General Introduction, Methods of Purification, Qualitative and Quantitative Analysis

SHORT ANSWER QUESTIONS

1. How are carbon and hydrogen of the organic compound detected ?

A. **Detection of carbon and hydrogen :**

The given organic compound is heated with cupric oxide (CuO) strongly, carbon is oxidized to carbondioxide and hydrogen to water.

$$C + 2CuO \longrightarrow CO + 2Cu$$

$$2H + CuO \longrightarrow H_2O + Cu$$

Carbondioxide is detected by lime water which develops white turbidity indicates the presenceof C

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

when water is treated with anhydrous copper sulphate which turns blue indicates the presenceof H

$$\underset{\text{white}}{5H_2O} + CuSO_4 \longrightarrow \underset{\text{blue}}{CuSO_4\ 5H_2O}$$

2. Explain the estimation of carbon and hydrogen by Liebig's method.

A. In this method a known weight of organic compound is heated with three times its weight of anhydrous copper oxide in a current of O_2

$$C_xH_y = (x + y/4) \longrightarrow xCO_2 + y/2\,H_2O$$

Carbon is converted into CO_2 and hydrogen is into H_2O

These gases are passed through already weighed U tubes containing anhydrous $CaCl_2$ aqueous KOH respectively. The increased weights of these two tubes give the weight of H_2O formed and weight of CO_2 formed. From the above data carbon and hydrogen are estimated by using the following formulae.

$$\%\ of\ C = \frac{12}{44} \times \frac{\text{Weight of carbondioxide}}{\text{Weight of organic compound}} \times 100$$

$$\%\ of\ H = \frac{2}{18} \times \frac{\text{Weight of water}}{\text{Weight of organic compound}} \times 100$$

3. How is nitrogen present in an organic compound estimated by Duma's method ?

A. **Estimation of Nitrogen :**

Duma's method :

In this method a known weight of organic compound is heated strongly with cupric oxide. Carbon and hydrogen get oxidized to carbondioxide and water vapour respectively. Nitrogen present is converted to nitrogen gas. Some amount of nitrogen is also converted to its oxides, they are reduced by hot copper gauze into nitrogen. The product gases are collected over a solution of potassium hydroxide. CO_2 is absorbed by KOH solution. Nitrogen is collected over potassium hydroxide solution and its volume is caluculated.

P = Pressure of gas collected over water

P = Aqueous tension

Pressure of dry N_2 gas $P_1 = P - p$

V = volume of nitrogen in ml at STP = $\frac{P_1 V_1}{T_1} \times \frac{273}{760}$

% of nitrogen in the organic compound = $\frac{28 \times V \times 100}{a \times 22400}$

a = Weight of the organic compound

Volume of nitrogen gas at STP

4. Explain the estimation of Nitrogen by Kjeldahl's method.

A. **Kjeldahls' method :**

In this method, the compound is heated with concentrated sulphuric acid in the presence of small amount of $CuSO_4$ to convert nitrogen into ammonium sulphate. The contents of the flask are transferred to another flask and heated with excess of sodium hydroxide solution to liberate ammonia gas. Ammonia gas so liberated is passed and absorbed in a known volume of known concentrated sulphuric acid. Now, the excess of acid remained after the neutralization by NH_3 is titrated against a standard solution of alkali. From the above, the amount of H_2SO_4 used to neutralize NH_3 is calculated. From this percentage of nitrogen is calculated by using the formula given below.

Organic compound + $H_2SO_4 \longrightarrow (NH_4)_2 SO_4$

$(NH_4)_2 SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O + 2NH_3$

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2 SO_4$

Percentage of Nitrogen = $\frac{14 \times M \times 2\left(V - \frac{V_1}{2}\right)}{1000} \times \frac{100}{a}$

a = weight of the organic compound

M = molarity of H_2SO_4 solution

V = Volume of H_2SO_4 solution

V_1 = Volume of H_2SO_4 solution consumed by NaOH

5. How are halogens of an organic compound estimated.

A. Halogens can be estimated by Carius method

In this method a known weight of the organic compound is heated with fuming nitric acid in presence of $AgNO_3$ in a hard glass tube. Carbon and hydrogen are oxidized to CO_2 and H_2O. Halogens are converted into silver halides. The silver halide is filtered off, washed, dried and weighed.

Calculation : Mass of the organic compound = 'a' g

Mass of silver halide formed (AgX) = b g

1 mole of AgX contains 1 mole of X

$\therefore$ Mass of halogen in 'b'g of AgX ……. .?

$$= \frac{(\text{Atomic mass of X} \times \text{b})}{\text{Molecular mass of AgX}} = \text{'C'g}$$

a g of organic compound has 'C' g of halogen

$\therefore$ 100 g or organic compound has ?

$$= \frac{100 \times C}{a} = \frac{100 \times \text{b} \times \text{Atomic mass of X}}{\text{a} \times \text{Molecular mass of AgX}}$$

(Molecular masses : AgCl = 143.5 (108 + 35.5) ; AgBr = 188 (108 + 80) ; AgI = 235 (108 + 127)

6. Explain the estimation of phosphorus, sulphur and oxygen in the given organic compound.

A. **Estimation of sulphur :** A known mass of the organic compound is heated with sodium peroxide in a Carius tube. Then 'S' is oxidized to H_2SO_4. The acid is precipitated as $BaSO_4$ by adding excess of $BaCl_2$ aqueous solution. The precipitate is filtered, washed, dried and weighed.

Calculations :

Mass of organic compound = a g

Mass of barium sulphate = b g

Molecular weight of $BaSO_4$ = 233

1 mole of $BaSO_4$ or 233g of $BaSO_4$ contains 32g of sulphur

∴ 'b'g of $BaSO_4$ contains …… ?

$$= \frac{32 \times b}{233} \text{g of sulphur}$$

a g of organic compound contains $\frac{32 \times b}{233}$ g of sulphur

∴ 100g organic compounds …… ?

$$= \frac{100 \times 32 \times b}{a \times 233} \text{g of sulphur} (\% \text{of S})$$

Estimation of Phosphorus: A known mass of organic compound is heated with fuming nitric acid in a Carius tube. Then phosphorus is oxidized to phosphoric acid. The acid is precipitated as ammonium phosphomolybdate by adding ammonia and ammonium molybdate solutions.

Calculation :

Mass of organic compound = a g

Mass of ammonium phosphomolybdate = b g

Molecular weight of ammoniumphosphomolybdate = 1877

1877 g of ammoniumphosphomolybdate contains 31 g of phosphorus

∴ 'b'g of …… ?

$$= \frac{31 \times b}{1877} \text{g of phosphorus}$$

'a' of organic compound contains $\frac{31 \times b}{1877}$ g of phosphorus

∴ 100g of organic compound contains …… ?

$$= \frac{100 \times 31 \times b}{1877} \text{g of } P (\% \text{of } P)$$

Estimation of Oxygen :

A known weight of organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red hot coke to convert all oxygen in those oxides to CO. Then the mixture is passed through hot iodine pentoxide to convert CO into CO_2 and iodine liberates.

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{other gaseous products}$$

$$2C + O_2 \xrightarrow{1373K} 2CO \; ; \; I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

Calculations :

Mass of organic compound = a g

Mass of Carbondioxide = b g

44g of CO_2 contains 32g of oxygen

$\therefore$ b g of CO_2 …….. ?

$$= \frac{b \times 32}{44} \text{g of oxygen}$$

'a' g of organic compound contains $\frac{b \times 32}{44}$ g of oxygen

$\therefore$ 100g of organic compound contains …… ?

$$= \frac{100 \times b \times 32}{a \times 44} \text{g of oxygen} \left(\% \text{ of oxygen}\right)$$

LONG ANSWER QUESTIONS

1. Write any four methods of purification of organic compounds.

A. I. Purification methods of solids :

a) Crystallisation :

The principle used here is that the impurities are insoluble or soluble in the given solvent at any temperature but the substance to be purified is sparingly soluble at room temperaturebut highly solubleat highest temp i,e almost near the boiling temp.of the solvent

b) Sublimation **:**

This is used for the purification method of solids. This process is used for those solids which convert directly into vapour on heating without converting into liquid and vapours upon cooling give back solid state.

Iodine, Camphor, Naphthalene, ammonium salts are sublimating solids.

The impure compound is taken in a beaker covered with a watch glass and heated on an electric plate. The compound sublimates and solidifies on the lower surface of the watch glass. Impurities settle in the beaker. The pure compound is separated by scratching the watch glass.

II. Purification methods of liquids :

a) Distillation :

This process is useful for the purification of liquids contaminated with non volatile impurities.

The impure liquid is boiled in distillation flask and the vapours are condensed and collected in a receiver. This method can also be used to separate liquid if only their boiling points differ by above $40°C$

i) Fractional distillation :

It is used to separate a liquid mixture which contains the components that have boiling point difference less than $40°C$

Let a mixture of liquids A and B is taken as a distillation flask which is fitted with a fractionating column at its mouth. The upper end of the column is connected to the water condenser. When the mixture is heated, the vapours of both A and B pass through the fractionating column. While moving through the long fractionating column the vapours of liquid which has high boiling point (say A) condenses and come back to the distillation flask. The vapours of other liquid (say B) which has low boiling point still in vapour state and move out of the column as pure vapours of B to the condenser. Vapours of B condense and get collected in the receiver.

Eg : Water (boiling point $100°C$) and alcohol (boiling point $78°C$) can be separated by this method.

ii) Distillation under reduced pressure :

This method is used to purify such liquids which decompose below their normal boiling points.

If the external pressure is reduced the liquid boils at lower temperature than its normal boiling point without decomposition. At reduced pressure the boiling point of a liquid is also reduced, hence its decomposition is avoided.

Eg : Glycerol and H_2O_2 are purified by this method.

iii) Steam distillation :

This method is used to such liquids which are insoluble in water and possess high vapour pressure at the boiling point of water.

In this method steam is passed into the hot liquid mixture taken in the distillation flask. The liquid with low boiling point comes out along the steam by leaving behind the liquid which has comparatively high boiling point. They are passed through the condenser and condensed, finally collected in the receiver. The water layer and the organic liquid layer are separated using a separating funnel.

Aniline can be purified by this method

Principle of this method :

The proportion of the organic substance that distills over with steam is related to the vapour pressure as well as molecular masses as

$$\frac{\omega_1}{\omega_2} = \frac{P_1 M_1}{P_2 M_2}$$

Here P_1 and P_2 represent vapour pressures of organic liquid and steam respectively. M_1 and M_2 represent molar mass of organic compound and water respectively if their corresponding weights are ω_1 and ω_2

III) Solvent extraction :

It is used to separate an organic compound present in aqueous medium by using a solvent which is immiscible in water and in which organic substance is more soluble.

The aqueous solution of impure organic compound is shaken with a suitable solvent. Organic compound goes into the organic solvent which is immiscible with water. The organic layer is separated and distilled to remove the liquid solvent. The compound remains with distillation flask.

IV) Chromatography :

It is a modern technique for the separation of coloured pigments from plants, mixtures containing cations of lanthanides and actinides, etc.

This method is based on the principle of selective adsorption or distribution of components of a mixture generally between two phases i.e, the stationary phase and the mobile phase.

The mobile phase may be liquid or a gas while the stationary phase is either a solid or liquid supported over a solid.

Chromatography involves the three steps given below :

a) Adsorption and retention of a mixture of substances on the stationary phase and their separation by mobile phase.

b) Recovery of the substances separated by a continuous flow of the mobile phase (known as elution) and

c) Qualitative and quantitative analysis of the eluted substances

Two general chromatography techniques are :

i) Adsorption chromatography

ii) Partition chromatography

Adsorption chromatography is based on the adsorption of different compounds on an adsorbent to different extent.

Generally used adsorbents are silica gel and alumina

A mobile phase is allowed to move over a stationary phase. The components of the mixture move to different distances over the stationary phase.

Different adsorption principle is used in (a) column chromatography and (b) thin layer chromatography.

a) Column chromatography :

In the column chromatography the components of a mixture are separated by a column of adsorbent (stationary phase) packed in a glass tube.

The mixture is placed at the top of the stationary phase. A suitable eluant, either a single solvent or a mixture of solvents is allowed to flow down the column slowly.

The most readily adsorbed substances are retained near the top and others come down accordingly to various distances.

b) Thin layer chromatography (TLC) :

Here the adsorbent used in silica gel or alumina coated over a glass plate of suitable size. The plate is called TLC plate or chromoplate.

The solution of the mixture to be separated is applied as a small spot at about 2cm from the bottom of the plate. The plate is then kept in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along the eluant to various distances depending on their degree of adsorption.

The relative adsorption of a component of the mixture is expressed in terms of its RETARDATION FACTOR $\left(R_f\right)$ value.

$$R_f = \frac{\text{Distance moved by substance from base line}(\text{X})}{\text{Distance moved by the solvent from base line}(\text{Y})}$$

Partition Chromatography :

This is based on continuous differential separation of components of a mixture between the stationary phase and the mobile phase.

In this method chromatography paper (contains water trapped in it) used as the stationary phase

The chromatography paper spotted with the solution of the mixture at the base, is suspended in a suitable solvent. This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and moves over the spot. The paper selectively retains different compounds as per their differing partition in mobile and stationary phases. The paper strip so developed is known as chromatogram. The spots of the separated coloured compounds are detected and for colourless compounds other methods like spraying suitable reagent, are used.

Classification of chromatography methods :

Based on the physical states of the stationary phase and mobile phase chromatography processes are classified into several types.

Classification :

S.No.	Type of Chromatography	Mobile phase	Stationary phase
1	Adsorption or Column chromatography	Liquid	Solid
2	Thin layer chromatography	Liquid	Solid (or) Liquid
3	Ion Exchange chromatography	Liquid	Solid
4	Gas liquid chromatography (G.L.C) Gas solid chromatography (G.S.C)	Gas	Liquid Solid
5	Paper or partition chromatography	Liquid	Liquid
6	Liquid – Liquid chromatography	Liquid	Liquid

2. Explain the detection of Nitrogen, Halogens, Sulphur phosphorous and oxygen in an organic compound.

A. **Detection of the elements :**

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by **Lassaigne's test.**

1) Preparation of Lassaigne's extract or sodium extract :

The organic compound is fused with a small piece of Na metal. The red hot tube is plunged in distilled water, boiled and filtered. The filtrate is called Lassaigne's extract or sodium extract.

The elements presents in the organic compound are converted from covalent form into the ionic form according to the following reactions.

$$Na + C + N \rightarrow NaCN$$

$$2Na + S \rightarrow Na_2S$$

$$Na + X \rightarrow NaX \qquad (X = Cl, Br \text{ or } I)$$

Note : Usually the sodium extract is alkaline

(A) Test for Nitrogen :

The sodium fusion extract is boiled with iron (II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.

The Prussian tube colour obtained in Lassaigne's test is due to formation of Ferric ferro cyanide.

$$6NaCN + FeSO_4 \longrightarrow Na_4\left[Fe(CN)_6\right] + Na_2SO_4$$

$$3Na_4\left[Fe(CN)_6\right]+4FeCl_3 \longrightarrow Fe_4\left[Fe(CN)_6\right]_3+12\,NaCl$$

Note :

$Fe_4\left[Fe(CN)_6\right]_3$ = Iron (III) hexa cyano Ferrate (II)

(B) Test for Nitrogen and Sulphur together :

If the organic compound contains nitrogen and sulphur together, sodium thiocyanate formed in the sodium extract gives blood red colouration with Fe^{+3} ions due to the formation of Ferric thiocyanate.

$$Na + C + N + S \rightarrow NaCNS$$

(C) Test for Sulphur :

(i) Sodium nitroprusside test : A small portion of the Lassaigne's filtrate is treated with a few drops of sodium nitroprusside solution. It gives violet colouration indicates the presence of sulphur.

$$Na_2S + Na_2\left[Fe(CN)_5\,NO\right] \longrightarrow \underset{\text{(violet colour)}}{Na_4\left[Fe(CN)_5\,NOS\right]}$$

(ii) Lead acetate test :

a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur in the given compound.

$$Na_2S + \left(CH_3COO\right)_2 Pb \longrightarrow \underset{\text{(Black ppt)}}{PbS} + 2CH_3COONa$$

(D) Test for Halogens :

The sodium extract is boiled with dilute HNO_3 cooled and a few drops of silver nitrate solution are added

$$NaX + AgNO_3 \longrightarrow \underset{\text{Silver halide}}{AgX} + NaNO_3$$

(a) A white precipitate of AgCl soluble in ammonium hydroxide indicates the presence of chlorine $AgCl + 2NH_4OH \longrightarrow \left[Ag\left(NH_3\right)_2\right]Cl + 2H_2O$

(b) A pale yellow precipitate of AgBr partially soluble in NH_4OH indicates the presence of bromine

(c) A yellow precipitate of AgI partially soluble in NH_4OH indicates the presence of iodine

E) Detection of phosphorus :

The compound is heated with an oxidizing agent (sodium peroxide.) The 'P' in the organic compound is oxidized to PO_4^{3-}. The solution is boiled with HNO_3 and treated with

ammonium molybdate. The formation of canary yellow precipitate indicates the presence of phosphorus in the compound.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2 MoO_4 + 21HNO_3 \longrightarrow \underset{\text{ammonium phosphomolybdate}}{(NH_4)_3 PO_4 .12MoO_3} + 12H_2O$$

F) Detection of oxygen :

There is no direct test for oxygen.The organic compound is tested for the presence of functional groups like OH, CHO, COOH, NO, etc, from this oxygen is detected.

Determining the percentage composition of all elements in the compounds if it does not come to 100% , the remaining is of oxygen.

ORGANIC CHEMISTRY(2nd part)

UNIT 1

1 Classification and IUPAC Nomenclature of Organic compounds
2 Electronic displacements in a covalent bond : Inductive effect, Electrometric effect ; Resonance and Hyperconjutation

Very Short Answer Questions :

1. What is functional group isomerism ? Give an example ?

A. The isomers differing in functional groups are called functional group isomers and phenomenon is called functional isomerism.

Ex : CH_3-CH_2-OH (Ethyl alcohol) and CH_3-O-CH_3 (Dimethyl Ether), both with molecular formula C_2H_6O

2. Give the structural formulae and names of the isomers with the molecular formula C_5H_{12}

A. C_5H_{12} has 3 chain isomers

i)

$$CH_3-CH_2-CH_2-CH_2-CH_3$$

n – pentane

ii)

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

iso - pentane

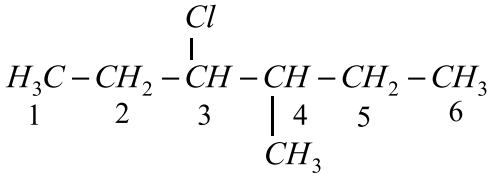
iii)

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

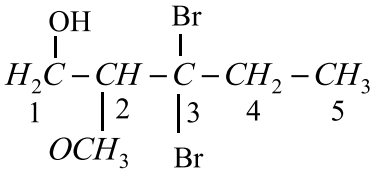
neo - pentane

3. Write the structures of 3 – chloro – 4 – methyl hexane and 2 – methoxy – 3, 3 – dibromo – 1 – pentanol.

A. a) 3 – chloro – 4 – methyl hexane



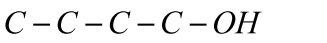
b) 2 – methoxy – 3, 3 – dibromo – 1 – pentanol.



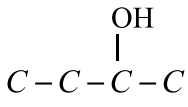
4. What type of functional group isomers are possible from a molecular formula $C_4H_{10}O$? Give the names of the isomers.

A. $C_4H_{10}O$ exhibit alcohol ether functional group isomers. Since it resembles $C_nH\ 2n+2$

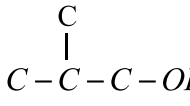
Alcohols



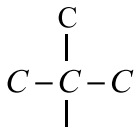
$P-$butyl alcohol



sec – butyl ether

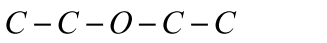


iso – butyl alcohol

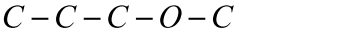


ter - butyl alcohol

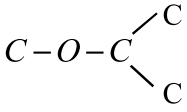
Ethers



Diethyl ether



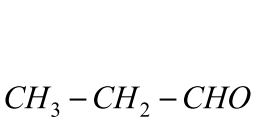
methyl propyl ether



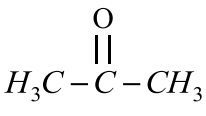
methyl isopropyl ether

5. Name the functional group isomers of molecular formula C_3H_6O. C_3H_6O has aldehyde and ketone isomers since it resembles $C_nH_{2n}O$

A. **Aldehyde** **Ketone**



Propanal



Propanone

6. What is Metamerism ? Give an example.

A. Compounds having same molecular formula but differ in nature of allyl groups attached to functional group are metamers. The phenomenon is known as Metamerism.

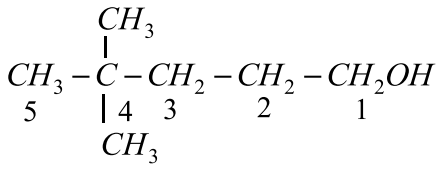
Example :

$CH_3 - CH_2 - O - CH_2 - CH_3$ Diethyl ether

$H_3C - CH_2 - CH_2 - O - CH_3$ Methyl propyl ether

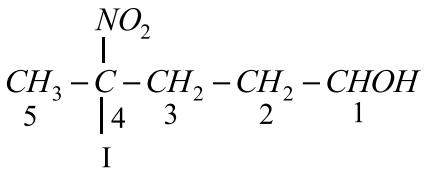
7. Give the names of the following compounds according to IUPAC names.

A. a)



Ans) 4, 4 – Dimethyl – pentanol – 1

b)



Ans) Iodo – 4 – Nitro pentanoic acid

8. What is position isomerism ? Give an example ?

A. Isomers having same carbon skeleton but differs in the position of the substituent (or) functional groups.

Ex : $CH_3 - CH_2 - CH_2 - Cl$ 1 – Chloro propane

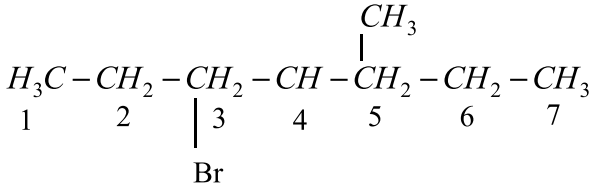
$CH_3 - \underset{\displaystyle Cl}{CH} - CH_3$ 2 – Chloro propane

9. Write the structural formulae of the following compounds

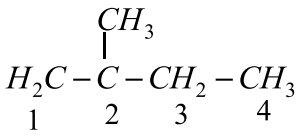
a) 3 – Bromo 4 – methyl heptane **b) 2 – Methyl – 1 – butane**

c) 2 – amino propanoic acid **d) 2, 3 – dimethyl hexanal**

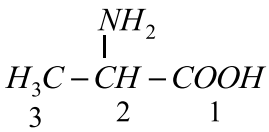
A. a) 3 – Bromo 4 – methyl heptane



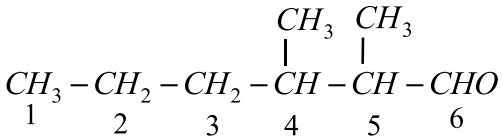
b) 2 – Methyl – 1 – butane



c) 2 – amino propanoic acid

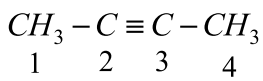


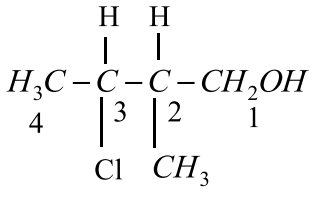
d) 2, 3 – dimethyl hexanal

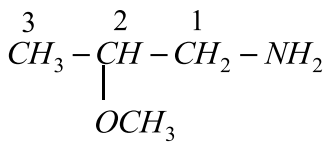


10. Give the names of the following compounds according to IUPAC rules.

A. a) $CH_3 - CH_2 - CH = CH_2$:1 - Butene

b)  : 2 – Butyne

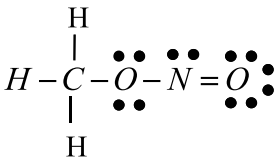
c)  : 3 – chloro – 2 – methyl – Butanol

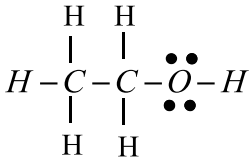
d)  : 2 – Methoxyl propananine

11. Write the Lewis structure of methyl Nitrate and ethyl alcohol

A. Methyl Nitrate

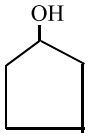
Formula : CH_3NO





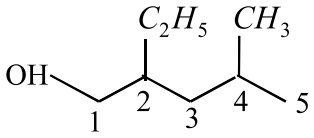
(-) denotes a shared electron pair bond

12. Write bond line formulae for cyclopentanol and 2 – ethyl methylpentanol



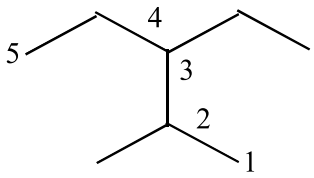
A. Cyclopentanol

2 - ethyl - 4 - Methyl pentanol



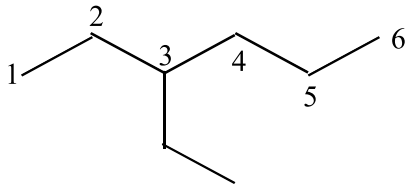
13. Write IUPAC names of

(a)



3 - ethyl - 2 - Methyl pentane

(b)



3 - ethyl - 4 - methyl hexane

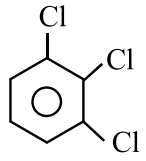
14. Write the isomers of $C_2H_3Cl_3$

A. 1) CH_3CCl_3 1, 1, 1 – trichloroethane

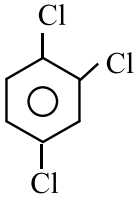
2) $CH_2ClCHCl_2$ 1, 1, 2 – trichloroethane

These are position isomers

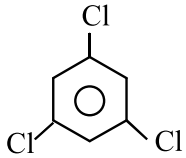
15. Write the structural isomers of $C_6H_3Cl_3$

A. 

1, 2, 3 - trichloro benzene



1, 2, 4 - trichloro benzene



1, 3, 5 - trichloro benzene
These are position isomers

SHORT ANSWER QUESTIONS

1. Explain inductive effect.

A. **Inductive effect :**

It is a permanent displacement of σ electrons along the chain of carbon atoms due to the presence of some electron donating or electron withdrawing group.

Inductive effect is defined as the polarization of σ bond caused by the polarization of adjacent σ bond.

It is generally represented as $\overset{\delta_+}{C}-\overset{\delta_-}{Cl}$ or - C ⟶ Cl

Salient features of inductive effect :

1) It is permanent in nature

2) It occurs through σ bonds

3) Its effect decreases gradually along the carbon chain and negligible after the third carbon

4) Influences chemical reactivity

5) It effects physical properties

Types of inductive effect :

1) Electron withdrawing groups are said to exhibit negative inductive effect (- I)

Eg : $-NO_2, -CHO, -COOH$, Halogens - $-OH, -NH_2$

2) Electron donating groups are said to exhibit positive inductive effect (+I)

Alkyl groups are electron donating groups

$-CH_2CH_3, -CH_3$

2. Explain Electromeric effect.

A **Electromeric effect :**

It is defined as the complete transfer of a shared pair of π electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.

Salient features of electromeric effect :

1) it is denoted by E and observed only in organic compounds with multiple bonds (a double or triple bond) in the presence of attacking reagent

2) The effect is not observed when the attacking reagent is removed from the domain of the reaction. Hence, it is a temporary effect.

3) This effect is shown by a curved arrow.

Types :

+ E effect : When the transfer of electrons takes place towards the attacking reagent, the effect is called + E effect.

Eg : The addition of acids to alkenes

- E effect : When the transfer of electrons takes place away from the attacking reagent, the effect is called – E effect.

Eg : Addition of cyanide ion to carbonyl compounds

3. Write a brief note on Mesomeric effect.

A. **Mesomeric effect :**

Electrons in a molecule try to delocalize as far as possible to get stability. Atoms with lone pairs and conjugated systems exhibit to greater extent.

The electron pair displacement caused by an atom or group along a chain by a conjugative mechanism is called the mesomeric effect of that atom or group.

Salient features of the mesomeric effect :

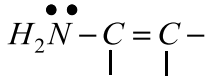
i) Permanent effect operating in the ground state of the molecule

ii) Lone pairs and π electrons are involved and operate through conjugative mechanism of electron displacement

iii) It influences the physical properties, reaction rates etc

+ M effect :

Groups which tend to increase the electron density of the rest of the molecule are said to have (+M) effect. Such group tend to possess lone pairs of electrons.

Ex : 

Hence $-NH_2$ group has + M effect

- M effect :

Groups that decrease the electron density of the rest of the molecule are said to have (-M) effect.

Unsaturated groups having polar character have – M effect.

Here C = O group decreases the electron density of the remaining molecule

It has – M effect

Halogens have – I effect but with lone pairs they have (+ M). These two operate in opposite directions.

4. Write a brief note on Resonance effect

A. **Resonance effect :**

It is the polarity produced in a molecule by the interactions of two π bonds or between a π bond and a lone pair of electrons present on adjacent atoms. This effect is transmitted through the chain.

If the transfer of electrons is away from the atoms or substituent group attached to the conjugated system, then the molecule gets some of its positions high electron density as in aniline and it is given (+R). If the shift of electrons are towards the atom or substituent group it is (-R) as in nitrobenzene.

Groups showing

(+R) are X, - OH, - COOH, $-NH_2$, etc

(-R) effect are – COOH, - CHO, > C = O, - CN, $-NO_2$

Resonance energy :

Resonance energy is the difference in energy between the actual energy of the molecule and that of the most stable canonical form.

5. What is hyperconjugation ? Explain its examples.

A. **Hyperconjugation :**

When alkyl group with atleast one C – H bond is attached to C = C, or a benzene nucleus, it involves delocalization of σ electrons of C – H bond in conjugation with π bonds. This is called hyperconjugation. It is also known as no bond resonance.

Eg : methyl benzene

Effects of hyper – conjugation :

1) **Stability of alkyl carbo cations :** Graeter the alkyl groups attached to the positively charged carbon atom, higher is the stability through hyperconjugation. Due to this, the stability of alkyl cations is

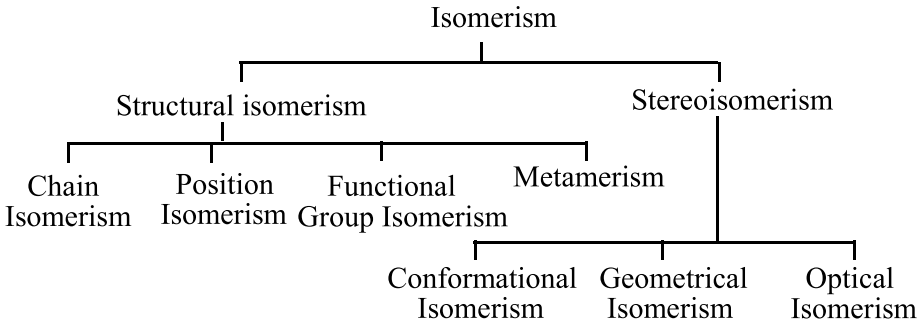
$1° < 2° < 3°$

2) Hyperconjugation may be due to C – H bond possessing partial ionic character because of resonance

LONG ANSWER QUESTIONS:

1. Define isomerism. Write the types of isomerism. Explain with examples of different types of structural isomerism.

A. Different compounds with the same molecular formula are called isomers. This phenomenon is called isomerism. Isomerism arises due to the difference in the arrangement of the atoms or in their spatial orientation in the molecule. It is mainly two types.



Structural isomerism : It arises due to the difference in the atoms or groups in the molecule. It is four types.

1) Chain isomerism : It arises due to the difference in the arrangement of atoms in the carbon chain. It is observed in the compounds with more than 3 carbon atoms.

Ex 1 : C_4H_{10} **Butane**

1) $CH_3-CH_2-CH_2-CH_3$ (n−butane)

2)

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

2 - methyl propane (isobutane)

Ex 2 : C_5H_{12} **Pentane**

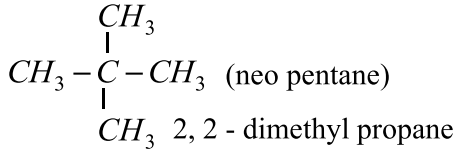
1) $CH_3-CH_2-CH_2-CH_2-CH_3$ (n−pentane)

2)

$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ (isopentane)

2 - methyl butane

3)



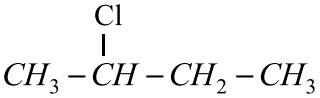
(neo pentane)

2, 2 - dimethyl propane

2) Position isomerism : It arises due to the difference in the position of a substituent or functional group or multiple bond.

Ex 1 : C_4H_9Cl **Chlorobutane**

1) $CH_3 - CH_2 - CH_2 - CH_2 - Cl$
1 – Chlorobutane

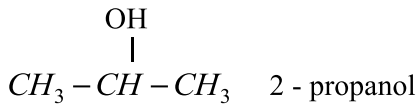


2) 2 - Chlorobutane

Ex 2 : C_3H_7OH **Propanol**

1) $CH_3 - CH_2 - CH_2OH$ 1 - propanol

2)



2 - propanol

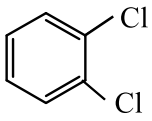
Ex 3 : C_4H_8 **Butene**

1) $CH_3 - CH_2 - CH = CH_2$ 1 - butene

2) $CH_3 - CH = CH - CH_3$ 2 - butene

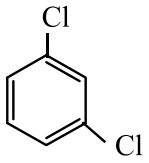
Ex 4 : $C_6H_4Cl_2$ **dichlorobenzene**

1)



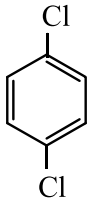
o - dichlorobenzene

2)



m - dichlorobenzene

3)



p - dichlorobenzene

3) Functional group isomers :

Compounds with same molecular formula but having different functional groups are called functional isomers. This phenomenon is called functional isomerism.

i) Alcohols and ethers are functional isomers

Ex : C_2H_6O C_2H_5OH ethanol

CH_3OCH_3 methoxy methane

ii) Aldehydes and Ketones are functional isomers

Ex : C_3H_6O CH_3CH_2CHO propanal

CH_3COCH_3 propanone

iii) Acids and esters are functional isomers

Ex : $C_4H_8O_2$ $CH_3-CH_2-CH_2-COOH$ butanoic acid

$CH_3COOCH_2CH_3$ ethyl ethanoate

iv) Alkynes and Alkadienes are functional isomers

Ex : C_4H_6 $CH_3-CH_2-C\equiv CH$ 1 – butyne

$CH_2=CH-CH=CH_2$ 1, 3 – Butadiene

v) Cyanides and isocyanides are functional isomers

C_2H_3N CH_3CN Ethanenitrile

CH_3NC Methane carbylamine

4) Metamerism : It arises due to the difference in the nature of the alkyl groups attached to divalent functional groups.

Ex : i) ethers $C_2H_5OC_2H_5$ - ethoxy ethane

$C_4H_{10}O$ (Diethyl ether)

$C_3H_7OCH_3$ Methoxy propane (Methyl propyl ether)

ii) amines $CH_3CH_2-NH-CH_2CH_3$ (Diethyl amine)

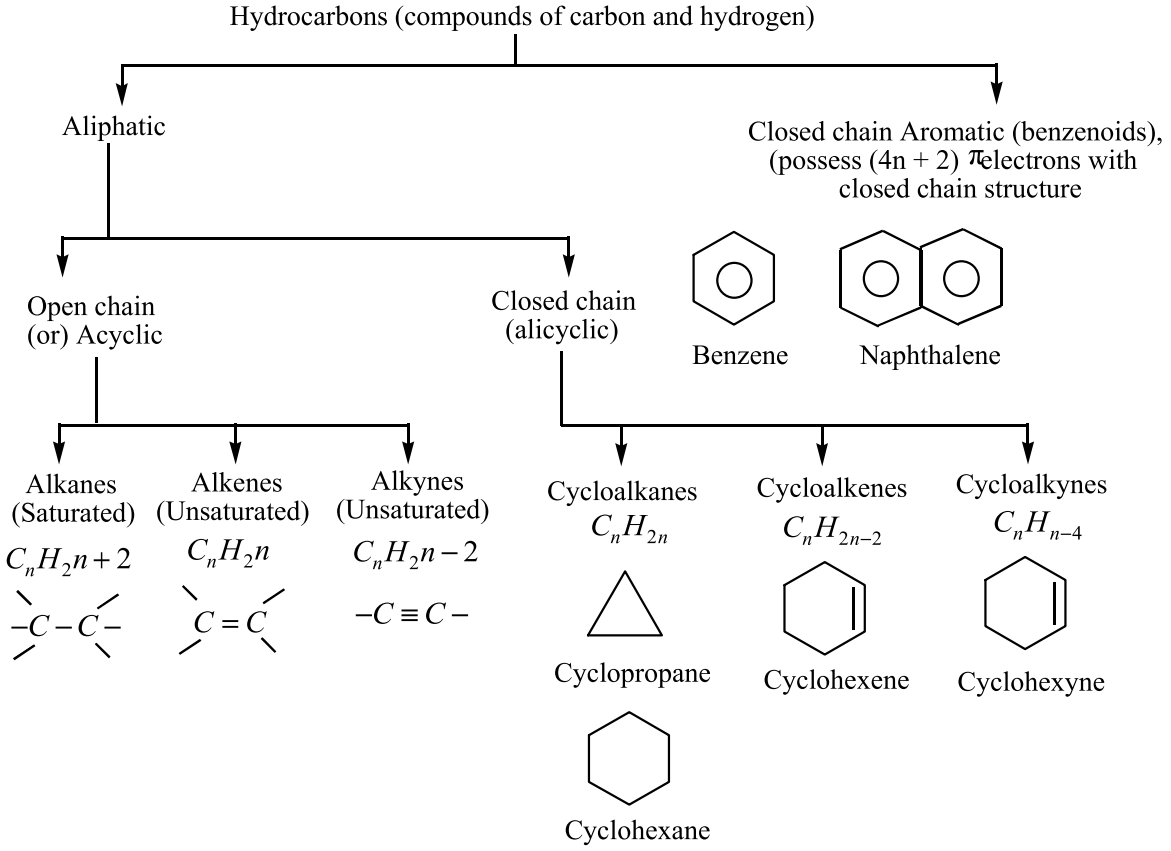
$C_4H_{11}N$ $CH_3NH-CH_2CH_2CH_3$ (Methyl n – propyl amine)

iii) Ketones $C_2H_5COC_2H_5$ (Diethyl ketone)

$C_5H_{10}O$ $CH_3COC_3H_7$ (Methyl ketone)

2. Explain the classification of hydrocarbons.

A. Classification of hydrocarbons : Hydrocarbons are classified as aliphatic hydrocarbons and aromatic hydrocarbons. Aliphatic hydrocarbons are again classified as open change hydrocarbons and closed chain hydrocarbons i.e, cylcohydrocarbons. Both open chain and closed chain hydrocarbons are again classified as hydrocarbons containing C – C single bonds. > C = C < compounds, - C ≡ C – hydrocarbons. Aromatic compounds are called benzenoids as they are related to benzene.



ORGANIC CHEMISTRY
UNIT: 2

1. Fission of covalent bond: hemolytic and heterolytic fissions
2. Types of reagents Electrophiles, Nucleophiles and free radicals examples, reactive intermediates
3. Common types of organic reactions – Substitution, Addition, Elemination and Rearrangement reactions with examples

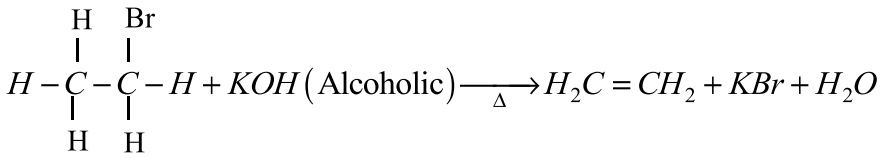
Very Short Answer Questions:

1. What is dehydro halogenation? Give the corresponding equation for the formation of alkene from alkyl halide.

A. Removal of hydrogen and halogen from the adjacent carbon atoms is called dehydrohalogenation.

Alkene from alkyl halide:

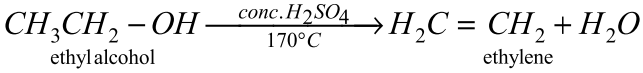
When ethyl chloride is heated with alcoholic KOH, ethylene is formed due to dehydrohalogenation.



2. What is dehydration reaction? How is ethylene is prepared from ethyl alcohol?

A. Removal of water molecules is called Dehydration.

Dehydration of Ethanol: When ethanol is heated to $170°C$ with conc H_2SO_4, it undergoes dehydration and ethylene is formed.



SHORT ANSWER QUESTIONS

1. Explain the types of organic reactions with examples.

A. **Common types of organic reactions:**

Organic reactions are mainly classified into four types known as

i) Addition reactions

ii) Substitution reactions

iii) Elimination reactions

iv) Molecular arrangements

i) Addition reaction:

In these reactions the reagent and the substrate combine together to give a single product

Example:

Depending on the reagent added in the slow rate-determining step, addition reactions are again classified as

a) Electrophilic addition reactions

b) Nucleophilic addition reactions

c) Free radical addition reactions

ii) Substitution reactions:

In these reactions an atom or a group of the substrate species is replaced by another atom or group These are again classified as

a) Electrophilic substitution

b) Nucleophilic substitution

c) Free radical substitution reactions on the basis of the reagent involved in the rate determining step

iii) Elimination reactons:

In these reactions two or more atoms or groups of an organic substrate are removed to form multiple bonds

iv) Molecular rearrangements:

Here one organic species (generally less stable) rearranges to other species (generally more stable)

$$NH_4CNO \longrightarrow CO(NH_2)_2$$

Ammonium cyanate Urea

Fries rearrangement:

In the acylation of phenol with carboxylic acid anhydrides in the presence of sulphuric acid, and it rearranges in the presence of $AlCl_3$ catalyst to O – acyl isomer that is more stable. Here aryl esters are converted to aryl ketones by rearrangement.

2. Discuss the fission of a covalent bond in Carbon compounds.

A. Fission of a covalent bond – Homolytic and Heterolytic fissions:

a) Heterolytic fission: This involves the breaking of a covalent bond in such away that both the electrons of the shared pair are carried away by one of the atoms.

This fission leads to the formation of charged (or) ionic species

e.g: $H_3C:Cl \longrightarrow \underset{\text{carboniumion}}{H_3\overset{\oplus}{C}} + Cl^-$

b) Homolytic fission: This involves the breaking of a covalent bond in such a way that each separates with one electron of the shared pair, (i.e) each atom acquires its initial configuration.

This fission leads to the formation of free radicals

e.g: $Cl:Cl \xrightarrow[\text{sunlight}]{\text{energy}} \underset{\text{free radicals}}{\overset{\bullet}{Cl} + \overset{\bullet}{Cl}}$

3. What do you understand by organic reaction mechanism?

A. Organic reaction mechanism: In organic reactions the reactants reacts with an attacking reagent ad forms one or more intermediates and finally products.

$$\text{Reactant} \xrightarrow{\text{Reagent}} [\text{Intermediate}] \begin{cases} \nearrow \text{product} \\ \searrow \text{By product} \end{cases}$$

Reaction mechanism involves the sequential account of each step, describing the details of electron movements, energy changes during bond breaking and bond formation and the rates at which reactants are converted into products (i.e) kinetics of the reaction. This helps in understanding the reactivity of compounds and in planning the synthesis of these compounds.

4. Explain the types of organic reagents. A) Electrophiles b) Nucleophiles c) Free radicals with examples

A. These are the reagents that attack a point of high electron density or-ve site. They are electron deficient and act as Lewis acids. They may be+vely charged ions or neutral species with one atom in them containing an empty orbital to accept electrons. The reaction involvling an electrophile is called electrophillic reaction.

Ex: $X^+.R^+.RCO^+.AlCl_3, SO_3$ etc.

b**) Nucleophiles**: These are the reagents that attack a site of low electron density or+ve centres. They are electron- hating species. They are –vely charged or neutral species containing a lone pair of electrons. They act as Lewis bases.

Ex: $Cl^-, Br^-, OH^-, CN^-, NH_3, H_2O$ etc.

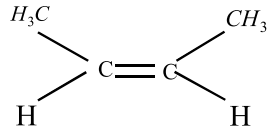
C) **Free radicals**: These are the reagents which possess odd electrons.

Ex: $\ddot{\text{C}}\text{l}\cdot$,R- $\ddot{\text{O}}\cdot$, $\text{Na}\cdot$ etc.

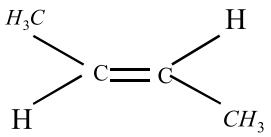
Long Answer Questions

1. What do you understand about Geometrical Isomerism? Explain the geometrical isomers of 2-butene.

A. Geometrical isomerism arises due to difference in the arrangement of atoms or groups around doubly bonded carbon atoms. 2- Butene has the following two structures.



Cis – 2- Butene



Trans- 2- Butene

This isomer in which same groups or atoms are on the same side of the C=C is called cis-isomer while the isomer having same groups or atoms on the opposite sides of the C=C is called trans-isomer. In cis-2- Butene the two methyl group are on one side while the two hydrogen atoms are on other side. In Trans-2 butene two methyl groups and two hydrogen atoms are present opposite to the double bond.

ORGANIC CHEMISTRY(3rd part)

UNIT: 3

1. classification of Hydrocarbons
2. ALKANES – Nomenclature , isomerism, conformations
3. Methods of preparation of ETHANE
4. Physical properties, Chemical reactions including free radical mechanism Halogenation , combustion and pyrolysis of ETHANE
5. CYCLOHEXANE: preparations and properities

Very Short Answer Questions :

1. Give an example for wurtz's reaction.

A. Sodium metal reacts with methyl halide in the presence of dry ether to give ethane. It is known as wurtz reaction.

Ex : $2CH_3Cl + 2Na \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaCl$

2. What is the product formed when sodium propionate is heated with sodalime ?

A. Ethane gas is obtained

$\underset{\text{Sodium propionate}}{CH_3CH_2COONa} + NaOH \xrightarrow{CaO} \underset{\text{Ethane}}{CH_3 - CH_3} + Na_2CO_3$

3. Calculate the volume of CO_2 formed at STP when one litre of ethane burns in oxygen completely.

A. $C_2H_6 + 3\frac{1}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

1 Lit : $3\frac{1}{2}$ Lit : 2 Lit : 3 Lit at STP

4. Name the product formed when ethyl alcohol is heated to $170°C$ with conc. H_2SO_4. How does this product react with HCl ?

A. Ethyl alcohol on heating with conc. H_2SO_4 at $170°C$ gives ethylene

$$C_2H_5OH \xrightarrow[170°C]{\text{conc.}H_2SO_4} H_2C = CH_2 \,(\text{or})\, C_2H_4$$

Ethylene reacts with HCl and gives ethyl chloride

$\underset{\text{Ethylene}}{C_2H_4} + HCl \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl}$

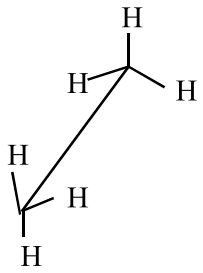
SHORT ANSWER QUESTIONS :

1. Discuss the conformation of ethane.

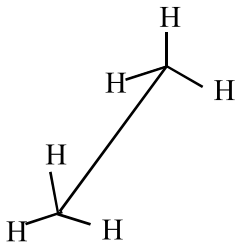
A. **Conformation of Ethane :**

Out of the infinite number of possible conformations of ethane, only two extreme conformations, i.e, staggered and eclipsed are important.

Saw – Horse projection

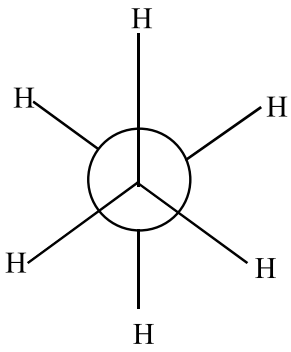


Staggered

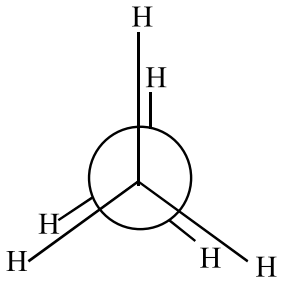


Eclipsed

Newman's projection



Staggered



Elipsed

Staggered conformation :

The C – H bonds are so arranged that each one bisects the angle defined by two C – H bonds on the adjacent carbon. Thus, the hydrogen atoms on adjacent carbons are farthest apart from each other. i.e, they are staggered.

Eclipsed conformation :

Here C – H bond is aligned (eclipsed) with a C – H bond on the adjacent carbon

In these two conformations, the basic structure of the ethane molecule and its various bond angles and bond lengths remain to be same

The repulsions between the non – bonded hydrogen atoms on the two carbons are minimum in the staggered conformation, therefore, staggered conformation is more stable than the eclipsed conformation by about $3.0\,k\,cal\,mol^{-1}$

Angle strain :

The compression of the bond angle results angle strain and causes increase in potential energy of the molecule. For example in cyclopropane expected bond angle according to sp^3 hybridization is $109°28'$. But observed is $60°$. Hence it experience the angle strain.

Torsional strain :

In eclipsed conformations of a molecule, there are repulsions between the aligned electron pairs of the eclipsed bonds. The strain due to this is known as torsional strain.

Cyclopropane and cyclobutane are relatively more reactive than cyclohexane due to angle strain and torsional strain.

2. Describe any two methods of preparation of ethane. Give any three reactions of ethane.

A. **1) Decarboxylation of sodium propionate :** Ethane is prepared by heating sodium propionate with sodalime. Sodalime is a mixture of CaO and NaOH

$$CH_3CH_2COONa + NaOH \xrightarrow[\Delta]{CaO} C_2H_6 + Na_2CO_3$$

2) Wurtz reaction : Ethane is prepared by heating methyl iodide with sodium metal in dry ehter

$$CH_3 - I + 2Na + I - CH_3 \xrightarrow{\text{dry ether}} CH_3 - CH_3 + 2NaI$$

3) Kolbe's electrolysis : Ethane is obtained by the electrolysis of aqueous sodium or potassium acetate solution

$$2CH_3COOK + 2H_2O \longrightarrow \underset{\text{At anode}}{C_2H_6} + 2CO_2 + \underset{\text{At cathode}}{2KOH} + H_2$$

4) Sabatier – Senderen's reaction : On a large scale ethane is prepared by the catalytic hydrogenation of ethylene and the reaction is called Sabatier – Senderen's reduction reaction.

$$\underset{\text{Ethylene}}{H_2C = CH_2} + H_2 \xrightarrow[300°C]{Ni} \underset{\text{Ethane}}{C_2H_6}$$

5) Reduction of ethyliodide : Ethane is prepared by the reduction of ethyl iodide by Zn – Cu couple in ethyl alcohol

$$C_2H_5I + 2H \xrightarrow[C_2H_5OH]{Zn-Cu} C_2H_6 + HI$$

CHEMICAL PROPERTIES :

Nitration :

Ethane reacts with nitric acid vapours at $400 - 450°C$ to give nitro ethane

$$C_2H_6 + HNO_3 \xrightarrow{400-450°C} C_2H_5NO_2 + H_2O$$

Pyrolysis :

The decomposition of higher alkanes on strong heating in the absence of air into lower alkanes, alkenes, etc is called pyrolysis or cracking.

$$C_{12}H_{26} \xrightarrow[973\,K]{Pt/Pd} C_7H_{16} + C_5H_{10} + \text{other products}$$

Dodecane

$$C_2H_6 \xrightarrow{450^\circ C} C_2H_4 + H_2$$

Controlled oxidation :

In the presence of a special catalyst at high pressure alkanes undergo controlled oxidation to give different products.

$$2C_2H_6 \xrightarrow[\Delta]{(CH_3COO)_2\ Mn} 2CH_3COOH + 2H_2O$$

Manganese acetate is the catalyst

Combustion :

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O + \text{energy}$$

3. Name the product formed when ethyl alcohol is heated to 170^oC with conc. $H_2SO_4^+$. How does this product react with HCl ?

A. Ethyl alcohol on heating with conc. H_2SO_4 at 170^oC gives ethylene.

$$C_2H_5OH \xrightarrow[170^oC]{Conc.H_2SO_4} H_2C = CH_2\,(or)\,C_2H_4$$

Ethylene reacts with HCl and gives ethyl chloride.

$$C_2H_4 + HCl \longrightarrow C_2H_5Cl$$

Ethylene Ethyl chloride

4. What is natural gas ? How is it useful ? Explain the distillation of crude oil.

A. The gas which occurs in earth crust is natural gas.

Natural gas is rich in methane and also contains ethane, propane and low molecular weight alkanes

Petroleum is a liquid mixture containing about 150 hydrocarbons and half of them are cycloalkanes

Distillation of crude oil gives several fractions as given below which contain several hydrocarbons

Petroleum refining involves distillation, cracking and reforming.

Cracking :

Higher molecular weight hydrocarbons are broken at C – C bonds to form lower molecular weight hydrocarbons.

This is induced by heat (thermal cracking) or by catalysis (catalytic cracking)

Reforming :

Reforming converts the hydrocarbons in them to aromatic hydrocarbons and highly branched alkanes. These are with less knocking tendency than unbranched alkanes or cycloalkanes.

5. Explain the free radical substitution of halogens in ethane with mechanism.

A. **1) Halogenation :**

Ethane reacts with halogens in the presence of sunlight to give a mixture of halogen derivatives

$$C_2H_6 + Cl_2 \xrightarrow{hv} C_2H_5Cl + HCl$$

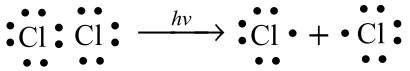
The above reaction proceeds further, finally it gives C_6Cl_6

Halogenation takes place by free radical mechanism

Mechanism :

The chlorination of ethane takes place in three steps

i) Chain initiation : In this step Cl_2 molecule absorbs energy and splits into free radicals



homolytic cleavage

ii) Chain propagation : Chlorine free radicals formed above react with ethane molecule

$$CH_3 - CH_3 + \dot{C}l \rightarrow CH_3 - \dot{C}H_2 + HCl \quad \text{..... (a)}$$

$$CH_3 - \dot{C}H_2 + Cl - Cl \rightarrow CH_3 - CH_2Cl + \dot{C}l \quad \text{..... (b)}$$

(a) and (b) repeat several times making the reaction a chain reaction and these steps are called propagation steps. In these steps the main products are formed.

iii) Chain termination : When free radicals directly combine, the chain reaction steps down

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$

$$\dot{C}_2H_5 + C_2\dot{H}_5 \longrightarrow C_4H_{10}$$

$$H_2\dot{C} - CH_3 + \dot{C}l \longrightarrow CH_3CH_2Cl \text{ etc}$$

LONG ANSWER QUESTIONS

1. Describe any two methods of preparation of ethane. Give any three reactions of ethane.

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In the presence of a special catalyst at high pressure alkanes undergo controlled oxidation to give different products.

$$2C_2H_6 \xrightarrow[\Delta]{(CH_3COO)_2\ Mn} 2CH_3COOH + 2H_2O$$

Manganese acetate is the catalyst

Combustion :

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O + \text{energy}$$

2. Write the preparations and properties of cyclohexane.

.A. Cycloalkanes are hydrocarbons whose molecules have their carbons arranged in one or more rings

They also, like alkanes have only C – C single bonds with sp^3 carbon atoms. Cycloalkanes with only one ring have the general formula C_nH_{2n}

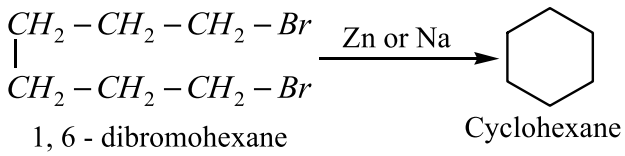
They also known as polymethylenes

Note : For nomenclature of cycloalkanes and bicyclic compounds refer page no 170

Preparation methods :

1. Freunds methods :

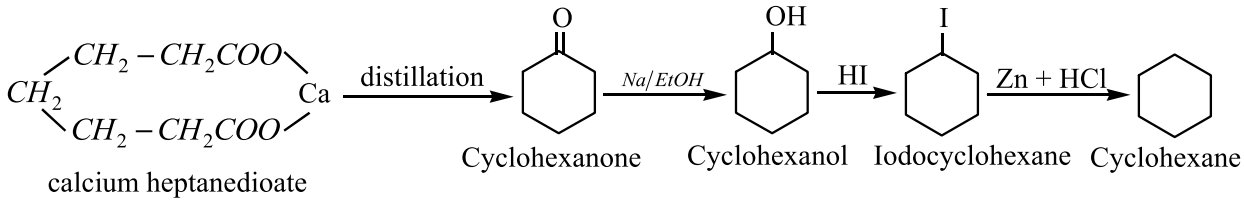
1, 3 to 1, 6 – dihaloalkanes react with metallic sodium or zinc to form the corresponding cycloalkanes



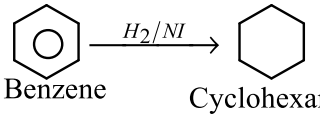
1, 6 - dibromohexane Cyclohexane

2. Wislicenus method :

Calcium or barium salts of dicarboxylic acids on distillation give the corresponding cycloketones. Cycloketones are reduced to cyclo alkanes.



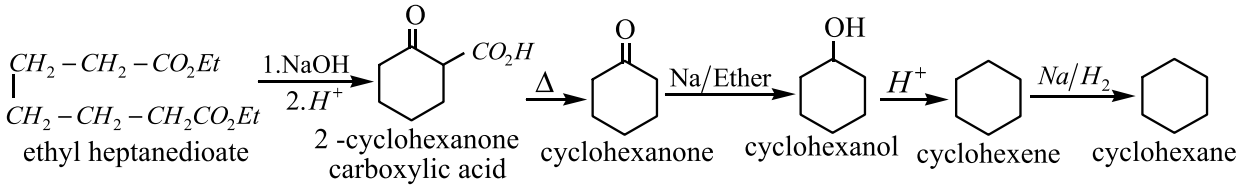
3. The reduction of aromatic hydrocarbons :



In the presence of Ni Benzene reacts with hydrogen to give cyclohexane

4. Dieckmann condensation reaction :

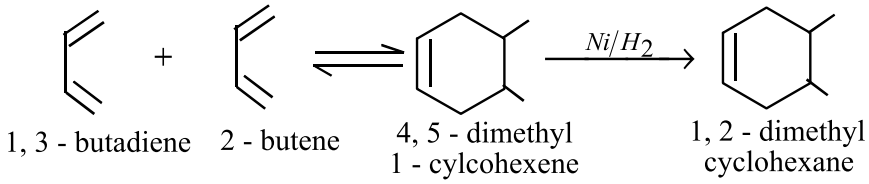
Five, six, seven membered rings are prepared from esters of dicarboxylic acids. This is an intramolecular condensation. The α - carbon atom and the ester group for the condensation come from the same molecule.



5. Diels – Alder reaction :

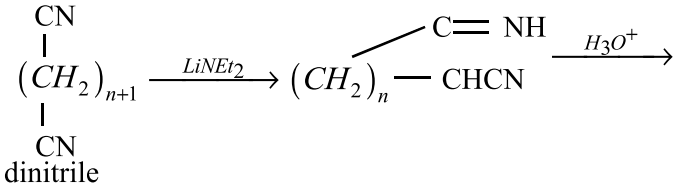
A conjugated diene (a 4π electron compound) and dienophile (a 2π electron compound) combine to give an addict which is a 6 membered cyclic compound with a double bond.

Examples :

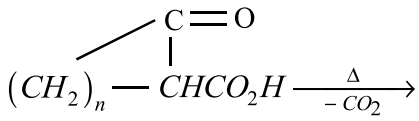


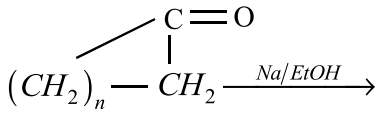
6. Ziegler reaction :

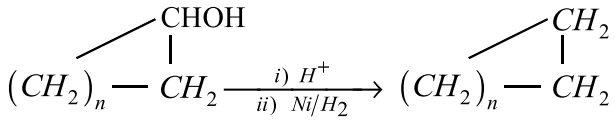
A dinitrile is treated with diethyl lithium amide. An imminonitrile is formed which is converted to cyclocketone by acid – catalysed hydrolysis and decarboxylation.



dinitrile





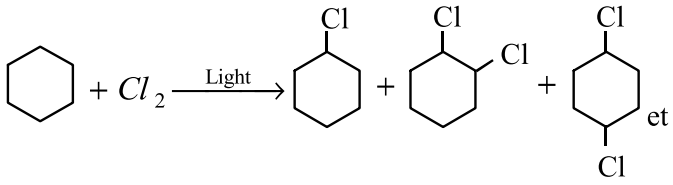


cycloalkane

Properties :

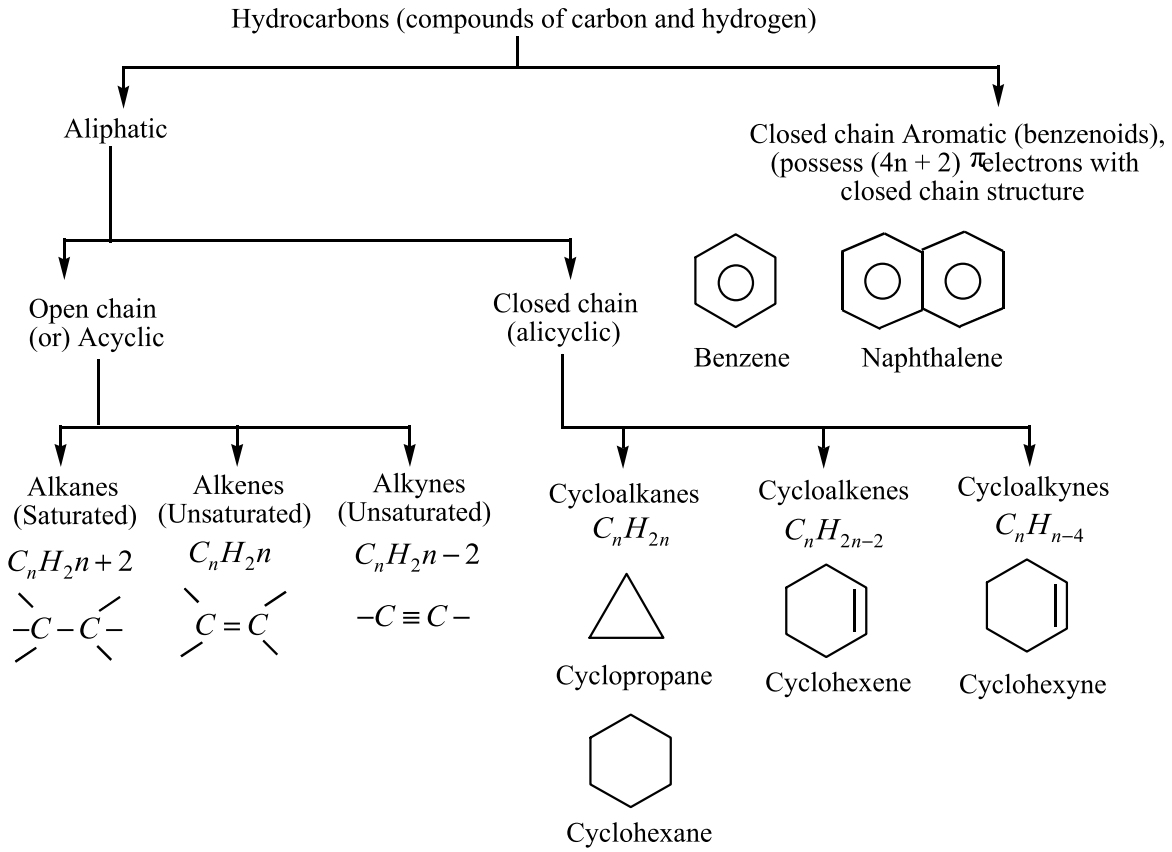
1. Cyclohexane behaves like hexane.

2. Halogenation of cyclochexane is free radical substitution similar to alkanes. Here a mixture of cyclohexanes are formed with cyclohexane.



3. Explain the classification of hydrocarbons.

A. **Classification of hydrocarbons :** Hydrocarbons are classified as aliphatic hydrocarbons and aromatic hydrocarbons. Aliphatic hydrocarbons are again classified as open change hydrocarbons and closed chain hydrocarbons i.e, cylcohydrocarbons. Both open chain and closed chain hydrocarbons are again classified as hydrocarbons containing C – C single bonds. > C = C < compounds, - C ≡ C – hydrocarbons. Aromatic compounds are called benzenoids as they are related to benzene.



4. Describe any two methods of preparation of ethane. Give any three reactions of ethane.

A. **Methods of preparation of ethane :**

1. Decarboxylation :

Ethane is prepared by heating sodium propionate with sodalime

$$\underset{\text{Sodium propionate}}{C_2H_5COONa} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Ethane}}{C_2H_6} + Na_2CO_3$$

2. Kolbe's electrolysis :

Ethane is obtained by the electrolysis of potassium acetate solution

$$\begin{bmatrix} CH_3 \\ CH_3 \end{bmatrix} COO\,K\,OH + \begin{bmatrix} H \\ H \end{bmatrix} \longrightarrow \underset{\text{Ethane}}{\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}} + 2CO_2 + 2KOH + H_2$$

H_2 gas evolves at cathode

Ethane and CO_2 are formed at anode

Chemical properties of ethane :

1. Halogenation :

Ethane reacts with chlorine in the presence of sunlight. Hydrogen atoms are substituted by halogen atoms successively. The final product is Hexachloro ethane.

$$C_2H_6 + Cl_2 \xrightarrow{\text{Sun light}} C_2H_5Cl + HCl \text{ (or)}$$

$$C_2H_6 + 6Cl_2 \xrightarrow{\text{Sun light}} C_2Cl_6 + 6HCl$$

2. Nitration :

Ethane reacts with nitric acid at $400°C$ and gives nitroethane

$$C_2H_6 + HNO_3 \xrightarrow[\Delta]{400°} \underset{\text{Nitro ethane}}{C_2H_5NO_2} + H_2O$$

3. Pyrolysis :

When ethane is heated in the absence of oxygen it decomposes giving ethylene and hydrogen

$$C_2H_6 \xrightarrow[\Delta]{400°} H_2C = CH_2 + H_2$$

5. What is the difference between conformation and configuration in open chain molecules?

A. Stereo isomers are of two types : 1) Configurational isomers 2) Conformational isomers .

Difference : Configurational isomers possess certain types of rigidity in the molecules. These molecules can be intercoverted only by bonds breaking and reforming of new bonds.

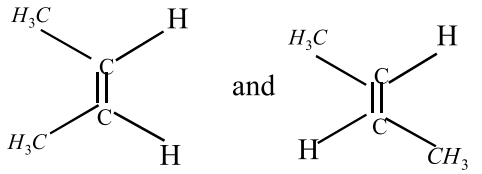
Conformations can be easily interconverted by simply rotating about C-C sigma bonds.

Explanation :

Configurational isomers are of two types : A) Geometrical isomers and B) Optical isomers.

A) Geometrical isomers : This is due to the difference in the spatial arrangement of groups about the doubly bonded carbon atoms in the molecules.

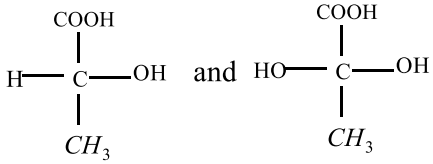
Ex : Cis -2 – Butene and Trans -2 – Butene



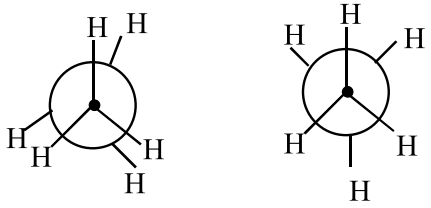
Cis – 2- Butene Trans – 2- Butene

B) Optical isomers : This is due to the different spatial arrangements of four different atoms or radicals in the molecules.

a. Ex : (+) Lactic acid (1) and (-) Lactic acid



2) **Conformations** : As a results of rotations about single C-C bond, the atoms or groups of a molecule assume different spatial arrangements. These different atomic arrangements are called, conformations.
3) Ex : Eclipsed (E) and staggered (S) conformations of ethane.



Eclipsed (E) Staggered (S)

ORGANIC CHEMISTRY
UNIT: 4

1. ALKENES : Nomenclature, structure of double bond (Ethene), geometrical isomerism , physical properties
2. Methods of preparation of ETHYLENE

3. Physical properties , chemical reactions : Addition of hydrogen , halogen, water, hydrogen halides (Markownikoff's addition and peroxide Effect) Ozonzlysis, Oxidation , Mechanism and electrophillic addition

Very Short Answer Questions

1. Give an example for polymerization.

A. Reaction in which several molecules of a substance combine with one another forming a big molecule is called polymerisation.

Ex : $\underset{\text{Ethylene}}{nC_2H_4} \xrightarrow[1500-2000\ \text{atm}]{O_2, 200^\circ C} \underset{\text{Polyethene}}{(C_2H_4)_n}$

2. Name the product formed when ethyl alcohol is heated at $170^\circ C$ with come sulphuric acid. How does the product react with HCl?

A. Ethylene gas is obtained

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{conc\ H_2SO_4/170^\circ C} \underset{\text{Ethylene}}{CH_2 = CH_2} + H_2O$$

It is known as dehydration reaction

$$CH_2 = CH_2 + HCl \longrightarrow \underset{\text{Ethyl chloride}}{H_3C - CH_2 - Cl}$$

3. How do you prepare ethyl chloride from ethylene?

A. Ethyl chloride is obtained when ethylene gas is treated with HCl

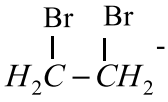
$$CH_2 = CH_2 + HCl \longrightarrow \underset{\text{Ethyl chloride}}{H_3C - CH_2 - Cl}$$

Ethyl chloride gives ethane by reduction with Zn – Cl in Ethyl alcohol.

4. Write the names of the products A and B formed in the following reaction.

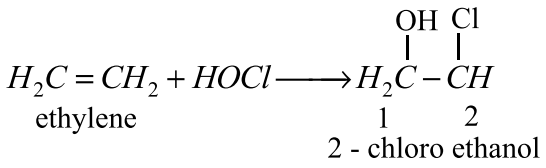
$$C_2H_5Cl \xrightarrow{Alc\ KOH} A \xrightarrow{Br_2} B$$

A. A = C_2H_4 - Ethylene

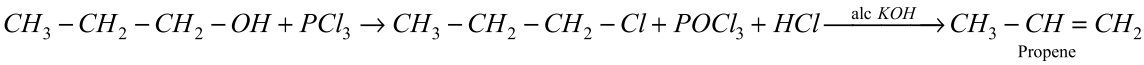
B =  - 1, 2 - dibromo ethane

5. Name the hydrocarbon which gives 2 – chloroethane-1-ol on treating with hypochlorous acid.

A. Ethylene gives 2 – chloroethanol with hypochlorous acid.



6. Give the structural formula of the product formed when n – propyl alcohol reacts with PCl_3 and alcoholic KOH. Write the equation for the reactions.

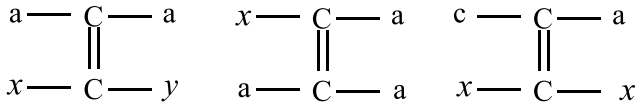
A. 

SHORT ANSWER QUESTIONS

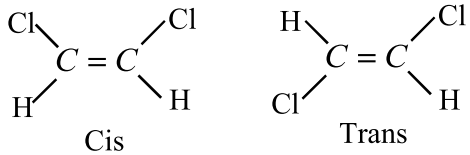
1. What do you understand about geometrical isomerism?

A. **Geometrical isomerism:** Compounds having same molecular formula but differ in spatial arrangement of atoms or groups above and below plane are called geometrical isomers and the phenomenon is called geometrical isomerism. It is also called as cis, trans isomerism.

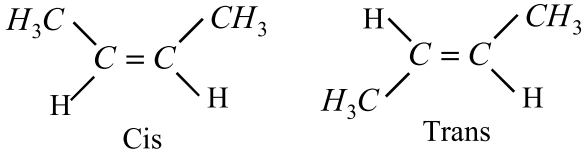
The geometrical isomerism is possible only when each of the doubly bonded carbon atom has two different groups. Thus the following type will not show geometrical isomerism.



Ex :- 1, 2 dichloro Ethylene

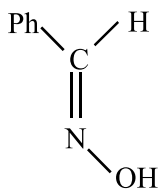


Ex :- 2 Butene

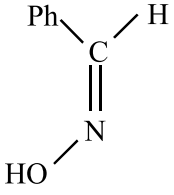


In the above example both methyl groups are present on same plane which is called Cis isomer. If the methyl groups are present in opposite plane, it is trans isomer. The prefixes Cis and trans are from Latin in which Cis means "on same side" and trans means across. Geometrical isomerism is possible even in molecules which do not possess a C = C

Example: It is found in oximes. If the lighter groups are an same side it is called Syn. But if they are an opposite side, they are called anti.

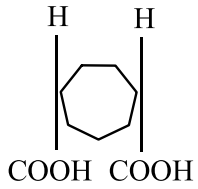


Syn - benzaldoxime

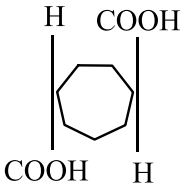


Ante - benzaldoxime

Other example:



cis - 1, 4 - Cyclohexane dicarboxylic acid



Trans - 1, 4 - Cyclohexane dicarboxylic acid

Note: The above isomers are non mirror images. Hence, they are diesteriomers

2. Describe two methods of preparations of ethylene. Give equation for the reactions of ethylene with the following.

a) O_3 **b) HOCl** **c) Baeyer's reagent** **d) Heated with** O_2 **at high pressure**

A. **Preparation methods of ethylene:**

1. Dehydration of ethyl alcohol:

Ethylene is obtained when ethyl alcohol is heated with concentrated sulphuric acid at $170°C$ or with Al_2O_3 at $350°C$. This reaction is also called β - elimination reaction as 'H' is eliminated from β carbon.

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[170°C]{Conc.\ H_2SO_4} \underset{\text{ethylene}}{H_2C=CH_2} + H_2O$$

2. Dehydrohalogenation of ethyl halides:

When ethyl alcohol or ethyl bromide or ethyl iodide is heated with alcoholic potassium hydroxide, ethylene is formed.

$$\underset{\text{ethyl bromide}}{CH_3CH_2Br} + KOH\,(ac) \xrightarrow{\Delta} H_2C=CH_2 + KBr + H_2O$$

This reaction is called β - eliminations as H – atom is eliminated from the β carbon atom

3. Dehalogenation:

When 1, 2 – dibromo – ethane is heated with zinc dust in an alcoholic solution and ethylene is obtained

4. Controlled hydrogenation of acetylene:

When acetylene is hydrogenated in the presence of Lindlar's catalyst, ethylene is obtained

$$H-C\equiv C-H+H_2 \xrightarrow[\text{Quinoline}]{Pd-BaSO_4} \underset{\text{Ethylene}}{H_2C=CH_2}$$

Lindlar's catalyst: It is a mixture of palladium coated charcoal and barium sulphate in the presence of quinoline.

5. Industrial method:

Ethene is prepared by pyrolysis of ethane which is obtained from natural gas. This is the industrial preparation of ethylene.

$$H_3C-CH_3 \xrightarrow{\Delta} H_2C=CH_2+H_2$$

CHEMICAL PROPERTIES:

a) Ozonolysis:

The formation of ozonide and its reduction with $(Zn+H_2O)$ is called ozonolysis

The addition product of unsaturated hydrocarbons with O_3 is called as ozonide

The double bonded carbons give > C = O groups (carbonyl compounds)

Based on the carbonyl compounds obtained the alkaline structure is given

On ozonolysis

1) Ethylene gives two formaldehyde molecules

2) Propene gives acetaldehyde and formaldehyde

3) Isobutylene gives one mole of acetaldehyde and one mole of formaldehyde

4) 2 – methyl 2 – butane gives one mole of acetaldehyde and one mole of acetone

b) HOCl:

Addition of hypochlorous acid to ethylene gives ethylene chlorohydrin

c) Oxidation:

a) Cold and dilute alkaline $KMnO_4$ is called Baeyer's reagent

At 273K ethylene reacts with Baeyer's reagent to form ethylene glycol

$$CH_2 = CH_2 \xrightarrow{\text{cold dil alk } KMnO_4} \underset{\text{ethylene glycol}}{CH_2OH - CH_2OH}$$

Potassium permanganate decolorizes

This reactions is used to detect carbon – carbon double bond or multiple bond under the name Baeyer's test

Acidic $KMnO_4$ or $K_2Cr_2O_7$ oxidizes alkenes to ketones or acids, depending on the nature of alkene

d) Heated with O_2 at high pressure:

Polymerisation:

The process in which simple molecule of same substance or different substances join together to form large molecules without elimination of small molecules is called polymerization and the product is called polymer.

$$\underset{\text{Ethene}}{nCH_2 = CH_2} \xrightarrow[O_2,\ 200°C]{1500-200\ atm} \underset{\text{Polythene or polyethylene}}{(C_2H_4)_n}$$

3. How does ethylene reacts with the following reagents.

a) Hydrogen b) HCl c) Bromine/CCl_4 d) water e) O_2/Ag

A. **a) Addition of hydrogen (hydrogenation) :**

Alkenes react with hydrogen in the presence of Pt, Pd and Ni catalyst to form alkanes

$$CH_2 = CH_2 + H \xrightarrow{Pt/Pd/Ni} CH_3 - CH_3$$

b) HCl :

Addition of hydrogen chloride of ethylene gives ethyl chloride

$$H_2C = CH_2 + HCl \longrightarrow H_3C - \underset{\text{Ethyl chloride}}{CHCl}$$

c) Bromine:

Ethylene decolourises red colour of bromine dissolved in CCl_4. This test is used in laboratory for the detection of unsaturation of organic compound.

d) Water (Hydration):

Ethyl gas on passing through dil H_2SO_4 adds a molecule of water giving ethyl alcohol

$$H_2C = CH_2 + H - Cl \xrightarrow{\text{Dil } H_2SO_4} CH_3 - CH_2 - OH$$

e) O_2/Ag :

When ethylene is heated with Ag in the presence of air it gives ethylene oxide (epoxide) (or) oxirane or epoxyethane

4. Discuss Markownikoff's rule and Kharasch effect?

A. **Addition of hydrogen halides:**

Addition of HX to a double bond generally follows Markownikoff rule

Statement of Markownikoff's rule:

The rule states the addition of hydrogen halides to unsymmetrical alkenes takes place in such a manner that the positive part of the reagent attaches itself to that carbon atom which has more number of hydrogen atoms.

Explanation :

It follows electrophilic addition mechanism

$$CH_2-CH=CH_2+HBr \xrightarrow{H^+} \underset{\text{less stable } 1^\circ}{CH_3-CH_2-{}^+CH_2} + \underset{\text{more stable } 2^\circ}{CH_3-{}^+CH-CH_3}$$

Since 2° carbocation is more stable than 1° carbocation, the major product formed is 2 – Bromo propane

$$Br^- + CH_3-{}^+CH-CH_3 \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

Note: Markownikoff's rule is only applicable for unsymmetrical alkenes

Anti Markownikoff's rule or peroxide effect or Kharasch effect:

In the presence of peroxide (R – O – O – H) the addition of HBr to unsymmetrical alkene like propene takes place in such a way that the negative part of the reagent attach itself to that carbon atom which has more number of hydrogen atoms.

$$CH_3-CH=CH_2+HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-CH_2-CH_2Br$$

Mechanism:

It follows free radical addition mechanism:

Step – 1:

$$CH_3-CH=CH_2+\dot{B}r$$

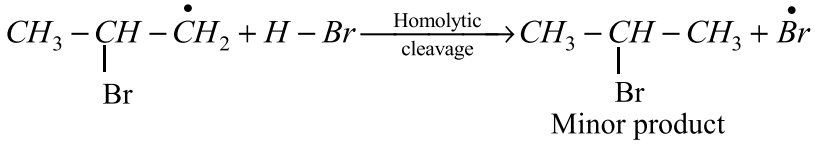
$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\dot{C}H_2 \qquad CH_3-\dot{C}H-CH_2-Br$$

Less stable — More stable

Step – 2:

$$CH_3-\dot{C}H-CH_2Br+HBr \xrightarrow[\text{cleavage}]{\text{Homolytic}} \underset{\text{Major product}}{CH_3-CH_2-CH_2Br} + \dot{B}r$$

Step – 3:



Stability of free radicals follows as $3° > 2° > 1°$ Therefore,1 – bromopropane is major product

Uses of Ethylene

Ethylene is used

i) In the manufacture of ethyl alcohol, polythene, etc

ii) In the preparation of ethylene glycol an antifreeze

iii) In the preparation of mustard gas

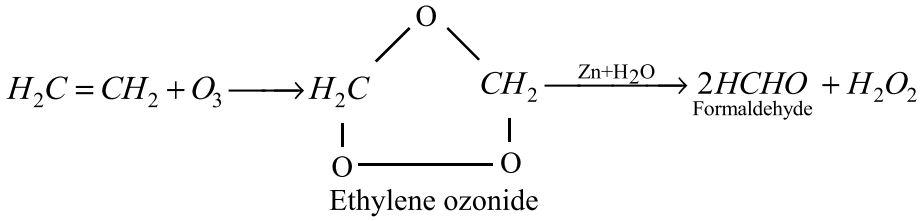
$$C_2H_4 + S_2Cl_2 \rightarrow Cl - CH_2 - CH_2 - S - CH_2 - CH_2 - Cl(\text{mustard gas}) + S$$

5. What is ozonolysis? Which type of compounds react with ozone ? Explain with an example.

A. 1) Unsaturated hydrocarbons react with ozone and form addition compound called ozonide. On hydrolysis and ozonide gives carbonyl compound. This is called ozonolysis.

2) Unsaturated hydrocarbons usually react with ozone. Ozonolysis is used for the location of the double bond in unsaturated compounds like alkene, alkyne and benzene.

Example: Ethylene undergoes addition reaction with ozone and form ozonide. If, on hydrolysis, in presence of Zn dust, gives formaldehyde and H_2O_2



LONG ANSWER QUESTIONS

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