m_1}{m_2} = \frac{W_1 p_1}{W_2 p_2} \Rightarrow$ $P_T = P_1 + P_2$ *or* $P_2 = 760-240 = 520mmHg$ *and*

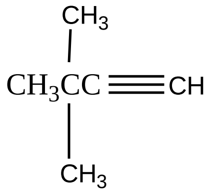
$m_1 = 100 - 90.8 = 9.2$

$$\frac{9.2}{90.8} = \frac{18 \times 240}{W_2 \times 520} \quad \therefore W_2 = 81.99g$$

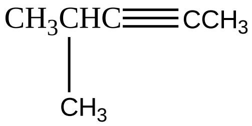
(ii) $(C_3H_5)_n = 82$ *or* $n = \frac{82}{41} = 2 \Rightarrow$ *M.F of X is* C_6H_{10}

(iii) *The isomers are*

$CH_3CH_2CH_2CH_2C{\equiv}CH$ $\quad CH_3CH_2CH_2C{\equiv}CCH_3$ $\quad CH_3CH_2C{\equiv}CCH_2CH_3$

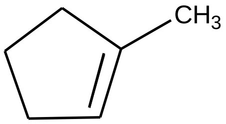


$CH_3C(CH_3)_2C{\equiv}CH$



$CH_3CH(CH_3)C{\equiv}CCH_3$

$CH_2{=}CHCH_2CH_2CH{=}CH_2$



N.B. *Check Physical Chemistry Textbook for more questions in order to practice*

CHAPTER TWO

ALKANES

These are hydrocarbons which form a homologous series of saturated nature with a general formula C_nH_{2n+2}. Successive members differ in composition by a methylene group

The main sources of Alkanes include:

- Natural gas which mainly contains methane with low amounts or propane and butane
- Petroleum products which are separated by fractional distillation during a process of refining

Cracking

This is the breaking down of long chain organic molecules (hydrocarbon) into two or small molecules which are useful products.

Cracking can be done using a catalyst (catalytic cracking) or by using high temperature (thermal cracking), the alkenes are used to make other chemical and alkanes are used for fuels.

NOMENCLATURE/NAMING OF ALKANES

With exception of the first four members of the homologous series, the straight chain members are named by taking prefix appropriate to the number of the carbons and adding the ending �ane.

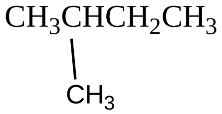
For branched members, the longest chain is selected and prefix is added to the name of the main of the chain, the position of the substituent is also indicated by appropriate number

Examples

Name the following organic compounds according IUPAC system:

(a) $CH_3CH_2CH_2CH_3$ (b) $CH_3CH_2CH_2CH_2CH_3$ (c) $CH_3(CH_2)_5CH_3$

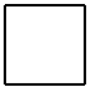
(d)



$CH_3\underset{\displaystyle | \atop CH_3}{C}HCH_2CH_3$

(e) $(CH_3)_4C$

(f)



Solution

(a) Butane (b) Pentane (c) Heptane (d) 2-methylbutane

(e) 2, 2-dimethylpropane (f) Cyclobutane

ISOMERISM IN ALKANES

Alkane�s posse�s structural isomers of class chain isomers from Butane.

Example

A hydrocarbon Q has a vapour density of 36 with empirical formula C_5H_{12}.

(a) Determine the molecular formula of Q

(b) Write down the possible isomers of Q and their IUPAC names

Soln:

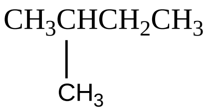
(a) Molecular mass = 36x2 = 72g

$(C_5H_{12})_n = 72 \Rightarrow 72n = 72 \therefore n = 1$ *M.F of Q is C_5H_{12}*

(b)

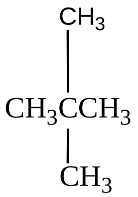
$CH_3CH_2CH_2CH_2CH_3$

Pentane



$CH_3CH(CH_3)CH_2CH_3$

2-methylbutane



$CH_3C(CH_3)_2CH_3$

2,2-dimethylpropane

PREPARATION OF ALKANES

1. HYDROGENATION OF ALKENES AND ALKYNES

This method provides one of the most suitable methods for preparing Alkanes. It used to deduce the number of the double or triple bond in the unsaturated hydrocarbon.

The method requires catalyst such as Nickel, Platinum or Palladium. Nickel requires an elevated temperature of 150°C whereas Platinum and Palladium requires ordinary temperature.

This reaction is used to determine the molecular mass of the Alkanes or Alkenes or Alkynes based upon the stoichiometry of the reaction

$$C_nH_{2n} + H_2 \xrightarrow[150^oC]{Ni} C_nH_{2n+2}$$

e.g.

$$CH_3CH{=}CHCH_3 \xrightarrow[150^oC]{H_2 / Ni} CH_3CH_2CH_2CH_3$$

Or

$$C_nH_{2n-2} + 2H_2 \xrightarrow[150^oC]{Ni} C_nH_{2n+2}$$

e.g.

$$CH_3C{\equiv}CCH_3 \xrightarrow[150^oC]{2H_2 / Ni} CH_3CH_2CH_2CH_3$$

Example

2.24dm^3 of Hydrogen gas at s.t.p reacts with 8.4g of hydrocarbon Q as represented by the equation below:

$$RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3$$

(a) Identify the functional group in the hydrocarbon Q

(b) *Determine the molecular mass of Q hence that of R*

(c) *Write the:*

- *(i) Molecular formula of Q*
- *(ii) Possible isomers of Q and their IUPAC names*

(1 mole of a gas occupies 22.4dm^3)

Soln:

(a) *Alkenes*

(b) *Moles of Hydrogen gas reacted =* $\frac{2.24}{22.4} = 0.1$

$\Rightarrow$ *Moles of the Alkenes = 0.1 (since the mole ratio is 1: 1) hence the RFM = 0.1x8.4 = 84*

Molecular mass of Q = 84g

$\Rightarrow$ *R + 2(12) + 3(1) = 84 thus R = 57g*

(c) *(i) From the general formula of Alkenes* C_nH_{2n}

$\Rightarrow n(12) + 2n(1) = 84$ *or* $n = 6$ $\therefore$ *M.F of Q is* C_6H_{12}

(ii)

$CH_3CH_2CH_2CH_2CH{=}CH_2$

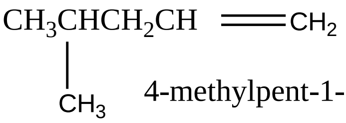
Hex-1-ene

$CH_3CH_2CH_2CH{=}CHCH_3$

Hex-2-ene

$CH_3\ CH_2CH{=}CHCH_2CH_3$

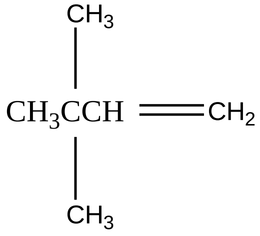
Hex-3-ene



$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2CH{=}CH_2$

4-methylpent-1-ene

and



$CH_3\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}CH{=}CH_2$

3,3-dimethylpropene

2. KOLBES SYNTHESIS

When aqueous solution of sodium salt of the carboxylic acid is electrolysed, an alkane is liberated at the anode and carbondioxide at the cathode.

This suitable for preparing symmetrical alkane of the R-R .

i.e.

$$2\ RCOO^- \longrightarrow R\text{-}R + 2CO_2 + 2e$$

e.g.

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

3. DECARBOXYLATION METHOD

The sodium salt of the carboxylic acid is heated with soda lime which contains sodium hydroxide and calcium oxide.

This reaction decreases the carbon chain by one carbon

$$RCOONa \xrightarrow[\text{Heat}]{\text{Sodalime}} RH + Na_2CO_3$$

$$CH_3COONa \xrightarrow[\text{Heat}]{\text{NaOH (s)}} CH_4$$

4. FROM ALKYL HALIDES

Reduction of alkyl halides also generates Alkanes. This can be done by using Zinc-Copper couple in ethanol or using lithium aluminium hydride in dry ether.

i.e.

$$RX \xrightarrow[\text{Dry Ether}]{LiAlH_4} RH + LiAlX_4$$

$$RX + 2H^+ \xrightarrow[\text{Ethanol}]{\text{Zn-Cu Couple}} RH + Zn^{2+} + X^-$$

e.g.

$$CH_3CH_2Br \xrightarrow[\text{Dry Ether}]{LiAlH_4} CH_3CH_3$$

Hydrolysis of Grignard reagent also gives rise to alkane

$$RX + Mg \xrightarrow{\text{Dry Ether}} RMgX \quad \text{(Alkyl magnesium halide)}$$

$$RMgX + H_2O \xrightarrow[\text{or } H_2SO_4]{HCl} RH + Mg(OH)X$$

e.g.

$$CH_3MgCl \xrightarrow[H_2SO_4]{H_2O} CH_4$$

5. WURTZ REACTION

Haloalkanes react with metallic sodium in dry ether to yield Alkanes of higher molecular mass and the carbons atoms are in even numbers.

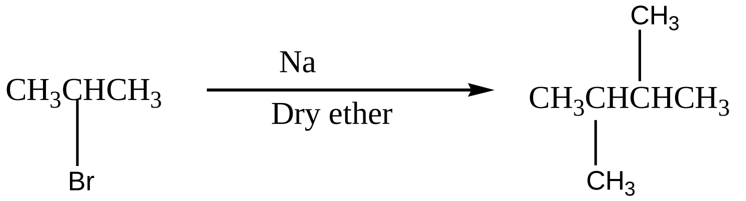
Greater yield is obtained when the alkane has a higher molecular mass.

i.e.

$$2RX + 2\,Na \xrightarrow{\text{Dry ether}} R\text{-}R + 2NaX$$

e.g.

$$CH_3CH_2CH_2Br \xrightarrow[\text{Dry ether}]{Na} CH_3CH_2CH_2CH_2CH_2CH_3$$



$$CH_3\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow[\text{Dry ether}]{Na} CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{C}HCH_3$$

FOR METHANE

Hydrolysis of Aluminium carbide with hot water or dilute mineral acids form methane

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

N.B. The diagonal carbide can also be used i.e. Beryllium carbide

PHYSICAL PROPERTIES OF ALKANES

The straight chainsAlkanes, C_1-C_4 are gases, C_5-C_7 are liquids and the remaining homologues are solids.

Boiling and Melting points increase with increasing molecular mass although the branched isomers are more volatile and degree of volatility increases with branching.

Alkanes are immiscible with polar solvents such as water but soluble in non-polar solvents such as chloroform, ether etc.

Density of the Alkanes increase with molecular mass but the factor reduces with increase in the branching.

REACTIONS OF ALKANES

Alkanes are generally unreactive compared to alkenes and alkynes.

Reasons:

- The C-C and C-H bonds are strong therefore unless heated to higher temperatures or subjected to ultraviolet light.
- Carbon and Hydrogen have nearly the same electronegativity value therefore the bonds are slightly polarized.
- There are no lone pairs of electrons in Alkanes therefore Alkanes are not attacked by acids.

However, under certain conditions, some of the reactions of Alkanes (paraffins) include:

1. **COMBUSTION**

Alkane�s burn in excess oxygen to form carbondioxide and water,the reaction is exothermic and it can be used to determine the molecular formula of the Alkanes.

$$C_nH_{2n+2} + (3n+1)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

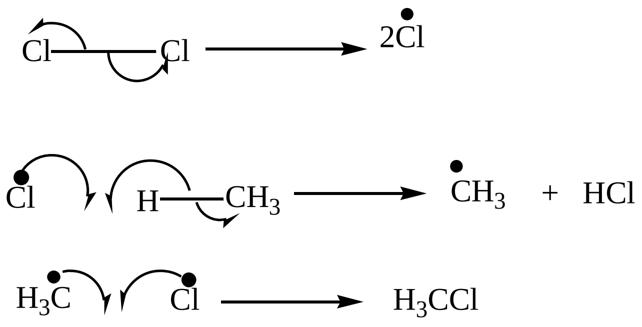
2. **CHLORINATION OR BROMINATION**

Alkanes react with halogens when heated at 250-400oC or in presence of Ultraviolet light to form a mixture of products which are difficult to separate.

The reactivity is the order of Fluorine> Chlorine> Bromine> Iodine. Iodine does not react with Alkanes while Fluorine reacts explosively.

$$CH_4 \xrightarrow[\text{U.V.light}]{Cl_2} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

Mechanism



N.B. The reaction mechanisms repeat to generate the rest of the products.

3. NITRATION REACTION

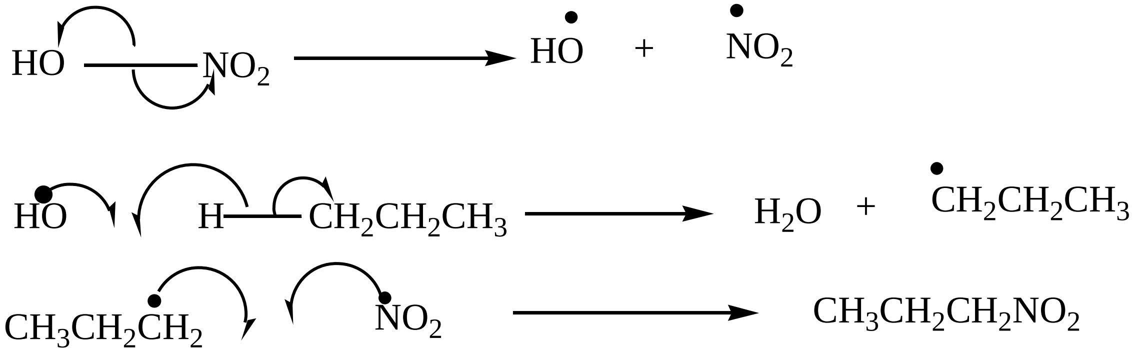
Alkanes react with nitric acid at about 400°C via free radical mechanism to form nitroalkane

$$RH \xrightarrow[400^oC]{HNO_3} RNO_2 + H_2O$$

e.g.

$$CH_3CH_2CH_3 \xrightarrow[400^oC]{HNO_3} CH_3CH_2CH_2NO_2$$

Mechanism



4. HALOGENATION USING SULPHURYL CHLORIDE

$$RH \xrightarrow[40\text{-}80^oC]{SO_2Cl_2} RCl + HCl + SO_2$$

CHAPTER THREE

ALKENES (OLEFINS)

Alkenes form a homologous series of unsaturated hydrocarbons containing a carbon-carbon double bond with the general formula C_nH_{2n} .

NOMENCLATURE OF ALKENES

In accordance with the IUPAC system, an alkene is named by dropping the ending *ane* from the corresponding alkane and replacing it with suffix *ene.*

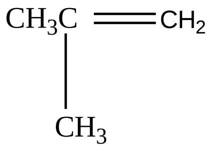
Where required, the position of the double bond is specified by appropriate number between the stem name and ending *ene* except for ethene and propene without positional isomers

Example

Name the following organic compounds using the IUPAC System:

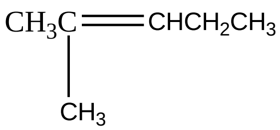
(a) $CH_3CH{=}CH_2$ (b) $CH_3CH_2CH{=}CH_2$ (c) $CH_3CH{=}CHCH_3$

(d)



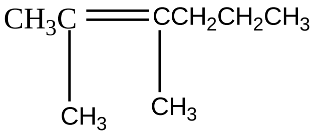
$CH_3\underset{\substack{|\\ CH_3}}{C}{=}CH_2$

(e)



$CH_3\underset{\substack{|\\ CH_3}}{C}{=}CHCH_2CH_3$

(f)



$CH_3\underset{\substack{|\\ CH_3}}{C}{=}\underset{\substack{|\\ CH_3}}{C}CH_2CH_2CH_3$

Solution:

(a) Propene (b) But-1-ene (c) But-2-ene (d) 2-methylpropene

(e) 2-methylpent-2-ene (f) 2, 3-dimethylhex-2-ene

Question

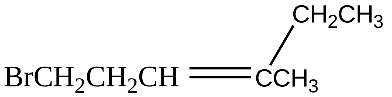
(a) Draw the structure of the following organic compounds:

(i) 3, 3-dimethylcyclopentene (ii) 6-bromo-2, 3-dimethylpent-2-ene (iii) 3, 6-dimethyloct-3-ene

(iv) 5-bromo-4-chlorohept-1-ene (v) 4-ethyl-3-methylcyclohexene

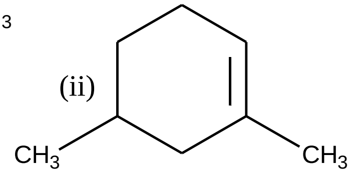
(b) Name the following organic compounds:

(i)

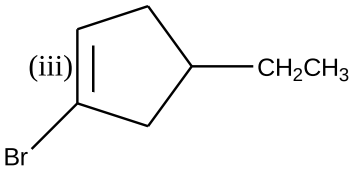


$BrCH_2CH_2CH{=}\overset{CH_2CH_3}{C}CH_3$

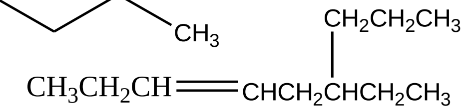
(ii)



(iii)



(iv)



$CH_3CH_2CH{=}CHCH_2\overset{CH_2CH_2CH_3}{CH}CH_2CH_3$

SYNTHETIC PREPARATIONS OF ALKENES

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

The ease of dehydration of alcohols is: 3^{o} Alcohol> 2^{o}>1^{o}Alcohol while the ease of dehydrohalogenation of halo alkanes is 3^{o}> 2^{o}>1^{o}

FROM ALCOHOLS

Alcohols are heated with excess concentrated sulphuric acid or orthophosphoric acid. The temperature of dehydration depends on the structure of the alcohol.

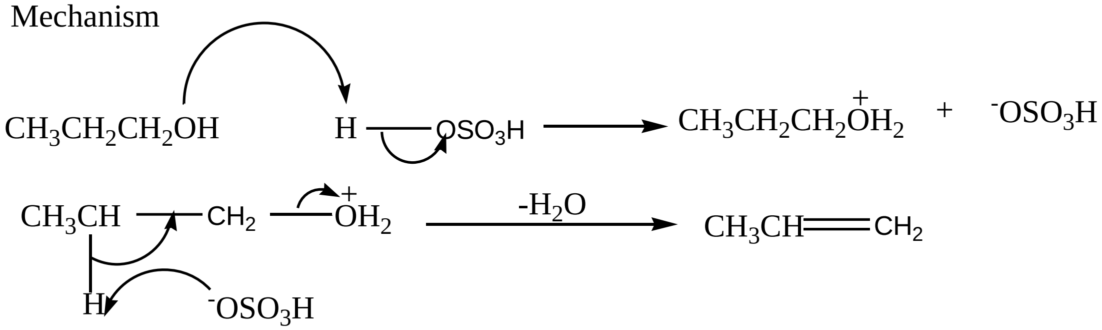
The reaction involves removal of water molecules hence known as *dehydration reaction*

The 1^{o} and 2^{o} Alcohols following the same mechanism while 3^{o} Alcohols undergoes partial ionization generating 3^{o}Carbocations

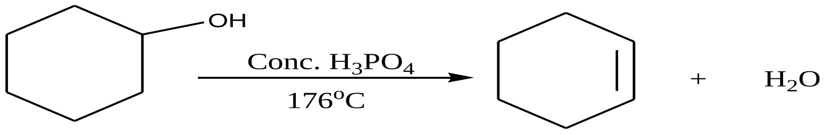
Example

$$CH_3CH_2CH_2OH \xrightarrow[180^{o}C]{Conc.H_2SO_4} CH_3CH{=}CH_2 \quad + \quad H_2O$$

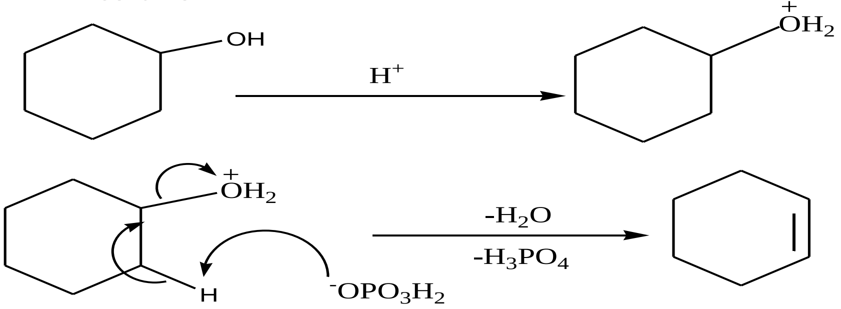
Mechanism



Example



Mechanism

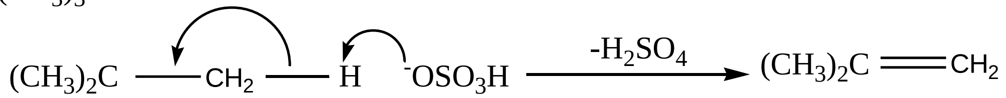


Example

$$(CH_3)_3C—OH \xrightarrow[170^oC]{Conc.H_2SO_4} (CH_3)_2C=CH_2 \quad + \quad H_2O$$

Mechanism

$$(CH_3)_3COH \rightleftharpoons (CH_3)_3\overset{+}{C}H \quad + \quad {}^-OH$$



$$(CH_3)_2C—CH_2—H \quad {}^-OSO_3H \xrightarrow{-H_2SO_4} (CH_3)_2C=CH_2$$

Example

$$CH_3(CH_2)_2CH_2OH \xrightarrow[180^oC]{Conc.\ H_2SO_4} CH_3CH=CHCH_3$$

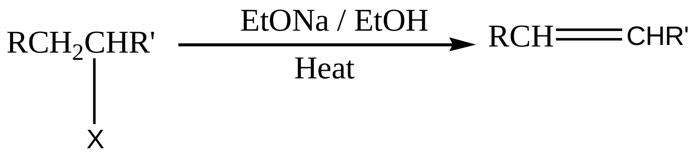
Write the mechanism of the above reaction.

2. FROM HALOALKANES

Halo alkanes are heated with a strong base to generate an alkene.

(i) Dehydrohalogenation of alkyl halides.

Halo alkanes are heated with a strong base such sodium amide in liquid ammonia or sodium ethoxide in ethanol in order to remove hydrogen halide i.e.

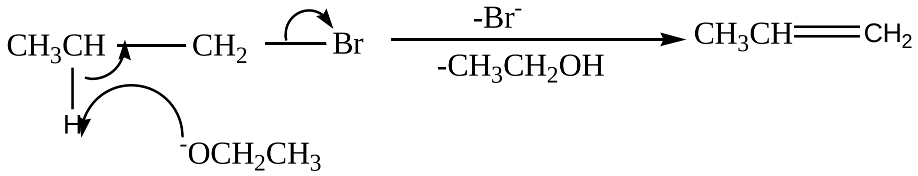


$$RCH_2CH(X)R' \xrightarrow[\text{Heat}]{\text{EtONa / EtOH}} RCH{=}CHR'$$

Example

$$CH_3CH_2CH_2Br \xrightarrow[\text{Heat}]{CH_3CH_2OK\ /\ CH_3CH_2OH} CH_3CH{=}CH_2$$

Mechanism

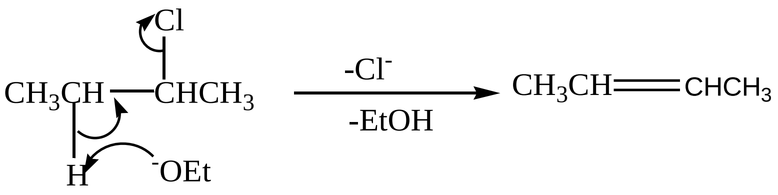


Example

$$CH_3CH_2CH(Cl)CH_3 \xrightarrow[\text{Heat}]{\text{KOH / EtOH}} CH_3CH{=}CHCH_3$$

Mechanism

$$KOH + EtOH \longrightarrow EtOK + H_2O$$

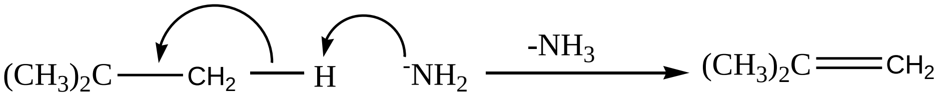


Example

$$(CH_3)_3C{-}Br \xrightarrow[\text{Heat}]{NaNH_2\ /\ Liq.NH_3} (CH_3)_2C{=}CH_2$$

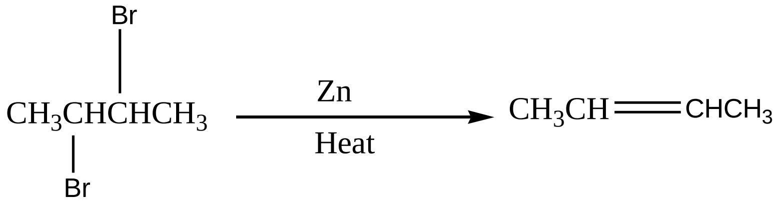
Mechanism

$$(CH_3)_3C{-}Br \rightleftharpoons (CH_3)_3C^+ + Br^-$$



(ii) Dehalogenation of Vicinal dihalides

When vicinal dihalides are heated with Zinc, alkenes are formed i.e.



$$CH_3CH(Br)CH(Br)CH_3 \xrightarrow[\text{Heat}]{\text{Zn}} CH_3CH{=}CHCH_3$$

N.B. On a large scale, alkenes are obtained by cracking of petroleum products

REACTIONS OF ALKENES

Alkenes undergo Electrophilic addition since they are electron rich species.

Some of the addition reactions include:

1. ADDITION OF HYDROGEN

Hydrogenation of alkenes generate alkanes

$$RCH{=}CHR' \xrightarrow[150^oC]{H_2 / Ni} RCH_2CH_2R'$$

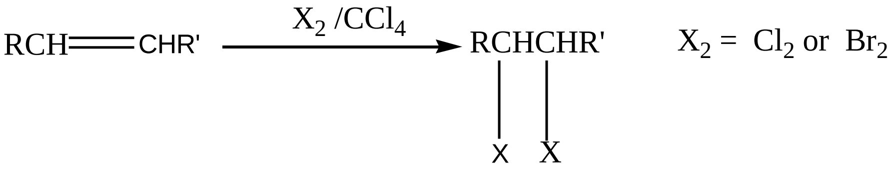
e.g.

$$CH_3CH{=}CH_2 \xrightarrow[150^oC]{H_2 / Ni} CH_3CH_2CH_3$$

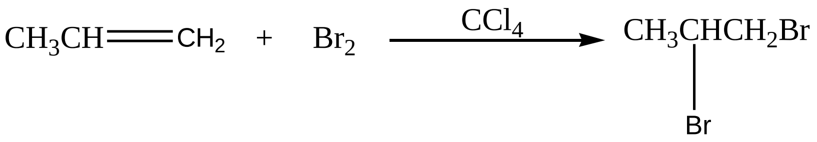
2. ADDITION OF HALOGENS

This reaction is usually carried out in an inert solvent such carbon tetrachloride. Chlorine and Bromine reacts but Iodine fails to react.

The reddish- brown colour of bromine is turned colourless therefore the reaction is used to test for presence of carbon-carbon double bond and the number of double bonds since the mole ratio is 1:1(Alkene : Bromine)

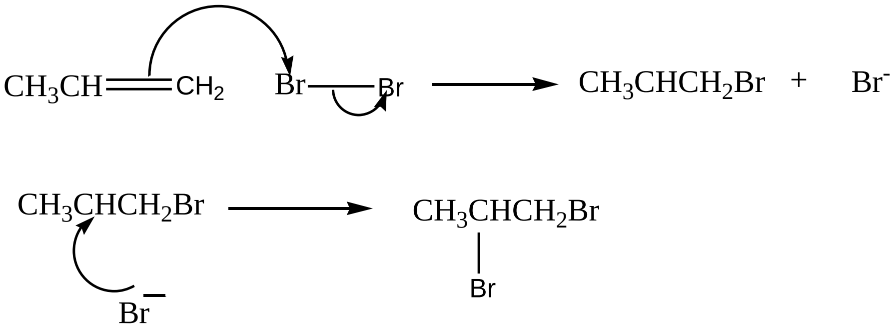


$$RCH{=}CHR' \xrightarrow{X_2/CCl_4} \underset{X}{RCH}\underset{X}{CHR'} \qquad X_2 = Cl_2 \text{ or } Br_2$$



$$CH_3CH{=}CH_2 + Br_2 \xrightarrow{CCl_4} CH_3\underset{Br}{C}HCH_2Br$$

Mechanism

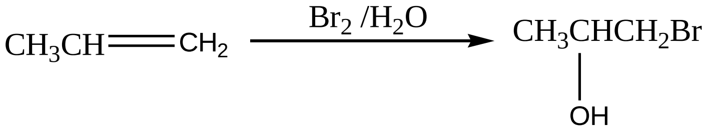


$$CH_3CH{=}CH_2 \quad Br{-}Br \longrightarrow CH_3\overset{+}{C}HCH_2Br + Br^-$$

$$CH_3CHCH_2Br \quad Br^- \longrightarrow CH_3\underset{Br}{C}HCH_2Br$$

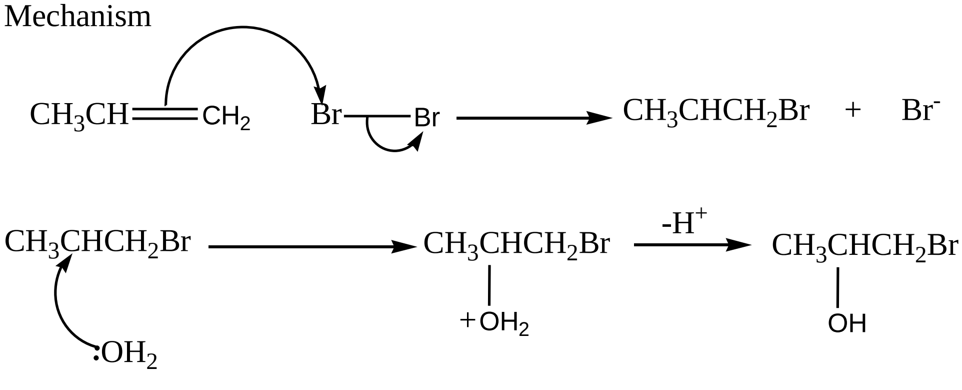
3. HALOHYDRIN FORMATION

Bromination or Chlorination of alkenes in water generates bromoalcohol or chloroalcohol



$$CH_3CH{=}CH_2 \xrightarrow{Br_2/H_2O} CH_3\underset{OH}{C}HCH_2Br$$

Mechanism



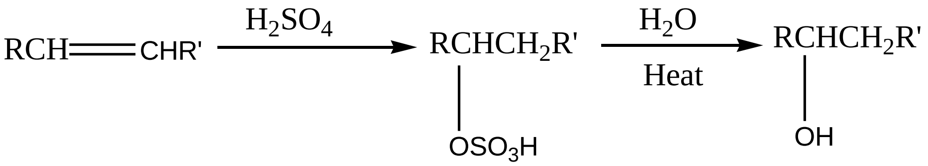
$$CH_3CH{=}CH_2 \quad Br{-}Br \longrightarrow CH_3CHCH_2Br + Br^-$$

$$CH_3CHCH_2Br \quad :OH_2 \longrightarrow CH_3\underset{+OH_2}{C}HCH_2Br \xrightarrow{-H^+} CH_3\underset{OH}{C}HCH_2Br$$

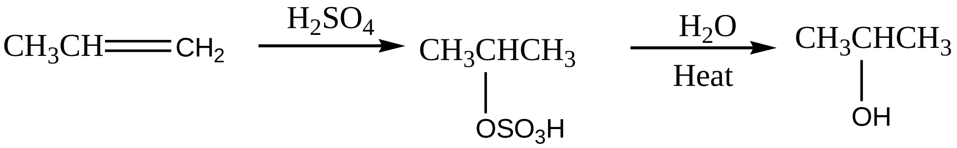
N.B. The mechanism is the same when chlorine water is used.

4. ADDITION OF WATER / HYDRATION

Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphate which reacts with water on heating alcohol



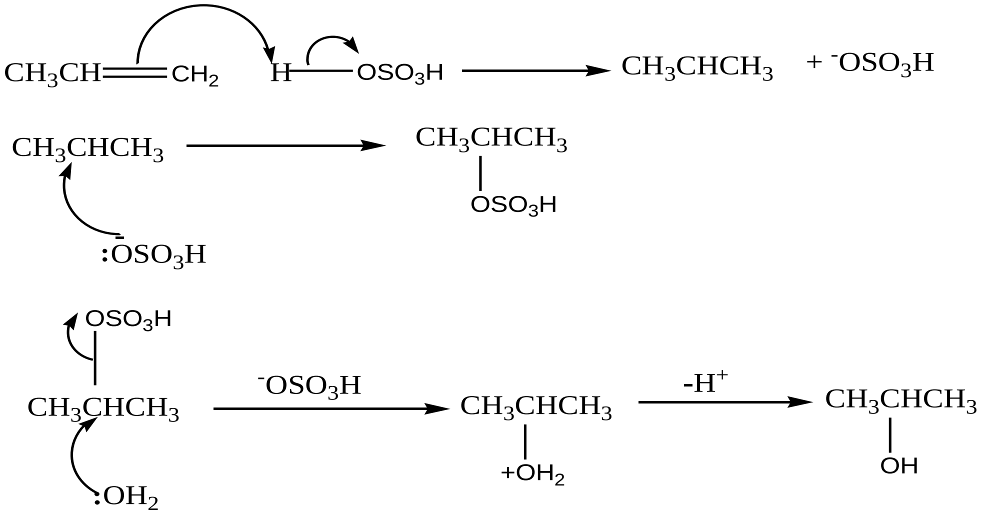
$$RCH{=}CHR' \xrightarrow{H_2SO_4} \underset{\displaystyle OSO_3H}{RCHCH_2R'} \xrightarrow[Heat]{H_2O} \underset{\displaystyle OH}{RCHCH_2R'}$$



$$CH_3CH{=}CH_2 \xrightarrow{H_2SO_4} \underset{\displaystyle OSO_3H}{CH_3CHCH_3} \xrightarrow[Heat]{H_2O} \underset{\displaystyle OH}{CH_3CHCH_3}$$

Mechanism

The mechanism follow markovnikov rule.



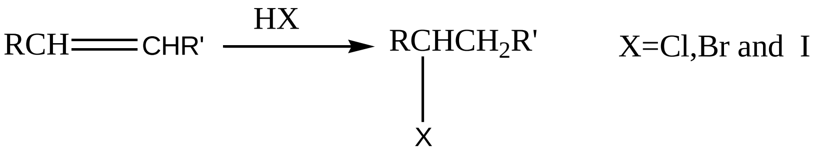
$$CH_3CH{=}CH_2 \quad H{-}OSO_3H \longrightarrow CH_3\overset{+}{C}HCH_3 + {}^{-}OSO_3H$$

$$CH_3\overset{+}{C}HCH_3 \xrightarrow{:\bar{O}SO_3H} \underset{\displaystyle OSO_3H}{CH_3CHCH_3}$$

$$\underset{\displaystyle :OH_2}{\overset{\displaystyle OSO_3H}{CH_3CHCH_3}} \xrightarrow{{}^{-}OSO_3H} \underset{\displaystyle +OH_2}{CH_3CHCH_3} \xrightarrow{-H^+} \underset{\displaystyle OH}{CH_3CHCH_3}$$

5. ADDITION OF HYDROGEN HALIDES

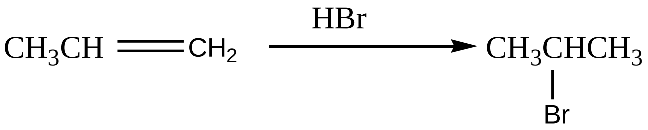
Hydrogen halides react with alkenes forming alkyl halides.



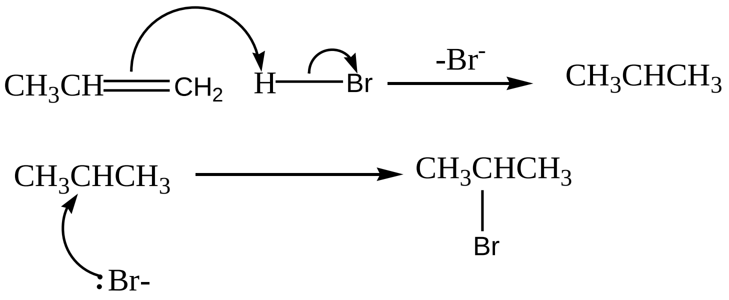
$$RCH{=}CHR' \xrightarrow{HX} \underset{\displaystyle X}{RCHCH_2R'} \qquad X=Cl, Br \text{ and } I$$

In the reaction above, the hydrogen atom from hydrogen halide adds itself to the carbon atom of the double bond with the larger number of hydrogen atoms.

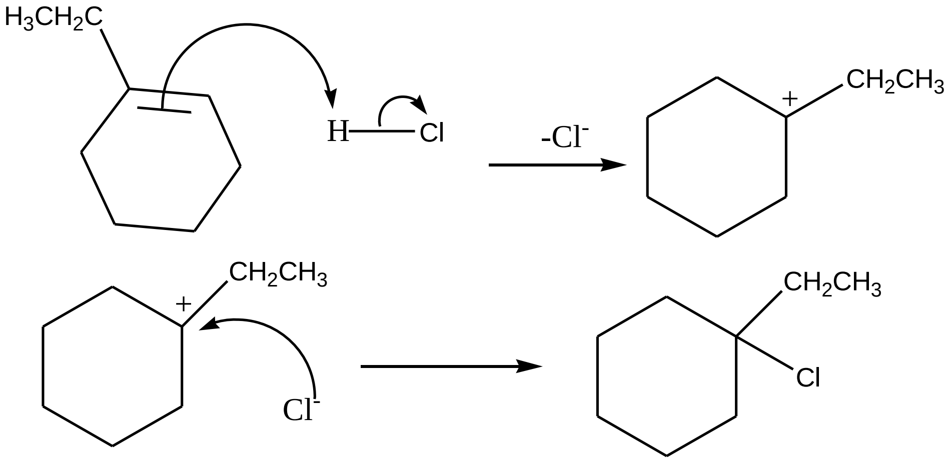
Also the halogen adds itself to the carbon atom in double bond with lower number of hydrogen atom thus these are known as Markovnikov rule.



$$CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$



Example



N.B. The hydrogen bromide are usually generated by action of concentrated Sulphuric acid on sodium bromide

6. ADDITION OF HYDROGEN BROMIDE IN PRESENCE OF PEROXIDE

In this reaction, the bromine atom adds itself to the carbon atom of the double bond having higher number of hydrogen atoms with hydrogen atom (from Hydrogen bromide) to lower carbon atom.

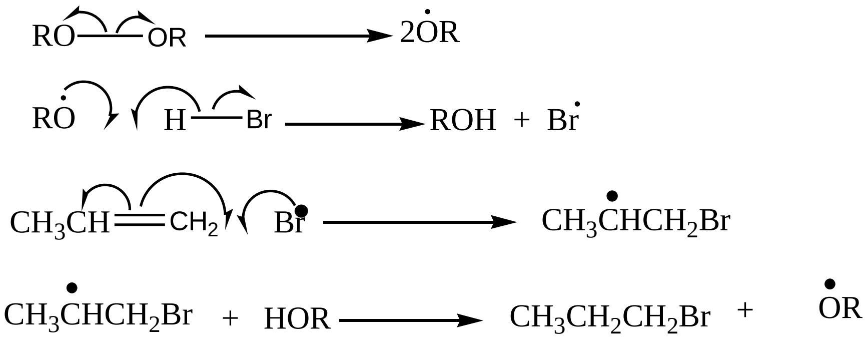
This observation is known as anti-markovnikov rule.

$$RCH{=}CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} RCH_2CH_2Br$$

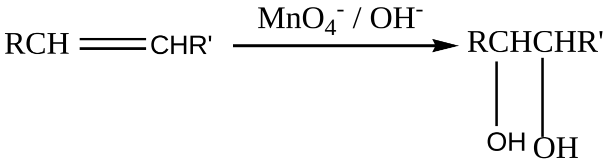
e.g.

$$CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} CH_3CH_2CH_2Br$$

Mechanism



7. WITH ALKALINE POTASSIUM MANGANATE (VII). Manganate (VII) is a weak oxidising agent therefore it oxidizes alkenes to diols. The purple colour turns colourless.



$$RCH{=}CHR' \xrightarrow{MnO_4^- / OH^-} RCH(OH)CH(OH)R'$$

$$CH_2{=}CH_2 \xrightarrow{MnO_4^- / OH^-} HOCH_2CH_2OH$$

Ethane-1,2-diol

The reaction is also used to test for unsaturated compounds. It can also occur if the reagent is in acidic medium.

8. OZONOLYSIS

Alkenes react with ozone to form ozonide which on hydrolysis generates carbonyl compounds.

The reaction is used to determine the structural formula of the alkene.

Alkenes with terminal double bond form methanal (HCHO), those with structure RCH= form Aldehydes (RCHO) while those of structure RR'C= form Ketones. i.e

$$RCH{=}CH_2 \xrightarrow[\text{(ii) } H_2O\,/\,Zn]{\text{(i) } O_3\,/CCl_4} RCHO + HCHO$$

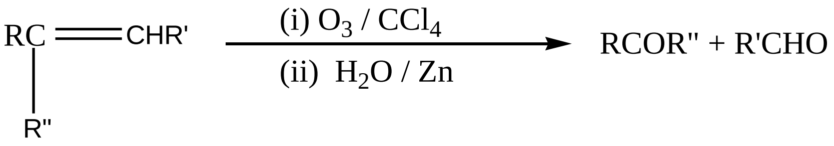
e.g.

$$CH_3CH{=}CH_2 \xrightarrow[\text{(ii) } H_2O\,/\,Zn]{\text{(i) } O_3\,/\,CCl_4} CH_3CHO + HCHO$$

$$RCH{=}CHR' \xrightarrow[\text{(ii) } H_2O\,/\,Zn]{\text{(i) } O_3/CCl_4} RCHO + R'CHO$$

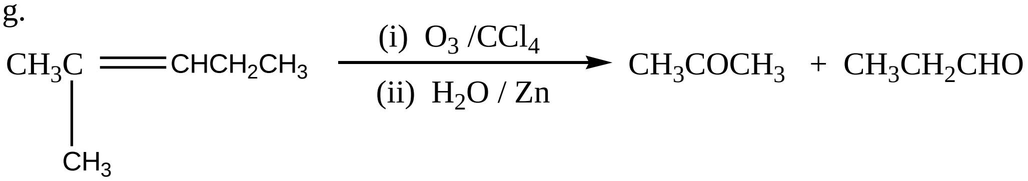
e.g.

$$CH_3CH{=}CHCH_2CH_3 \xrightarrow[\text{(ii) } H_2O\,/\,Zn]{\text{(i) } O_3\,/\,CCl_4} CH_3CHO + CH_3CH_2CHO$$



$$\underset{\displaystyle R''}{\underset{|}{RC}}{=}CHR' \xrightarrow[\text{(ii) } H_2O\,/\,Zn]{\text{(i) } O_3\,/\,CCl_4} RCOR'' + R'CHO$$

e.g.



$$\underset{\displaystyle CH_3}{\underset{|}{CH_3C}}{=}CHCH_2CH_3 \xrightarrow[\text{(ii) } H_2O\,/\,Zn]{\text{(i) } O_3\,/CCl_4} CH_3COCH_3 + CH_3CH_2CHO$$

N.B. Ozonolysis is the formation of ozonide followed by hydrolysis to generated carbonyl compounds.

8. POLYMERISATION REACTION

Alkenes undergo addition polymerization to form polymers.

Ethenepolymerises to form polyethene which is an important plastic material used as packing material.

$$n\,CH_2{=}CH_2 \xrightarrow[\text{1500atom, } 200^oC]{O_2 \text{ or Peroxide}} *\!-\!\left(CH_2CH_2\right)_n\!-\!*$$

Sample Question

*A hydrocarbon **A** contains 87.8% carbon. Its relative molecular mass is 82. A decolorizes bromine and in presence of Nickel it reacts with hydrogen to form **B**. 0.1g of **A** was found to absorb 27.3cm^3 of hydrogen (measured at s.t.p). **B** does not decolorize bromine.*

(a) Determine the:

(i) Empirical formula

(ii) Molecular formula of A.

(b) Calculate the:

(i) Number of moles hydrogen that reacted with one mole of A

(ii) Number of double bonds in the molecule of A

(c) Write the possible Isomers of A.

CHAPTER FOUR

ALKYNES OR ACETYLENES

Alkynes are unsaturated hydrocarbons having a triple bond between carbon atoms. The general formula of the homologous series is C_nH_{2n-2}.

NOMENCLATURE OF ALKYNES

The IUPAC names of the alkynes are obtained by taking the corresponding alkane name and replacing the ending with suffix “-*yne*”*.*The position of the triple bond is indicated by inserting the appropriate number between the stem and the ending “-*yne*”

Question:

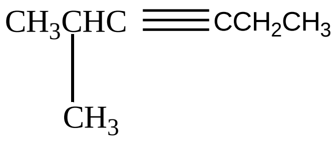
Name the following organic compounds using the IUPAC system.

(a) $HC\equiv CH$

(b) $CH_3C\equiv CH$

(c) $CH_3CH_2C\equiv CCH_3$

(d)



$CH_3\underset{\underset{CH_3}{|}}{C}HC\equiv CCH_2CH_3$

PHYSICAL PROPERTIES

The physical properties of alkynes are similar to those of alkanes and alkenes; however they boil at a higher temperature than alkenes and alkanes with the same number of carbon atoms due short bond length.

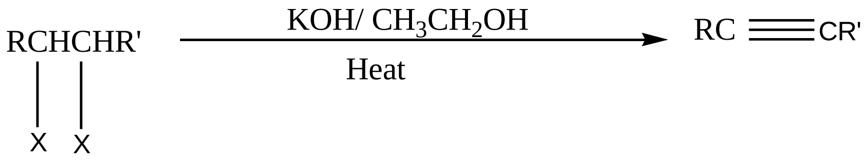
Alkyne	Bpt (^oC)	M.p.t (^oC)	Alkene	B.p.t (^oC)
Ethyne	-75	-82	Ethene	-104
Propyne	-23	-101.5	Propene	-47
But-1-yne	9	-122	But-1-ene	-6.3
Hex-1-yne	72	-124	Hex-1-ene	63

Synthetic Preparation

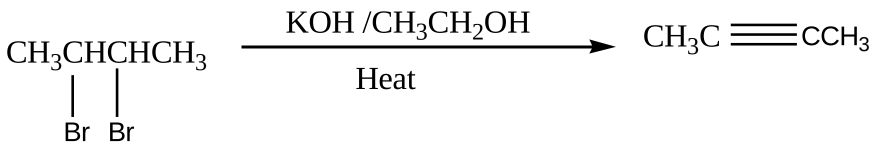
Alkynes are usually prepared by dehydrohalogenation of dihalogencompounds.

The dihalogen compounds are heated using strong bases which include:

- Sodium ethoxide in ethanol
  - Sodium amide in liquid ammonia (solution of sodium in liquid ammonia)
  - Potassium hydroxide in ethanol (contains ethoxide ions but not aqueous Potassium hydroxide or aqueous sodium hydroxide)



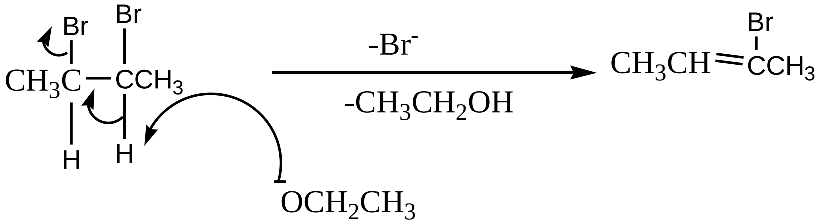
$$R\underset{\substack{| \\ X}}{C}H\underset{\substack{| \\ X}}{C}HR' \xrightarrow[\text{Heat}]{KOH/\ CH_3CH_2OH} RC\equiv CR'$$

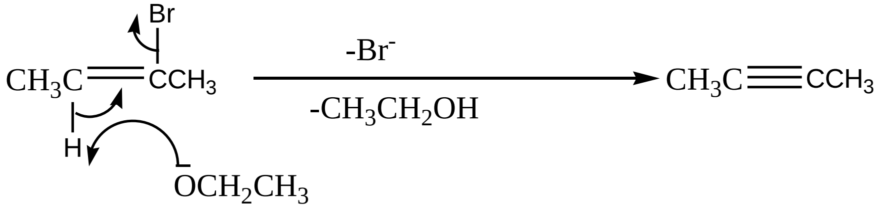


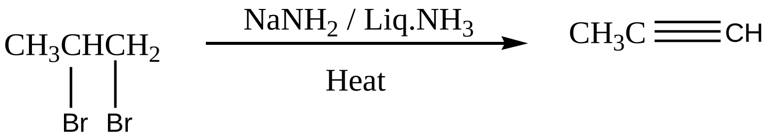
$$CH_3\underset{\substack{| \\ Br}}{C}H\underset{\substack{| \\ Br}}{C}HCH_3 \xrightarrow[\text{Heat}]{KOH\ /CH_3CH_2OH} CH_3C\equiv CCH_3$$

Mechanism

$$KOH + CH_3CH_2OH \longrightarrow CH_3CH_2OK + H_2O$$





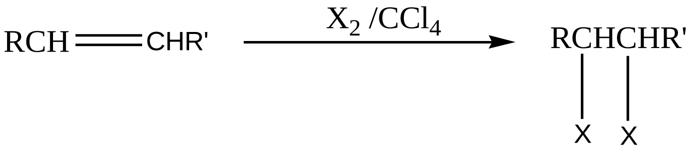


$$\underset{Br}{CH_3CH}\underset{Br}{CH_2} \xrightarrow[\text{Heat}]{NaNH_2 / Liq.NH_3} CH_3C\equiv CH$$

Qn: Write the mechanism of the reaction above.

Note: The dihalogen compounds are prepared by:

(a) Bromination or Chlorination of Alkenes



$$RCH=CHR' \xrightarrow{X_2 /CCl_4} R\underset{X}{CH}\underset{X}{CH}R'$$

(b)Carbonyl compounds

$$CH_3CH_2CHO \xrightarrow{PCl_5} CH_3CH_2CHCl_2$$

INDUSTRIAL PREPARATION OF ETHYNE

(a) Treatment of Calcium dicarbide with water

Calcium dicarbide is obtained by reducing Quicklime, obtained from Limestone, with coke in electric furnace 2000-3000^{o}C

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2$$

$$CaO + 3C \xrightarrow{2000^oC} CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$$

(b) Partial combustion of Methane

In this method, ethyne is separated by passing the gases product through Propanoneor Ammonia

$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2$$

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$2CH4 \xrightarrow{1500^oC} HC\equiv CH + 3H_2$$

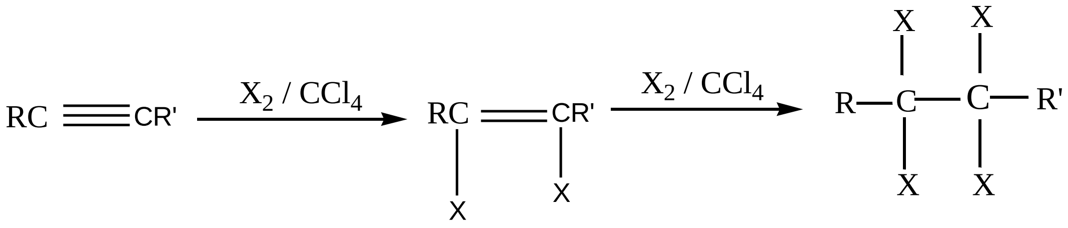
REACTIONS OF ALKYNES

Just like Alkenes, Alkynes also undergo Electrophilic addition due to availability of loosely held Π electron. Addition of hydrogen, Halogens and Hydrogen halide to alkynes is very much like addition to alkenes except that here two molecules of reagent can be consumed.

1. **Addition of hydrogen**

$$RC\equiv CR' \xrightarrow[\text{Heat}]{2H_2 / Ni} RCH_2CH_2R'$$

2. **Addition of Halogens**

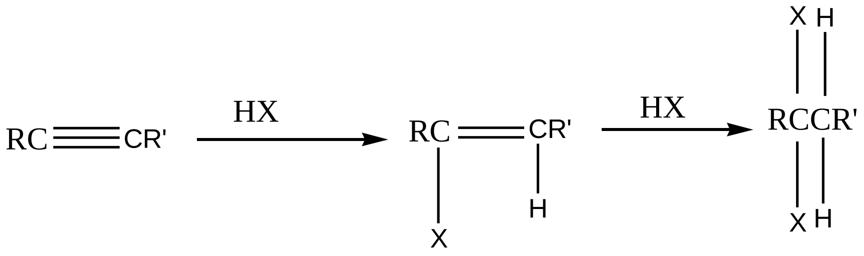


$$RC\equiv CR' \xrightarrow{X_2 / CCl_4} RC(X)=C(X)R' \xrightarrow{X_2 / CCl_4} R-CX_2-CX_2-R'$$

$X_2 = Cl_2$ or Br_2

Qn: *Write the mechanism of the above reaction*

3. **Addition of Halogen halides**



$$RC{\equiv}CR' \xrightarrow{HX} RC(X){=}C(H)R' \xrightarrow{HX} RCX_2CH_2R'$$

HX= HCl, HBr and HI

Qn: *Write the mechanism of the above reaction*

4. **Addition of hydrogen Bromide in presence of peroxides**

$$RCH_2C{\equiv}CH \xrightarrow[\text{Peroxide}]{HBr} RCH_2CH{=}CHBr$$

This reaction resemble that of alkenes to generate anti-markovnikov product

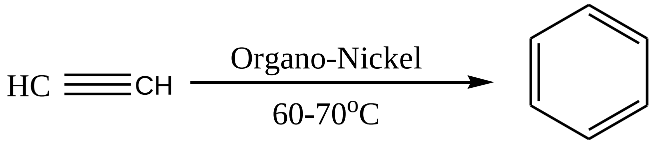
5. **Addition of water. Hydration**

$$HC{\equiv}CH \xrightarrow[HgSO_4,\ 60^oC]{H_2O,\ \text{dil.}H_2SO_4} CH_3CHO$$

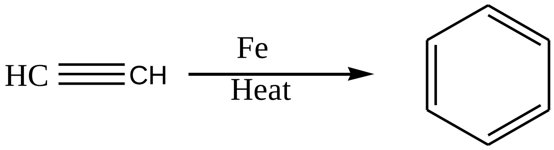
$$CH_3C{\equiv}CH \xrightarrow[HgSO_4,\ 60^oC]{H_2O,\ \text{dil.}H_2SO_4} CH_3COCH_3$$

Ethyne is the only alkyne that forms Aldehydes (ethanal) while the rest form Ketones on hydration.

6. **Polymerization of Ethyne**



or



7. **Substitution reaction of Acidic Hydrogen**

Alkynes which have a triple bond at the end of the chain (terminal alkynes) have a replaceable acidic hydrogen atom.

a) With Ammoniacal Silver nitrate Solution

Terminal Alkynes react to form white precipitate.

$$HC\equiv CH \; + \; 2\,Ag^{+} \longrightarrow \underset{\text{silver dicarbide}}{AgC\equiv CAg} \; + \; 2\,H^{+}$$

$$RC\equiv CH \; + \; Ag^{+} \longrightarrow RC\equiv CAg \; + \; H^{+}$$

This reagent is used to differentiate terminal alkynes from Non-terminal alkynes

b) With Ammoniacal Copper (I) Chloride solution

Terminal Alkynes react to form red precipitate

$$RC\equiv CH \; + \; \left[Cu(NH_3)_2\right]^{+} \; + \; -OH \xrightarrow{H_2O} RC\equiv CCu \; + \; 2NH_3$$

-

Also, ammoniacal copper (I) chloride solution is used to differentiate terminal alkynes from non-terminal.

c) Sodium Acetylide formation

Terminal Alkynes react with sodium in liquid ammonia to form sodium acetylide which can be used to synthesize the higher homologue by reacting with alkyl halides.

$$RC\equiv CH \; + \; 2Na \xrightarrow{\text{liq. } NH_3} 2\,RC\equiv CNa \; + \; H_2$$

$$RC\equiv CNa \xrightarrow{R'X} RC\equiv CR' \; + \; NaX$$

Sample Question

(a) Write equation(s) to show how the following compounds can be synthesized .In each cases indicate the mechanism for the reactions where possible.

(i) $(CH_3)_2C=CH_2$ from 2-bromo-2-methylpropane

(ii) $HC\equiv CH$ from Bromoethane

(b) Name the reagent(s) that can be used to differentiate between the following compounds. In each case, state what would be observed if the reagent is treated with compounds

(i) $CH_3CH_2C\equiv CH$ and $CH_3C\equiv CCH_3$

(ii) $CH_3CH{=}CH_2$ and $CH_3CH_2CH_3$

When 400cm^3 of the mixture of ethane and ethyne measured at room temperature was bubbled in to mixture of aqueous ammonia and silver nitrate solution. 2.4g of a white solid was formed.

(i) Write an equation for the reaction that took place and name the white solid

(ii) Calculate the percentage by volume of ethane in the mixture

(d) (i) Define the structural isomerism

(ii) Using suitable example(s), State the classes of structural isomerism

CHAPTER FIVE

AROMATIC HYDROCARBONS- BENZENE

Introduction

In the last chapter, we considered unsaturated compounds-Alkenes and Alkynes. There is another important class of unsaturated compounds that needs to be considered separately because their properties are so different from those of alkenes and alkynes.

This class of compounds is called the Aromatic hydrocarbon and its simplest member is *Benzene.*

The name Aromatic was originally used because some derivatives of these hydrocarbons have pleasant smells. Its is now known that just many of them have unpleasant and in any case the aromatic vapours are toxic

Therefore the name Aromatic has been retained to indicate certain chemical characteristics rather than odorous properties.

The structure of Benzene

Since 1834, molecular mass determination generated the molecular formula of benzene as C6H6. The exact structural formula, however posed a problem for many years.

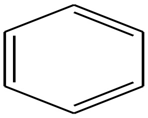
With such a high ratio of C: H, benzene must be a highly unsaturated with a possible structure of hexatetraene e.g.

$CH_2{=}C{=}CHCH{=}C{=}CH_2$

$CH_3C{\equiv}CCH_2C{\equiv}CH$

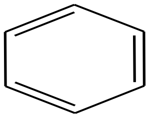
$CH_2{=}CHC{\equiv}CCH{=}CH_2$

However, benzene does not undergo addition reactions across the double bond as alkenes therefore Kekule (1865) proposed a ring structure in which alternate carbon atoms were joined by double bond as:



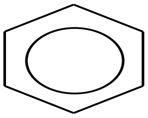
1

or



2

or



3

Bond lengths

X-ray diffraction studies show that benzene is planar and all the C-C bonds are the same.

Some of the bond lengths are:

C-C bond length in all bonds in benzene, 0.139nm

C-C bond length in cyclohexane, 0.154nm

C-C bond length in cyclohexene, 0.133nm

Kekule model would suggest unequal carbon-carbon lengths, alternating between double and single bond values. In fact the constant bond length is found between single and double bond.

Question: Explain the variation in the bond length between cyclohexane, cyclohexene and benzene.

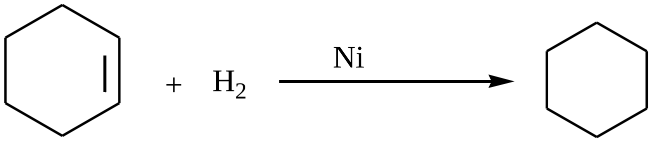
Soln: From Molecular orbital terms, Benzene is a planar molecular with all the six hydrogen and six carbon atoms lying in the same plane. Each Carbon atom is sp2 hybridized and explains why structure 3 is preferred.

Also, the variation can be attributed to resonance energy which indicates than benzene is more stable than cyclohexene and all carbon □ bond lengths in benzene are equal.

Thermochemistry of Benzene

Benzene is more stable than expected and this is illustrated using the enthalpy of hydrogenation to cyclohexane. i.e.

The enthalpy of hydrogenation of cyclohexene is -119KJ/mol



ΔH= -119KJ/mol

Considering Benzene as Cyclohexa-1, 3, 5-triene which has three double bonds then, we expect its enthalpy of hydrogenation to be = 3 (-119) = -357KJ/mol.

However, the experimental value observed was = -207KJ/mol.

The difference in the values (-357 + 207) = -150KJ/mol and it indicates that Benzene is more stable than cyclohexa-1, 3, 5-triene. The difference in the values is known as Resonance or Delocalization energy

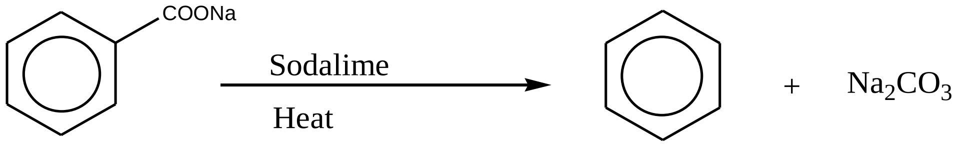
Sources of Benzene

Benzene is obtained from petroleum oil by fractional distillation.

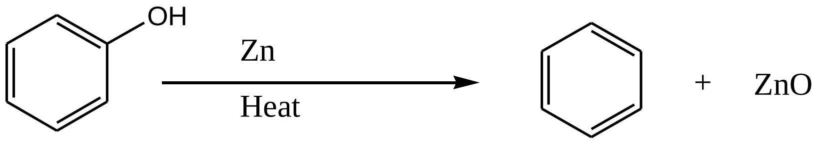
Synthetic Preparation

Owing to the great abundance of Benzene from Industrial sources, it is rarely prepared but may be prepared by the following methods.

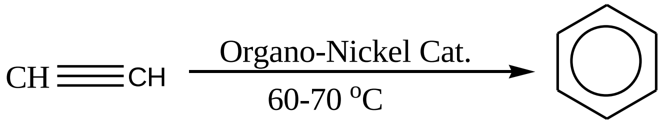
1. Decarboxylation of Sodium Salts



2. Reduction of Phenol



3. Polymerization of Ethyne



Physical properties Of Benzene

Benzene is a colourless liquid with a characteristic Aromatic smell. It is immiscible with water but highly soluble in organic solvents as well as being used as solvent itself.

Like all Aromatic compounds, it burns with a sooty flame owing to its relatively high carbon content

Reactions of benzene

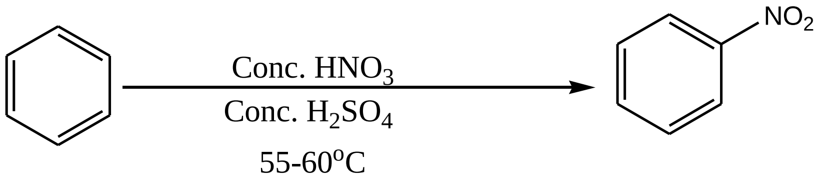
The availability of the pie electrons in benzene serves as a source of electrons which are donated to electron deficient species (Electrophiles). The reactions therefore are characterized by Electrophilic substitution reactions which differ from Addition reactions of Alkenes.

1. Nitration reaction

This is the reaction of Benzene with nitrating mixture containing equal molar quantities of concentrated Nitric acid and sulphuric acid.

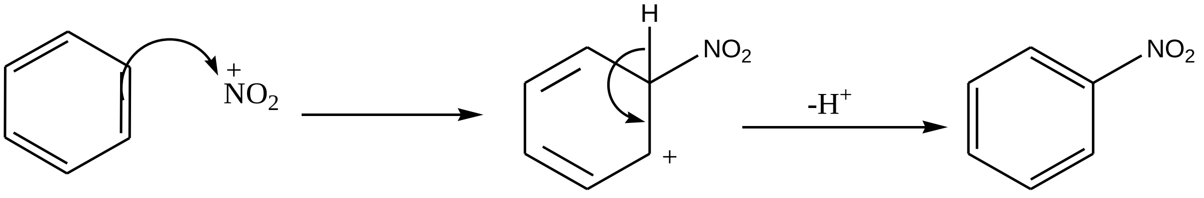
In this reaction, the hydrogen atom is substituted by a nitro group to generate Nitrobenzene.

Concentrated Sulphuric acid is used to protonate weaker Nitric acid such that Nitroniumcation is produced.



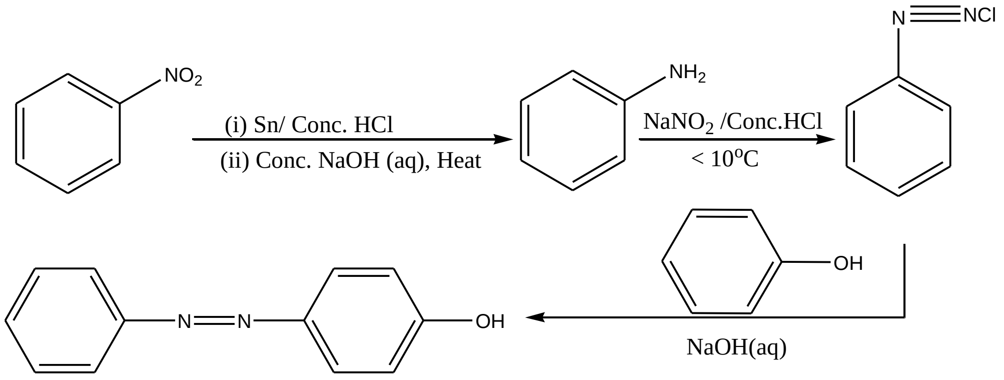
Mechanism

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons \overset{+}{N}O_2 + H_3\overset{+}{O} + 2HSO_4^-$$



Nitrobenzene is used to produce Phenylamine (Aniline) by reduction process which is used to manufacture azo-dyes.

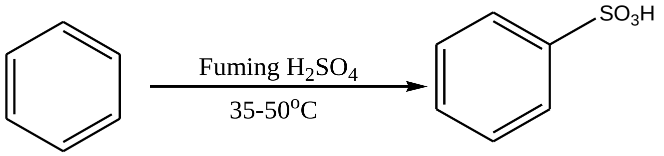
An example of an azo-dye is 4-hydroxyazobenzene which is orange solid synthesized from Nitrobenzene as shown below.



4-Hydroxyazobenzene
(Orange solid)

2. Sulphonation reaction

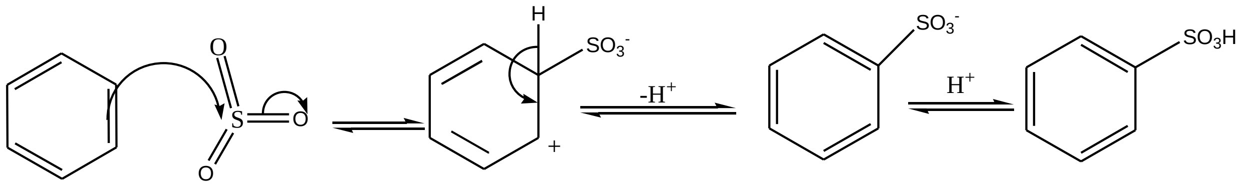
This is carried out by using fuming sulphuric acid. Concentrate sulphuric acid can be used but requires refluxing for several hours.



Benzenesulphonic acid

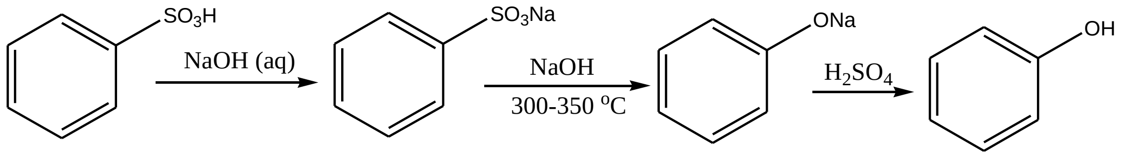
Mechanism

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3\overset{+}{O} + HSO_4^-$$



N.B The overall reaction is reversible with the equilibrium tending to the left.

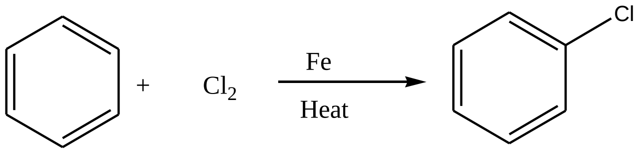
BenzeneSulphonic acid is used in the manufacture of phenol.i.e.



3. Halogenation

Substitution by chlorine or bromine takes place readily at room temperature in presence of halogen carriers e.g iron, aluminium chloride or iodine. Iodine does not easily substitute.

The halogen carrier functions as a Lewis acid inducing a certain degree of polarity in the halogen molecule.

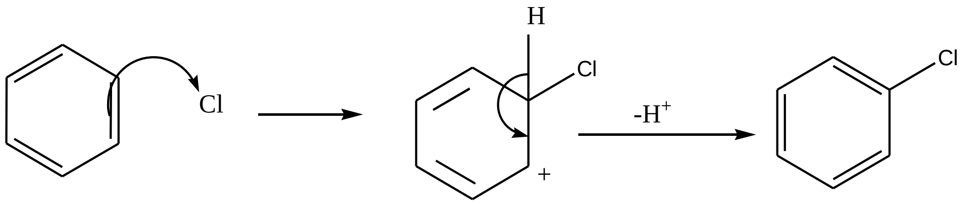


Chlorobenzene

Mechanism

$$2\,Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

$$Cl_2 + FeCl_3 \longrightarrow Cl + FeCl_4^-$$

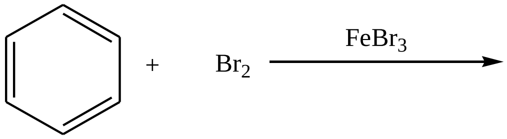


$$H^+ + FeCl_4^- \longrightarrow HCl + FeCl_3$$

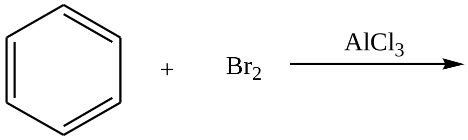
N.B. Bromine in presence of Iron (III) bromide follows the same mechanism.

Qn. Complete the reaction below, name the major product and write the acceptable mechanism of the reaction.

(a)

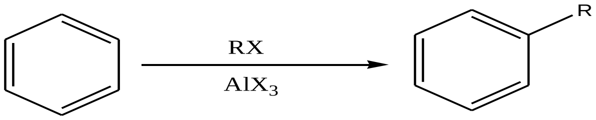


(b)

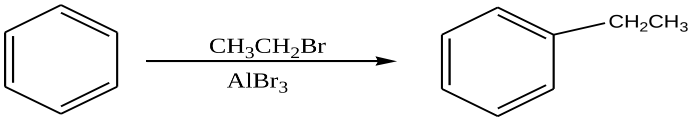


4. Friedel -Crafts Alkylation

Benzene reacts with alkyl halides in presence of Aluminium halides as Lewis acid to form alkyl benzene.

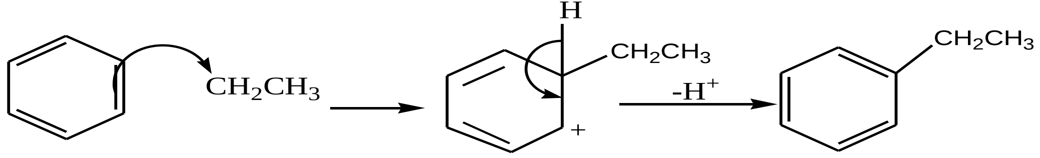


Example



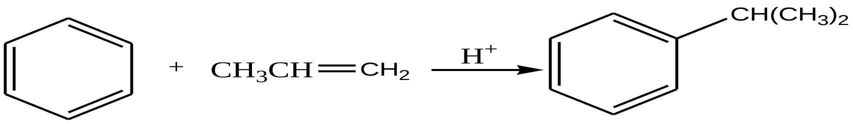
Mechanism

$$CH_3CH_2Br + AlBr_3 \longrightarrow CH_3CH_2^{+} + AlBr_4^{-}$$



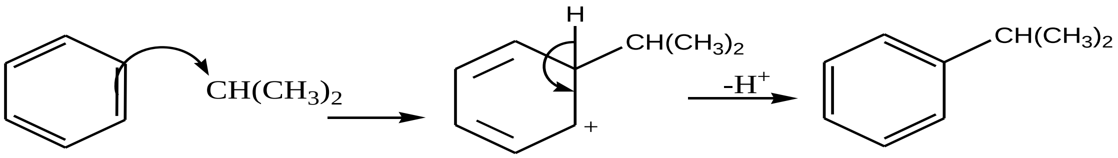
$$H^{+} + AlBr_4^{-} \longrightarrow HBr + AlBr_3$$

The Haloalkanes can be replaced by other compounds such as Alkenes and Alcohols e.g

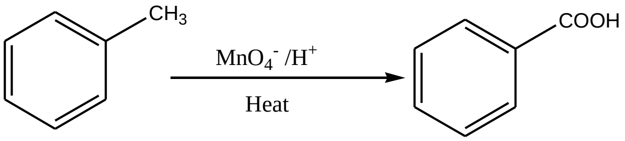


Mechanism

$$CH_3CH{=}CH_2 + H^{+} \longrightarrow CH_3CHCH_3$$

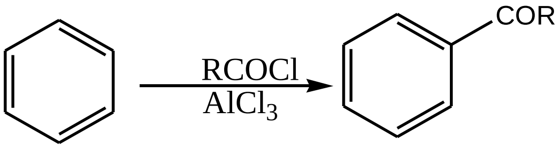


N.B. The alkyl group can be oxidized to carboxylic acid by Acidified $KMnO_4$ or dilute nitric acid

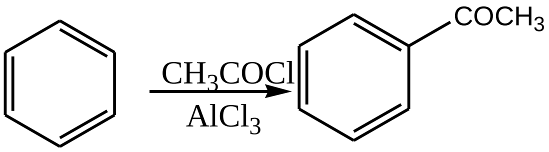


5. Friedel-Crafts Acylation

Acid Halides react with Benzene in presence of Aluminium Chloride to generate Aromatic Ketones.



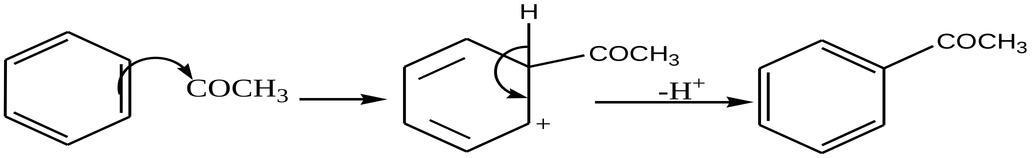
Example



Acetophenone

Mechanism

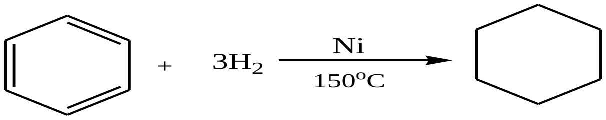
$$CH_3COCl + AlCl_3 \longrightarrow COCH_3 \quad + AlCl_4^-$$



N.B. Acid anhydrides i.e. $(RCO)_2O$ are generally preferred because they are easily obtained in a state of high purity, is more easily handled and resulting Ketones is more easily separated by distillation

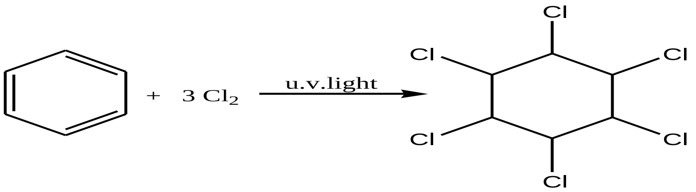
Other Important Addition reactions of Benzene include:

1. with Hydrogen



2. with Chlorine

Like Alkanes, Benzene undergo Addition reaction with chlorine in presence of sunlight or Ultraviolet radiation to form 1, 2, 3, 4, 5, 6-hexacyclohexane.



Position of Substitution in Benzene Derivatives

When a second atom or group of atoms is attached to monosubstituted benzene, the position of substitution is determined by the nature of the substituent already attached.

In fact, any substituent group attached to a benzene ring affects the rate and position at which further substitution occurs.

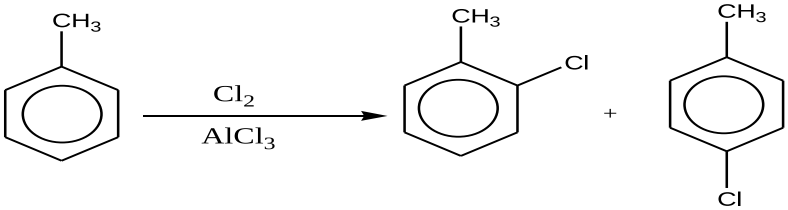
The position of substitution of the second substituent is governed largely by whether or not the atom or group already present is donating electrons to the ring or withdrawing electrons from it.

Electron-donating groups enhance the availability of the pie electrons hence *it activates the ring* generating products at position *2-(ortho) and 4-(Para).*

Examples of electron-donating groups include:

—R, —OH, —OR, —NH_2 —NHR, —NR_2

Example of substitution reaction with electron-donating group includes.



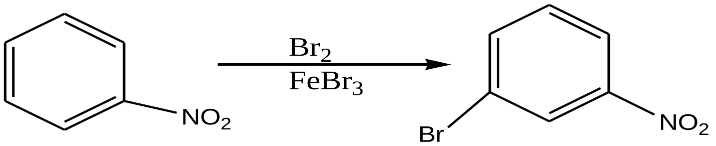
Presence *of halogens* on the benzene ring *deactivates t*he ring to products at positions 2- or 4- on substitution.

Electron- withdrawing groups reduce the availability of the pie-electrons hence deactivate the ring therefore on substitution position 3- preferred.

Examples of electron-withdrawing groups include:

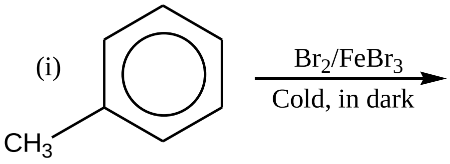
—NO_2 —CN —CHO —COR —COOH and —SO_3H

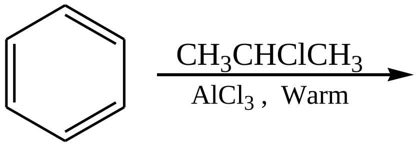
Example includes:



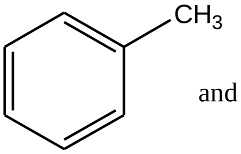
Question

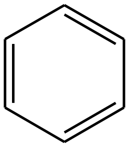
(a) Complete the following reactions and in each case write the acceptable mechanism;

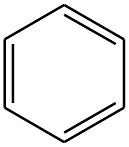
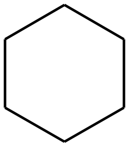
(i) 

(ii) 

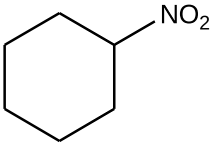
(b) How would distinguish between the following members of the pairs of compounds. In each case, state what would be observed when the reagent is treated with each member of the series.

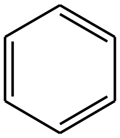
(i) 

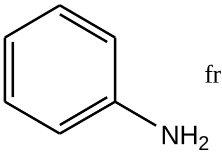
and 

(ii) 
and 

(c) Write equation(s) to show how the following compounds can be synthesized. In each case , indicate the condition(s)/reagent necessary.

(i) 

from 

(ii) 

from CH_3CH_2OH

(iii) $CH_3CH(Br)CH_3$ from CH_3CH_2Br

CHAPTER SIX

HALOHYDROCARBONS

Introduction

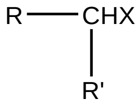
Organic halogen compounds are halogen derivatives of alkanes. Monohalo derivatives (Alkyl halides) have a general molecular formula $C_nH_{2n+1}X$ (X= Cl, Br and I). Fluorine is excluded because C-F bond is strong due to high electronegativity therefore C-F bond is unreactive.

Consequently fluorocarbon compounds are extremely inert and non-flammable.

Alkyl halides are divided into three classes depending on the number of the alkyl groups attached to the carbon atom bonded to the halogen i.e.

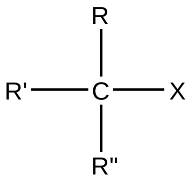
RCH_2X

Primary Alkyl halide, (1^o)



$R-CHX(R')$

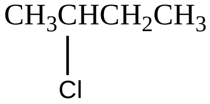
Secondary, (2^o)



$RR'R''C-X$

Tertiary, (3^o)

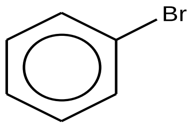
$CH_3CH_2CH_2Br$

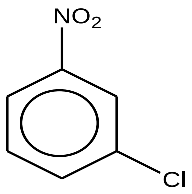


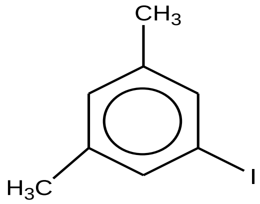
$CH_3CH(Cl)CH_2CH_3$

$(CH_3)_3C-I$

Aryl halides are halogen compounds in which the halogen atom is directly attached to the aromatic ring (Benzene). They are generally represented as ArX e.g.







If two halogen atoms are attached to adjacent carbon atom, the alkyl dihalides is known as Vicinal Dihalides while if are attached to the same carbon then it is known as germinal dihalides.

N.B Vinyl halides are compounds in which halogen is attached to a doubly bonded carbon e.g chloroethene while allyl halides are unsaturated halogen compounds.

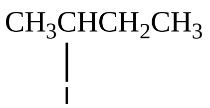
Nomenclature

Organic halogen compounds are named using the prefixes fluoro, chloro, bromo or iodo-. Numbers are used to indicate the position of the halogen atom in the carbon containing molecule.

Example

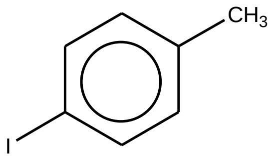
Name the following organic compounds

(a) CH_3CH_2Br

(b) 
$\underset{\displaystyle I}{CH_3\underset{|}{C}HCH_2CH_3}$

(c) $(CH_3)_3C—Cl$

(d) $C_6H_5CH_2Cl$

(e) 

Soln:

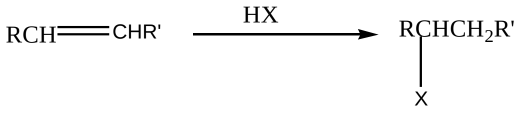
(a) Bromoethane (b) 2-iodobutane (c) 2-chloro-2-methylpropane
(d) Chloromethylbenzene

(e) 4-iodomethylbenzene

Synthetic Preparation

For Alkyl halides:

1. From Alkenes


$$RCH{=}CHR' \xrightarrow{HX} R\underset{\displaystyle X}{\underset{|}{C}}HCH_2R'$$

(See Alkenes for mechanism and detailed position for addition product)

2. From Alcohols

$$ROH \xrightarrow{SOCl_2} RCl + SO_2 + HCl$$

$$ROH \xrightarrow{PCl_5} RCl$$

$$CH_3CH_2OH \xrightarrow{SOCl_2} CH_3CH_2Cl$$

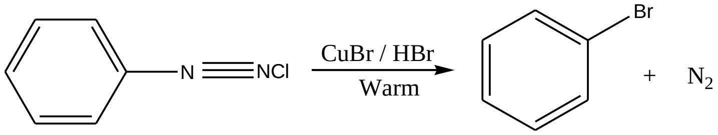
3. From Alkanes

Substitution with halogens in presence of sunlight or ultraviolet light is not suitable method since it generates a mixture of products.

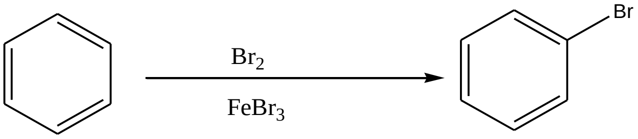
For Aryl Halides

1. From Diazonium salt

The salt is warmed with appropriate copper (I) halide e.g.



2. Direct Halogenation of Benzene



(See Benzene for Mechanism and other halogen and Halogen carriers)

Physical Properties

Because of the polarity of the carbon-halogen bond due to electronegativity difference which enhances dipole-dipole interaction in liquid phase, Haloalkanes have a higher boiling point than alkanes of comparable molecular mass.

Most Haloalkanes are liquids (except Iodomethane) and their boiling points depend on the alkyl group and halogen atom. Fluoroethane and chloroethane are gases.

For corresponding halogen atoms, boiling points increases with increasing molecular mass. Densities decreases in the same order due to close packing of smaller molecules in the liquid phase.

Haloalkanes and Aryl halides are both insoluble in water but soluble in organic solvent due to inability to form hydrogen bonds with water.

Reactions

The Haloalkanes are fairly reactive compounds due to polarity of the Carbon-halogen bonds therefore the electron deficient carbon atom is susceptible to attack by electron rich species hence their reactions are characterized by Nucleophilic substitution reactions.

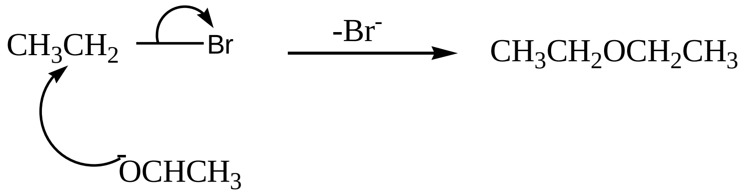
Some of the Nucleophilic substitution reactions include:

1. Ether Formation

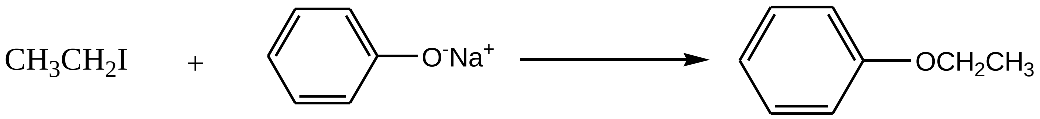
This reaction provides the suitable method for preparation of alkoaromatics and alkoalkanes.

$$CH_3CH_2Br \xrightarrow{CH_3CH_2\bar{O}Na^+} \underset{\text{ethoxyethane}}{CH_3CH_2OCH_2CH_3}$$

Mechanism



$$(CH_3)_2CH—Br \xrightarrow{CH_3CH_2O^-Na^+} (CH_3)_2CHOCH_2CH_3$$



Write the mechanism for the above reactions.

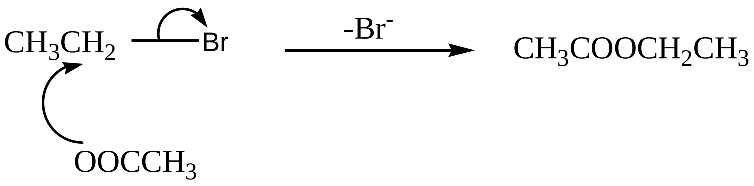
N.B. Sodium or Potassium Alkoxideare prepared by dissolving alkali metal in the excess appropriate alcohol.

2. Ester Formation

If the haloalkane is warmed with alcoholic solution of silver salt of carboxylic acid, an ester (sweet fruity smell) is formed. Silver halide is precipitated.

$$CH_3CH_2Br \xrightarrow[\text{warm}]{CH_3COO^-Ag^+/\text{ ethanol}} \underset{\text{ethylethanoate}}{CH_3COOCH_2CH_3}$$

Mechanism



The reaction cannot be used to generate phenyl esters.

N.B. A solution of Silver ethanoate in ethanol can be used to distinguish Haloalkanes from Acryl halides.

3. Amine Formation

When concentrated Ammonia solution is heated when Haloalkane in a sealed tube, different classes of amines are generated.

$$CH_3CH_2Br \xrightarrow[\text{Heat in sealed tube}]{NH_3} CH_3CH_2NH_2$$

$$CH_3CH_2NH_2 + CH_3CH_2Br \longrightarrow CH_3CH_2NHCH_2CH_3$$

$$(CH_3CH_2)_2NH + CH_3CH_2Br \longrightarrow (CH_3CH_2)_3N$$

To generate Primary amine, excess ammonia is used.

The reaction is limited to haloalkanes although aryl halides react if electron-withdrawing groups are present in 2- or 4- positions.

4. Cyanide (Nitrile) Formation

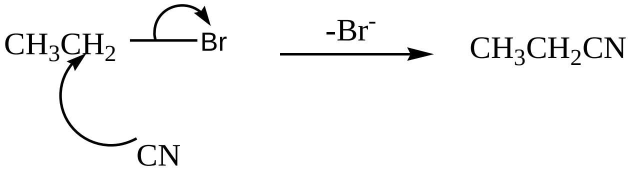
When heated, haloalkanes react with potassium cyanide in an alcohol to generate alkanenitrile.

$$RX \xrightarrow[\text{heat}]{\text{KCN/ EtOH}} RCN + KX$$

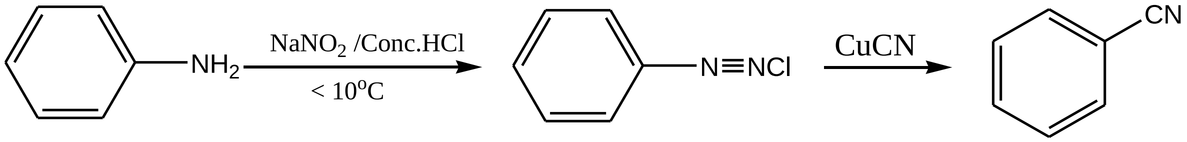
Example

$$CH_3CH_2Br \xrightarrow[\text{Heat}]{\text{KCN /EtOH}} CH_3CH_2CN$$

Mechanism



Aromatic nitriles are not prepared from aryl halides but from benzene Diazonium salts. i.e



Alkanenitrile are usually used to generate carboxylic acid of higher carbon chain. i.e.

$$\text{RCN} \xrightarrow[\text{reflux}]{H_2O\ /H^+} \text{RCOOH}$$

Example

$$CH_3Br \xrightarrow[\text{heat}]{\text{KCN / EtOH}} CH_3CN \xrightarrow[\text{reflux}]{H_2O\ /H^+} CH_3COOH$$

5. Higher Alkyne formation

Haloalkanes react with sodium salt of acidic alkyne to form higher non-terminal alkynes.

$$R'X + \quad RC\equiv C^-Na^+ \longrightarrow RC\equiv CR' \ + NaX$$

6. Grignard Reagent Formation.

Both haloalkanes and Aryl halides react with Magnesium in presence of dry ether to generate Grignard reagent.

$$R'X \xrightarrow[\text{dry ether}]{\text{Mg}} \underset{\text{Alkyl magnesium halide}}{R'MgX}$$

The reagent is widely used to generate alkanes, alkenes, alkynes, alcohols, Aldehydes, Ketones and carboxylic acid.

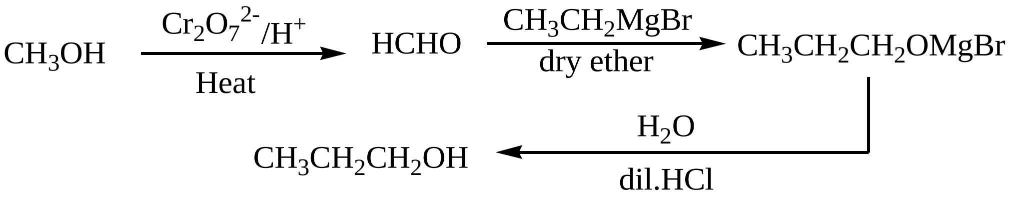
For Alkanes:

$$R'X \xrightarrow[\text{dry ether}]{\text{Mg}} R'MgX \xrightarrow[\text{dil.HCl}]{H_2O} \underset{\text{Alkane}}{R'H} + MgXOH$$

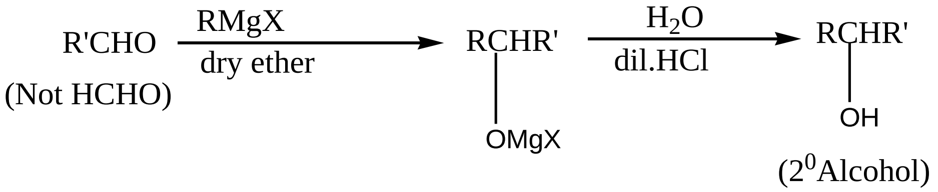
For Alcohols:

$$RMgX + \underset{\text{(methanal)}}{HCHO} \xrightarrow{\text{dry ether}} RCH_2OMgX \xrightarrow[\text{dil. HCl}]{H_2O} \underset{(1^o\text{Alcohol})}{RCH_2OH}$$

Example:



$$CH_3OH \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}/H^+} HCHO \xrightarrow[\text{dry ether}]{CH_3CH_2MgBr} CH_3CH_2CH_2OMgBr \xrightarrow[\text{dil.HCl}]{H_2O} CH_3CH_2CH_2OH$$



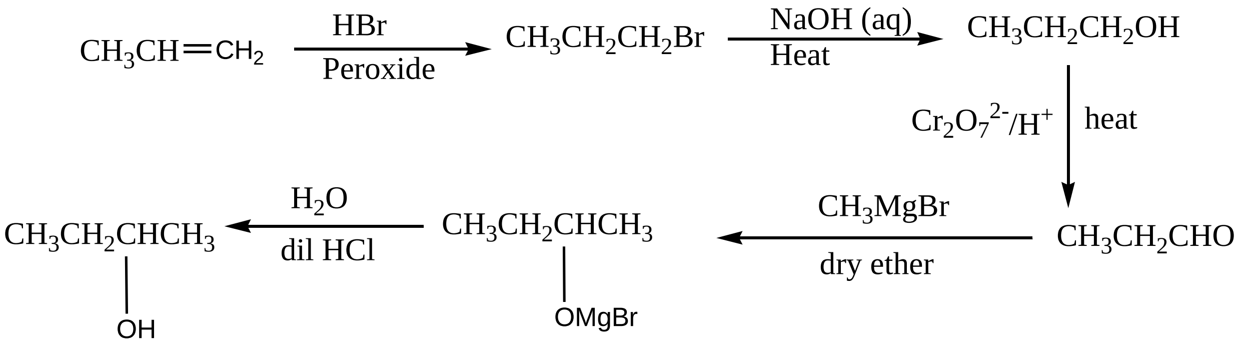
$$\underset{\text{(Not HCHO)}}{R'CHO} \xrightarrow[\text{dry ether}]{RMgX} \underset{OMgX}{RCHR'} \xrightarrow[\text{dil.HCl}]{H_2O} \underset{OH}{RCHR'}$$

(2⁰Alcohol)

Example

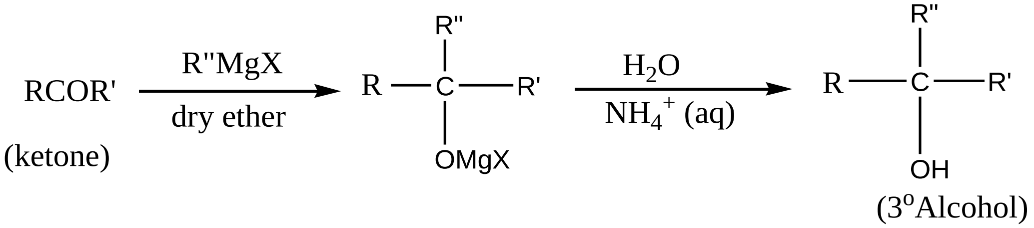
Write equations showing how Propene can be converted to Butan-2-ol.

Sol:



$$CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br \xrightarrow[\text{Heat}]{\text{NaOH (aq)}} CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} CH_3CH_2CHO \xrightarrow[\text{dry ether}]{CH_3MgBr} \underset{OMgBr}{CH_3CH_2CHCH_3} \xrightarrow[\text{dil HCl}]{H_2O} \underset{OH}{CH_3CH_2CHCH_3}$$

Example



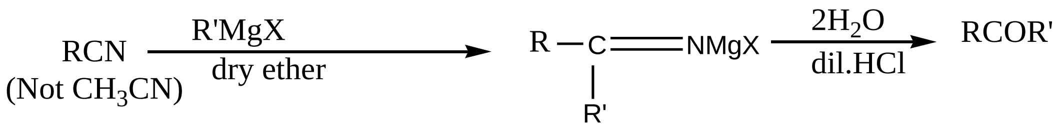
$$\underset{\text{(ketone)}}{RCOR'} \xrightarrow[\text{dry ether}]{R''MgX} R-\overset{R''}{\underset{OMgX}{C}}-R' \xrightarrow[NH_4^+ \text{(aq)}]{H_2O} R-\overset{R''}{\underset{OH}{C}}-R'$$

(3ᵒAlcohol)

N.B. Aqueous Ammonium salt is used in hydrolysis to generate 3ᵒAlcohol because the acid may dehydration to form Alkene.

Qn: Write equations showing how 2-methylpropan-2-ol can be synthesized from propan-2-ol.

For Ketones



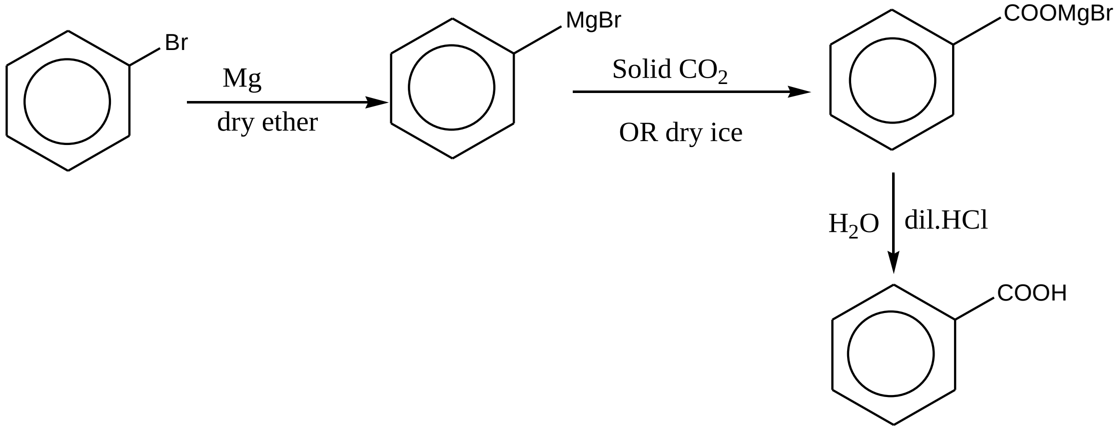
$$\underset{(\text{Not } CH_3CN)}{RCN} \xrightarrow[\text{dry ether}]{R'MgX} R-\underset{\displaystyle R'}{\underset{|}{C}}=NMgX \xrightarrow[\text{dil.HCl}]{2H_2O} RCOR'$$

For Carboxylic Acid

$$RMgX + CO_2 \xrightarrow{\text{dry ether}} RCOOMgX \xrightarrow[\text{dil.HCl}]{H_2O} \underset{(\text{Carboxylic acid})}{RCOOH} + Mg(OH)X$$

Example

Write equations showing how Benzoic acid can be prepared from Bromobenzene



7. Alcohol Formation

On heating, Alkyl halides react with sodium hydroxide solution on heating to form an alcohol.

For 3° Alkyl halide, the kinetic studies show that it is First order with respect to the alkyl halides consequently the rate determining step involves only the haloalkane therefore the mechanism and reaction is known as *Substitution Nucleophilicunimolecular (S_N1)*

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

Mechanism

$$(CH_3)_3C-Br \rightleftharpoons (CH_3)_3C^+ + Br^-$$

$$(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3C-OH$$

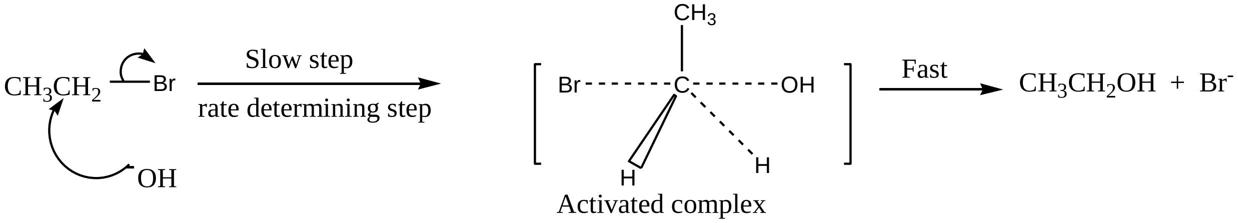
Qn: Draw a well labelled energy profile diagram for the reaction and State rate law for the reaction above.

For 1°haloalkane alkaline hydrolysis, the kinetic studies show that it is second order reaction therefore the dependent on the concentration of Haloalkane and hydroxide ions.

Consequently the rate determining step involves both species therefore the mechanism and reaction is known as *Substitution Nucleophilic bimolecular (S_N2)*

$$CH_3CH_2Br \xrightarrow[\text{heat}]{\text{NaOH (aq)}} CH_3CH_2OH$$

Mechanism



Qn: Draw a well labelled energy profile diagram for the reaction and State rate law for the reaction above.

Secondary haloalkanes show a mixture of both second and first order kinetics with the former predominating.

8. Alkene Formation or Elimination reaction

The reaction involves removal of halide ion and hydrogen to form the alkene. The hydrogen atom removed is the one bonded to the carbon atom adjacent to the one bonded to the halogen.

Unimolecular elimination (E_1)

This is undergone by 3°haloalkane to generate an alkene in presence of alcoholic potassium hydroxide and heat.

$$(CH_3)_3C{-}Br \xrightarrow[\text{heat}]{\text{KOH/ EtOH}} (CH_3)_2C{=}CH_2$$

Qn: Write the mechanism for the reaction

Bimolecular Elimination (E_2). This is undergone by 1°haloalkane and in the rate determining involves both the haloalkane and base to generate the alkene.

$$CH_3CH_2CH_2Br \xrightarrow[\text{Heat}]{KOH/\ CH_3CH_2OH} CH_3CH{=}CH_2$$

Qn: Write the mechanism for the reaction.

9. Reduction reaction

This can be done by:

(a) Using Lithium Aluminium hydride in dry ether.

$$RX \xrightarrow[\text{dry ether}]{LiAlH_4} RH$$

(b)Using sodium metal in dry ether (Wurtz reaction)

$$RX \xrightarrow[\text{dry ether}]{Na} R\text{-}R$$

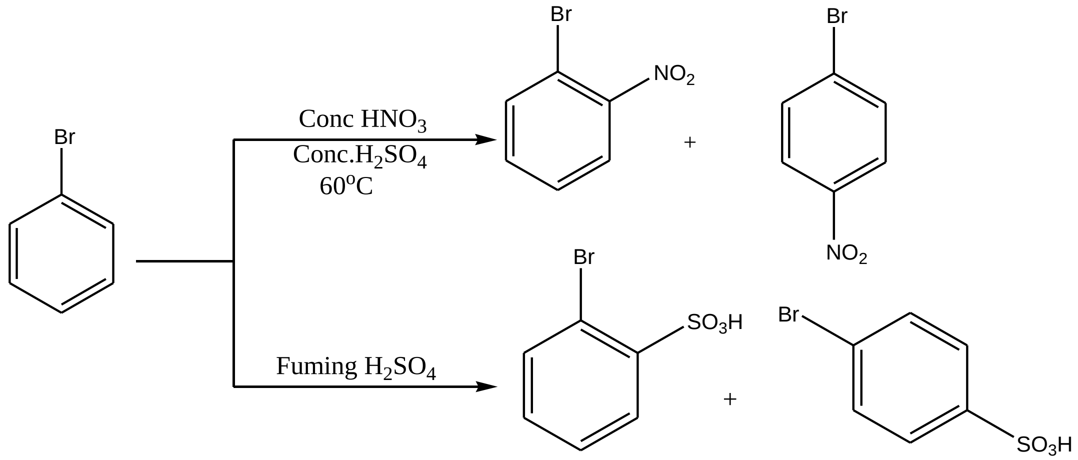
ELECTROPHILIC SUBSTITUTION REACTION OF ARYL HALIDES

Aryl halides differ in reaction from haloalkanes in that they do not undergo substitution of the halogen. This is because the lone pair of electrons on the halogen atom interacts with the delocalized electrons of the benzene ring. This strengthens the carbon-halogen bond or makes the carbon-halogen partly double bonded and difficult to break.

In the Alkyl halides, the carbon-halogen bond is polar because the halogen is a more electronegative atom therefore the carbon atom becomes partial positively charged atom. It is then attacked by electron rich species (Nucleophile) leading to substitution of the halogen atom.

Generally Aryl halides undergo Electrophilic substitution reaction to generate ortho and Para products.

Some of the reactions include:



Reagents used to distinguish Aryl halides from Alkyl halides include:

Hot silver ethanoate in ethanol or hot sodium hydroxide solution and silver nitrate solution

Sample Question:

1. Suggest Explanations for each of the following observations:

   a) Iodobenzene is more reactive than chlorobenzene towards but much less reactive than iodoethane.

   b) Tetrachloromethane is much less reactive towards Nucleophiles than chloromethane

   c) Iodo-and Bromo-compounds are much more useful as intermediates in synthesis than chloro-compounds.

2. Using equations indicating the required conditions to show how the following compounds can be synthesized:

   a) $CH_2{=}CH_2$ to CH_3CH_2COOH

   b) $CH_2{=}CH_2$ to $CH_3OCH_2CH_2OCH_3$

   c) $C_6H_5CH_3$ to $C_6H_5CH_2OH$

   d) CH_3CH_2Br to $CH_3CH_2CH_2OH$

3. (a) Methyl Benzene reacts with chlorine to form Chloromethylbenzene. State the conditions for the reaction

   (b) Under different conditions the product is phenyl chloromethane instead of Chloromethylbenzene.

   (i) State these conditions of the reaction (ii) Write a plausible mechanism for the reaction.

CHAPTER SEVEN

ALCOHOLS OR ALKANOLS AND PHENOL

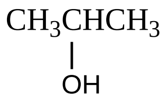
Introduction

Aliphatic Monohydric Alcohols are monohydroxyl derivatives of alkanes and have a general formula $C_nH_{2n+1}OH$ or $C_n H_{2n+2}O$

Aliphatic monools may be classified as 1°,2° or 3° according to the nature of the carbon atom to which the hydroxyl group is attached i.e.

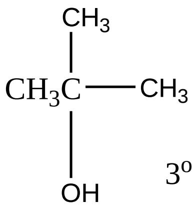
CH_3CH_2OH

1°



$CH_3\underset{\underset{OH}{|}}{C}HCH_3$

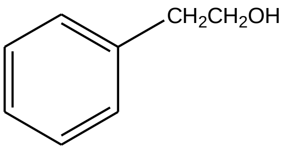
2°



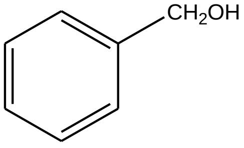
$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$

3°

Aromatic Alcohols have aryl group attached to aliphatic portion of the alcohol separated by at least a methylene group. E.g

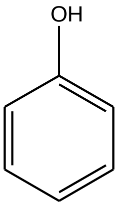


2-Phenylethanol

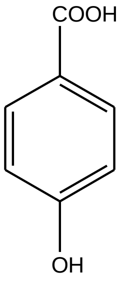


Phenylmethanol

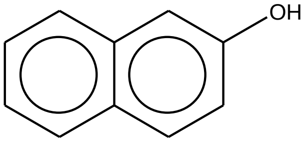
Compounds in which the hydroxyl group is attached directly to the benzene (Aromatic)ring are classified as **Pheno**l. E.g



Phenol



p-Hydroxybenzoic acid

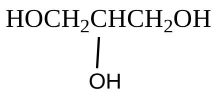


2-Napthol

Alcohols containing two hydroxyl groups are described as **dihydric alcohols or diols** and those with three hydroxyl groups are **triols** while those containing many hydroxyl groups are **polyols**. E.g.

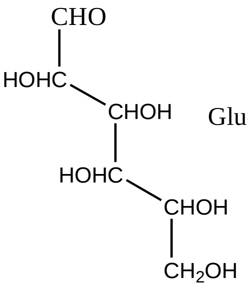
$HOCH_2CH_2OH$

Ethane-1,2-diol



$HOCH_2CH(OH)CH_2OH$

Propane-1,2,3-triol



Glucose

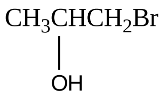
NOMENCLATURE OF ALCOHOLS

The IUPAC Names are obtained by dropping the ending ��**e** �of alkane and replacing it with suffix �**-ol**�. The position of the hydroxyl group is indicated by inserting an appropriate number between the stem name and ol.

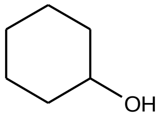
Example:

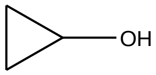
Name the following compounds using the IUPAC System

(a) CH_3OH (b) CH_3CH_2OH (c) $CH_3CH_2CH_2OH$ (d) $(CH_3)_3CCH_2OH$

(e) 

$CH_3CH(OH)CH_2Br$

(f) $CH_3CH_2CH(CH_3)CH_2OH$ (g) 

(h) 

Solution

(a) Methanol (b) Ethanol (c) Propan-1-ol (d) 2,2-dimethylpropan-1-ol

(e) 1-bromopropan-2-ol (f) 2-methylbutan-1-ol (g) Cyclohexanol (h) Cyclopropanol

ISOMERISM

Aliphatic monools have structural isomers .i.e. Chain, functional and Positional Isomers.

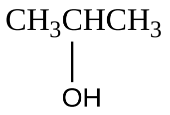
Ethers are functional isomers of monools.

Example:

A compound X has molecular formula C_3H_8O. Write down the structural formulae and names of the possible isomers of X.

Solution:

$CH_3CH_2CH_2OH$
Propan-1-ol



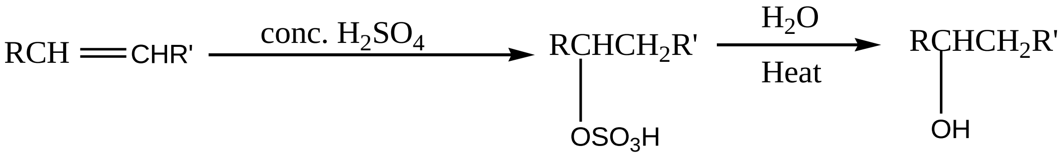
$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

Propan-2-ol

$CH_3OCH_2CH_3$
Methoxyethane

SYNTHETIC PREPARATION OF ALCOHOLS

1. **From Alkenes**



$$RCH{=}CHR' \xrightarrow{\text{conc. } H_2SO_4} R\underset{\displaystyle OSO_3H}{\underset{|}{C}}HCH_2R' \xrightarrow[\text{Heat}]{H_2O} R\underset{\displaystyle OH}{\underset{|}{C}}HCH_2R'$$

$$CH_2{=}CH_2 \xrightarrow{\text{conc.}H_2SO_4} CH_3CH_2OSO_3H \xrightarrow[\text{Heat}]{H_2O} CH_3CH_2OH$$

2. **From Alkyl halides**

$$RX \xrightarrow[\text{heat}]{\text{NaOH (aq)}} ROH \quad + NaX$$

$$CH_3CH_2Br \xrightarrow[\text{Heat}]{\text{NaOH (aq)}} CH_3CH_2OH$$

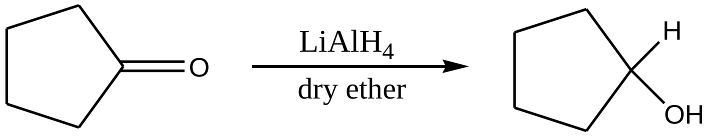
3. **From Carbonyl compounds**

   Reduction of carbonyl compounds generates alcohol. Aldehydes are reduced to Primary Alcohol while Ketones to Secondary Alcohol.

   The reducing agents commonly used are Na/ethanol, $LiAlH_4$ in dry ether, $NaBH_4$ and water, amalgamated Zinc and concentrated Hydrochloric acid, finely divided Ni or Pt with hydrogen gas.

   Lithium Aluminium hydride does reduce a double bond if it is present in the carbonyl compound.

$$CH_3CH_2CHO \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2CH_2OH$$



4. **Grignard Reagent Synthesis**

   See Reactions of Haloalkanes.

5. **Reduction Of Carboxylic acids**

   Carboxylic acids are reduced to Primary Alcohols using $LiAlH_4$ in dry ether.

$$RCOOH \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2OH$$

$$CH_3CH_2COOH \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2CH_2OH$$

6. **From Esters**

   Esters are hydrolysed by aqueous sodium hydroxide solution to generate an alcohol. However this is not usually done since esters are obtained from alcohols.

$$RCO_2R' \xrightarrow[\text{heat}]{OH^-(aq)} RCOO^-(aq) + R'OH$$

7. **Cannizzaro Reaction**

   Aromatic Aldehydes without α -hydrogen atoms undergo self-reduction and oxidation in sodium hydroxide solution.

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$$

DOMESTIC PRODUCTION OF ETHANOL

Ethanol is mainly prepared by fermentation process. Fermentation is a process where starch or sugar is converted to ethanol by yeast enzymes.

The main sources of the starch materials include maize, millet, cassava, sorghum, potatoes, banana, rice, molasses, etc.

The enzymes that participate in the fermentation process and their stages include:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)n} \quad + n\,H_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CH_3CH_2OH + 2CO_2$$

Qn:

a) Describe the processes involved in the production of ethanol from a named material domestically

b) State briefly how the purification of the ethanol produced can be done

c) State four uses of ethanol

d) State two effects of over consumption of ethanol on the human body.

Physical Properties of Alcohols

a) Solubility

Lower members of the series are soluble however, solubility decreases as the hydrocarbon portion increases. The miscibility of alcohols is due to ability of the formation of hydrogen bond with water molecule.

b) Boiling Points

Alcohols boil at higher temperatures expected because the molecules associate through hydrogen bonding which requires an extra energy to break.

Within the series, boiling points increase with molecular mass.

c) Density

Density increases with increasing molecular mass although branching reduces the factor. Aliphatic alcohols are less dense than water while Aromatic alcohols tend to be slightly denser than water.

REACTIONS OF ALCOHOLS

1. With Electropositive Metals

Although Alcohols are neutral to neutralization indicators, the hydroxyl group can be replaced by metals of Group I and II of the periodic table. The products are hydrogen gas and metal Alkoxide.

$$2ROH + Na \longrightarrow 2RO^{-}Na^{+} + H_2$$

$$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^{-}Na^{+} + H_2$$

2. Halogenation

This can be done by:

a) Using Hydrogen Halide

They react with hydrogen halides to form alkyl halides. The order of reactivity for alcohols is $3^o>2^o>1^o$ while for hydrogen halides is HI>HBr>HCl.

$$ROH \xrightarrow{HX} RX + H_2O$$

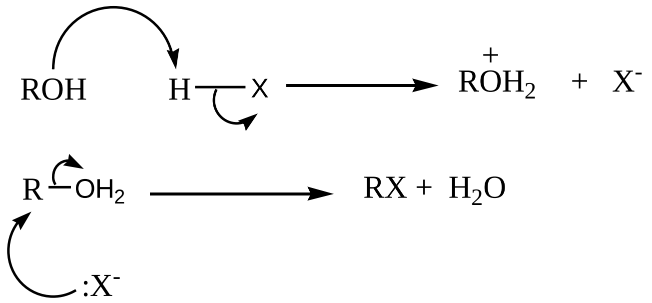
1^o Alcohols undergo bromination with hydrogen bromide which is generated from sodium bromide and concentrated sulphuric acid.

In case of hydrogen chloride, the reaction is carried by using anhydrous Zinc chloride and concentrated hydrochloric acid. (Luca's Reagent)

The reagent is used to distinguish the classes of monools i.e.

- 3^0 Alcohol forms a cloudy solution immediately
- 2^oAlcohols forms cloudiness between 5-10minutes
- 1^o Alcohol no observable change.

Mechanism



b) Using Phosphorous Halides

$$ROH \xrightarrow{PX_3} RX + H_3PO_3 \quad \text{where X= Br or I}$$

c) Using Thionyl chloride

Thionyl Chloride and Phosphorous pentachloride generate alkyl chloride.

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

3. Concentrated Sulphuric acid

The products of the reaction depend on the conditions of the reaction under which it is carried out.

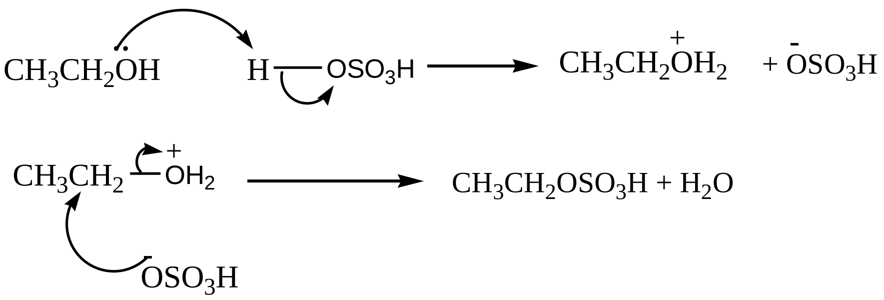
a) At lower temperatures (below 140°C), alkyl hydrogen sulphate is obtained

$$ROH \xrightarrow{\text{Conc. } H_2SO_4} ROSO_3H + H_2O$$

$$CH_3CH_2OH \xrightarrow{\text{Conc.}H_2SO_4} CH_3CH_2OSO_3H + H_2O$$

(ethyl hydrogen sulphate)

Mechanism

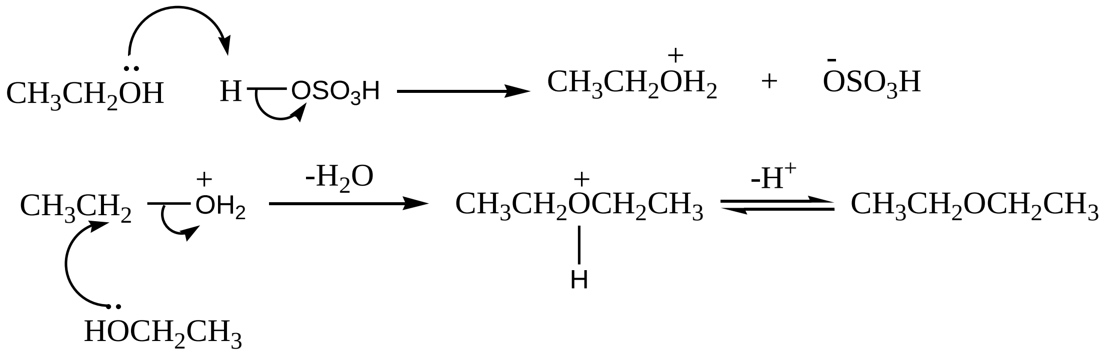


b) At about 140°C when excess alcohol, ether is obtained.

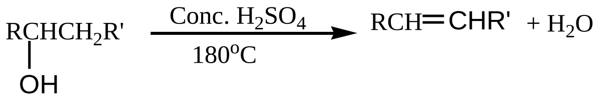
$$ROH \xrightarrow[140^{o}C]{\text{Conc. } H_2SO_4} ROR + H_2O$$

$$CH_3CH_2OH \xrightarrow[140^oC]{Conc.H_2SO_4} CH_3CH_2OCH_2CH_3$$

Mechanism



c) When the reaction is carried out at about 180°C, an alkene is obtained. Aluminium Oxide at 350°C or concentrated orthophosphoric acid can be used.



$$\underset{OH}{RCHCH_2R'} \xrightarrow[180^oC]{Conc.\ H_2SO_4} RCH{=}CHR' + H_2O$$

$$CH_3CH_2OH \xrightarrow[Heat]{Conc.H_2SO_4} CH_2{=}CH_2$$

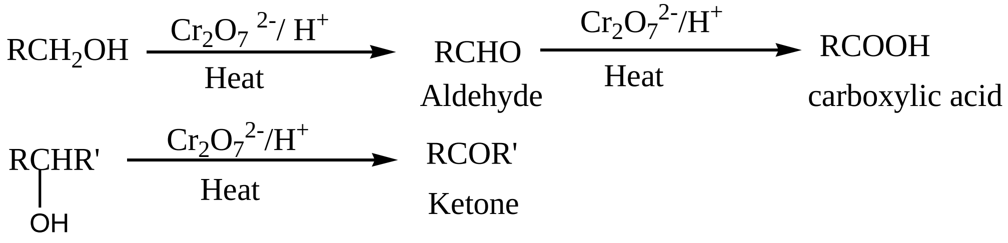
4. Oxidation reaction

The product oxidation depends on the type of alcohol and partly the power of oxidizing agent.

Primary Alcohols are oxidized to Aldehydes and the reaction proceeds to carboxylic acid while Secondary Alcohols are oxidized to Ketones.

Tertiary Alcohols are resistant to oxidation.

The oxidizing agents commonly used are acidified potassium dichromate or acidified chromium (VI) oxide



$$RCH_2OH \xrightarrow[Heat]{Cr_2O_7{}^{2-}/\ H^+} \underset{Aldehyde}{RCHO} \xrightarrow[Heat]{Cr_2O_7{}^{2-}/H^+} \underset{carboxylic\ acid}{RCOOH}$$

$$\underset{OH}{RCHR'} \xrightarrow[Heat]{Cr_2O_7{}^{2-}/H^+} \underset{Ketone}{RCOR'}$$

5. Esterification reaction

The process whereby a primary alcohol reacts with a monocarboxylic acid is known as esterification.

The reaction usually takes place in presence of concentrated sulphuric acid and it is reversible reaction.

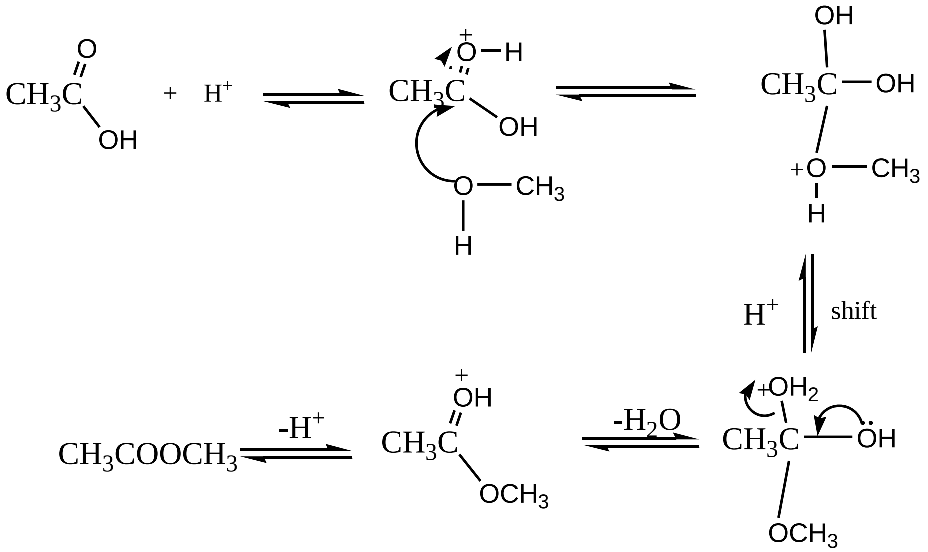
$$\mathrm{RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O}$$

Example:

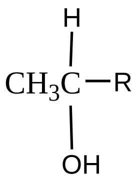
$$\mathrm{CH_3CO_2H + CH_3OH \rightleftharpoons CH_3CO_2CH_3 + H_2O}$$

Mechanism:

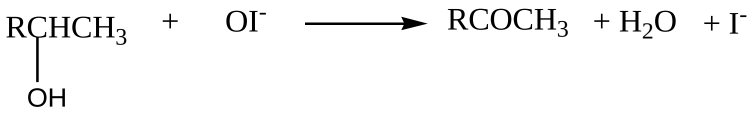
This was determined using radioactive Oxygen (18). The primary alcohol containing oxygen-18 is reacted with monocarboxylic acid. The mass spectrometer is used to analyse the ester and water formed. The oxygen-18 is found in the ester only and not water indicating that carbon-oxygen single bond in the acid and oxygen-hydrogen bond in the alcohol are bonded.



6. Iodoform reaction

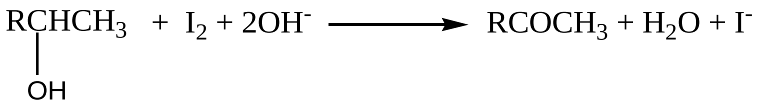
Alcohols of the form  $CH_3CH(OH)R$ react with iodine in presence of sodium hydroxide solution to form a yellow solid.

Iodine is an oxidizing agent and can oxidize alcohols to Aldehydes or Ketones.



$$RCH(OH)CH_3 + OI^- \longrightarrow RCOCH_3 + H_2O + I^-$$

OR



$$RCH(OH)CH_3 + I_2 + 2OH^- \longrightarrow RCOCH_3 + H_2O + I^-$$

Ethanol is the only primary alcohol which gives a positive.

N.B. Chlorine forms chloroform which is colourless liquid, Bromine forms bromoform which is reddish-brown.

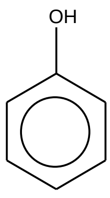
PHENOL

Introduction

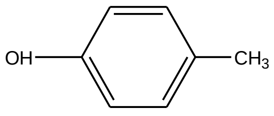
These are compounds containing a hydroxyl group attached directly to aromatic nucleus (Benzene) and have a general formula *ArOH.*

Like alcohols they may be monools or polyols depending on the number of the hydroxyl groups they contain.

Examples include:



Phenol



4-Methylphenol

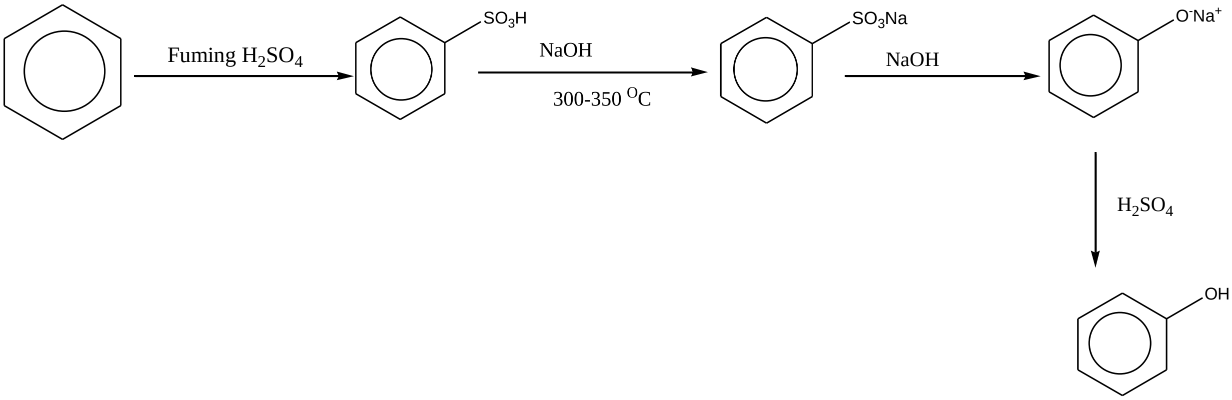
Physical Properties

Phenol is colourless crystalline solid although often found red tint due to presence of oxidation products. It is slightly soluble but very soluble in organic solvents.

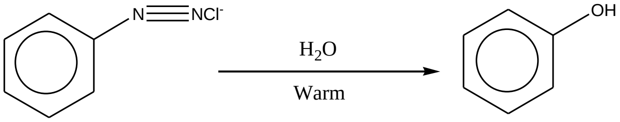
N.B. The introduction of the hydroxyl group into an already substituted aromatic ring especially in position-4 produces a marked increase in the boiling point. E.g. the greater volatility of 2-nitrophenol is attributed to intramolecular hydrogen bonding while the higher boiling points of 3- and 4- isomers are direct result of intermolecular hydrogen bonding.

Preparation of Phenol

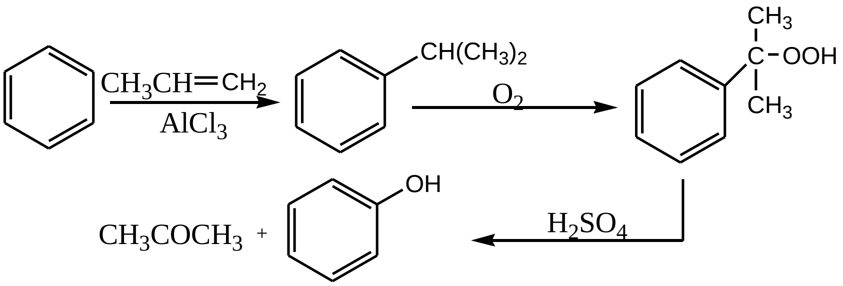
a) From Benzene sulphonic acid



b) From Benzene Diazonium salt.



c) Cumene process



Reactions of Phenol

Phenol undergoes two distinct reactions i.e.

a) Side-chain substitution reactions which generally involves replacement of the acidic proton

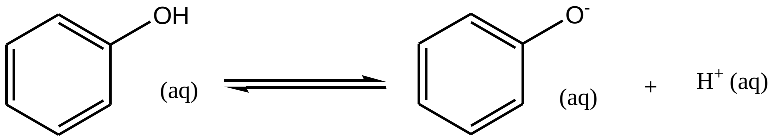
b) Electrophilic substitution in the ring.

Phenol as an acid

Phenol is a stronger acid than alcohols but weaker acid compared to carboxylic acid.

Qn: Explain briefly why phenol is more acidic compared to Ethanol

Soln: In phenol, the lone pair of electrons on the oxygen atom interacts with delocalized electrons of the benzene ring. This strengthens the carbon-hydrogen bond while weakening the oxygen-hydrogen bond consequently; phenol loses a proton easily making it acidic.



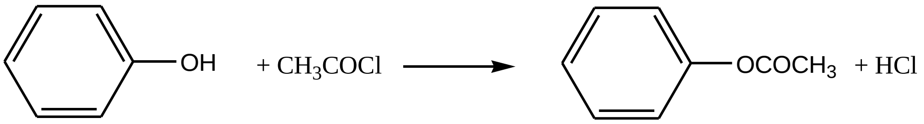
In ethanol, the oxygen-hydrogen bond is not weakened and the proton is not easily lost. This is because there are no delocalized electrons to interact with lone pairs of electrons on the electrons.

Note: Due to the above reason, phenol differs from alcohols in that it does not react with halogen acids or Phosphorus halides and does not undergo elimination reaction

a) **Side-chain reactions include**:

1) **Esterification reaction**

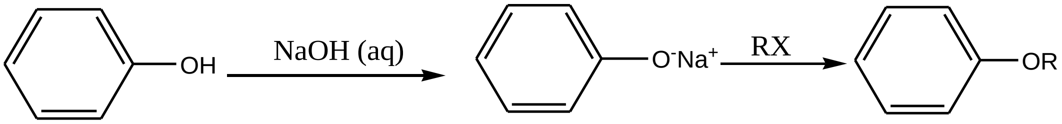
Phenol reacts with acid chlorides and acid anhydrides to form esters



Phenylethanoate

2) **Ether Formation**

Sodium phenate (Sodium phenoxide) reacts with alkyl halides to form ethers



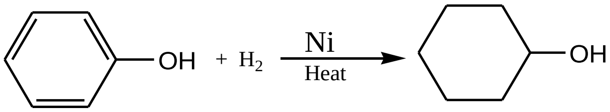
3) With Neutral Iron (III)chloride solution

Phenol reacts with neutral Iron (III) chloride solution to form a violet colouration due to a complex formed.

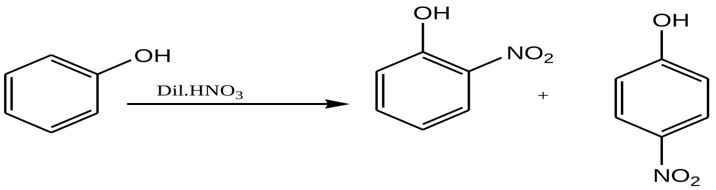
b) Electrophilic Substitution of the ring

Phenol is more reactive towards Electrophilic reagent than Benzene since it activates position 2- and 4- therefore the products formed at those positions.

1) Reduction reaction



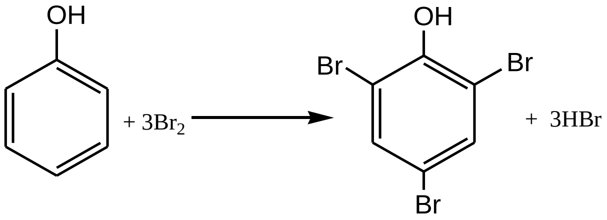
2) Nitration reaction



3) Bromination

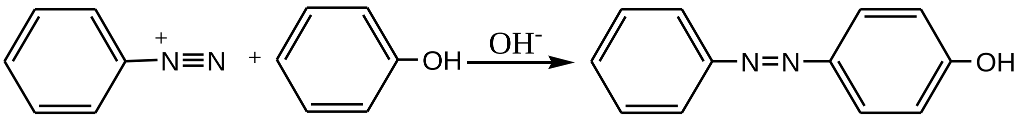
In aqueous solution, phenol reacts with bromine to form a white precipitate of 2, 4, 6-tribromophenol.

This reaction is used also to test for presence of phenol and estimate phenol quantitatively.



4) Coupling with Benzene Diazonium salts

Benzene Diazonium salt solution is added to alkaline solution of phenol to generate bright yellow precipitate of 4-hydroxyphenylazobenzene.



4-hydroxphenylazobenzene

Question

1. Explain the following observation:
    a) Ethanol is more acidic than 2-methylpropan-2-ol but less acidic than phenol
    b) Phenol is easily nitrated using nitric acid whereas Benzene is nitrated using a mixture of concentrated nitric acid and sulphuric acid
    c) Butan-1-ol is more soluble in 5M hydrochloric acid than in water
    d) The boiling point of ethanol (78^{o}C) is greater than Ethoxyethane (35^{o}C)
2. Write the half and overall equation of reaction for:
    a) Ethanol and acidified potassium dichromate solution
    b) Ethene and acidified potassium manganate (VII) solution

CHAPTER EIGHT

CARBONYL COMPOUNDS

Introduction

Aldehydes and Ketones are referred to as Carbonyl compounds as both contain the carbonyl functional group.

The saturated aliphatic series are homologous and correspond to a general molecular formula $C_nH_{2n}O$.

Aldehydes possess single hydrogen attached to the carbonyl carbon whereas Ketones always contain two hydrocarbon groups

Aldehydes are more reactive therefore easily oxidized and also more susceptible to Nucleophilic addition.

Nomenclature of Aldehydes and Ketones

For Aldehydes, the IUPAC names are obtained by dropping the ending **�-e�**of the corresponding alkane and replacing it with suffix **�-al�** for Aldehydes name.

The IUPAC names for Ketones is also obtained by dropping the ending�-e� of alkanes and replacing it with suffix**�-one�**

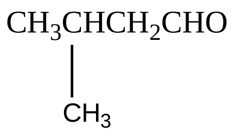
The position for carbonyl group is indicated by inserting an appropriate number between stem name and �one.

Example

Name the following organic compounds:

(a) CH_3CH_2CHO

(b)



$$\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HCH_2CHO}$$

(c) $CH_3COCH_2CH_2CH_3$

PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS

Simple aliphatic Aldehydes and Ketones with exception of methanal are all colourless liquids. The lower Aldehydes possess rather unpleasant smell whereas Ketones and Benzenecarbaldehyde have pleasant, sweet odours.

Methanal is a gas at room temperature and rest are liquids. Carbonyl group is polar therefore Aldehydes and Ketones have a higher boiling points but lower than those of alcohols since they do not form strong hydrogen bonds with each other.

Lower Aldehydes and Ketones are appreciably soluble in water due to their ability to form hydrogen bonds with water molecules and the resultant solution is neutral to litmus.

The density of the aliphatic compounds of both series is less than that of water but it increases with increase in molecular mass.

Synthetic Preparations

1) Oxidation of Alcohols

1^{o} Alcohols are oxidized to Aldehydes while 2^{o} Alcohols are oxidized to Ketones using acidified potassium dichromate or acidified chromium (VI) oxide.

$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}/\,H^+} \underset{\text{ethanal}}{CH_3CHO} \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}/\,H^+} \underset{\text{ethanoic acid}}{CH_3COOH}$$

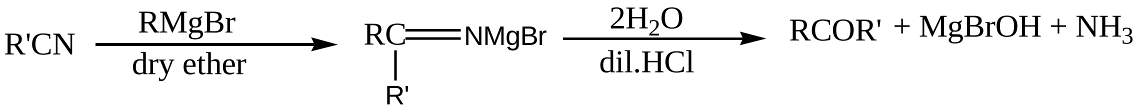
$$\underset{\text{Propan-2-ol}}{(CH_3)_2CHOH} \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}/\,H^+} \underset{\text{propanone}}{(CH_3)_2CO}$$

Oxidization can also be accomplished by dehydrogenation of the alcohol using copper catalyst heated at about $300^{o}C$

$$RCH_2OH \xrightarrow[300^{o}c]{Cu} RCHO$$

2) From Grignard reagent.

When Grignard reagent reacts with cyanide compounds and on hydrolysis a Ketones are obtained.



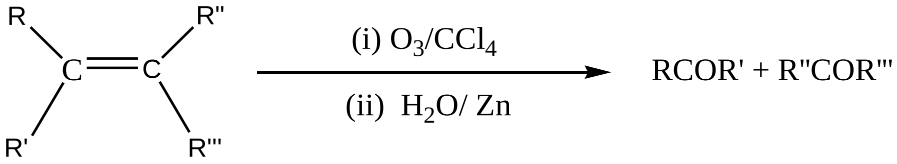
$$R'CN \xrightarrow[\text{dry ether}]{RMgBr} \underset{R'}{\underset{|}{RC}}{=}NMgBr \xrightarrow[\text{dil.HCl}]{2H_2O} RCOR' + MgBrOH + NH_3$$

3) Decarboxylation method of Calcium salts

$$(CH_3COO)_2Ca \;+\; (HCOO)_2Ca \xrightarrow{\text{heat}} 2CH_3CHO + 2CaCO_3$$

$$(CH_3COO)_2Ca \xrightarrow{\text{heat}} CH_3COCH_3 \;+ CaCO_3$$

4) Ozonolysis of Alkenes



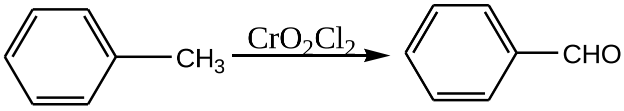
$$CH_3CH{=}CHCH_3 \xrightarrow[\text{(ii) } H_2O/\ Zn]{\text{(i) } O_3\ /CCl_4} CH_3CHO$$

5) Hydration of Alkynes

$$RC{\equiv}CR' \xrightarrow[HgSO_4,\ 60^oC]{H_2O,\ \text{dil. } H_2SO_4} RCOCH_2R'$$

$$CH{\equiv}CH \xrightarrow[HgSO_4\ ,\ 60^oC]{H_2O,\ \text{dil.}H_2SO_4} CH_3CHO$$

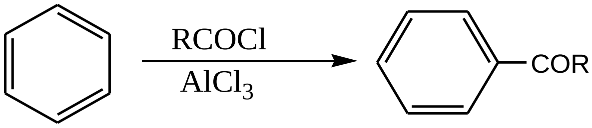
6) From methyl benzene



methylbenzene benzylaldehyde

QN: Show methyl benzene can be converted to Benzoic acid using equation (s) of reactions.

7) Acylation method



Question:

a) Write the mechanism of the reaction above

b) Using equations show how 1-phenyl ethanol can be prepared from benzene.

c) Write equations showing how Benzene can be obtained from 1-phenylethanol.

Reactions of Carbonyl compounds

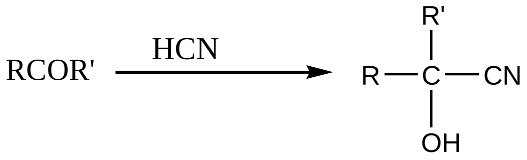
In carbonyl compounds, the carbonyl carbon has a partial positive charge because it is bonded to a more electronegative oxygen atom therefore it is attacked by a Nucleophile.

The susceptibility of the carbonyl carbon to Nucleophilic attack is reduced by its attachment to electron-releasing alkyl or aryl groups which reduces the degree of positive charge on the carbon.

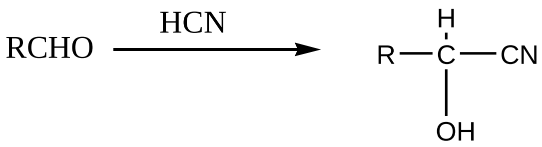
Steric hindrance by the hydrocarbon groups impedes the approach of the attacking Nucleophile and reduces the reactivity.

Some of the Nucleophilic addition reactions include;

1) Addition of Hydrogen cyanide:



$$\mathrm{RCOR'} \xrightarrow{\mathrm{HCN}} \mathrm{R{-}\underset{OH}{\overset{R'}{C}}{-}CN}$$

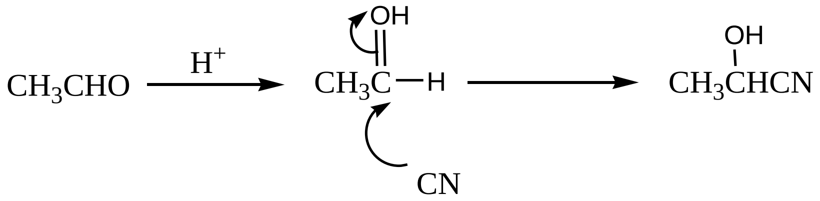


$$\mathrm{RCHO} \xrightarrow{\mathrm{HCN}} \mathrm{R{-}\underset{OH}{\overset{H}{C}}{-}CN}$$

Hydrogen cyanide is usually prepared during a reaction of dilute sulphuric acid on alkali metal cyanide.

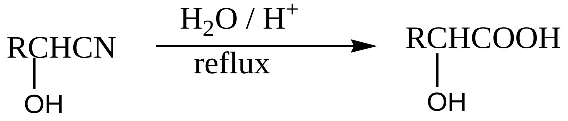
$$\mathrm{CH_3CHO} \xrightarrow{\mathrm{HCN}} \mathrm{CH_3\underset{H}{\overset{OH}{C}}{-}CN}$$

Mechanism



$$CH_3CHO \xrightarrow{H^+} CH_3\overset{OH}{\overset{\|}{C}}-H \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCN$$

Cyanohydrins are used to synthesize 2-or α -hydroxy acids on hydrolysis.

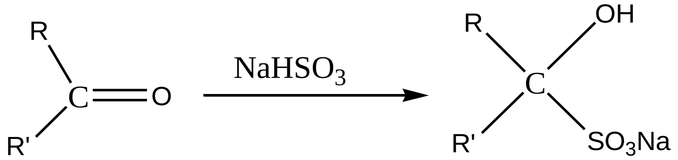


$$R\underset{OH}{\underset{|}{C}}HCN \xrightarrow[\text{reflux}]{H_2O\ /\ H^+} R\underset{OH}{\underset{|}{C}}HCOOH$$

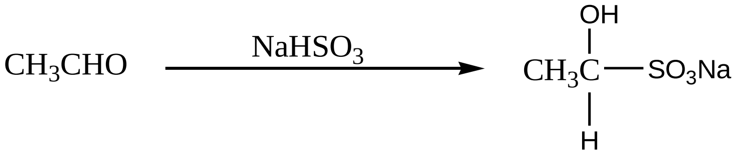
Qn: Using equations indicating the necessary conditions show Ethene can be converted to 2-hydroxypropanoic acid.

2) Addition of saturated sodium hydrogen sulphite solution

The reaction occurs readily with most Aldehydes and some Ketones especially methyl Ketones to form white solids of Aldehydes or Ketones hydrogen sulphite.

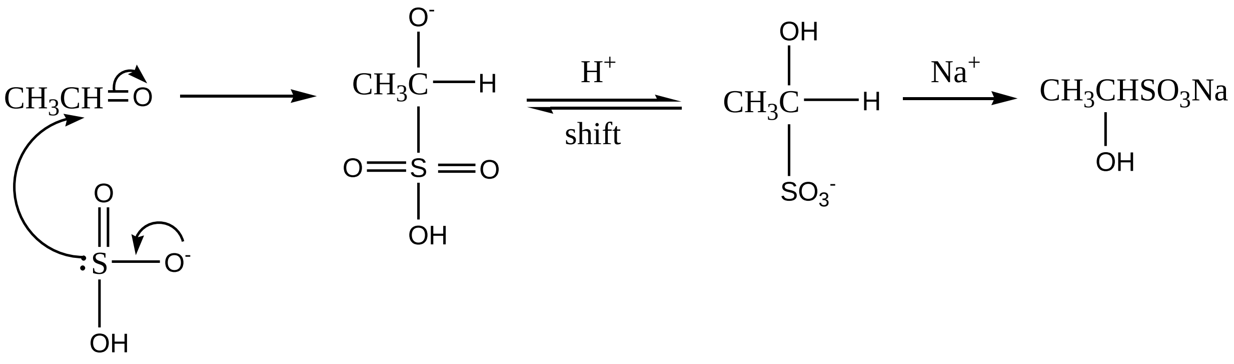


Aldehyde or Ketone hydrogen sulphite



$$CH_3CHO \xrightarrow{NaHSO_3} CH_3\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-SO_3Na$$

Mechanism



$$CH_3CH{=}O \longrightarrow CH_3\overset{O^-}{\overset{|}{C}}-H \underset{\text{shift}}{\overset{H^+}{\rightleftharpoons}} CH_3\overset{OH}{\overset{|}{\underset{SO_3^-}{\underset{|}{C}}}}-H \xrightarrow{Na^+} CH_3\underset{OH}{\underset{|}{C}}HSO_3Na$$

Qn: Write equation showing show Propanone can be converted to Propanone hydrogen sulphite and indicate the mechanism of the reaction.

3. **Condensation reaction or Elimination of water molecules.**

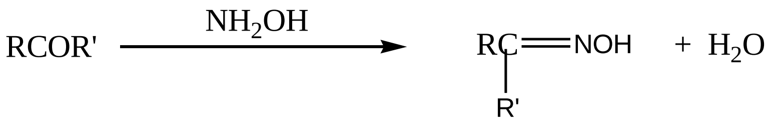
In this reaction, carbonyl compounds react with derivatives of ammonia of general form X-NH2 to release water molecules.

The final products are usually solids which are easily isolated and purified by recrystallisation.

Some of the addition reagents include:

a) **With Hydroxylamine,NH_2OH**

The product formed is white solid is Aldehydes or Ketone oxime.



$$RCOR' \xrightarrow{NH_2OH} R\underset{\underset{R'}{|}}{C}{=}NOH + H_2O$$

$$CH_3CHO \xrightarrow{NH_2OH} \underset{\text{ethanal oxime}}{CH_3CH{=}NOH} + H_2O$$

Qn: Write the mechanism of the reaction above and show how the product formed can be converted to:

(i) $CH_3CH_2NH_2$

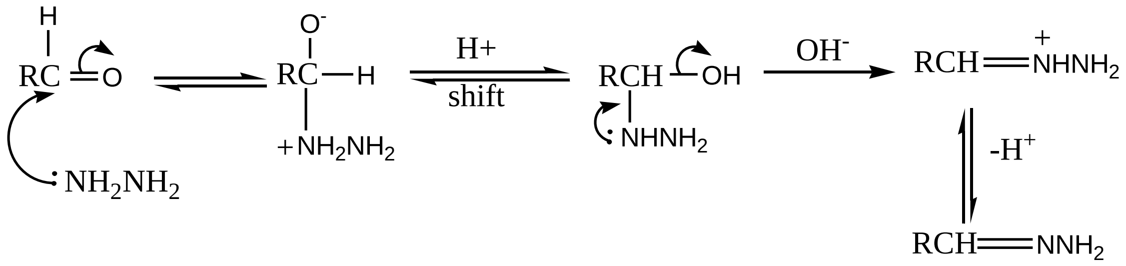
(ii) CH_3COOH

b) **With hydrazine, NH_2NH_2**

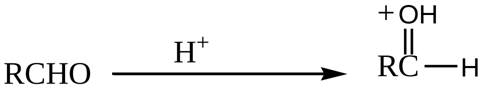
The product is Aldehydes or Ketoneshydrazone which in excess yield azine.

$$RCHO \xrightarrow{NH_2NH_2} \underset{+\,H_2O}{RCH{=}NNH_2} \xrightarrow{RCHO} RCH{=}NN{=}CHR + H_2O$$

Mechanism



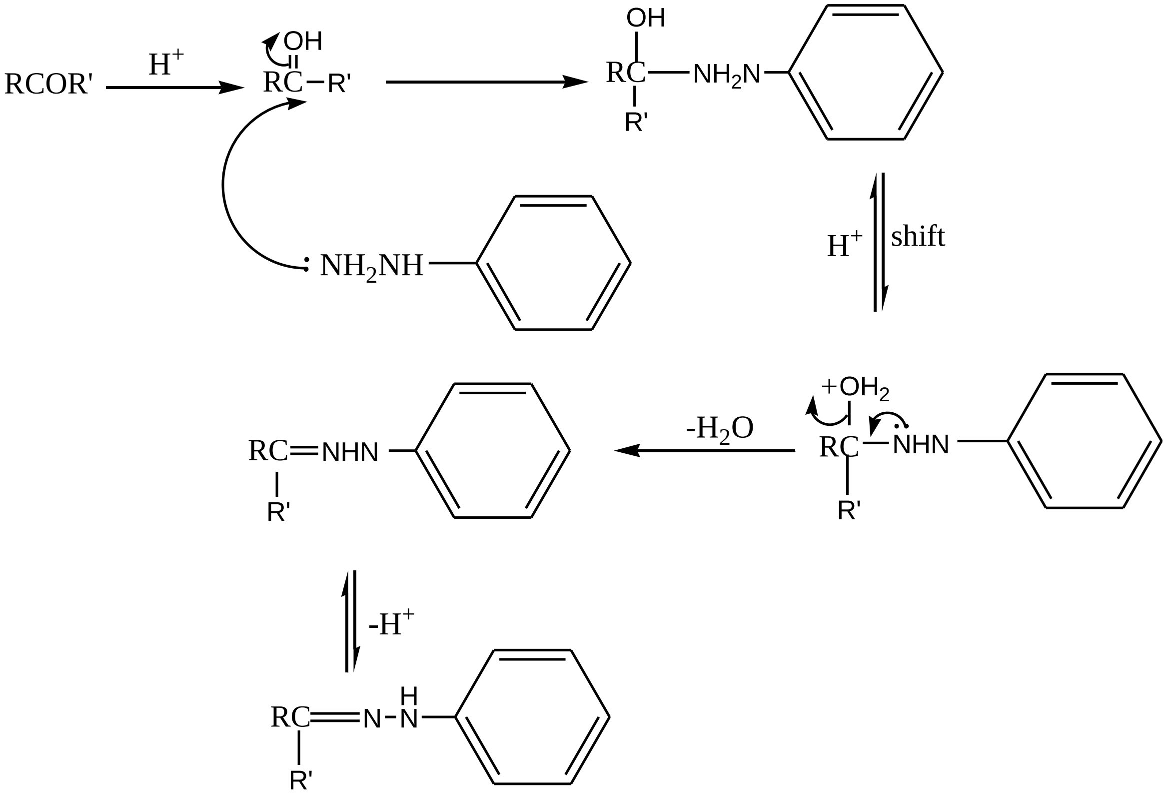
N.B. In presence of an acid, protonation is the first stage



$$RCHO \xrightarrow{H^+} R\overset{+OH}{\overset{\|}{C}}-H$$

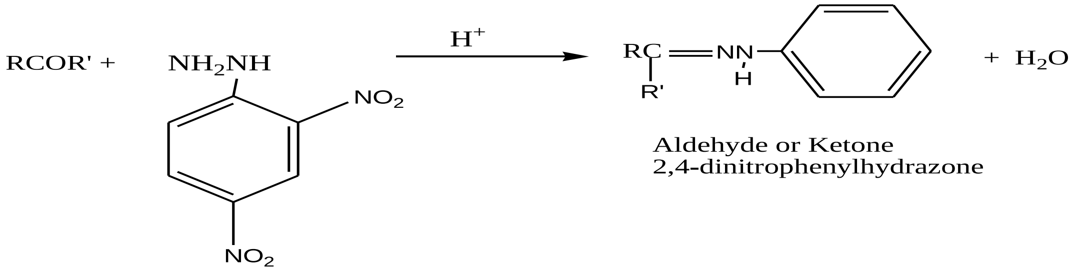
c) With Phenyl hydrazine $C_6H_5NHNH_2$

Carbonyl compounds generate phenyl hydrazone derivatives which are low melting point solids. The reaction occurs with or without an acid.

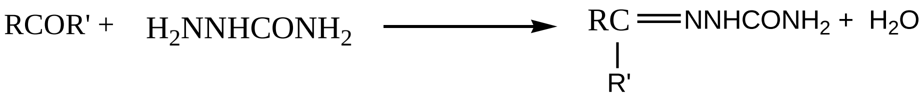


d) With 2,4-dinitrophenylhydrazine

2,4-dinitrophenylhydrazine is utilized in Brady's reagent for detection of a carbonyl functional group. Yellow or orange solid crystallizes out in the form of 2,4-dinitrophenylhydrazone.



e) With semicarbazide, $NH_2NHCONH_2$



$$RCOR' + H_2NNHCONH_2 \longrightarrow \underset{\displaystyle R'}{RC}{=}NNHCONH_2 + H_2O$$

semicarbazone

4. Reaction with Primary amines.

Aldehydes react with primary amines to form imines.

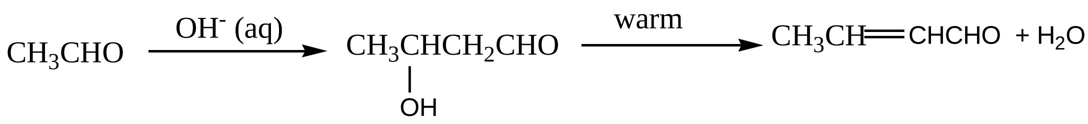
$$RCHO + H_2NR' \longrightarrow RCH{=}NR' + H_2O$$

$$CH_3CHO \xrightarrow{C_6H_5CH_2NH_2} CH_3CH{=}NCH_2C_6H_5 + H_2O$$

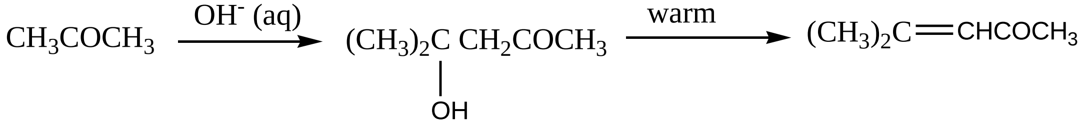
5. Aldol condensation

Aldehydes react with alkali to generate Aldol product which dimerises on warming to enal.

The reaction is undergone by carbonyl compounds with at least one-α-hydrogen atom.



$$CH_3CHO \xrightarrow{OH^-\,(aq)} CH_3\underset{\displaystyle OH}{CH}CH_2CHO \xrightarrow{warm} CH_3CH{=}CHCHO + H_2O$$

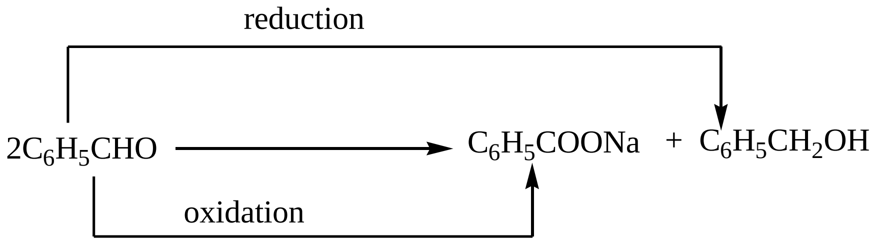


$$CH_3COCH_3 \xrightarrow{OH^-\,(aq)} (CH_3)_2\underset{\displaystyle OH}{C}\,CH_2COCH_3 \xrightarrow{warm} (CH_3)_2C{=}CHCOCH_3$$

6. Cannizzaro reaction

Aldehydes without at least one-α-hydrogen atom react with sodium hydroxide solution to undergo self-oxidation and reduction reaction.

This reaction is limited to aromatic and aliphatic compounds in which the carbonyl carbon is attached to tertiary alkyl carbon atom.



$$2C_6H_5CHO \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$$

7. Oxidation reaction

Aldehydes are oxidized to carboxylic acids by oxidising agents such as acidified potassium dichromate solution, acidified chromium (VI) oxide solution or dilute nitric acid.

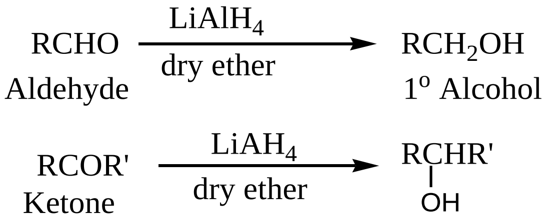
Ketones are resistant to oxidation by common oxidising agents.

$$\mathrm{RCHO} \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} \mathrm{RCOOH}$$

8. Reduction reaction

Aldehydes are reduced to Primary alcohol while Ketones are reduced to Secondary Alcohol.

Reducing agents commonly used are $LiAlH_4$/ dry ether, Hydrogen /Nickel at 150^{O}C, Amalgamated Zinc and concentrated hydrochloric acid, $NaBH_4$/ Water.



$$\underset{\text{Aldehyde}}{\mathrm{RCHO}} \xrightarrow[\text{dry ether}]{LiAlH_4} \underset{1^{o}\ \text{Alcohol}}{\mathrm{RCH_2OH}}$$

$$\underset{\text{Ketone}}{\mathrm{RCOR'}} \xrightarrow[\text{dry ether}]{LiAH_4} \underset{\mathrm{OH}}{\underset{|}{\mathrm{RCHR'}}}$$

9. Halo form reaction

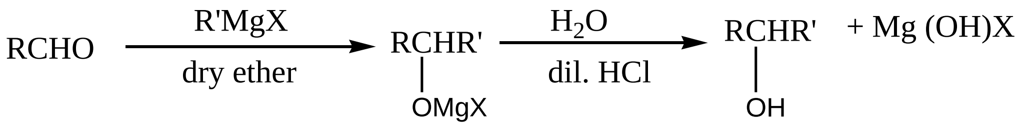
Ethanal and Methyl Ketones react with iodine in presence of sodium hydroxide solution to form a yellow solid.

$$RCOCH_3 + 3I_2 + 4NaOH \longrightarrow RCOONa + 3H_2O + CHI_3\,(s) + 3I^-$$

This reagent is used to differentiate between the structure of Aldehydes and methyl Ketones.

10. Addition of Grignard reagent

Aldehydes generate Secondary Alcohol except ethanal while Ketones generate tertiary alcohol.



$$RCHO \xrightarrow[\text{dry ether}]{R'MgX} \underset{OMgX}{RCHR'} \xrightarrow[\text{dil. HCl}]{H_2O} \underset{OH}{RCHR'} + Mg(OH)X$$

$$HCHO \xrightarrow[\text{dry ether}]{R'MgX} R'CH_2OMgX \xrightarrow[\text{dil.HCl}]{H_2O} RCH_2OH$$

11. **With Phosphorous penta chloride**

Carbonyl compounds generate dichloride.

$$RCHO \xrightarrow{PCl_5} RCHCl_2$$

$$RCOR' \xrightarrow{PCl_5} RCCl_2R'$$

Distinguishing between Aldehydes and Ketones

Aldehydes can be differentiated from Ketones by various reagents that are oxidizing agent's i.e.

a) **Ammoniacal Silver nitrate solution.**

The reagent consists of silver nitrate in presence of excess ammonia solution.

Aldehydes react with ammoniacal silver nitrate form a silver mirror along side a clean test tube on warming whereas no observable change for Ketones.

Ethanal reacts almost immediately.

$$RCHO + 2Ag(NH_3)_2OH \longrightarrow RCOONH_4 + 2Ag + H_2O + 3NH_3$$

b) **Fehling's test.**

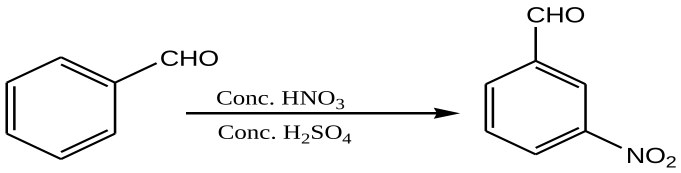
Aliphatic Aldehydes reduce copper (II) ions to reddish-brown copper (I) oxide on heating.

$$RCHO + 2Cu^{2+} + NaOH + H_2O \longrightarrow RCOONa + Cu_2O + 4H^+$$

Ketones and aromatic Aldehydes give no observable change.

Reactions of Aromatic Aldehydes and Ketones involving substitution in Ring

Carbonyl group is deactivating group therefore the reaction involving the benzene ring generatemeta-derivative product.



CHAPTER NINE

CARBOXYLIC ACIDS

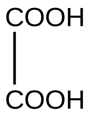
Introduction

Aliphatic monocarboxylic acids form a homologous series corresponding to the general molecular formula, $C_nH_{2n+1}COOH$.

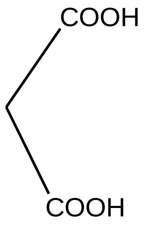
Carboxylic acids are organic compounds contain the carboxyl group that is made of carbonyl group and hydroxyl group.

The number of the carboxyl group present in acid classifies acids as: Monocarboxylic acids which are monobasic have one carboxyl while dicarboxylic acid are dibasic.

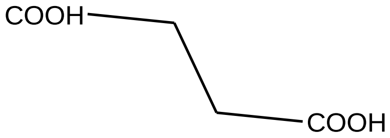
The simplest dicarboxylic acid are:



Ethanedioic acid



Propane-1,3-dioic acid (Malonic acid)



Butane-1,4-dioic acid (Succinic acid)

Nomenclature

The IUPAC names are afforded by taking the name of the appropriate alkane and replacing the ending ⍰⍰e⍰ with the suffix ⍰oic acid⍰. Positions of the substitution are denoted in the usual way by numbering the longest unbranched chain containing the carboxyl group.

Sturcture	**Name**
HCOOH	methanoic acid
CH_3CH_2COOH	Propanoic acid
$CH_3(CH_2)_2COOH$	Butanoic acid
$(CH_3)_2CHCOOH$	2-methylpropanoic acid
$CH_3(CH_2)_{14}COOH$	Hexadecanoic acid
$C_6H_5CH_2COOH$	2-phenylethanoic acid
HOOCCOOH	ethanedioic acid
$HOOCCH_2COOH$	Propane-1,3-dioic acid

Synthetic Preparations

1) Oxidation of Primary Alcohol or Aldehydes

Primary Alcohols or Aldehydes are oxidized by acidified potassium dichromate solution or acidified chromium (VI) oxide to carboxylic acid.

$$\underset{1^{o}\text{Alcohol}}{RCH_2OH} \xrightarrow[\text{heat}]{CrO_3\ /H^+} \underset{\text{Aldehyde}}{RCHO} \xrightarrow[\text{heat}]{CrO_3\ /H^+} \underset{\text{Carboxylic acid}}{RCOOH}$$

Orange solution turns green due to reduction of chromium (VI) ions to chromium (III) ions.

2) Grignard synthesis

$$RBr \xrightarrow[\text{dry ether}]{Mg} RMgBr \xrightarrow[\text{dry ether}]{CO_2} RCOOMgBr \xrightarrow[\text{dil.HCl}]{H_2O} RCOOH + MgBrCl$$

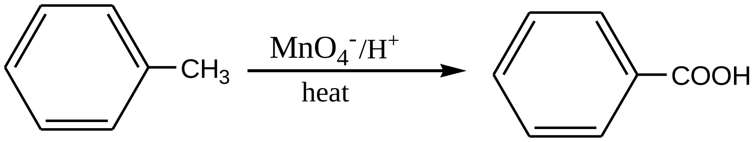
R may be $1^{o}, 2^{o}, 3^{o}$ or Aromatic

Example

$$CH_3CH_2Br \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2MgBr \xrightarrow[\text{dry ether}]{CO_2} CH_3CH_2COOMgBr \xrightarrow[\text{dil.}H^+]{H_2O} CH_3CH_2COOH$$

In Preparation of Benzoic acid, solid carbondioxide or dry ice is used.

3) From Methyl Benzene



4) **From Cyanide compounds.**

$$RX \xrightarrow[\text{heat}]{\text{KCN/EtOH}} RCN \xrightarrow[\text{Reflux}]{H_2O/H^+} RCOOH$$

$$\begin{tikzcd} CH_3CH{=}CH_2 \arrow[r, "HBr", "\text{peroxide}"'] & CH_3CH_2CH_2Br \arrow[r, "\text{KCN/EtOH}", "\text{heat}"'] & CH_3CH_2CH_2CN \arrow[d, "H_2O\ /H^+"', "\text{reflux}"] \\ & & CH_3CH_2CH_2COOH \end{tikzcd}$$

The reaction is unsuitable for preparation of aromatic carboxylic acid.

5) **Cannizzaro reaction**

Aromatic Aldehydes and aliphatic ones containing no α-hydrogen atom undergo self oxidation and reduction.

$$\begin{tikzcd} HCHO \arrow[r, "\text{NaOH (aq)}"] & HCOONa \arrow[d, "\text{dil.}H^+"] + CH_3OH \\ & HCOOH \end{tikzcd}$$

6) **Alkali Hydrolysis of Esters**

The hydrolysis of Esters generates the corresponding alcohol and Acid.

The method is not commonly used since esters are obtained from carboxylic acid.

$$\begin{tikzcd} RCOOR' \arrow[r, "\text{NaOH (aq)}"] & RCOONa \arrow[d, "\text{dil.}H^+"] + R'OH \\ & RCOOH \end{tikzcd}$$

Physical Properties of Carboxylic acids

All simple aliphatic acids as far as C_{10} are liquids at room temperature while aromatic acids are crystalline solids. Ethanoic acid has a sharp, pungent odour.

Boiling points of the acids increase with increase molecular mass. The boiling points are higher than expected because of the ability of the molecule to associate through hydrogen bonding which requires extra energy to break.

The first four aliphatic acids are completely miscible with water due to the ability of the functional group to form hydrogen bonds with water molecules.

Because of their greater hydrocarbon hence covalent character, the higher homologues become progressively less soluble in water.

Benzoic acid is only slightly soluble in cold water but dissolves readily in hot.

N.B. The molecular mass determination of carboxylic acids using Colligative properties such as freezing point in non-polar solvents gives the results that are twice than expected due dimerisation of the molecule through hydrogen bonding in such solvents.

Acidic nature of carboxylic acids

Carboxylic acids are weak acids which partially dissociate in aqueous solutions. However, they are stronger acids than alcohols and phenols.

The acidic strength of carboxylic acids depend on degree of ionisation and the acid dissociation constant denoted K_a defined as

$K_a = \frac{[H^+][X^-]}{[HX]}$ for a weak monobasic HX acid.

The Nature of the groups close to the carboxyl group has a great effect on the acid strength therefore a phenomenon known as inductive effect.

Electron withdrawing groups e.g halogens makes carboxylic acid stronger thus oxygen-hydrogen bond becomes weaken hence release of hydrogen ions in aqueous solution. i.e.

Acid	CH_3COOH	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH
K_a	$1.7x\ 10^{-5}$	$1.3x10^{-3}$	$5.0x10^{-2}$	$2.3x10^{-1}$
P^{Ka}	4.76	2.86	1.29	0.65

Electron releasing groups e.g alkyl groups makes carboxylic acid weaker thus oxygen-hydrogen bond strengthen hence less amount of hydrogen ions in aqueous solution.

Reactions of carboxylic acids

The reactions of carboxylic acids involve the hydroxyl group which either undergoes the loss of proton or replaced by another atom or group.

Some of the reactions include:

1) **With Bases**

The react to form salts and water

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

2) **With electropositive metals.**

The react to form salts and hydrogen

$$2\,RCOOH + Mg \longrightarrow (RCOO)_2Mg + H_2$$

3) **With sodium carbonate or Sodium hydrogen carbonate**

They react to liberate carbondioxide gas. They are stronger acids than carbonic acid.

$$2RCOOH + Na_2CO_3 \longrightarrow 2RCOONa + CO_2 + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

4) **With Primary Alcohols**

Carboxylic acids react with primary alcohols in presence of concentrated sulphuric acid as catalyst to form esters.

$$RCOOH + R'OH \underset{heat}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$$

(*See Alcohols for mechanism of the reaction*)

5) **With Phosphorous Halides**

They react to acid chlorides.

$$RCOOH \xrightarrow{PCl_5} RCOCl + POCl_3 + HCl$$

$$RCOOH \xrightarrow{PCl_3} RCOCl + H_3PO_3$$

6) With Thionyl chloride

They react also to form acid chlorides. This is the convenient method for preparation of acid chlorides since the other two products are gaseous.

$$RCOOH \xrightarrow{SOCl_2} RCOCl + SO_2 + \underset{\text{(white fumes)}}{HCl}$$

7) With Iron (III) chloride solution

They react forming a reddish-brown precipitate or solution. Lower molecular mass acids form a solution.

$$3RCOO^- + Fe^{3+} \longrightarrow (RCOO)_3Fe$$

$$3C_6H_5COO^-(aq) + Fe^{3+}(aq) \longrightarrow (C_6H_5COO)_3Fe_{(s)}$$

8) Reduction reaction

Carboxylic acids are reduced to primary alcohols using lithium aluminium hydride.

$$RCOOH \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2OH$$

9) Reaction of the Alkyl group

When chlorine gas is bubbled through hot carboxylic acid in presence of ultraviolet light, one or all the hydrogen atoms adjacent are substituted.

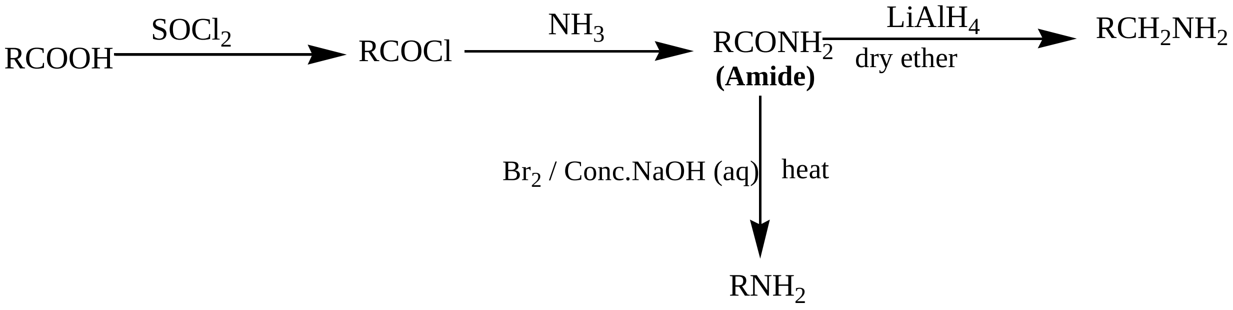
$$CH_3COOH \xrightarrow[\text{U.V.light}]{Cl_2} ClCH_2COOH \xrightarrow[\text{U.V.light}]{Cl_2} Cl_2CHCOOH \xrightarrow[\text{U.V.light}]{Cl_2} Cl_3CCOOH$$

10) Decarboxylation reaction.

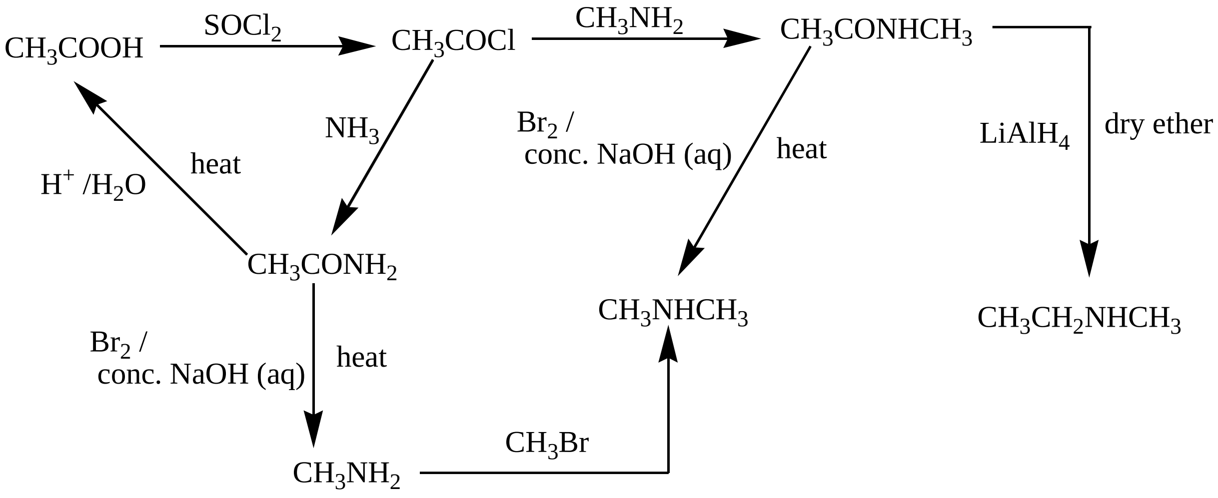
This reaction decreases the carbon length of the sodium salt of carboxylic acid to form an alkane.

$$RCOONa \xrightarrow[\text{heat}]{\text{sodalime}} \underset{\text{(Alkane)}}{RH} + Na_2CO_3$$

11) Amide formation.



Sample reaction scheme is shown below



12) With Ammoniacal Silver nitrate solution

Methanoic acid is the only carboxylic acid that reacts with ammoniacal silver nitrate solution on warming due to presence of Aldehydes group to form silver mirror along side a clean test tube.

$$HCOOH + 2Ag^+ \longrightarrow CO_2 + 2H^+ + Ag$$

13) Dehydration reaction

Methanoic acid and Ethanedioic acid are the only carboxylic acid that can be dehydrated using concentrated sulphuric acid.

$$HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$$

$$(COOH)_2 \xrightarrow{\text{conc.} H_2SO_4} CO + CO_2 + H_2O$$

Question

1. How would one carry out the following conversions in the laboratory? Indicate the necessary conditions of the reaction.

    (a) CH_3CHO to CH_3COOCH_3
    (b) $CH_2{=}CH_2$ to CH_3CH_2COOH
    (c) CH_3COOH to $CH_3CH_2NHCH_3$
    (d) $C_6H_5CH_3$ to $C_6H_5COOCH_3$

2. Three isomeric acids **A, B** and **C** have molecular formula **$C_8H_6O_4$** and all contain a benzene ring. In each case, one mole of the acid will react with 2moles of sodium hydroxide. Suggest structures for the acids. When the three acids are separately heated, **A** and **B** melt without decomposing, but **C** loses a molecule of water at about 250°C to form D,**$C_8H_4O_3$**.Suggest structures of **C** and **D**

3. Explain the following observations:

    a) When dilute hydrochloric acid is added to aqueous solution of soap, a white insoluble substance is formed.

    b) Butane, Propan-1-ol, Propanal and Ethanoic acid have approximately the same molecular mass yet their boiling points are 273, 370 and 391K respectively.

    c) Methanoic acid reacts with ammoniacal silver nitrate solution while Ethanoic acid does not.

    d) Ethanedioic acid decolorizes potassium manganate (VII) solution on warming while Ethanoic acid does not.

READ ON THE FOLLOWING ASPECTS

DERIVATIVES OF CARBOXYLIC ACIDS

- *AMIDES*
- *ACID CHLORIDES*
- *ACID ANHYDRIDES AND ESTERS*

CHAPTER TEN

AMINES

Introduction

Amines are alkyl or aryl derivatives of ammonia, and may be classified as Primary, secondary and tertiary according to the number of alkyl or aryl groups attached to the nitrogen atom.

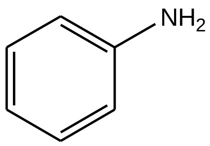
Aromatic amines are amines in which the nitrogen atom is attached directly to the aromatic ring.

Compounds containing two amine groups are known as diamines.

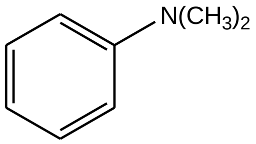
Examples of amines are their classes include

CH_3NH_2
methylamine, 1°

CH_3NHCH_3
dimethylamine, 2°



Phenylamine,1°



N,N-dimethylphenylamine, 3°

$(CH_3)_3N$
Trimethylamine,3°

Nomenclature

Both aliphatic and aromatic amines can be named by inserting the ending "amine" to the name of alkane or other appropriate hydrocarbon.

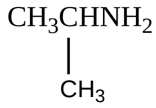
Examples include:

CH_3NH_2
Merthylamine

$CH_3CH_2NH_2$
Ethylamine

$(CH_3)_2NH$
Dimethylamine

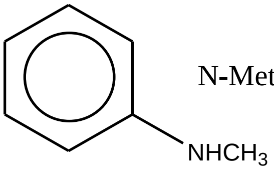
$CH_3CH_2CH_2NH_2$
Propylamine



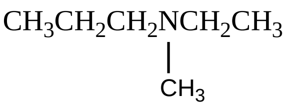
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HNH_2$

1-methylethylamine

$CH_3CH_2NHCH_3$
Ethylmethylamine



N-Methylphenylamine



$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{N}}CH_2CH_3$

N-ethyl-N-methylpropylamine

More complex tertiary amines with different alkyl groups are named as derivatives of the longest chain and "N" is inserted before the named of each group.

For aromatic amines, the names are derived from the simplest aromatic amine i.e. Phenylamine.

Methylphenylamines are collectively termed as Toluidines.

Synthetic Preparation

1) From Alkyl halides

This method generates a mixture of amines. Therefore their separation fractional distillation is used.

However better yield are obtained when Primary amine reacts with haloalkane compounds to generate secondary or tertiary amine.

The method also is suitable for preparation of Aromatic amine since aromatic halides do not react with ammonia under normal condition.

$$RCH_2X \xrightarrow{NH_3} RCH_2NH_2 + HCl$$

$$RCH_2NH_2 + RCH_2X \longrightarrow RCH_2NHCH_2R + HCl$$

$$RCH_2NHCH_2R + RCH_2X \longrightarrow (RCH_2)_3N + HCl$$

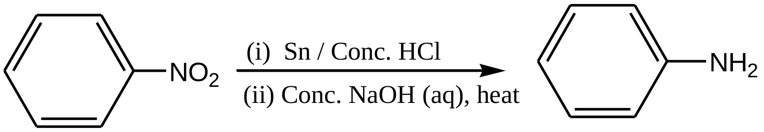
2) Reduction of Nitro compounds

Nitro compounds are reduced to Primary amines using Lithium Aluminium hydride or hydrogen gas in presence of a catalyst.

$$RCH_2NO_2 \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2NH_2$$

$$CH_3CH_2NO_2 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2NH_2$$

For aromatic amines, tin and concentrated hydrochloric acid is used for reduction of aromatic nitro compounds.



3) Reduction of Nitriles

Nitriles are reduced to primary amines by lithium aluminium hydride or hydrogen in presence of a catalyst.

$$\mathrm{RCN} \xrightarrow[\text{dry ether}]{\mathrm{LiAlH_4}} \mathrm{RCH_2NH_2}$$

$$\mathrm{CH_3CH_2Br} \xrightarrow[\text{heat}]{\text{KCN / EtOH}} \mathrm{CH_3CH_2CN} \xrightarrow[\text{dry ether}]{\mathrm{LiAlH_4}} \mathrm{CH_3CH_2NH_2}$$

A further application is reduction of Oximes.

$$\mathrm{RCHO} \xrightarrow{\mathrm{H_2NOH}} \mathrm{RCH{=}NOH} \xrightarrow[\text{dry ether}]{\mathrm{LiAlH_4}} \mathrm{RCH_2NH_2}$$

4) **Hofmann degradation of Amides.**

This reaction gives a good yield of primary amine of a lower carbon chain.

$$\mathrm{RCONH_2} \xrightarrow[\text{heat}]{\mathrm{Br_2}\text{ / Conc. NaOH (aq)}} \mathrm{RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O}$$

$$\underset{\text{Ethanamide}}{\mathrm{CH_3CONH_2}} \xrightarrow[\text{heat}]{\mathrm{Br_2}\text{ / Conc. NaOH (aq)}} \underset{\text{methylamine}}{\mathrm{CH_3NH_2}}$$

5) **Reduction of amides**

Primary or Secondary or tertiary amides are reduced to their respective amines using lithium aluminium hydride in dry ether.

$$\mathrm{RCONH_2} \xrightarrow[\text{dry ether}]{\mathrm{LiAlH_4}} \mathrm{RCH_2NH_2}$$

Properties of Amines

Simple aliphatic amines are gases and possess a characteristic smell of ammonia. However most of the higher homologues are liquids with rotten fish smell.

They are polar compounds and the molecules form intermolecular hydrogen bonds with each other except tertiary amines.

For isomeric amines, the boiling points decrease in the order of 1o>2o>3o due to progressive decrease in intermolecular hydrogen bond.

The hydrogen bonds in alcohols are stronger than those in amines because oxygen is more electronegative than nitrogen atom therefore the boiling points of alcohols are higher those of amines of relatively the same molecular mass.

Lower molecular mass amines are soluble in water because the molecules form hydrogen bond with water molecules and the resultant solution is basic .i.e. turns red litmus blue.

Basic Strength of Amines

The basic strength of amines depends on availability of lone pair of electrons on the nitrogen atom for protonation. Primary amines are more basic than ammonia due to presence of alkyl group which is electron releasing group therefore great salvation.

Secondary amines are more basic than Primary amines since they have two electron releasing groups hence more solvation.

Tertiary amines are less basic than both Primary and Secondary amines but more basic ammonia since they have three alkyl groups which are electron releasing groups hence greater positive inductive effect or more electron releasing hence less solvation due to steric hinderance.

Aromatic amines are weaker or less basic than aliphatic amines because of the presence of benzene ring where the lone pair of electrons on the nitrogen atom gets delocalized.Thus lone pair of electrons on the nitrogen atom becomes less available for protonation.

The Table gives the base dissociation and their boiling points of amines.

Amines	**M.p.t (^oC)**	**B.p.t(^oC)**	**K_b**
$CH_3CH_2NH_2$	-84	17	$5.6X10^{-4}$
$CH_3CH_2NHCH_2CH_3$	-48	56	$9.6X10^{-4}$
$(CH_3CH_2)_3N$	-115	90	$5.7X10^{-4}$
$C_6H_5N(CH_3)_2$	3	194	$11.5X10^{-5}$

Reaction of Amines

Majority of the reactions of amines indicate aminesaselectron rich species (Nucleophiles). Therefore some of the reactions of amines include:

1) Salt formation

As bases, amines react with acids to form salts.

$$RNH_2 + HX \longrightarrow R\overset{+}{N}H_3X^-$$

$$CH_3CH_2NH_2 \xrightarrow{HCl} CH_3CH_2\overset{+}{N}H_3Cl^-$$

Generally the salts are soluble in water but insoluble in organic solvents. Therefore amines are soluble in dilute mineral acids.

2) Amide formation

Both aliphatic and aromatic primary or secondary amines readily acylated using acyl halides or acid anhydrides

$$RCOCl + R'NH_2 \longrightarrow RCONHR' + HCl$$

$$CH_3COCl + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + HCl$$

$$RNH_2 + (R'CO)_2O \longrightarrow RNHCOR' + R'COOH$$

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

Qn: Write the mechanism of the above reaction

3) Alkylation of amines

Primary and secondary halides react with amines to form alkylated amine.

$$RCH_2X + R'CH_2NH_2 \longrightarrow RCH_2NHCH_2R' + HX$$

$$(RCH_2)_2NH + R'CH_2X \longrightarrow (RCH_2)_2NCH_2R' + HX$$

Qn: Write the mechanism of the above general reactions.

4) With Nitrous acid

Nitrous acid is unstable at room temperature therefore usually prepared in the reaction mixture using sodium nitrite and concentrated hydrochloric acid at low temperatures usually below 10^oC.

The reaction mixture is used to differentiate between the classes of amines.

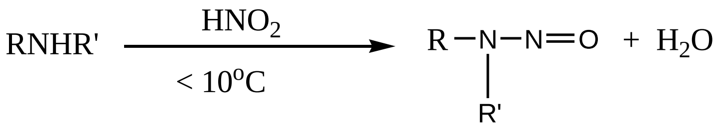
a) With Primary Aliphatic amines

They react to unstable alkyl Diazonium salt that decomposes to a colourless solution and bubbles of colourless gas.

$$RNH_2 \xrightarrow[< 10^oC]{HNO_2} ROH + N_2 + \text{mixture of ethers, alkene,haloalkane}$$

b) With Secondary amines

Both aliphatic and aromatic secondary amines react forming yellow oily liquids.



$$RNHR' \xrightarrow[< 10^oC]{HNO_2} R-\underset{\displaystyle R'}{\underset{|}{N}}-N=O + H_2O$$

N- nitrosoamines

c) With Tertiary amines

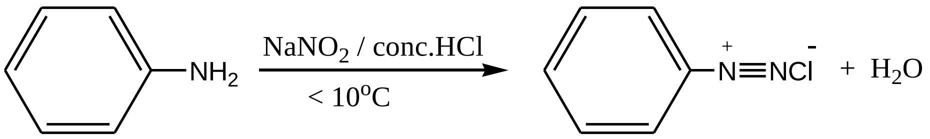
They with nitrous acid forming a colourless solution without evolution of bubbles of a colourless gas

$$R_3N \xrightarrow[< 10^oC]{HNO_2} R_3\overset{+}{N}H\overset{-}{NO_2}$$

d) With Primary Aromatic amines

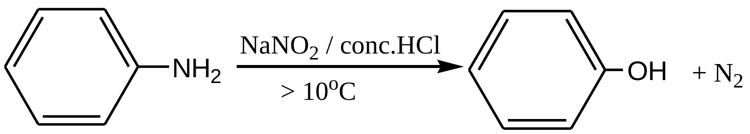
They react forming benzene Diazonium salt which is a stable colourless solution below 10°C.

The reaction between primary aromatic amine with nitrous below 10°C is known as diazotization.



Benzene diazonium salt

Above 10°C, there is effervescence of a colourless gas and colourless liquid of phenol.



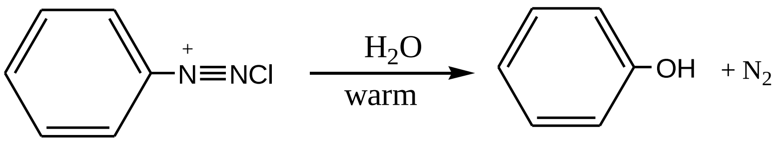
Reactions of Benzene Diazonium salt

Benzene Diazonium salt are prepared by action of nitrous acid on Phenylamine below 10oC.

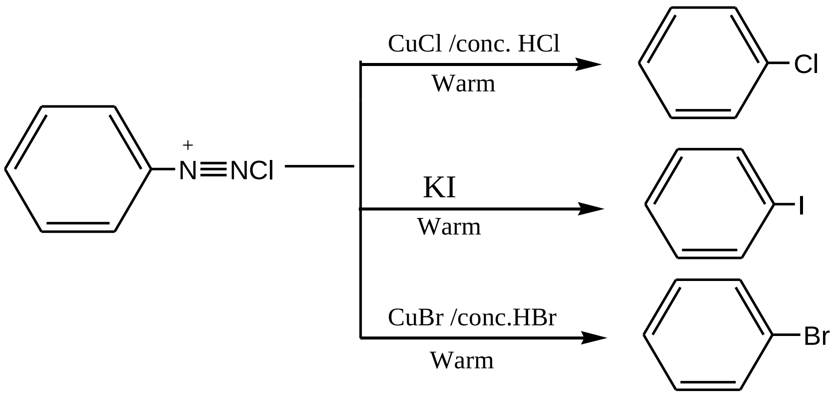
They undergo two types of reactions i.e.

1) Nucleophilic substitution reaction

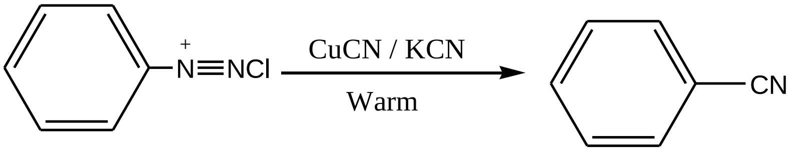
a) With water.



b) Halogen substitution



c) Cyanide substitution

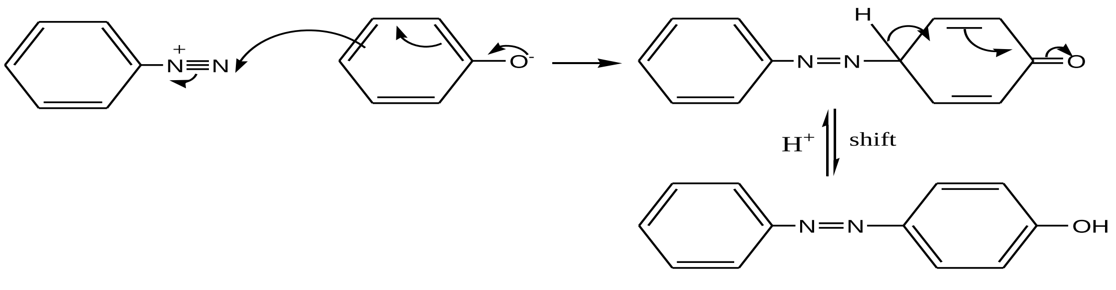


2) Coupling reactions

These reactions are usually used to generate azo dyes.

a) With Phenol

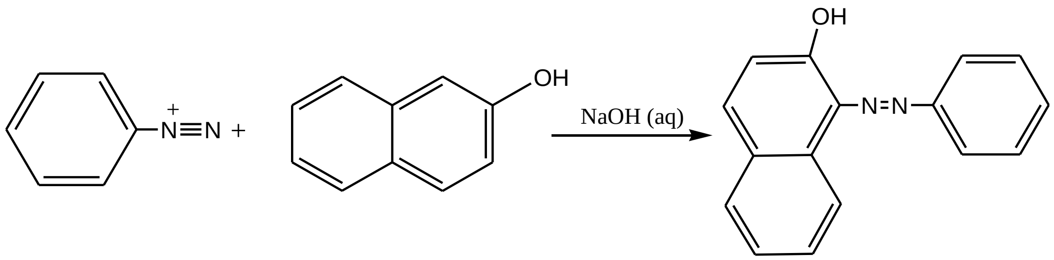
In alkaline medium benzene Diazonium salt react with phenol form a yellow azo dye.



4-hydroxphenylazobenzene
(Yellow solid)

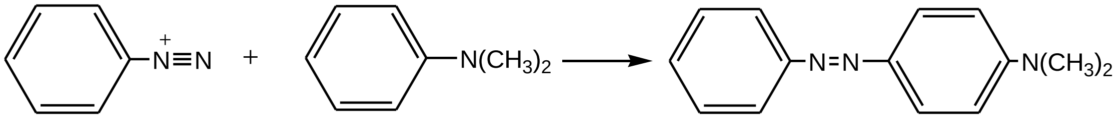
b) With Napth-2-ol

Benzene Diazonium salt forms a red azo dye in presence of alkaline medium also.



1-phenyl-2-azo-napthol
(red solid)

c) With amines



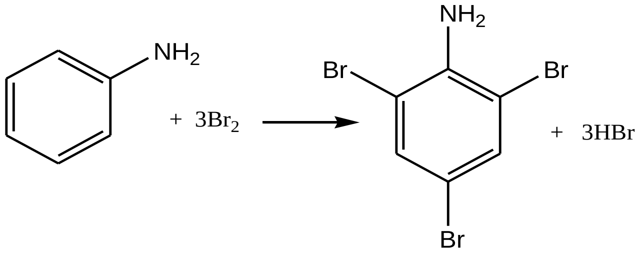
4-dimethylaminoazobenzene
(Yellow solid)

Qn: Write the mechanism of this reaction

Reaction of Aromatic amines (Substitution in the Benzene ring)

The amino group directs the incoming group to position 2 and 4 and activates the benzene ring towards Electrophilic substitution reactions.

Phenylamine reacts with Bromine forming a white precipitate of 2,4,6-tribromophenylamine.



CHAPTER ELEVEN

SOAP AND DETERGENTS

SOAP

Sodium salt of long carboxylic acid is known as soap. Soap is usually obtained from Fats or Oils.

Fats and Oils are complex mixtures of glycerol with a long chain carboxylic acid. Fats are solids at room temperature while Oils are liquids.

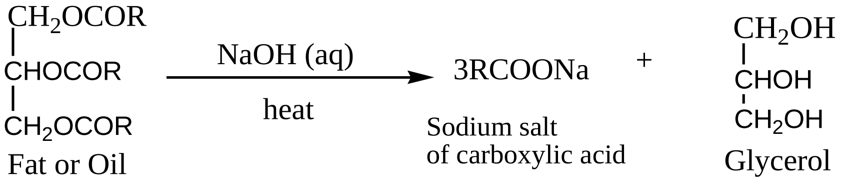
Fats tend to contain greater proportion of unsaturated acids while Oils tend to contain greater proportion of saturated acids.

The sources of oils are cotton seed, simsim, groundnut, sunflower seed, soya beans and coconut etc while fats are obtained from animals such as Pigs, Sheep or Cows.

Preparation of Soap

Soap is prepared by a reaction known as *saponification.*

Roast the dry seeds; crush/grind to make paste. Boil with water until oil floats on top and decant off the oil. Mix the oil with excess sodium hydroxide solution and boil while constant stirring for a long time.



$$\begin{matrix}CH_2OCOR\\ |\\ CHOCOR\\ |\\ CH_2OCOR\end{matrix} \xrightarrow[\text{heat}]{NaOH\,(aq)} 3RCOONa + \begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}$$

Add concentrated sodium chloride solution (Brine) to precipitate out the soap.

Cleansing Action of Soap

Soap lowers the surface tension between water and oil or insoluble material. They do so because they contain a polar group ($-COO^-$) and a non-polar alkyl chain (R-). The molecule of water congregates near the polar end while the molecules of oil congregate around the alkyl group. The non-polar oil particles are emulsified into suspension and removed.

N.B. Hard water affects the cleansing action of soap. Hard water contains calcium or magnesium ions. These ions react with soap to form a precipitate known as Scum.

$$\mathrm{2RCOONa\ (aq)} + \mathrm{Ca^{2+}\ (aq)} \longrightarrow \mathrm{(RCOO)_2Ca\ (s)} + \mathrm{Na^{+}\ (aq)}$$

Lather cannot be formed when the entire calcium or magnesium ions are completely removed as scum. This wastes soap in hard water.

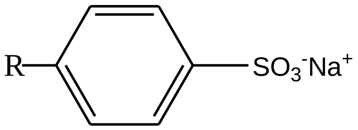
DETERGENTS

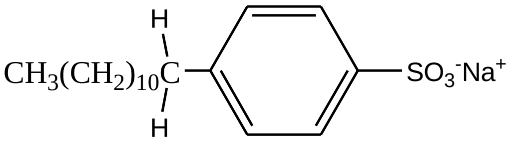
These are substances which improve the cleansing properties of water since they are sodium salts of long chain alkyl sulphonate or alkyl sulphate

Features of Detergents

Detergents have along chain hydrocarbon end which is oil or Fat soluble and hydrophilic part which is the sulphonate group. Thus detergents are sodium salts of sulphonic acids.

Since Detergents are alkyl benzene sulphonate examples include:





Common detergents include Nomi, Omo, surf, teepol etc.

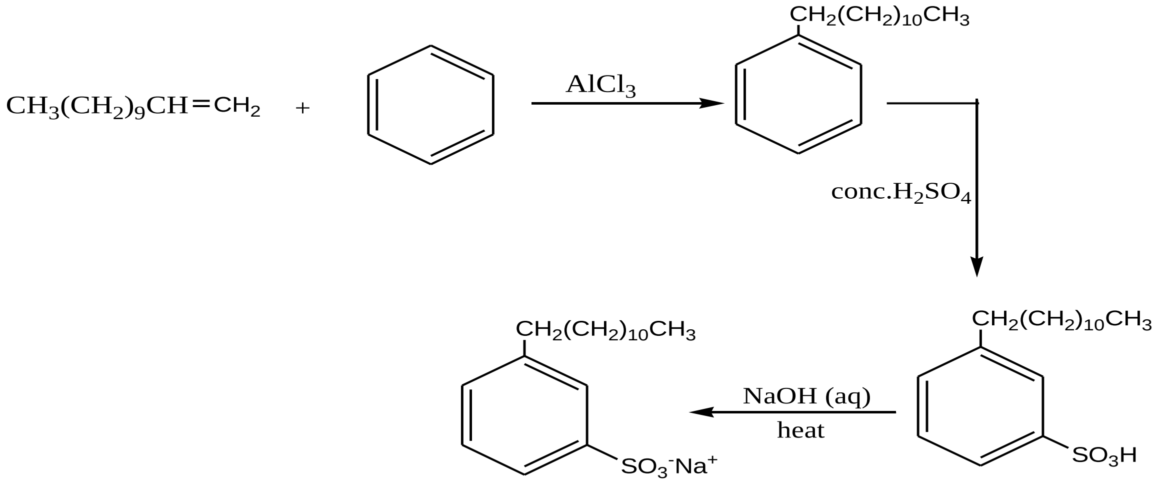
Properties of detergents

1. They are highly soluble in water
2. Detergents are emulsifying agents.

Preparation of Alkyl Benzene sulphonate

Soap less detergent is prepared as follows:

Benzene is alkylated in presence of a halogen carrier. The alkylated benzene is then sulphonated with concentrated sulphuric acid and the sulphonic acid formed is reacted with sodium hydroxide solution to form the detergent. i.e.



The table below shows the types of detergents and their uses.

Types	**Nature**	**use**
Anionic detergent	These have negative heads e.g $CH_3(CH_2)_{11}CH_2OSO_3^-Na^+$	Used for manufacture of toothpaste and shampoo
Cationic detergent	These have positive heads e.g $C_{15}H_{31}N(CH_3)_3Br$	Used for hair conditioners
Non-ionic detergents	These are neutral in water i.e. these carry no charge	Used for making liquid detergents

Action of Detergents on Fabrics

The action of detergents on fabrics is the same as that of soap.

Detergent Additives

1) **Sodium Sulphate:** This is used to increase the bulk of the detergent.

2) **Detergent builders (Inorganic phosphate):** These are used as water softeners because they form soluble complexes with calcium or magnesium ions in hard water.

3) **Peroxyborates:** These are used as bleaching agents.

Advantages of Soap over detergents

a) Soap is biologically degradable

b) Soap can be used for both bathing and washing

Disadvantage of Soap over detergents

They form undesirable scum with hard water which leads to wastage of soap

Advantages of detergents over soap

a) They are used in any of water.

b) Detergents have a brighter cleansing effect

Disadvantages of detergents over soap

a) Detergents are non biodegradable

b) Detergents contain fertilizer materials such as phosphates which nourish the growth of algae hence reducing oxygen supply in water.

Question:

a) Some oils are used in the manufacture of soap.

i. Name the reaction leading to the formation of soap

ii. Outline how soap is manufactured from oil.

iii. Write an equation of reaction between hard water and soap

iv. Explain briefly why soap is not commonly used in washing aluminium utensils

v. A sample of soap was prepared from 9.5g of oil containing an ester of hexadecanoic acid ($C_{15}H_{31}COOH$). Calculate the mass of soap formed.

b) Synthetic detergents are gradually replacing soap as cleansing agents.

i. Write equations to show how a soap less detergent can be prepared from $CH_3(CH_2)_5CH=CH_2$

ii. What problem does detergent cause to the environment

iii. State one structural difference between soap and detergent

iv. Describe the cleansing action of Omo as a detergent

v. $0.6cm^3$ of Jik was dissolved in water and solution made in $250cm^3$ volumetric flask. $25cm^3$ of this solution was acidified and $10cm^3$ of 0.2M potassium iodide solution added.

The iodine liberated required 5.0cm^3 of 0.2M Sodium thiosulphate solution for complete reaction. Calculate the mass of Chlorine in 1dm^3 of Jik.

POLYMERISATION

This is the building of large molecules (polymer) by linking together very many small molecules (monomers) with or without loss of small molecules such as water, ammonia etc.

Polymers are long chain molecules with recurring structural units formed by polymerization process.

When the recurring units are different, a co-polymer is formed.

Factors that determine the properties of Polymers

- Chain length: Strength and melting points of polymers increase with increase chain length
- Branching: Increased branching reduces the molecular strength and lowers the melting point
- Cross linkage: Polymers with a cross link between the chains form a rigid network which increases the strength.
- Intermolecular forces: Stronger intermolecular forces between the chains result into higher melting points.

Types of Polymers

1. Natural Polymers

These are polymers whose formation is not controlled by man. These include Cellulose material (Cotton, paper), Protein material (wool, silk), Natural rubber and Rayon.

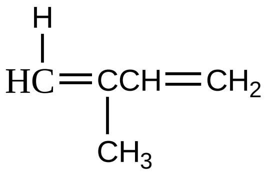
2. Synthetic Polymers

These are polymers that are man made. These include Plastics and fibers, addition polymers (polyethene, polypropene, and polyvinylchloride), Condensation polymers (Polyesters, nylon 6, 6)

Natural Rubber

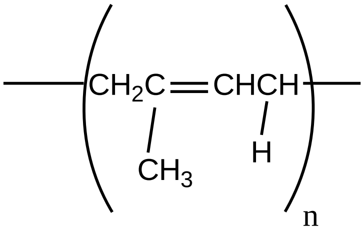
Rubber is obtained naturally from rubber trees as milky liquid called latex.

Natural rubber is a polymer derived from 2-methylbut-1, 3-diene I,e



$\overset{H}{HC}{=}\underset{CH_3}{C}CH{=}CH_2$

2-methylbut-1,3-diene
(monomer)



$-\!\left(CH_2\underset{CH_3}{C}{=}\underset{H}{C}H\right)_n\!-$

Natural rubber (polymer)

Natural rubber is very soft and of little use. It is made hard and tough by heating it with sulphur by a process known as Vulcanisation.

Vulcanisation

This is the process of improving on the qualities of rubber by heating it with sulphur.

The sulphur atoms add to some double bonds of two neighbouring rubber molecules to form vulcanized rubber.

The hardness of vulcanized rubber is directly proportional to the amount of sulphur added.

The following are the effects of heating natural rubber with sulphur:

- It improves on temperature working range
- It improves on toughness
- It improves on elasticity
- It improves on Bulkiness

Vulcanized rubber therefore is used for making car tyres, shoe sole, gloves and insulating electric cables.

Synthetic Polymer

Addition Polymers

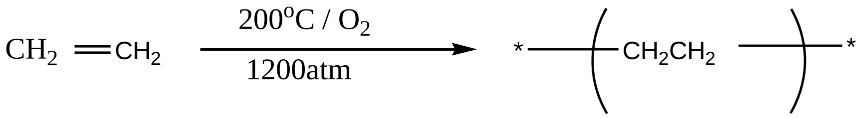
Addition Polymerization

This is the building up of a large molecule from a number of unsaturated monomers to form a single product.

Addition polymers include:

Polyethene: These exsit in two forms i.e. High density and lower density polymer.

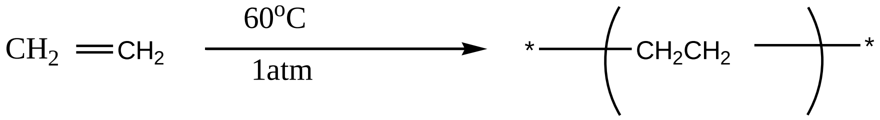
Low density polymer: This is formed in presence of a catalyst i.e.



$$CH_2{=}CH_2 \xrightarrow[1200atm]{200^oC / O_2} *\!-\!\left(CH_2CH_2\right)\!-\!*$$

Low density polyethene is used for making plastic bags, packing materials, electric cables, insulators.

High density polyethene: This is formed when ethene undergoes polymerization at 60^{o}C and 1 atmosphere. i.e.



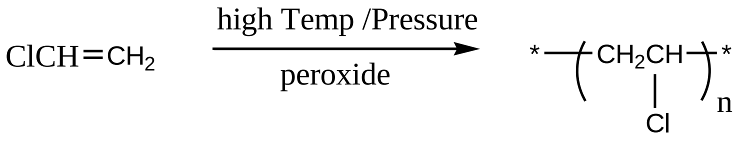
$$CH_2{=}CH_2 \xrightarrow[1atm]{60^oC} *\!-\!\left(CH_2CH_2\right)\!-\!*$$

High density polyethene is used for manufacture of water tanks, plastic pipes, plastic bottles, crates, buckets and kitchen ware.

Polyethenedon'trot, insoluble in most common solvents and less dense than water.

Polyvinylchloride (PVC)

The monomer is chloroethene. Chloroethene undergoes polymerization at high pressure and temperature in presence of peroxide i.e.



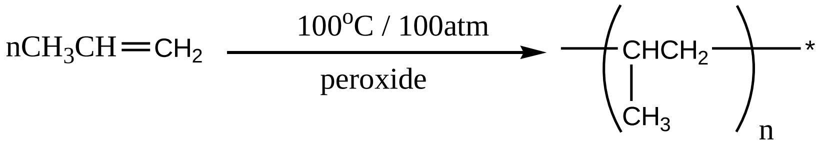
$$ClCH{=}CH_2 \xrightarrow[peroxide]{high\ Temp\ /Pressure} *\!-\!\left(CH_2\underset{\displaystyle Cl}{\underset{|}{CH}}\right)_n\!-\!*$$

The properties of PVC are water proof, non-degradable, not attacked and easily destroyed on heating.

PVC is used for making plastic coats, umbrellas, electronic equipments, suitcases and insulating electric cables.

Polypropene

This is formed from propene at 100^{o}C and 100atmosphere in presence of peroxide.



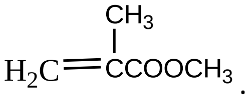
$$nCH_3CH{=}CH_2 \xrightarrow[\text{peroxide}]{100^{o}C\ /\ 100atm} -\left(\underset{CH_3}{\underset{|}{CH}}CH_2 \right)_n\!-*$$

Polypropene is used for making beer bottle crates, drinking straws, ropes and surfaces of all weather football and hockey pitches.

Polystyrene / Polyphenylethene

The monomer is phenylethene. Polystyrene is used for making combs, packing materials, ceilings and toys.

Perspex

This is an addition polymer whose monomer is  $H_2C{=}\overset{CH_3}{\overset{|}{C}}COOCH_3$.

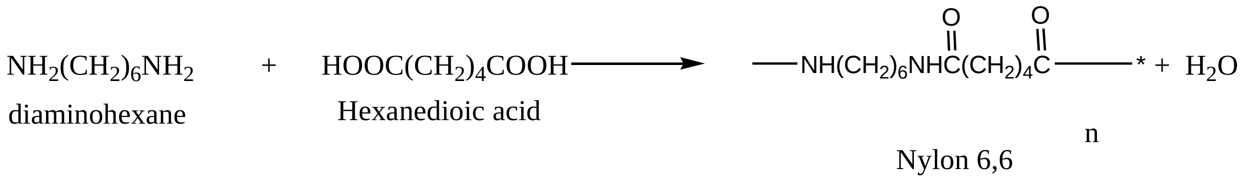
Perspex is used for making lenses, laboratory glass ware, windows of cars and airplanes, corrugated roof lights and in packaging.

Condensation Polymers

Condensation polymerization occurs when molecules that are bifunctional or polyfunctional react together to form a polymer and another product with small molecules.

Nylon 6,6

The monomers are diaminohexane and hexanedioic acid. It is called Nylon 6, 6 because each of the monomers has got six carbon atoms.



$$NH_2(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow -NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-*_{n} + H_2O$$

Nylon 6,6 has the following properties:

- It is water repellent hence dries easily
- It has got a hard warring tendency
- Insoluble in most solvents

- Fuses at temperatures above 200°C

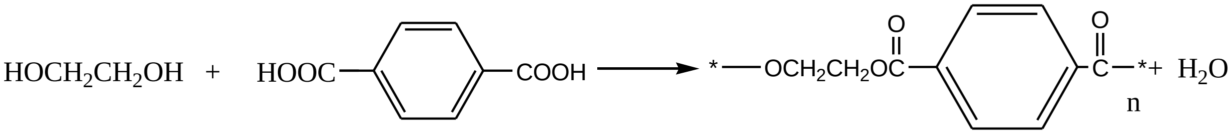
Nylon 6,6 is used for making of stockings, gloves, clothes, carpets and fishing nets.

N.B. Nylon 6,10 has monomers 1,6-diaminohexane and decanedicyldichloride and it is used for making surgical gloves, curtains , fishing nets and carpets.

Nylon polymers are also known as polyamides since they contain the peptide bond with in the molecule.

Polyester / Terylene

Made by condensing Ethane-1,2-diol and Benzene-1,4-dicarboxylic acid with loss of water molecules. i.e.



It is used for making clothes (textiles), ropes, safety belts and tents.

Differences between Addition polymerization and Condensation polymerization

	Addition polymerization	**Condensation polymerization**
1	Addition polymers are linear	Condensation polymers are non-linear
2	The monomers used are similar	Monomers used are different
3	Addition polymerization can be reversed	Condensation polymerization is irreversible

Advantages of Synthetic polymers over natural polymers

- Easier to manufacture
- Relatively stronger than the corresponding natural polymer

Disadvantages of Synthetic polymers over Natural polymers

- Non-biodegradable
- Its manufacture involves release of toxic fumes which cause a health hazards to Human.

Plastics

A plastic is a substance which when heated becomes soft and can be moulded into different shapes.

Properties of Plastics

- Become soft on heating
- Non-biodegradable
- Not attacked by acids or alkali

The properties of plastics can be modified by addition of:

- Plasticizers: these are substances which soften and make plastics easily moulded.
- Dyes and pigments: used to colour plastics
- Fillers: are used to increase the bulk of Plastics.

Types of plastics

1) Thermosofthening plastics (Thermoplastics)

These are plastics which when heated soften and can be remoulded into different shapes. This is because the binding forces between the polymer chains are weak and also have fewer cross-linkages between the polymer chains (or linear pattern arrangement).

Thermoplastics include Polypropene, polyethene, polystyrene, polyvinylchloride etc.

2) Thermosetting plastics (Thermosets)

These are plastics which when heated donot soften but harden and can not be remoulded in to different shapes. This is because they are held together by much cross-linkage between the polymer chains.

Thermosets include Bakelite used for making electric plugs, sockets and switches.

Advantages of Plastics over metals

- Plastics are resistant to attacks by acids, alkalis and atmospheric oxygen (corrosion).
- Easier to be recycled.
- Lighter than metals

Disadvantages of Plastics over metals

- Plastics items easily burn
- Pollutants since they are non-biodegradable
- You are provided with organic substance **Z** whose nature is required to be determined. Record your observation(s) and deduction(s) in the table below

Sample OrganicPractical's

Sample one

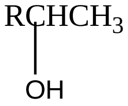
You are provided with organic substance **Z** whose nature is required to be determined. Record your observation(s) and deduction(s) in the table below

TEST	OBSERVATION(S)	DEDUCTION(S)
(a) Burn a small amount of **Z** on crucible lid.	*Burns with non-sooty flame*	*Aliphatic compound present*
b) To 1cm^3 of **Z**, add 2cm^3 of water and shake the mixture. Test with litmus.	*Soluble in water. Solution is neutral to litmus*	*Alcohols, carbonyl compounds present*
c) To 1cm^3 of **Z**, add five drops of Brady's reagent.	*No observable change* *Or* *No yellow precipitate formed*	*Carbonyl compound absent*
(d) To 2cm^3 of **Z**, add acidified Potassium dichromate and warm.	*Orange solution turns green*	*Primary, secondary alcohol probably present*
(e) To 2cm^3 of **Z**, add Lucas reagent.	*Cloudiness formed after a short time.*	*Secondary alcohol present*
(e) To 2cm^3 of **Z**, add conc. Sulphuric acid, heat and pass the vapour through acidified Potassium permanganate solution.	*Colourless gas turns acidified Purple solution turns colourless*	*Dehydration of alcohol leading to formation of an alkene.*

(f) To 1cm^3 of **Z**, add Iodine solution followed by sodium hydroxide solution drop wise until the Iodine is discharge and warm.	*Yellow precipitate*	*Secondary alcohol contains a methyl radical adjacent to the carbon atom carrying the functional group*

Comment on the nature of **Z**

Z is an aliphatic secondary alcohol with structure



$$\underset{\displaystyle OH}{RCHCH_3}$$

Sample Practical Two

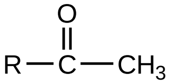
You are provided with organic substance **K**. You are required to identify the nature of **K**. Carry out the following tests on **K** and record your observations and deductions in the table below.

TEST	OBSERVATION(S)	DEDUCTION(S)
(a) Burn a spatula end -ful of **K** on a porcelain dish.	*Burns with non-sooty flame*	*Aliphatic compound present*
(b) Shake 3cm^3 of **K** with 2cm^3 of water and allow to it stand. Test with litmus.	*Soluble in water. Solution is neutral to litmus*	*Alcohol , Carbonyl compounds probably present*
(c)To 2cm^3 of **K** in test tube, add Brady's reagent.	*Yellow precipitate formed*	*Carbonyl compound present*
(d)To 2cm^3 of **K**, add saturated sodium hydrogen sulphite solution.	*White precipitate formed*	*Carbonyl compound present*
(e) To 1cm^3 of **K** in the test tube, add acidified potassium dichromate and warm.	*No observable change*	*Aldehydes absent* *Or* *Ketones present*
(f) To 3cm^3 of silver nitrate solution, add 2cm^3 of sodium	*No silver mirror formed*	*Aldehydes absent*

hydroxide then ammonia drop wise until the precipitate dissolves followed by 3cm^3 of **K**. Then warm.	*Or* *No observable change*	*Or* *Ketones present*
(g) To 2cm^3 of **K**, add iodine followed by sodium hydroxide until the colour is discharged. Warm the mixture and cool under water.	*Yellow precipitate formed*	*Methyl radical attached to the carbon atom carrying the functional group.*

(h) Comment on the nature of **K**

K is aliphatic carbonyl compound with a structure of



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

__Sample Practical Three__

You are provided with an organic substance **J** whose nature is required to be determined. Carry out the following test on J.

TEST	OBSERVATION(S)	DEDUCTION(S)
a) Burn a small amount of **J** in a spatula.	*Burns with yellow sooty flame*	*Aromatic compound present*
b) To a half spatula end ful of **J**, add 1cm^3 of water and with test with methyl orange indicator.	*Slightly soluble in water.* *Solution turns methyl orange pink / red*	*Phenol or Carboxylic acid present*
c) To a half spatula end ful of **J**, add 2-3 drops of iron (III) chloride solution.	*No violet colouration formed*	*Phenol absent*

d) Boil a spatula end ful of **J** with sodium hydroxide solution for three minutes.	*Dissolves to form a colourless solution*	*Acidic compound present Therefore carboxylic acid present.*
e) Add sodium carbonate solution to about a spatula end ful of **J**.	*Slight effervescence* *Or* *Bubbles of colourless gas*	*Carboxylic acid present*
f) Add a spatula endful of **J** in about 2cm^3 of water followed by acidified potassium manganate(VII) solution	*Purple solution turns colourless*	*Compound is Unsaturated*
f) Add 1cm^3 of ethanol to a spatula end ful of **J** followed by concentrated sulphuric acid. Boil the mixture and pour into a beaker of water.	*Sweet fruity smell formed*	*Esterification occurred Therefore Carboxylic acid present.*
g) Add 3cm^3 of water to a spatula end-ful of J in a test tube. Then add soda lime and Heat strongly.	*Colourless gas formed*	*Decarboxylation occurred Therefore Carboxylic acid present.*

(h) Comment on the nature of **J**

J is an aromatic unsaturated compound with a carboxyl group attached.

<u>Sample Practical Four</u>

You are provided with an organic compound Q. You are required to determine the nature of Q. Carry out the following tests on Q and record your observations and deductions in the table below.

Tests	**Observations**	**Deductions**
a) Burn a small amount of Q on crucible lid	*Burns with a yellow sooty flame*	*Aromatic compound present*

b)Add a spatula end-ful of Q to about 3cm^3 of dilute sodium hydroxide solution and shake	*Soluble to form a colourless solution*	*Acidic compound present. Therefore Phenol ,carboxylic acid probably present*
c) To a spatula end ful of Q in a test tube add 4cm^3 of water. Shake vigorously and warm. Test the solution with litmus paper and divide the resultant solution into three portion	*Slightly soluble in cold water and soluble on warming.* *Turns blue litmus red*	*Phenol, Carboxylic acid probably present*
(i) To the first portion, add three drops of 2,3-dinitrophenylhydrazine	*No observable change* *Or* *No yellow precipitate formed*	*Carbonyl compound absent*
(ii) To the second portion, add 3 drops of iron (III) chloride solution	*Violet colouration formed*	*Phenol absent*
(iii) To the third portion, add endful of solid sodium hydrogen carbonate	*Effervescence occurred* *Or* *Bubbles of colourless gas*	*Carboxylic acid present*
d) To 3cm^3 of methanol, add a spatula end-ful of Q and shake. Add 3-4 drops of concentrated sulphuric acid and warm the mixture	*Sweet fruity smell*	*Esterification occurred* *Therefore carboxylic acid confirmed.*

(e) Comment on the nature of Q

Aromatic compound with a hydroxyl and carboxyl groups attached to benzene ring.

Sample Practical Five

You are provided with organic substance **J** whose nature is required to be determined.

Carry out the following tests on J and identify the functional groups in J.

TEST	OBSERVATION(S)	DEDUCTION(S)
a) Burn a small amount of J in a crucible lid.	*Burns with yellow sooty flame*	*Aromatic compound present*

b) To 2cm^3 of J, add 2cm^3 of water and warm the mixture and test with litmus paper. Divide the warm solution into four parts.	*Slightly soluble in water.* *Solution is neutral to litmus.*	*Alcohol or Carbonyl compound probably present*
(i) To the first part, add 2-3 drops of sodium carbonate solution.	*No observable change*	*Carboxylic acid absent*
(ii) To the second part, add 2-3 drops of iron (III) chloride solution.	*No observable change* *Or* *No violet colouration formed*	*Phenol absent*
(iii)To the third part add 2,4-dinitrophenylhydrazine solid followed by 2cm^3 of ofconcentrated sulphuric acid.	*Yellow precipitate formed*	*Carbonyl compound present*
(iv) To the fourth part, add 2-3drops of acidified potassium dichromate solution and warm.	*Orange solution turns green*	*Aldehydes present* *Or* *Ketones absent*
c) To 2cm^{3}of J, add silver nitrate solution followed by sodium hydroxide solution then ammonia solution until the solid dissolves. Warm the mixture.	*Silver mirror formed*	*Aldehydes present*
d) To 3cm^3 of J, add iodine solution followed by sodium hydroxide solution and warm the mixture	*No observable change* *Or* *No yellow precipitate formed*	*Methyl Aldehyde absent*
e) To 3cm^3 of J, add Fehling solution and heat the mixture	*Brown precipitate formed*	*Aldehyde present*
f) To 3cm^3 of J, add acidified potassium manganate (VII) solution.	*Purple solution turns colourless*	*Compound is unsaturated*

e) Comment on the nature of **J**

J is an unsaturated aromatic compound with a carbonyl group attached.

Sample Practical Six

You are provided with an organic substance **Q**. Carry out the following tests on **Q** to identify its nature.

Record your observations and deductions in the table below.

Tests	Observations	Deductions
(a) Burn a small amount of **Q** on a spatula end	*Burns with a yellow sooty flame*	*Aromatic compound present*
(b) Shake 3 drops of **Q** with about 3cm^3 of water and test with litmus	*Slightly soluble in water.* *Solution turns red litmus to blue*	*Basic Compound present* *Therefore Amines present*
(c) Place 2cm^3 of dilute hydrochloric acid in a test tube followed by 3 drops of **Q**	*White fumes are formed.* *Soluble in acid*	*Amines present*
(d) To 3drops of **Q** add concentrate hydrochloric acid until the mixture is just acidic the add 1cm^3 of sodium nitrite solution followed by 2-napthol in sodium hydroxide solution	*Red precipitate formed*	*Azo dye formed* *Primary aromatic amine present*
(e) To 3drops of **Q** in a test tube add concentrate hydrochloric acid until it dissolves. Then add bromine water drop by drop until in excess.	*White precipitate*	*Primary Aromatic amine*

(f) To three drops of Q in a test tube,add acidified potassium manganate(VII) solution.	*Purple solution turns colourless*	*Unsaturated compound present.*

Comment on the nature of **Q**

Q is unsaturated primary aromatic amine.