Foundations of

Organic Chemistry

G Katumba

2017

CHAPTER 1: INTRODUCTION.

This is a branch of chemistry that deals with study of compounds that largely contain carbon. These compounds contain carbon combined with one or more elements, especially hydrogen, oxygen and nitrogen.

Compounds like carbon monoxide, carbon dioxide, carbonates and hydrogencarbonates are usually not considered as organic chemicals, but this is a matter of convenience, not a strict rule.

Naturally, carbon occurs in wood, coal, petroleum mines, and swamps.

1.1. Uniqueness of Carbon.

a) Carbon has the ability to form a variety of chains (straight chains and branched chains). The ability of similar atoms to form chains is called *catenation*. Note: Other elements can catenate, e.g. sulphur, silicon, boron and some metals; but no other element is able to make as wide a variety of chains as carbon.

b) Carbon has the ability to form bonds of nearly equal stability with hydrogen, nitrogen, oxygen and the halogens though hydrogen is electropositive and the rest are electronegative.

c) Carbon has the ability to form four bonds leaving no unpaired valence electrons.

d) Carbon has the ability to form multiple bonds (*double and triple bonds*) or rings between its atoms and even with atoms of other elements.

1.2. Hybridisation

It is the single mathematical mixing of orbitals to produce degenerate atomic orbitals.

 (*Degenerate meaning atomic orbitals of equal energy*).

Different types of hybridization lead to different types of carbon – carbon bonds, i.e. single, double or triple bonds.

The whole process starts with excitation. This is when an electron in the 2S orbital absorbs energy and jumps to the 2P orbital. Now depending on how many 2P orbitals

mix with the 2S orbital, different hybrid orbitals are formed hence different carbon – carbon bond.

1.2.1. Types of Hybridisation

a) SP^3 Hybridisation.

Here three P orbitals mix with one S orbital. The atomic orbitals produced arrange themselves tetrahedrally around the carbon atom. The carbon atom then uses these orbitals to get bonded to other carbon atoms to form a single carbon – carbon bond (e.g. in ethane, diamond, propane etc.). Or with hydrogen like in methane.

b) SP^2 Hybridisation.

Here two P orbitals mix with one S orbital. The carbon atom then uses these orbitals to get bonded to other carbon atoms to form a sigma bond while the orbitals that did not hybridise now link to form a pi bond. The combination of the sigma and the pi bond forms the carbon – carbon double bond seen in compounds like ethene, propene etc.

c) SP Hybridisation.

Here one P orbital mixes with one S orbital. The carbon atom then uses these orbitals to get bonded to other carbon atoms to form a sigma bond while the orbitals that did not hybridise now link to form two pi bonds. The combination of the sigma bond and the two pi bond forms the carbon – carbon triple bond seen in compounds like ethyne, propyne etc.

1.3.   Terms Used In Organic Chemistry.

a) Homologous series.

Is a group of organic compounds with the same general formular but each member differs from the next by a methylene group. ($-CH_2-$ group).

Examples include; alkanes, alkenes, alkynes, alcohols etc.

b) Functional group

An atom or a group of atoms which determine the chemical properties of a homologous series.

Examples;

Homologous series		Functional group
Name	**General formular**	
Alkanes	C_nH_{2n+2}	-H
Alkenes	C_nH_{2n}	C=C
Alkynes	C_nH_{2n-2}	C≡C
Alkyl halides	$C_nH_{2n+1}X$	-X (X = F, Cl, Br, I)
Alcohols	$C_nH_{2n+1}OH$	-OH
Carboxylic acids	$C_nH_{2n+1}COOH$	$-\overset{\displaystyle \,}{\underset{\parallel}{C}}-OH$ $\;\;O$
Esters	$C_nH_{2n}O_2$	$-\underset{\parallel}{C}-O-$ $\;\;O$
Ethers	$C_nH_{2n+1}O$	-O-
Amines	$C_nH_{2n+1}NH_2$	$-NH_2$
Amides	$C_nH_{2n+1}CONH_2$	$-\underset{\parallel}{C}-NH_2$ $\;\;O$
Carbonyl compounds	$C_nH_{2n}O$	Aldehydes	$-\underset{\parallel}{C}-H$ $\;\;O$
		ketones	$-\underset{\parallel}{C}-$ $\;\;O$

c) Radical

An atom or a group of atoms with unpaired electrons. E.g. Ċl chlorine radical, ĊH$_3$ methyl radical.

d) Mechanism

Is the stepwise exposure of the path taken by reactants and intermediates towards formation of products.

e) Electrophile

Is an electron deficient species.

Positive electrophiles carry a positive sign e.g. ^{+}H, $^{+}CH_3$.

Neutral electrophiles carry no charge.

All electrophiles attack sites that are rich in electrons.

f) Nucleophile

Is an electron rich species.

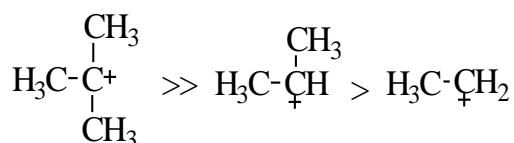Negative nucleophiles have an electron pair and negatively charged. E.g. Br^{-}, ^{-}CN

Neutral nucleophiles have a lone pair of electrons but not charged. E.g. $\overset{..}{N}H_3$ and $H_2\overset{..}{\underset{..}{O}}$

g) Carbocation.

A substance in which the carbon atom carries a positive charge.

The stability of carbo cations is in the order: tertiary>>secondary>primary.

1° carbocation has one alkyl group, 2° has two alkyl groups while 3° has three alkyl groups attached to the carbon carrying the positive charge. E.g.

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}+ \quad >> \quad H_3C-\underset{+}{\overset{\overset{CH_3}{|}}{C}H} \quad > \quad H_3C-\overset{.}{C}H_2$$

h) Carbo anion.

A substance in which the carbon atom carries a negative charge. E.g. $CH_3\overset{-}{C}H_2$.

i) Saturated compound.

A compound with only carbon – carbon single bonds e.g. alkanes.
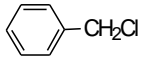
j) Unsaturated compound

A compound with a carbon – carbon double or triple bond e.g. alkenes and alkynes.

k) Aliphatic compound

A compound in which carbon atoms are joined in straight chains or branched chains. E.g. Chloroethane, CH_3CH_2Cl.

l) Aromatic compound

A compound with a benzene ring in its structure. E.g. benzyl choride,

1.4. Isomerism

The existence of two or more compounds with the same molecular formular but different structural formulae. Such compounds are referred to as *isomers*.

1.4.1. Types of Isomerism.

There are two types of isomerism namely; **structural isomerism** and **stereo isomerism.**

1.4.1.1. Structural Isomerism

This is when two or more compounds with the same molecular formular but different structural formulae.

Structural isomerism has four classes i.e.

a) Chain isomerism

This is when two or more compounds with the same molecular formular but different arrangement of carbon atoms. It gives rise to branched chains, unbranched chains or rings. Examples;

C_5H_{12}
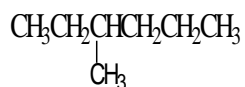
$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane
$CH_3CH_2CHCH_2CH_2CH_3$ $\quad\quad\mid$ $\quad\quad CH_3$	3-methylpentane.
	Cyclohexane

b) Position isomerism

This is when two or more compounds with the same molecular formular and functional group but only differ in the position of the functional group.

Examples;

C$_4$H$_9$OH CH$_3$CH$_2$CH$_2$CH$_2$OH Butan-1-ol

C$_4$H$_9$OH CH$_3$CHCH$_2$CH$_2$CH$_3$ Butan-2-ol
                    |
                   OH

c) Functional group isomerism

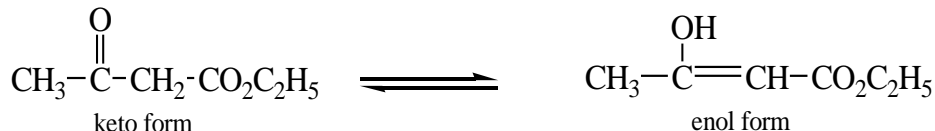This is when two or more compounds have the same molecular formular but with different functional groups.

Examples;

C$_3$H$_6$O$_2$ CH$_3$CH$_2$COOH Propanoic acid

C$_3$H$_6$O$_2$ CH$_3$COOCH$_3$ Methyl ethanoate

d) Tautomerim

This is exhibited by isomers that are in dynamic equilibrium. An example is ethyl 3-oxobutanoate; the two isomers rapidly interconvert.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CO_2C_2H_5 \rightleftharpoons CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH-CO_2C_2H_5$$

keto form   enol form

1.4.1.2.   Stereo Isomerism

This is when two or more compounds with the same molecular formular and same structural formular but with different spatial arrangement. (*Arrangement in space*).

Stereo isomerism has two classes i.e.
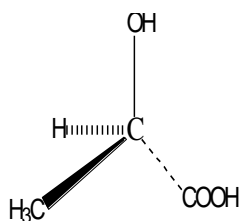
a) Optical isomerism

This is when two or more compounds with the same molecular formular and same structural formular but one is not super imposable on the other. One isomer is a mirror image of the other. The rotate a plane of plane polarized light differently.

(L) or (-) isomers rotate it to the left while (D) or (+) isomers rotate it to the right.

Examples;
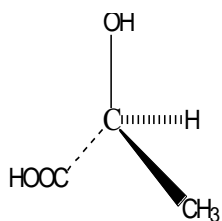
(-)-2-hydroxypropanoic acid   (+)-2-hydroxypropanoic acid
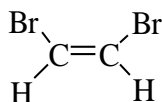
b) Geometrical isomerism

Occurs in isomers in which free rotation is prevented by the presence of a double bond.

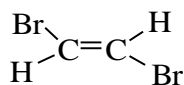The structures of geometrical isomers differ only in configuration thus;

Cis isomers: These have similar atoms on the same side of the double bond.

Trans isomers: These have different atoms on the same side of the double bond
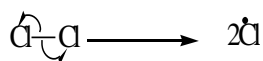
Examples:

Cis-1,2-dibromobutene   Trans-1,2-dibromobutene

1.5. Types of Reactions

a) Bond cleavage

A covalent bond can be broken in two ways i.e.

i. **Homolytic cleavage:** This is happens when there is negligible or no difference in the electronegativity of the two covalently bonded atoms. It leads to formation of free radicals. E.g.

ii. **Heterolytic cleavage:** It occurs when one of the atoms in a covalent bond is more electronegative than the other. It leads to formation of ions. E.g.

$$H\text{–}Br \longrightarrow H^+ + Br^-$$
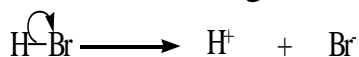
Br is more electrogative than H.

b) Electrophilic addition reaction.

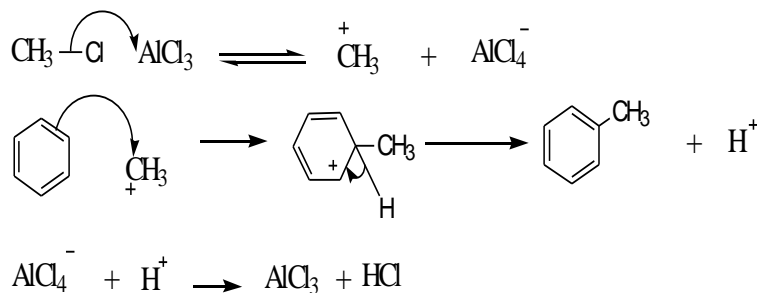A reaction in which an electrophile is added to an unsaturated compound to form a saturated compound. E.g.

$$H_2C\!:\!CH_2 \xrightarrow{HBr} CH_3CH_2Br$$

Mechanism.

$$CH_2\!\!=\!\!CH_2 \xrightarrow{} CH_3\overset{+}{C}H_2 + Br^- \qquad \bigg| \qquad CH_3CH_2 \xrightarrow{} CH_3CH_2Br$$
$$H\text{–}Br \qquad\qquad\qquad\qquad\qquad\qquad Br^-$$

c) Electrophilic substitution reaction.

A reaction in which an electrophile replaces a hydrogen atom on a benzene ring. E.g.

$$\bigcirc \xrightarrow{CH_3Cl/AlCl_3} \bigcirc\!\!-\!CH_3$$

Mechanism.

$$CH_3\text{–}Cl \quad AlCl_3 \rightleftharpoons \overset{+}{C}H_3 + AlCl_4^-$$

$$\bigcirc\!\!\!\text{–}CH_3 \longrightarrow \bigcirc\!\!\!\overset{CH_3}{\underset{H}{+}} \longrightarrow \bigcirc\!\!\!-CH_3 + H^+$$
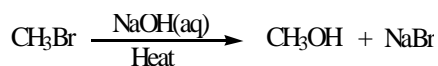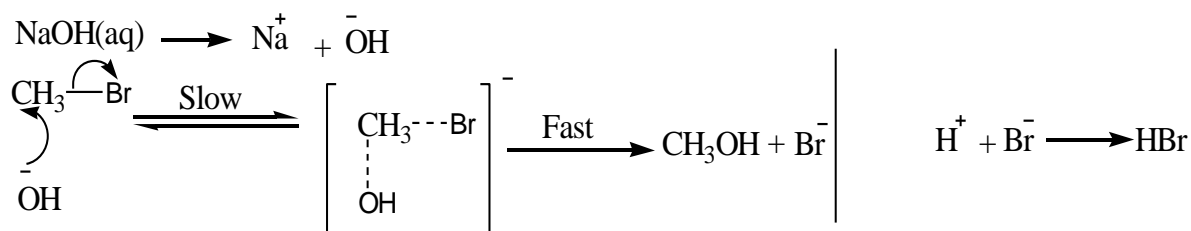
$$AlCl_4^- + H^+ \longrightarrow AlCl_3 + HCl$$

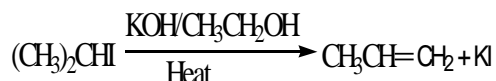## d) Nucleophilic substitution reaction.

A reaction in which a nucleophile replaces an atom or a group of atoms to form a compound with a different functional group. E.g.
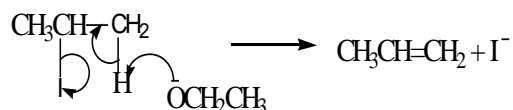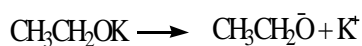
$$CH_3Br \xrightarrow[\text{Heat}]{NaOH(aq)} CH_3OH + NaBr$$

$$NaOH(aq) \longrightarrow \overset{+}{Na} + \overset{-}{OH}$$

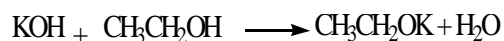$$\overset{+}{H} + \overset{-}{Br} \longrightarrow HBr$$

e) Nucleophilic elimination reaction.

A reaction in which a nucleophile eliminates an atom or a group of atoms to form an unsaturated compound. E.g.

$$(CH_3)_2CHI \xrightarrow[\text{Heat}]{KOH/CH_3CH_2OH} CH_3CH=CH_2 + KI$$

Mechanism.

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

$$CH_3CH_2OK \longrightarrow CH_3CH_2\overset{-}{O} + K^+$$

$$CH_3CH=CH_2 + I^-$$
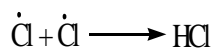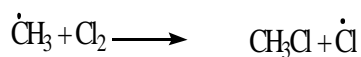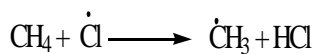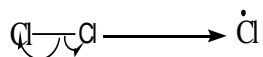
$$\overset{+}{K} + I^- \longrightarrow KI$$

f) Chain reaction.

A reaction that proceeds in several steps whereby each step produces a reactive particle that initiates the next step until the final step. E.g. chlorination of methane.

$$CH_4 + \text{Limited } Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$$

Mechanism.

$$CH_4 + \overset{\cdot}{Cl} \longrightarrow \overset{\cdot}{CH_3} + HCl$$

$$\overset{\cdot}{CH_3} + Cl_2 \longrightarrow CH_3Cl + \overset{\cdot}{Cl}$$

$$\overset{\cdot}{Cl} + \overset{\cdot}{Cl} \longrightarrow HCl$$

EER.

a) Define the term *Organic chemistry*. Why *Organic chemistry?*
   (5 marks).

b) Discuss the two types of bond cleavage. (*Your answer should include one example in each*)

(*4 marks*).

c) Discuss the two types of isomerism (*Your answer should include one example in each*).

(*20 marks*).

d) UNEB 2011 P.2 No.5. *Question on types of reactions* (*20 marks*).

1.6.   Empirical and Molecular Formular of Organic Compounds.

a) Empirical Formular.

The formular that shows the ratio of the atoms of the elements present in the compound in their simplest ratio.

b) Molecular Formular.

The formular that shows the exact number of atoms of each element in the formular of the compound.

1.6.1. Combustion Analysis to Determine the Empirical and Molecular Formulae.

A. When an organic compound is completely burnt in oxygen, only carbon dioxide and water are formed.

Knowing either the mass or volume of water and carbon dioxide produced, the mass of hydrogen in the compound can be calculated from water while that of carbon from carbon dioxide. Then that of oxygen or any other element can be obtained by subtraction from the mass of the organic compound.

Examples.

1. 0.88g of an organic compound **Z** that contains carbon, hydrogen and oxygen and vapour density of 22 on combustion gave 1.76g of carbon dioxide and 0.72g of water. Determine the;

a) Empirical formular of **Z** (C=12, O=16, H=1) (*Ans. EF is C_2H_4O*).

b) Molecular formular. (*Ans. MF is C_2H_4O*).

a) A hydrocarbon **Q** of molecular mass 58 on combustion gave $9.6dm^3$ of carbon dioxide and 9g of water at room temperature. Determine the;

   i.   Empirical formular of **Q** (C=12, O=16, H=1) (*Ans. EF is C_2H_5*).

   ii.   Molecular formular. (*Ans. MF is C_4H_{10}*).

b) Write all the structural formulae of isomers of **Q.**

2. 0.5g of an organic compound **P** that contains carbon, hydrogen and oxygen and vapour density of $1.43×10^{-3}gcm^{-3}$ in the vapour phase at STP, on combustion gave 0.6875g of carbon dioxide and 0.5625g of water.

a) Determine the;

   i.   Empirical formular of **P** (C=12, O=16, H=1) (*Ans. EF is CH_4O*).

   ii.   Molecular formular. (*Ans. MF is CH_4O*).

b) Write the structural formular of **P.**

B. Formular of a Compound by Explosion with Oxygen.

A hydrocarbon with a formular C_xH_y explodes in oxygen according to the equation.

$$CxHy + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$
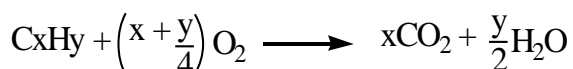
A compound with a formular $C_xH_yO_z$ explodes in oxygen according to the equation.

$$CxHyOz + \left(x + \frac{y}{4} - \frac{z}{2}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$
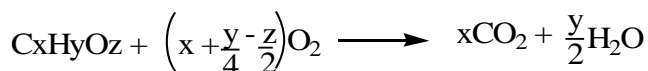
Applying Avogadro's hypothesis;

Volume of CO_2 produced = x × (volume of C_xH_y).

Volume of O_2 used = (x + y/4) × (volume of C_xH_y)

It's worth noting that;

1. Volume of CO_2 is always obtained from absorption with a strong alkalis e.g. KOH or NaOH.

2. Volume of O_2 used is obtained by subtraction of the volume of residual gases after absorption from the original volume of O_2.

3. Contraction = [volume of C_xH_y + volume of O_2] – volume of CO_2

Examples.

1. $60cm^3$ of oxygen were added to $10cm^3$ of a gaseous hydrocarbon. After explosion and cooling the residual gases occupied $50cm^3$. After absorption with KOH solution, $30cm^3$ of the gaseous products remained. Determine the molecular formular of the hydrocarbon. *Ans. MF is C_2H_4.*

2. $150cm^3$ of oxygen and $30cm^3$ of a gaseous hydrocarbon were exploded and cooling the residual gases occupied $105cm^3$. After absorption with NaOH solution, a diminition of $60cm^3$ of the gaseous products was produced. Determine the molecular formular of the hydrocarbon.

   Ans. MF is C_2H_6.

3. (a) $10cm^3$ of a gaseous hydrocarbon **Q** was exploded with excess oxygen. On cooling, the reduction in volume was $25cm^3$. If the vapour density of **Q** is $3.482 \times 10^{-3} gcm^{-3}$ at s.t.p. Calculate the molecular formular of **Q.**

   (b) Write equations to show how 2-phenylpropan-2-ol can be synthesized from **Q.**

4. (a) $20cm^3$ of a gaseous hydrocarbon **R** was exploded with excess oxygen. On cooling, the contraction in volume was $30cm^3$. If the vapour density of **R** is 13. Calculate the molecular formular of **R**.

   (b) Write equations to show how benzophenone can be synthesized from R.

5. A saturated organic compound **M** contains carbon, hydrogen and oxygen only. When $20cm^3$ of **M** was exploded with excess oxygen and cooled, there was a contraction of $70cm^3$ which occurred. When the residual gases were treated with conc. KOH solution, there was a further contraction of $120cm^3$ which occurred.in another experiment, $20cm^3$ of **M** when exploded in excess oxygen, $120cm^3$ of steam was formed.

a) Determine the molecular formular of **M.**

b) **M** is neutral to litmus but reacts with sodium metal to form a compound **N** and hydrogen gas.

Identify **M** and **N.**

c) Write the equation and suggest a mechanism for the reaction between;

    i.   **M** and hot phosphoric acid.

    ii.   **M** and ethanoyl chloride.

    iii.   **N** and phenylchloromethane.

d) **M** was warmed with acidified chromium (VI) oxide.

    i.   State what was observed. ii). Write equation for the reaction.

    ii.   Name the main organic product.

6. **W** is an organic compound of the $C_nH_{2n}O$ series. $40cm^3$ of **W** was exploded with $180cm^3$ of oxygen, the residual gases produced at room temperature were passed through conc. KOH solution. The final volume was found to be $20cm^3$.

a) Determine the molecular formular of **W.**

b) Write two structural formulae and IUPAC names of the isomers of **W.**

c) **(i)** Name a reagent that can be used to distinguish the isomers in (b) above.

(ii)State what would be observed when the reagent named in c (i) above is treated with each isomers. (iii)   Write equation(s) for the reaction(s) that occurs in c (ii) above.

d) (i) Name one inorganic reagent that reacts with both isomers in (b) above to give the same observation. State the observation.

CHAPTER 2: ALKANES.

Alkanes are hydrocarbons that conform to the general formular C_nH_{2n+2}. Where n = 1, 2, 3…

The functional group is hydrogen atom, C-H.

2.1. Nomenclature of Alkanes

Chemical compounds are named basing on the International Union of Pure and Applied Chemistry, (IUPAC) rules.

Note. The carbon number is counted as:

Carbon number	Naming	Carbon number	Naming
1	Meth-	6	Hex-
2	Eth-	7	Hept-
3	Prop-	8	Oct-
4	But-	9	Non-
5	Pent-	10	Dec-

Rules followed when naming alkanes.

1. The name of any alkane ends with **"ane".**

2. Identify the longest continuous chain of carbon atoms and take this to be the parent structure upon which the compound is built. E.g.

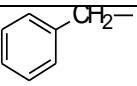CH_4 Methane

CH_3CH_3 Ethane

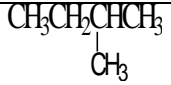$CH_3CH_2CH_3$ Propane
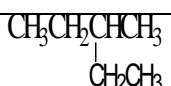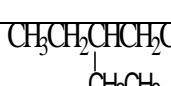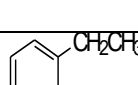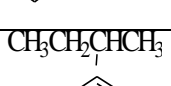
$CH_3CH_2CH_2CH_3$ Butane

3. When there is an alkyl group (for aliphatic compound) or aryl group (for aromatic compound), identify it by its nature and position on the chain.

4. Number the parent chain starting from a side that gives the carbon atom carrying the alkyl/aryl group the smallest number. A hyphen (-) is used to separate a number and a letter.
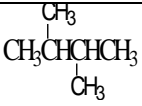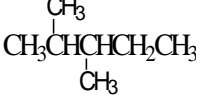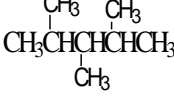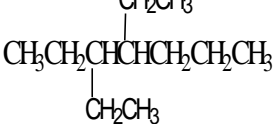
Common alkyl and aryl groups include;   **Examples.**

Alkyl groups		Aryl groups	
-CH_3	Methyl		Phenyl
-CH_2CH_3	Ethyl	CH_2-	benzyl
-$CH_2CH_2CH_3$	Propyl		
-$CH(CH_3)_2$	Isopropyl		
-$C(CH_3)_3$	Isobutyl		

$CH_3CH_2CHCH_3$ $\quad\ \ CH_3$	2-methylbutane
$CH_3CH_2CHCH_3$ $\quad\ \ CH_2CH_3$	2-methylpentane
$CH_3CH_2CHCH_2CH_3$ $\quad\ \ CH_2CH_3$	2-ethylpentane
CH_2CH_3	Phenylethane
$CH_3CH_2CHCH_3$ 	2-phenylbutane

5. (a) If there are two or more alkyl/aryl groups in the chain, they are identified by their nature and position and the prefix di-, tri-, tetra-, penta- etc.is used. A comma (,) is used to separate a two numbers e.g.

CH_3 $CH_3CHCHCH_3$ $\quad\ \ CH_3$	2,3-dimethylbutane
CH_3 $CH_3CHCHCH_2CH_3$ $\quad\ \ CH_3$	2,3-dimethylpentane
$CH_3\ \ CH_3$ $CH_3CHCHCHCH_3$ $\quad\ \ CH_3$	2,3,4-trimethylpentane
CH_2CH_3 $CH_3CH_2CHCHCH_2CH_2CH_3$ $\quad\quad\ \ CH_2CH_3$	3,4-diethylheptane

(b) If the alkyl/aryl groups are different, they are still identified by their nature and

$\underset{\underset{CH_2CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{CH_3CHCHCH_2CH_3}}$	3-ethyl-2-methylpentane	$\underset{\underset{CH_2CH_3}{\mid}}{\overset{\overset{CH_2CH_2CH_3}{\mid}}{CH_3CH_2CHCHCH_2CH_2CH_3}}$	3-ethyl-4-propylheptane

position and the naming follows alphabetical order. E.g.

6. For cyclic compounds a prefix "**cyclo**" is put before the name of the parent chain. E.g.

△	Cyclopropane	⬠	Cyclopentane
☐	Cyclobutane	⬡	Cyclohexane

2.2. Occurrence of Alkanes.

1. The first 4 alkanes occur naturally as gases and can be found in areas where crude petroleum is mined or in swamps. They include methane (used in gas cookers as natural gas), ethane, propane and butane (used in gas cookers and Bunsen burners).

2. The next 13 (C_5-C_{17}) are liquids at room temperature and include petrol, kerosene, diesel etc.

3. Those with more than 17 carbon atoms occur as solids at room temperature e.g. candle wax, grease, and petroleum jellys.

4. Members in this homologous series can be separated by fractional distillation owing to their different boiling points.
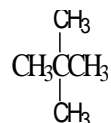
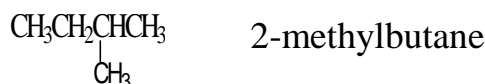## 2.3. Isomerism in Alkanes.

Alkanes exhibit chain isomerism.

Examples.

1. Write all the structures and IUPAC names of the isomers of the compounds with molecular formular C_5H_{12}.
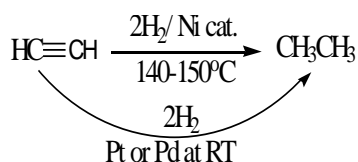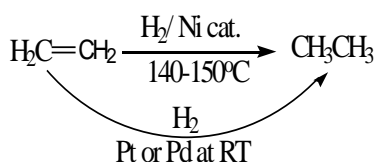
   Solution.

   $CH_3CH_2CH_2CH_2CH_3$ Pentane

   $$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3$$ 2,2-dimethylpropane

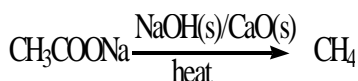 $$CH_3CH_2\underset{\displaystyle CH_3}{CH}CH_3$$ 2-methylbutane

EER: Write all the structures and IUPAC names of the isomers of the compounds with molecular formular C_6H_{14}.

2.4. Synthesis of Alkanes.

1. By hydrogenation of alkenes and alkynes using hydrogen gas in presence of nickel catalyst at 140-150ºC in presence of platinum or palladium catalyst at room temperature. E.g.

   $$H_2C{=}CH_2 \xrightarrow[\substack{H_2 \\ Pt\,or\,Pd\,at\,RT}]{\substack{H_2/\,Ni\,cat. \\ 140\text{-}150ºC}} CH_3CH_3 \qquad HC{\equiv}CH \xrightarrow[\substack{2H_2 \\ Pt\,or\,Pd\,at\,RT}]{\substack{2H_2/\,Ni\,cat. \\ 140\text{-}150ºC}} CH_3CH_3$$

2. By decarboxylation of sodium salts of carboxylic acids using heated sodium hydroxide and solid calcium oxide or carboxylic acid using excess heated concentrated sodium hydroxide solution. E.g.

   $$CH_3COONa \xrightarrow[\text{heat}]{NaOH(s)/CaO(s)} CH_4 \qquad CH_3COOH \xrightarrow[\text{heat}]{Excess\,Conc.NaOH(aq)} CH_4$$

3. By reacting alkyl halides with a zinc-copper couple suspended in an alcohol. E.g.

   $$CH_3CH_2Cl \xrightarrow[\text{ethanol}]{Zn\text{-}Cu\,couple} CH_3CH_3$$

   Zn-Cu/ethanol mixture reacts to produce hydrogen that displaces the halogen to produce the alkane.

4. From Grignard's reagent.

   Grignard's reagent is obtained by reacting an alkyl halide with magnesium in presence of dry ether. E.g.
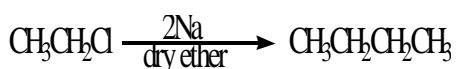
$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

Ethylmagnesium bromide, a grignard's reagent

The Grignard's reagent is then hydrolised (reacted with water) in the presence of an acid to form the alkane. E.g.
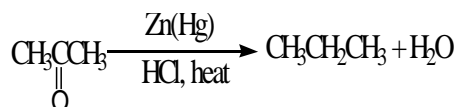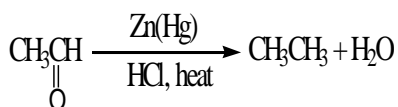
$$CH_3CH_2MgBr \xrightarrow{H^+/H_2O} CH_3CH_3$$

5. From Wurtz reaction.

   An alkyl halide is reacted with sodium metal in dry ether. The reaction doubles the chain. E.g.

$$CH_3CH_2Cl \xrightarrow[\text{dry ether}]{2Na} CH_3CH_2CH_2CH_3$$

6. By reduction of an alkyl halide using zinc and concentrated hydrochloric acid. E.g.

$$CH_3CH_2Cl \xrightarrow{Zn/Conc.HCl} CH_3CH_3 + ZnCl_2$$

7. By reacting carbonyl compounds with hot amalgamated zinc and hydrochloric acid. E.g.

$$CH_3\underset{\underset{O}{\|}}{C}H \xrightarrow[\text{HCl, heat}]{Zn(Hg)} CH_3CH_3 + H_2O \qquad CH_3\underset{\underset{O}{\|}}{C}CH_3 \xrightarrow[\text{HCl, heat}]{Zn(Hg)} CH_3CH_2CH_3 + H_2O$$

2.5.   Physical Properties of Alkanes.

a) Alkanes are insoluble in water but soluble in organic solvents such as benzene.

b) Density increases with increase in molecular but branching reduces this flow.

c) Melting and boiling points increase with increase in molecular mass since magnitude of Van der Waal's forces increase. Branched alkanes have lower mp and bp compared to straight alkanes of same molecular mass. Even numbered alkanes have higher mp compared to odd numbered alkanes of same molecular mass.

Qn. Explain why branched alkanes have lower mp and bp compared to straight alkanes of same molecular mass.

Ans. *Increased branching gives the molecule a more nearly spherical shape, reducing the extent of contact between the neighbouring carbon atoms. Consequently, the attractive forces are reduced in number hence mp and bp reduce.*

Qn. Explain why even numbered alkanes have higher mp compared to odd numbered alkanes of same molecular mass.

Ans. *This is because in the crystalline state, even numbered molecules adopt a highly ordered arrangement in which carbon atoms form a zigzag pattern, causing different chains to pack closer together so that the attractive forces become stronger for even numbered alkanes and more energy is needed to break them hence a higher mp than odd numbered alkanes.*

2.6. Chemical Properties of Alkanes [Reactions of Alkanes].

The relative strength of the carbon-hydrogen bond in alkanes makes these saturated hydrocarbons rather unreactive even towards the strongest oxidizing agents such as potassium permanganate and concentrated sulphuric acid.

Qn. Alkanes are unreactive even towards the strongest oxidizing agents. Explain.

Ans. *For a reaction to occur bonds must be broken first, the strength of a bond depends on the difference in the electronegativities of the bonded atoms, the bigger the difference, the weaker the bond. But in a carbon-hydrogen bond, there is a very small difference in the electronegativities of carbon and hydrogen atoms and the electrons are placed almost symmetrically between the two atoms making the bond nonpolar hence alkanes are unreactive.*

However, under drastic conditions such as high temperature and presence of ultraviolet (UV) light, alkanes undergo certain reactions.

1. Combustion.

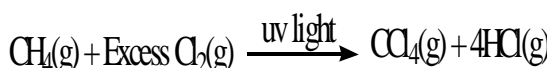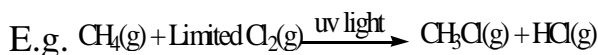- Alkanes burn in excess oxygen to form carbon dioxide and water.

$$C_xH_y + 1/2(2x + y/2)O_2 \longrightarrow xCO_2 + y/2\,H_2O$$

E.g. $C_2H_6(g) + 7/2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

- Alkanes burn in limited oxygen to form carbon monoxide and water.

$$CxHy + 1/2(x+y/2)O_2 \longrightarrow xCO + y/2 H_2O$$

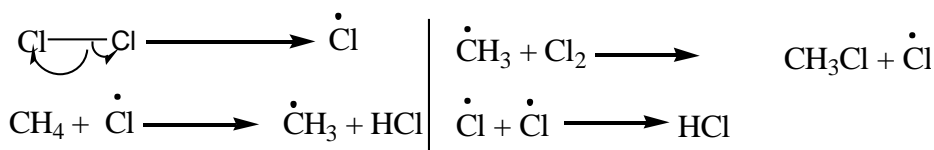E.g. $C_2H_6(g) + 5/2O_2(g) \longrightarrow 2CO(g) + 3H_2O(l)$
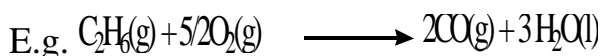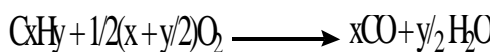
2. Chlorination.

Alkanes react with chlorine only if the mixture is exposed to direct sunlight (UV light) or heated. The reaction proceeds via free radical mechanism.

E.g. $CH_4(g) + Limited\ Cl_2(g) \xrightarrow{uv\ light} CH_3Cl(g) + HCl(g)$

$CH_4(g) + Excess\ Cl_2(g) \xrightarrow{uv\ light} CCl_4(g) + 4HCl(g)$

Mechanism;

EER. Complete and write a mechanism.
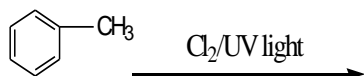
Chlorination of alkanes can also be done using heated sulphur dichloride dioxide (SO_2Cl_2) in the presence of dibenzene carbonyl peroxide. E.g.

$CH_4 + SO_2Cl_2 \xrightarrow[heat]{dibenzene\ carbonyl\ peroxide} CH_3Cl + SO_2 + HCl$
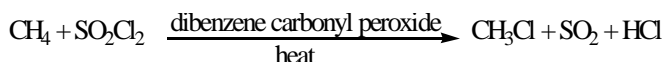
3. Nitration.

Introducing a nitro group ($-NO_2$) into an alkane is done using concentrated nitric acid in vapour phase at 300ºC. E.g.

$CH_4 + HNO_3(g) \xrightarrow{300ºC} CH_3NO_2$
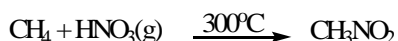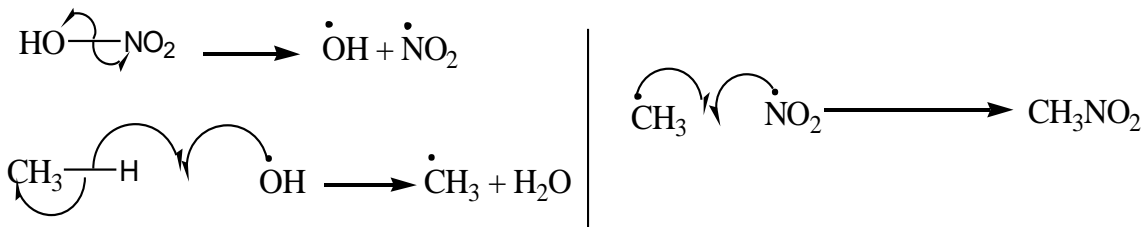
Mechanism:

EER. Complete and write a mechanism.

2.7. Uses of Alkanes.

a) Methane is used to make synthesis gas (CO and H_2) where H_2 is needed for Haber process.

b) Methane is used to make dichloromethane, an important solvent.

c) Ethane and propane are sources of ethene and propene respectively.

d) Methane and butane are used as fuel in gas stoves.

e) Higher alkanes are used to make grease and candle wax.

f) Liquid alkanes are used as fuel in auto mobiles.

CHAPTER 3: ALKENES.

Alkenes are unsaturated hydrocarbons with general formular, C_nH_{2n} where n = 2, 3, 4….

The functional group is the carbon-carbon double bond C=C.

3.1 Nomenclature of Alkenes.

a) The ending **"ane"** in alkanes is replaced with **"ene"** in the corresponding alkene. E.g.

Alkane   Alkene

Ethane   Ethene

Propane   Propene

b) The position is identified by numbering the chain in such that the carbon atom with the double bond is given the smallest number. E.g.

$CH_3CH=CHCH_2CH_3$	Pent-2ene
$CH_3CH_2CH=CHCH_2CH_3$	Hex-3-ene
$CH_3CH_2CH_2CH=CHCH_2CH_3$	Hept-3-ene

c) Alkyl/aryl or any other group on the ring are identified the same way as in alkanes. E.g.

$CH_3C=CHCH_3$ $\quad\|$ $\quad CH_3$	3-methylbut-2-ene	$\qquad CH_2CH_3$ $CH_3CH_2CH=CHCCH_2CH_3$ $\qquad\quad\|$ $\qquad\quad CH_3$	5-ethyl-5-methylhept-3-ene

$CH_3C{=}CCH_3$ with CH_3 above left carbon and CH_3 below	2,3-dimethylbut-2-ene	$CH_3C{=}CCH_3$ with Cl above left carbon and CH_3 below	2-chloro-3-methylbut-2-ene

d) Cyclic alkenes are named with a prefix "cyclo" before the parent chain. E.g.

(triangle with double bond)	Cyclopropene	(hexagon)	Cyclohexene
(pentagon)	Cyclopentene	(pentagon with CH_3)	1-methylcyclopentene

3.2 Isomerism in Alkenes.

Alkenes exhibit chain, position, geometrical and functional group isomerism.

Example.

Write the structural formulae and IUPAC names of all the isomers of C_5H_{10}.

Solution.

$CH_3CH_2CH_2CH{=}CH_2$	Pent-1-ene	$CH_3CH_2C{=}CH_2$ with CH_3 below	2-methylbut-1-ene
$CH_3CH_2CH{=}CHCH_3$	Pent-2-ene	$CH_3CHCH{=}CH_2$ with CH_3 below	3-methylbut-1-ene
$CH_3C{=}CHCH_3$ with CH_3 below	2-methylbut-2-ene	(pentagon) Cyclopentane.	*Note: alkenes are isomeric to cyclic alkanes.*

EER: C_6H_{12}.

3.3 Synthesis of Alkenes.

1 a) Dehydration of alcohols using concentrated sulphuric acid at 170-180°C. E.g.

i. $CH_3CH_2CH_2OH \xrightarrow[170-180°C]{Conc.H_2SO_4} CH_3CH=CH_2 + H_2O$

$CH_3CH_2CH_2\ddot{O}H \quad \overset{\curvearrowright}{H-OSO_3H} \longrightarrow CH_3CH_2CH_2-\overset{+}{O}H_2 + \overset{-}{O}SO_3H$

$CH_3CH_2CH_2\overset{+}{O}H_2 \underset{-(H_2O)}{\rightleftharpoons} CH3CH_2-\overset{+}{C}H_2 \quad \Big| \quad CH3CH-\overset{+}{C}H_2 \longrightarrow CH_3CH=CH_2 + H_2SO_4$

$\overset{H}{\underset{OSO_3H}{}}$
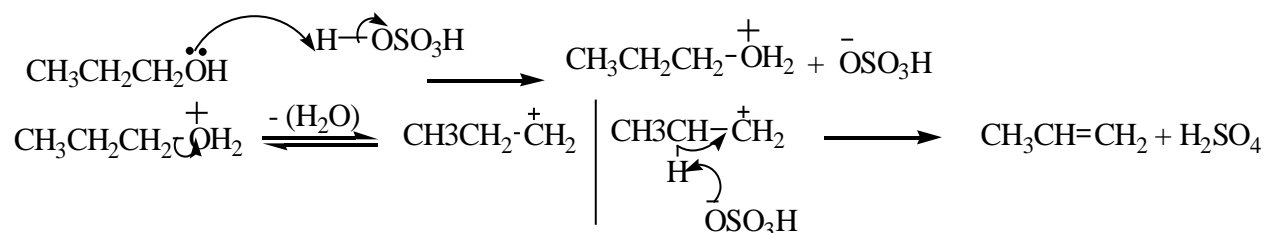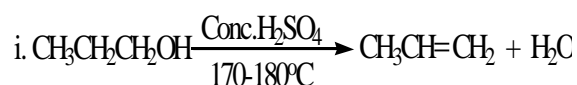
Order of Stability of Carbo cations.

The stability of carbo cations depends on the number and size of the alkyl group present.

$3°$ carbo cations are most stable because they have three alkyl groups, $2°$ carbo cations are more stable than $1°$ carbo cations because they have two alkyl groups while $1°$ carbo cations have only one alkyl group.
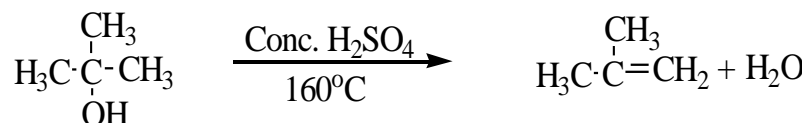
Alkyl group have the ability to direct electrons towards the carbon atom where they are attached, a property called *positive inductive effect.* The higher the number of alkyl groups the greater the positive inductive effect hence the order of stability $3°>2°>1°$.

Also the magnitude of inductive effect is proportional to the size of the alkyl group i.e. propyl>ethyl>methyl etc.

Therefore, the mechanism via a more stable carbocation is more favourable and so the product formed is the major product. If there is a possibility of two carbo cations being formed as intermediates during a reaction, the one via a more stable carbocation is taken, the other route is neglected.

Reactions via the most carbo cations require less vigorous conditions.

Examples.

$$\underset{\underset{OH}{\overset{CH_3}{|}}}{H_3C\cdot\overset{|}{C}\cdot CH_3} \xrightarrow[160°C]{Conc.\ H_2SO_4} \underset{\overset{CH_3}{|}}{H_3C\cdot\overset{|}{C}=CH_2} + H_2O$$

Qn. Dehydration of butan-1-ol using concentrated sulphuric acid occurs at 180°C while that of 2-hydroxy-2-methylpropane occurs at 160°C. Explain.

Ans. Butan-1-ol has one propyl group with a positive inductive effect while 2-hydroxy-2-methylpropane has three methyl groups each with a positive inductive effect. The positive inductive effect from the three methyl groups is greater than that from one propyl group in butan-1-ol. The tertiary carbocation from 2-hydroxy-2-methylpropane is there for more stable than the primary carbocation from butan-1-ol. Hence dehydration of butan-1-ol occurs at 180ºC while that of 2-hydroxy-2-methylpropane occurs at 160ºC.

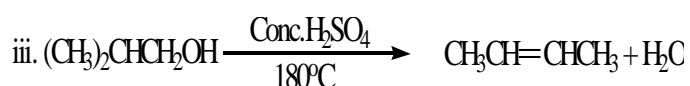ii. $CH_3CH_2CH_2CH_2OH \xrightarrow[180ºC]{Conc.H_2SO_4} CH_3CH=CHCH_3 + H_2O$

Mechanism. (Hydride shift, stability of carbocation is $3^º >> 2^º > 1^0$).

iii. $(CH_3)_2CHCH_2OH \xrightarrow[180ºC]{Conc.H_2SO_4} CH_3CH=CHCH_3 + H_2C$

Mechanism. (Methyl shift, stability of carbocation is $3^º >> 2^º > 1^0$).

b. Ethene is prepared by passing ethanol vapour over aluminium oxide at 300ºC.

$CH_3CH_2OH \xrightarrow[300ºC]{Al_2O_3} CH_2=CH_2 + H_2C$
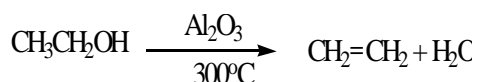
2. Dehydrohalogenation of $2^º$ or $3^º$ halogen alkanes using hot alcoholic potassium hydroxide. E.g.

CH_3CHCH_3 (with Cl below) $\xrightarrow[Heat]{KOH/CH_3CH_2OH} CH_3CH=CH_2 + KCl$

Mechanism.

$KOH + CH_3CH_2OH \longrightarrow CH_3CH_2OK + H_2O$

$CH_3CH_2OK \longrightarrow CH_3CH_2\overset{-}{O} + \overset{+}{K}$

$\longrightarrow CH_3CH=CH_2 + \overset{-}{Cl}$

b. $CH_3\overset{CH_3}{\underset{Cl}{C}}CH_3 \xrightarrow[Heat]{KOH/CH_3CH_2OH} CH_3\overset{CH_3}{C}=CH_2 + KCl$

Mechanism.

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

$$CH_3CH_2OK \longrightarrow CH_3CH_2\bar{O} + K^+$$

$$(CH_3)_3C-Cl \rightleftharpoons (CH_3)_3\overset{+}{C} + \bar{C}l$$

$$CH_3\overset{+}{C}-CH_3 \longrightarrow CH_3C=CH_2$$
$$\underset{OCH_2CH_3}{CH_2-H} \qquad CH_3$$

Note: primary halogen alkanes with the hot alcoholic potassium hydroxide yield not alkenes but rather ethers. E.g.

$$CH_3CH_2CH_2Cl \xrightarrow[\text{Heat}]{KOH/CH_3CH_2OH} CH_3CH_2OCH_2CH_3 + KCl$$

Mechanism.

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

$$CH_3CH_2OK \longrightarrow CH_3CH_2\bar{O} + K^+$$

$$CH_3CH_2-Cl$$
$$CH_3CH_2\bar{O} \longrightarrow CH_3CH_2OCH_2CH_3 + \bar{C}l$$

$$\overset{+}{K} + \bar{C}l \longrightarrow KCl$$

3. Reduction of alkynes using hydrogen in presence of nickel heated to 140°C or platinum or palladium at room temperature. E.g.

$$CH≡CH \xrightarrow[140-150°C]{H_2/\,Ni\,cat.} CH_2=CH_2$$
$$\xrightarrow[\text{Pt or Pd at RT}]{H_2}$$

Note: Higher alkynes are reduced using hydrogen in presence of Lindler's catalyst. (Lindler's catalyst is Pd/CaCO₃/Quinoline). E.g.

$$CH_3C≡CH \xrightarrow{H_2/\text{Lindler's cat.}} CH_3CH=CH_2$$

3.4 Reactions of Alkenes.

1. Combustion.

Alkenes burn in oxygen with a slightly sooty flame to form water and carbon dioxide. The soot is a result of incomplete combustion of carbon due to a high carbon-hydrogen ratio of the alkenes. E.g.
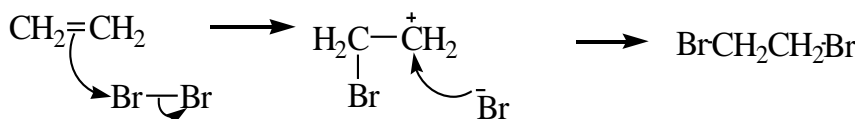
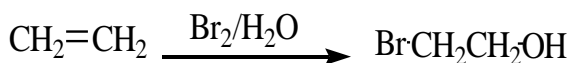$$C_2H_4(g) + 3O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

2. Halogenation.

a) Alkenes undergo electrophilic addition with halogen in the presence of carbon tetrachloride to form dihalo alkanes. E.g.
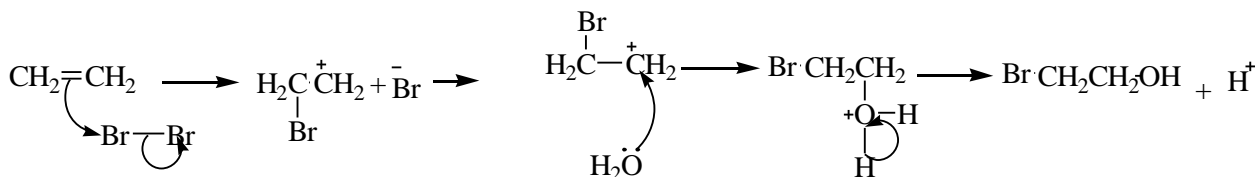
$$CH_2{=}CH_2 \xrightarrow{\text{Br}_2/CCl_4} Br{\cdot}CH_2CH_2{\cdot}Br$$
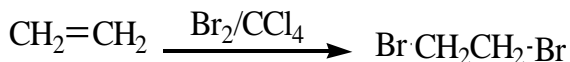
Mechanism.

b) Alkenes undergo electrophilic addition with halogen in the presence of water to form substituted alkanes. E.g.

$$CH_2{=}CH_2 \xrightarrow{\text{Br}_2/H_2O} Br{\cdot}CH_2CH_2OH$$
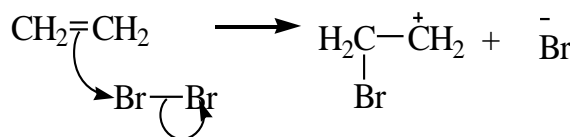
Mechanism.

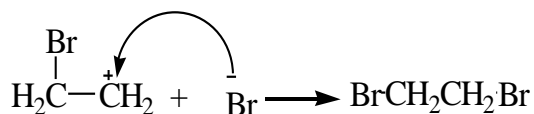**Qn. Addition of bromine in presence of CCl₄ to propene yields 1,2-dibromopropane as the major product while in presence of water, yields 1-bromo-2-hydroxypropane. Explain.**

Ans. Propene reacts with bromine forming a carbocation and a bromide ion.

In the presence of CCl₄, the bromide ion reacts with the carbocation to form 1,2-dibromopropane as the major product.

In the presence of water, there is much more water than the bromide ions in the solution, water having a lone pair of electrons on oxygen atom, the reaction with water predominates, hence 1-bromo-2-hydroxypropane is the major product.

$$H_2\overset{+}{C}-\overset{+}{C}H_2 \longrightarrow CH_2CH_2 \longrightarrow Br\cdot CH_2CH_2OH + \overset{+}{H}$$
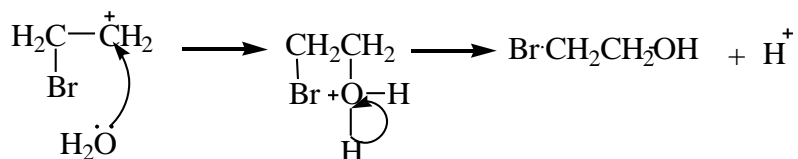
Qn. *Addition of bromine in presence of sodium chloride to propene yields 1-bromo-2-chloropropane as the major product and 1,2-dibromopropane as the minor product. Explain.*
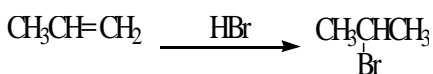
3. Hydrohalogenation.

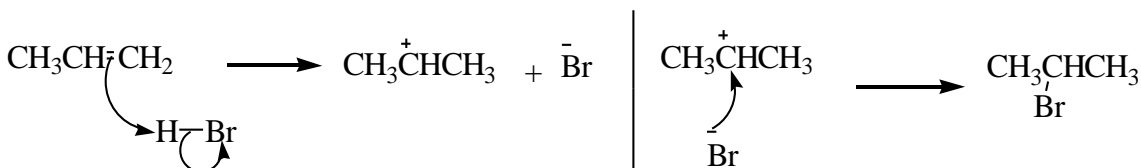Alkenes undergo electrophilic addition with halogen acids to form halogen alkanes.

The electrophilic addition of halogen acids to alkenes follows Markovnikov rule.

Markovnikov rule state that "*The hydrogen atom of the halogen acid bonds to the carbon atom of the double bond with more hydrogen atoms*".

Example:

$$CH_3CH=CH_2 \xrightarrow{\quad HBr \quad} CH_3\underset{Br}{CH}CH_3$$

Mechanism.

$$CH_3CH=CH_2 \longrightarrow CH_3\overset{+}{C}HCH_3 + \bar{Br} \quad \bigg| \quad CH_3\overset{+}{C}HCH_3 \longrightarrow CH_3\underset{Br}{CH}CH_3$$
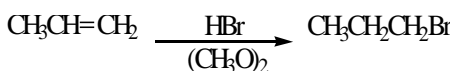
Anti-Markovnikov states that "*The hydrogen atom of the halogen acid bonds to the carbon atom of the double bond with less hydrogen atoms*".*it occurs in presence of a peroxide, ROOR e.g.H_2O_2, CH_3OOCH_3 etc. it follows a free radical mechanism.*
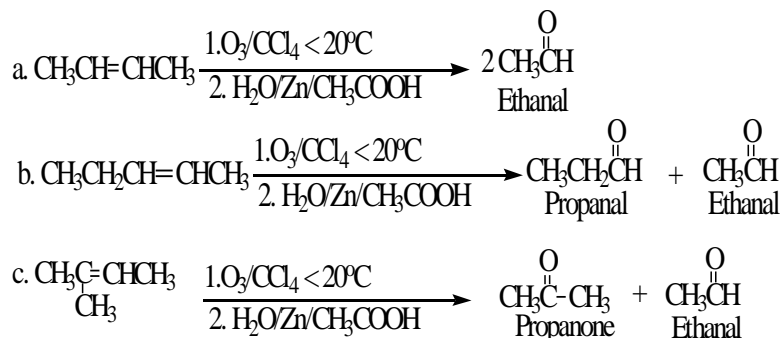
Example.

$$CH_3CH=CH_2 \xrightarrow[\text{(CH}_3\text{O)}_2]{\quad HBr \quad} CH_3CH_2CH_2Br$$

Mechanism.

$CH_3\overset{\frown}{O}\overset{\frown}{O}CH_3 \longrightarrow 2\overset{\bullet}{O}CH_3$

$CH_3\overset{\bullet}{O} + H-Br \longrightarrow CH_3OH + \overset{\bullet}{B}r$

$CH_3CH=CH_2 \longrightarrow CH_3\overset{\bullet}{C}HCH_2Br$
with Br

$CH_3\overset{\bullet}{C}HCH_2Br + H-Br \longrightarrow CH3CH_2CH_2Br + \overset{\bullet}{B}r$

$CH_3\overset{\bullet}{O} + \overset{\bullet}{B}r \longrightarrow CH_3OBr$

4. Hydrogenation.

Hydrogen adds to an alkene in the presence of nickel heated to 140-150°C or platinum or palladium at room temperature. E.g.

$H_2C=CH_2 \xrightarrow[140-150°C]{H_2/Ni\ cat.} CH_3CH_3$
$\xrightarrow[Pt\ or\ Pd\ at\ RT]{H_2}$

5. Acid hydrolysis of alkenes.

Alkenes react with concentrated sulphuric acid in presence of water and mixture warmed to form alcohols. E.g.

$CH_2=CH_2 \xrightarrow[H_2O/Warm]{Conc.H_2SO_4} CH_3CH_2OH$ Usually written as $CH_2=CH_2 \xrightarrow[Warm]{H^+/H_2O} CH_3CH_2OH$

Mechanism:

$CH_2=CH_2 \xrightarrow{H^+} CH_3\overset{+}{C}H_2 \xrightarrow{:OH_2} CH_3CH_2\overset{+}{\underset{H}{O}}-H \longrightarrow CH_3CH_2OH + H^+$

EER.

1. Complete the following and write mechanism.

a. $CH_3CH=CH_2 \xrightarrow[Warm]{H^+/H_2O}$

b. (cyclohexene with CH_3 group) $\xrightarrow[Warm]{H^+/H_2O}$

6. Ozonolysis of alkenes.

Alkenes react with ozone to form an ozonide, the ozonide is unstable and very explosive and so the reaction is carried out in in an inert solvent, CCl_4 at less than 20°C. When the ozonide is hydrolised in presence of zinc and ethanoic acid (*to*

prevent further oxidation to carboxylic acids by H_2O_2 formed), carbonyl compounds are formed.

Examples.

a. $CH_3CH=CHCH_3 \xrightarrow[\text{2. }H_2O/Zn/CH_3COOH]{\text{1. }O_3/CCl_4 < 20^\circ C} 2\,CH_3\overset{\overset{O}{\|}}{C}H$
Ethanal

b. $CH_3CH_2CH=CHCH_3 \xrightarrow[\text{2. }H_2O/Zn/CH_3COOH]{\text{1. }O_3/CCl_4 < 20^\circ C} CH_3CH_2\overset{\overset{O}{\|}}{C}H \;+\; CH_3\overset{\overset{O}{\|}}{C}H$
Propanal   Ethanal

c. $CH_3\underset{\underset{CH_3}{|}}{C}=CHCH_3 \xrightarrow[\text{2. }H_2O/Zn/CH_3COOH]{\text{1. }O_3/CCl_4 < 20^\circ C} CH_3\overset{\overset{O}{\|}}{C}\text{-}CH_3 \;+\; CH_3\overset{\overset{O}{\|}}{C}H$
Propanone   Ethanal

7. **Oxidation of alkenes.**

   a. Alkenes are oxidized by dilute, alkaline potassium manganite (VII) solution to diols. The purple solution turns green and a black solid deposited due to formation of manganate(VI) ions and manganese(IV)oxide respectively.

   Examples.

   i) $CH_3CH_2CH=CH_2 \xrightarrow[\text{Heat}]{OH^-(aq)/MnO_4^-(aq)} CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2OH + MnO_4^{2-} + MnO_2$

   ii) $\xrightarrow[\text{Heat}]{OH^-(aq)/MnO_4^-(aq)}$ $+ MnO_4^{2-} + MnO_2$
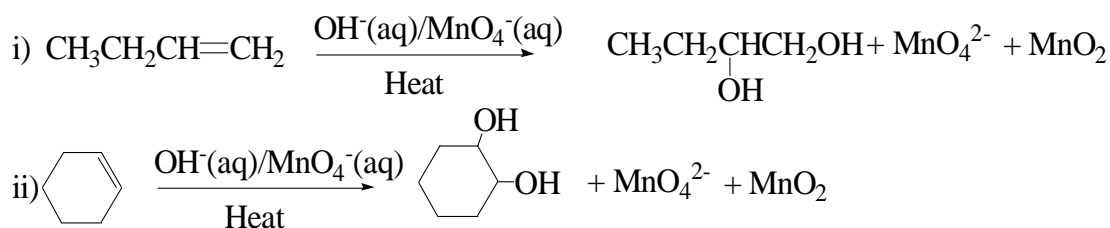
   b. Alkenes are oxidized by acidified potassium manganite (VII) solution to organic acids. The purple solution turns colourless due to formation of manganese(II) ions. E.g.

   i) $CH_3CH_2CH=CH_2 \xrightarrow[\text{Heat}]{H^+(aq)/MnO_4^-(aq)} CH_3CH_2COOH + CO_2 + Mn^{2+}$

   ii) $\xrightarrow[\text{Heat}]{H^+(aq)/MnO_4^-(aq)} HOOC(CH_2)_4COOH + Mn^{2+}$
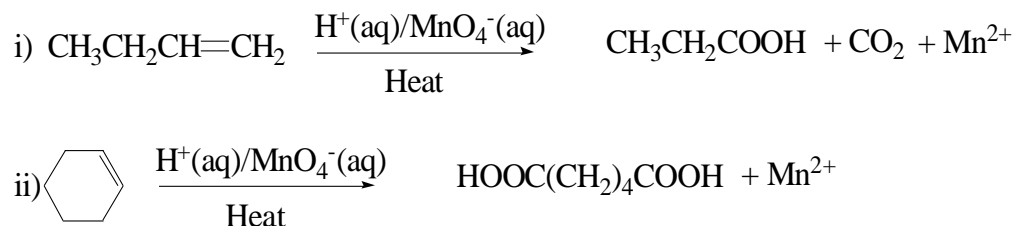
3.5 Distinguishing Alkenes from Alkanes.

Reagent:

Liquid Bromine

Observation:

Alkenes- Brown colour of liquid bromine turns colourless.

Alkanes- No observable change.

Reagent:

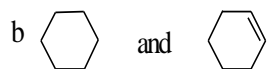*Acidified potassium manganate (VII) solution.*

Observation:

Alkenes- Purple colour turns colourless.

Alkanes- No observable change.

Examples.

1. Name a reagent that can be used to distinguish between the following pairs of compounds. In each case, state what is observed when the named reagent is reacted with each compound.

a. $CH_3CH=CH_2$ and $CH_3H_2CH_3$

b. $\hexagon$ and $\hexagon$

3.6. Uses of alkenes.

1) Used to make plastics like polyethene from ethene.

2) Used to make alcohols like ethanol from ethene.

3) Ethene is used to make epoxyethane which is used to make detergents.

4) Also used to make ethene-1,2-diol, an anti-knock agent in the petrol engine.

CHAPTER 4: ALKYNES.

Alkynes are unsaturated hydrocarbons with general formular, C_nH_{2n-2} where n = 2, 3, 4….

The functional group is the carbon-carbon tripple bond, $C{\equiv}C$.

4.1 Nomenclature of Alkynes.

a. The ending **"ane"** in alkanes is replaced with **"yne"** in the corresponding alkyne. E.g.

Alkane   Alkyne

Ethane   Ethyne

Propane   Propyne
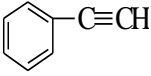
b. The position is identified by numbering the chain in such a way that the carbon atom with the tripple bond is given the smallest number. E.g.

$CH_3C{\equiv}CCH_2CH_3$ Pent-2-yne

$CH_3CH_2C{\equiv}CCH_2CH_3$ Hex-3-yne

$CH_3CH_2CH_2C{\equiv}CCH_2CH_3$ Hept-3-yne

c. Alkyl/aryl or any other group on the ring are identified the same way as in alkanes. E.g.

$CH_3CHC{\equiv}CH$ $\quad\mid$ $\quad CH_3$	3-methylbut-1-yne	$\qquad CH_2CH_3$ $CH_3CH_2C{\equiv}CCH_2CH_3$ $\qquad CH_3$	5-ethyl-5-methylhept-3-yne
$\quad CH_3$ $\quad\mid$ $CH_3CC{\equiv}CH$ $\quad\mid$ $\quad CH_3$	3,3-dimethylbut-1-yne	⬡$-C{\equiv}CH$	Phenylethyne

4.2 Isomerism in Alkynes.

Alkynes exhibit chain, position and functional group isomerism.

Example.

Write the structural formulae and IUPAC names of all the isomers of C_5H_8.

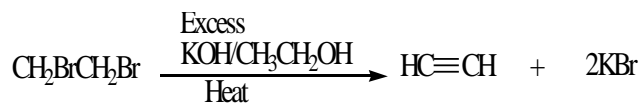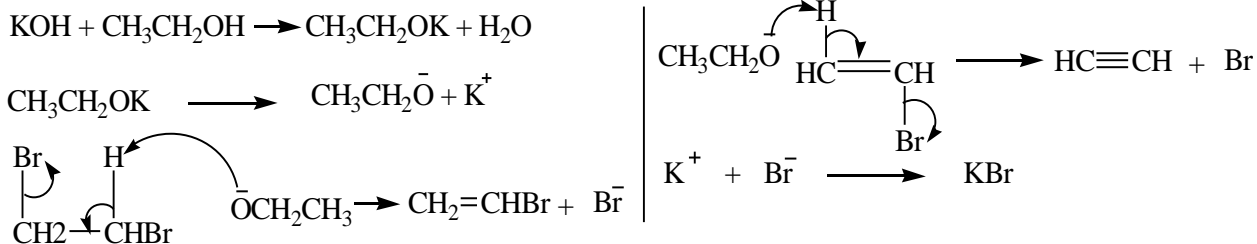| $CH_3CH_2CH_2C{\equiv}CH$	Pent-1-yne	$CH_3CHC{\equiv}CH$ $\qquad CH_3$	3-methylbut-1-yne
$CH_3CH_2C{\equiv}CCH_3$	Pent-2-yne	⬠ Cyclopentene.	*Note: alkynes are isomeric to cyclic alkenes.*

EER: C_6H_{10}.

4.3 Synthesis of Alkynes.

1. Ethyne is prepared by reacting calcium dicarbide with cold water. The calcium dicarbide is obtained by reacting calcium oxide with coke in an electric furnace at 2500-3000°C.

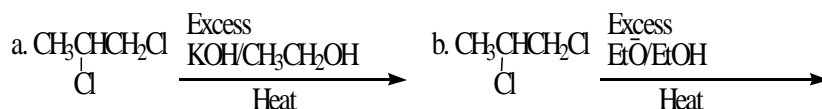$$CaO \ + \ 3C \ \xrightarrow[3000°C]{} \ CaC_2 \ + \ CO$$

$$CaC_2 \ + \ 2H_2O \longrightarrow HC{\equiv}CH \ + \ Ca(OH)_2$$
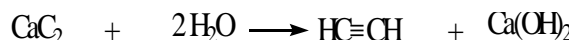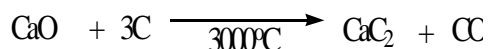
2. Reacting vicinal dihalo alkanes with excess, hot, alcoholic potassium hydroxide. E.g.

$$CH_2BrCH_2Br \ \xrightarrow[\text{Heat}]{\substack{\text{Excess}\\ \text{KOH/CH}_3\text{CH}_2\text{OH}}} \ HC{\equiv}CH \ + \ 2KBr$$

Mechanism:

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

$$CH_3CH_2OK \longrightarrow CH_3CH_2\bar{O} + K^+$$

$$\bar{O}CH_2CH_3 \longrightarrow CH_2{=}CHBr + \bar{Br}$$

$$K^+ + \bar{Br} \longrightarrow KBr$$

EER. Complete and write mechanism

a. CH_3CHCH_2Cl $\overset{\text{Excess}}{\underset{\text{Heat}}{KOH/CH_3CH_2OH}}$ with Cl

b. CH_3CHCH_2Cl $\overset{\text{Excess}}{\underset{\text{Heat}}{Et\bar{O}/EtOH}}$ with Cl

3. By reacting sodium acetylides with alkyl halides. Sodium acetylides are formed by reacting terminal alkynes with sodium in liquid ammonia.

Examples.

$$CH_3CH_2C{\equiv}CH \xrightarrow{Na/Liquid\ NH_3} CH_3CH_2C{\equiv}CNa + H_2$$
$$\text{Sodium butylide}$$

$$CH_3CH_2C{\equiv}CNa \xrightarrow{CH_3Br} CH_3CH_2C{\equiv}CCH_3 + NaBr$$
$$\text{Pent-2-yne}$$

Summarized as;

$$CH_3CH_2C{\equiv}CH \xrightarrow[2.CH_3Br]{1.Na/Liquid\ NH_3} CH_3CH_2C{\equiv}CCH_3$$
$$\text{Pent-2-yne}$$
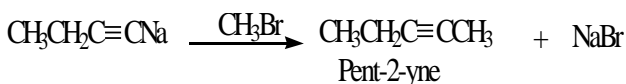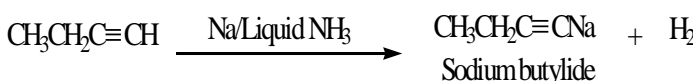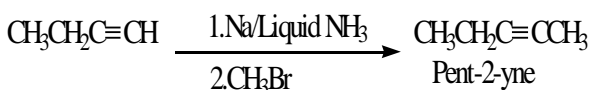
Note: T*his method increases the carbon skeleton.*

4. Indirect route. E.g. show how propyne can be synthesized from propan-1-ol.

Solution.

$$CH_3CH_2CH_2OH \xrightarrow[180^oC]{Conc.H_2SO_4} CH_3CH{=}CH_2 \xrightarrow{Br_2/CCl_4} CH_3\overset{Br}{CH}CH_2Br \xrightarrow{\overset{\text{Excess}}{KOH/CH_3CH_2OH}} CH_3C{\equiv}CH$$

4.4 Chemistry of the Tripple Bond.

Alkynes have a small bond length between the two hybrid carbon atoms that bear the tripple bond. The increase in the S-character in the SP hybrid atomic orbitals

bring about a stronger binding force between the two bonded carbon atoms such that the electrons are more strongly held between the two carbon atoms. This makes alkynes less reactive towards electrophiles compared to alkenes, though one would think that there is a bigger electron cloud in the tripple bond than in a double bond. The electrons in the tripple bond are not readily available for attack by electrophiles.

Nevertheless, alkynes undergo typical electrophilic addition reactions just like alkenes to form saturated compounds in a two stage process.

4.5 Reactions of Alkynes.

1. **Combustion.**

Alkynes burn in oxygen with a sooty flame due to a high carbon to oxygen ratio to form carbon dioxide and water.

$$2HC \equiv CH(g) \; + \; 5O_2(g) \longrightarrow \; 4CO_2(g) \; + \; 2H_2O(g)$$

2. **Hydrogenation.**

Alkynes are hydrogenated using hydrogen gas in presence of nickel catalyst at 140-150°C or in presence of platinum or palladium catalyst at room temperature to form
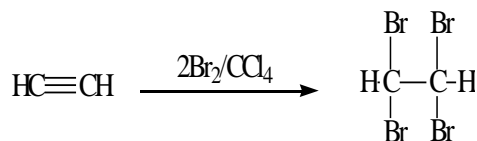
$$HC \equiv CH \xrightarrow[\text{140-150°C}]{2H_2/ \text{Ni cat.}} CH_3CH_3$$
$$\xrightarrow[\text{Pt or Pd at RT}]{2H_2}$$
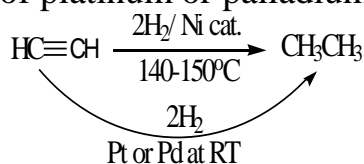
alkanes. E.g.

NB: *Higher alkynes are reduced to alkenes using Lindler's catalyst. E.g.*

$$CH_3CH_2C \equiv CCH_3 \xrightarrow{H_2/\text{Lindler's catalyst}} CH_3CH_2CH = CHCH_3$$
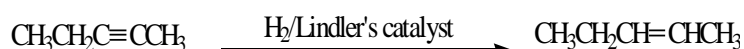
3. **Halogenation.**

Electrophilic addition of chlorine, bromine and iodine to alkynes is the same as for alkenes. E.g.

$$HC \equiv CH \xrightarrow{2Br_2/CCl_4} \underset{\overset{|}{Br} \; \overset{|}{Br}}{\overset{\overset{Br}{|} \; \overset{Br}{|}}{HC - C\text{-}H}}$$

Mechanism: *See halogenation of alkenes.*

4. **Hydrohalogenation.**

Electrophilic addition of halogen acids to alkynes is the same as for alkenes. E.g.

$$CH_3C\equiv CH \xrightarrow{2HCl} CH_3\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}CH_3$$
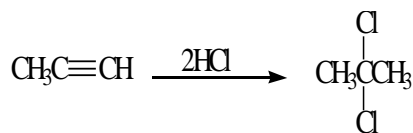
Mechanism: *See Hydrohalogenation of alkenes following Markovnikov rule.*

$$CH_3C\equiv CH \xrightarrow[ROOR]{2HCl} CH_3\overset{}{\underset{\underset{Cl}{|}}{CH}}CH_2Cl$$

Mechanism: *See Hydrohalogenation of alkenes following Anti-Markovnikov rule.*

5. **Polymerisation of ethyne.**

Ethyne polymerizes to benzene when heated to 400ºC. Or when heated with iron as catalyst. Or When heated to 60-70ºC with organo-nickel catalyst.
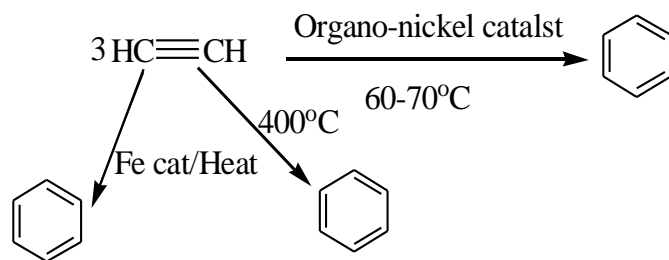
6. Reaction of alkynes with water in the presence of concentrated sulphuric acid and mercury (II) sulphate as a catalyst at 60ºC. Ethyne forms ethanal while other alkynes form ketones. E.g.

$$HC\equiv CH \xrightarrow[HgSO_4,\ 60ºC]{H_2O/Conc.H_2SO_4} CH_3\overset{\overset{O}{\|}}{CH} \qquad CH_3C\equiv CH \xrightarrow[Hg^{2+},\ 60ºC]{H_2O/H^+} CH_3\overset{\overset{O}{\|}}{C}CH_3$$

Mechanism:
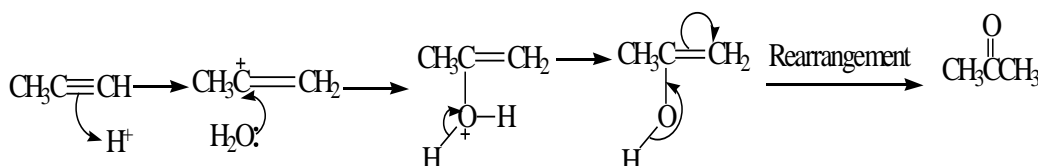
4.6 Distinguishing Between Alkynes and Alkanes.

Reagent:

Liquid Bromine

Observation:

Alkynes- Brown colour of liquid bromine turns colourless.
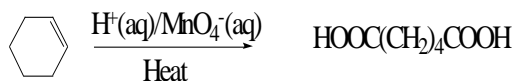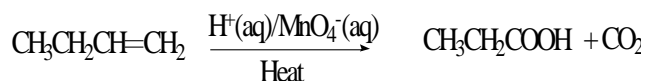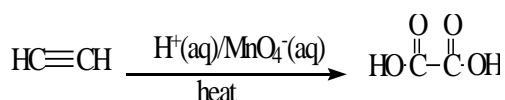
Alkanes- No observable change.

Reagent:

Acidified potassium manganate (VII) solution.

Observation:

Alkynes- Purple colour turns colourless.

Alkanes- No observable change.

NOTE: *The reaction of ethyne with acidified potassium manganite (VII) solution is a little different from that of ethene. Oxidation takes place, but the product is instead ethanedioic acid (oxalic acid) not ethane-1,2-diol.*

$$HC\equiv CH \xrightarrow[\text{heat}]{H^+(aq)/MnO_4^-(aq)} HOOC-COOH$$

$$CH_3CH_2CH=CH_2 \xrightarrow[\text{Heat}]{H^+(aq)/MnO_4^-(aq)} CH_3CH_2COOH + CO_2$$

$$\bighexagon \xrightarrow[\text{Heat}]{H^+(aq)/MnO_4^-(aq)} HOOC(CH_2)_4COOH$$

Examples.

1. Name a reagent that can be used to distinguish between the following pairs of compounds. In each case, state what is observed when the named reagent is reacted with each compound.

   $CH_3CH_2CH_3$ and $CH_3C\equiv CH$

4.7 Distinguishing Between Terminal Alkynes and Non-terminal Alkynes.

Example:

1. Name a reagent that can be used to distinguish between the following pairs of compounds. In each case, state what is observed when the named reagent is reacted with each compound.

$CH_3CH_2C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$

Solution.

Reagent: *Ammoniacal silver nitrate solution (Tollen's reagent).*

Observation: *Terminal alkynes (e.g. $CH_3CH_2C{\equiv}CH$) - White precipitate of silver acetylides.*

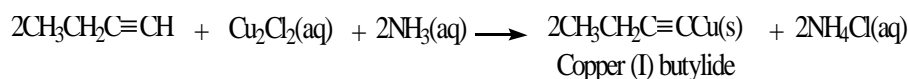$$CH_3CH_2C{\equiv}CH + AgNO_3(aq) + NH_3(aq) \longrightarrow CH_3CH_2C{\equiv}CAg(s) + NH_4NO_3(aq)$$
$$\text{Silver butylide}$$
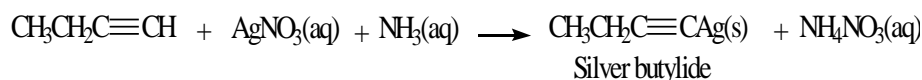
- *Non-terminal alkynes (e.g. $CH_3C{\equiv}CCH_3$) - No observable change.*

Alternatively:

Reagent: *Ammoniacal copper (I) chloride solution.*

Observation: *Terminal alkynes (e.g. $CH_3CH_2C{\equiv}CH$) – Red precipitate of copper (I) acetylides.*

$$2CH_3CH_2C{\equiv}CH + Cu_2Cl_2(aq) + 2NH_3(aq) \longrightarrow 2CH_3CH_2C{\equiv}CCu(s) + 2NH_4Cl(aq)$$
$$\text{Copper (I) butylide}$$

- *Non-terminal alkynes (e.g. $CH_3C{\equiv}CCH_3$) - No observable change.*

Note: Ethyne shows similar observations as terminal alkynes.
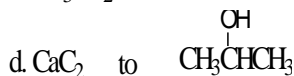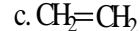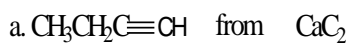
- With *ammoniacal silver nitrate solution (Tollen's reagent), ethyne gives a white precipitate of silver acetylide (silver dicarbide).*

$$HC{\equiv}CH + 2AgNO_3(aq) + 2NH_3(aq) \longrightarrow AgC{\equiv}CAg(s) + 2NH_4NO_3(aq)$$
$$\text{Silver dicarbide}$$
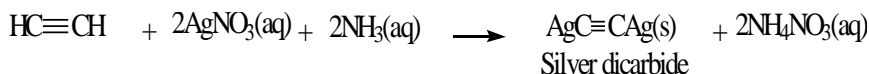
- *With ammoniacal copper (I) chloride solution, ethyne gives a red precipitate of copper (I) dicarbide.*

$$HC{\equiv}CH + Cu_2Cl_2(aq) + 2NH_3(aq) \longrightarrow CuC{\equiv}CCu(s) + 2NH_4Cl(aq)$$
$$\text{Copper(I)dicarbide}$$
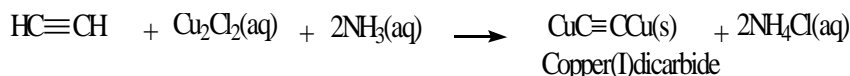
EER: Show how the following syntheses can be effected.

a. $CH_3CH_2C{\equiv}CH$ from CaC_2 b. $CH_3C{\equiv}CH$ from $CH_3CH_2CH_2OH$ c. $CH_2{=}CH_2$ to [benzene ring]

d. CaC_2 to $CH_3\overset{\underset{\displaystyle |}{OH}}{C}HCH_3$

4.8. Uses of alkynes.

Ethyne is used in oxyacetylene welding due to high temperatures produced when ethyne is bunt in oxygen.

Ethyne is used to make benzene which is needed in manufacture of plastics.

CHAPTER 5: HALOGEN ALKANES.

These are saturated organic compounds that conform to the general formular $C_nH_{2n+1}X$ where n is 1, 2, 3… and X is Cl, Br or I.

The functional group is –X.

5.1: **Classes of Halogen Alkanes.**

There are 3 classes of halogen alkanes namely; primary (1°), secondary (2°) and tertiary (3°) halogen alkanes.
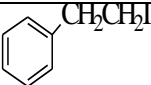
✓ **Primary halogen alkanes:** These have one alkyl/aryl group attached to the carbon atom that has the halogen atom. i.e. $R-CH_2-X$.

✓ **Secondary halogen alkanes:** These have two alkyl/aryl groups attached to the carbon atom that has the halogen atom. i.e. $R-\underset{R}{\overset{}{C}}H-X$.

✓ **Tertiary halogen alkanes:** These have three alkyl/aryl groups attached to the carbon atom that has the halogen atom. i.e. $R-\underset{R}{\overset{R}{C}}-X$.

5.2: Nomenclature of Halogen Alkanes.

1. They are named as halogen-alkane, where the longest continuous chain is taken as the parent chain. E.g. CH_3Cl Chloromethane, CH_3CH_2Br Bromoethane, C_6H_5I Iodobenzene.

2. The carbon atom with the halogen atom is given the smallest number when numbering. E.g. $CH_3CH_2CH_2CH_2Br$ 1-bromobutane, $CH_3\overset{Br}{\overset{|}{C}}HCH2CH_2CH_3$ 2-bromopentane etc.

3. The alkyl/aryl groups present are identified by nature and position. If they are more than one and similar, prefixes di-, tri-, tetra- etc. are used. If they are more than one and different, alphabetical order is followed.

CH₃ CH₃CHCH₂Br	1-bromo-2-methylpropane.	CH₂CH₃ CH₃CHCH₂CHCH₂CH₂Cl CH₃	1-chloro-3-ethyl-5-methylhexane.
CH₃ CH₃CCH₂Br CH₃	1-bromo-2,2-dimethylpropane.	CH₂CH₂I ⬡	1-iodo-2-phenylethane.

5.3: Isomerism in Halogen Alkanes.

Halogen alkanes exhibit chain and position isomerism.

Example.

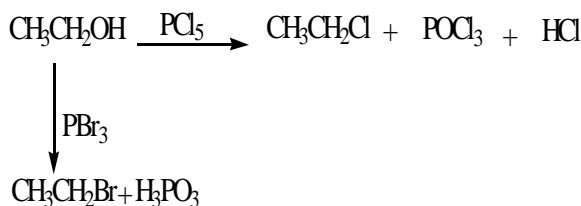Write the structural formulae and IUPAC names of all the possible isomers that conform to $C_5H_{11}Br$.

CH₃CH₂CH₂CH₂CH₂Br	1-bromopentane.	Br CH₃CH₂CH₂CHCH₃	2-bromopentane.
CH₃ CH₃CH₂CH₂CHBr	1-bromo-1-methylbutane.	Br CH₃CH₂CHCH₂CH₃	3-bromopentane.
CH₃ CH₃CH₂CHCH₂Br	1-bromo-2-methylbutane.	Br CH₃CH₂CCH₃ CH₃	2-bromo-2-methylbutane.
CH₃ CH₃CHCH₂CH₂Br	1-bromo-3-methylbutane.	Br CH₃CHCHCH₃ CH₃	2-bromo-3-methylbutane.

Qn. Write the structural formulae and IUPAC names of all the possible isomers that conform to $C_6H_{13}Cl$.
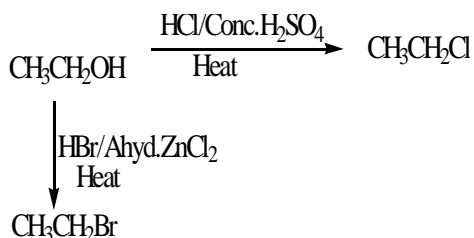
5.4: Synthesis of Halogen Alkanes.

1. **From alcohols.**

a) Reacting an alcohol with halides of phosphorous e.g. PCl_3, PCl_5 and PBr_3. E.g.

$$CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl + POCl_3 + HCl$$

$$\downarrow PBr_3$$

$$CH_3CH_2Br + H_3PO_3$$

b) Heating an alcohol with a halogen acid e.g. HCl in the presence of a dehydrating agent like concentrated sulphuric acid or anhydrous zinc chloride. E.g.
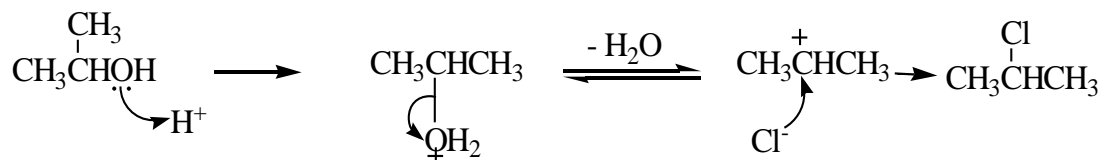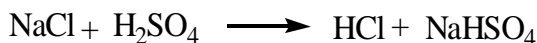
$$CH_3CH_2OH \xrightarrow[\text{Heat}]{HCl/Conc.H_2SO_4} CH_3CH_2Cl$$

$$\downarrow \substack{HBr/Ahyd.ZnCl_2 \\ Heat}$$

$$CH_3CH_2Br$$

c) Heating an alcohol with sulphur dichloride oxide (thionyl chloride, $SOCl_2$). Little pyridine, C_5H_5N is put to absorb the hydrogen chloride. E.g.
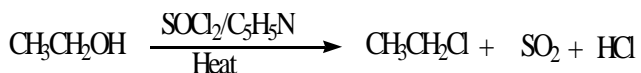
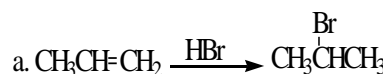$$CH_3CH_2OH \xrightarrow[\text{Heat}]{SOCl_2/C_5H_5N} CH_3CH_2Cl + SO_2 + HCl$$

d) Heating an alcohol with a metal halide e.g. NaCl in the presence of concentrated sulphuric acid or anhydrous zinc chloride. E.g.
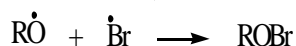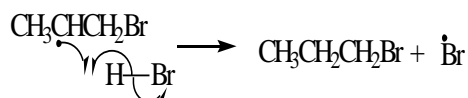
$$\underset{CH_3\overset{\overset{CH_3}{|}}{C}HOH}{} \xrightarrow[\text{Heat}]{NaCl/Conc.H_2SO_4} \underset{CH_3\overset{\overset{CH_3}{|}}{C}HCl}{}$$

Mechanism:

$$NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$$

$$HCl \longrightarrow H^+ + Cl^-$$

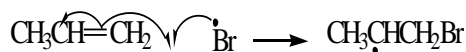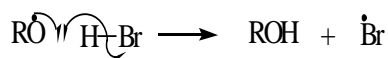$$\overset{\overset{CH_3}{|}}{CH_3CHOH} \longrightarrow CH_3CHCH_3 \xrightarrow{-H_2O} CH_3\overset{+}{C}HCH_3 \longrightarrow \overset{\overset{Cl}{|}}{CH_3CHCH_3}$$

2. By reacting alkenes with halogen acids. E.g.

a. $CH_3CH=CH_2 \xrightarrow{HBr} CH_3\overset{\overset{Br}{|}}{C}HCH_3$

Mechanism.

b. $CH_3CH=CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2-Br$

Mechanism.

$CH_3CH=CH_2 \longrightarrow CH_3\overset{+}{C}HCH_3 + \overset{\cdot}{B}r$

with $H-Br$ below

$CH_3\overset{+}{C}HCH_3 \longrightarrow CH_3\overset{|}{C}HCH_3$ (with Br)

$\overset{\cdot}{B}r$

$RO-OR \longrightarrow 2\overset{\cdot}{O}R$

$R\overset{\cdot}{O} + H-Br \longrightarrow ROH + \overset{\cdot}{B}r$

$CH_3CH=CH_2 + \overset{\cdot}{B}r \longrightarrow CH_3\overset{\cdot}{C}HCH_2Br$

$CH_3\overset{\cdot}{C}HCH_2Br \longrightarrow CH_3CH_2CH_2Br + \overset{\cdot}{B}r$

with $H-Br$

$R\overset{\cdot}{O} + \overset{\cdot}{B}r \longrightarrow ROBr$
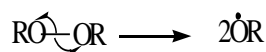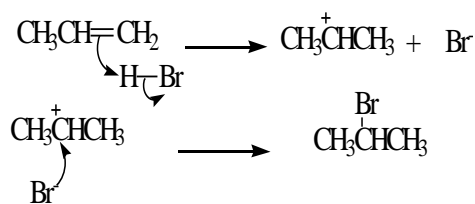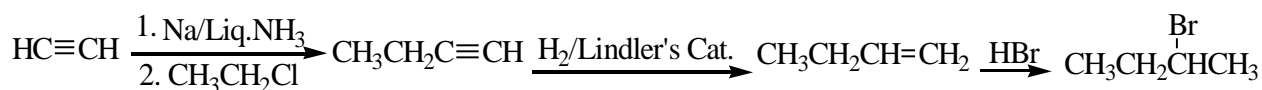
3. By reacting alkanes with chlorine or bromine in presence of ultra-violet light. E.g.

$CH_4 + \text{Limited } Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$

$Cl-Cl \longrightarrow 2\overset{\cdot}{C}l$

$CH_4 + \overset{\cdot}{C}l \longrightarrow \overset{\cdot}{C}H_3 + HCl$

$\overset{\cdot}{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \overset{\cdot}{C}l$

$\overset{\cdot}{C}l + \overset{\cdot}{C}l \longrightarrow HCl$
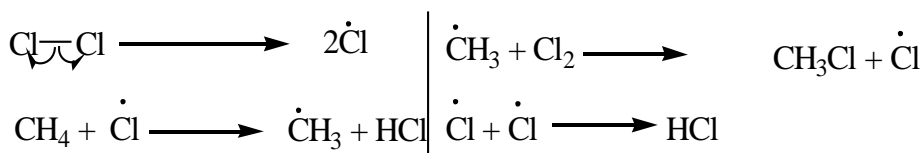
4. Indirect method. E.g. write equation indicating reagents and conditions to show how ethyne can be converted to 2-bromobutane.

$HC\equiv CH \xrightarrow[\text{2. }CH_3CH_2Cl]{\text{1. Na/Liq.NH}_3} CH_3CH_2C\equiv CH \xrightarrow{H_2/\text{Lindler's Cat.}} CH_3CH_2CH=CH_2 \xrightarrow{HBr} CH_3CH_2\overset{Br}{\overset{|}{C}H}CH_3$

EER:

1. Show how the following conversions can be effected.

a) Benzene from calcium dicarbide.

b) Cyclohexanol to chlorobutane.

5.5: Physical Properties of Halogen Alkanes.

Chloromethane, Chloroethane bromomethane are colourless gases at RT. The other lower members are colourless liquids with a sweet smell. Iodides have a higher bp than bromides, which, in turn, boil at higher temperatures than chlorides. [Why?].

They are less dense than water, but the bromides and iodides are denser.

They have higher bp than the corresponding alkanes (*Why? Increased magnitude of van der Waals forces due to increased molecular masses*), though lower than the
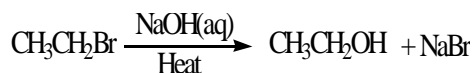
corresponding alcohols. (*Why? Alcohols exhibit hydrogen bonding that are stronger than van der Waals forces*).

5.6: Reactions of Halogen Alkanes.

1. Substitution Reactions.

a) Halogen alkanes react with hot aqueous NaOH or KOH to form alcohols.

Example 1.

$$CH_3CH_2Br \xrightarrow[\text{Heat}]{\text{NaOH(aq)}} CH_3CH_2OH + NaBr$$
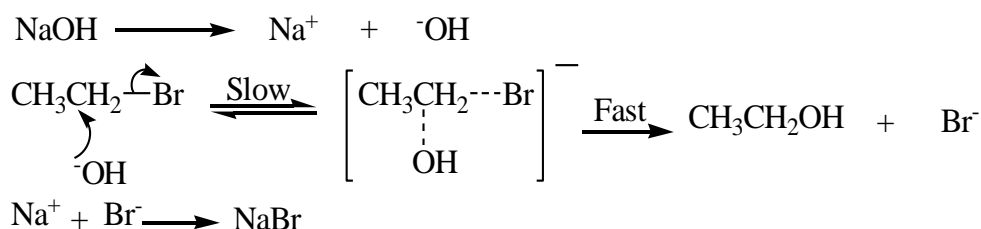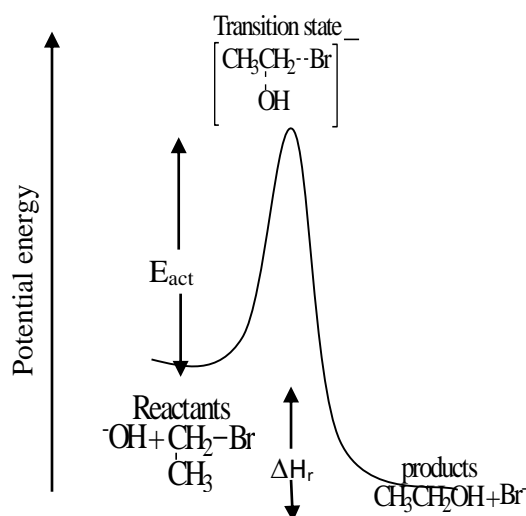
Mechanism:

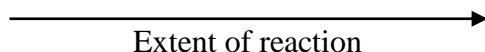$1°$ halogen alkanes undergo S_N2 mechanism.

S_N2 mechanism is Nucleophilic substitution bimolecular mechanism. Here, two species take place in the rate determining step (slow step) to form an unstable intermediate that then breaks down fast to form the products.
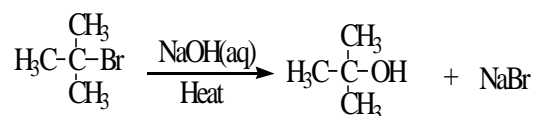
$$NaOH \longrightarrow Na^+ + {}^-OH$$

$$CH_3CH_2-Br \xrightarrow[]{\text{Slow}} \left[\begin{array}{c} CH_3CH_2{\cdots}Br \\ \vdots \\ OH \end{array} \right]^- \xrightarrow{\text{Fast}} CH_3CH_2OH + Br^-$$
$$^-OH$$

$$Na^+ + Br^- \longrightarrow NaBr$$

Potential energy diagram for S_N2 mechanism.

At first, more energy is needed to break the C-Br bond than is supplied by formation of the new C-O bond, so the energy increases. A peak is reached, corresponding to the situation in which the C-Br bond is 'half-broken' and the C-O bond is 'half-formed'; the system is described as being at its **transition state**. The energy then decreases, corresponding to the completion of the formation of the C-O bond. The energy difference between the reactants and the transition state is the **activation energy (E_{act}).** The energy difference between the reactants and the products is the **energy of reaction (ΔH_r).**

Example 2.

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow[\text{Heat}]{\text{NaOH(aq)}} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \quad + \quad NaBr$$
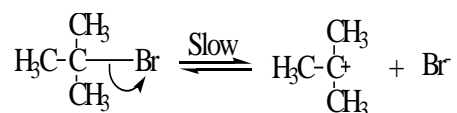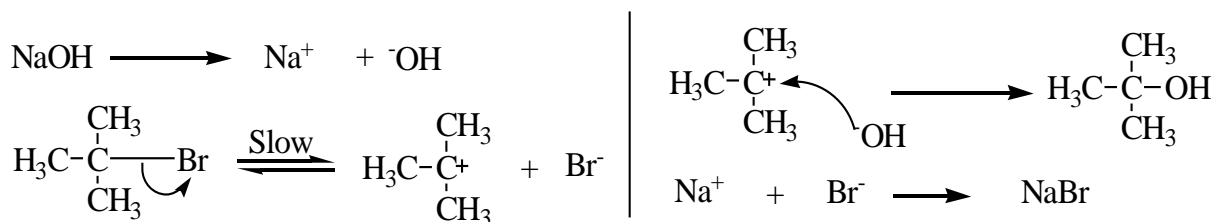
Mechanism:

3° halogen alkanes undergo S_N1 mechanism.

S_N1 mechanism is Nucleophilic Substitution unimolecular mechanism. Here, one species take place in the rate determining step (slow step) to form an unstable intermediate.
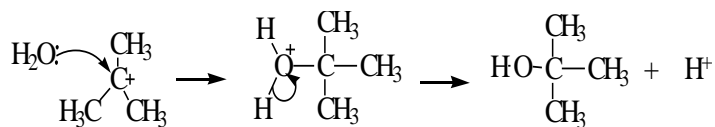
The 3° halogen alkanes spontaneously ionize in solution, forming a carbonium ion and a halide ion, for example:
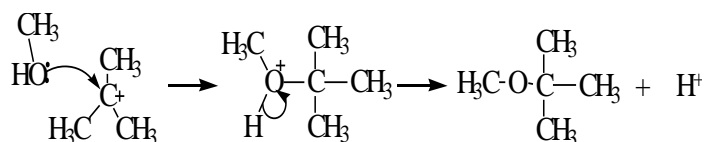
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \overset{\text{Slow}}{\rightleftharpoons} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}^{+} \quad + \quad Br^-$$

The carbonium ion is very reactive and is attacked by other nucleophiles which may be present.

$$NaOH \longrightarrow Na^+ \quad + \quad {}^-OH$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \overset{\text{Slow}}{\rightleftharpoons} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}^{+} \quad + \quad Br^-$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}^{+} \xleftarrow{\quad} \quad \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$
$$\quad \quad \quad OH$$
$$Na^+ \quad + \quad Br^- \longrightarrow NaBr$$

i. For example, if water is the solvent, water itself acts as the nucleophile and an alcohol is formed.

$$H_2O: \quad \underset{H_3C}{\overset{CH_3}{\diagdown}}C^+ \longrightarrow \quad \underset{H}{\overset{H}{\underset{|}{\overset{|}{O}}}}^+-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + H^+$$

ii. If alcohol is the solvent, alcohol itself acts as the nucleophile and an ether is formed.

$$\underset{H_3C}{\overset{CH_3}{\underset{|}{HO}}} \quad \underset{H_3C}{\overset{CH_3}{\diagdown}}C^+ \longrightarrow \quad \underset{H}{\overset{H_3C}{\underset{|}{\overset{|}{O}}}}^+-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow H_3C-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + H^+$$

Potential energy diagram for S_N1 mechanism.
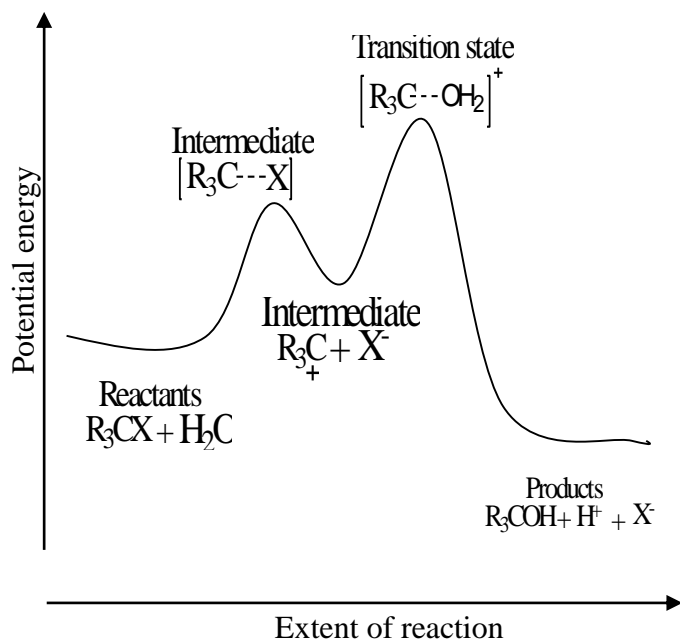
The slow step is the breaking of the C-Br bond to form the carbonium ion. This can then revert to the reactants by recombining with the bromide ion, or give products by reacting with a nucleophile like water. Both these steps are fast, and although the recombination with the bromide ion has the lower activation energy, most of the carbonium ions react with water because it is in far higher concentration than the bromide ions. The overall reaction is described as **unimolecular** because only one molecule is involved in the transition state of the slow step.

b) Reaction of Halogen alkanes with ammonia.

Halogen alkanes react on heating with concentrated ammonia to form a mixture of amines. E.g.

$$CH_3CH_2-I \xrightarrow[100°C]{Conc.NH_3} CH_3CH_2NH_2 + HI$$
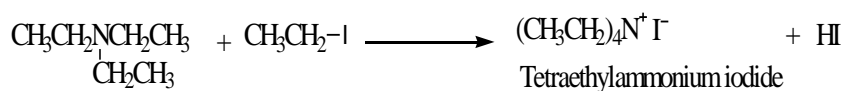$$\text{Ethylamine}$$
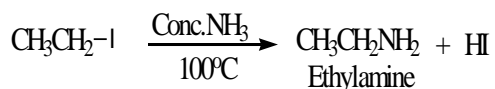
In presence of more halogen alkane, the formed 1° amine (Ethylamine) acts as a nucleophile and reacts with halogen alkane to form a 2° amine (Diethylamine).
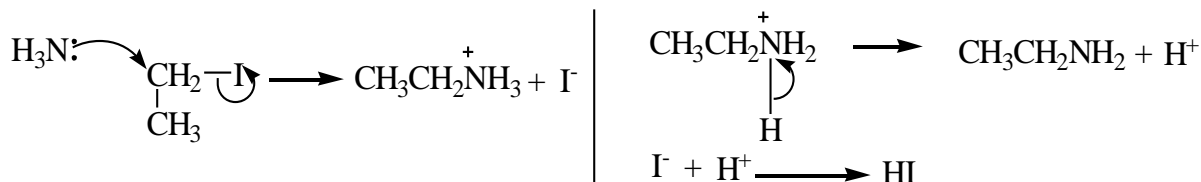
$$CH_3CH_2NH_2 + CH_3CH_2-I \longrightarrow CH_3CH_2NHCH_2CH_3 + HI$$
$$\text{Diethylamine}$$
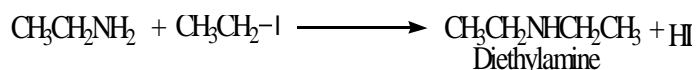
In presence of more halogen alkane, the formed 2° amine (Diethylamine) acts as a nucleophile and reacts with halogen alkane to form a 3° amine (Triethylamine).

$$CH_3CH_2NHCH_2CH_3 + CH_3CH_2-I \longrightarrow (CH_3CH_2)_3N + HI$$
$$\text{Triethylamine}$$
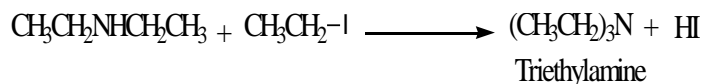
In presence of more halogen alkane, the formed 3° amine (Triethylamine) acts as a nucleophile and reacts with halogen alkane to form a 4° amine (Tetraethylamine ammonium iodide).
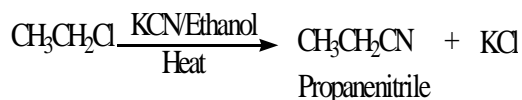
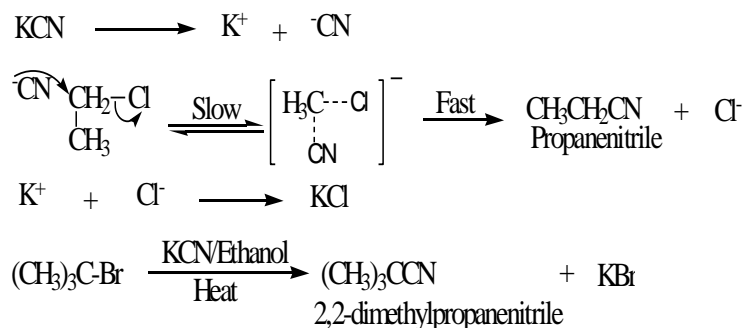$CH_3CH_2NCH_2CH_3$ + CH_3CH_2-I $\longrightarrow$ $(CH_3CH_2)_4N^+I^-$ + HI
$\overset{|}{C}H_2CH_3$ Tetraethylammonium iodide

Mechanism:

$H_3N:$

CH_2-I $\longrightarrow$ $CH_3CH_2\overset{+}{N}H_3$ + I^- $CH_3CH_2\overset{+}{N}H_2$ $\longrightarrow$ $CH_3CH_2NH_2$ + H^+
$\overset{|}{C}H_3$

                                                           H

                                        I^- + H^+ $\longrightarrow$ HI

c) Reaction of Halogen alkanes with potassium cyanide.

By refluxing a solution of the halogen alkane and potassium cyanide in ethanol, nitriles are formed. E.g.

CH_3CH_2Cl $\xrightarrow[\text{Heat}]{\text{KCN/Ethanol}}$ CH_3CH_2CN + KCl
                                       Propanenitrile

Mechanism:

KCN $\longrightarrow$ K^+ + ^-CN

CN CH_2-Cl $\underset{}{\overset{\text{Slow}}{\rightleftharpoons}}$ $\left[H_3C\text{---}Cl \right]^-$ $\xrightarrow{\text{Fast}}$ CH_3CH_2CN + Cl^-
   $\overset{|}{C}H_3$ $\overset{|}{C}N$ Propanenitrile

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

$(CH_3)_3C-Br$ $\xrightarrow[\text{Heat}]{\text{KCN/Ethanol}}$ $(CH_3)_3CCN$ + KBr
                               2,2-dimethylpropanenitrile
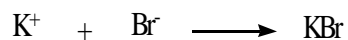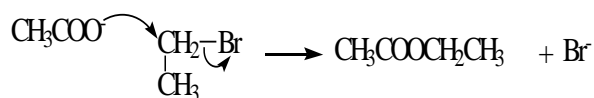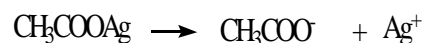
Mechanism:

(Follow S_N1 mechanism).

d) Reaction with a silver salt of organic acid.

Halogen alkanes with a silver salt of organic acid (e.g. silver ethanoate) on heating to form esters.
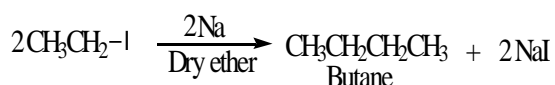
Example:

CH_3CH_2-Br + CH_3COOAg $\xrightarrow{\text{Heat}}$ $CH_3COOCH_2CH_3$ + AgBr
                Silver ethanoate   ethylethanoate   pale yellow ppt

Mechanism:

$$CH_3COOAg \longrightarrow CH_3COO^- + Ag^+$$

$$CH_3COO^- \overset{\frown}{} CH_2\!-\!Br \longrightarrow CH_3COOCH_2CH_3 + Br^-$$
$$\underset{CH_3}{\big|}$$

$$K^+ + Br^- \longrightarrow KBr$$
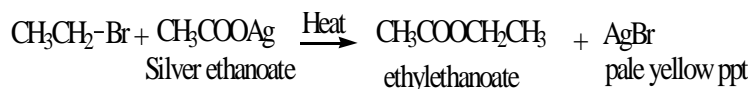
2. Reaction of halogen alkanes with metals.

a) Halogen alkanes react with sodium in dry ether in a **Wurtz** reaction to give alkanes. E.g.

$$2CH_3CH_2\!-\!I \xrightarrow[Dry\ ether]{2Na} \underset{Butane}{CH_3CH_2CH_2CH_3} + 2NaI$$

Note: *The **Wurtz** reaction doubles the carbon chain and therefore useful in synthesis of even numbered alkanes.*

b) Halogen alkanes react with magnesium in dry ether, to form **Grignard's reagents** (alkylmagnesium halides). E.g.

$$CH_3CH_2\!-\!I \xrightarrow[Dry\ ether]{Mg} \underset{Ethylmagnesium\ iodide}{CH_3CH_2MgI} + MgI_2$$

3. Elimination reaction.

Reaction with hot alcoholic potassium or sodium hydroxide solution.

a) 1° halogen alkanes like chloropropane react in an S_N2 reaction to form ethers. E.g.

$$CH_3CH_2CH_2Cl \xrightarrow[Heat]{KOH/CH_3CH_2OH} CH_3CH_2OCH_2CH_3 + KCl$$

Mechanism.

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

$$CH_3CH_2OK \longrightarrow CH_3CH_2\bar{O} + K^+$$

$$CH_3CH_2\!-\!Cl$$
$$CH_3CH_2\bar{O} \longrightarrow CH_3CH_2OCH_2CH_3 + \bar{Cl}$$

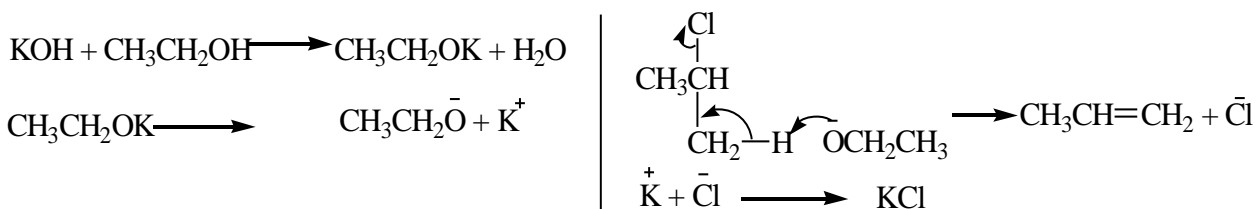$$\overset{+}{K} + \bar{Cl} \longrightarrow KCl$$
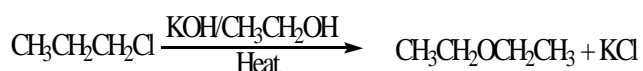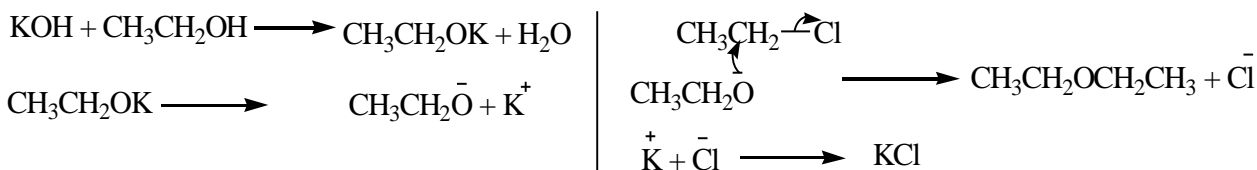
3° halogen alkanes and to some extent 2° halogen alkanes undergo elimination, though the 2° halogen alkanes are intermediate between E1 and E2 mechanism.
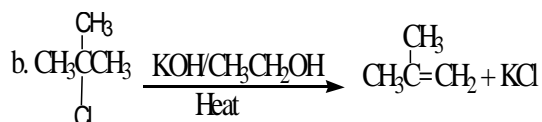
b) 2° halogen alkanes like 2-chloropropane react in an E2 (Elimination Bimolecular: because two molecules are involved in the formation of the transition state) reaction to form alkenes. E.g.
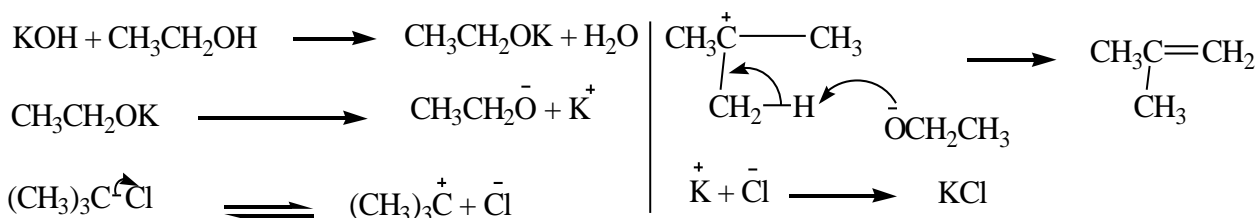
$$CH_3\overset{|}{\underset{Cl}{C}}HCH_3 \xrightarrow[\text{Heat}]{KOH/CH_3CH_2OH} CH_3CH=CH_2 + KCl$$

Mechanism.

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

$$CH_3CH_2OK \longrightarrow CH_3CH_2\bar{O} + K^+$$
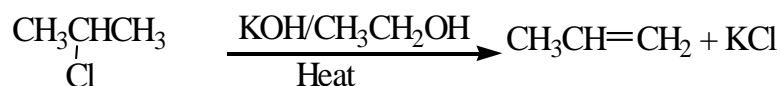
c) 3° halogen alkanes like 2-chloro-2-methylpropane react in an E1 (Elimination Unimolecular: because one molecule is involved in the formation of the transition state) reaction to form alkenes. E.g.

$$b.\ CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}CH_3 \xrightarrow[\text{Heat}]{KOH/CH_3CH_2OH} CH_3\overset{CH_3}{\underset{}{C}}=CH_2 + KCl$$

Mechanism.

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

$$CH_3CH_2OK \longrightarrow CH_3CH_2\bar{O} + K^+$$

$$(CH_3)_3C\!-\!Cl \rightleftharpoons (CH_3)_3\overset{+}{C} + \bar{C}l$$

5.7. Differentiating reactivity of alkyl and aromatic halogen alkanes.

Reagent:

Hot sodium hydroxide solution followed by dilute nitric acid followed by silver nitrate solution.

- Hot sodium hydroxide serves to substitute the halide ion (e.g. chloride, bromide or iodide ion), thereby releasing the halide ion in solution.

- Dilute nitric acid is added to prevent precipitation of other insoluble salts of silver such as silver carbonate, silver hydroxide etc.by reacting with any anion besides the halide ion.

- Silver nitrate solution serves the silver ions that react with any halide ions to precipitate the insoluble silver halide salt.

Observation:

- Chloroalkanes: white precipitate of silver chloride. The precipitate is soluble in excess ammonia solution. E.g.

$$CH_3CH_2Cl + NaOH(aq) + AgNO_3(aq) \longrightarrow CH_3CH_2OH + NaNO_3(aq) + \underset{\text{white ppt}}{AgCl(s)}$$
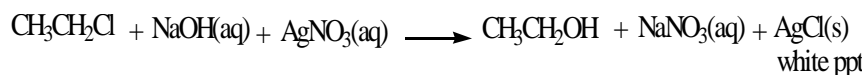
- Bromoalkanes: pale yellow precipitate of silver bromide. The precipitate is insoluble in ammonia solution. E.g.

$$CH_3CH_2Br + NaOH(aq) + AgNO_3(aq) \longrightarrow CH_3CH_2OH + NaNO_3(aq) + \underset{\text{pale yellow ppt}}{AgBr(s)}$$
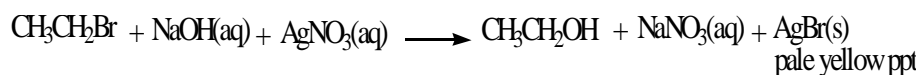
- Iodoalkanes: yellow precipitate if silver iodide. The precipitate is insoluble in ammonia solution. E.g.

$$CH_3CH_2I + NaOH(aq) + AgNO_3(aq) \longrightarrow CH_3CH_2OH + NaNO_3(aq) + \underset{\text{yellow ppt}}{AgI(s)}$$

- Aromatic halogen alkanes with the halogen atom directly attached on the ring: No observable change (**Why?**)

    Ans: The lone pair of electrons on the halide atom gets involved in delocalization with the pi electrons of the benzene ring. This makes the C-X bond strong and much hard to substitute with the hydroxide ion. The alkyl groups have a positive inductive effect. This increases the electron density around the C-X bond making it weak and easy to substitute with the hydroxide ion.

Question:

1. For the compounds:
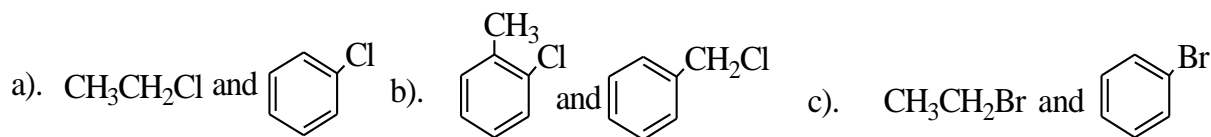
a). CH_3CH_2Cl and b). and c). CH_3CH_2Br and

  i.   Name one reagent that can be used to distinguish between the two compounds.

ii.   State what is observed in each case when each compound is treated with the named reagent.

iii.   Write equation for the reaction if any. Explain your observations in each case.

5.8. Uses of halogen alkanes.

Halogen alkanes are of great value in organic synthesis because of the compounds which can be made from them by nucleophilic substitution and via Grignard's reagents.

CHAPTER 6: ALCOHOLS.

These are organic compounds that conform to the general formular $C_nH_{2n+1}OH$ where n is 1, 2, 3…. The functional group is the hydroxyl group (-OH).

6.1: Classes of Alcohols.

There are 3 classes of alcohols namely; primary (1°), secondary (2°) and tertiary (3°) alcohols.

✓ **Primary alcohols:** These have one alkyl/aryl group attached to the carbon atom that has the hydroxyl group. i.e. $R-CH_2OH$.

✓ **Secondary alcohols:** These have two alkyl/aryl groups attached to the carbon atom that has the hydroxyl group. i.e. $\underset{R}{R-CH-OH}$.

✓ **Tertiary alcohols:** These have three alkyl/aryl groups attached to the carbon atom that has the hydroxyl group. i.e.

$$R-\underset{R}{\overset{R}{C}}-OH$$.
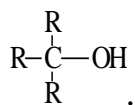
6.2: Nomenclature of Alcohols.

e) The ending **"e"** in alkanes is replaced with **"ol"** in the corresponding alcohols. E.g.

Alkane	Alcohol
Ethane	Ethanol
Methane	Methanol

f) The position of the functional group is identified by numbering the chain in such that the carbon atom with the double bond is given the smallest number. E.g.

$CH_3CH_2CH_2OH$	Propan-1-ol	$CH_3CH_2CH_2CH_2OH$	Butan-1-ol
OH CH_3CHCH_3	Propan-2-ol	OH $CH_3CHCH_2CH_3$	Butan-2-ol

g) Alkyl/aryl or any other group on the ring are identified the same way as in alkanes. E.g.

CH₃
CH_3CHCH_2OH 2-methylpropan-1-ol
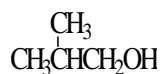
−CH_2OH Phenyl methanol
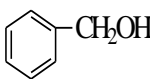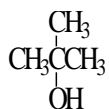
CH₃
CH_3CCH_3
OH   2-methylpropan-2-ol

h) Cyclic alcohols are named with a prefix "cyclo" before the parent chain. E.g.

−OH   Cyclopropanol
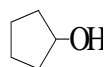
−OH   Cyclopentanol
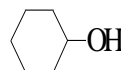
−OH   Cyclohexanol

6.3: Isomerism in alcohols.

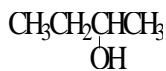Alcohols exhibit chain, position and functional group isomerism.

Example. Write the structural formulae and IUPAC names of all the possible isomers that conform to C_4H_9OH.

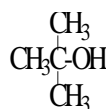$CH_3CH_2CH_2CH_2OH$ Butan-1-ol
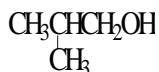
CH_3CH_2CHOH
CH₃   1-methylpropan-1-ol

$CH_3CH_2CHCH_3$
OH   Butan-2-ol

CH₃
CH_3C-OH
CH₃   2-methylpropan-2-ol

CH_3CHCH_2OH
CH₃   2-methylpropan-1-ol
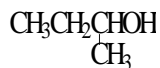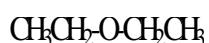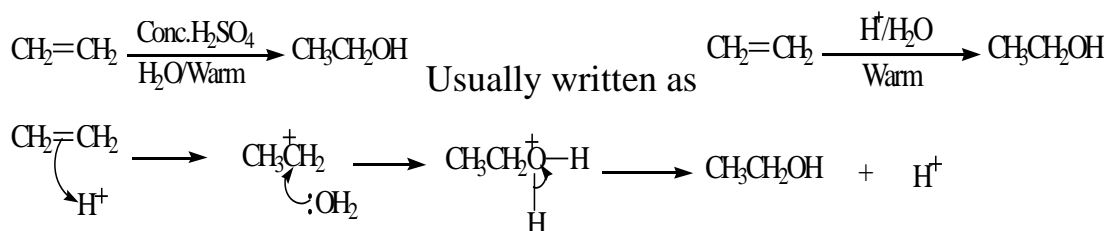
$CH_3CH_2-O-CH_2CH_3$ Diethylether

Qn. Write the structural formulae and IUPAC names of all the possible isomers that conform to $C_5H_{11}OH$.
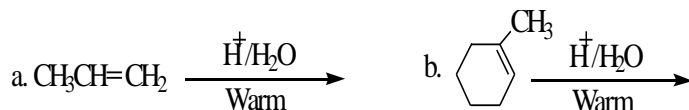
6.4: Physical Properties of Alcohols.

- Lower members are liquids, higher members in solids with a characteristic alcoholic smell.

- Higher boiling point than alkanes and halogen alkanes of similar molecular masses. Because alcohols possess hydrogen bonds in their molecules, that require more energy to break.

- Soluble in water though solubility increases with increase in molecular mass. Because alcohols possess hydrogen bonds in their molecules and water molecules.

6.5: Synthesis of alcohols.

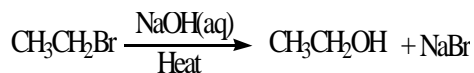1. Warming of alkenes with concentrated sulphuric acid in presence of water. E.g.

$$CH_2=CH_2 \xrightarrow[H_2O/Warm]{Conc.H_2SO_4} CH_3CH_2OH \qquad \text{Usually written as} \qquad CH_2=CH_2 \xrightarrow[Warm]{H^+/H_2O} CH_3CH_2OH$$

$$CH_2=CH_2 \xrightarrow{H^+} CH_3\overset{+}{C}H_2 \xrightarrow{:OH_2} CH_3CH_2\overset{+}{O}-H \xrightarrow{} CH_3CH_2OH + H^+$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H$$

Qn. Complete the following and write mechanism.

a. $CH_3CH=CH_2 \xrightarrow[Warm]{H^+/H_2O}$

b. (cyclohexene with CH_3) $\xrightarrow[Warm]{H^+/H_2O}$
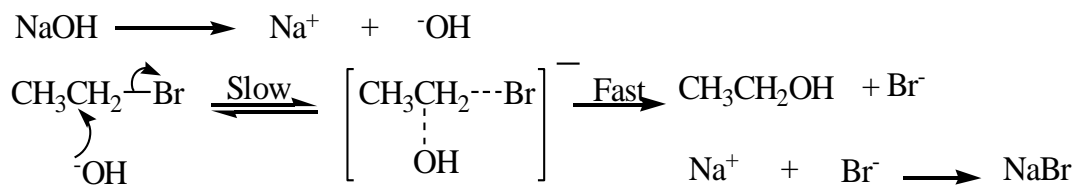
2. Reacting halogen alkanes with hot sodium/potassium hydroxide solution. E.g.

Example 1.
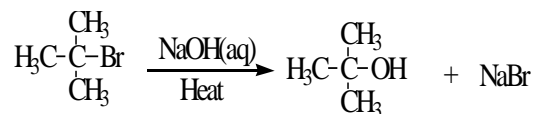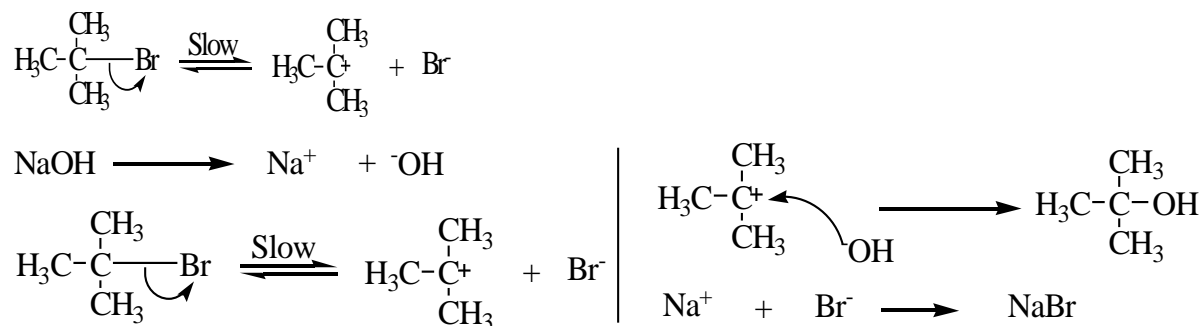
$$CH_3CH_2Br \xrightarrow[Heat]{NaOH(aq)} CH_3CH_2OH + NaBr$$

Mechanism:

$$NaOH \longrightarrow Na^+ + {}^-OH$$

$$CH_3CH_2\text{—}Br \xrightarrow{\text{Slow}} \left[CH_3CH_2\text{---}Br \atop \overset{|}{OH} \right]^- \xrightarrow{\text{Fast}} CH_3CH_2OH + Br^-$$

${}^-OH$

$$Na^+ + Br^- \longrightarrow NaBr$$

Example 2.

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Br \xrightarrow[\text{Heat}]{NaOH(aq)} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH + NaBr$$

Mechanism:

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}Br \xrightarrow{\text{Slow}} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{}^+ + Br^-$$

$$NaOH \longrightarrow Na^+ + {}^-OH$$

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}Br \xrightarrow{\text{Slow}} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{}^+ + Br^-$$

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{}^+ \quad {}^-OH \longrightarrow H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$$

$$Na^+ + Br^- \longrightarrow NaBr$$
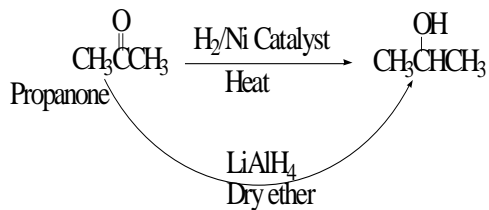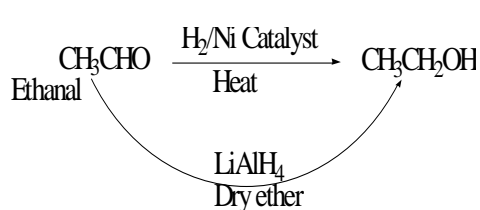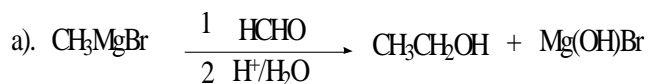
3. Reduction of carboxylic acids with lithium tetrahydridoaluminate in dry ether gives a primary alcohol. E.g.

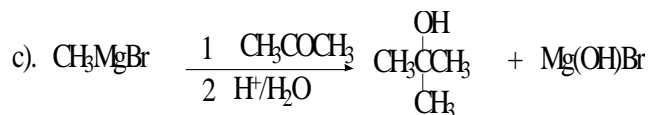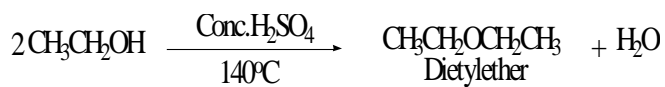$$CH_3COOH \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2OH$$
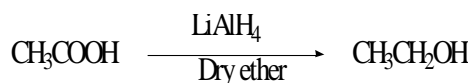
4. Reduction of carbonyl compounds acids with hydrogen gas over heated nickel catalyst or with lithium tetrahydridoaluminate in dry ether gives a primary alcohol. E.g.

$$CH_3CHO \xrightarrow[\text{Heat}]{H_2/Ni\ Catalyst} CH_3CH_2OH$$
Ethanal

$$\xrightarrow[\text{Dry ether}]{LiAlH_4}$$

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \xrightarrow[\text{Heat}]{H_2/Ni\ Catalyst} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$$
Propanone

$$\xrightarrow[\text{Dry ether}]{LiAlH_4}$$

5. By reacting a Grignard's reagent with aldehyde or ketone, followed by acid hydrolysis. E.g.

a). $CH_3MgBr \xrightarrow[\text{2 } H^+/H_2O]{\text{1 } HCHO} CH_3CH_2OH + Mg(OH)Br$

b). $CH_3MgBr \xrightarrow[\text{2 } H^+/H_2O]{\text{1 } CH_3CHO}$ $CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$ + $Mg(OH)Br$

c). $CH_3MgBr \xrightarrow[\text{2 } H^+/H_2O]{\text{1 } CH_3COCH_3}$ $CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$ + $Mg(OH)Br$

6.6: Reactions of Alcohols.

1. Reaction of alcohols with sulphuric acid.

a. At 170-180°C, alcohols are dehydrated by concentrated sulphuric acid to form alkenes. E.g.

i. $CH_3CH_2CH_2OH \xrightarrow[\text{170-180°C}]{\text{Conc.}H_2SO_4}$ $CH_3CH=CH_2$ + H_2C

Mechanism.

ii. $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{180°C}]{\text{Conc.}H_2SO_4}$ $CH_3CH=CHCH_3$ + H_2O

Mechanism. (Hydride shift, stability of carbocation is $3^o >> 2^o > 1^0$).

iii. $(CH_3)_2CHCH_2OH \xrightarrow[\text{180°C}]{\text{Conc.}H_2SO_4}$ $CH_3CH=CHCH_3$ + H_2O

Mechanism. (Methyl shift, stability of carbocation is $3^o >> 2^o > 1^0$).

b. At 140°C, alcohols are dehydrated by concentrated sulphuric acid to form ethers. E.g.

$$2\,CH_3CH_2OH \xrightarrow[140°C]{Conc.H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$
Dietylether

Mechanism:

c. At 0°C, alcohols are dehydrated by concentrated sulphuric acid to form alkyl hydrogensulphates. E.g.

$$CH_3CH_2OH \xrightarrow[0°C]{Conc.H_2SO_4} CH_3CH_2OSO_3H + H_2O$$
Ethyl hydrogensulphate
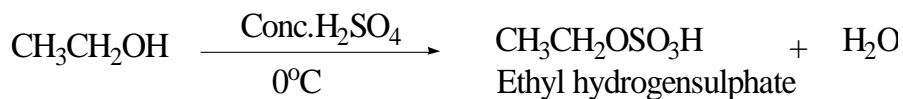
Mechanism:
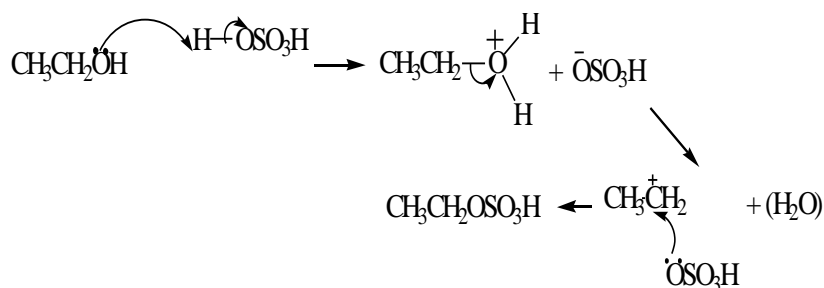
2. Oxidation of alcohols.

Primary alcohols are oxidized in a two stage to carboxylic acids and $2°$ to ketones respectively by strong oxidizing agents like acidified potassium/sodium dichromate (VI) solution or acidified potassium/sodium permanganate solution. E.g.
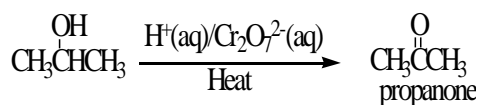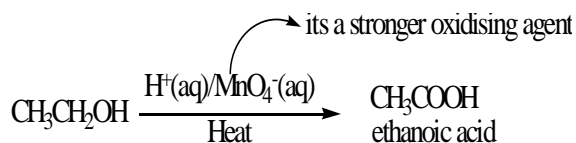
Note: *Tertiary alcohols do not undergo oxidation under similar conditions.*

3. Esterification.

a. Alcohols react with organic acids in presence of concentrated sulphuric acid to form esters. E.g.

$$CH_3OH + CH_3COOH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOCH_3 + HCl$$
methanol   methyl ethanoate
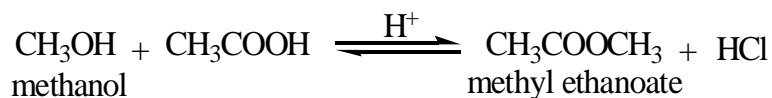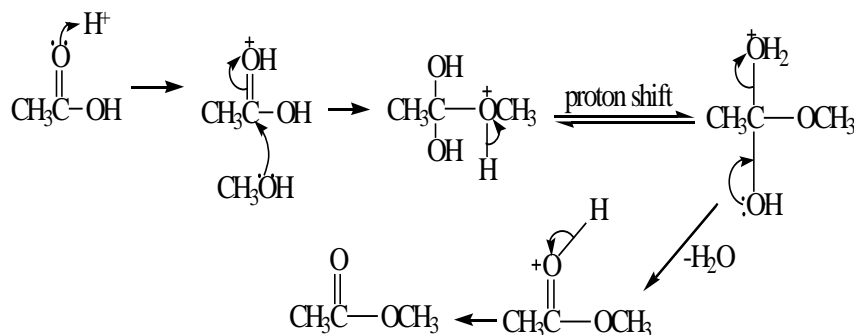
Mechanism:

b. Alcohols react with acid chlorides or acid anhydrides form esters. E.g.

$$CH_3OH + CH_3COCl \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOCH_3 + HCl$$
methanol   ethanoyl   methyl ethanoate
        chloride

Mechanism:

EER.

$$CH_2\text{-}\overset{O}{\overset{||}{C}}\text{-O-}\overset{O}{\overset{||}{C}}\text{-}CH_3 + CH_3OH \longrightarrow \ ?$$
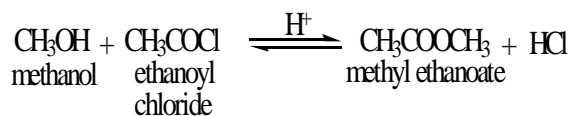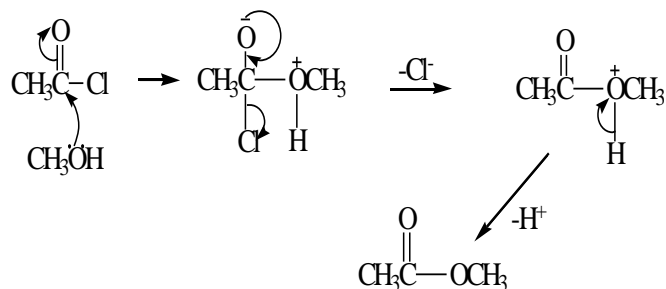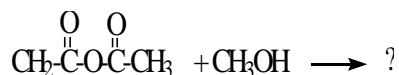
4. Substitution reactions.

These are reactions of the –OH group.

a) Reacting an alcohol with halides of phosphorous e.g. PCl_3, PCl_5 and PBr_3 produces a halogen alkane. E.g.

$$CH_3CH_2OH \xrightarrow{\quad PCl_5 \quad} CH_3CH_2Cl + POCl_3 + HCl$$

$$\downarrow PBr_3$$

$$CH_3CH_2Br + H_3PO_3$$

b) Heating an alcohol with a halogen acid e.g. HCl in the presence of a dehydrating agent like concentrated sulphuric acid or anhydrous zinc chloride produces a halogen alkane. E.g.
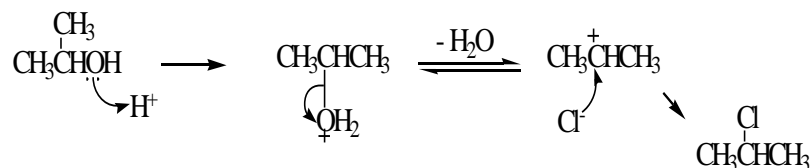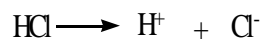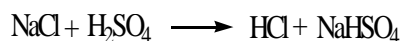
$$CH_3CH_2OH \xrightarrow[\text{Heat}]{\text{HCl/Conc.H}_2\text{SO}_4} CH_3CH_2Cl$$

$$\downarrow \begin{array}{c}\text{HBr/Ahyd.ZnCl}_2\\ \text{Heat}\end{array}$$

$$CH_3CH_2Br$$
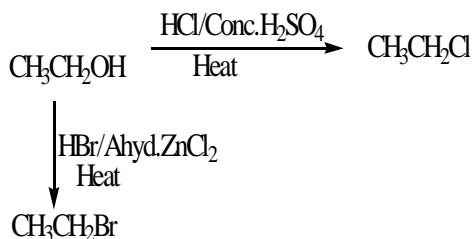
c) Heating an alcohol with sulphur dichloride oxide (thionyl chloride, $SOCl_2$) produces a chloroalkane. Little pyridine, C_5H_5N is put to absorb the hydrogen chloride. E.g.
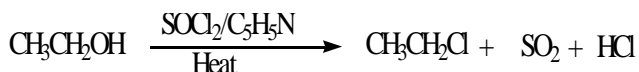
$$CH_3CH_2OH \xrightarrow[\text{Heat}]{\text{SOCl}_2/\text{C}_5\text{H}_5\text{N}} CH_3CH_2Cl + SO_2 + HCl$$

d) Heating an alcohol with a metal halide e.g. NaCl in the presence of concentrated sulphuric acid or anhydrous zinc chloride produces a halogen alkane. E.g.
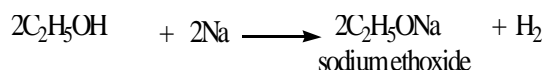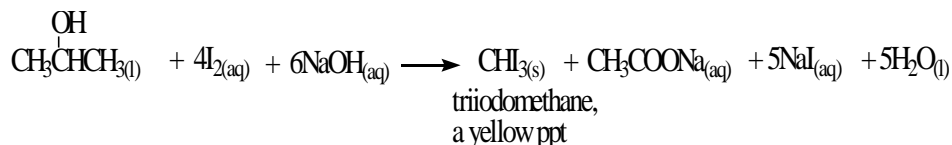
$$\overset{\overset{\displaystyle CH_3}{|}}{CH_3CHOH} \xrightarrow[\text{Heat}]{\text{NaCl/Conc.H}_2\text{SO}_4} \overset{\overset{\displaystyle CH_3}{|}}{CH_3CHCl}$$

Mechanism:

$$NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$$

$$HCl \longrightarrow H^+ + Cl^-$$

$$\overset{\overset{\displaystyle CH_3}{|}}{CH_3CHOH} \longrightarrow CH_3CHCH_3 \underset{}{\overset{-H_2O}{\rightleftharpoons}} CH_3\overset{+}{C}HCH_3 \searrow$$

$$\overset{\displaystyle Cl}{\underset{}{CH_3CHCH_3}}$$

e) Alcohols react with sodium metal to form hydrogen gas and sodium alkoxides. i.e.

$$2C_nH_{2n+1}OH + 2Na \longrightarrow 2C_nH_{2n+1}ONa + H_2$$

e.g.

$$2C_2H_5OH \; + \; 2Na \longrightarrow \underset{\text{sodium ethoxide}}{2C_2H_5ONa} \; + \; H_2$$

f) Iodoform reaction. Ethanol and Methyl alcohols react with iodine solution and sodium hydroxide solution to form a yellow precipitate of triiodomethane. E.g.

$$\underset{\underset{OH}{|}}{CH_3CHCH_{3(l)}} + 4I_{2(aq)} + 6NaOH_{(aq)} \longrightarrow \underset{\substack{\text{triiodomethane,} \\ \text{a yellow ppt}}}{CHI_{3(s)}} + CH_3COONa_{(aq)} + 5NaI_{(aq)} + 5H_2O_{(l)}$$

EER: For the compounds:

a). CH_3CH_2OH and $CH_3CH_2CH_2OH$

b). $\underset{\underset{OH}{|}}{CH_3CHCH_3}$ and $\underset{\underset{OH}{|}}{CH_3CH_2CHCH_2CH_3}$

iv.   Name one reagent that can be used to distinguish between the two compounds.

v.   State what is observed in each case when each compound is treated with the named reagent.

vi.   Write equation for the reaction if any.

vii.   Explain your observations in each case.

6.7.   Differentiating between the 3 classes of alcohols.

Reagent: *anhydrous zinc chloride in concentrated hydrochloric acid (Lucas reagent).*

Observations:

1°. No observable change at room temperature.

2°. A cloudy solution between 5-10 minutes.

3°. immediate cloudy solution.

EER: For the compounds:
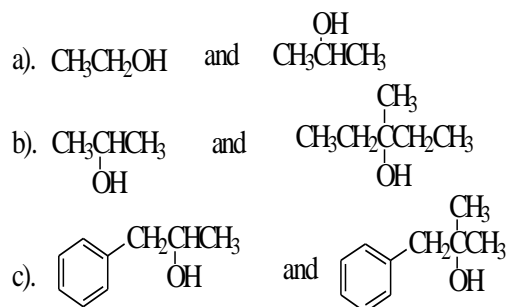
a). CH_3CH_2OH and $CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$

b). $CH_3\overset{\overset{\displaystyle }{}}{C}HCH_3$ and $CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}CH_2CH_3$
   $\quad\quad\;\;|$ $\quad\quad\quad\quad\quad\quad\;\;|$
   $\quad\quad OH$ $\quad\quad\quad\quad\quad\quad OH$

c).

CH_2CHCH_3 and $CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}CH_3$
$\quad\quad|$ $\quad\quad\quad\quad\quad\quad|$
$\quad OH$ $\quad\quad\quad\quad\quad OH$

i. Name one reagent that can be used to distinguish between the two compounds.

ii. State what is observed in each case when each compound is treated with the named reagent.

6.8. Comparison of the reactivity of an aromatic alcohol like phenol and an aliphatic alcohol like ethanol.

The lone pair of electrons on the oxygen atom in phenol participate in delocalization with the pi electrons of the benzene ring. This strengthens the C-O bond and weakens the O-H bond in phenol. This makes phenol partially ionise in water, to form an

acidic solution.

$$\text{(phenol)} + H_2O \rightleftharpoons \text{(phenoxide ion)} + H_3O^+$$
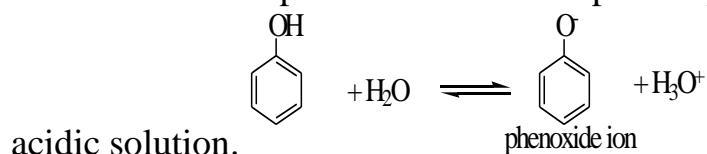
Hence phenol reacts with sodium hydroxide forming sodium phenoxide.

Generally, phenol undergoes substitution reactions like aliphatic alcohols though with less vigour.

Uses of ethanol

a) Used as a disinfectant.
b) Used as a liquid in thermometers.
c) Used as a beverage/drink.
d) Ethanol is used as a solvent for perfumes, vanishes, paints.
e) It is used in manufacture of organic compounds such as ethanoic acid.
f) Ethanol is used as a fuel.
g) Used as an aesthetic.

Assignment:

Identify reagents that can be used to test for the presence of the hydroxyl group in alcohols. For each reagent, state the observations.

CHAPTER 7: AROMATIC COMPOUNDS.

These are compounds that contain at least one benzene ring.
Important members include;

benzene

CH_3

methylbenzene (Toluene)

OH

hydroxybenzene (Phenol)

NO_2

Nitrobenzene

NH_2

Aminobenzene (Aniline)

X

Halobenzene eg chlorobenzene
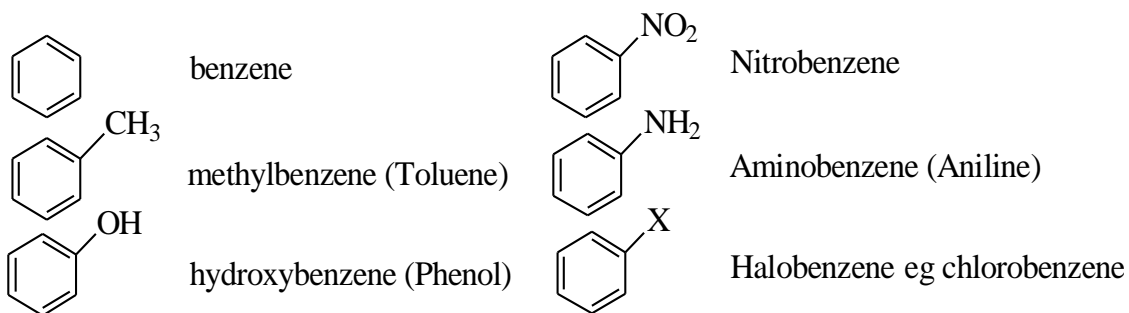
a) Benzene, C₆H₆,

The structure of benzene is thought to be a resonance hybrid of several forms with the most important ones being the Kekule structures.

Kekule structures of benzene.

He suggests that the carbon atoms of benzene are in a 6 membered ring each carbon atom joined to the other by alternating single and double bonds with a hydrogen atom bonded to each carbon.
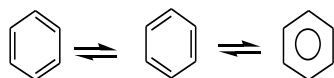
Stability of benzene.

Benzene is more stable than what Kekule structures suggest and doesn't undergo electrophilic addition reactions like alkenes do.

To prove this, thermochemical data is taken.

The heat of hydrogenation of benzene is less than expected if benzene molecule truly contained 3 C-C double bonds depicted by the Kekule structures.

The heat of hydrogenation of cyclohexene to cyclohexane is -120kJmol^{-1}.
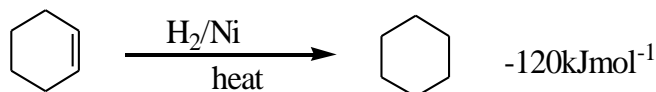
Benzene that is theoretically known to have 3 double bonds would be expected, when hydrogenated to cyclohexane, to give (-120×3kJmol^{-1} = -360kJmol^{-1}) but the experimental value is only +210kJmol^{-1}.
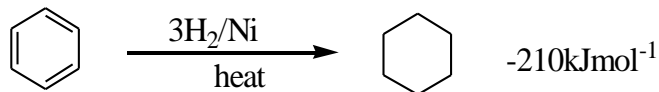
The difference in energies (-360-(-210) = -150kJmol^{-1}) is called the resonance/delocalization energy of benzene.

So, the stability of benzene is due to delocalization of the pi electrons. I.e. the alternation of the single and double bonds. The carbon-carbon bonds in benzene (single and double) have a short, fixed bond length, 139pm. The carbon-carbon single bond in cyclohexene is 154pm long while the double bond id 134pm long.

Question: The heat of hydrogenation of cyclohexene and benzene to cyclohexane are

-120 kJmol^{-1}and -210 kJmol^{-1} respectively. Explain. (3 marks)

Physical properties of benzene.

a) Colourless liquid. Its toxic and long exposure causes anemia and leukemia.

b) Insoluble in water, soluble in organic solvents.

c) Mp is 5-5.7°C and Bp is 80-80.3°C.

d) Density is $0.87gcm^{-3}$.
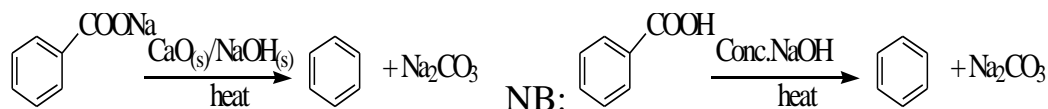
Synthesis of benzene.
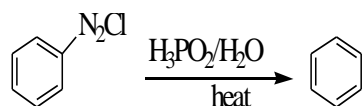
1. Passing phenol vapour over heated zinc dust.
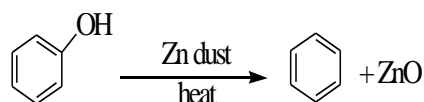
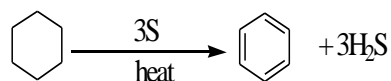2. Passing ethyne over heated iron catalyst or over organo-nickel catalyst heated to 60-70°C.
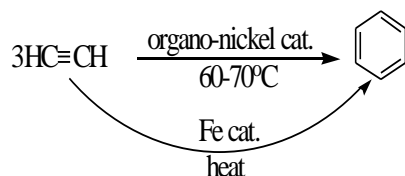
3. Decarboxylation of sodium benzoate by heating it with solid calcium oxide and sodium hydroxide.

4. Hydrolyzing of benzene diazonium chloride with hypophsporous acid and water.

5. Heating cyclohexane with sulphur.
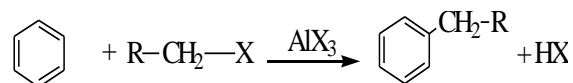

Reactions of benzene.

1. Combustion.

Benzene burns with a yellow, heavily sooty flame to form carbon dioxide and water.

$$2C_6H_{6(l)} + 15O_{2(g)} \longrightarrow 12CO_{2(g)} + 6H_2O_{(l)}$$
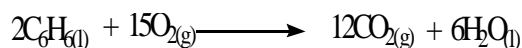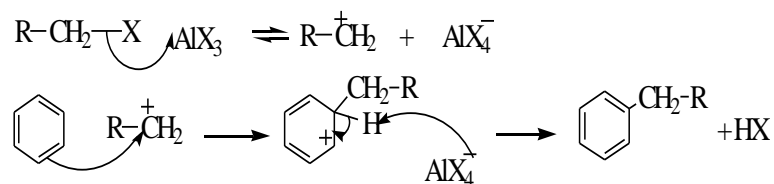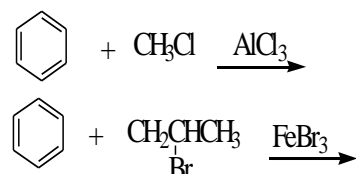
2. Friedel-Crafts alkylation reaction.

Benzene reacts with alkyl halides in the presence of a halogen carrier e.g. $AlCl_3$, $AlBr_3$, $FeBr_3$…etc. to form alkyl benzenes.
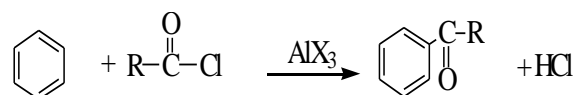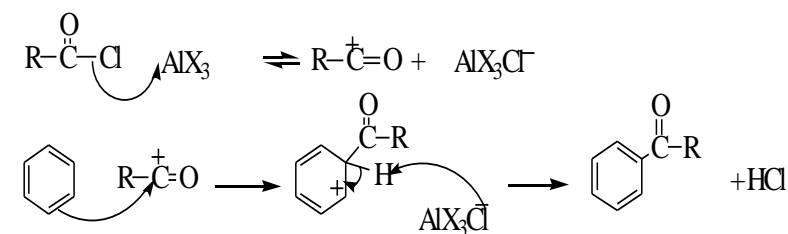

Mechanism.

Examples.

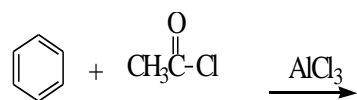

3. Friedel-Crafts acylation reaction.

Benzene reacts with acid chlorides in the presence of a halogen carrier e.g. $AlCl_3$, $AlBr_3$, $FeBr_3$…etc. to form acylated benzenes.
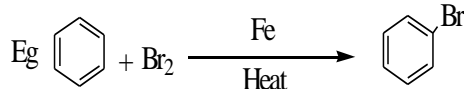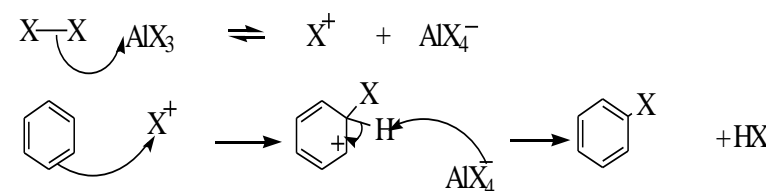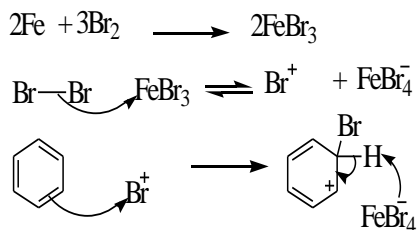

Mechanism

Examples.

4. Halogenation reaction.

Benzene reacts with halogens in the presence of a halogen carrier e.g. $AlCl_3$, $AlBr_3$, $FeBr_3$...etc. to form halogen benzenes.

Mechanism

Eg

Mechanism

$$2Fe + 3Br_2 \longrightarrow 2FeBr_3$$

5. Nitration reaction.

Benzene reacts with a mixture of concentrated nitric acid and concentrated sulphuric acid at 60°C to form nitrobenzene.

The role of sulphuric acid.

1. Concentrated sulphuric acid protonates nitric acid making it easy for the reactive electrophiles (nitronium ions) to be generated.

2. Concentrated sulphuric acid also prevents possible dilution of concentrated nitric acid by removing water produced during the reaction.
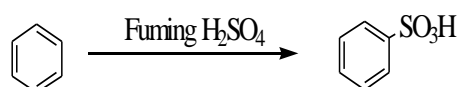
$$HNO_3 + 2H_2SO_4 \rightleftharpoons \overset{+}{N}O_2 + 2HSO_4^- + H_3\overset{+}{O}$$
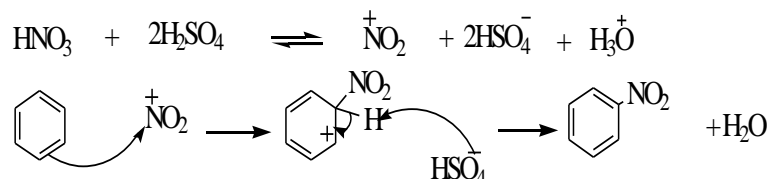
6. Sulphonation reaction.

Benzene reacts with fuming sulphuric acid to form benzenesulphonic acid.

The important electrophile from fuming sulphuric acid that attacks the benzene ring is sulphur trioxide.

Mechanism

$$2H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3\overset{+}{O}$$
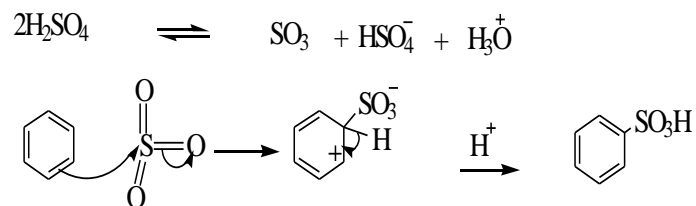
7. Hydrogenation reaction.

Benzene reacts with hydrogen catalysed by heated nickel to form cyclohexane.

b) METHYLBENZENE (TOLUENE), $C_6H_5CH_3$,

Synthesis of Methylbenzene

1. Friedel-Crafts alkylation reaction.

By alkylation of benzene with a halogen methane in the presence of a halogen carrier e.g. $AlCl_3$, $AlBr_3$, $FeBr_3$...etc.

Mechanism.
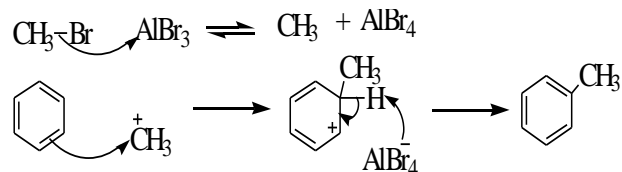
2. By Wurtz-Fittig's reaction.

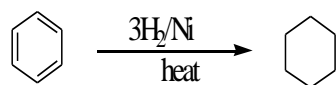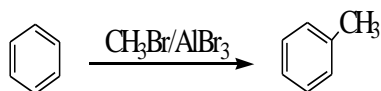Bromobenzene is reacted with bromomethane in presence of sodium in dry ether.
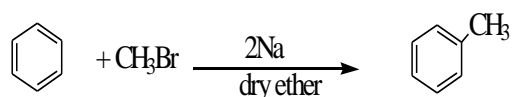
Reactions of Methylbenzene

Effect of substituent group on the reactivity of the ring and direction of the incoming group.

The positions on a benzene ring in reference to a given attached group are labeled with numbers 2, 3 and 4, also called ortho, Meta and para respectively.
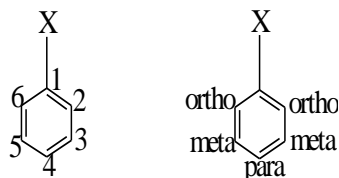
Electron donating groups (those with a positive inductive effect) activate the ring and are ortho-para directors.

Electron withdrawing groups (those with a negative inductive effect) deactivate the ring and are Meta directors.

Examples of;

Groups that direct *ortho* and *para*	CH_3	NH_2	OH	OCH_3	$NHCOCH_3$	Cl	Br	I

Groups that
direct *meta*

NO$_2$ COOH   CHO   SO$_3$H

Note: The halogen groups, the amino group and hydroxyl group all have electron withdrawing effects (those with a negative inductive effect) since the atoms attached to carbon are more electronegative than carbon but they are ortho-para directors while one would think of them as meta directors. This is because the halogens, oxygen and nitrogen have lone pairs of electrons that participate in delocalization with the pi electron cloud of the ring. This tends to stabilize the ortho and para complexes at the expense of the meta complex.

1. Electrophilic substitution reactions on the ring.

NB: the methyl group (-CH$_3$) is an activating group and an ortho-para director.

Nitration, sulphonation, Friedel-Crafts alkylation and acylation and halogenation of toluene is the same as that for benzene, the major products being the ortho and para products. (Examples).

Physical properties of Methylbenzene

a) Colourless liquid. Its toxic and long exposure causes anemia and leukemia.

b) Insoluble in water, soluble in organic solvents.

c) Mp is -95°C and Bp is 111°C.

Note: The mp of methylbenzene is lower than that of benzene although methylbenzene has the highest molecular weight. This is because the planar molecules of benzene can pack closely together in the crystal and the cohesive forces are strong, while the methyl group in methylbenzene prevents such close packing.

Qn: The mp of methylbenzene (-95°C) is lower than that of benzene although methylbenzene (5.7°C) has the highest molecular weight. Explain.

2. Reactions of the side chain (-CH$_3$).

i.   Oxidation.

Methylbenzene is oxidized by hot strong oxidising agents like H^+/MnO_4^- and $H^+/Cr_2O_7^{2-}$ to benzoic acid
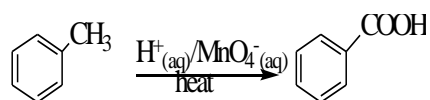
Methylbenzene is oxidized by mild oxidising agents like H^+/MnO_2 and $CrCl_2O_2$ (chromyl chloride) to benzaldehyde.
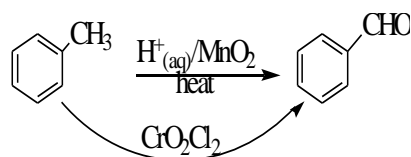
ii.   Halogenation.

Methylbenzene is halogenated with chlorine or bromine in presence of UV light to produce substituted products.
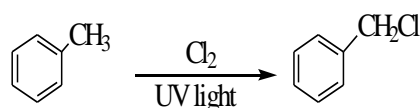
iii.   Hydrogenation.

Methylbenzene is hydrogenated with hydrogen in presence of heated nickel catalyst to form methyl cyclohexane.
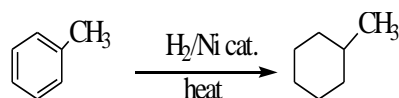
c) HYDROXYBENZENE, (PHENOL), C_6H_5OH
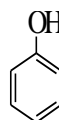
Synthesis of phenol.

1. From phenyl amine.

The phenylamine is diazotized to benzenediazonium chloride (using sodium nitrite in conc. HCl at 0°C) followed by hydrolysis at 50°C.
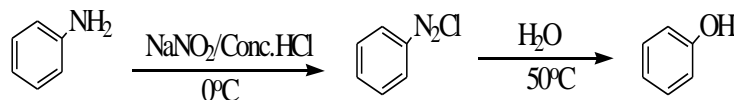
2. By reacting aromatic halides with sodium hydroxide in the presence of copper(II)chloride catalyst at 300°C and 200 atm followed by dilute mineral acid.

NB:
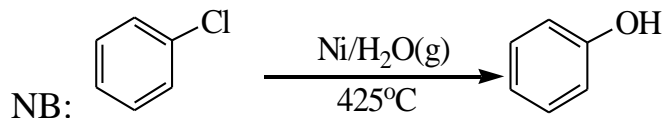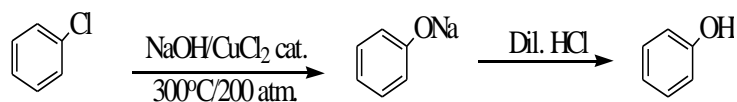
3. By reacting sodium salt of benzenesulphonic acid with sodium hydroxide at 300°C followed by dilute mineral acid.
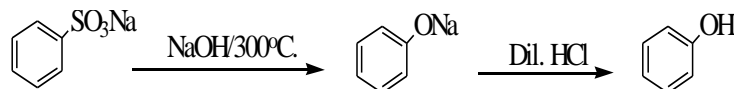
4. Cumene process.

Benzene is first alkylated with propene using concentrated phosphoric acid or aluminium chloride catalyst to form Cumene. Cumene is then oxidized by oxygen to Cumene hydroperoxide that is then hydrolysed by dilute sulphuric acid to phenol and acetone (Propanone).
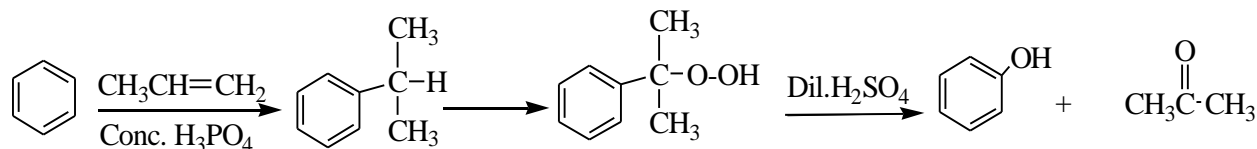
Physical properties of phenol.

a) Colourless crystalline liquid.

b) Slightly soluble in water, soluble in organic solvents.

c) Mp is 39.5-41°C and Bp is 182°C.

Reactions of phenol.

1. Reactions on the ring.

NB: The hydroxyl group (-OH) is a deactivating group but an ortho-para director.

Nitration*, sulphonation, Friedel-Crafts alkylation and acylation and halogenation of phenol is the same as that for benzene, the major products being the ortho and para products. (Examples).

* o or p nitrophenol is obtained with dilute nitric acid.

* With concentrated nitric acid yields 2,4,6-trinitrophenol (picric acid)

2. Reactions of the side chain (-OH).

Note: the vigour of the reactions of phenol is less compared to that with alcohols. Why ?.

a) Ether formation.

Phenol reacts with halogen alkanes in the presence of alkalis to form ethers.

OH $+ CH_3Br$ $\xrightarrow{NaOH_{(aq)}}$ OCH$_3$ methyl phenoxide

mechanism

$NaOH_{(aq)} \longrightarrow Na^+ + \bar{O}H$

$\longrightarrow$ $\bar{O}$ $+ H_2O$

$\longrightarrow$ $\bar{O}$ CH$_3$–Br $\xrightarrow{slow}$ $\left[\text{–O---CH}_2\text{--Br} \right]^{-}$ $\xrightarrow{fast}$ OCH$_3$
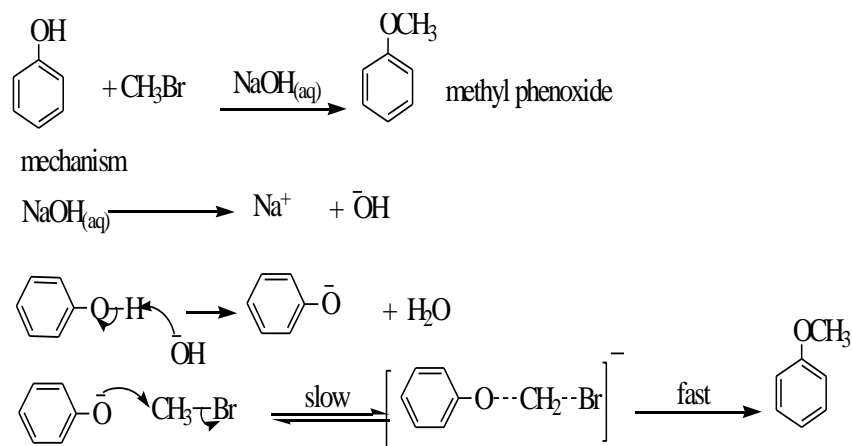
b) Ester formation

i. From acid chlorides.

OH $+$ $CH_3\overset{O}{\overset{\|}{C}}\text{-Cl}$ $\longrightarrow$ OOCCH$_3$ phenyl ethanoate

mechanism

ii. From organic acids.

OH $+$ $CH_3\overset{O}{\overset{\|}{C}}\text{-OH}$ $\xrightarrow{OH^-}$ OOCCH$_3$ phenyl ethanoate

mechanism
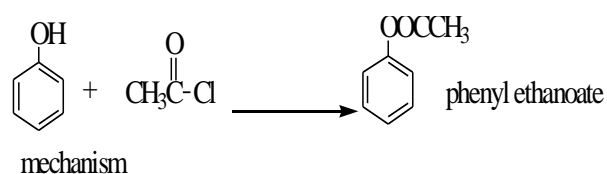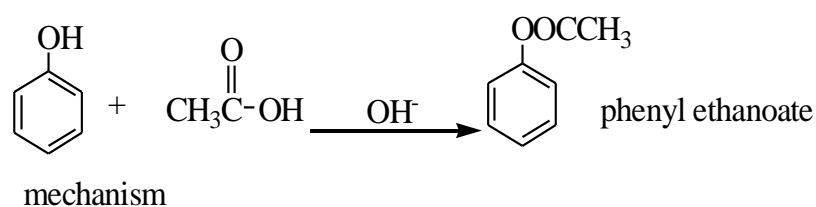
Note: the esterification of phenol with organic acids does not occur in acidic medium.

c) Phenol reacts with PCl$_5$ to form chlorobenzene.

OH → (PCl$_5$) → Cl   chlorobenzene
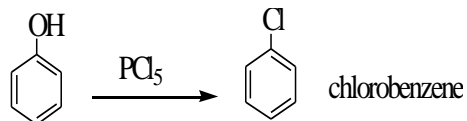
d) Phenol reacts with sodium metal to form sodium phenoxide and hydrogen gas.

OH → (Na) → ONa + H$_2$
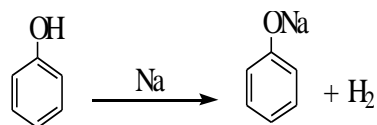
e) Phenol reacts with heated zinc dust to form benzene.

OH → (Zn dust / heat) → + ZnO
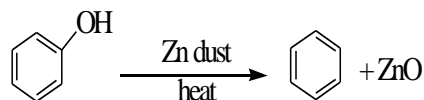
f) Phenol forms a weakly acidic solution, it reacts with sodium hydroxide to form sodium phenoxide and water.

OH → (NaOH) → ONa + H$_2$O
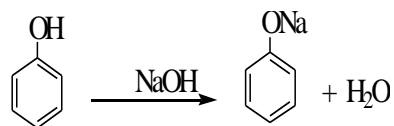
g) When phenol heated with ammonia and zinc chloride at 200°C, aniline is formed.

OH → (NH$_3$/ZnCl$_2$ / 200°C) → NH$_2$ + H$_2$O
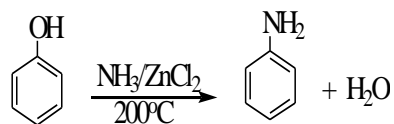
h) Hydrogenation.

Phenol is hydrogenated with hydrogen in presence of heated nickel catalyst to form cyclohexanol.

OH → (3H$_2$/Ni cat. / Heat) → OH
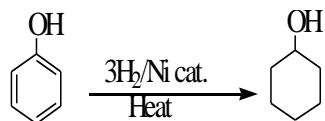
3. **Confirmatory reactions/tests of phenol.**

a) Reaction with bromine.

Phenol reacts with bromine to form a white precipitate of 2,4,6-tribromophenol.
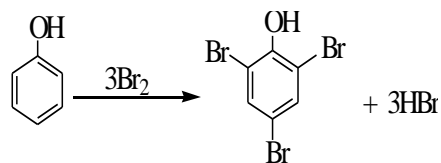
NOTE: This reaction confirms phenol only when aniline is absent.

b) Reaction with neutral iron(III)chloride solution.

Phenol reacts with neutral iron(III)chloride solution to form a violet solution. This reaction confirms phenol.

c) Reaction with sodium hydroxide solution.

Phenol is soluble in sodium hydroxide but insoluble in sodium carbonate. This distinguishes phenol from a carboxylic acid.

d) Coupling reaction.

Phenol reacts with benzenediazonium chloride in presence of an alkalis to form a brightly yellow azo dye.
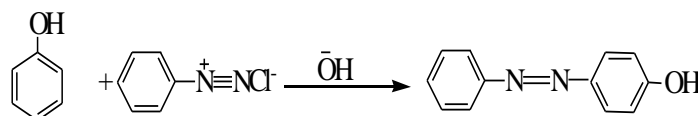
d) AMINOBENZENE (PHENYLAMINE) $C_6H_5NH_2$
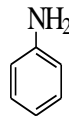
Synthesis of aminobenzene.

1. Aniline is prepared by reduction of nitrobenzene using a mixture of tin in concentrated hydrochloric acid followed by hot sodium hydroxide.
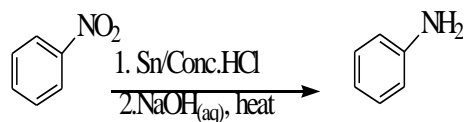
2. By Hofmann degradation reaction. The aromatic amide is heated with bromine and concentrated sodium hydroxide.
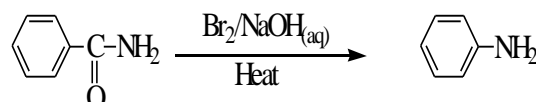
3. By heating phenol with ammonia and zinc chloride at 200°C, aniline is formed.
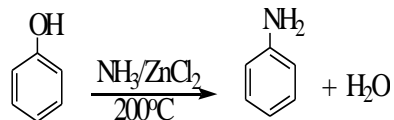
Reactions of aminobenzene.

1. Reactions on the ring.

NB: The amino group ($-NH_2$) is a deactivating group but an ortho-para director.

Nitration, sulphonation, Friedel-Crafts alkylation and acylation and halogenation of phenol is the same as that for benzene, the major products being the ortho and para products.

2. Other reactions.

a) Reaction with bromine.

Aniline reacts with bromine to form a white precipitate of 2,4,6-tribromoaminobenzene.
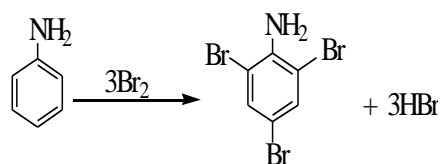
NOTE: This reaction differentiates aniline from benzene and other aromatic compounds except phenol.

b) Aniline reacts with nitrous acid (HNO_2) which is prepared and used in situ from sodium nitrite and concentrated hydrochloric acid at 0°C because nitrous acid is not stable at room temperature. Benzenediazonium chloride is produced.

Benzenediazonium chloride
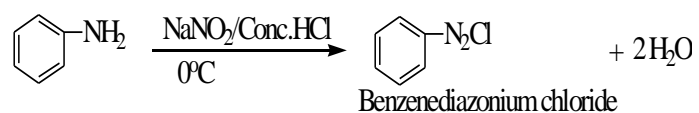
CHAPTER 8: CARBONYL COMPOUNDS.

These are organic compounds that conform to the general formular $C_nH_{2n}O$.

The functional group is the carbonyl group, $-\overset{\overset{\displaystyle O}{\|}}{C}-$.

Carbonyl compounds are made of two classes i.e. aldehydes $R-\overset{\overset{\displaystyle O}{\|}}{C}H$ and ketones, $R-\overset{\overset{\displaystyle O}{\|}}{C}R$.

Nomenclature of carbonyl compounds.

1. Aldehydes.

a) IUPAC names of aldehydes are obtained by replacing the ending "**a**" in the corresponding alkane with "**al**" in aldehydes.

b) The carbonyl carbon in aldehydes is always at position one.

c) The attached groups are identified by their nature and position.

Examples.

$\overset{\overset{\displaystyle O}{\|}}{H}CH$ Methanal

$CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$ Ethanal

$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$ Propanal

Phenylmethanal (Benzaldehyde)

2-phenylpropanal
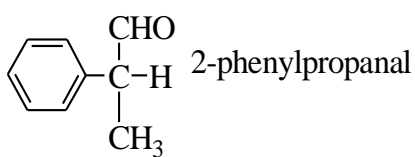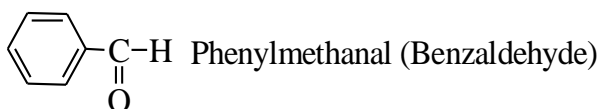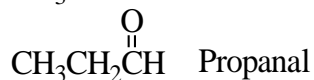
2. Ketones.

a) IUPAC names of ketones are obtained by replacing the ending "**a**" in the corresponding alkane with "**one**" in ketones.

b) The position of the carbonyl carbon is specified. Numbering of the longest continuous chain is done so as to give the carbonyl carbon the smallest number.

c) The attached groups are identified by their nature and position.

Examples.

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 \quad \text{Propanone}$$

Acetophenone: phenyl-$\overset{\overset{\displaystyle }{}}{C}\text{-}CH_3$ with $=O$

$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 \quad \text{Butanone}$$

Benzophenone: phenyl-$\overset{\overset{\displaystyle O}{\|}}{C}$-phenyl
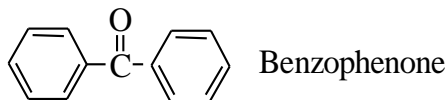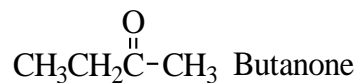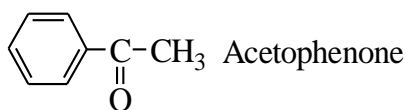
Isomerism in carbonyl compounds.

Carbonyl compounds exhibit chain and position isomerism.

Example: Write the IUPAC names and structural formulae of all isomers to $C_5H_{10}O$.

Synthesis of carbonyl compounds.

1. Oxidation.

a) Controlled oxidation of 1° alcohols yields aldehydes while 2° alcohols yields ketones.

Examples.

$$CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{\overset{\text{limited}}{H^+_{(aq)}/Cr_2O_7^{2-}{}_{(aq)}}} CH_3CH_2CHO$$

$$\underset{\overset{\displaystyle |}{OH}}{CH_3CHCH_3} \xrightarrow[\text{heat}]{\overset{\text{limited}}{H^+_{(aq)}/Cr_2O_7^{2-}{}_{(aq)}}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3$$
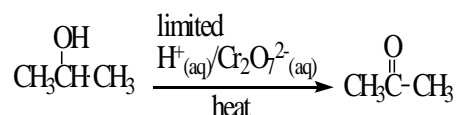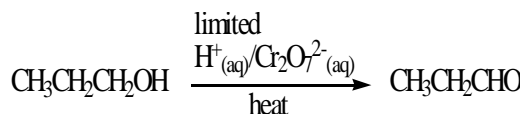
The Wacker process.

b) Oxidation of ethene with palladium(II)chloride in water.

$$H_2C{=}CH_2 \xrightarrow{PdCl_2/H_2O} CH_3CHO$$
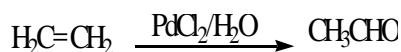
c) Oxidation of alcohols in gas phase over silver metal catalyst at 500°C.

$$CH_3CH_2CH_2OH \xrightarrow[500°C]{O_2/Ag} CH_3CH_2CHO$$
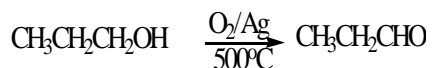
2. From ozonolysis of alkenes.

Alkenes react with ozone to form an ozonide, the ozonide is unstable and very explosive and so the reaction is carried out in in an inert solvent, CCl_4 at less than

20°C. When the ozonide is hydrolised in presence of zinc and ethanoic acid, carbonyl compounds are formed.

Examples.

a. $CH_3CH=CHCH_3 \xrightarrow[\text{2. } H_2O/Zn/CH_3COOH]{\text{1. } O_3/CCl_4 < 20°C}$ 2 $CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$
Ethanal

b. $CH_3CH_2CH=CHCH_3 \xrightarrow[\text{2. } H_2O/Zn/CH_3COOH]{\text{1. } O_3/CCl_4 < 20°C}$ $CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$ + $CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$
Propanal   Ethanal

c. $CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}=CHCH_3 \xrightarrow[\text{2. } H_2O/Zn/CH_3COOH]{\text{1. } O_3/CCl_4 < 20°C}$ $CH_3\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ + $CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$
Propanone   Ethanal
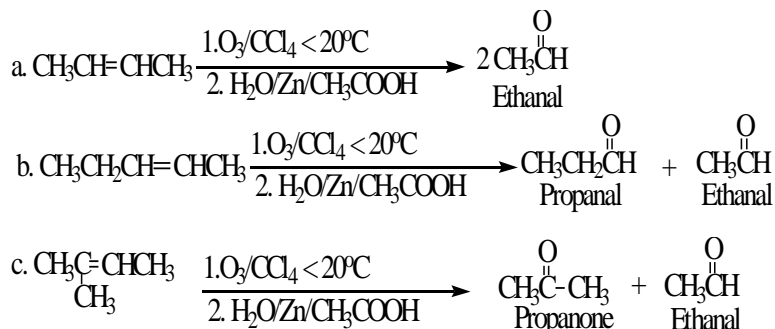
3. By reaction of alkynes with water in the presence of concentrated sulphuric acid and mercury (II) sulphate as a catalyst at 60°C. Ethyne forms ethanal while other alkynes form ketones. E.g.

$HC\equiv CH \xrightarrow[\text{HgSO}_4, 60°C]{H_2O/\text{Conc.}H_2SO_4}$ $CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$ $CH_3C\equiv CH \xrightarrow[\text{Hg}^{2+}, 60°C]{H_2O/H^+}$ $CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

Mechanism:

$CH_3C\equiv CH \longrightarrow CH_3\overset{+}{C}=CH_2 \longrightarrow CH_3C=CH_2 \longrightarrow CH_3C=CH_2$ Rearrangement $CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$
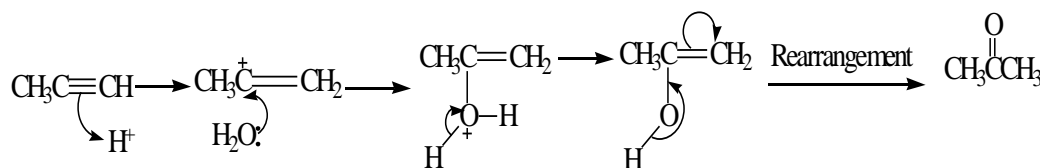
4. By hydrolysis of gemi dichlorides.
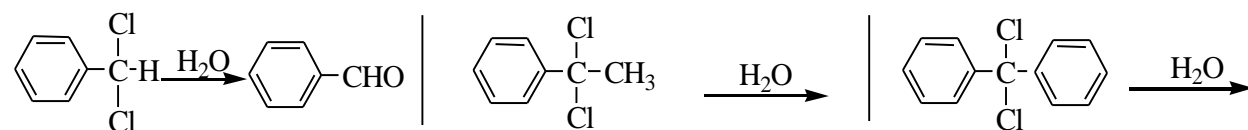
NOTE: The method is convenient for aromatic carbonyl compounds due to the difficulty of obtaining aliphatic dichlorides. It's easy to obtain aromatic dichlorides e.g. by chlorination of toluene in UV light.

5. Decarboxylation of calcium salts of organic salts.

a) Heating calcium salts of organic salts alone yields **ketones.**

$(CH_3COO)_2Ca \xrightarrow{\text{heat}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$
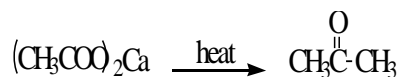
b) Heating calcium salts of organic salts with calcium methanoate yields **aldehydes.**

$$(CH_3COO)_2Ca \xrightarrow[\text{heat}]{(HCOO)_2Ca} CH_3\overset{\displaystyle O}{\overset{\|}{C}}\text{-H}$$
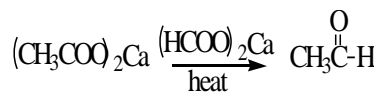
Physical properties of carbonyl compounds.

a) Lower aliphatic carbonyl compounds are soluble in water due to their ability to form hydrogen bonds with water molecules. Higher members are insoluble in water but soluble in organic solvents due to a large oil group.

b) They are less dense than water and their density increases with increase in molecular weight.

c) They have higher bps than corresponding alkanes due to their ability to form hydrogen bonds between their molecules.

d) They are more volatile than the corresponding alkanes.

Reactions of carbonyl compounds.
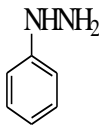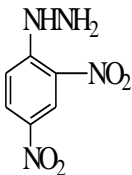
Note: Aldehydes are more reactive than ketones. Why?

Both aldehydes and ketones have the same carbonyl group that is polarized since oxygen is more electronegative than carbon. Ie oxygen atom has a partial negative charge and the carbon atom has a partial positive charge. In a Nucleophilic addition reaction, nucleophiles attack the electron deficient carbon atom.

In aldehydes is one alkyl group bonded to the carbonyl carbon while in ketones are two alkyl groups bonded to the carbonyl carbon. These alkyl groups have a positive inductive effect thus reduce the positive charge on the carbonyl carbon. Thus any attacking nucleophile is less attracted in ketones than in aldehydes.

a) Reaction between carbonyl compounds and compounds of the form NH₂-Y.

Carbonyl compounds react with compounds of the form NH_2-Y in presence of a mineral acid catalyst to form brightly coloured crystalline products with sharp melting points.

Reagent	Product	
Hydroxyamine NH_2OH	$R-\overset{\overset{O}{\|}}{C}-R', H^+$	$\underset{R'}{\overset{R}{>}}C=NHOH$ Oxime
Hydrazine NH_2NH_2		$\underset{R'}{\overset{R}{>}}C=NHNH_2$ Hydrazone
Semi carbazine $NH_2NHCONH_2$		$\underset{R'}{\overset{R}{>}}C=NHNHCONH_2$ Semi carbazone
Phenylhydrazine $\underset{}{\overset{NHNH_2}{\text{⬡}}}$		$\underset{R'}{\overset{R}{>}}C=N-N\overset{}{\underset{H}{}}\text{⬡}$ Phenylhydrazone
2,4-dinitrophenylhydrazine		2,4-dinitrophenylhydrazone

Mechanism;
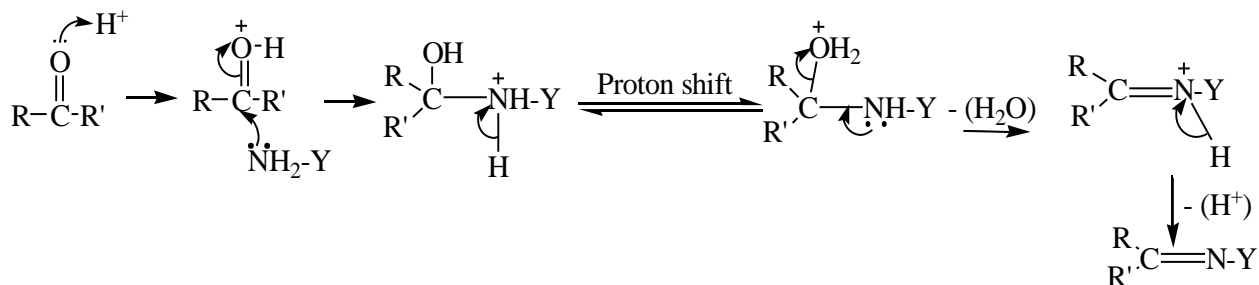
Note: Should also write a mechanism in absence of an acid catalyst.

b) Reduction.

Carbonyl compounds are reduced to corresponding alcohols by lithium tetrahydridoaluminate ($LiAlH_4$) in dry ether.

a) $CH_3CHO \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2OH$ b) $CH_3\overset{\overset{O}{\|}}{C}\text{-}CH_3 \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3\overset{\overset{OH}{\|}}{CH}\text{-}CH_3$
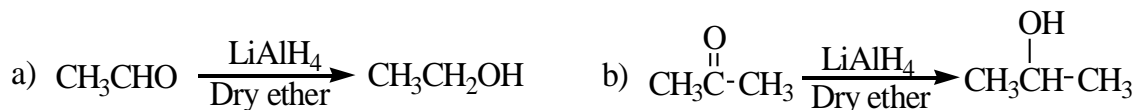
c) Reaction with sodium hydrogen sulphite solution.

Carbonyl compounds react with sodium hydrogen sulphite solution to form white crystalline solids.

a) $CH_3CHO \xrightarrow{NaHSO_{3(aq)}} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HSO_3Na$ Ethanal sodium hydrogensulphite

b) $CH_3\overset{\overset{\displaystyle O}{||}}{C}\text{-}CH_3 \xrightarrow{NaHSO_{3(aq)}} CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{-}SO_3Na$ propanone sodium hydrogensulphite

Mechanism.

$NaHSO_3 \longrightarrow Na^+ + HSO_3^-$
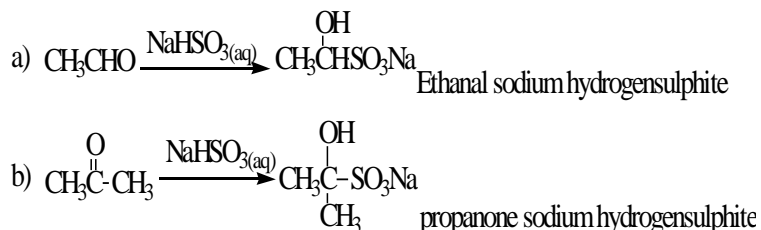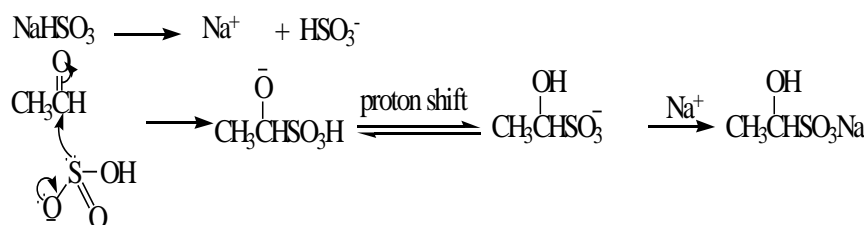
d) Reaction with phosphorous pentachloride.

Carbonyl compounds react with phosphorous pentachloride to form gemi-dichlorides.

a) $CH_3CHO \xrightarrow{PCl_5} CH_3\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}H$
1,1-dichloroethane

b) $CH_3\overset{\overset{\displaystyle O}{||}}{C}\text{-}CH_3 \xrightarrow{PCl_5} CH_3\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}\text{-}CH_3$
2,2-dichloropropane
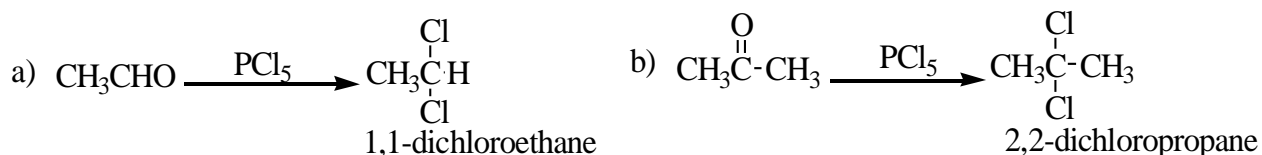
e) Reaction with ammonia.

Aliphatic aldehydes (except methanal) react with ammonia in dry ether to form hydroxyl amines.

$CH_3CHO \xrightarrow[\text{dry ether}]{NH_3} CH_3\overset{\overset{\displaystyle OH}{|}}{C}H\text{-}NH_2$ 1-hydroxyaminoethane
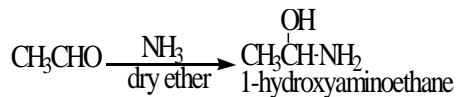
Mechanism.
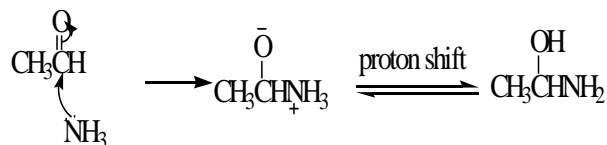
f) Reaction with hydrogen cyanide.

Carbonyl compounds react with hydrogen cyanide to form hydroxyl nitriles. Hydrogen cyanide is formed and used in situ from an alkali metal cyanide and concentrated sulphuric acid since it is very poisonous.

$$CH_3CHO \xrightarrow{KCN/Conc.\ H_2SO_4} \overset{\displaystyle OH}{CH_3\overset{|}{C}H\cdot CN}$$

2-hydroxypropanenitrile

Mechanism.

$$KCN + H_2SO_4 \longrightarrow HCN + KHSO_4$$

$$HCN \longrightarrow H^+ + {}^-CN$$
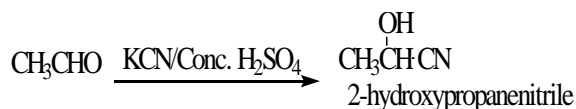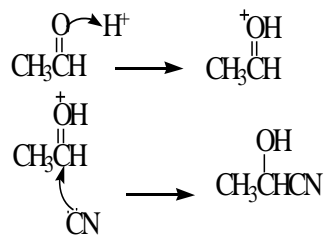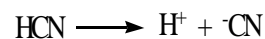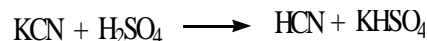
g) Reaction with Grignard's reagents.

Carbonyl compounds react with Grignard's reagents in ether to form alcohols on acid hydrolysis.
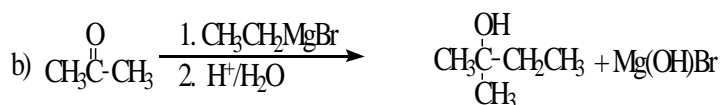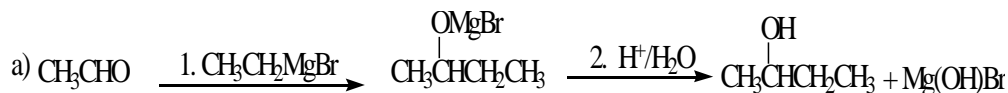
Reading areas.

Aldo condensation, Carnizzaro and halogenation reactions of carbonyl compounds.

Confirmatory test for carbonyl compounds.

Reagent. *2,4-dinitrophenylhydrazine solution.*

Observations. *Yellow precipitate with aliphatic carbonyl compounds*

Brown precipitate with aromatic carbonyl compounds

Distinguishing between aldehydes and ketones.

Reagent.

a) Ammoniacal silver nitrate solution (Tollen's reagent). (Silver mirror test for aldehydes only)

Aldehydes reduce silver(I) ions in the solution to metallic silver which coats the test tube.

$$CH_3CHO_{(aq)} + 2Ag(NH_3)_2^+{}_{(aq)} + 3\bar{O}H_{(aq)} \rightarrow 2Ag_{(s)} + CH_3CO\bar{O}_{(aq)} + 4NH_{3(g)} + 2H_2O_{(l)}$$
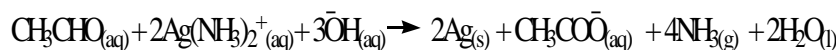
Observations.

A silver mirror with aldehydes.

No observable change with ketones.

b) Fehling's or Benedict's solution. (For aliphatic aldehydes only)

Aliphatic aldehydes reduce Cu^{2+} held as a complex in Fehling's or Benedict's solution to copper(I)oxide (Cu_2O), a red solid.

$$CH_3CHO_{(aq)} + 2Cu^{2+}{}_{(aq)} + 4\bar{O}H_{(aq)} \rightarrow Cu_2O_{(s)} + CH_3COOH_{(aq)} + 2H_2O_{(l)}$$
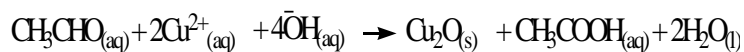
Observations.

Red precipitate with aliphatic aldehydes.

No observable change with ketones and aromatic aldehydes.

c) Iodine solution followed by sodium hydroxide solution. (Iodoform reagent)

It tests for aldehydes, ketones and alcohols of the form CH_3-CO-, and CH_3-CH(OH)- called methyl alcohols, methyl aldehydes or methyl ketones. All produce a yellow precipitate of triiodomethane.

$$\underset{CH_3\overset{\overset{\displaystyle O}{\|}}{C}\cdot CH_3}{} + 4I_2(aq) + 6NaOH(aq) \longrightarrow CHI_3(s) + CH_3COONa(aq) + 5NaI(aq) + 5H_2O(l)$$

Triiodomethane
yellow ppt
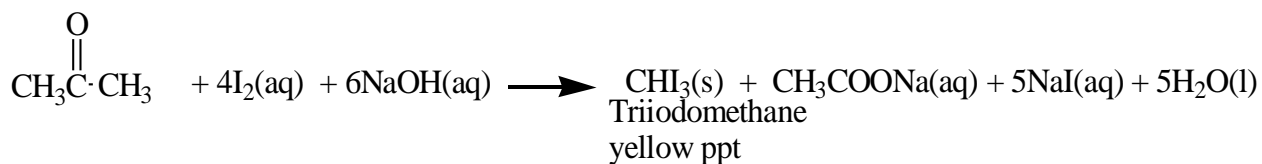
Non-methyl alcohols, aldehydes or ketones give no observable change.

CHAPTER 8: CARBOXYLIC ACIDS.

8.1. These are saturated organic compounds with general formular, RCOOH where R is an alkyl or aryl group.

The functional group is the carboxyl group, -COOH.

8.2. Nomenclature of carboxylic acids.

1. The ending **"e"** in alkanes is replaced with **"oic"** in the corresponding carboxylic acid. E.g.

CH_3COOH Ethanoic acid

CH_3CH_2COOH Propanoic acid

C_6CH_5COOH Benzoic acid

2. Any other group on the chain are identified by its nature and position. Numbering starts from the carboxyl group. The position of the carboxyl group is not mentioned since it's always at the end of the chain. E.g.

 CH_2COOH 2-phenylethanoic acid

$\overset{OH}{CH_3CH_2\overset{|}{C}HCOOH}$ 2-hydroxybutanoic acid

$\overset{NH_2}{CH_3CH_2\overset{|}{C}HCOOH}$ 2-aminobutanoic acid
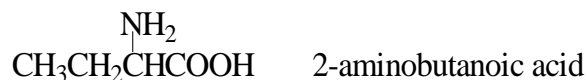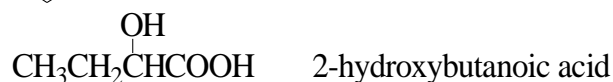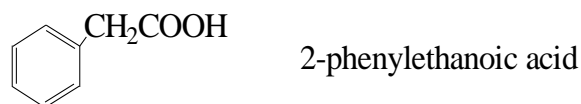
8.3. Isomerism in Carboxylic acids.

Carboxylic acids exhibit chain and functional group isomerism.

Example.

Write the structural formulae and IUPAC names of all the isomers of $C_3H_6O_2$.

Solution.

CH_3CH_2COOH propanoic acid

CH_3COOCH_3 methyl ethanoate

Notice that carboxylic acids are isomeric to esthers.

EER. Write the structural formulae and IUPAC names of all the isomers of $C_4H_8O_2$.

8.4. Synthesis of carboxylic acids.

1. a) Oxidation of primary alcohols in a two stage process or aldehydes by strong oxidizing agents like acidified potassium/sodium dichromate (VI) solution or acidified potassium/sodium permanganate solution. E.g.

$$CH_3CH_2OH \xrightarrow[\text{Heat}]{\substack{\text{limited} \\ H^+(aq)/Cr_2O_7^{2-}(aq)}} \underset{\text{ethanal}}{CH_3CHO} \xrightarrow[\text{Heat}]{\substack{\text{excess} \\ H^+(aq)/Cr_2O_7^{2-}(aq)}} \underset{\text{ethanoic acid}}{CH_3COOH}$$

its a stronger oxidising agent

$$CH_3CH_2OH \xrightarrow[\text{Heat}]{H^+(aq)/MnO_4^-(aq)} \underset{\text{ethanoic acid}}{CH_3COOH}$$

$$CH_3CH_2MgBr \xrightarrow[\text{2.}H^+(aq)/H_2O(l)]{\text{1.}CO_2(g)/ether} CH_3CH_2COOH + Mg(OH)Br$$
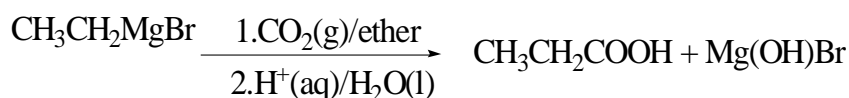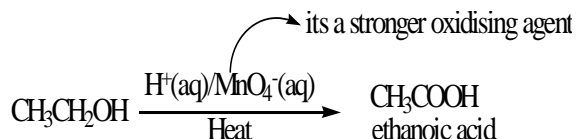
b) Oxidation of methyl benzene using hot alkaline potassium permanganate followed by dilute hydrochloric acid.
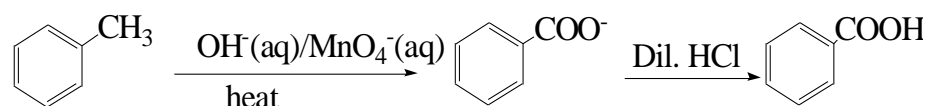
NOTE: Acidified potassium permanganate is also used.
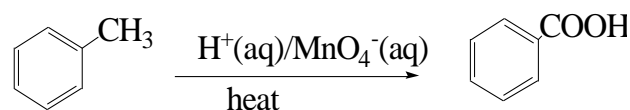
Note:
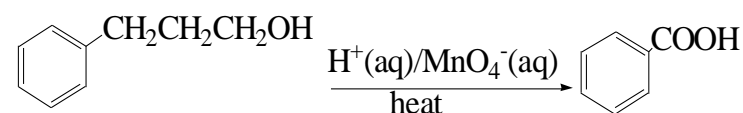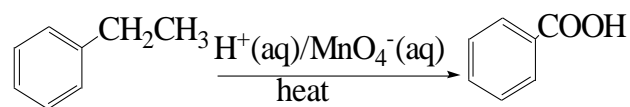
2. From Grignard's reagent.

The Grignard's reagent is reacted with carbon dioxide in the presence of ether followed by acid hydrolysis. E.g.

$$CH_3CH_2MgBr \xrightarrow{CO_2(g)/ether} CH_3CH_2COOMgBr \xrightarrow{H^+(aq)/H_2O(l)} CH_3CH_2COOH + Mg(OH)Br$$

Or simply as;

$$CH_3CH_2MgBr \xrightarrow[2.H^+(aq)/H_2O(l)]{1.CO_2(g)/ether} CH_3CH_2COOH + Mg(OH)Br$$
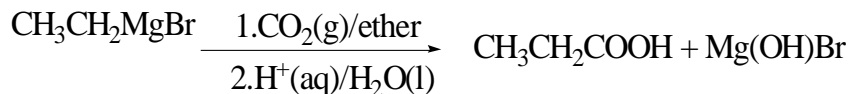
3. By hydrolysis of nitriles.

When nitriles are heated with a dilute mineral acid like HCl or H_2SO_4 or with alkalis like NaOH or KOH, carboxylic acids are formed. E.g.

$$CH_3CH_2CN \xrightarrow[heat]{H^+(aq)/H_2O(l)} CH_3CH_2COOH$$
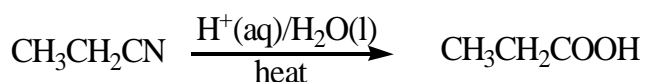
4. By hydrolysis of esters with water or base. Best for the lower members of the series. E.g.

$$CH_3CH_2COOCH_3 \xrightleftharpoons[heat]{H_2O(l)} CH_3CH_2COOH + CH_3OH$$
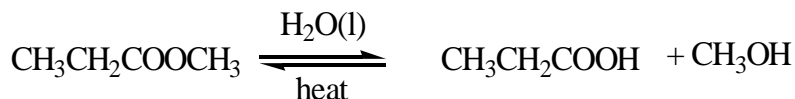
Mechanism???

8.5. Physical properties of carboxylic acids.

a) Aliphatic acids as far as C_{10} are liquids with pungent odours at room temperature, but anhydrous Ethanoic acid freezes to an ice-like solid below 17°C and has a vinegar smell. Aromatic acids are crystalline solids.

b) The 1st 4 aliphatic acids are completely miscible with water. This is due to their ability to form hydrogen bonds with water. Higher homologues become progressively immiscible with water due to their greater hydrocarbon tail thus covalence character. Benzoic acid is only slightly soluble in cold water but readily soluble in hot water. All carboxylic acids dissolve in suitable organic solvents.

c) They have higher bps than alkanes of similar formular weight due to their ability to form dimers via hydrogen bonds. E.g. Ethanoic acid, (Mr = 60) has b.p of 118°C while butane, (Mr = 58) has b.p of -0.5°C.

8.6. Chemical properties of carboxylic acids.

a) The chemistry of the O-H bond.

Carboxylic acids are weak acids compared to mineral acids because they ionize partially in water to set up an equilibrium as follows.

$$RCOOH(aq) + H_2O(l) \rightleftharpoons RCOO^-(aq) + H_3O^+(aq)$$

The equilibrium constant, Ka is given by:

$$Ka = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

The bigger the Ka value, the stronger the acid. They therefore turn blue litmus paper to red.

b) Effect of substituent groups on the strength of the acid.

Comparison of some organic acids.

Acid Name	Formular	Ka at 25ºC (moldm^{-3})
Methanoic acid	HCOOH	1.6×10^{-4}
Ethanoic acid	CH_3COOH	1.75×10^{-6}
Propanoic acid	CH_3CH_2COOH	1.3×10^{-8}
Chloroethanoic acid	$Cl\text{-}CH_2COOH$	1.3×10^{-3}
Trichloroethanoic acid	$Cl_3\text{-}CCOOH$	2.3×10^{-1}

The presence of an electron withdrawing group like a halogen atom bonded to a carbon atom adjacent to the carboxyl group makes the carboxylic acid stronger. For this reason, Chloroethanoic acid is a stronger acid than Ethanoic acid. (cf Ka values). Trichloroethanoic acid is even a stronger acid. This is because the halogen atom has a negative inductive effect, it withdraws electrons from the carboxyl group, reducing the electron cloud around the O-H bond, and this weakens which makes the acid to easily release a hydrogen ion in solution.

Qn: Chloroethanoic acid is a stronger acid than Ethanoic acid. Explain.

Qn: The Ka of chloroethanoic acid is 1.3×10^{-3} while that of ethanoic acid is 1.75×10^{-6}. Explain.

The acid strength decreases with presence and increase in length of the alkyl group bonded to the carboxyl group. This is because there is a greater positive inductive effect with increasing number of carbon atoms in the alkyl group. When electrons are pushed towards the O-H bond, the electron density of this bond increases hence becomes stronger. Increased branching on the alkyl groups will also have the same effect.

Qn: Methanoic acid is a stronger acid than ethanoic acid. Explain.

Qn: The Ka of methanoic acid is 1.6×10^{-4} while that of ethanoic acid is 1.75×10^{-6}. Explain.

c) **Reactions of carboxylic acids.**

1. Carboxylic acids react with highly electropositive metals like Na, K, Mg, Ca etc. to form an organic salt of the metal and hydrogen.

$2\ CH_3COOH(l) + Mg(s) \longrightarrow (CH3COO)_2Mg(s) + H_2(g)$
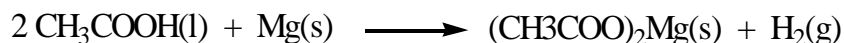
2. They react with bases to form a salt and water.

i.e $RCOOH(aq) + NaOH(aq) \longrightarrow RCOONa(aq) + H_2O(l)$

e.g $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$
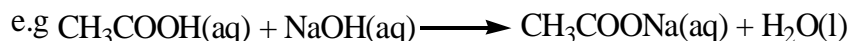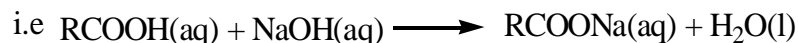
3. They react with carbonates and hydrogencarbonates with evolution of carbon dioxide, a salt and water. This is the confirmatory test for carboxylic acids.

i.e $RCOOH(aq) + Na_2CO_3(aq) \longrightarrow RCOONa(aq) + H_2O(l) + CO_2(g)$

e.g $CH_3COOH(aq) + Na_2CO_3(aq) \longrightarrow CH_3COONa(aq) + H_2O(l) + CO_2(g)$
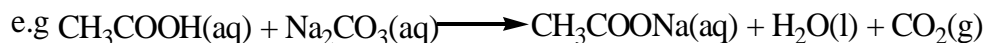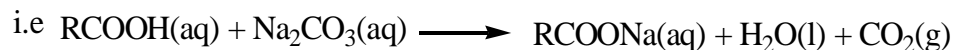
4. Esterification. Organic acids react with alcohols in presence of concentrated sulphuric acid to form esters. E.g.

$$CH_3OH + CH_3COOH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOCH_3 + HCl$$
methanol — methyl ethanoate

Mechanism:

$$CH_3\overset{\overset{O}{\|}}{C}\text{-}OH \xrightarrow{\;H^+\;} CH_3\overset{\overset{+}{O}H}{\underset{\;}{C}}\text{-}OH \longrightarrow CH_3\overset{OH}{\underset{\underset{CH_3OH}{OH}}{C}}\overset{+}{O}CH_3 \xrightarrow{\text{proton shift}} CH_3\overset{\overset{+}{O}H_2}{\underset{:OH}{C}}\text{-}OCH_3$$

$$\downarrow -H_2O$$

$$CH_3\overset{\overset{O}{\|}}{C}\text{-}OCH_3 \longleftarrow CH_3\overset{\overset{+}{O}\;H}{C}\text{-}OCH_3$$
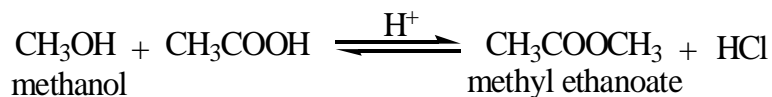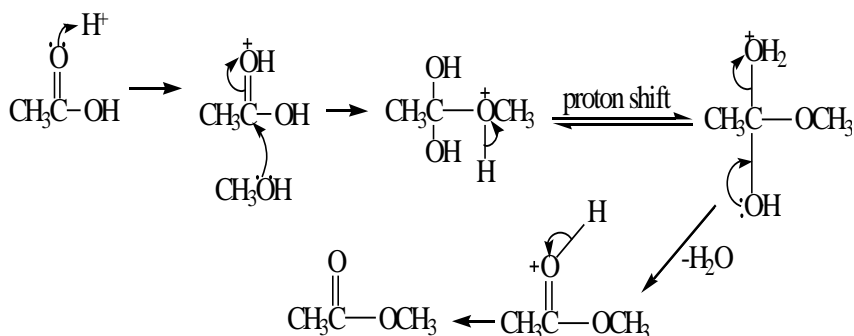
5. They react with phosphorous halides like PCl_5, PBr_5 (given as Red P/Br_2) or thionyl chloride, $SOCl_2$ to form acid halides.

$$RCOOH(aq) \xrightarrow{\;PCl_5\;} RCOCl + POCl_3 + HCl$$

$$RCOOH(aq) \xrightarrow{PBr_5 \text{ (or Red P/Br}_2)} RCOBr + POBr_3 + HBr$$

$$RCOOH(aq) \xrightarrow{\;SOCl_2\;} RCOCl + SO_2 + HCl$$
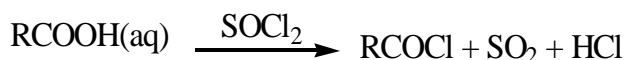
6. Reduction. Reduction of carboxylic acids with lithium tetrahydridoaluminate in dry ether gives a primary alcohol. E.g. $CH_3COOH \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2OH$
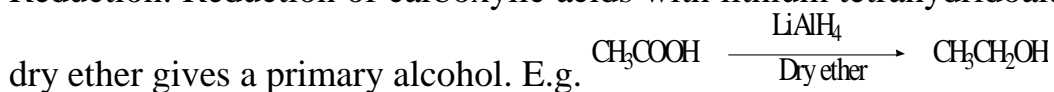
However, unlike aldehydes and ketones, they are not reduced by sodium tetrahydridoborate, $NaBH_4$ in water.

7. Carboxylic acids with beta hydrogens (i.e. hydrogens adjacent to the carboxyl group) can be substituted with chlorine when chlorine gas is passed into the hot acid in the presence of ultraviolet light. E.g.

$$(CH_3)_2\overset{H}{\underset{\;}{C}}\text{-}COOH \xrightarrow[\text{Heat}]{Cl_2(g)/\,UV\,light} (CH_3)_2\overset{Cl}{\underset{\;}{C}}\text{-}COOH \;+ HCl$$
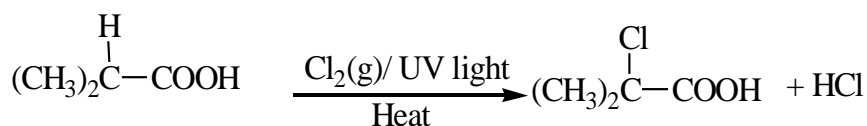
When there are more than one beta hydrogens, further substitution occurs. E.g. in CH_3COOH, chloroethanoic, dichloroethanoic and trichloroethanoic are formed.

8. Decarboxylation. Carboxylic acids are heated with solid sodium hydroxide and solid calcium oxide or excess concentrated sodium hydroxide solution. E.g.

$$CH_3COOH \xrightarrow[\text{heat}]{NaOH(s)/CaO(s)} CH_4 \qquad CH_3COOH \xrightarrow[\text{heat}]{\text{Excess Conc.NaOH(aq)}} CH_4$$
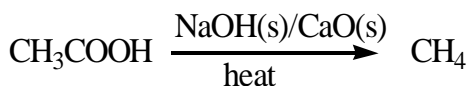
Note: Although carboxylic acids contain the carbonyl group, C=O, they don not undergo the addition reaction with, e.g. $NaHSO_3$ or the condensation reactions with, e.g. hydroxylamine, NH_2OH which are characteristic of this group in aldehydes and ketones.

This is because an orbital on the oxygen atom of the hydroxyl group which contains two unshared electrons in the carboxyl group interacts with the *p* orbital of the adjacent carbon atom. This provides extra delocalization in the molecule, as compared with that in aldehyde or ketone, which would be lost by addition of a reagent to the carboxyl group, so that a carboxylic acid is more resistant to addition than an aldehyde or a ketone.

Qn: Unlike aldehydes and ketones, carboxylic acids do not undergo addition reactions. Explain.

8.7.   Uniqueness of methanoic acid.

Methanoic acid differs from other carboxylic acids in the following ways.

1. It is dehydrated by concentrated sulphuric acid.

$$HCOOH \xrightarrow{\text{Conc. } H_2SO_4} CO + H_2O$$
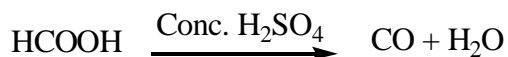
This is the basis of the laboratory preparation of carbon monoxide.

2. On warming, it reduces Fehling's or Benedict's solution to copper (I) oxide, a red solid while itself is oxidized to carbon dioxide.

$$HCOOH(aq) + 2Cu^{2+}(aq) + 4OH^-(aq) \longrightarrow \underset{\text{Red solid}}{Cu_2O(s)} + CO_2(g) + 3H_2O(l)$$
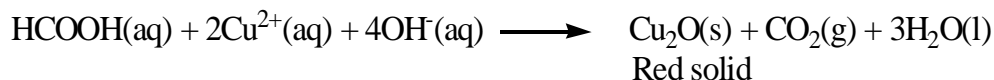
3. On warming, it reduces ammoniacal silver nitrate solution to silver and ammonia, while it is oxidized to carbon dioxide.

$$HCOOH(aq) + 2Ag(NH_3)_2^+(aq) + 2OH^-(aq) \longrightarrow \underset{\text{Silver Mirror}}{2Ag(s)} + CO_2(g) + 2H_2O(l) + 4NH_3(g)$$
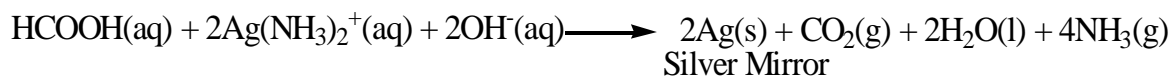
4. On warming, it reduces acidified potassium permanganate solution, (which is purple) to manganese (II), (which is colourless), while it is oxidized to carbon dioxide.

$$5HCOOH(aq) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5CO_2(g) + 8H_2O(l)$$

5. On warming, it reduces acidified potassium dichromate solution, (which is orange) to chromium (III), (which is green), while it is oxidized to carbon dioxide.

$$3HCOOH(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3CO_2(g) + 7H_2O(l)$$

Methanoic acid is able to undergo these reactions because it has an easily oxidized aldehydic group, H-C=O.

Qn: Name a reagent you can use distinguish between HCOOH and CH_3COOH. In each case, state your observations and write equation of reaction that takes place.

Qn: Methanoic acid was warmed with ammoniacal silver nitrate solution. State what was observed. Explain your observation (s) using a chemical equation.

Qn: Methanoic acid was warmed with Fehling's solution. State what was observed. Explain your observation (s) using a chemical equation.

Qn: Methanoic acid was warmed with acidified potassium manganate (VII) solution. State what was observed. Explain your observation (s) using a chemical equation.

Qn: Methanoic acid was warmed with acidified potassium dichromate (VI) solution. State what was observed. Explain your observation (s) using a chemical equation.

8.8. Uses of carboxylic acids.

1. Ethanoic acid is used in the manufacture of ethenyl ethanoate, required for the production of poly(ethenyl ethanoate) used to make things like office glue and envelop adhesive. Ethanoic acid is also used to manufacture ethanoic anhydride, required for making cellulose ethanoate used as a frame material for eye glasses, manufacture of cigarette filters and playing cards among others.

2. Long chain monocarboxylic acids are used in manufacture of soap.

3. They make up a series of essential fatty acids which are not produced by the body.

4. Used in food industry for the production of soft drinks, food products etc. e.g. ethanoic acid is used in making vinegar.

5. In pharmaceutical industries, organic acids are used in many drugs such as aspirin, phenacetin etc.

6. They are used in making dye stuff, perfumes and rayon.

8.9.   SOAPS AND DETERGENTS.

8.9.1. SOAP.

Soap is a sodium salt of a long chain carboxylic acid/ester.

a) How soap is manufactured.

Saponification.

A process by which soap is made by heating a fat/oil and sodium hydroxide solution (potassium hydroxide).

<u>Raw materials.</u>

➢ Vegetable oil from;	➢ Animal fats from;	➢ Sodium hydroxide/potassium hydroxide solution
• Simsim. • Ground nuts. • Sun flower. • Coco nut. • Castor oil.	• Mutton. • Lard.	

<u>Procedure.</u>

- The named fat/oil is mixed with concentrated potassium/sodium hydroxide solution.
- The mixture is heated until a thick white mass appears.
- The mixture is allowed to cool and during cooling, a suitable colour and perfume is added.
- Concentrated sodium chloride solution is then added to precipitate (seed out soap).
- The formed soap is now removed and moulded into desired forms.

$$CH_2-O\cdot COR$$
$$CH-O\cdot COR \quad +3NaOH \longrightarrow$$
$$CH_2-O\cdot COR$$
fat/oil

$$CH_2-O\cdot H$$
$$CH-O\cdot H \quad +3RCOONa$$
$$CH_2-O\cdot H \qquad \text{soap}$$
Propane-1,2,3-triol
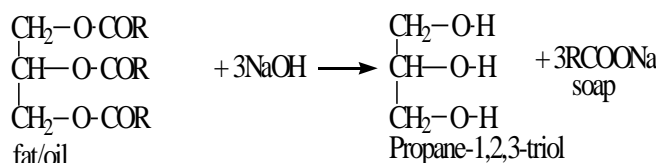
b) <u>Differences between fats and oils.</u>

- Fats are solids at room temperature while oils are liquids.

- Fats are saturated while oils are unsaturated.

c) <u>The cleansing action of soap (How soap works).</u>

- Soap first lowers the surface tension between water and the fat/oil. They do so because they contain both a water hating part called ***hydrophobic end*** (the alkyl chain) and a water loving part called ***hydrophilic end*** ($-COO^-$).
- Then, the dirt bonds to the hydrophobic end while water bonds to the hydrophilic end hence the dirt is removed from the cloth.

d) <u>Advantages and disadvantages of soap.</u>

Advantages	Disadvantages
• Biodegradable.	• Forms scum with hard water.
• Soap is cheap.	• It does not form lather easily with hard water.

8.9.2. <u>DETERGENTS.</u>

A detergent is a cleansing agent that does not form scum with hard water.

<u>How to make a detergent</u>

- Raw materials: **castor oil, concentrated sulphuric acid and sodium hydroxide.**
- Concentrated sulphuric acid is added to ice cold castor oil in a beaker while stirring.
- The acid is added until the mixture turns from yellow to brown.
- Concentrated sodium hydroxide solution is added to the mixture forming the detergent.

NB: The commonest detergents contained alkyl benzene sulphonates made from a polymer of propene by a Friedel-Crafts alkylation reaction; followed by sulphonation and neutralisation of the sulphonic acid with sodium hydroxide.

$$CH_3 \left(\overset{\overset{CH_3}{|}}{CH}-CH_2 \right)_3 CH=CH_2 \ + \ \bigcirc \longrightarrow CH_3 \left(\overset{\overset{CH_3}{|}}{CH}-CH_2 \right)_3 \overset{\overset{CH_3}{|}}{CH}-\bigcirc$$

1. Fuming H_2SO_4
2. $NaOH_{(aq)}$

$$CH_3 \left(\overset{\overset{CH_3}{|}}{CH}-CH_2 \right)_3 \overset{\overset{CH_3}{|}}{CH}-\bigcirc-SO_2^-\bar{O}N\overset{+}{a}$$
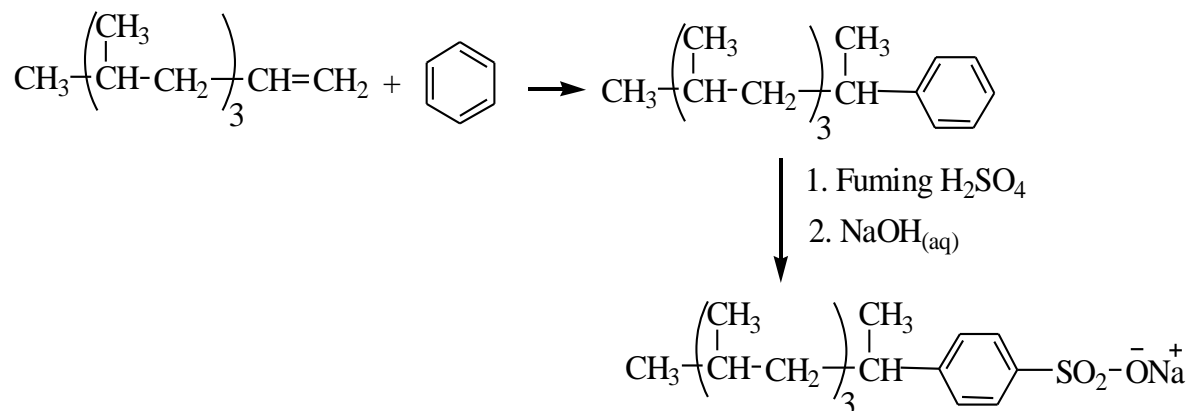
How a detergent works.

See action of soap.

Advantages of detergents over soap.

- They are more soluble in cold water than soap.
- They do not form scum with hard water.
- They form more lather with water than soap.

Disadvantages of detergents over soap.

- They are non-biodegradable hence cause pollution.
- They cause foaming in rivers and streams.
- They are expensive.

CHAPTER 8: ESTERS.

These are organic compounds that conform to the general formular RCOOR' where R and R' are alkyl or aryl groups.

8.1. Nomenclature of esters.

They are named as alkyl carboxylates.

Examples.

$H\text{-}COO\text{-}CH_3$	Methyl methanoate	$CH_3CH_2\text{-}COO\text{-}CH_3$	Methyl propanoate

H-COO-CH$_2$CH$_3$	Ethyl methanoate	CH$_3$CH$_2$-COO-CH$_2$CH$_3$	Ethyl propanoate
CH$_3$-COO-CH$_3$	Methyl ethanoate	C$_6$H$_3$-COO-CH$_3$	Methyl benzoate

8.2. Physical properties of esters.

1. Esters are neutral liquids with pleasant, fruity smells.

2. They are insoluble in water but are soluble in organic solvents.

3. Their mps and bps are below those of corresponding carboxylic acids because ester molecules, unlike acid molecules, are not associated by hydrogen bonding.

8.3. Laboratory synthesis of esters.

1. Esterification.

By the reaction between alcohols and organic acids in presence of a strong acid like concentrated sulphuric acid as a catalyst. E.g.

$$CH_3OH + CH_3COOH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOCH_3 + HCl$$
methanol   methyl ethanoate
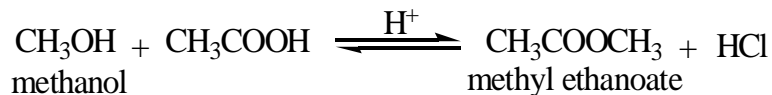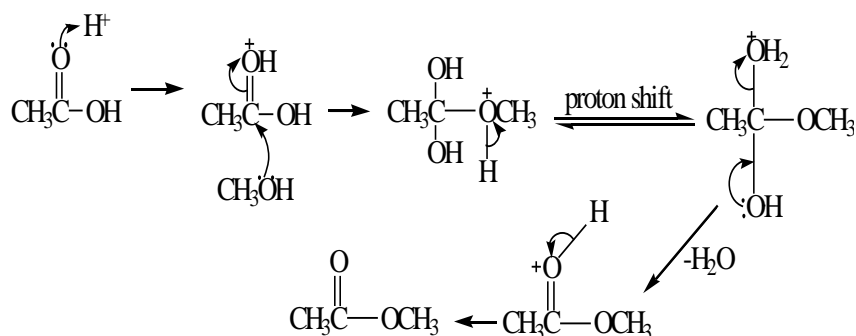
Mechanism:

2. By the reaction between alcohols and acid chlorides e.g. ethanoyl chloride or acid anhydrides e.g. ethanoic anhydride. For example.

$$CH_3OH + CH_3COCl \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOCH_3 + HCl$$
methanol   ethanoyl   methyl ethanoate
    chloride

Mechanism:

$$CH_3\overset{O}{\underset{CH_3\ddot{O}H}{\overset{\|}{C}}}-Cl \longrightarrow CH_3\overset{\bar{O}}{\underset{Cl}{\overset{\|}{C}}}-\overset{+}{\underset{H}{O}}CH_3 \xrightarrow{-Cl^-} CH_3\overset{O}{\overset{\|}{C}}-\overset{+}{\underset{H}{O}}CH_3 \xrightarrow{-H^+} CH_3\overset{O}{\overset{\|}{C}}-OCH_3$$

EER.

$$CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CH_3OH \longrightarrow \ ?$$
Ethanoic anhydide
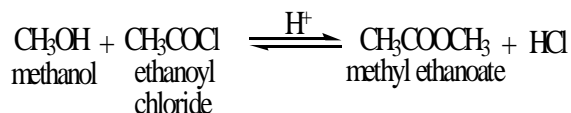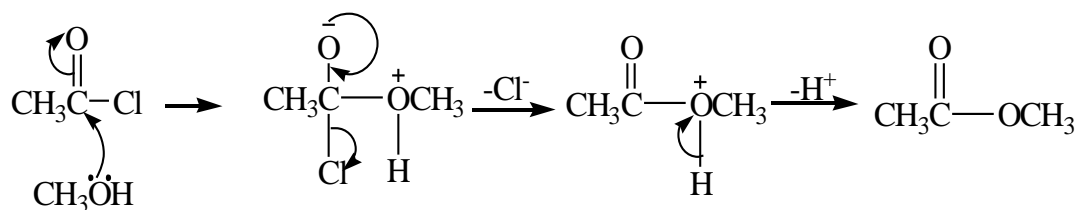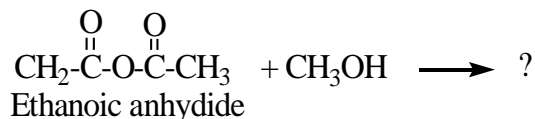
3. By the reaction between silver salts of organic acids e.g. silver ethanoate and halogen alkanes e.g. chloroethane. For example.

$$CH_3\overset{O}{\overset{\|}{C}}\text{-}OAg + CH_3CH_2Cl \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_3 + AgCl$$

Mechanism.

$$CH_3\overset{O}{\overset{\|}{C}}\text{-}OAg \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\text{-}\bar{O} + Ag^+$$

$$\begin{array}{c} CH_3CH_2\text{—}Cl \\ \\ CH_3\overset{O}{\overset{\|}{C}}\text{-}O \end{array} \underset{\xrightarrow{\text{Slow}}}{\rightleftharpoons} \left[\begin{array}{c} O \\ \| \\ CH_3\underset{Cl}{CH}\text{- - - -}O\overset{}{C}\text{-}CH_3 \end{array} \right]^- \xrightarrow{\text{Fast}} CH_3\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_3 + Cl^-$$

$$Ag^+ + Cl^- \longrightarrow AgCl$$
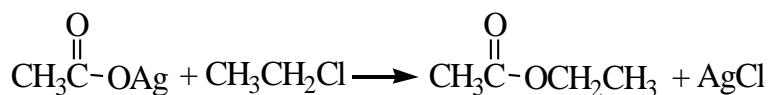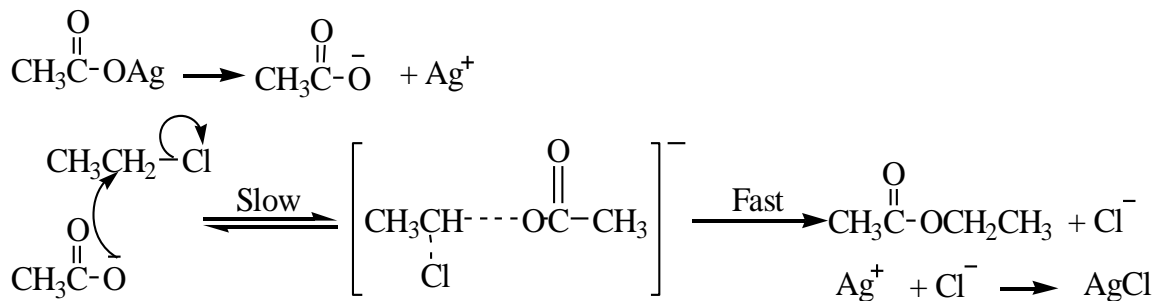
8.4.   Reactions of esters.

1. Hydrolysis.

Esters are hydrolysed by heating with water and a mineral acid as a catalyst. The reaction is the exact opposite of esterification.

For example.

Acid catalysed hydrolysis.

$$CH_3COOCH_3 + H_2O \underset{\xleftarrow{\hspace{1cm}}}{\overset{H^+}{\rightleftharpoons}} CH_3COOH + CH_3OH$$

Mechanism.

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

$$H_2O{:}\!\!\curvearrowleft\overset{+}{C}H_3 \rightleftharpoons CH_3\overset{+}{O}\!\!\diagup^{H}_{\diagdown H}$$

$$CH_3\overset{+}{O}\diagdown^{H}_{H\curvearrowleft :OH_2} \rightleftharpoons CH_3OH + H_3O^+$$

The reaction mechanism diagrams for acid catalysed hydrolysis are shown.

$$CH_3\overset{O{:}\curvearrowleft H\curvearrowleft\overset{+}{O}H_2}{\underset{}{C}}{-}O{-}CH_3 \rightleftharpoons CH3\overset{\overset{+}{O}H}{\underset{}{C}}{-}O{-}CH_3 + H_2O$$

$$CH3\overset{\overset{+}{O}H}{\underset{}{C}}{-}O{-}CH_3 \rightleftharpoons CH_3\overset{O}{\underset{}{C}}{-}OH + \overset{+}{C}H_3$$
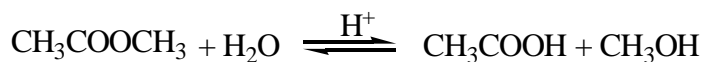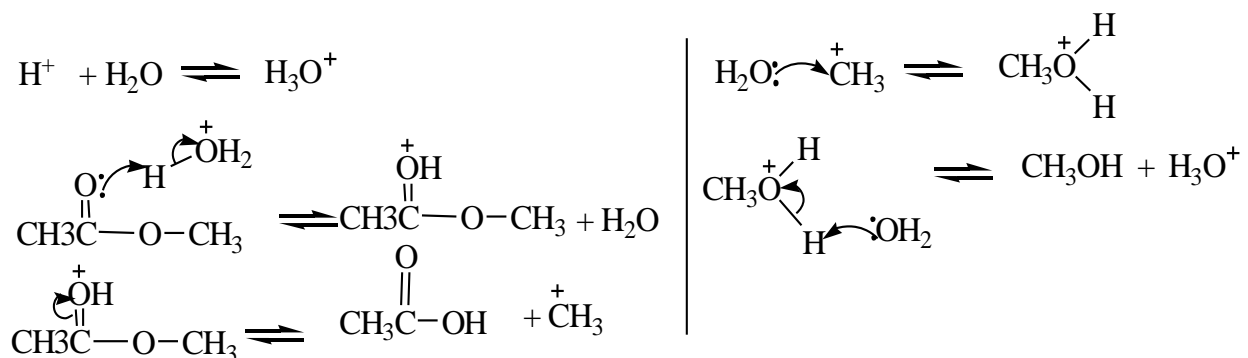
Base catalysed hydrolysis.

The reaction proceeds faster in the alkaline conditions. When the acid molecules are formed, OH⁻ ions react with them to form a salt. Salt formation removes the acid molecules from the equilibrium mixture. The hydrolysis reaction therefore goes to completion in the presence of a base. The base is used up in the reaction.

$$CH_3COOCH_3 + H_2O \overset{\bar{O}H}{\rightleftharpoons} CH_3CO\bar{O} + CH_3OH$$

Mechanism.

$$CH_3\overset{O}{\underset{}{C}}{-}OCH_3 \rightleftharpoons CH_3\overset{\bar{O}{:}}{\underset{OH}{C}}{-}OCH_3 \rightleftharpoons CH_3\overset{O}{\underset{}{C}}{-}OH + \bar{O}CH_3$$

$$CH_3\overset{O}{\underset{}{C}}{-}O\curvearrowleft H\curvearrowleft :\bar{O}CH_3 \longrightarrow CH_3\overset{O}{\underset{}{C}}{-}\bar{O} + CH_3OH$$
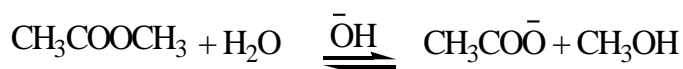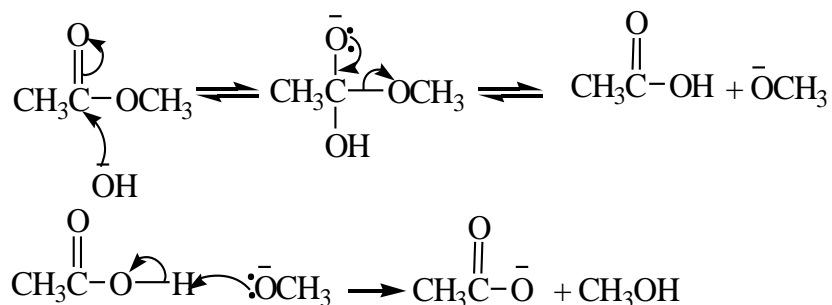
2. Reduction.

+ Like organic acids, esters are reduced with lithium tetrahydridoaluminate in dry ether, LiAlH₄ but not with sodium tetrahydridoborate, NaBH₄ to form alcohols.

$$CH_3CH_2COOCH_3 \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2CH_2OH + CH_3OH$$
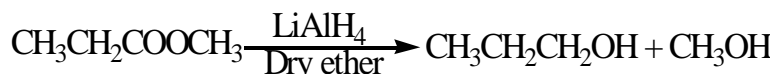
+ Esters can also be reduced by sodium in ethanol to form alcohols.

$$CH_3CH_2COOCH_3 \xrightarrow[\text{Ethanol}]{Na} CH_3CH_2CH_2OH + CH_3OH$$
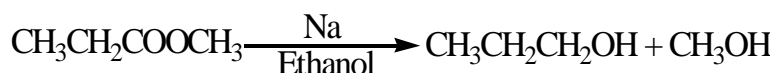
3. Ammonolysis.

Esters react with ammonia, either in concentrated aqueous or alcoholic solution, to form acid amides.

$$CH_3CH_2COOCH_3 \xrightarrow{\text{Conc. NH}_3(aq)} \underset{\text{Propanamide}}{CH_3CH_2CONH_2} + CH_3OH$$

$$CH_3CH_2COOCH_3 \xrightarrow{\text{NH}_3/\text{Ethanol}} \underset{\text{Propanamide}}{CH_3CH_2CONH_2} + CH_3OH$$
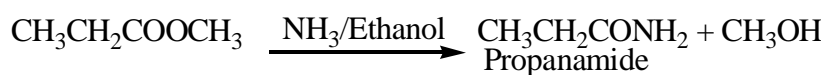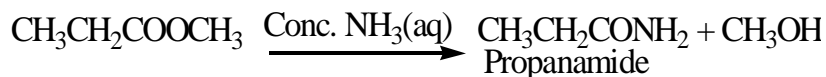
Mechanism:
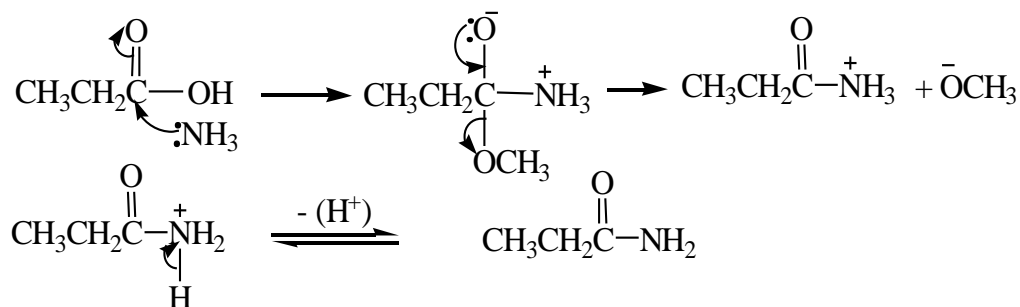
8.5.   Uses of esters.

1) Used to prepare artificial flavouring essences and scents e.g. 3-metrhylbutyl ethanoate to prepare pear essence and ethyl methanoate to prepare raspberry essence.

2) Used as solvents and special lubricants.

3) Waxes are esters of higher carboxylic acids and higher alcohols e.g. beer wax is $C_{15}H_{31}COOC_{31}H_{63}$.

4) Fats and oils are esters of higher carboxylic acids and propane-1,2,3-triol, some are used to make soap.

CHAPTER 9: AMINES.

These are organic compounds that conform to the general formular $C_nH_{2n+1}NH_2$ where n is 1, 2... The functional group is the amino group ($-NH_2$).

6.1: Classes of Amines.
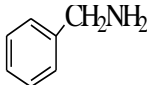
There are 3 classes of amines namely; primary (1º), secondary (2º) and tertiary (3º) amines.

✓ **Primary amines:** These have one alkyl/aryl group attached to the carbon atom that has the amino group. i.e. $R-CH_2-NH_2$.

✓ **Secondary amines:** These have two alkyl/aryl groups attached to the carbon atom that has the amino group. i.e.
$$R-\underset{\underset{R}{|}}{CH}-NH_2 \ .$$

✓ **Tertiary amines:** These have three alkyl/aryl groups attached to the carbon atom that has the amine group. i.e.

$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-NH_2 \ .$$
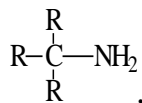
6.2: Nomenclature of Amines.

Simple amines are usually named by adding the word "amine" to the names of the groups to which the nitrogen atom is attached. Examples.

CH_3NH_2	Methylamine
$CH_3CH_2NH_2$	Ethylamine
CH_3NHCH_3	Dimethylamine
$CH_3CH_2NHCH_3$	Ethylmethylamine
$(CH_3)_3N$	Trimethylamine

$C_6H_5-CH_2NH_2$ Phenylmethylamine (benzylamine)

Note: *an alternative nomenclature employs a prefix "amino".*

Examples.

CH_3NH_2 aminomethane

$CH_3CH_2NH_2$ aminoethane

$CH_3CHCH_2CH_3$ 2-aminobutane
  |
  NH_2

      CH_3
      |
$CH_3CCH_2CH_3$ 2-amino-2-methybutane
      |
      NH_2

6.3.   Synthesis of amines.

1. By heating halogen alkanes with ammonia in an alcohol.

$$R-Br \xrightarrow[\text{heat}]{NH_3/alcohol} R-NH_2 + HBr$$
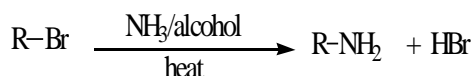
Note:

✓ The method is not suitable because a mixture of primary, secondary and tertiary amines and quaternary ammonium salts is obtained. The hydrogen bromide evolved reacts with the ammonia and the formed amines to form salts.

✓ Aromatic amines cannot be made in this way because aryl halides are unreactive towards ammonia.

2. Reduction of a nitro compound using lithium tetrahydridoaluminate ($LiAlH_4$) in dry ether or hydrogen, catalysed by nickel.

$$R-NO_2 \xrightarrow{LiAlH_4/dry\ ether} R-NH_2$$

$$R-NO_2 \xrightarrow[\text{Heat}]{H_2/Ni\ cat} R-NH_2 + H_2O$$
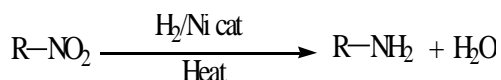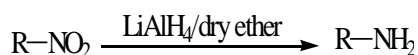
NB: Aromatic amines are not reduced in this way.

Nitrobenzene is reduced to aminobenzene by a mixture of tin in concentrated hydrochloric acid followed by hot sodium hydroxide.
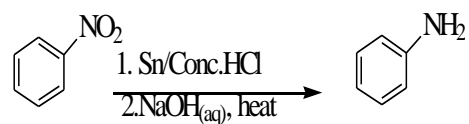
3. Reduction of nitriles lithium tetrahydridoaluminate ($LiAlH_4$) in dry ether.

$$R-CN \xrightarrow{LiAlH_4/dry\ ether} R-CH_2NH_2$$
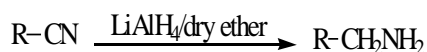
4. Reduction of amides using lithium tetrahydridoaluminate ($LiAlH_4$) in dry ether.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{\quad LiAlH_4/dry\ ether \quad} R-CH_2NH_2$$
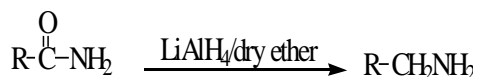
5. By Hofmann degradation reaction. The amide is heated with bromine and concentrated sodium hydroxide, it yields a primary amine with a reduced chain.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[heat]{\quad Br_2/NaOH_{(aq)} \quad} R-NH_2$$
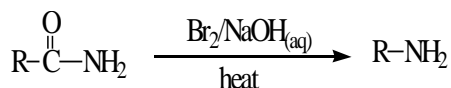
6.4. Physical properties of amines.

a) Lower aliphatic amines are gases.

b) Their bps are lower than those of corresponding alcohols. Because the N-H bond is less polar than O-H bond in alcohols hence amines form weaker intermolecular hydrogen bonds than alcohols.

c) Lower amines smell like ammonia. Higher members have a smell of "bad" fish because amines are formed when proteins decompose. Higher amines are found in decaying meat.

d) They are soluble in water due to ability to form hydrogen bonds.

e) Aromatic amines are liquids or solids with high bps. They have a characteristic smell and are soluble in organic solvents but almost soluble in water.

6.5. Chemical properties of amines.

Basicity of amines.

Amines are bases. Amines, like ammonia, give alkaline solution in water as a result of the equilibrium:

$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + \overset{-}{O}H$$
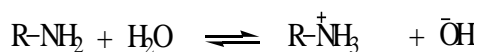
Amines are bases because they possess a lone pair of electrons on the nitrogen atom that accepts a proton. The basic strength of amines depends on how available is the lone pair of electrons to accept a proton. The higher the positive inductive effect of the alkyl group on the amines, the more available the lone pair of electrons and hence the more basic the amine. Hence the basicity of the amines is in the order $3^o >> 2^o > 1^o$.

The basic strength can also be determined using the base dissociation constant, K_b of the amine. The larger the K_b value, the stronger the basic nature of the amine. Hence the smaller the pK_b value, the stronger the base since $pK_b = -\log K_b$.

Effect of substituent group on the basicity of amines.

a) Electron donating group.
The availability of the unshared electron pair on nitrogen, we expect to see an increase in basic strength in the order $NH_3 < RNH < R_2NH < R_3N$, due to the increasing positive inductive effect of successive alkyl groups.
Introduction of an alkyl group into ammonia increases the basic strength markedly as expected. The introduction of a second alkyl group further increases the basic strength, but the net effect of introducing the second alkyl group is very much less marked than with the first. The introduction of a third alkyl group to yield a tertiary amine, however, actually decreases the basic strength. This is due to the fact that the basic strength of an amine in water is determined not only by electron - availability on the nitrogen atom, but also by the extent to which the cation, formed by uptake of a proton, can undergo solvation, and so become stabilized. The more the hydrogen atoms attached to nitrogen in the cation, the greater the possibilities of powerful solvation via hydrogen bonding between these ions and water, thus on going along the series
$NH_3 < RNH < R_2NH < R_3N$, the inductive effect will tend to increase the basicity, but progressively less stabilisation of the cation by hydration will occur which will tend to decrease the basicity. The net replacing effect of introducing successive alkyl groups thus becomes progressively smaller, and an actual changeover takes place on going from a secondary to a tertiary amine. For this explanation, no such changeover should be observed if measurements of basicity are made in a solvent in which hydrogen - bonding cannot take place; it has, indeed, been found that in chlorobenzene the order of basicity of the butylamines is
$BuNH < Bu_2NH < Bu_3N$.

b) Electron withdrawing group.
The effect of introducing electron withdrawing groups, e.g. Cl, NO_2, close to a nitrogen atom decreases the basicity, due to their electron withdrawing inductive effect. Thus the amine is found to be virtually none – basic.
This can well be explained on the basis of more 's' character on lone pair of N.
The change is also pronounced with C=O, for not only is the nitrogen atom, with its electron pair, bonded to an electron withdrawing group through an *SP* hybridised carbon atom but an electron withdrawing mesomeric effect can also operate: Thus

amides are found to be only very weakly basic in water [pKb for ethanamide (acetamide) is » 0.5], and if two C=O groups are present the resultant imides, far from being basic, are often sufficiently acidic to form alkali metal salts, e.g. benzene-1,2–dicarboximide.

Aromatic Bases: (Aromatic Amines)

Aniline is a very weak base compared with ethylamine. This is because the lone pair of electrons on the nitrogen atom in phenylamine involves in the delocalization with the pi-electrons of the ring, this makes the lone pair of electrons on the nitrogen atom less available to accept a proton. Ethylamine on the other hand, has two methyl groups that have positive inductive effect which increase the electron density around the nitrogen atom, hence increases availability of the lone pair of electrons to accept a proton.

A group with a more powerful (electron - withdrawing) inductive effect, e.g. NO_2 is found to have rather more influence. Electron withdrawal is intensified when the nitro group is in the o- or p-position, for the interaction of the unshared pair of the amino nitrogen with the delocalized pi electron system of the benzene is then enhanced.

Sample question.

1. Explain the following:

a) The basicity of methylamine, dimethylamine and trimethylamine in benzene is in the order;

$(CH_3)_3N \gg (CH_3)_2NH > CH_3NH_2$

b) The basicity of methylamine, dimethylamine and trimethylamine in water is in the order;

$(CH_3)_3N < (CH_3)_2NH > CH_3NH_2$

c) Ethylamine is a stronger base than ammonia.

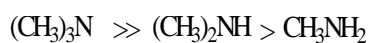d) The pK_b of ammonia 4.8 while that of ethylamine is 3.4.

e) Ethylamine is a stronger base than phenylamine.

This is because the lone pair of electrons on the nitrogen atom in phenylamine involves in the delocalization with the pi-electrons of the ring, this makes the lone

pair of electrons on the nitrogen atom less available to accept a proton. Ethylamine on the other hand, has two methyl groups that have positive inductive effect which increase the electron density around the nitrogen atom, hence increases availability of the lone pair of electrons to accept a proton.

Reactions of amines.

1. Reaction with halogen alkanes.

Amines like concentrated ammonia react with halogen alkanes to form a mixture of amines. E.g.

a. CH_3I $\xrightarrow[100°C]{Conc.NH_3}$ CH_3NH_2 (Methylamine) + HI

Mechanism:

$CH_3\overset{\frown}{-}I$
$\overset{\curvearrowleft}{:}NH_3$
+

$\longrightarrow$ $CH_3\overset{+}{N}H_3$ + I^-

$CH_3\overset{+}{N}H_2$ $\longrightarrow$ CH_3NH_2 + H^+
H

H^+ + I^- $\longrightarrow$ HI

b. $CH_3CH_2NH_2$ $\xrightarrow[Pressure]{CH_3Cl}$ $CH_3CH_2NHCH_3$ (Ethylmethylamine) + HCl

Mechanism:

$CH_3\overset{\frown}{-}Cl$
$\overset{\curvearrowleft}{:}NH_2CH_2CH_3$

$\longrightarrow$ $CH_3CH_2\overset{+}{N}H_3$ + Cl^-

$CH_3CH_2\overset{+}{N}H_2$ $\longrightarrow$ $CH_3CH_2NHCH_3$ + H^+
H

H^+ + Cl^- $\longrightarrow$ HCl
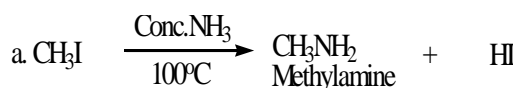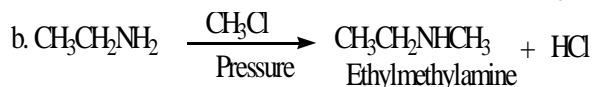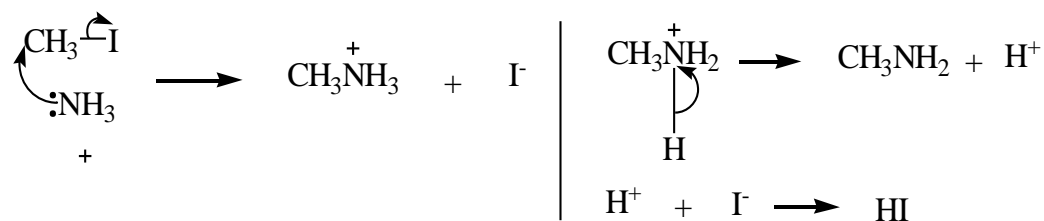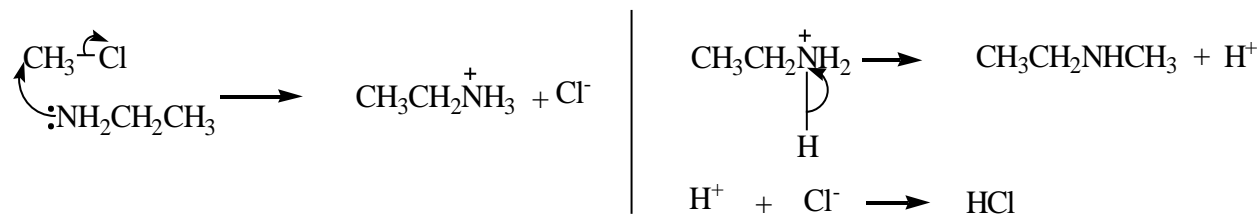
2. Reaction with acid chlorides.

Amines react with acyl chlorides like ethanoyl chloride to form amides. E.g.

$CH_3CH_2NH_2$ (ethylamine) + CH_3COCl (ethanoyl chloride) $\longrightarrow$ $CH_3CH_2NHCOCH_3$ (N-ethylethanamide) + HCl

Mechanism:

The mechanism shows:

$$CH_3CH_2\overset{..}{N}H_2 + \underset{CH_3}{\overset{O}{\overset{\|}{C}}}-Cl \longrightarrow CH_3CH_2\overset{+}{N}H_2\overset{O}{\overset{\|}{C}}CH_3 \quad CH_3CH_2\overset{+}{N}HCCH_3 \longrightarrow CH_3CH_2NH\overset{O}{\overset{\|}{C}}CH_3 + H^+$$
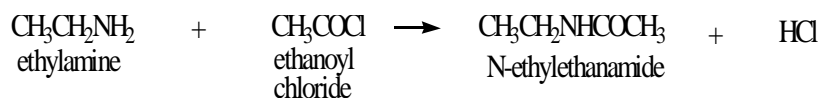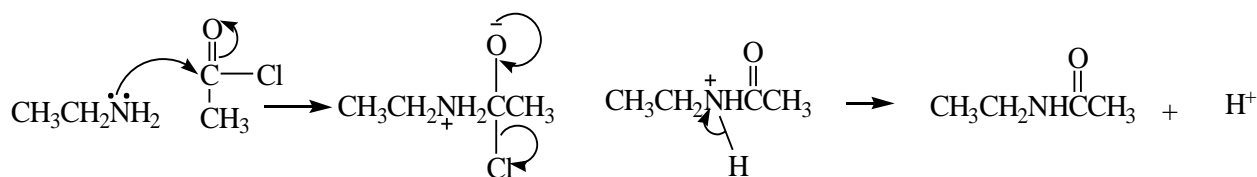
Qn: Complete and write mechanism.

$$CH_3CH_2NH_2 + \bigodot\!\!-COCl \longrightarrow$$
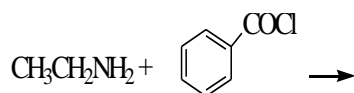
6.6. Distinguishing between classes of amines.

Reagent.

Sodium nitrite and concentrated hydrochloric acid at 0ºC. (Nitrous acid, HNO_2. Nitrous acid is unstable and so formed and used in situ)

Observations.

- *$1º$ aliphatic amine give bubbles of a colourless gas (nitrogen gas). E.g.*

$$CH_3CH_2NH_2 \xrightarrow[0ºC]{NaNO_2/Conc.HCl} CH_3CH_2OH + N_2 + H_2O$$
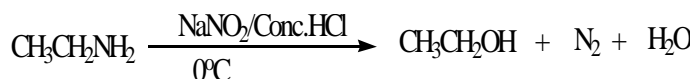
- *$1º$ aromatic amine give colourless solutions of diazonium salts. E.g.*

$$\bigodot\!\!-NH_2 \xrightarrow[0ºC]{NaNO_2/Conc.HCl} \bigodot\!\!-N_2Cl + 2H_2O$$

Benzenediazonium chloride
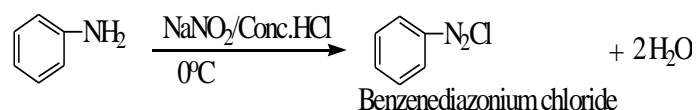
- *$2º$ amines, both aliphatic and aromatic give yellow oily products called nitroso compounds. E.g.*

$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} \xrightarrow[0ºC]{NaNO_2/Conc.HCl} \underset{\text{N-nitrosodimethylamine}}{(CH_3)_2N-N=O}$$
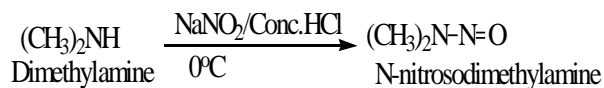
- *$3º$ amines show no observable change.*

Qn: Name a reagent that can be used to distinguish between the following. In each case, give the observations, and write equation of reaction if the reagent is used.

a. $CH_3CH_2NH_2$ and $(CH_3)_2NH$

b. $CH_3CH_2NH_2$ and $\bigodot\!\!-NH_2$
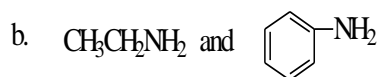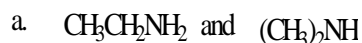
6.7. Uses of amines.

Amines are used in manufacture of;

- Plastics e.g. nylon-6,6.

- Dye-stuffs e.g. azo dyes from primary aromatic amines.

- Medicines e.g. Paludrine, an antimalarial.

- Amines are used as inhibitors to prevent deterioration of rubber through oxidation by atmospheric oxygen.

CHAPTER 10: POLYMERS AND POLYMERISATION.

A polymer is a substance of high molecular mass built from many repeating monomers which are connected by covalent bonds.

Polymerisation is a process by which monomers link to form a polymer with or without loss of small molecules.

10.1. Types of Polymerization.

1. Addition Polymerization.

Linking of many unsaturated monomers to form a polymer whose molecular mass is a simple integral multiple of the mass of the monomer without loss of any small molecule. The polymers are called *addition polymers.*

Examples of addition polymers.

a) **Polyethene**

Low density polyethene is formed when ethene is heated to $200^{\circ}C$ and 1500 atmosphere in presence of oxygen as catalyst.

$$nCH_2=CH_2 \xrightarrow[\text{O}_2 \text{ cat.}]{200^{\circ}C/1500 \text{ atm.}} \left(CH_2-CH_2 \right)_n ^*$$
$$\text{low density polyethene}$$
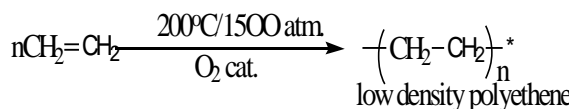
High density polyethene is made by passing ethene in an aromatic hydrocarbon solvent containing triethylaluminium and titanium (IV) chloride catalyst at $60^{\circ}C$ and 1 atm.

$$nCH_2=CH_2 \xrightarrow[(CH_3)_3Al + TiCl_4 \text{ cat.}]{60^{\circ}C/1atm.} \left(CH_2-CH_2 \right)_n ^*$$
$$\text{high density polyethene}$$
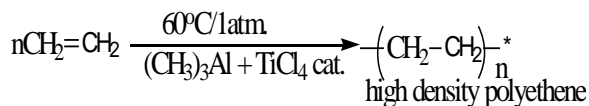
High density polyethene has a greater rigidity and higher softening point than low density polyethene.

b) Polypropene

Formed by passing propene in heptane as a solvent containing a trialkylaluminium compound and titanium (III) chloride at 100°C and 10 atmosphere.

$$nCH_3CH_2{=}CH_2 \xrightarrow[\text{100°C, 10 atm.}]{\text{AlR}_3 + \text{TiCl}_3 \text{ as cat.}} \left(CH_2{-}CH_2 \right)^{*}_{n} \overset{CH_3}{|}$$

polypropene
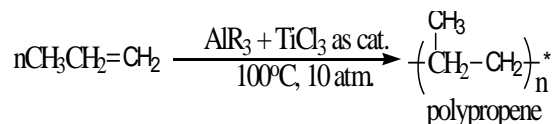
c) Polyphenylethene (polystyrene).

Formed by heating phenylethene (styrene) with dibenzoyl peroxide to initiate the polymerisation to 100°C.

$$n\;C_6H_5{-}CH{=}CH_2 \xrightarrow[\text{100°C}]{\text{dibenzoyl peroxide cat.}} {*}{-}\left(CH_2{-}CH_2 \right)^{*}_{n}$$

polystyrene
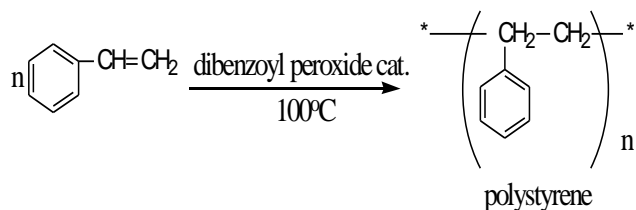
d) Polychloroethene (Polyvinyl chloride, PVC)

Formed by heating chloroethene (vinyl chloride) in an inert solvent with dibenzoyl peroxide to initiate the polymerisation.

$$nCH_2{=}CHCl \xrightarrow[\text{heat}]{\text{dibenzoyl peroxide cat.}} \left(\underset{Cl}{CH}{-}CH_2 \right)^{*}_{n}$$

PVC
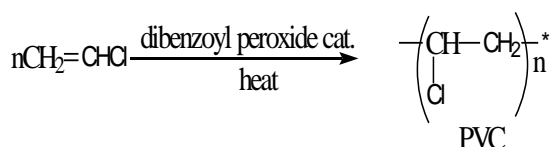
e) Polytetrafluoroethene (PTFE) (Teflon).

PTFE is formed by heating tetrafluoroethene under pressure in the presence of ammonium peroxosulphate as catalyst.

$$n\;CF_2{=}CF_2 \xrightarrow[\text{heat}]{(NH_4)_2S_2O_8 \text{ as cat.}} {*}\left(\underset{F}{\overset{F}{C}}{-}\underset{F}{\overset{F}{C}} \right)_{n}{*}$$

PTFE
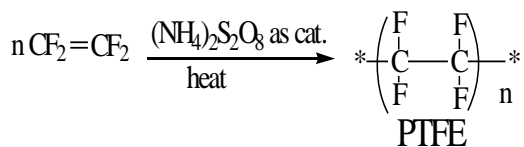
f) Poly (methyl 2-methylpropenoate), Perspex or Diakon.

Formed by heating Methyl 2-methylpropenoate with dibenzoyl peroxide to initiate the polymerisation to 100ºC.

Perspex
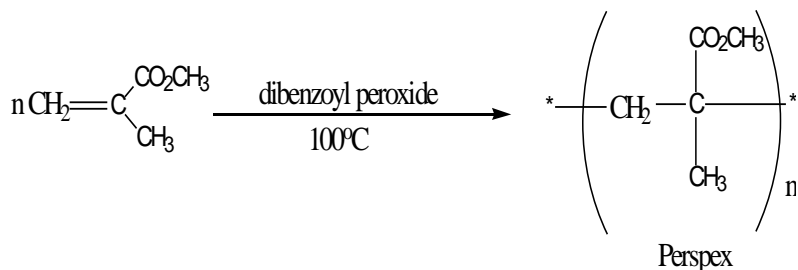
Summary of physical properties and uses of these addition polymers.

Polymer	Monomer	Physical properties of polymer	Uses of polymer
Polyethene $-(CH_2-CH_2)_n^*$	Ethene $CH_2=CH_2$	Less dense than water. Does not corrode. Insoluble in all solvents Unreactive with common reagents.	As insulator. For making packagings like bags. As a film for coating.

Polypropene $$\left(\text{CH}_2-\text{CH}_2\right)_n^{*}$$ with CH_3	Propene $\text{CH}_3\text{CH}=\text{CH}_2$	Stronger than polyethene. Lighter than polyethene. Has a higher softening point than polyethene. Have higher tensile strength.	For making carpets. For making ropes. For making drinking straws. For making packagings such as plastic bottles.
Polystyrene (polyphenylethene) $$*-\left(\text{CH}_2-\text{CH}_2\right)_n'$$	Phenylethene $-\text{CH}=\text{CH}_2$	Less dense than water. Does not corrode. Insoluble in most solvents.	For making light-weight packagings. For making house hold goods like egg boxes. As a lining material for refrigerators.
Polyvinyl chloride, PVC $$\left(\overset{|}{\underset{Cl}{\text{CH}}}-\text{CH}_2\right)_n^{*}$$	Chloroethene $\text{CH}_2=\text{CHCl}$	Water proof. Non-biodegradable. Resistant to fire. Resistant to weather. Resistant to chemicals.	As insulator for cables. For making artificial leather. For making house hold goods like curtains and table cloths. Used for guttering and water-down pipes.

Polytetrafluoroet hene PTFE $*\left(\begin{array}{cc} F & F \\ | & | \\ C & C \\ | & | \\ F & F \end{array}\right)_n*$	Tetrafluoroethene $CF_2{=}CF_2$	Resistant to chemicals. Has a higher softening point. Has anti-stick properties.	For making gaskets and seals. As a surface coating for cooking equipment.
Poly (methyl 2-ethylpropenoate) $*\left(\begin{array}{c} CO_2CH_3 \\ | \\ CH_2{-}C{-} \\ | \\ CH_3 \end{array}\right)_n*$	Methyl 2-methylpropenoate $CH_2{=}C\begin{array}{l} CO_2CH_3 \\ CH_3 \end{array}$	It's light. It's strong. It's transparent.	For making transparent packagings. Making aeroplane windows. Making lenses. Making corrugated roof lights. Making car wind screens.

2. Condensation Polymerization.

Linking of two types of bifunctional monomers to form a polymer with loss of small molecules like water, methanol, hydrogen chloride etc. The polymers are called *condensation polymers.*

Examples of condensation polymers.

a) Nylon-6.6

Made by heating hexane-1,6-dioic acid with hexane-1,6-diamine. Water is the small molecule lost. It's called nylon-6.6 because each of the monomers has six carbon atoms. It's a polyamide.

$$n\,HOOC(CH_2)_4COOH + n\,H_2N(CH_2)_6NH_2 \xrightarrow{\text{heat}} *\left(\begin{array}{cccc} O & O & H & H \\ || & || & | & | \\ C(CH_2)_4C & - & N(CH_2)_6N \end{array}\right)_n* + n\,H_2C$$
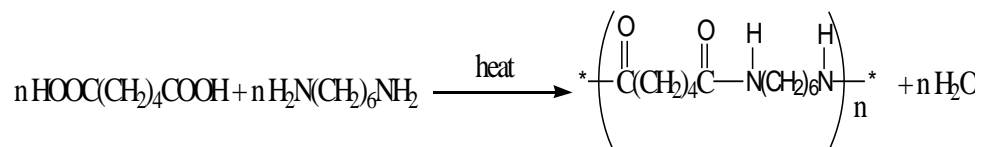
Other forms of nylon with a peptide link include nylon-6.10.

Nylon-6.10, prepared by heating decane-1,10-dioic acid with hexane-1,6-diamine has similar properties to nylon-6.6.

$$n\,HOOC(CH_2)_8COOH + n\,H_2N(CH_2)_6NH_2 \xrightarrow{heat} *\left(\!\!\begin{array}{c} O \quad\;\; O \;\; H \quad H \\ \| \qquad \| \quad | \qquad | \\ C(CH_2)_8C - N(CH_2)_6N \end{array}\!\!\right)_{\!n}^{\!*} + n\,H_2O$$
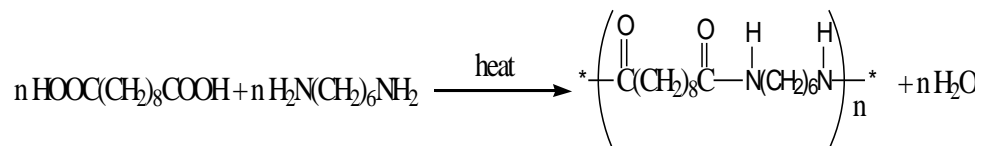
Nylon-6.10, is also prepared by heating decanedioyl chloride with hexane-1,6-diamine. Hydrogen chloride is lost.

$$n\,ClOC(CH_2)_8COCl + n\,H_2N(CH_2)_6NH_2 \xrightarrow{heat} *\left(\!\!\begin{array}{c} O \quad\;\; O \;\; H \quad H \\ \| \qquad \| \quad | \qquad | \\ C(CH_2)_8C - N(CH_2)_6N \end{array}\!\!\right)_{\!n}^{\!*} + n\,HCl$$
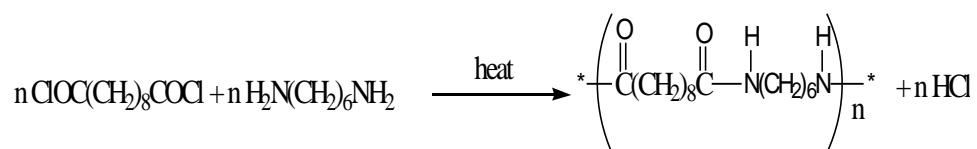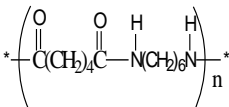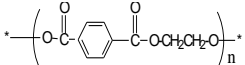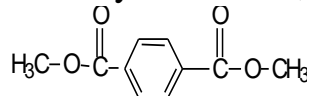
b) Terylene (Dacron).

Made by reacting dimethylbenzene-1,4-dioic acid with ethane-1,2-diol. It's a polyester. Methanol is lost.

$$n\,CH_3-O-\overset{\overset{\displaystyle O}{\|}}{C}-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle O}{\|}}{C}\cdot O\cdot CH_3 + n\,HO\text{-}CH_2CH_2\text{-}OH \longrightarrow *\left(\!\!O-\overset{\overset{\displaystyle O}{\|}}{C}-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle O}{\|}}{C}-O\text{-}CH_2CH_2\text{-}O\!\!\right)_{\!n}^{\!*} + n\,CH_3OH$$
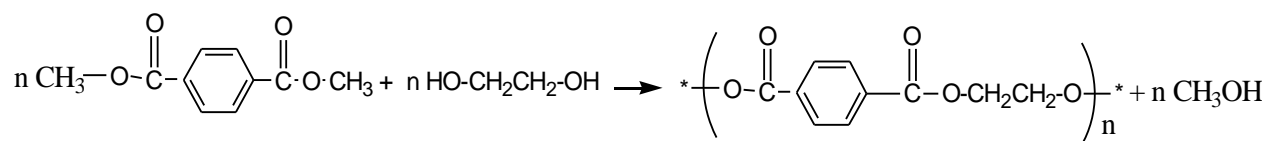
Summary of condensation polymers.

Polymer	Monomer	Uses
Nylon-6.6 $$*\!\!\left(\!\!\begin{array}{c} O \;\; O \; H \; H \\ \| \;\;\; \| \; | \;\; | \\ C(CH_2)_4C - N(CH_2)_6N \end{array}\!\!\right)_{\!n}^{\!*}$$	hexane-1,6-dioic acid $HOOC(CH_2)_4COOH$ and hexane-1,6-diamine. $H_2N(CH_2)_6NH_2$	Making clothes and woolen carpets. Making articles such as brushes. Making fishing nets and ropes.

| Terylene (Dacron)

 $*-\left(O-\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}-OCH_2CH_2-O\right)_n-*$ | dimethylbenzene-1,4-dioic acid

 $H_3C-O-\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}-O-CH_3$ and

 Ethane-1,2-diol.

 $HO-CH_2CH_2-OH$ | Making clothes and woolen carpets. |

Differences between addition and condensation polymers.

Addition polymers	Condensation polymers
Monomers have similar functional group.	Monomers have different functional group.
Monomers are unsaturated.	Monomers are saturated.
Polymer's RMM is a multiple of the monomer's RMM.	Polymer's RMM is not a multiple of the monomer's RMM due to loss of molecules.
Usually linear.	Are nonlinear.

10.2. Classes of Polymers.

a) Natural polymers.

Polymers whose formation is not controlled by man.

They include: natural rubber, protein material like silk, cellulose material of plant origin like cotton, paper, and starch.

b) Synthetic polymers.

These are man-made polymers.

Examples include:

Polyethene, Polypropene, PVC, PTFE, Nylon-6.6, Perspex, neoprene, Terylene, polystyrene etc.

10.3. Types of Polymers.

a) Natural polymers.

i.   Natural rubber.

Rubber is obtained naturally from rubber trees as latex, a milky liquid. It's a polymer derived from 2-methylbuta-1,3-diene as the monomer.

$$n\ CH_2{=}C{-}CH{=}CH_2 \longrightarrow *{-}\Big(CH_2{-}C{=}C{-}CH_2\Big)_n{-}$$

2-methylbuta-1,3-diene, monomer

naturalrubber, polymer.
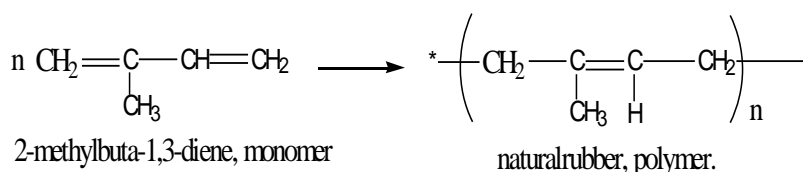
Natural rubber is soft and of little use so it's made tough by heating it with sulphur, a process called *vulcanization.*

During vulcanization, natural rubber is heated with sulphur to improve its qualities. Sulphur adds to the carbon-carbon double bonds of the two neighbouring rubber molecules to form vulcanized rubber.

rubber
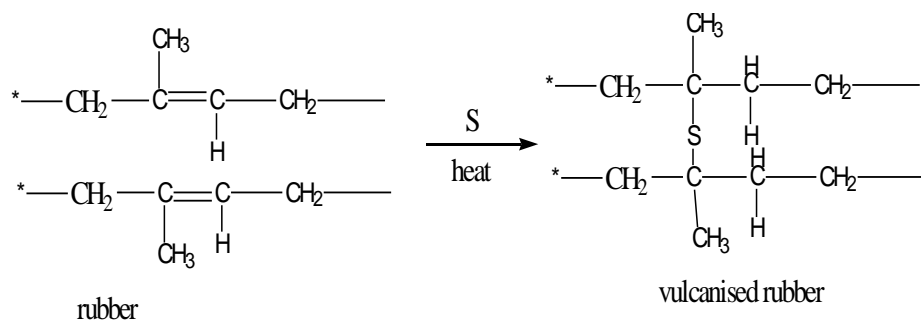
vulcanised rubber

Properties of Vulcanized Rubber.

Greater durability, greater tensile strength, and greater elasticity over a wide of temperatures.

Uses of Vulcanized Rubber.

Used for making; Shoe soles, Surgical gloves, Condoms, Car tyres, Cables of electric wires.

ii.   Synthetic Rubber.

This is a man-made rubber. The commonest example is **neoprene rubber**.

Neoprene rubber is resistant to organic solvents and strong.

It's used to make hoses and gaskets where oil resistance is needed.

Neoprene rubber is made from 2-chlorobuta-1,3-diene (chloroprene) by heating it with ammonium peroxosulphate as a catalyst.

$$n\ CH_2=\!\!\overset{\underset{\displaystyle Cl}{|}}{C}-CH=\!\!CH_2 \xrightarrow{S_2O_8^{2-}\ as\ cat.} *\!\!-\!\!\left(CH_2-\overset{\underset{\displaystyle Cl}{|}}{C}=\overset{\underset{\displaystyle H}{|}}{C}-CH_2\right)_n\!\!-$$

2-chlorobuta-1,3-diene, monomer   neoprene rubber, polymer.

b) Plastics.

i. Thermosoftening plastics.

These are plastics that become soft when heated and can then be moulded or remoulded.

They are linear polymers i.e. they are of the general structure –X-X-X-X-X-.

Where X is the monomer.

Many of the thermosoftening plastics are made by addition polymerisation.

Examples of thermosoftening plastics.

Polyethene from ethene, Polypropene from propene, PVC from chloroethene and Perspex from methyl 2-methylpropenoate.

Uses of thermosoftening plastics.

All the uses of individual examples

ii. Thermosetting plastics.

These plastics contain a three-dimensional network of bonds and are moulded during the polymerisation stage of their manufacture.

Unlike thermosoftening plastics, thermosetting plastics cannot be remoulded.

Examples of thermosetting plastics.

Bakelite from phenol and methanal, melamine from carbamide, $CO(NH_2)_2$ and methanal HCHO.

Uses of thermosetting plastics.

Bakelite is used for making electrical plugs, switches and tools owing to its electrical resistance.

Melamine is used table ware, trays, plates etc.

They are used in solution to strengthen paper and to improve the shrink resistance of cotton wool and rayon.

Used in ion-exchange resins to demineralize water as the free NH_2 groups combine with acidic groups in the water.

Used in production of chipboard used for kitchen tops and fire doors and in cavity-wall insulation to keep warmth and reduce condensation inside the house.

Environmental effects of plastics.

Plastics when burnt cause air pollution and global warming.

When poorly disposed, they cause soil infertility since they don't allow water leach the soil.

Biologically, plastics are sources of cancer.

Note: *The best way to deal with plastics is recycling.*

c) Fibres.

Fibres are the thin strands of thread.

Types of Fibres.

Natural fibres: The fibres which are obtained from plants and animals. Examples include starch, cotton, silk, proteins, and wool.

Artificial fibres: The fibres which are synthesized in the industry from simple chemicals obtained from petroleum. Examples include nylon, polyester (Terylene), propeno-nitrile etc.

EER: List uses of fibres.

Ans. See uses of individual examples of fibres.

Sample questions on polymers and polymerisation.

1. List factors affecting properties of polymers.

- Branching.
- Cross linking.
- Length of chains.
- Intermolecular forces.

2. Describe how the named factors affect the properties of polymers.

3. (a) Neoprene is a synthetic rubber. Write the structure and IUPAC name of the monomer of neoprene.

   (b) When 110g of the monomer was polymerized, 2.59×10^{-4} moles of neoprene was formed. Determine the number of monomer units that polymerized.

   (c) Sodium-4-dodecylbenzenesulphonate, $CH_3(CH_2)_{10}CH_2$—⬡—SO_3Na is a synthetic detergent. Starting with benzene, write equations to show how the detergent can be prepared.

4. The osmotic pressure of a solution containing 2.5g of a polymer X in 200cm^3 of a solution is 340Pa at 17°C.

   (a) Define the term Osmotic pressure.

   (b) Calculate the molecular mass of X

   (c) State any two assumptions made.

5. The osmotic pressure of a solution containing 1.4% of a polymer M in a solution is 9.0mmHg at 25°C.

   a) Define the term Osmotic pressure.
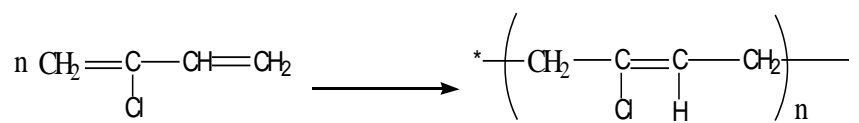
   b) Calculate the molecular mass of M.

   c) The structural formular of M is $\left(CH_2-CH_2 \right)_n^*$. Determine the value of n.

6. (a) A synthetic rubber Z was made from (n) monomers with structure
   $$CH_2{=}C-CH{=}CH_2$$
   $$\quad\quad\,|$$
   $$\quad\quad Cl$$

   i. State the conditions for the reaction.

ii.   Write the equation leading to the formation of Z.

(b) Name the type of reaction in a (ii).

(c) The osmotic pressure of a solution containing 5% of a polymer Z in a solution is 34kPa at 17°C.

   i.   Calculate the molecular mass of Z.

  ii.   Determine the number of monomers, n in Z.

7.   (a) A synthetic rubber, neoprene, was made by polymerisation of 2-chlorobuta-1,3-diene, $CH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2$ according to the following equation.

$$n\ CH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2 \longrightarrow *\left(CH_2-\underset{\underset{Cl}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_2\right)_n.$$

   i.   State the conditions for the reaction.

  ii.   Name the type of reaction leading to the formation of neoprene.

(b) The osmotic pressure of a solution containing $25gdm^{-3}$ of neoprene is 34kPa at 17°C.

   i.   Calculate the molecular mass of neoprene.

  ii.   Determine the number of monomers in neoprene.

8. (a) Nylon-6.6 is a synthetic polymer $*\left(\underset{}{\overset{O}{\overset{||}{C}}}(CH_2)_8\overset{O}{\overset{||}{C}}-\overset{H}{\overset{|}{N}}(CH_2)_6\overset{H}{\overset{|}{N}}\right)_n*$.

   i.   Name the type of the polymer.

  ii.   Write the structures and give the names of the monomers.

  (b) An aqueous solution containing 1.5% of nylon-6.6 exerts an osmotic pressure of 3.6×10^{-4} atmospheres at 25°C. Calculate the molecular mass of nylon-6.6.

9. *UNEB 2012 P.1 No.15.*

10. *UNEB 2010 P.1 No.6.*

11. UNEB 2009 P.2 No.7.

12. UNEB 2006 P.1 No.16.

13. UNEB 2005 P.1 No.14.

14. UNEB 2003 P.1 No.9.

15. UNEB 2001 P.1 No.17.

16. UNEB 1996 P.1 No.7.

17. UNEB 1995 P.1 No.17.

18.