CHAPTER NO 16

HYDROCARBONS

Q:- What are hydrocarbons? How they are classified?

Hydrocarbons:-

"Organic compounds which contain carbon and hydrogen only are called hydrocarbons"

→ **Catenation:-**

"The ability of carbon atoms to attach with each other to form a chain or ring is called catenation"

TYPES OF HYDROCARBONS

Hydrocarbons

- Open chain Hydrocarbons OR Acyclic Hydrocarbons
  - Saturated hydrocarbons
    - Alkanes e.g.:- (CH_4)
  - Unsaturated hydrocarbons
    - Alkenes e.g.:- $CH_2 = CH_2$ (Ethene)
    - Alkynes e.g.:- $CH \equiv CH$ [Ethyne]
- Closed Chain Hydrocarbons OR Cyclic Hydrocarbons
  - Alicyclic H.C. [Cycloalkanes] e.g.:- (Cyclohexane)
  - Aromatic H.C. e.g.:- [Benzene]

1- Open Chain Hydrocarbons :- [Aliphatic OR Acyclic H.C]

"The hydrocarbons in which carbon atoms are attached with each other to form open chains are called open chain hydrocarbons"

OR

"Hydrocarbons in which carbon atoms are attached without ring structure are called open chain hydrocarbons"

TYPES :-

They are further classified into two types

i- Saturated Hydrocarbons [Alkanes OR Paraffins]

ii- Unsaturated Hydrocarbons [Alkenes OR Olefins] AND [Alkynes]

EXPANATION AND EXAMPLES :-

SATURATED HYDROCARBONS	UNSATURATED HYDROCARBONS
⇒ Hydrocarbons in which there is a single bond b/w carbon atoms are called saturated hydrocarbons.	⇒ Hydrocarbons in which there is double or triple bond b/w carbon atoms are called unsaturated hydrocarbons
⇒ They have general formula: C_nH_{2n+2}	⇒ They have general formula: i- C_nH_{2n} (Alkenes) ii- C_nH_{2n-2} [Alkynes]
⇒ Each carbon atom is "sp^3" hybridized.	⇒ They hybridized "sp^2" for alkenes and "sp" for alkynes.
⇒ They may have straight chain or branched chain	⇒ They may have straight chain or branched chain.
⇒ Example: Alkanes i- $CH_3-CH_2-CH_2-CH_3$ n-Butane	⇒ Examples :- In case of Alkene:- i- $CH_2=CH-CH_2-CH_3$ [1-Butene]

ii- $CH_3-CH(CH_3)-CH_3$

2-Methyl Propane

⇒ No further atoms or groups of atoms can be attached to the carbon atoms of such hydrocarbons. That is why they are known as saturated hydrocarbons.

i- $CH_2=C(CH_3)-CH_3$

2-Methyl Propene

→ In case of Alkyne:-

i- $CH_3-C\equiv C-CH_3$

2-Butyne

ii- $H_3C-CH(CH_3)-C(CH_2CH_3)-C\equiv CH$

3-Ethyl-3-Methyl-1-Pentyne

2- Closed Chain Hydrocarbons
OR
Cyclic Hydrocarbons
OR
Ring Hydrocarbons :-

"Hydrocarbons in which carbon atoms are bonded in the form of rings structure are called closed chain hydrocarbons"

OR

"Hydrocarbons in which carbon atoms are attach with each other to form rings are called closed chain hydrocarbons"

TYPES :-

They are further classified into two types.

i- Alicyclic hydrocarbons

ii- Aromatic hydrocarbons

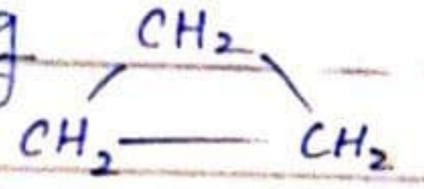
EXPLANATION AND EXAMPLES

Alicyclic Hydrocarbons

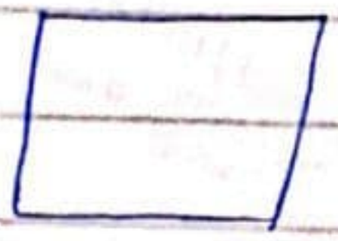
⇒ Closed chain hydrocarbons without benzene ring [NON-BENZOID] are called Alicyclic hydrocarbons

⇒ Alicyclic hydrocarbons possess two hydrogen atoms less than their corresponding open chain hydrocarbons

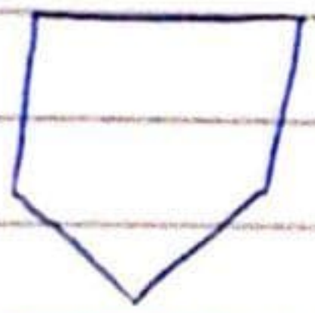
⇒ e.g



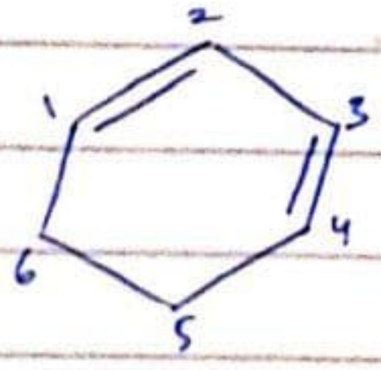
Cyclopropane



cyclobutane



Cyclopentane



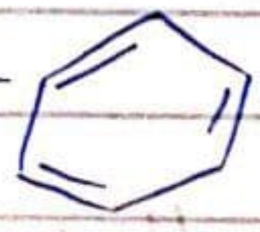
1,3-cyclohexa-diene

Aromatic Hydrocarbons

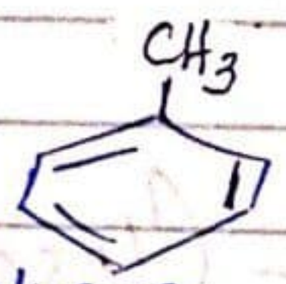
⇒ Closed chain hydrocarbons contains atleast one benzene ring [BENZOID] in their structure are called aromatic hydrocarbons.

⇒ Benzene, which is the simplest aromatic hydrocarbon, has a regular hexagonal structure with alternate single or double bonds b/w carbon atoms

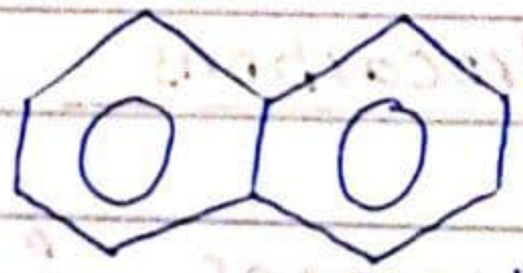
⇒ e.g:-



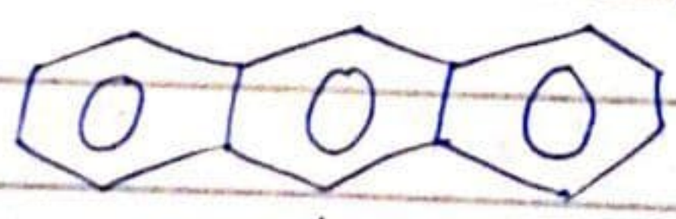
BENZENE



Toluene



Napthalene



Anthracene.

ALKANES and CYCLOALKANES

Alkanes:-

⇒ Simplest organic molecules with only "C" and "H" atoms.
⇒ Commercially important as fuels and oils.

NOMENCLATURE :-

[Nomenclature are saperately arranged on different notes]

Physical Properties of Alkane :-

1) First four Alkanes i-e Methane (CH_4), Ethane (C_2H_6), propane (C_3H_8) and Butane (C_4H_{10}) are colourless and odourless gases. "C_5-C_{17}" alkanes are colourless, odourless liquid. C_{18} and higher members are colourless, odourless waxy solids.

2) Alkanes are nonpolar, they are insoluble in polar solvents like water but soluble in organic solvents like benzene, carbontetrachloride [CCl_4] and petroleum ether.

3) Physical parameters like melting points, boilingspoint and density increases with. increase in no of carbom atoms. By the addition of each "CH_2" group, increase in melting points, boilingpoint is "20 - 30 °C". But solubility of Alkane decreases with increase in no of Carbon atom.

4) Straight chain alkane have high boiling points as compared to isomer of that Alkane in branched

form. e.g Boiling point of n-butane is greater than Isobutane

⇒ STRUCTURE :-

1) In Alkane, each carbon atom is sp^3 - hybridized.
2) They have general formula "C_nH_{2n+2}"
3) They are saturated hydrocarbons
4) n-butane and Isobutane are Isomer of each other

i- $CH_3 - CH_2 - CH_2 - CH_3$

n-butane

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

Isobutane

⇒ REACTIVITY OF ALKANE :-

⇒ Alkanes are also called "paraffins", param means "little", "affins" means "affinity", which means that they have low value of affinity.

⇒ They donot react with acid, bases, oxidizing agents and reducing agents at room temperature.

⇒ However under suitable condition, they undergo two types of reactions.

i- Substitution Reaction
ii- Thermal and Catalytic reaction

⇒ Reactivity of Alkane can be discussed on the basis of two factors.

1- Inertness of Sigmabond :-

In alkane there is sigmabond b/w carbon atom. It is formed by overlapping of atomic orbitals. Electron density exists b/w the two nuclei. These electrons are

not easily available for the attack of electrophile and nucleophile, because they are tightly arranged b/w the two nuclei.

2- Nonpolar nature of C-C or C-H bond:-

In Alkane there is C-C or C-H bond. They are non-polar because electronegativity of "C" is "2.5" and electronegativity of "H" is "2.1". Difference in electronegativity is zero (0) or very small. Therefore Alkanes are non-polar and less reactive hydrocarbons

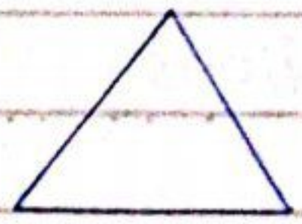
⟹ CYCLOALKANES:-

Another type of molecule containing sp^3 hybridized "C" and "H" atoms connected by single bonds is possible with a ring of 3 or more C atoms. These are the cycloalkanes which are fairly common in the world of organic chemistry, both man-made and natural.

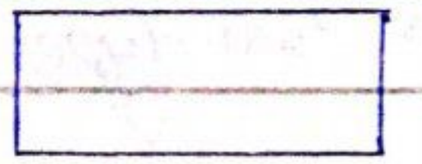
Nomenclature:-

According to IUPAC system, cycloalkanes with one ring are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring.

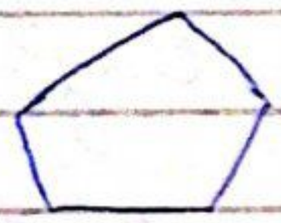
e.g:-



Cyclopropane



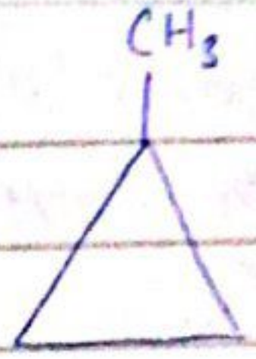
Cyclobutane



Cyclopentane

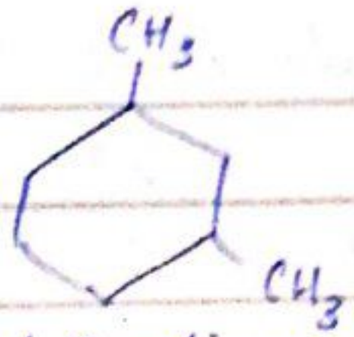
The substituents are numbered in such a way that the sum of numbers are kept minimum

e.g:- If the alicyclic hydrocarbon is unsaturated, the rules applied to alkenes (for double bond) or alkynes (for triple bond) are used. e.g.



Methyl cyclo propane

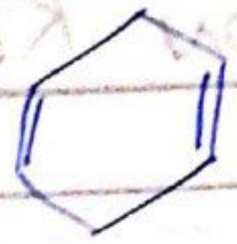
1-2-dimethyl cyclo butane



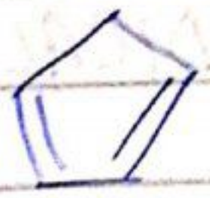
1,3-dimethyl cyclohexane

Multiple bonds are given the lowest possible number.

Cyclo peniene



Cyclo 1,4-hexadiene



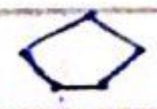
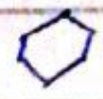
cyclo 1,3-peniadiene

-2) PHYSICAL PROPERTIES :-

Like alkanes, the low polarity of all the bonds in cycloalkanes means that the only intermolecular forces b/w molecules of cycloalkanes are the very weak induced dipole-induced dipole forces, also known as "London forces" which are easily overcome. Like alkanes, cycloalkanes also to have low melting and boiling points.

They have a geometric formula C_nH_{2n} [note: there is 2 less atom-H as compared to analogous alkane].

The C3 to C6 cycloalkanes are shown below in a variety of representations.

Cyclopropane	C_3H_6	
Cyclo butane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	

- 3) REACTIVITY :-

Very small reactivity to the closed related alkanes

which have the same type of bonds. Since "C" and "H" atoms have very similar electronegativities, both C-H and C-C bonds are non polar. As a result, cycloalkanes, like alkanes are not a very reactive functional group.

RADICAL SUBSTITUTION REACTIONS

i- Halogenation :-

1) Replacement of hydrogen atom by "Halogen" is called Halogenation

2) Reactivity order of Halogen are given below

$$F_2 > Cl_2 > Br_2 > I_2$$

3) For halogenation, chlorine (Cl_2) or bromine (Br_2) are used, Flourine (F_2) and Iodine (I_2) are not used because reaction of F_2 takes place voilenily (شدید) and reaction of I_2 with alkane are slow and reversible.

4) Extent of Halogenation depends upon amount of halogen used in a chemical reaction.

5) Halogenation of alkane take place in the presence of sunlight or ultraviolet radiation or at high temperature.

6) Reaction of alkane are "free radical mechanism"

REACTION MECHANISM:- [Radical chain mechanism]

⇒ It has three steps.

i- Iniation

ii- Propogation

iii- Termination.

EXAMPLE :-

⇒ Reaction of Methane (CH_4) with Bromine (Br_2):-

$$CH_4 + 4Br_2 \xrightarrow{h\nu} CBr_4 + 4HBr$$

Step 01 : Initiation :-

$$\overset{\frown}{Br}-\overset{\frown}{Br} \xrightarrow{h\nu} Br^{\bullet} + Br^{\bullet}$$

Step 02 : Propagation :-

$$\overset{\frown}{CH_3}-\overset{\frown}{H} \quad \overset{\vee}{Br^{\bullet}} \xrightarrow{h\nu} \dot{C}H_3 + HBr$$

$$\dot{C}H_3 \quad \overset{\vee}{Br}-Br \xrightarrow{h\nu} CH_3Br + Br^{\bullet}$$

$$\overset{\frown}{CH_3Br} \quad \overset{\vee}{Br^{\bullet}} \xrightarrow{h\nu} \dot{C}H_2Br + HBr$$

$$\dot{C}H_2Br \quad \overset{\vee}{Br}-Br \xrightarrow{h\nu} CH_2Br_2 + Br^{\bullet}$$

$$\overset{\frown}{CH_2Br_2} \quad \overset{\vee}{Br^{\bullet}} \xrightarrow{h\nu} \dot{C}HBr_2 + HBr$$

$$\dot{C}HBr_2 \quad \overset{\vee}{Br}-Br \xrightarrow{h\nu} CHBr_3 + Br^{\bullet}$$

$$\overset{\frown}{CHBr_3} \quad \overset{\vee}{Br^{\bullet}} \xrightarrow{h\nu} \dot{C}Br_3 + HBr$$

$$\dot{C}Br_3 \quad \overset{\vee}{Br}-Br \xrightarrow{h\nu} CBr_4 + Br^{\bullet}$$

Step 03 : Termination :-

$$\overset{\frown}{CH_3} \quad \overset{\vee}{Br^{\bullet}} \xrightarrow{h\nu} CH_3Br$$

$$Br^{\bullet} \quad \overset{\vee}{Br^{\bullet}} \xrightarrow{h\nu} Br-Br$$

$$\dot{C}H_3 \quad \overset{\vee}{\dot{C}H_3} \longrightarrow CH_3-CH_3$$

Oxidation - Reduction reaction / redox reaction

Oxidation :-

- Addition of oxygen i-e more "C-O" bond.
- Removal of hydrogen i-e less "C-H" bond.
- Loss of electron
- Increase in oxidation state i-e $+1 \longrightarrow +5$

Reduction :-

- Addition of hydrogen. i-e more "C-H" bond.
- Removal of oxygen i-e less "C-O" bond.
- Gain of electron.
- Decrease in oxidation state.

Very Important

ISOMERISM :-

"Different compounds having same molecular formula but different structural formula and properties are called isomers and the phenomena is known as isomerism"

⇒ Methane, Ethane and Propane has no. isomers because they have only one possible structure

⇒ Butane has two isomers.

⇒ Pentane has three isomers.

⇒ Hexane has five isomers.

. As the no of carbon atoms increases, no. of isomers are increases.

TYPES :-

There are two types of isomerism.

1- Structural Isomerism.

2- Stereo Isomerism.

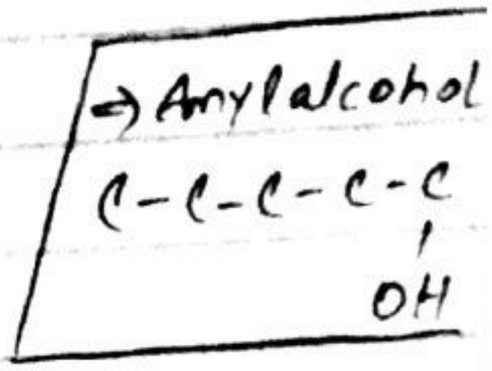
1- STRUCTURAL ISOMERISM :-

"Different compounds having same molecular formula but different structure are called structural isomers and the phenomena is known as structural isomerism"

It is further divided into five types.

i- Chain Isomerism.
ii- Position Isomerism.
iii- Functional Isomerism.
iv- Tautomerism.
v- Metamerism.

→ Amyl alcohol



i- Chain Isomerism :-

"Different compounds having same molecular formula but different carbon chain are called chain Isomers and the phenomena is known as chain Isomerism."

e.g :-

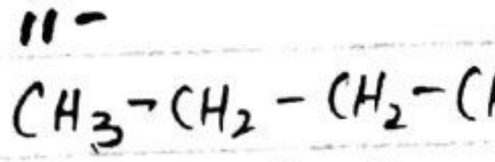
i- $CH_3 - CH_2 - CH_2 - CH_3$

• n-Butane

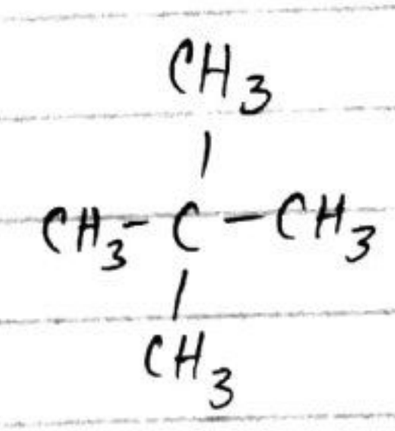
• Iso-butane

n-Butane and Isobutane are chain Isomers.

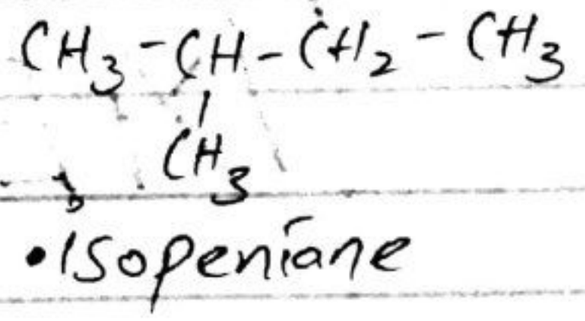
ii-



• n-Pentane



• Neopentane



• Isopentane

n-Pentane, Neopentane and Isopentane are chain isomers.

ii- Position Isomerism :-

"Different compounds having same molecular formula but different position of the same functional group are called position isomers and the phenomena is known as position isomerism."

i-

$CH_2=CH-CH_2-CH_3$

1-Butene

$CH_3-CH=CH-CH_3$

2-Butene

1-Butene & 2-Butene are position isomers.

ii-

$CH_3-CH_2-CH_2$ (OH)

1-Propanol

$CH_3-CH(OH)-CH_3$

2-Propanol

iii- Functional Isomerism:-

"Different compounds having same molecular formula but different functional group are called functional isomers and the phenomena is known as functional isomerism."

i-

CH_3-O-CH_3

Dimethyl ether.

CH_3-CH_2-OH

Ethyl alcohol.

Dimethyl ether & Ethylalcohol are functional isomers.

ii-

$CH_3-CH_2-C(=O)-H$

Propionaldehyde

$CH_3-C(=O)-CH_3$

Acetone.

Propionaldehyde & Acetone are functional isomers.

iii-

$CH_3-C(=O)-OH$

Acetic acid

$H-C(=O)-OCH_3$

Methyl formate

Acetic acid & Methyl formate are functional isomers.

iv- Metamerism :-

"Different compounds having same molecular formula but unequal distribution of C-atom on either side of functional group are called metamers and the phenomena is known as metamerism"

⇒ Metamers belongs to same homologous series.

e.g :-

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

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

Diethyl ether and Methylpropyl ether are metamers.

$CH_3-CH_2-NH-CH_2-CH_3$ — Diethyl amine

$CH_3-NH-CH_2-CH_2-CH_3$ — Methyl propyl amine

Diethyl amine and Methylpropyl amine are metamers.

v- Tautomerism :- [also called as equilibrium type]

"Type of isomerism in which one isomer is converted into other isomer due to the migration of hydrogen ion are called tautomerism."

Examples

1) $R-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-OH \rightleftharpoons R-\underset{\underset{\oplus NH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-O^-$

(Amino Acid) (Zwitter ion)

2) $CH_3-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{O}{||}}{C}-OC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{||}}{C}-OC_2H_5$

Ketoform (enol-form)

2- STEREOISOMERISM

"Different compounds having same molecular formula but different configuration i-e arrangement of the different atoms in the space are called stereoisomers and the phenomena is called stereoisomerism."

⇒ It is further classified into two types.

i- Geometric isomerism [Cis-Trans isomerism].

ii- Optical isomerism.

i- Geometric Isomerism :-

"Different compounds having same molecular formula but different positions of the identical group in space are called geometric isomers and the phenomena is called geometric Isomerism."

⇒ When two identical group lie on the same double bond, it is called **cis-form**.

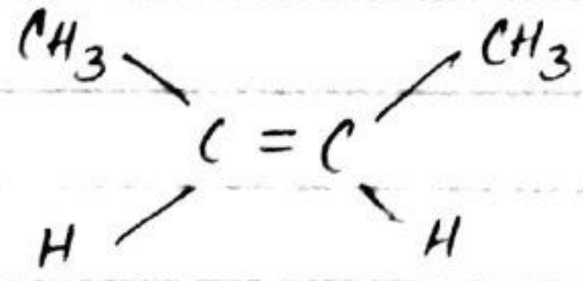
⇒ When two identical group lie on the opposite side of double bond, it is called **trans-form**.

⇒ Trans-form is more stable as compared to the Cis-form because in transform two bulky groups lie on the opposite side of the double bond. Due to which the steric repulsion decreases and as a result the stability increases

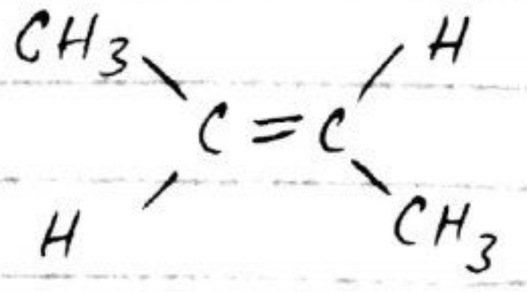
⇒ Trans-form has **zero** dipole moment and Cis-form has **non-zero** dipole moment.

e.g.:-

i- 2-butene shows geometric isomeoism

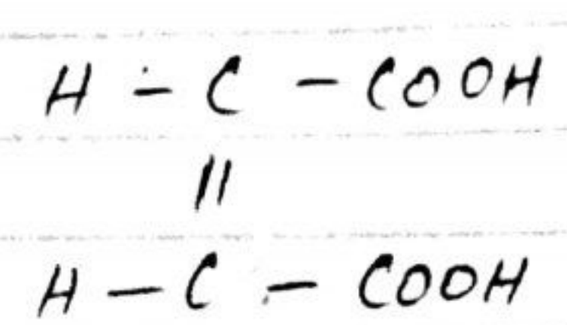


• Cis-2-butene

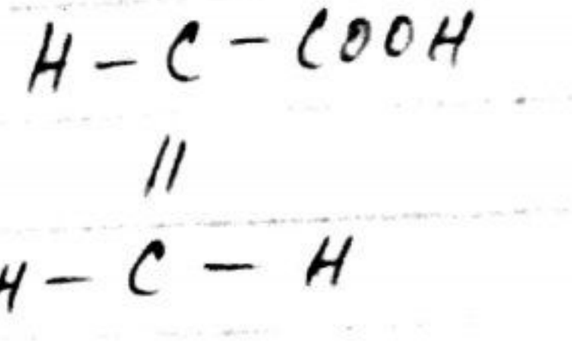


• Trans-2-butene.

ii. Maleic Acid and Fumeric Acid shows geometric isomerism

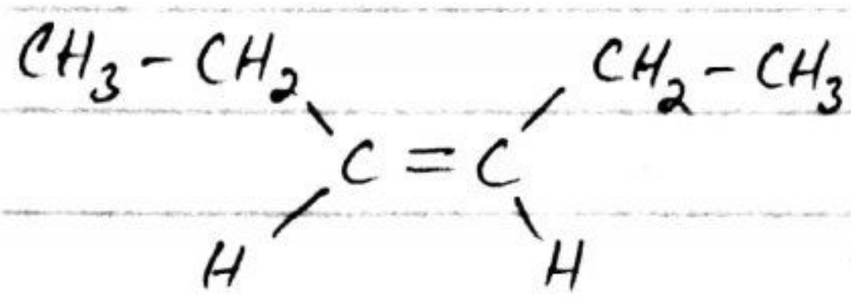


- Cis-2-buiene-1,4-dioic acid (Maleic acid)

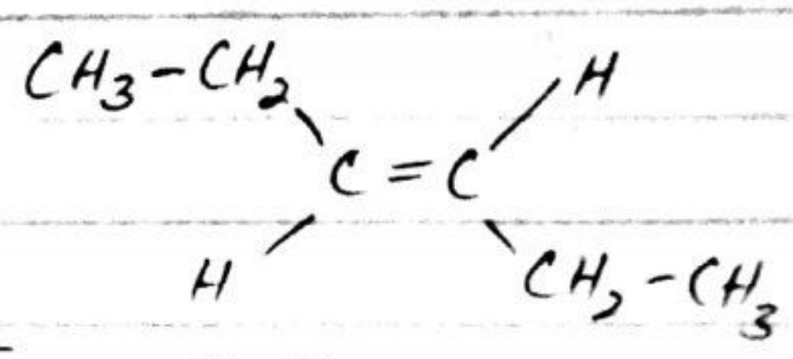


- Trans-2-buiene-1,4dioic acid (fumeric acid)

iii- 3-Hexene shows geometric isomerism.



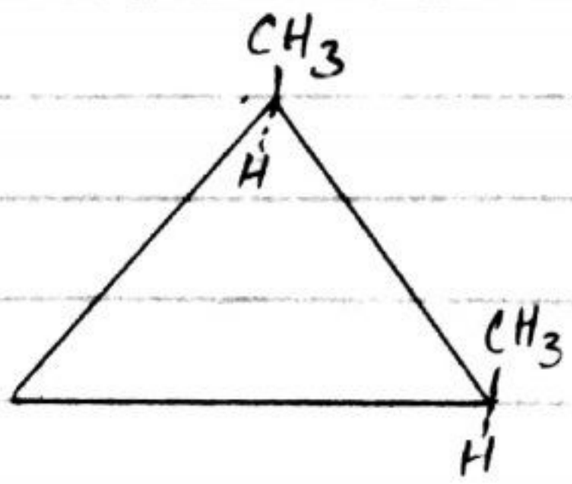
- Cis-3-Hexene



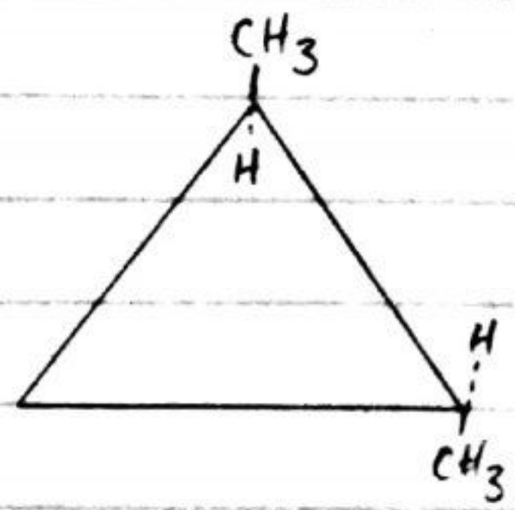
- Trans-3-Hexene

⇒ In cycloalkane, C-C bond should not rotate around its axis, therefore cycloalkane shows geometric isomerism.

⇒ Only single bond shows geometric isomerism in cycloalkane.



- Cis-form



- Trans-form

Note:- [⇒ Conditions for Geometric Isomerism]

1- Two groups attach with the the same carbon atom must be different

2- C-C bond should not rotate around its axis

Q- 1-butene donot show geometric isomerism but 2-butene show geometric isomerism - Why?

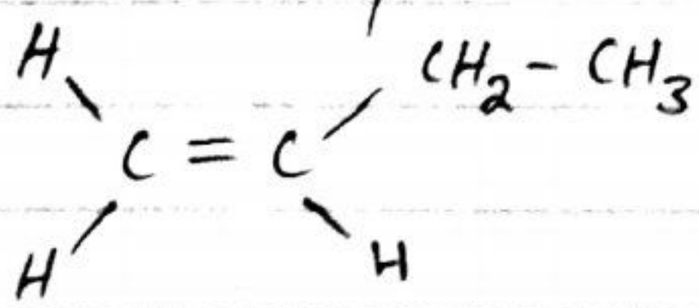
ANS:-

As we know that we have two conditions in geometric isomerism.

i- Two group attached with the same C-atom must be diff-

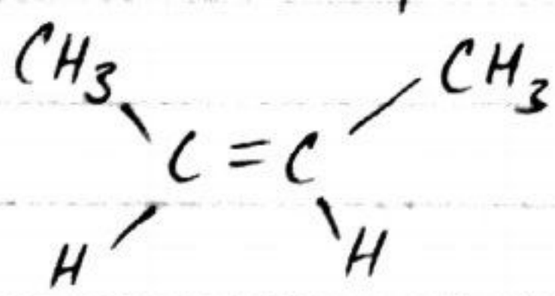
ii- C-C bond should not be rotate around its axis.

The structure of 1-butene is



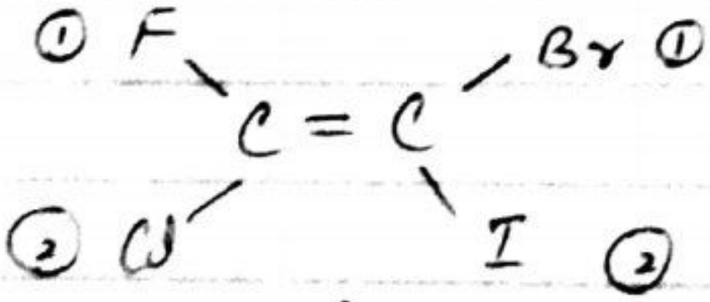
Muhammad Javed Iqbal
HOD Chemistry
Asharia Colleges Rwp.

The structure of 2-butene is

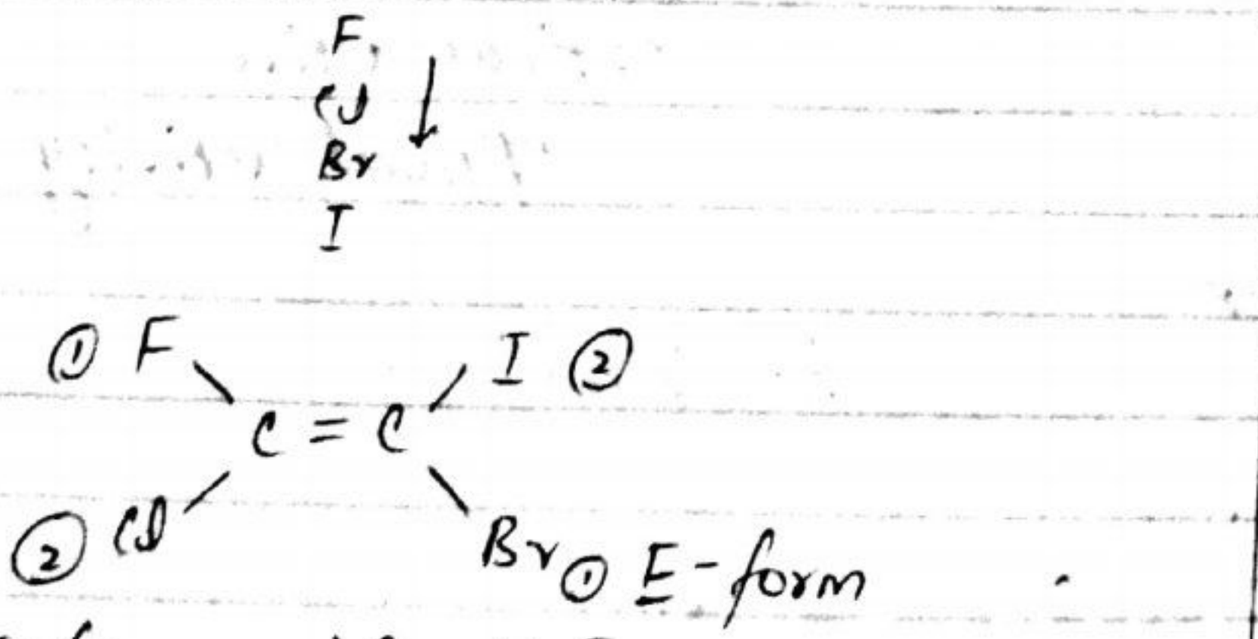


As the structure of 1-butene doesnot obeys the conditions but the structure of 2-butene fulfill both conditions.

FOR KNOWLEDGE ONLY-



Z-form



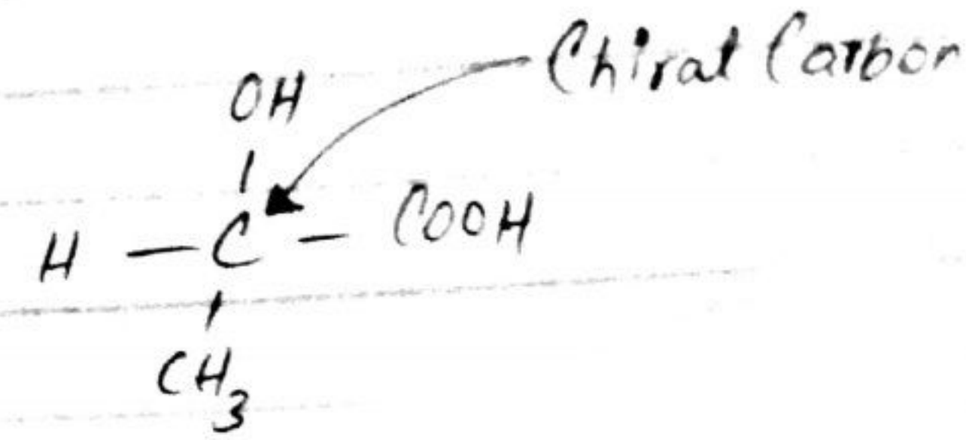
E-form

⇒ Z-form is the name of Cis-form, if all the groups are different.

⇒ E-form is the name of Transform, if all the groups are different.

2- OPTICAL ISOMRISM :-

Chiral Carbon
OR
Chiral Center



"Carbon atom which is bonded with four different groups is called Chiral center or Chiral carbon."

⇒ Compounds containing chiral carbon or chiral center shows optical isomerism.

⇒ These are Asymmerical molecule (different atoms attached).

Plane of Symmetry:-

"Plane which divide two object into two symmetric group called plane of symmetry".

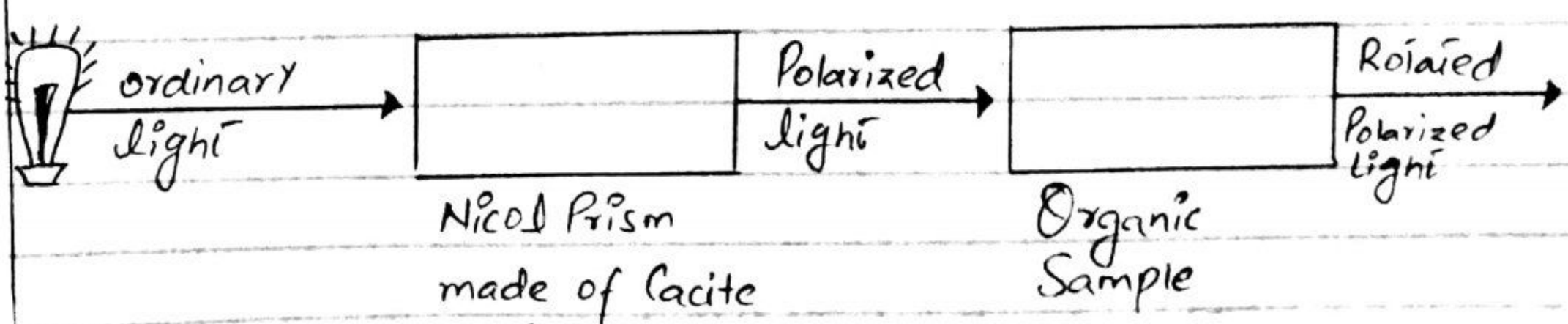
e.g:- A person or hat.

⇒ Compounds which have lack of plane of symmetry shows optical isomerism

Optical Activity :-

"Solution of some organic compounds has ability to rotate plane polarized light in opposite direction, such solutions are called **optical active**, and the phenomena is called **optical activity**"

⇒ Optical Activity of compounds is measured with the help of **Polarimeter**.



Defination of Optical Isomerism :-

" Optical active compounds exist in two different isomeric form which can rotate the plane polarized light in opposite direction. These compounds are called **optical isomers** and the phenomena is called **optical isomerism** "

⇒ Isomers which can rotate the plane polarized light in right side (clockwise) called dextrorotatory or positive isomers.

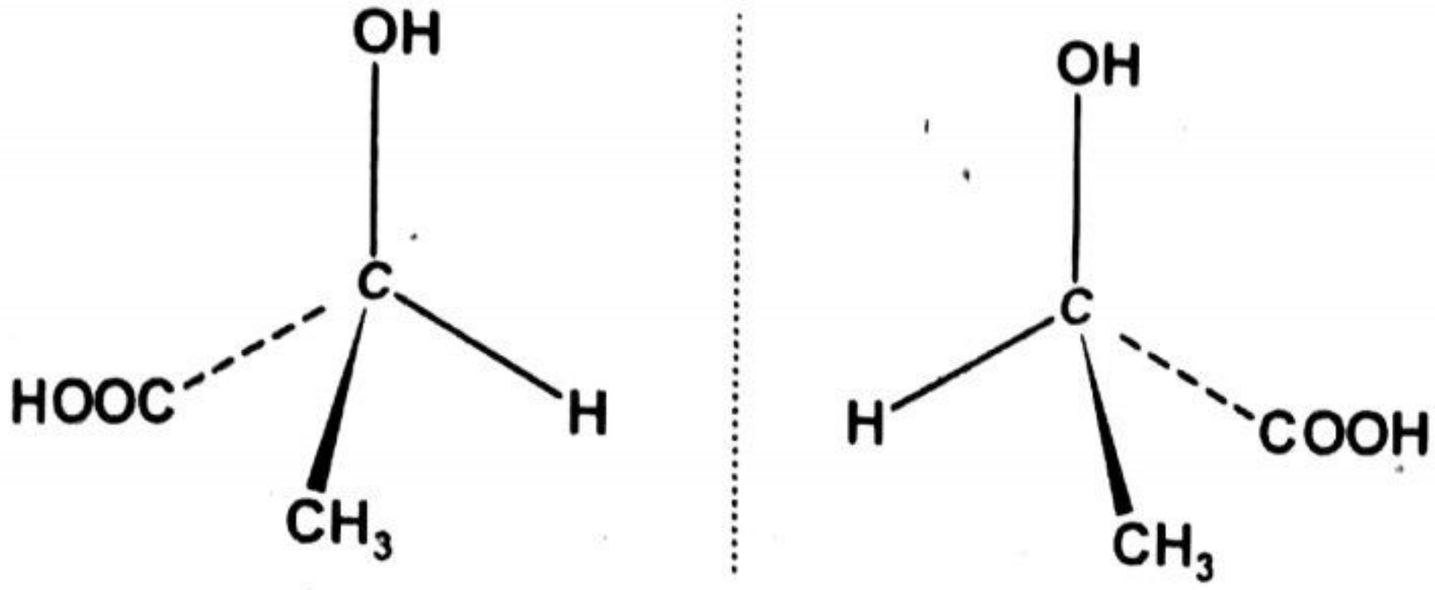
⇒ Isomers which rotate the plane polarized light in left side (anticlockwise) called Levorotatory or negative isomers.

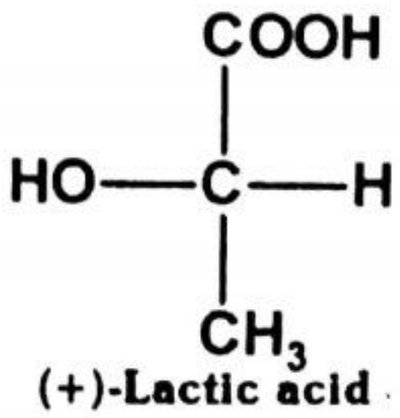
e.g :-

Lactic acid show optical Isomerism

Optical Isomerism of Lactic Acid

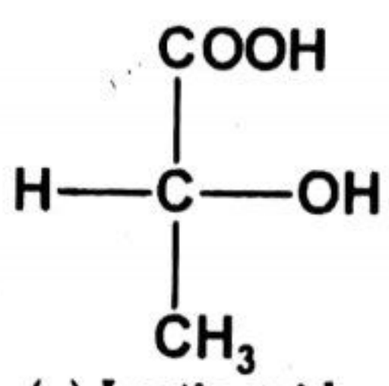
- Lactic acid (2-Hydroxypropaoic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom.
- Two three dimensional structures are possible for Lactic acid





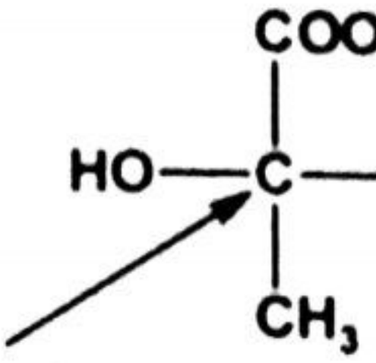
(+)-Lactic acid
m.p. = 26°C

(I)



(–)-Lactic acid
m.p. = 26°C

(II)



Asymmetric Carbon Atoms

Equimolar mixture of (+) and (-) forms is called racemic mixture. It is denoted as (±).

e.g. (±)-Lactic acid

(III)

- These structures are not identical because they cannot be superimposed on each other.
- The non-superimposable mirror images of each other and called *Enantiomers*.
- Equimolar mixture of two enantiomers is called racemic mixture. It is optically inactive and denoted by (±).
- Thus, three forms of lactic acid are known. Two are optically active and one is optically inactive.

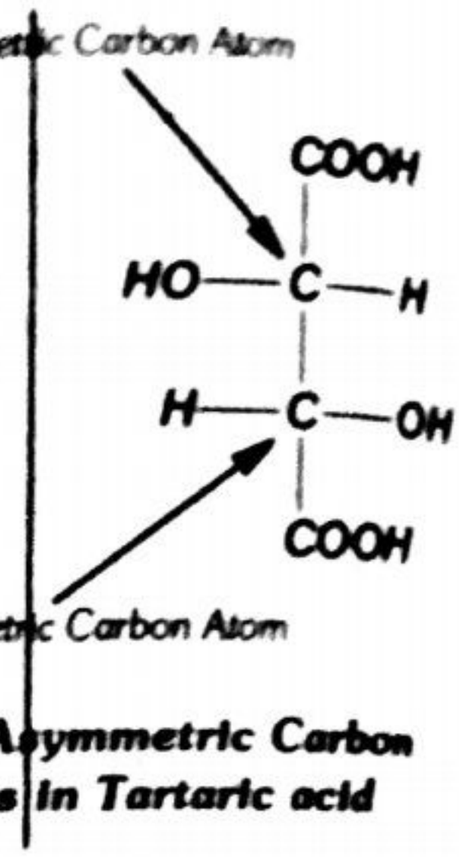
(+)-Lactic Acid: It rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory.

(–)-Lactic Acid: It rotates the plane of polarized light to the left (anticlockwise direction) is called laevorotatory (–)- Lactic acid is the mirror image of (+)-lactic acid and vice versa.

(±)-Lactic Acid: It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms. It is called racemic mixture.

Optical Isomerism of Tartaric Acid

Tartaric acid (2,3-Dihydroxybutanedioic acid) contains two asymmetric carbon atoms.



Two Asymmetric Carbon Atoms In Tartaric acid

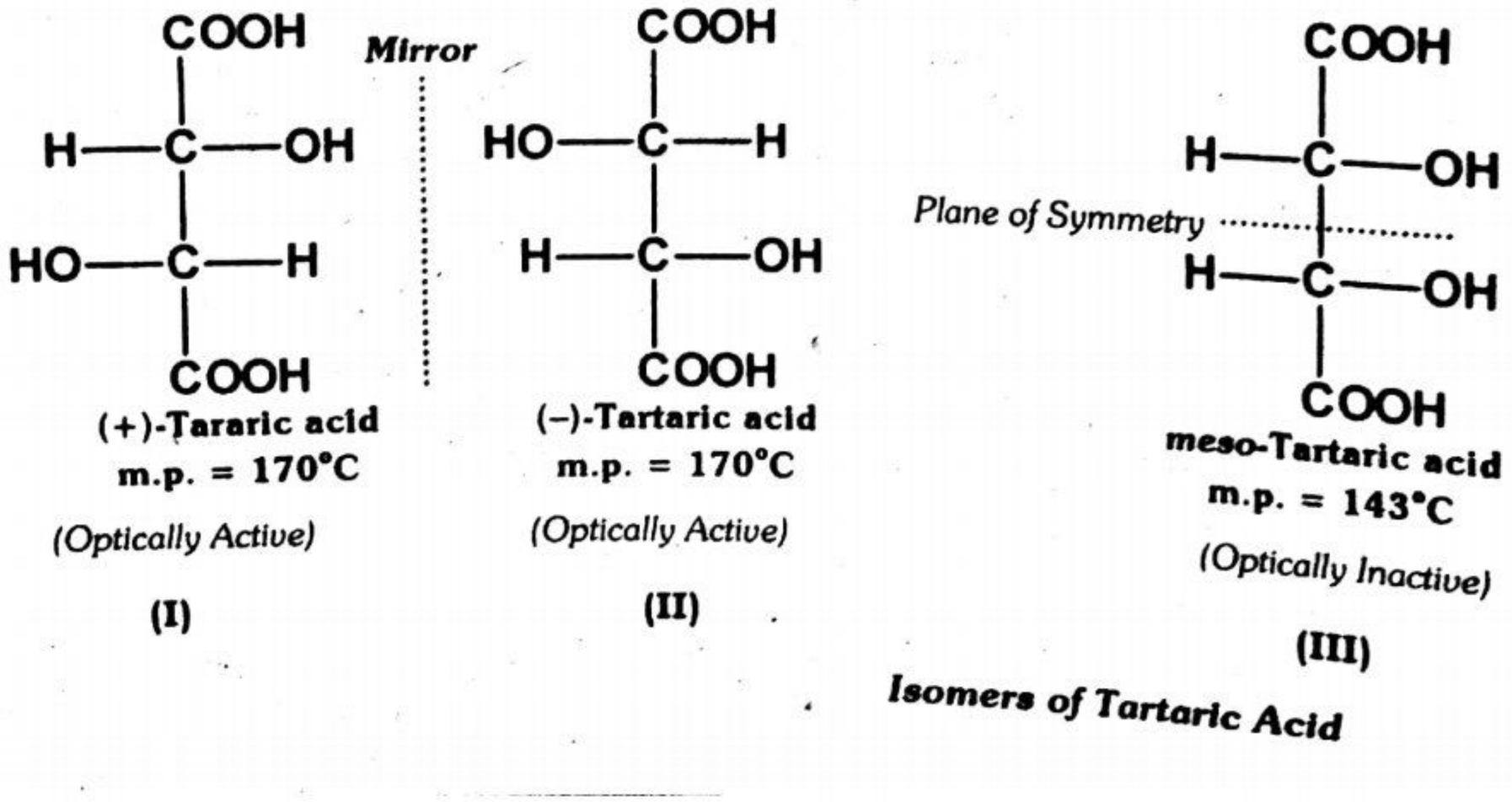
- Four forms of tartaric acid are known.
- Two of them are optically active and two are optically inactive.
- The optically active forms are related to each other as a non-superimposable mirror image of each other. They are enantiomers.

(+)-Tartaric Acid: It rotates the plane of polarized light to the left (anticlockwise direction) is called laevorotatory. (–) Lactic acid is the mirror image of (+) lactic acid and vice versa.

(-)-Tartaric Acid: It rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory.

(±)-Tartaric Acid: It does not rotate the plane of polarized light. Thus, it is optically inactive. It is an equi mixture of (+) and (-) forms (racemic mixture).

***meso*-Tartaric Acid:** It has plane of symmetry. So, it does not rotate the plane of polarized light. Thus optically inactive.



Isomers of Tartaric Acid

ALKENES

NOMENCLATURE :-

⇒ The notes of nomenclature of Alkene are separately available.

- Relative Stability :-

⇒ Conjugate Alkenes are more stable as compared to Iso-alkenes.

⇒ Trans Alkenes are more stable as compared to cis alkenes due to less steric-repulsion or due to bulky group.

⇒ More alkylated alkene are more stable as compared to normal Alkene e.g iso-butylene is more stable as compared to butylene.

-3- Structure :-

⇒ In alkenes, Carbon atoms linked through π-bond are sp^2 hybridized

⇒ Each C-atom carries three sp^2-hybridized and one p-orbital.

⇒ The p-orbital overlap to form π-bond and hybrid orbitals form σ-bond due to linear overlapping.

⇒ The C-C distance in ethene is shorter (1.34A) than the C-C bond distance of ethane (1.54A). It is due to the increased electron density between carbon atoms.

⇒ Carbon atoms are coplaner and the rotation of one carbon atom is with respect to other is restricted which results in cis-trans isomerism in alkene.

4- Methods of Preparation :-

There are two methods for the f preparation of alkene.

1) Dehydration of alcohols :-

⇒ Removal of water from the molecule is called dehydration.

⇒ For dehydration, dehydrating agents are used like Al_2O_3 , P_2O_5 , H_3PO_4 , H_2SO_4.

⇒ Ease of dehydation order alcohols are :

$$3^\circ\text{-alcohol} > 2^\circ\text{-alchohol} > 1^\circ\text{-alcohol}$$

⇒ REASON :-

Due to the stability of "carbocation" (C^+) .

$$3^\circ\text{-carbocation} > 2^\circ\text{-Carbocation} > 1^\circ\text{-carbocation} > \overset{\oplus}{C}H_3$$

⇒ EXAMPLES :-

⇒ $CH_3 - \overset{\beta}{C}H_2 - \overset{\alpha}{C}H_2 - OH \xrightarrow[140-170^\circ C]{H_2SO_4\ (75\%)} CH_3 - CH = CH_2 + H_2O$

1- Propanol.

⇒ $\overset{\beta}{C}H_3 - \overset{\alpha}{C}H(OH) - \overset{\beta}{C}H_3 \xrightarrow[100^\circ C]{H_2SO_4\ (60\%)} CH_2 = CH - CH_3 + H_2O$

(2-Propanol)

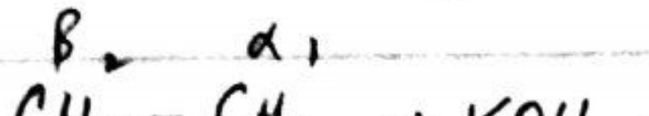
⇒ $CH_3 - \overset{CH_3}{\underset{OH}{C}} - CH_3 \xrightarrow[85\%]{H_2SO_4\ (20^\circ k)} CH_2 = \overset{CH_3}{C} - CH_3 + H_2O$

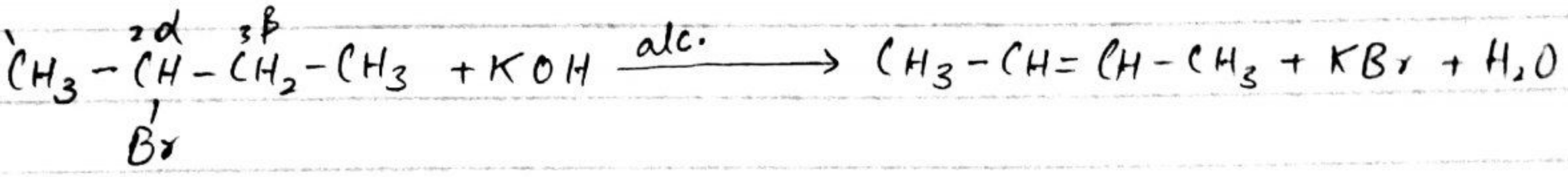
2-Methyl-2-Propanol

2) Dehydrohalogenation of Alkyl Halide:-

"Removal of hydrogen and halogen from the molecule is called dehydrohalogenation"

⇒ For dehydrohalogenation, Alcoholic "KOH" is used.





Reactivity Of Alkene:-

⇒ In Alkene, there is one sigma bond (σ) and one pi-bond (π). Sigma bond contains sigma electrons and Pi-bond contains pi-electrons. π-bond is formed by the parallel overlapping of atomic orbitals. So these pi-electrons are more exposed. Due to this, the attack of electrophile is easy. Hence ..... Alkenes are more reactive.

REACTIONS OF ALKENES

Generally, Alkenes undergoes the following reactions.

1- Addition Reactions — [5-subtypes (V)]
2- Oxidation Reactions — [2-subtypes]
3- Polymerization (1)

-1) Addition Reactions :-

⇒ There are five addition reactions of Alkenes.

i- Addition of Hydrogen [Hydrogenation]
OR
Sabatier Senderyn's reaction :-

⇒ Addition of hydrogen in the molecule is called hydrogenation.
⇒ Hydrogenation takes place in the presence of "Ni", Pt, Pd.
⇒ If "Ni" is used for hydrogenation, temp. 200-300°C is required.
⇒ If "Pt" or "Pd" is used for hydrogenation, reaction takes place at room temperature.
⇒ Mostly, Ni is used for hydrogenation, because it is cheaper than "Pt" or "Pd".
⇒ Hydrogenation is an exothermic process.
"Heat release is called heat of hydrogenation".
⇒ Heat of hydrogenation for one double bond to single bond is -120 KJ/mol.
⇒ Hydrogenation is very important in industry because vegetable ghee is prepared from vegetable oil by this process.
⇒ "Raney Nickel is more reactive than ordinary nickel."
It is prepared by

$$Ni\text{-}Al + NaOH + H_2O \longrightarrow \underset{\text{Raney Nickel}}{Ni} + NaAlO_2 + \frac{3}{2}H_2$$

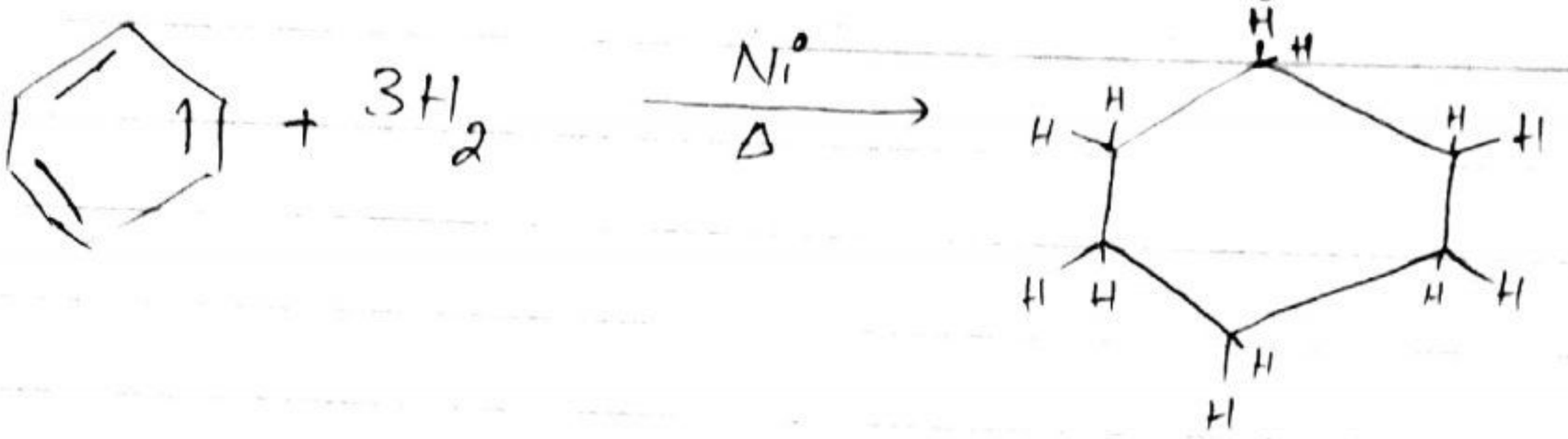
i- $CH_2=CH_2 + H-H \xrightarrow[200-300^\circ C]{Ni} CH_3-CH_3$
Ethene → Ethane

ii°- $CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 + H_2 \xrightarrow[200°C - 300°C]{Ni°} CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_3$

Isobutylene

2 - Methylpropane

iii°-



ii°- Hydrohalogenation [Addition of HX] :-

Reactivity order of acids is :-

$HI > HBr > HCl > HF$

$CH_2 = CH_2 + \overset{+\delta}{H} - \overset{-\delta}{Cl} \longrightarrow CH_3 - \underset{\underset{Cl}{|}}{CH_2}$

Mechanism :

Step 01 : $CH_2 = CH_2 + H^{+\delta} - Cl^{-\delta} \longrightarrow CH_3 - \overset{\oplus}{C}H_2 + Cl^-$

Step 02 : $CH_3 - \overset{\oplus}{C}H_2 + Cl^- \longrightarrow CH_3 - \underset{\underset{Cl}{|}}{CH_2}$

"Addition of hydrogen and halogen in the molecule is called hydrohalogenation"

Markonikov's Rule :- *when unsymmetrical reagent is added to unsymmetrical alkene*

According to this rule

"Negative part of the adding reagent goes to that carbon of Alkene, consist double bond which contains less no of hydrogen atoms"

e.g :-

$CH_3 - CH = CH_2 + \overset{+\delta}{H} - \overset{-\delta}{Cl} \longrightarrow CH_3 - \underset{\underset{Cl}{|}}{CH} - CH_3$

2-Methylbutene

2-Bromo-2-Methylbutane

iii- Addition of Sulphuric acid [H_2SO_4]

OR

Hydration of Alkene

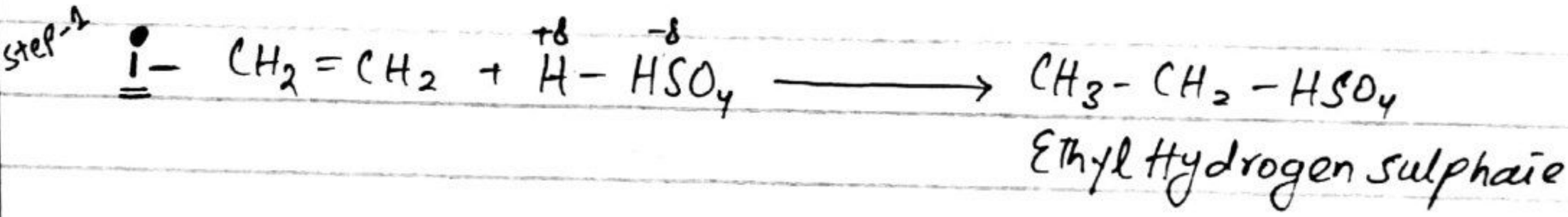
OR

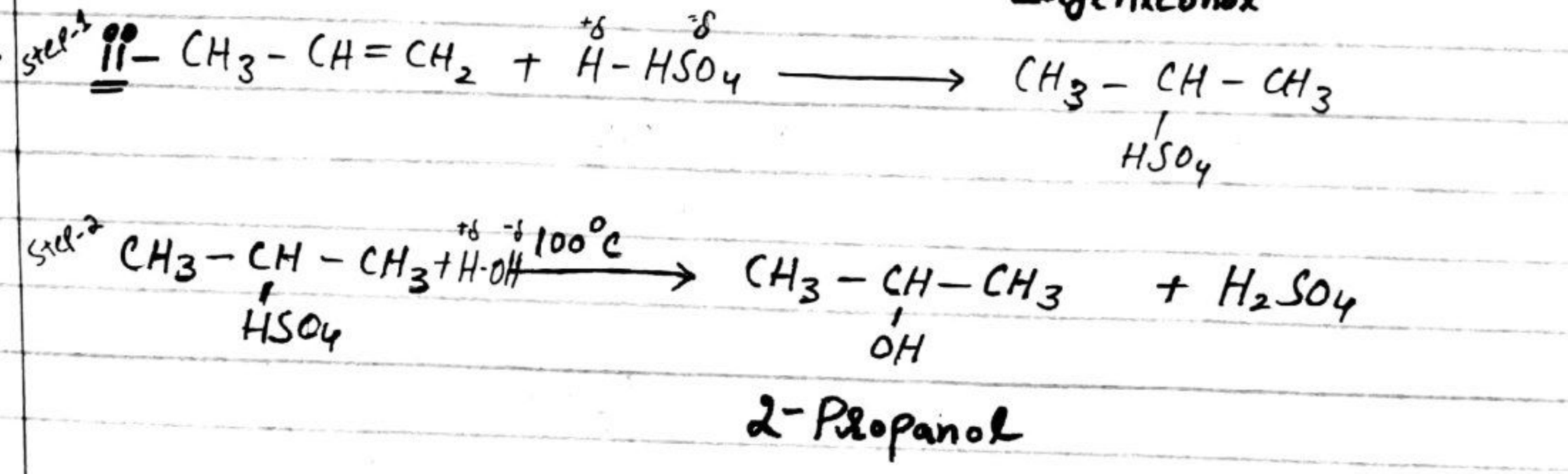
Q- How will you convert:

i- $CH_2 = CH_2 \longrightarrow$ Ethylalcohol

ii- Propene $\longrightarrow$ 2-Propanol

When alkene is reacted with conc. sulphuric acid, alkyl hydrogen sulphate is formed. When it is boiled with water at 100°C, alcohol is obtained





2-Propanol

V-V-V IMP

iv- Addition Of Halogen [Halogenation] OR Test for Unsaturation :-

⇒ "Addition of halogen in the molecule is called halogenation."

⇒ Halogenation of Alkene takes place in the presence of inert solvent CCl_4.

⇒ When alkene is reacted with bromine water, brown colour of bromine water is disappeared. Therefore, this reaction is used for "test for unsaturation".

1- $CH_3-CH=CH-CH_3 + Cl_2 \xrightarrow{CCl_4} CH_3-CH(Cl)-CH(Cl)-CH_3$

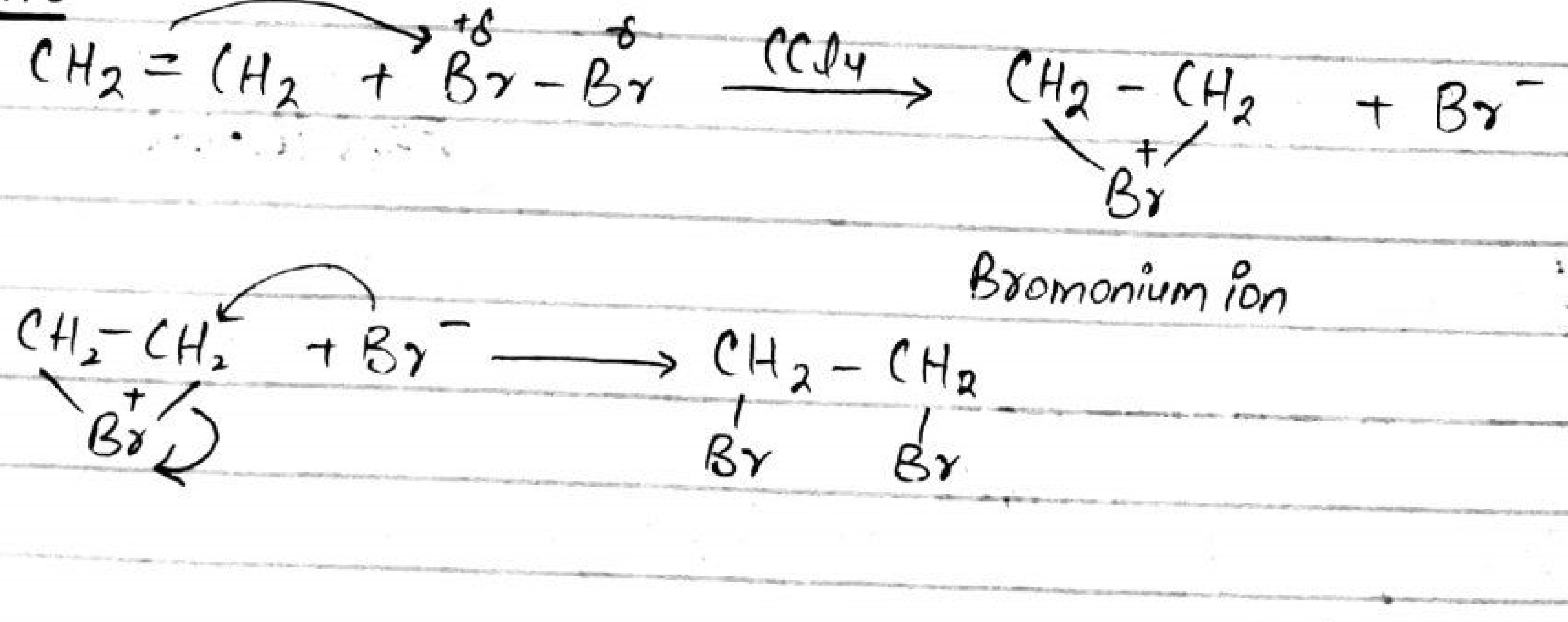
(Vicinal dihalide)

2- $CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} CH_2(Br)-CH_2(Br)$

Mechanism :-

Step 01 :

Step 02 :



⇒ Vicinal = 2 halogens on adjacent C-atom.

⇒ Geminal = 2-halogens on same carbon-atom.

V- Halohydration
OR
Addition of Hypochlorous acid [HOX] :-

⇒ "Addition of halogen and "OH" group in the molecule is called halohydration"

⇒ If halogenation of alkene take place in the presence of water as a solvent. In this case, water molecule also become reagent and product formed is called haloalcohol. They are also called "halohydrin"

i- $Cl_2 + H_2O \longrightarrow HCl + HOCl$

$CH_2=CH_2 + \overset{+\delta}{H}O\overset{-\delta}{Cl} \longrightarrow CH_2(OH)-CH_2(Cl)$

$CH_2=CH_2 + Cl_2 + H_2O \longrightarrow CH_2(OH)-CH_2(Cl) + HCl$

2-chloroethanol

ii- $Cl_2 + H_2O \longrightarrow HCl + HOCl$

$CH_3-CH=CH_2 + HOCl \longrightarrow CH_3-CH(OH)-CH_2(Cl)$

$CH_3-CH=CH_2 + Cl_2 + H_2O \longrightarrow CH_3-CH(OH)-CH_2(Cl) + HCl$

Propene

1-chloro-2-propanol

Q- How can you prepare 1-chloro-2-Propanol by Propene?

⇒ The above reaction No(ii) is the answer of this question.

(2) OXIDATION REACTIONS :-

There are two oxidation reactions of Alkene.

i- Addition of Oxygen [Epoxidation]

ii- Ozonolysis

i- Addition of OXYGEN OR EPOXIDATION :-

⇒ When Alkene is reacted with peracid of acetic acid or benzoic acid, epoxides of alkene are obtained

⇒ They are used as a starting material in industry for preparation of **glycol**

i- $CH_2=CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-O-OH \xrightarrow{CH_3Cl} CH_2-CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-OH$

Ethene PeroxyAceticacid

Epoxyethane
OR cyclic ether
OR epoxide of ethylene

OR

ii- $CH_3-CH=CH_2 + \frac{1}{2}O_2 \xrightarrow[300^\circ C]{Ag_2O} CH_3-CH-CH_2$ (O)

Propylene Epoxide
or
Epoxy Propane

ii- OZONOLYSIS OR

Test for the location of double bond in Alkenes-

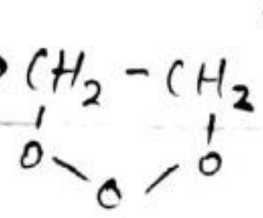
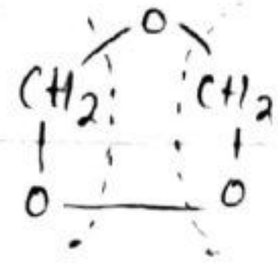
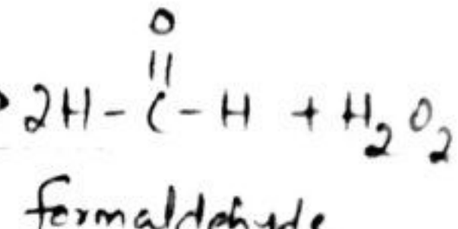
⇒ Ozone is allotropic form of oxygen

⇒ It react with alkene, form **Molozonide**, which is unstable

⇒ It rearrange itself in the presence of zinc acid and water

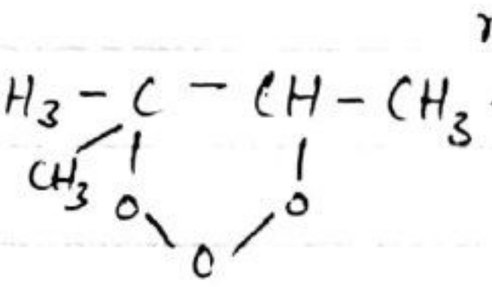
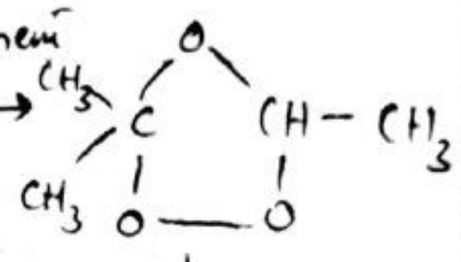
⇒ Ozonide is converted into carbonyl compounds (Aldehyde and Ketone).

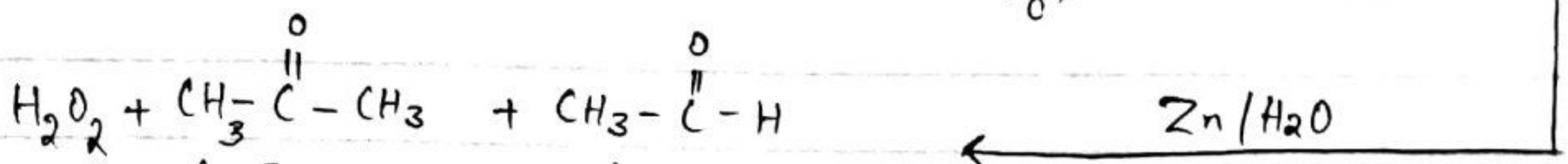
⇒ This test is used to locate the double bond position of Alkene.

i- $CH_2=CH_2 + O_3 \longrightarrow$  $\xrightarrow{\text{rearrangment}}$  $+ H_2O \xrightarrow{Zn}$ 

Molozonide — Ozonide — formaldehyde

$H_2O_2 + Zn \longrightarrow H_2O + ZnO$

ii- $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3 + O_3 \longrightarrow$  $\xrightarrow{\text{rearrangment}}$ 



Acetone — Acetaldehyde

$H_2O_2 + Zn \longrightarrow ZnO + H_2O$

i③ POLYMERISATION :-

Process in which small molecules called monomers combine with eachother form large molecule called polymer and the process is called polymerization.

For high quality polythene, $TiCl_4$ and $Al(C_2H_5)_3$ is used as a catalyst.

$$n\ CH_2=CH_2 \xrightarrow[0.2\%\ O_2\ (\text{trace amount})]{400^\circ C,\ 100 atm} -\{CH_2-CH_2\}_n-$$

Polythene OR Polyethylene

→ Conjugation (Link together)

CONJUGATED ALKENES:-

Double bond separated by only one single bond is called Conjugated Alkenes. e.g:- $CH_2=CH-CH=CH_2$

COMMULATED ALKENE :-

Double bond adjacent to each other, alkene are called commulated alkene. e.g:- $CH_2=C=CH_2$

Isolated Alkene:-

Double bond separated by more than one single bond are called isolated alkene

e.g $CH_2=CH-CH_3$

ALKYNE :-

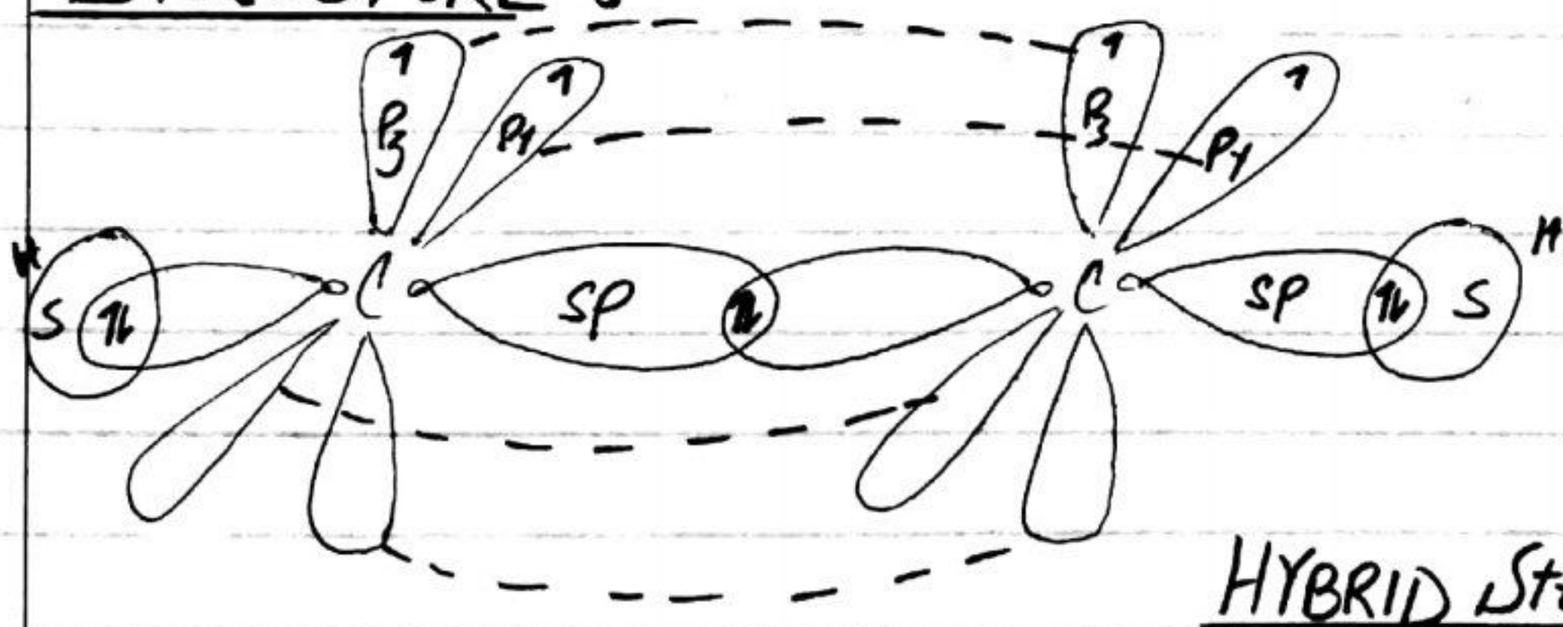
NOMENCLATURE :-

The rules of nomenclature are seperately available.

RELATIVE STABILITY :-

Alkynes are more stable than Alkene because in Alkene there is one sigma bond and one pi-bond but in Alkyne there is one sigma and two pi-bonds. One extra pi-bond makes Alkynes more stable. Therefore Alkynes are more stable than Alkenes.

STRUCTURE :-



HYBRID Structure of Ethyne

Methods Of Preparation :-

There are two methods for the preparation of Alkynes.

i- Dehydrohalogenation of Vicinal dihalides

ii- Dehydrohalogenation of Geminal dihalides.

Dehydrohalogenation of Vicinal dihalides :-

"Removal of hydrogen and halogen from the molecule is called dehydrohalogenation"

⇒ For dehydrchalogenation, Alcohlic KOH is used.

"Alkyl hallides having two halogen atoms on adjacent Carbon atoms called Vicinal dihalides"

i- $CH_2(Cl)-CH_2(Cl) + KOH \xrightarrow{\text{alcohlic}} CH(Cl)=CH_2 + KCl + H_2O$

$CH(Cl)=CH_2 + KOH \xrightarrow{\text{alcohlic}} CH \equiv CH + KCl + H_2O$

ii- $CH_3-CH(Br)-CH_2(Br) + 2NaNH_2 \xrightarrow[-33^\circ C]{\text{liq } NH_3} CH_3-C\equiv CH + 2NaBr + 2NH_3$

Dehydrohalogenation of Geminal dihalides :-

"Removal of hydrogen and halogen from the molecule is called dehydrohalogenation".

"Alkyl hallides having two halogen atom on the same C-atom called geminal dihalide"

i- $CH_3-CH(Cl)(Cl) + 2NaNH_2 \xrightarrow[-33^\circ C]{\text{liq } NH_3} CH \equiv CH + 2NaCl + 2NH_3$

ii- $CH_3-C(Br)(Br)-CH_3 + 2NaNH_2 \xrightarrow[-33^\circ C]{\text{liq } NH_3} CH_3-C\equiv CH + 2NaBr + 2NH_3$

PHYSICAL PROPERTIES :-

⇒ Alkynes are colourless, odourless, except "acetyle" which has garlic like odour.

⇒ Ethyne, Propyne, Butyne are gases - C_5-C_{13} alkynes are liquids. C_{13}-higher alkynes are solids (waxy solids).

⇒ Alkynes are non-polar, they are insoluble in polar solvents but soluble in organic solvents.

Acidity of Terminal Alkyne (1-Alkyne) :-

Ethyne or 1-Alkyne are acidic in nature because these alkynes are **sp-hybridized**. It contains **50% s**-character and **50% p**-character. Due to more **s**-Character as compare to sp^2 and sp^3-hybridized Carbons, there "**C**" are more **electronegative**. Therefore H attached become **electron defficient** ($2^{1}2e^{-}$) and behaves as **acidic**. These "H" are called **terminal hydrogen**.

Q:- Why 2-Butyne is not acidic but 1-Butyne is acidic in nature?

In 1-butyne, their is terminal hydrogen but in 2-butyne their is no terminal hydrogen

$$H-C\equiv C-CH_2-CH_3$$

1-Butyne

$$CH_3-C\equiv C-CH_3$$

2-Butyne

Electrophilic Substitution Reaction

OR

Reactions of Terminal Alkynes :-

Rule :-

e ⟶ ide

Muhammad Javed Iqbal
HOD Chemistry
Askaria Colleges Rwp.

i- Reaction with Sodium Metal :-

$$H-C\equiv C-H + 2Na \longrightarrow NaC\equiv CNa + H_2$$

Acetylene
or Ethyne

Disodium acetylide
Disodium ethynide or

$$2\ H-C\equiv C-CH_3 + 2Na \longrightarrow 2\ Na-C\equiv C-CH_3 + H_2$$

Propyne

Sodium Propynide

ii- Reaction with Sodaamide ($NaNH_2$) :-

$$H-C\equiv C-H + 2NaNH_2 \xrightarrow[-33^\circ C]{liq\ NH_3} NaC\equiv CNa + 2NH_3$$

Ethyne

$$H-C\equiv C-CH_3 + NaNH_2 \xrightarrow[-33^\circ C]{liq\ NH_3} Na-C\equiv C-CH_3 + NH_3$$

Propyne

iii- Reaction with Ammonical Silver Nitrate [$AgNO_3 + NH_4OH$]

OR

Identification test for 1-Alkyne :-

Ethyne or 1-Alkyne react with ammonical silvernitrate, form white precipitate of disilver acetylide or silver alkynide

$$H-C\equiv C-H + 2AgNO_3 + 2NH_4OH \longrightarrow AgC\equiv AgC + 2H_2O + 2NH_4NO_3$$

Ethyne

Disilver acetylide (C.N)
Disilver ethynide (IUPAC)
white p.p.t.

ii- $H-C\equiv C-CH_3 + AgNO_3 + NH_4OH \longrightarrow AgC\equiv \overset{-CH_3}{C} + H_2O + NH_4NO_3$

iv- Reaction with Amonical Cuprous Chloride [$Cu_2Cl_2 + NH_4OH$]

OR

Identification test for 1-Alkyne :-

Ethyne or 1-Alkyne react with amonical cuprous chloride, form reddish brown precipitate of dicopperacetylide or copper alkynide.

i- $H-C\equiv C-H + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC\equiv CuC + 2H_2O + 2NH_4Cl$

Dicopperacetylide

[Reddish brown ppt.]

ii- $H-C\equiv C-CH_3 + \frac{1}{2}Cu_2Cl_2 + NH_4OH \longrightarrow CuC\equiv C-CH_3 + H_2O + NH_4Cl$

Copper Propynide

[Reddish brown ppt]

Uses of Alkynides :-

$AgC\equiv CAg + 2HCl \xrightarrow{\Delta} H-C\equiv C-H + 2AgCl$

$CuC\equiv C-Cu + 2HCl \xrightarrow{\Delta} H-C\equiv C-H + Cu_2Cl_2$

⇒ These Alkynides are used for purification, preparation, saperation and identification of Alkynes.

$AgC\equiv CAg + 2HCl \xrightarrow{\Delta} HC\equiv CH + 2AgCl$

$CuC\equiv C-Cu + 2HCl \xrightarrow{\Delta} HC\equiv CH + Cu_2Cl_2$

How will you distinguish b/w 1-Pentyne, 2-Pentyne by mean of a chemical reaction?

Reaction with Amonical Silvernitrate ($AgNO_3 + NH_4OH$)

1 - Pentyne.

$$HC\equiv C\text{-}CH_2\text{-}CH_2\text{-}CH_3 + AgNO_3 + NH_4OH \rightarrow AgC\equiv C\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2O + NH_4NO_3$$

Silver pentynide
(white ppt)

2 - Pentyne -

No reaction

Q- How will you convert vicinal dihalide into a germinal dinalide?

Ans

$$CH_2(Cl)\text{-}CH_2(Cl) + KOH \xrightarrow{alc} CH(Cl)=CH_2 + KCl + H_2O$$

viccinal dihalide

$$CH(Cl)=CH_2 + KOH \xrightarrow{alc} CH\equiv CH + KCl + H_2O$$

alkyne

$$H-C\equiv C-H + H^{+\delta}\text{-}Cl^{-\delta} \longrightarrow CH_2=CH(Cl)$$

$$CH_2=CH(Cl) + H^{+\delta}\text{-}Cl^{-\delta} \longrightarrow CH_3\text{-}CH(Cl)_2$$

(germinal-dihalide)

(9)

2- Addition Reactions of Alkynes :-

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i- Addition of Hydrogen [Hydrogenation] :-

"Addition of hydrogen in the molecule is called hydrogenation"

⇒ Hydrogenation takes place in the presence of Nickel, Platinum, or Pladium. (Ni, Pt or Pd)

i- $HC \equiv CH + H_2 \xrightarrow[200-300^\circ C]{Ni^\circ} CH_2 = CH_2$

Ethyne

$CH_2 = CH_2 + H_2 \xrightarrow[200-300^\circ C]{Ni^\circ} CH_3 - CH_3$

Ethane

ii- $CH_3 - C \equiv C - CH_3 + H_2 \xrightarrow[200-300^\circ C]{Ni^\circ} CH_3 - CH = CH - CH_3$

2-Butyne — 2-butene

$CH_3 - CH = CH - CH_3 + H_2 \xrightarrow[200-300^\circ C]{Ni^\circ} CH_3 - CH_2 - CH_2 - CH_3$

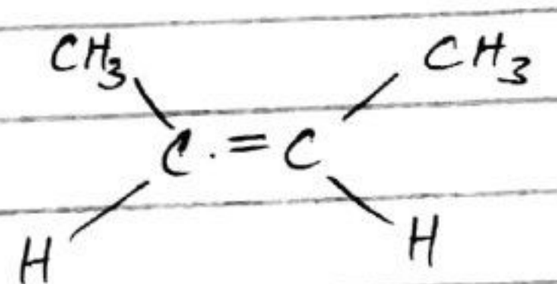
2-butene — n-butane

ii- Partial hydrogenation of Alkyne:-

Alkynes can be reduce to Cis-Alkane in the presence of Lindler's Catalyst ($Pd + BaSO_4 +$ Quinoline)

Alkynes can be reduce to Trans-Alkene in the presence of Na and liquid NH_3 at $-33^\circ C$

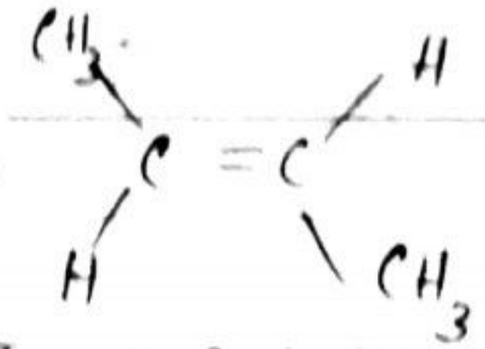
$CH_3 - C \equiv C - CH_3 + H_2 \xrightarrow[Quinoline]{Pd + BaSO_4}$



2-Butyne — Cis-2-butene

$$CH_3-C\equiv C-CH_3 + 2[H] \xrightarrow[-33^\circ C]{Na + liq\ NH_3}$$

2-butyne



Trans-2-butene.

iii- Hydrohalogenation :-

"Addition of HX in the molecule is called hydrohalogenation"

$$H-C\equiv C-H + \overset{+\delta}{H}-\overset{-\delta}{Cl} \longrightarrow CH_2=\underset{Cl}{CH}$$

$$CH_2=\underset{Cl}{CH} + \overset{+\delta}{H}-\overset{-\delta}{Cl} \longrightarrow CH_3-\underset{Cl}{\overset{Cl}{CH}}$$

(geminal dihalide)

iv- Hydration of Alkyne :-

When alkyne is reacted with water in the presence of $HgSO_4$ dissolved in H_2SO_4, at 75°C, carbonyl compound is obtained. In case of Ethyne, aldehyde is obtained. But in case of all other Alkynes, Ketone product is obtained.

$$H-C\equiv C-H + \overset{+\delta}{H}-\overset{-\delta}{OH} \xrightarrow[75^\circ C]{HgSO_4/H_2SO_4} CH_2=\underset{OH}{CH} \qquad CH_3-\underset{\underset{O}{\|}}{C}-H$$

Vinyl alcohol — Acetaldehyde

$$CH_3-C\equiv CH + \overset{+\delta}{H}-\overset{-\delta}{OH} \xrightarrow[75^\circ C]{HgSO_4/H_2SO_4} CH_3-\underset{OH}{C}=CH_2 \qquad CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

(Enol) — (Acetone)

2- Halogenation :-

"Addition of halogen in the molecule is called halogenation"

Halogenation takes place in the presence of CCl_4 as a solvent

$$H-C\equiv C-H + Cl_2 \xrightarrow{CCl_4} \underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{CH=CH}}}}$$

$$\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{CH=CH}}}} + Cl_2 \xrightarrow{CCl_4} \underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{CH-CH}}}}$$

1, 1, 2, 2-Tetrachloroethane

-3] Oxidation Reactions :-

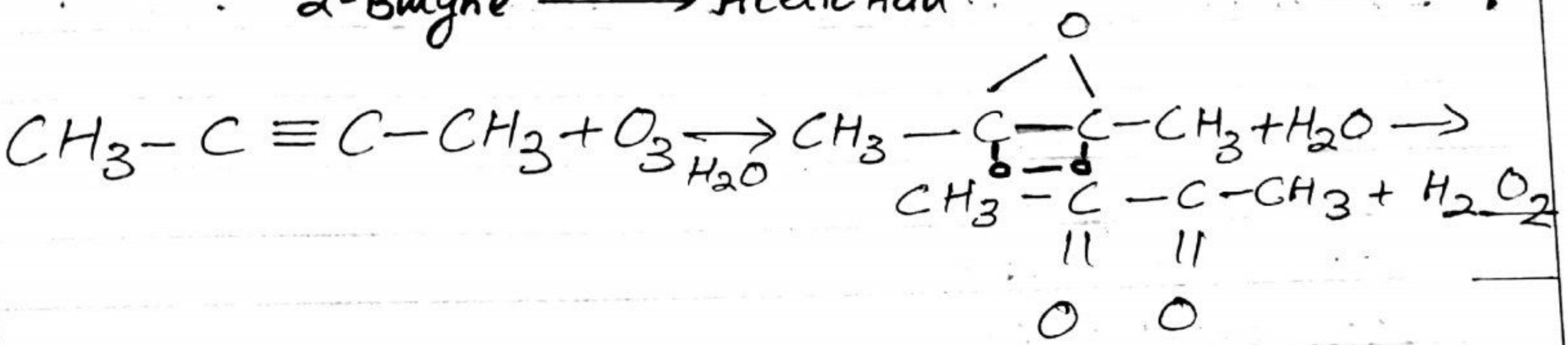
[Ozonolysis]

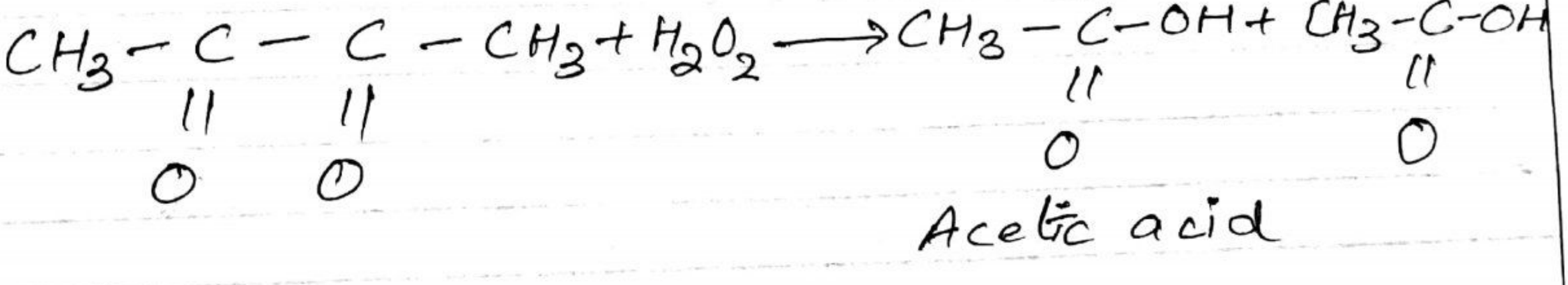
$$R-C\equiv C-R + O_3 \xrightarrow{H_2O} R-\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{/\backslash}{C-C}}}-R + H_2O$$

$$R-\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{||}{C}}}-\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{||}{C}}}-R + H_2O_2 \longrightarrow R-\underset{\displaystyle O}{\overset{||}{C}}-OH + R-\underset{\displaystyle O}{\overset{||}{C}}-OH$$

Conversion:-

2-Butyne ⟶ Acetic Acid





Acetic acid

BENZENE AND SUBSTITUTED BENZENE

Discovered by :- Micheal Faraday
Isolated by :- Hoffmann
Molecular formula :- C_6H_6
Molecular weight :- 78 amu
Special feature :- i- Resonance
ii- Electrophilic substitution reactions.

⇒ Benzene was discovered by Micheal Faraday in 1825 by destructive distillation of vegetable oil.
20 years later it was found in coal tar. by Hoffmann.

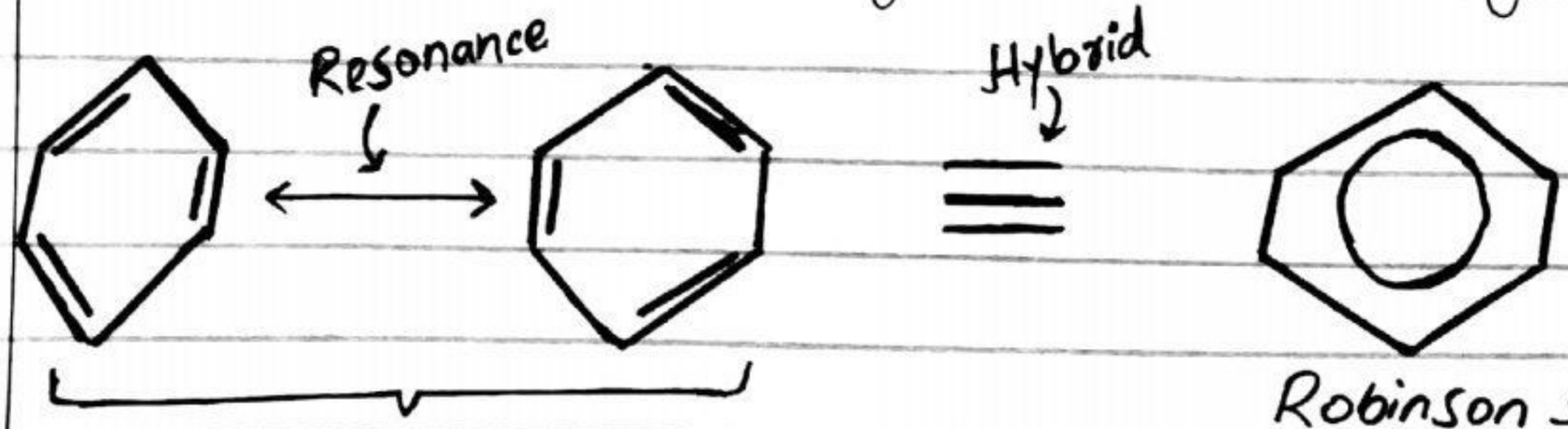
Note:-
⇒ As a functional group, benzene and their derivative are called "Arenes".

PHYSICAL PROPERTIES :-

In the absence of polar substitution, benzene behaves like hydrocarbons i-e They have low melting and boiling point and low solubility.

STRUCTURE :-

Structure of Benzene was proposed by Kekule in 1865
According to Kekule benzene has cyclic hexagonal planer structure containing 3 alternate single and double bond.



Molecular Orbital Treatment of BENZENE :-

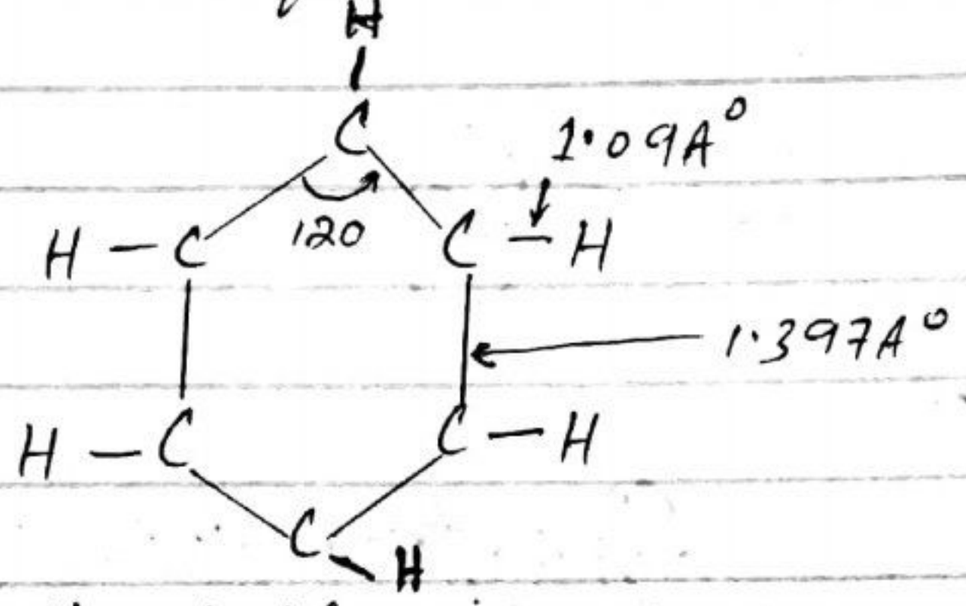
Kekule structure was failed to explain

1- Less reactivity of Benzene

2- Dual nature of Benzene i-e Addition and substitution reaction

3- Less heat of formation

4- Equal C-C bond length



⇒ According to X-ray study benzene has cyclic hexagonal planer structure

⇒ All C-C bond length are equal that is **1.397A°**

⇒ All C-H bond length are equal that is **1.097A°**

⇒ All angles are **120**

⇒ In Benzene each carbon is sp^2 hybridized

⇒ Each "C" has **three** hybrid orbitals and **one** un-hybrid orbital

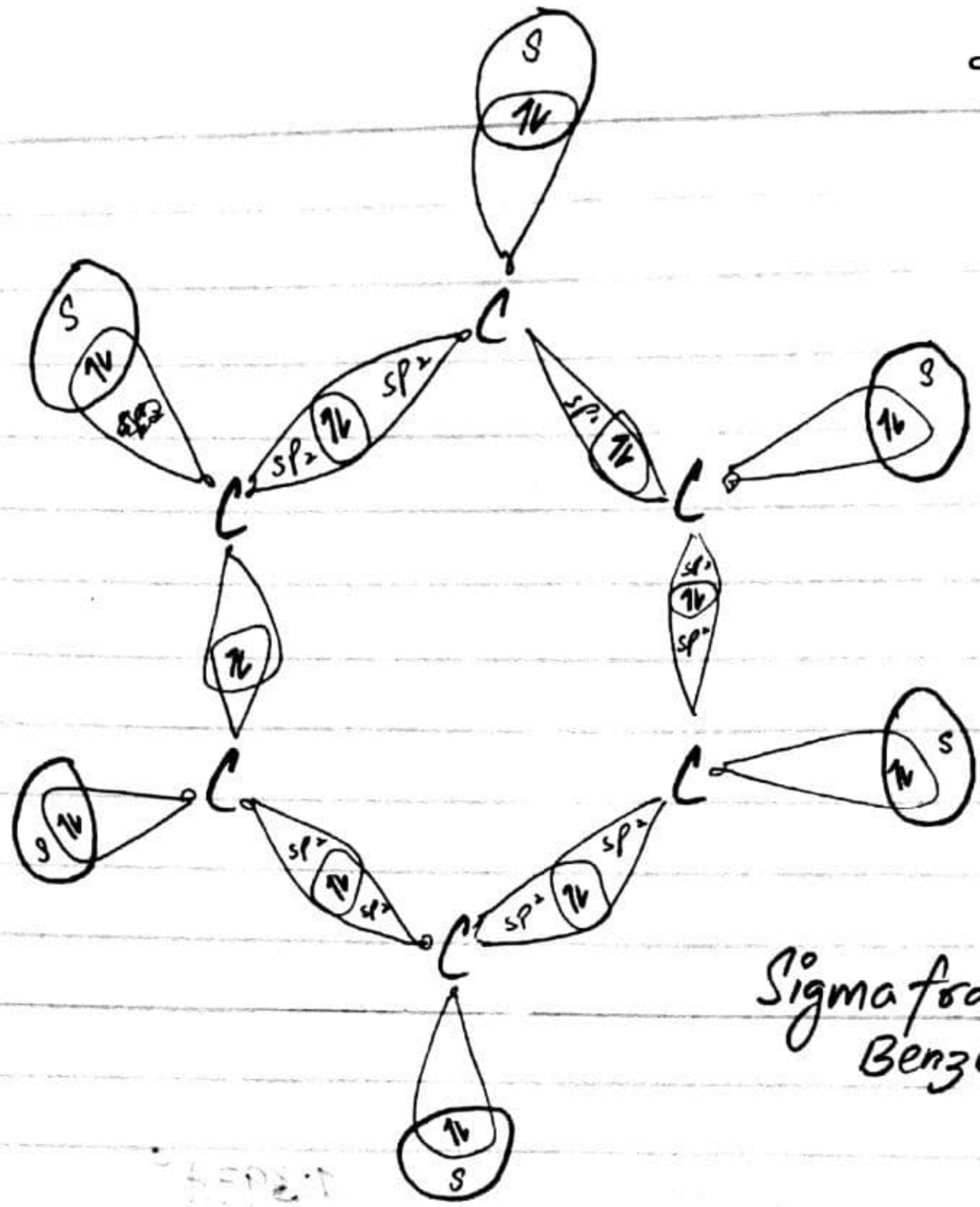
⇒ Hybrid Orbital form sigma (σ) bond. In Benzene, there is "**12**" sigma bonds.

→ **6** sigma bonds form by sp^2-sp^2 overlapping and

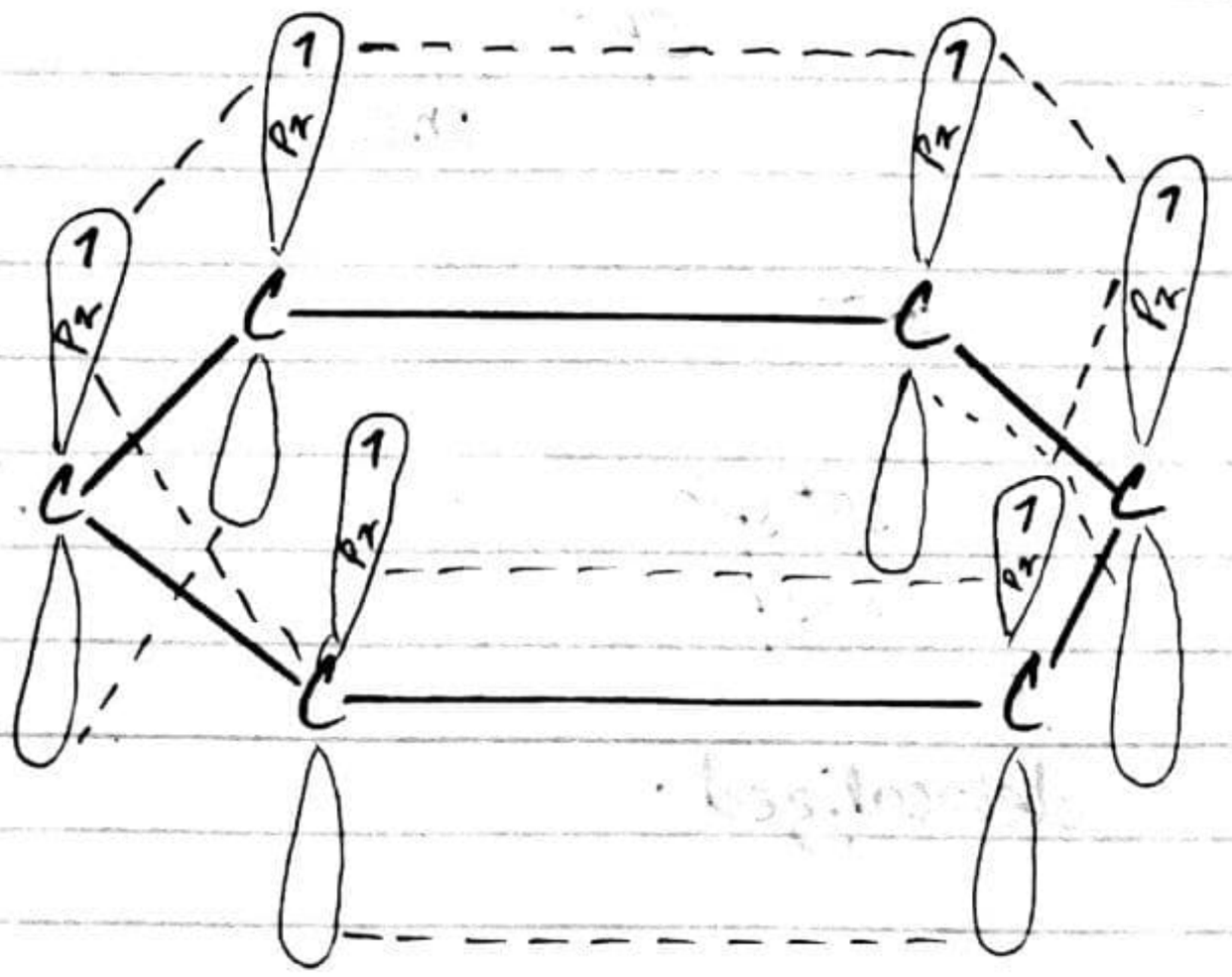
→ **6** sigma bonds form by s-sp overlapping

⇒ Unhybrid orbital form π- bond. In Benzene, there are **3** π- bond. which are **delocalized**.

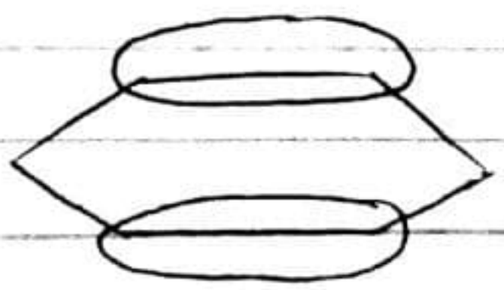
46



Sigma framework of Benzene



Unhybrid P_z Orbital



Delocalize π-orbitals

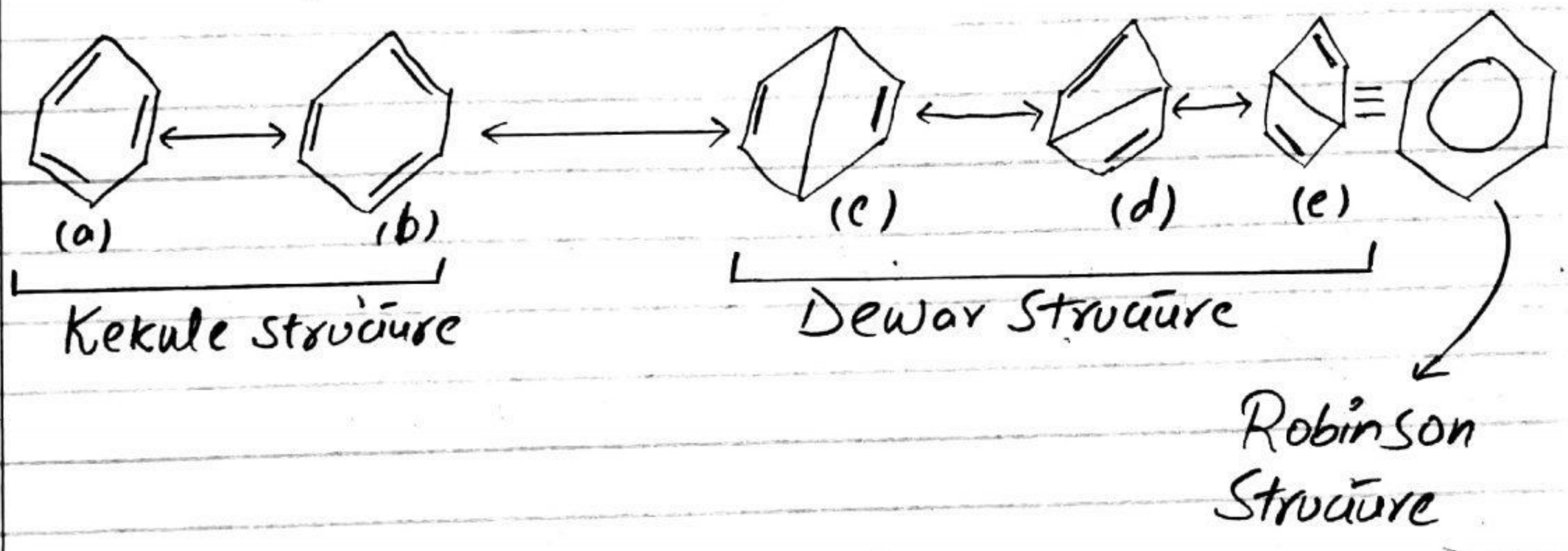
Stability of BENZENE on the basis of RESONANCE

RESONANCE :-

"Possibility of different pairing scheme of valence electron of an atom is called resonance"

⇒ Benzene has 5 resonance contributing structure.

⇒ Higher will be the resonance structure, higher will be the stability of the molecule.

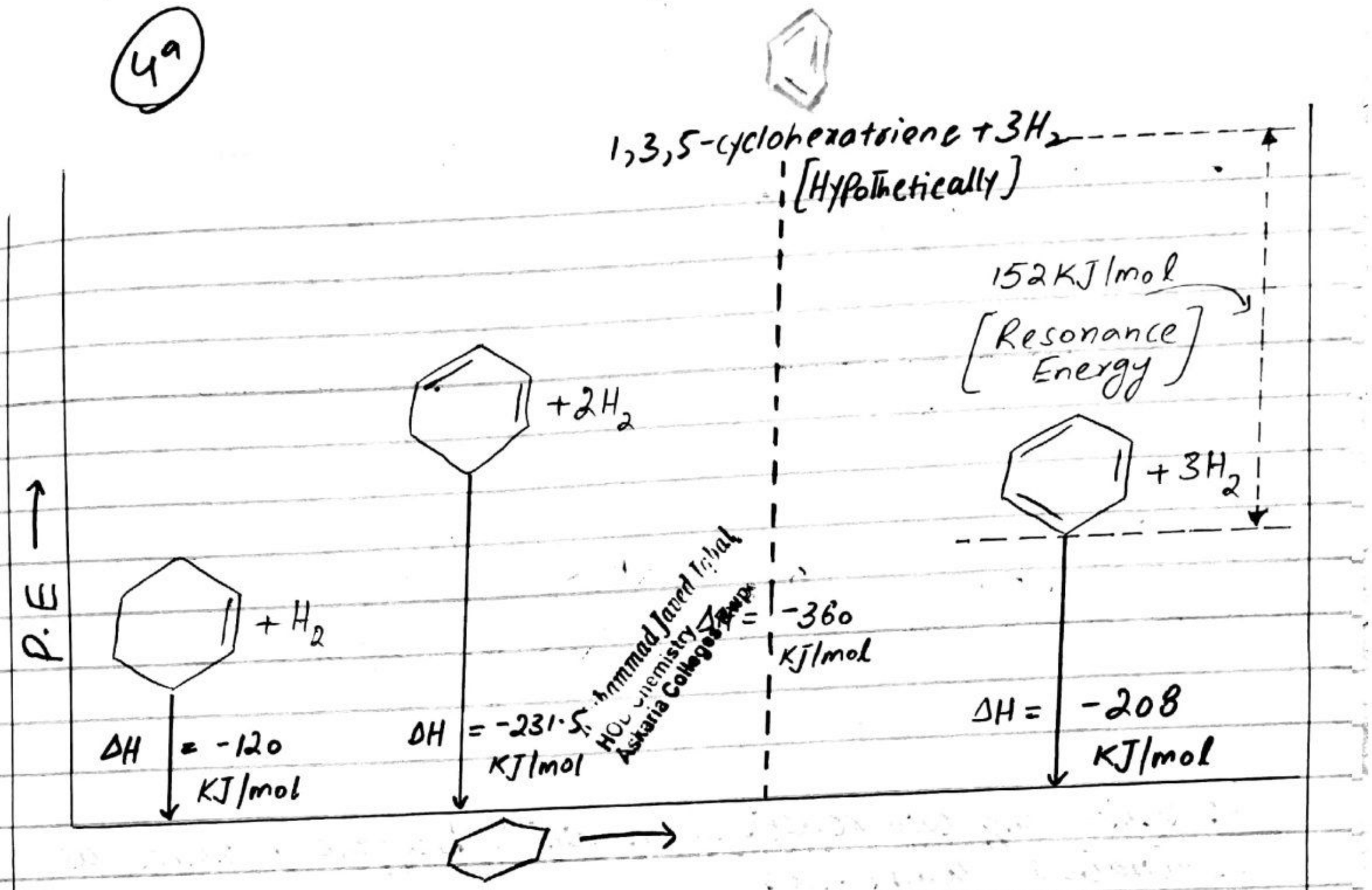


⇒ The structure (a) and (b) was proposed by Kekule.

⇒ (c), (d), (e) was proposed by Dewar.

⇒ Dewar structure was unstable, because in these structures opposite C-C bond length like (1-4), (2-5), (3-6) is greater than as compared to adjacent "C-C" bond length.

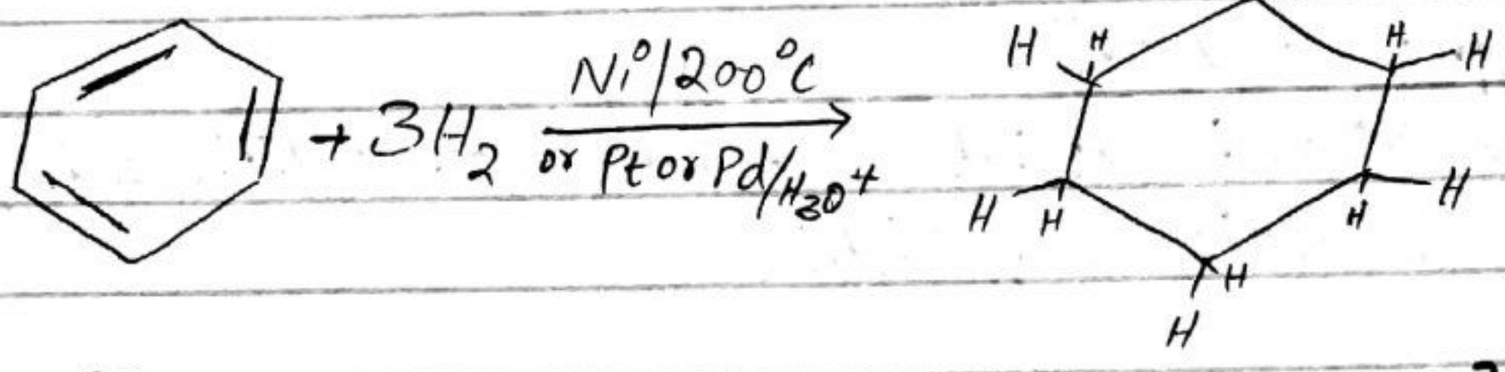
⇒ In actual structure of Benzene, contribution of Kekule is 80% and contribution of Dewar is 20%. Therefore structure of Benzene is denoted by Kekule or Robinson structure.



1- ADDITION REACTIONS

i- Addition of hydrogen [Hydrogenation]:-

"Addition of hydrogen in the molecule is called hydrogenation".

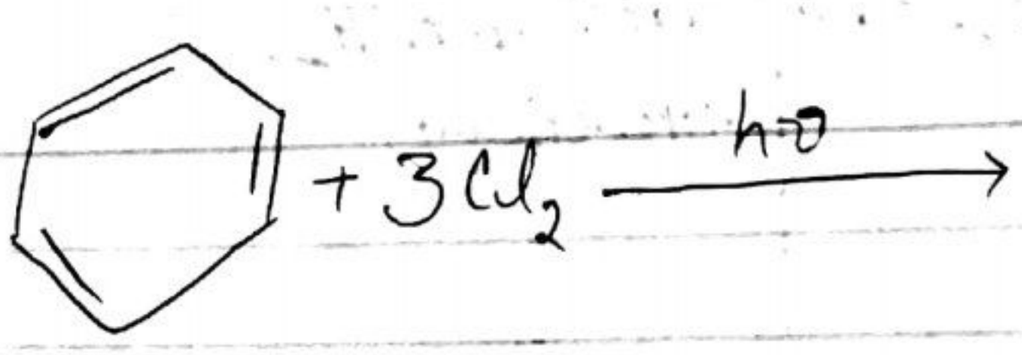


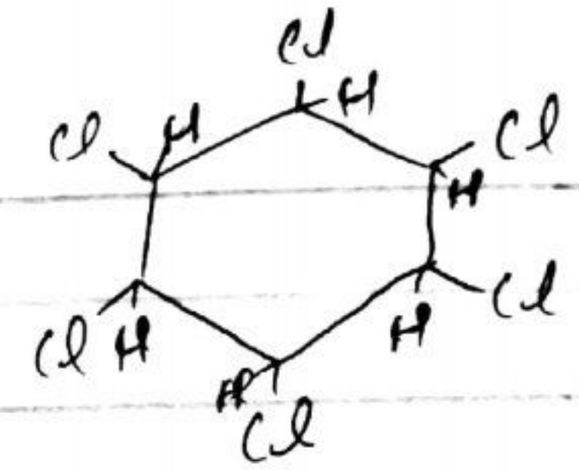
ii- Addition of Halogen [Halogenation]:-

"Addition of halogen in the molecule is called halogenation".

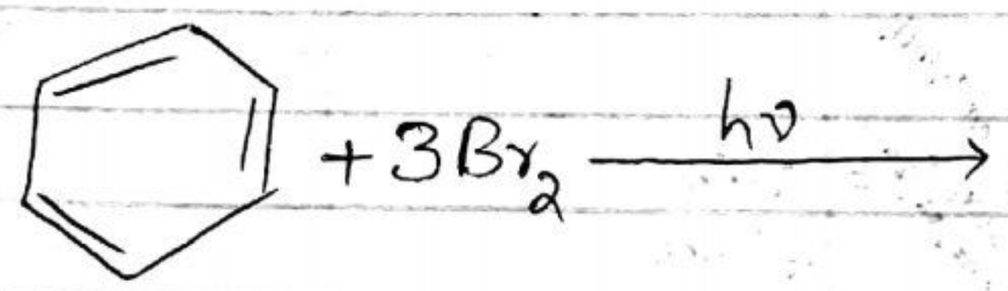
⇒ Halogenation performed in the presence of sunlight.

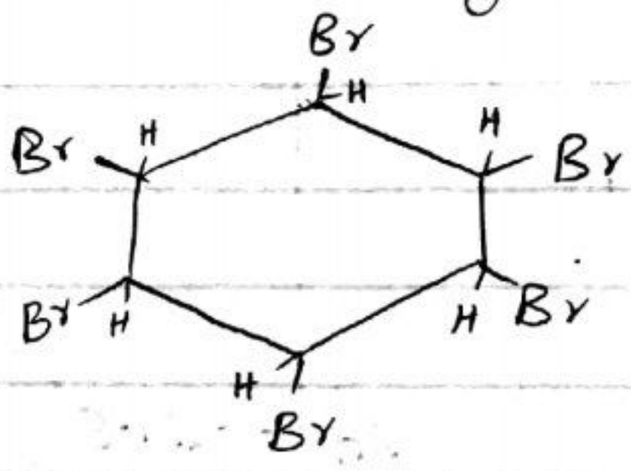
(50)





Hexachlorocyclohexane OR
Hexachlorocyclobenzene





Q: Write any two reactions in which benzene behaves as unsaturated compound?

Ans:- The above Hydrogenation and halogenation reactions are the answers of this questions

-3) OXIDATION REACTIONS:-

a- Catalytic Oxidation:-

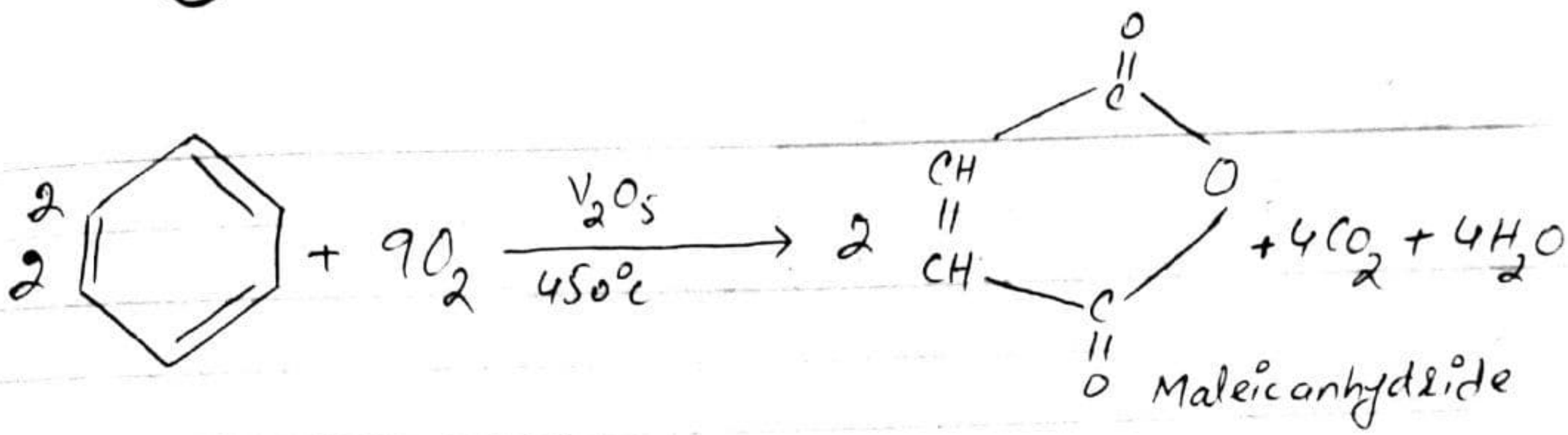
OR

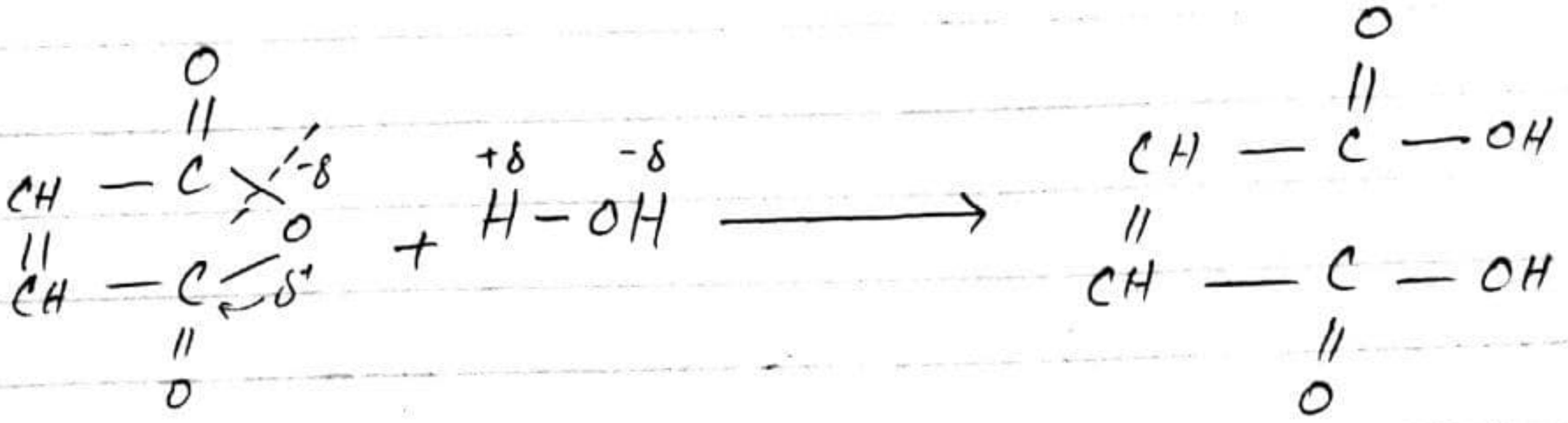
How will you convert

(i) Benzene ⟶ Maleic Acid (2-Butene-1,4 dioic acid)

(ii) Benzene ⟶ Maleic Anhydride

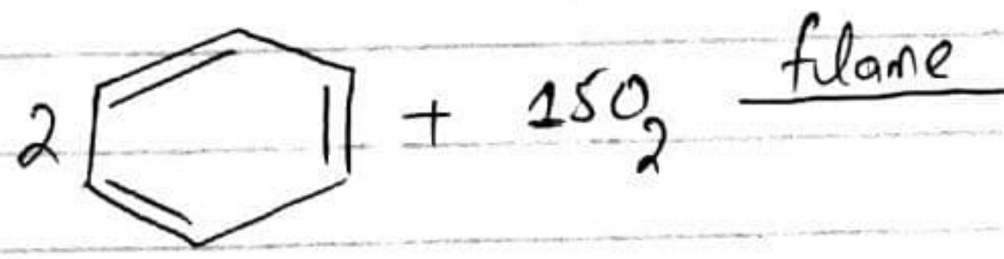
Benzene cannot oxidize with strong oxidizing agents like $KMnO_4$ or $K_2Cr_2O_7$. However Benzene ring is destroy in the presence of oxygen and V_2O_5 at high temperature.





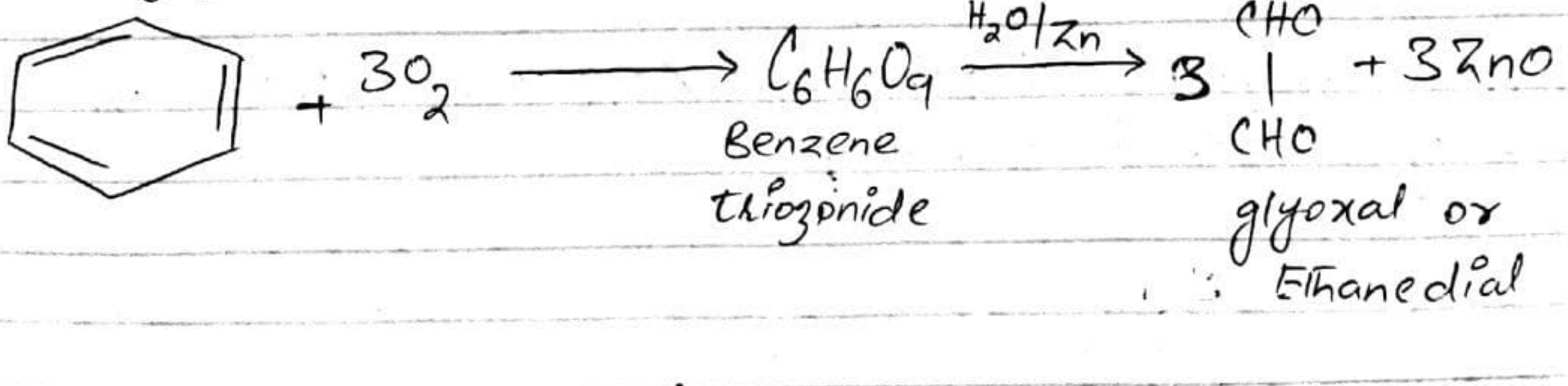
ii) Combustion :-

"Burning of compound in the presence of oxygen is called combustion."



iii) Ozonolysis :-

When benzene is reacted with Ozone, benzene ozonide is obtained. It react with water and zinc, form glyoxal.

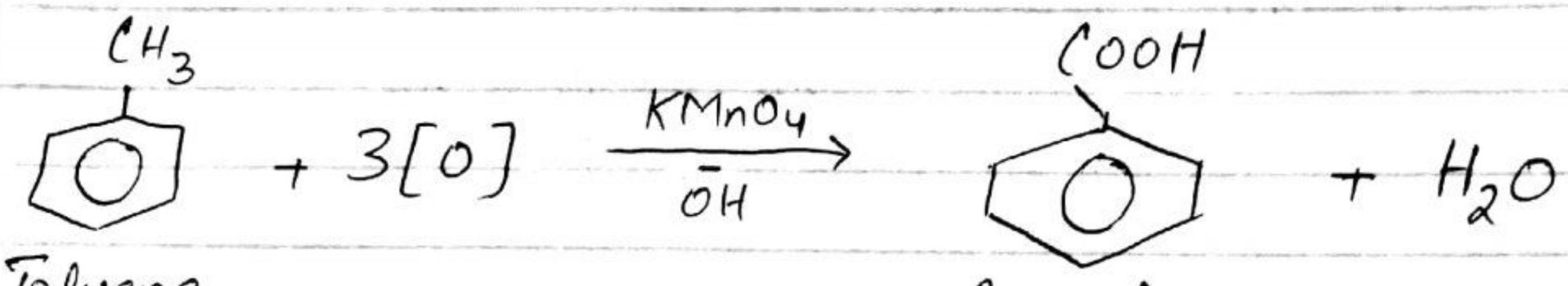


(v) Side Chain Oxidation :-

OR

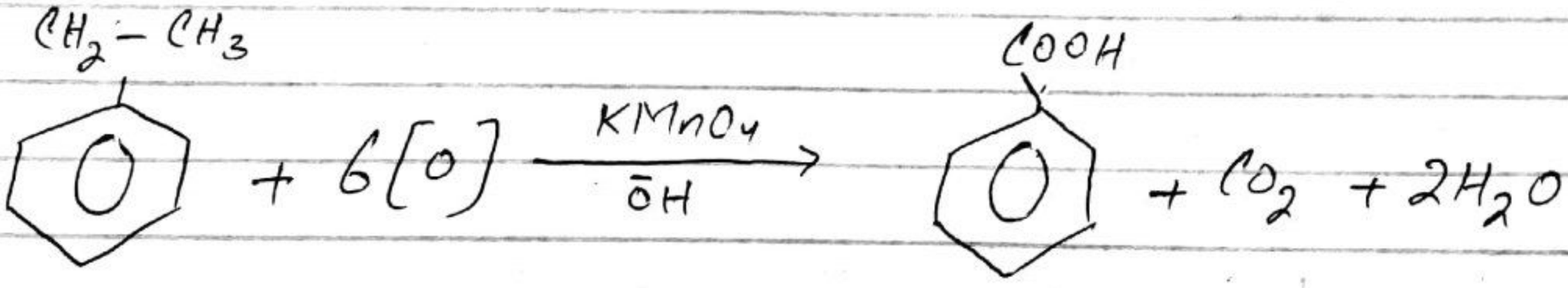
Identification test for Alkyl Benzene :-

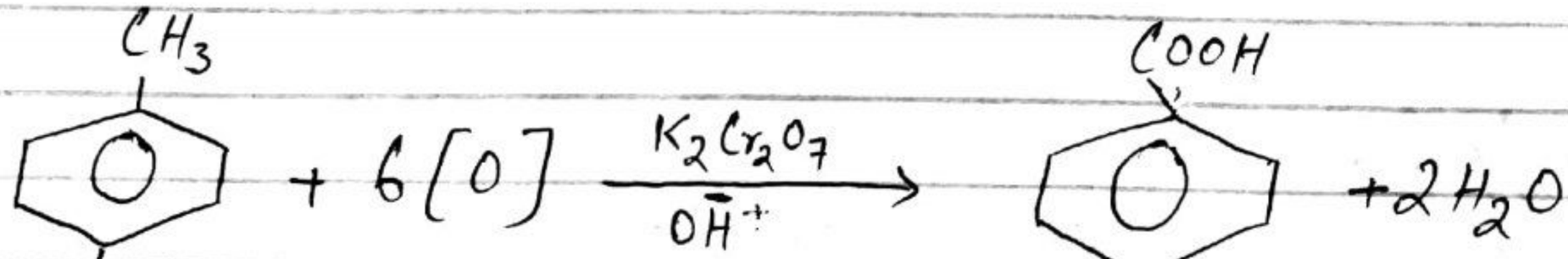
Benzene cannot oxidize with $KMnO_4$ or $K_2Cr_2O_7$. However, alkyl benzene are oxidized in the presence of $KMnO_4$ or $K_2Cr_2O_7$. Alkyl group present on benzene ring is converted into carboxylic group. Formation of carboxylic group doesnot depend upon the length of alkyl group.



Toluene

Benzoic Acid





P-Xylene

Q:- How will you distinguish b/w Benzene and toluene by means of chemical reaction?

Benzene cannot oxidize with $KMnO_4$ or $K_2Cr_2O_7$. But alkyl benzene are oxidized in the presence of $KMnO_4$ or $K_2Cr_2O_7$. As Toluene is an Alkyl benzene it will oxidized but benzene doesnot, in the presence of $KMnO_4$ or $K_2Cr_2O_7$. Hence

we can easily distinguish b/w benzene and toulene.

Electrophilic Substitution Reaction of BENZENE

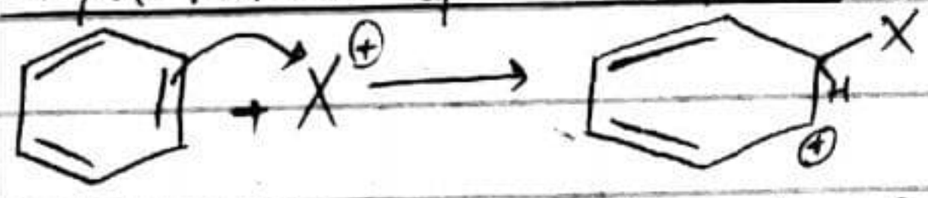
Q:- Write general mechanism of electrophilic substitution reaction of Benzene?

Step1: Formation of Electrophile:

$$X\overset{+\delta}{-}X\overset{-\delta}{} + FeX_3 \longrightarrow X^+ + FeX_4^-$$

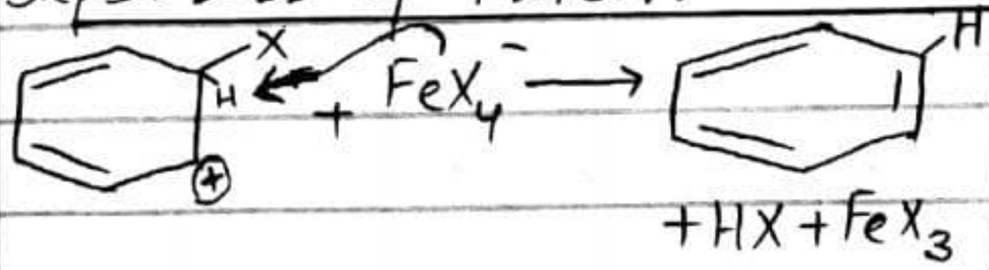
electrophile

Step2: Attack of Electrophile:



Benzonium ion

Step3: Loss of Proton:

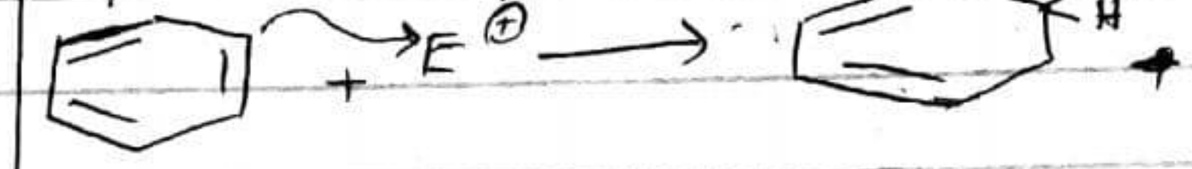


$+HX + FeX_3$

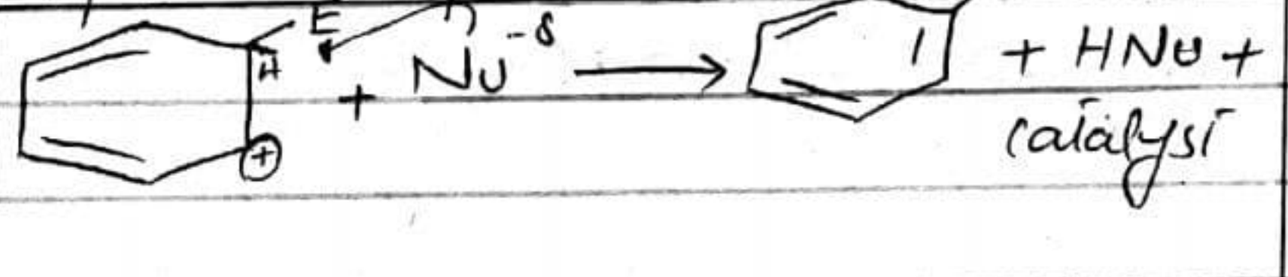
Step1: Formation of Electrophile:

$$E\overset{+\delta}{-}NU\overset{-\delta}{} + \text{catalyst} \longrightarrow E^+ + NU\text{-catalyst}^-$$

Step2: Attack of Electrophile



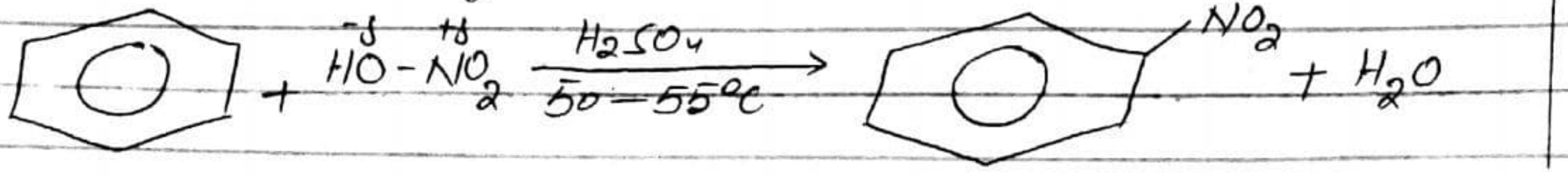
Step3: Loss of Proton



(9) Nitration:-

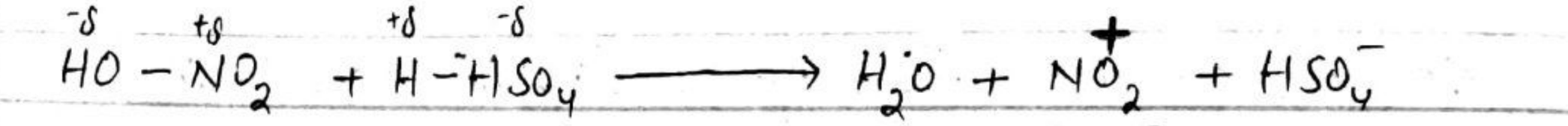
"Replacement of Hydrogen atom by (NO_2) nitro group is called nitration"

When benzene is reacted with HNO_3 in the presence of H_2SO_4 as a catalyst, nitro benzene is obtained

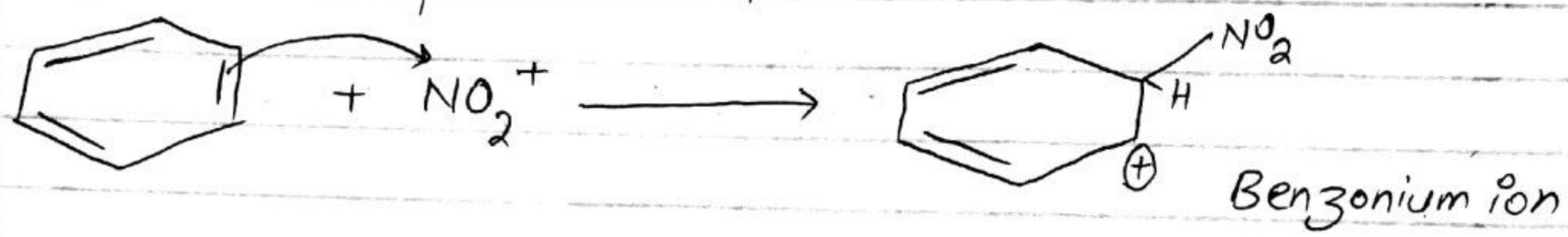


Mechanism:-

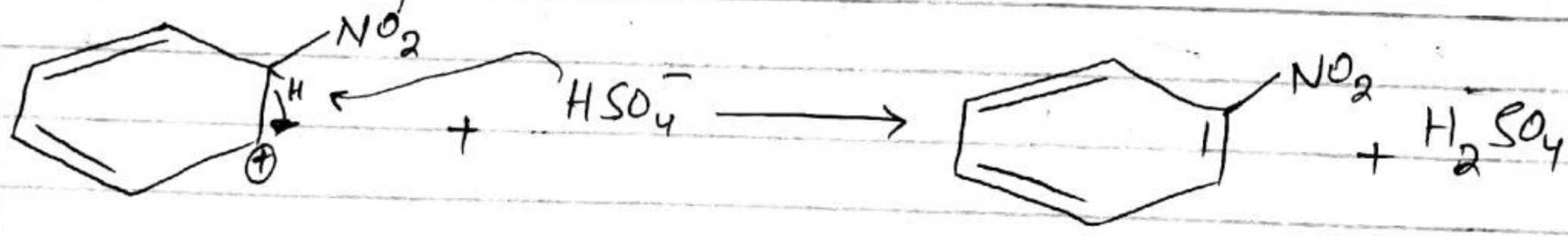
⇒ Step 1) Formation of Electrophile :-



⇒ Step 2) Attack of Electrophile :-

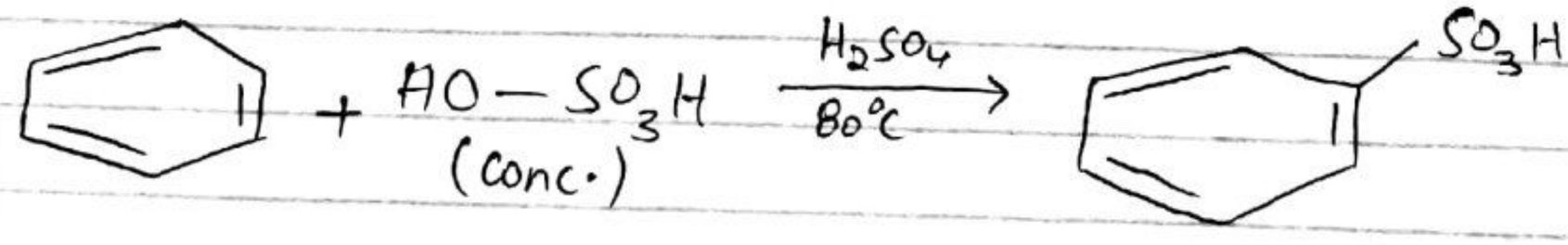


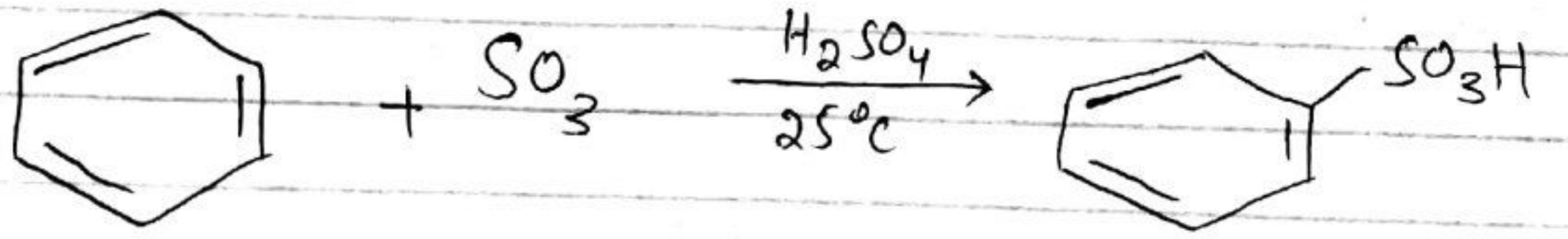
⇒ Step 3) Loss of Proton :



11- Sulphonation :-

"Replacement of Hydrogen atom by sulphonic ($-SO_3H$) group is called sulphonation"



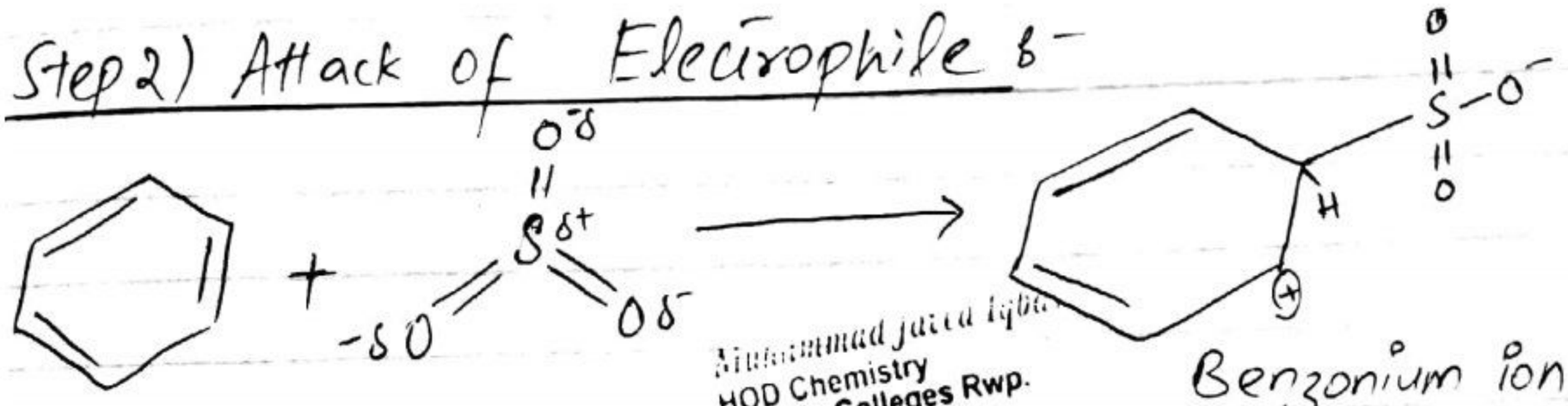


Mechanism:-

Step 1) Formation of Electrophile :

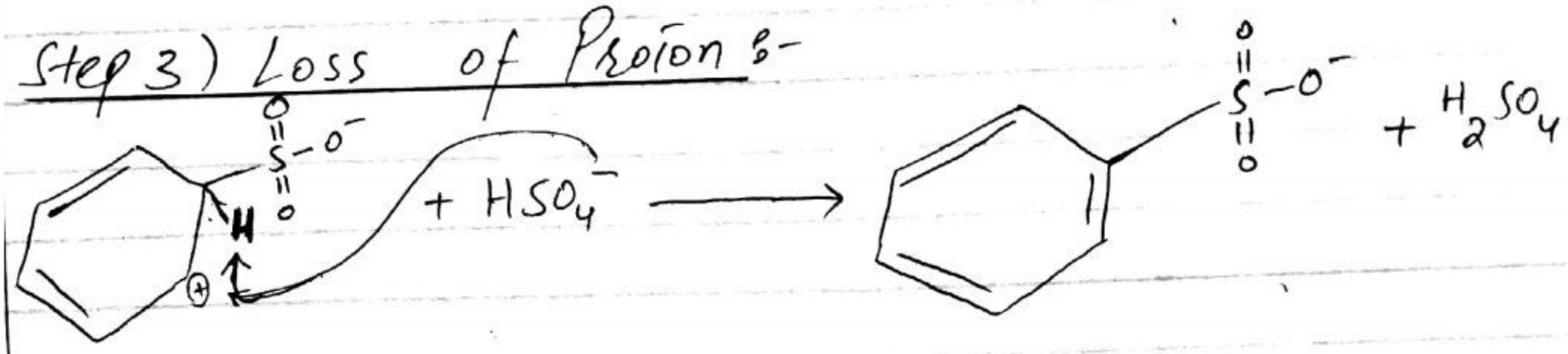
$$H_2SO_4 + H_2SO_4 \longrightarrow SO_3 + H_3O^+ + HSO_4^-$$

Step 2) Attack of Electrophile δ^-

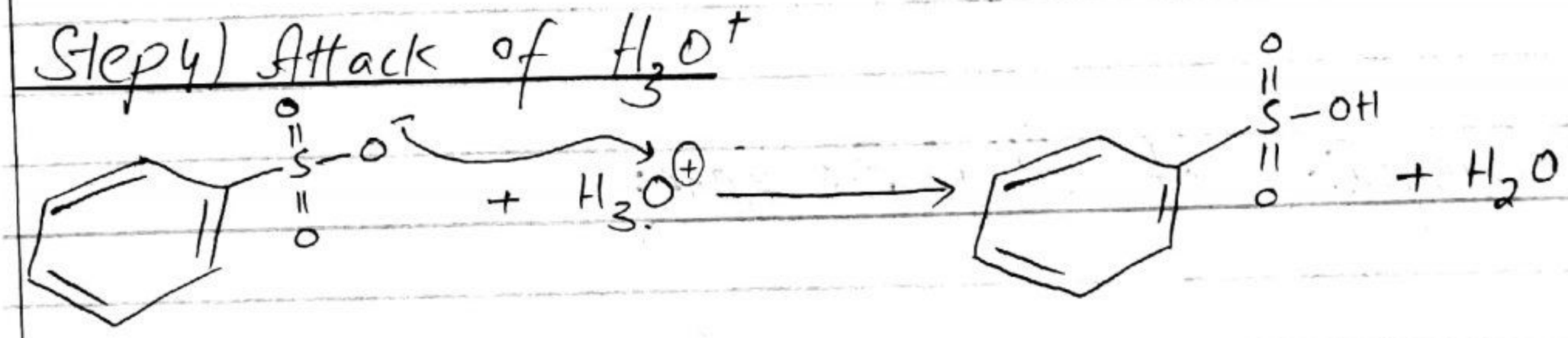


Benzonium ion

Step 3) Loss of Proton δ^-

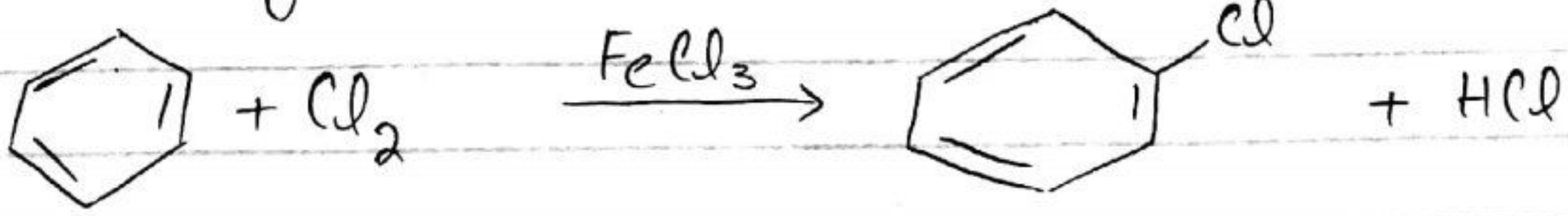


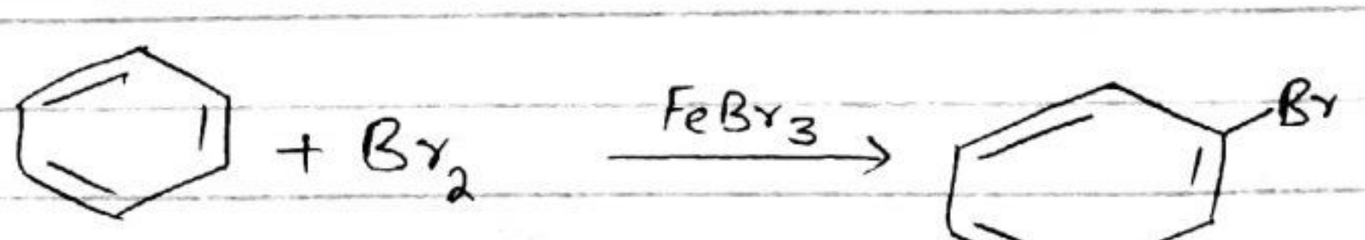
Step 4) Attack of H_3O^+



C-Halogenation:-

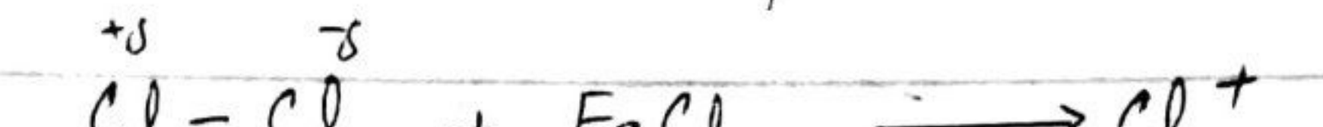
"Replacement of H-atom by halogen is called halogenation"



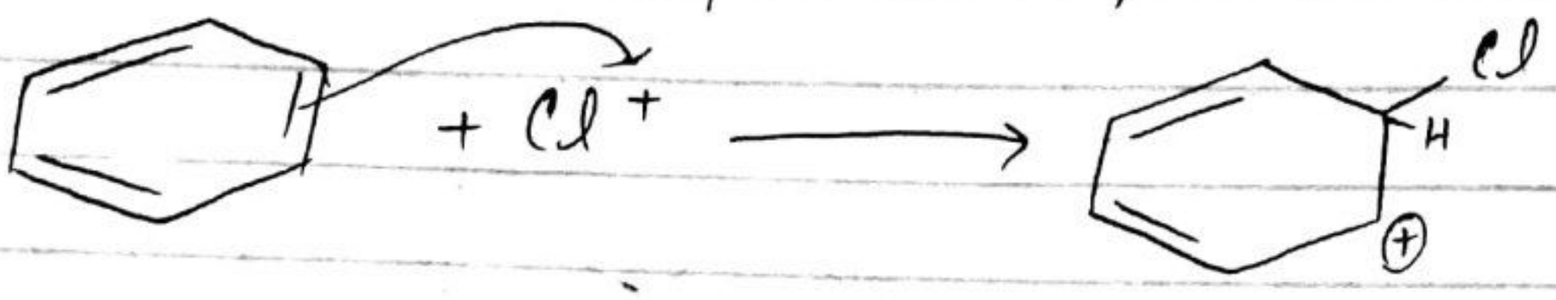


Mechanism :-

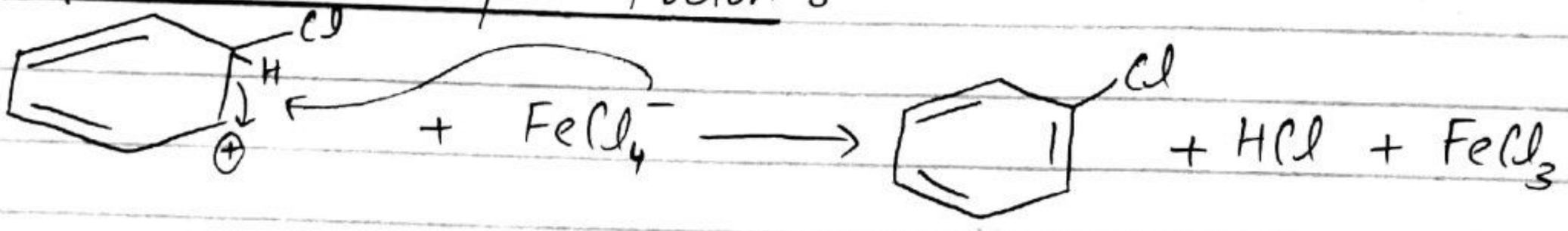
Step 1) Formation of Electrophile :-



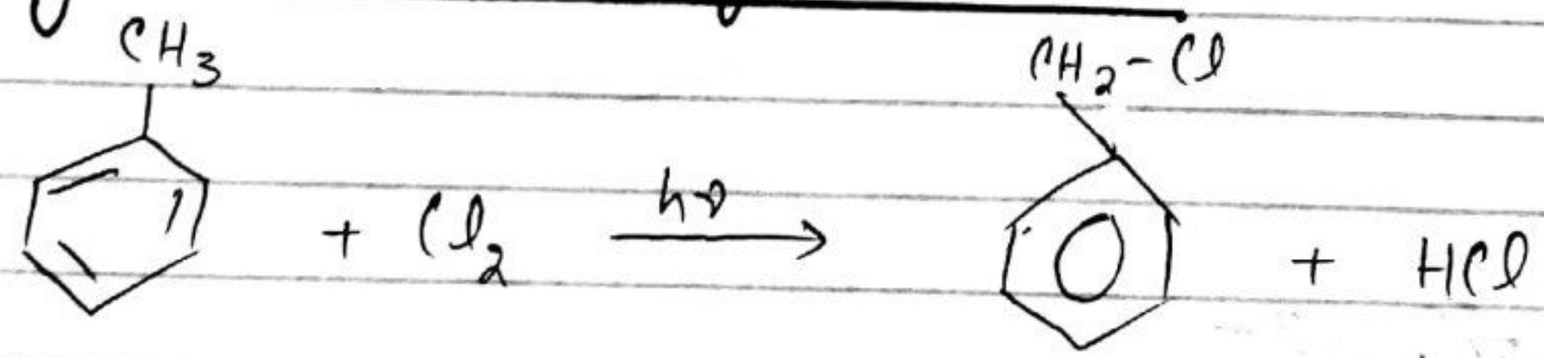
Step 2) Attack of Electrophile :-

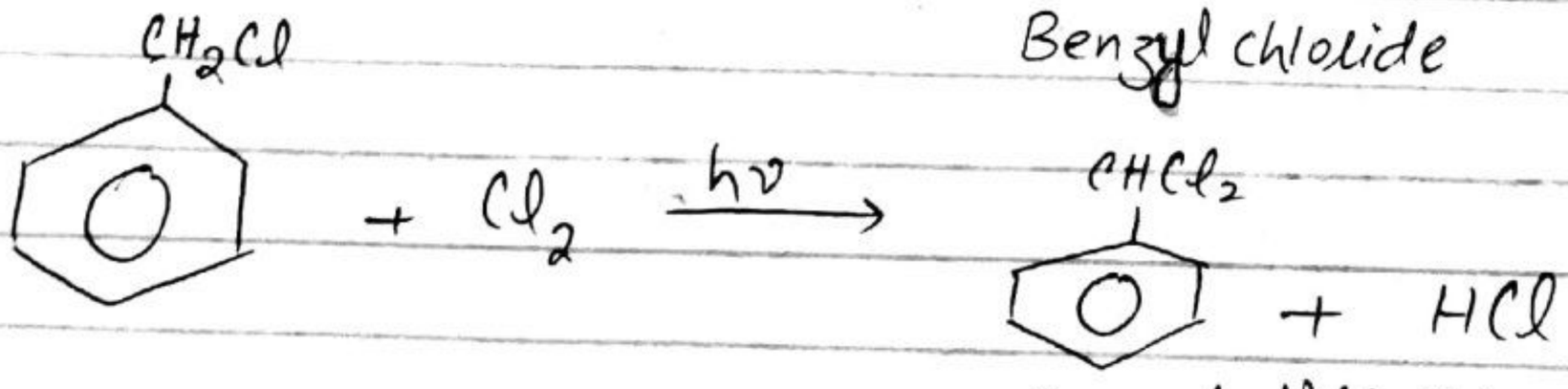


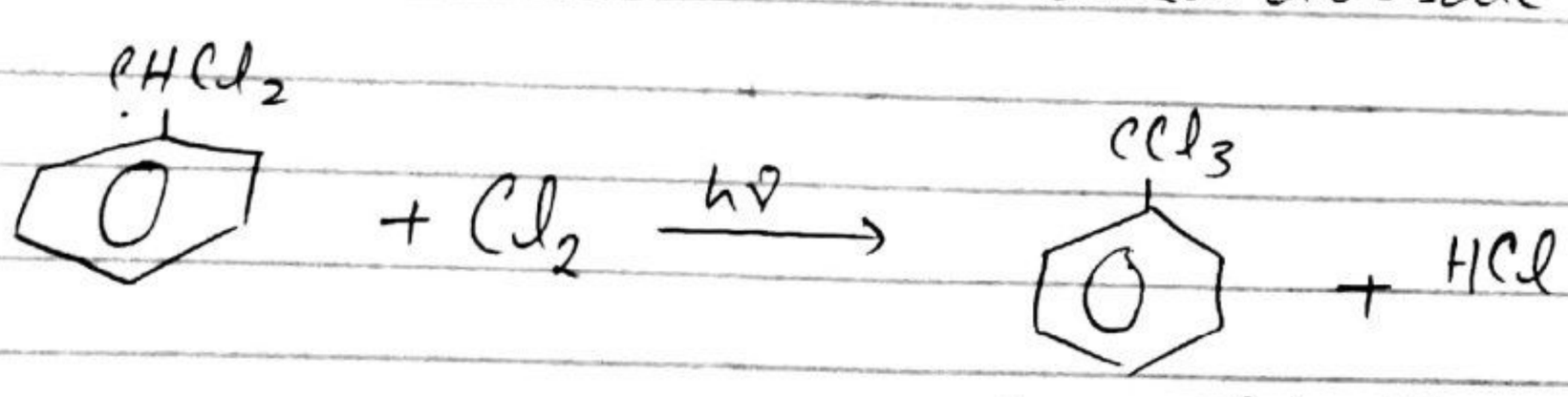
Step 3) Loss of Proton :-



Halogenation of Alkyl Benzene :-







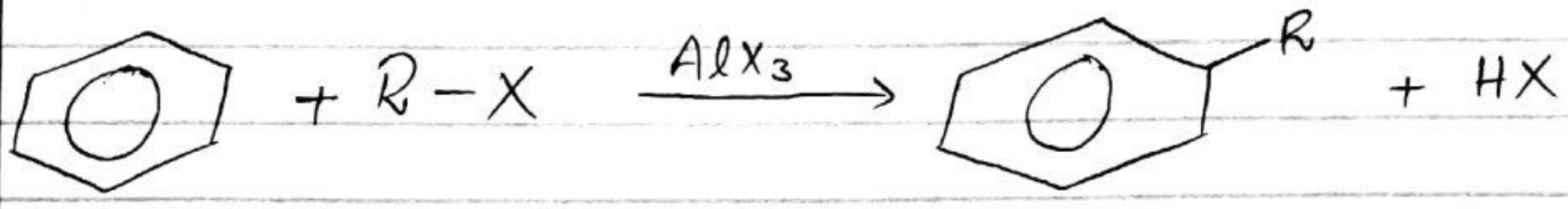
VVV imp

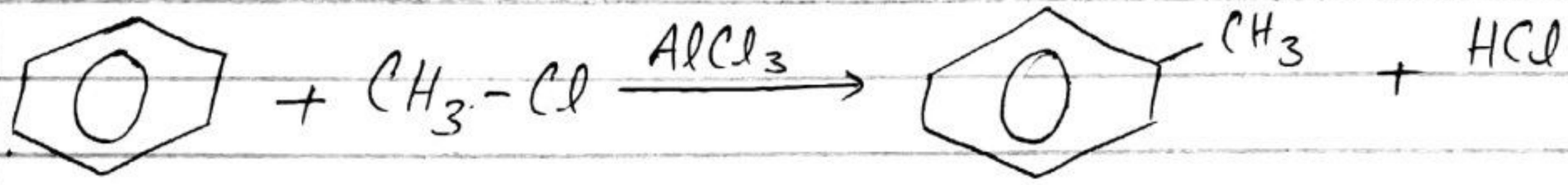
d) Friedal - Craft Reaction :-

"Alkylation and Acylation of Benzene is called "Friedal - Craft reaction"

→ Alkylation :-

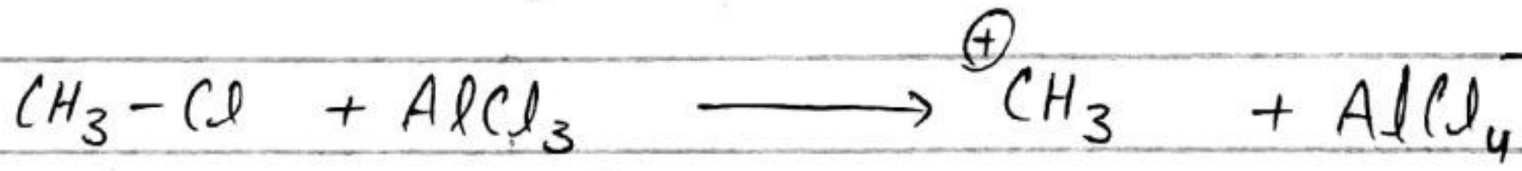
Replacement of hydrogen atom by Alkyl group is called "alkylation"



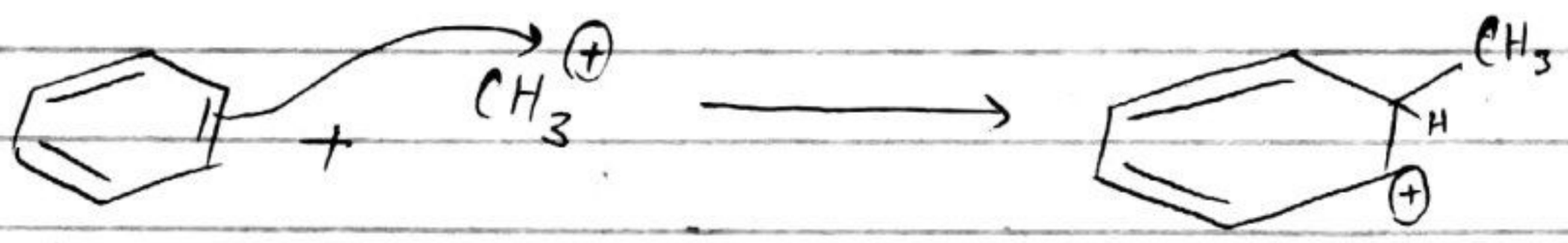


Mechanism :-

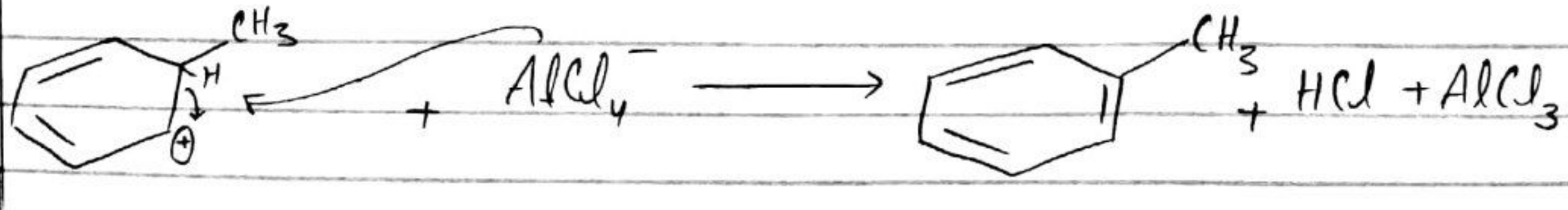
Step 1) Formation of Electrophile :-



Step 2) Attack of Electrophile :-

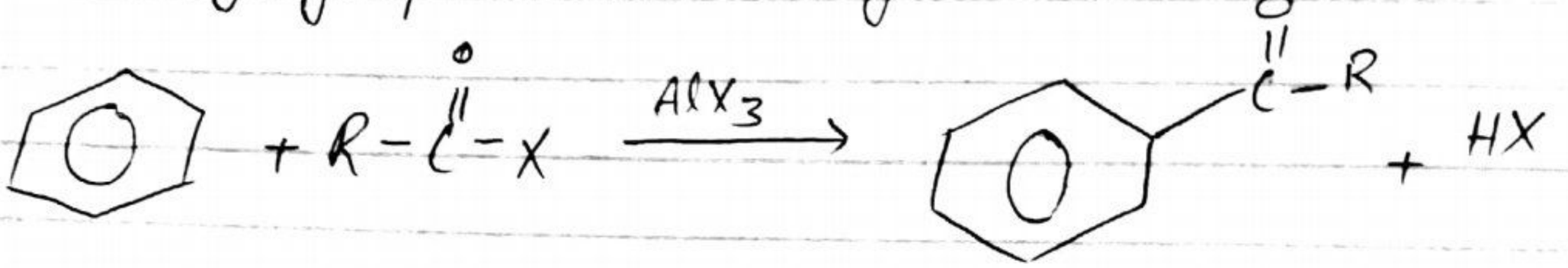


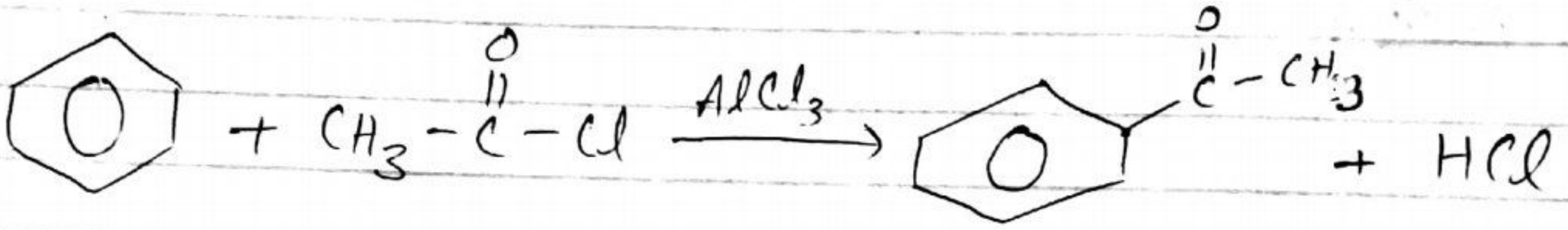
Step 3) Loss of Proton :-



→ ~~Atte~~ **Acylation:-**

"Replacement of Hydrogen by acyl group is called Accylation".

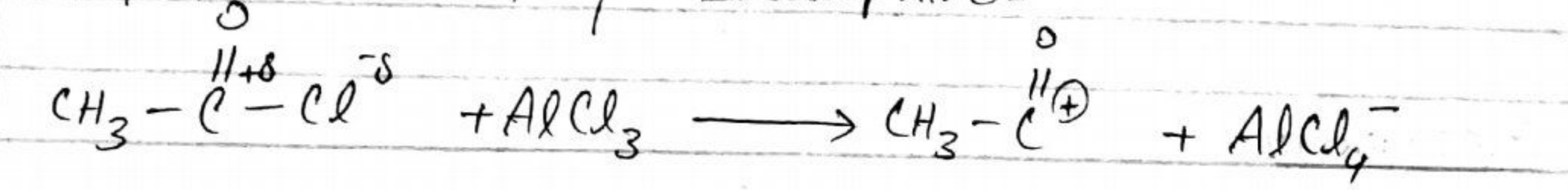




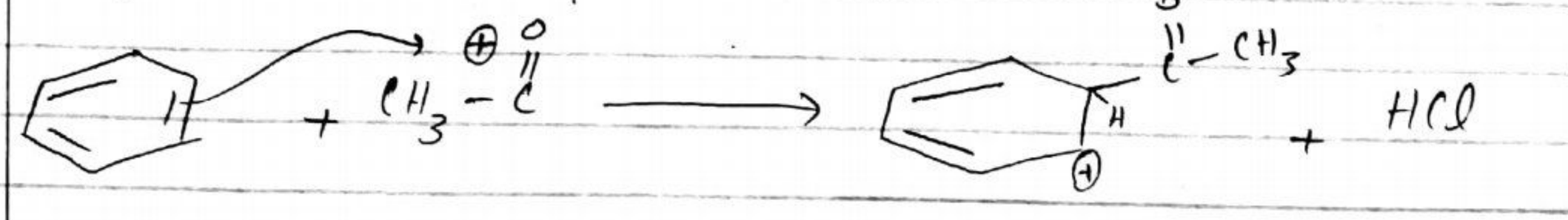
Acetophenone

Mechanism:-

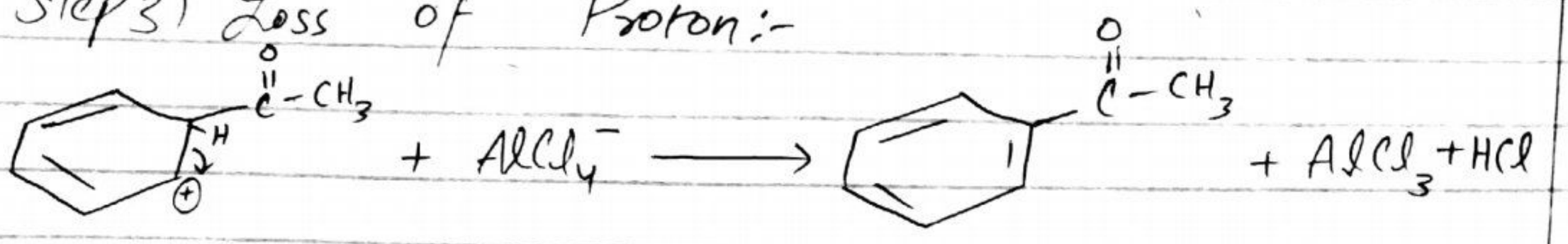
Step1) Formation of Electrophile:-



Step2) Attack of Electrophile:-



Step3) Loss of Proton:-



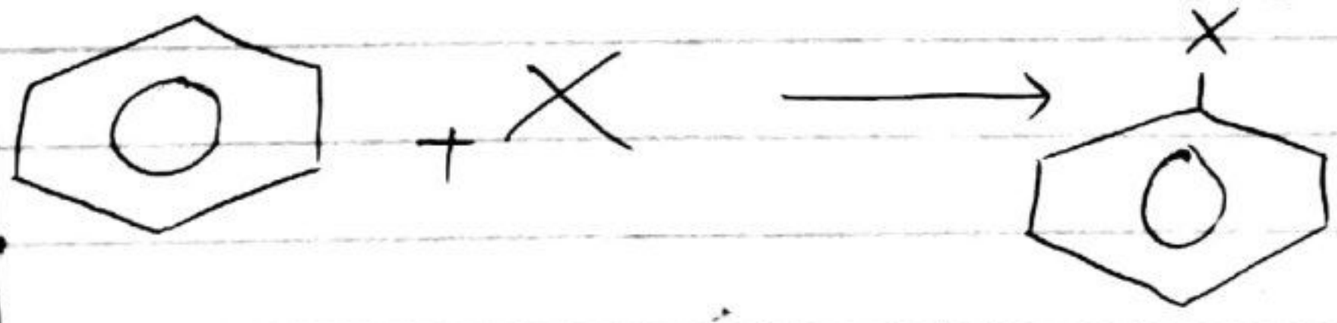
SUBSTITUTION EFFECT AND Making Disubstituted BENZENE:-

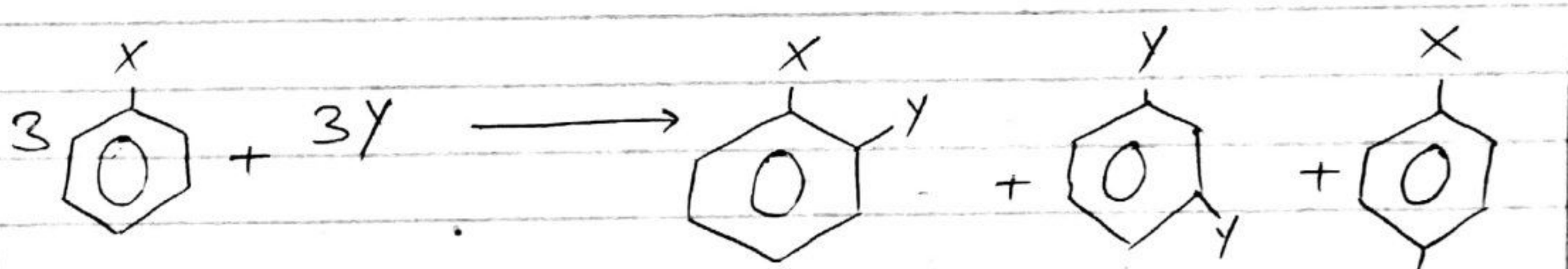
OR

ORIENTATION IN ELECTROPHILIC SUBSTITUTION

REACTIONS:-

When Benzene is reacted with any compound like X, it form monosubstituted product showing that the reactivity of all C-atom in Benzene ring are same.

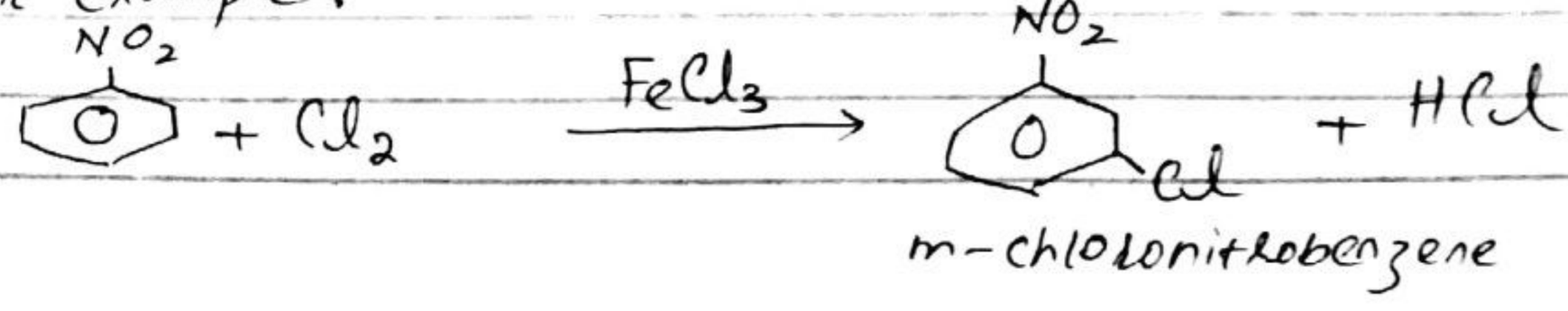




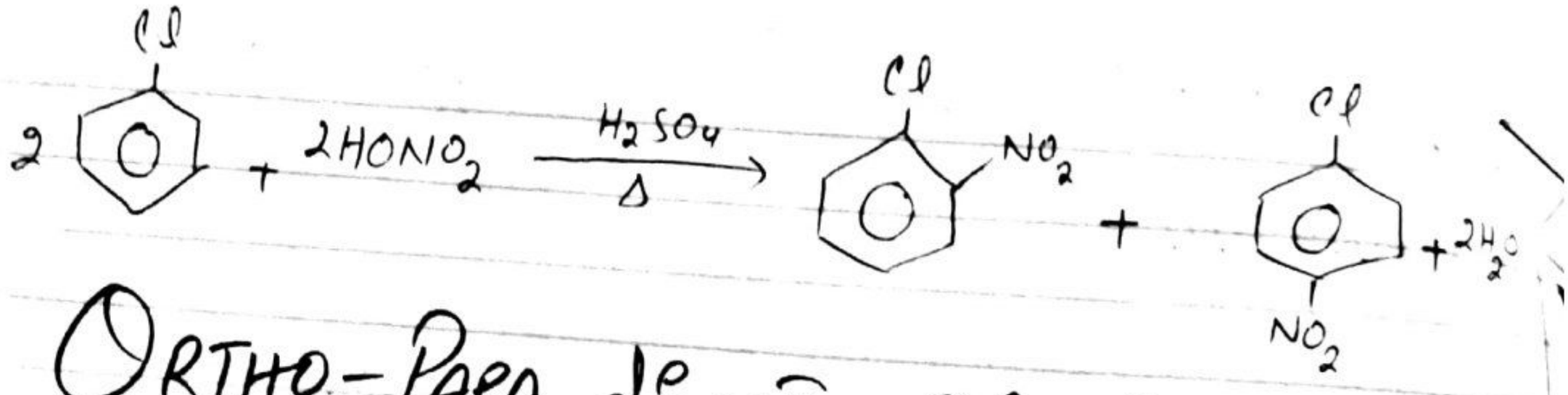
Disubstituted Products.

On the chance basis, there is 40% ortho, 40% meta and 20% para product is expected. But practically it is not possible, because nature of product depend upon group which is present already in Benzene.

For example:



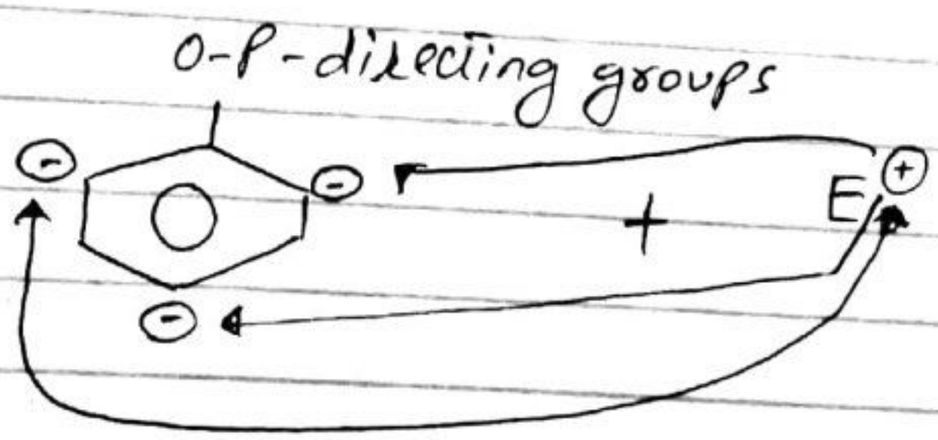
m-chloronitrobenzene



ORTHO-PARA directing group :-

" Group which direct the incomming group to ortho and para positions is called ortho-para directing groups "

⇒ They are electron donating or electron-releasing groups.
⇒ They donate electrons to benzene ring. Benzene ring become electron rich at ortho and para positions, therefore incomming electrophile attacks at ortho and para positions.

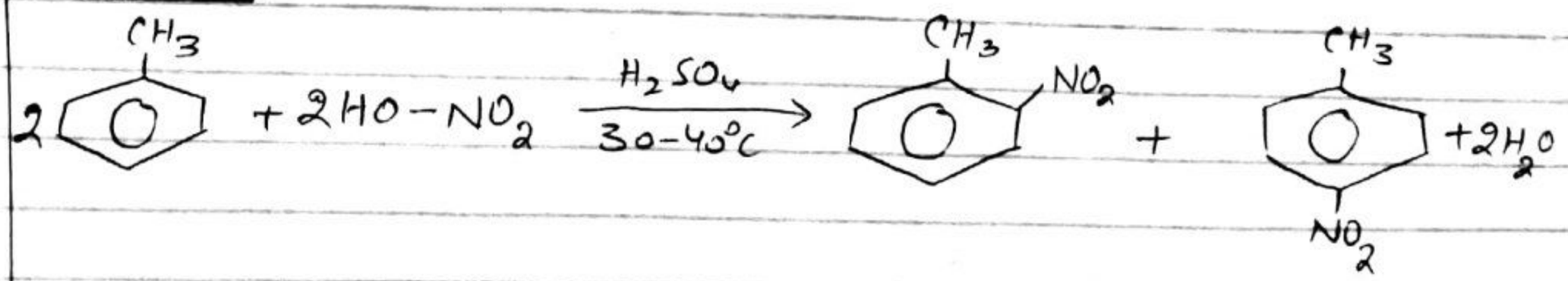


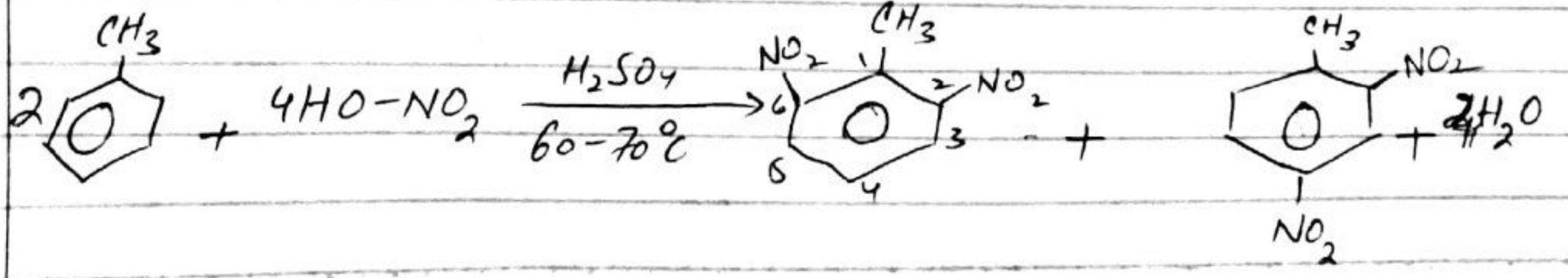
e.g :- NH_2, $-NHR$, $-NR_2$, $-OH$, $-OR$, $-R$, $-X$

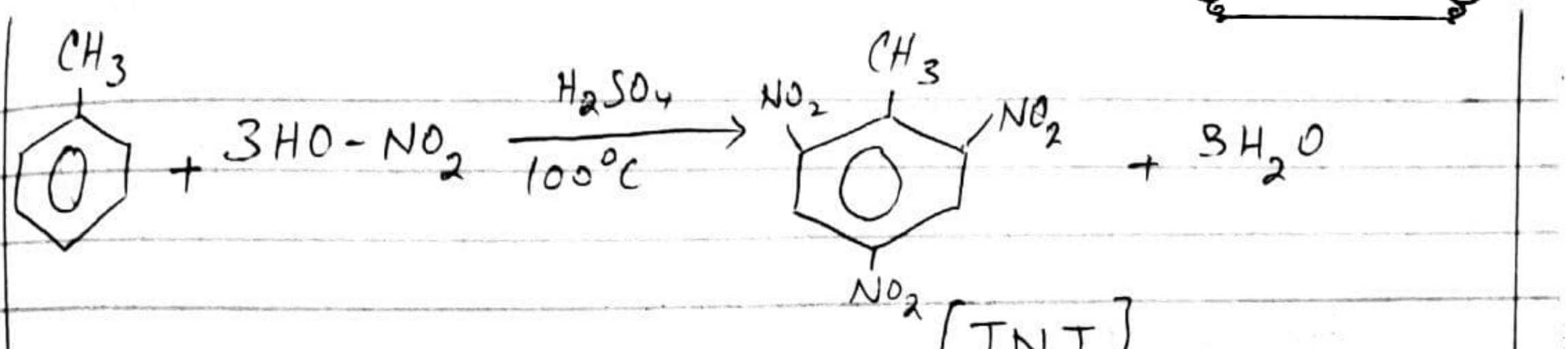
NH_2, $-NHR$, $-NR_2$, $-OH$, $-OR$, $-R$: Activators

$-X$: Deactivators.

EXAMPLES :-







[TNT]

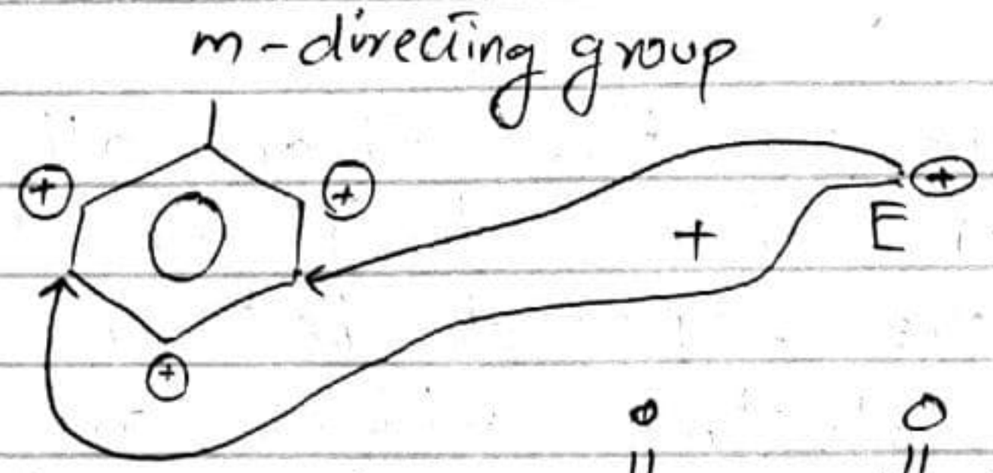
META-directing groups:-

"Groups which direct the incomming group to meta-positions are called meta-directing groups".

They are electron withdrawing and e⁻ attracting groups.

They are attract electrons from Benzene ring.

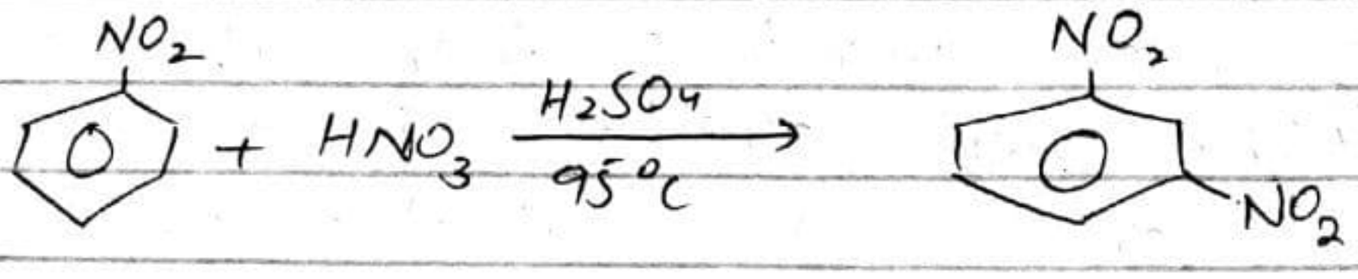
Benzene ring become electron defficient at ortho and para-positions. Therefore incomming electrophile attacks at meta-positions.



e.g:- $-NO_2$, $-SO_3H$, $-C\equiv N$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-R$, $-COOH$, $-\overset{\oplus}{N}R_3$

Deactivators

EXAMPLES:-



RULE :-

i- If directly bonded atom with benzene is less electronegative as compared to the other bonded atom, group is called meta-directing. e.g:- $-NO_2$

11- If directly bonded atom with benzene is more E.N as compared to the other. bonded atom, group is called. ortho-paradirecting group.

EXAMPLE :-

→ OH-group is ortho-para directing bcz oxygen is more E.N as compared to "H".

→ Similarly "NO_2" group is meta-directing bcz "N" is less electronegative as compared to oxygen.

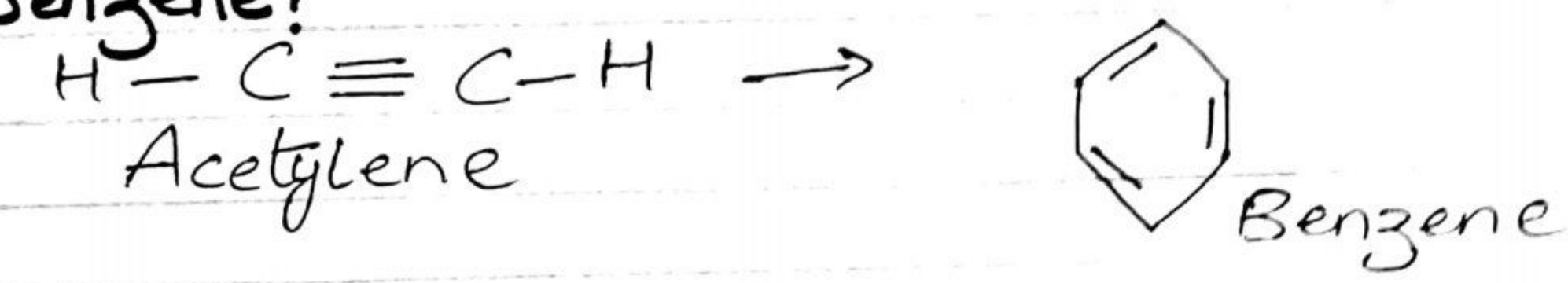
Justify the given order of reactivity. Alkene > Alkyne > Alkene?

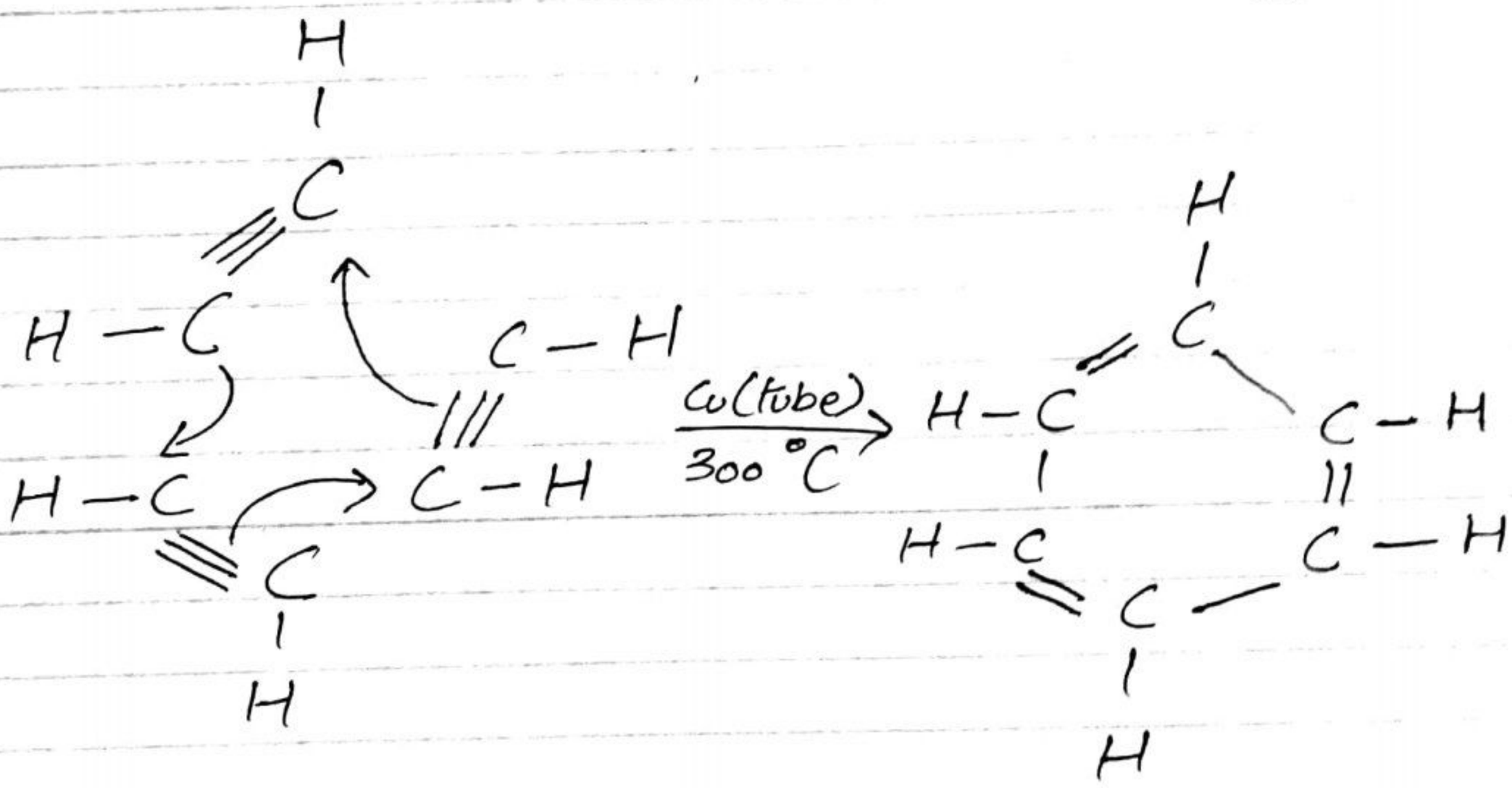
Alkene > Alkynes > Alkanes

alkene are more reactive than alkyne this is because in alkene their are π-electron which are more exposed but in alkyne there are π-electron which are less exposed due to shorter bond length between the carbon atom. These electron are not easily avaiable for the attack of electrophile.

Alkynes are more reactive than alkane because in alkyne there are π-electron but in alkane there are σ-electron which are tightly held between the two nuclei and not easily avaiable for the attack of electrophile.

How will you convert acetylene into benzene?





" EXERCISE "

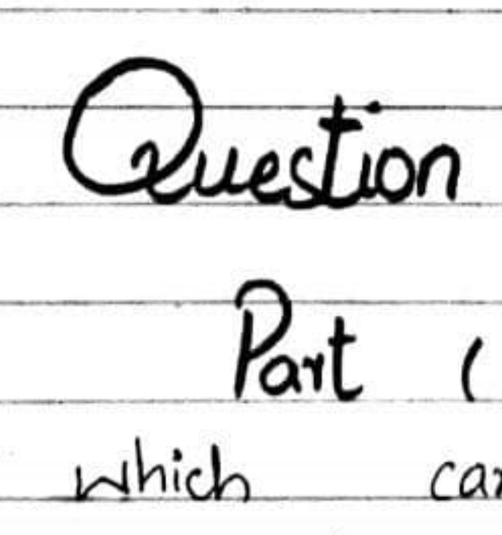
Question : 01

1- a
2- d
3- d
4- a
5- a
6- d
7- b
8- a
9- a
10- c
11- b
12- b
13- a
14- d
15- d
16- d
17- b
18- a
19- d
20- b
21- c
22- b
23- b & c
24- c
25- d

Question : 02

Part (1)

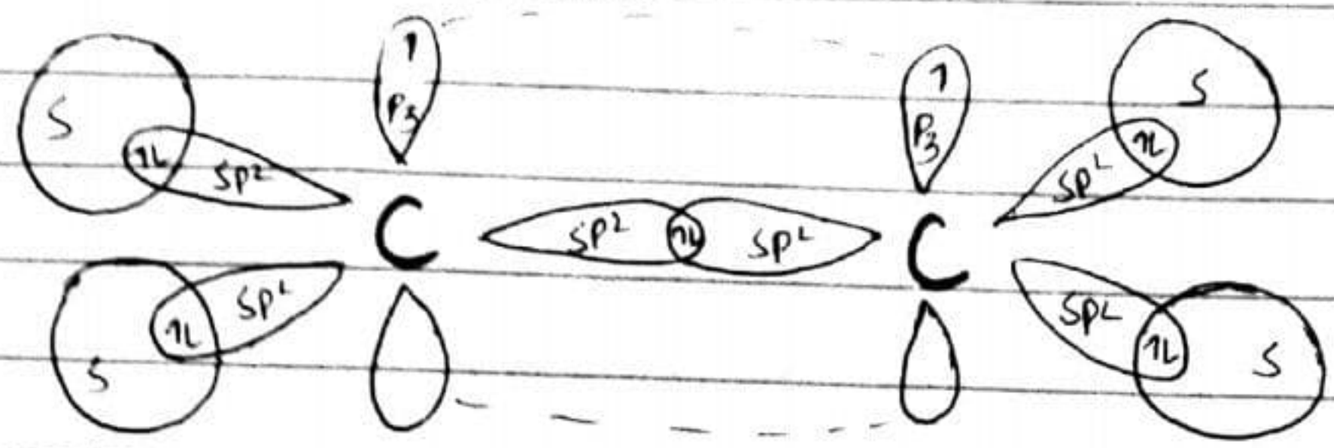
Compounds in which carbon forms 4 σ bonds. σ bonds are formed by linear overlapping of atomic orbitals. The orbitals formed by σ bonds are hybrid. So 4 σ bonds forms 4 hybrid orbitals which forms sp^3 hybridization.



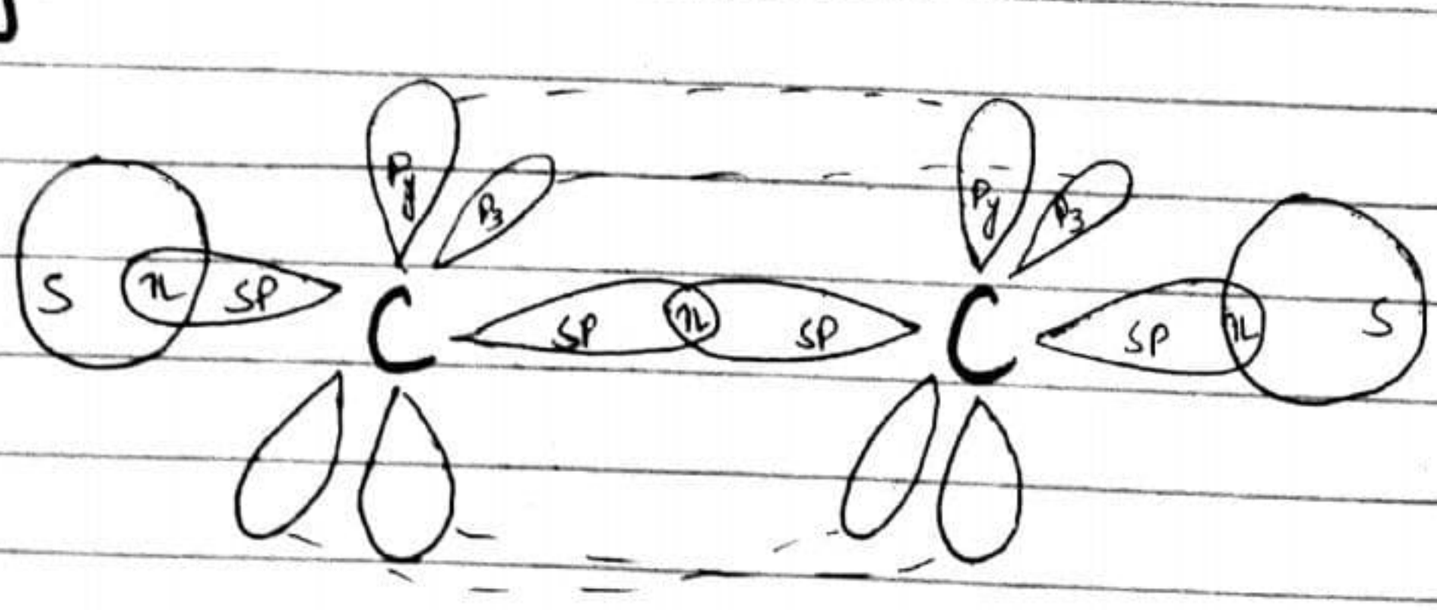
Tetrahedral geometry

Part (2)

In alkenes, there is 1S & 2P hybrid orbitals which forms sp^2 hybridization.
1 unhybrid orbital forms $\bar{\pi}$-bond by the parallel overlapping of atomic orbitals. **e.g;**



While in alkynes, there is 1S & 1P hybrid orbitals which forms sp hybridization.
2 unhybrid orbitals forms $\bar{\pi}$ bonds by parallel overlapping of atomic orbitals.
e.g;



Part (3)

See the topic "Geometric Isomerism".

Part (4)

See the topic "Inertness of sigma bond" in Alkanes.

Part (5)

Alkenes are unsaturated compounds. In alkenes, there is double bond b/w the C-C atoms. Therefore, on reaction, they undergo addition reaction.

Alkanes are saturated compounds. In alkanes, there is single bond b/w the C-C atoms. Therefore, on reaction, they undergo substitution reaction.

Example:

$$CH_2 = CH_2 + Br^{\delta+} - Br^{\delta-} \xrightarrow{CCl_4} CH_2(Br) - CH_2(Br)$$

(Ethene) (1,2-Dibromoethane)

$$CH_3 - CH_3 + Br_2 \xrightarrow{h\nu} CH_3 - CH_2(Br) + HBr$$

(Ethane)

In these reactions, when Br_2 reacts with ethene it is added by destroying the double bond & converting it into a single bond.

While in the case of ethane, Br is substituted by H atom. So alkanes undergo substitution reaction.

Part (6)

See the topic "Stereoisomerism".

Part (7)

See the topic "Optical Isomerism."

Part (8)

See the topic "Conjugated alkenes".

Part (9)

Alkenes are more reactive than alkynes. This is because in alkenes there are $\bar{\pi}$-electrons which are more exposed. But in alkynes there are $\bar{\pi}$- electrons which are less exposed due to shorter bond length b/w the C atoms. These electrons are not easily available for the attack of electrophile (E^+).

Part (10)

Alkenes > Alkynes > Alkanes

Alkenes are more reactive than alkynes. This is because in alkenes there are $\bar{\pi}$- electrons which are more exposed. But in alkynes there are $\bar{\pi}$- electrons which are less exposed due to shorter bond length b/w the C atoms. These electrons are not easily available for the attack of Electrophile (E^+).

Alkynes are more reactive than alkanes. Because in alkynes there are $\bar{\pi}$-electrons. But in alkanes there are $\bar{\sigma}$- electrons which are tightly held b/w the two nuclei & not easily available for the attack of electrophile (E^+).

(ii) Alcohols

$$\underset{\underset{OH}{|}}{CH_2 - CH_2 - CH_2 - CH_3} \xrightarrow[140-170C]{H_2SO_4\ (75\%)} CH_2 = CH - CH_2 - CH_3 + H_2O$$

(Butanol)

(iii) Electrolysis of Salt

$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH - C(=O) - ONa \\ | \\ CH_2 - C(=O) - ONa \end{array} + \begin{array}{l} H - OH \\ + \\ H - OH \end{array} \longrightarrow CH_2 = CH - CH_2 - CH_3 + 2NaOH + H_2 + 2CO_2$$

(iv) Vic - dihalides

$$\underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH} - CH_2 - CH_3 + Zn \xrightarrow{CH_3OH} CH_2 = CH - CH_2 - CH_3 + ZnCl_2$$

(b)

(i) Combustion

$$CH_3 - CH_2 - CH_3 + 5O_2 \xrightarrow{Flame} 3CO_2 + 4H_2O$$

(ii) Nitration

$$CH_3 - CH_2 - CH_3 + HO - NO_2 \xrightarrow[450^\circ C]{H_2SO_4} CH_3 - CH_2 - CH_2 - NO_2 + H_2O$$

Question : 03

(a)

See the topic " Halogenation in reactions of alkanes ".

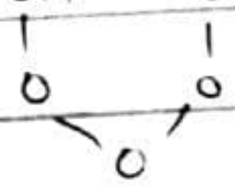
(b)

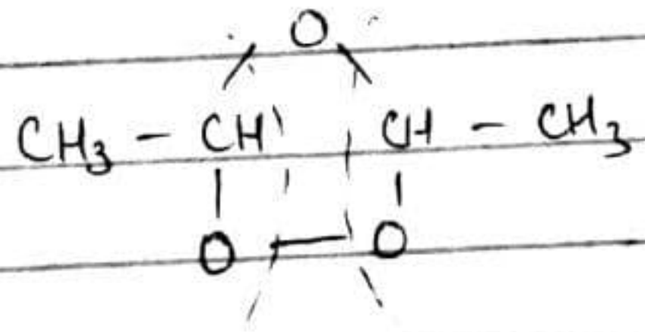
$$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_3 + Zn \xrightarrow{CH_3OH} CH_3-CH=CH-CH_3 + ZnCl_2$$

(2,3 - Dichlorobutane)

(2 - Butene)

$$CH_3-CH=CH-CH_3 + O_3 \longrightarrow CH_3-\underset{O}{\underset{|}{CH}}-\underset{O}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{rearrangement}}$$





$$\xrightarrow{H_2O/Zn} 2\ CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O_2$$

(Acetaldehyde)

$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$

Question : 05

See the topic "Friedal Graft acylation & alkylation."

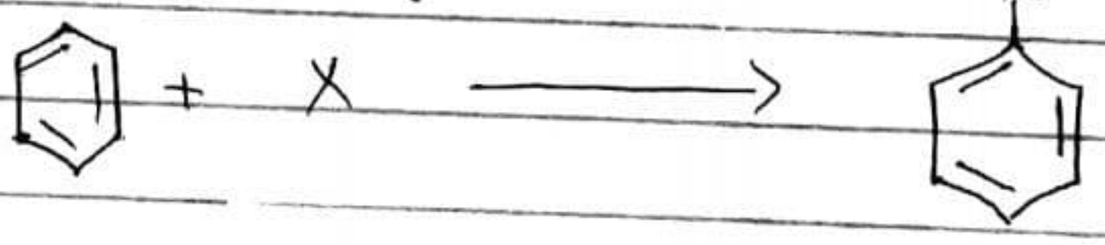
Question : 06

See the topics "Halogenation, Nitration & Sulphonation in reactions of benzene."

Question : 04

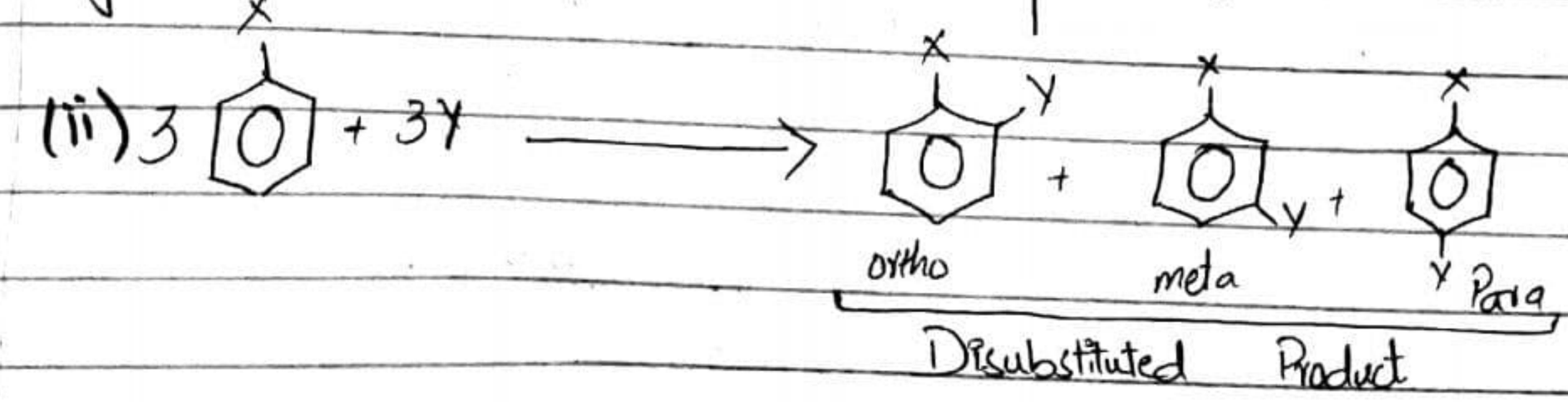
(a)

Structure of benzene was proposed by German chemist **Kekule** in 1865. According to kekule, benzene has cyclic hexagonal planar structure containing three alternate single & double bond. He proved his structure with the help of following experiment;

(i) 

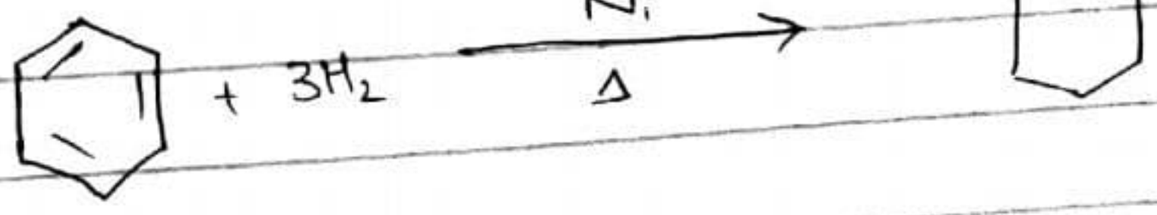
Monosubstituted Product

This experiment is showing that benzene has cyclic structure because it gives only one mono-substituted product. This experiment should give three mono-substituted products;

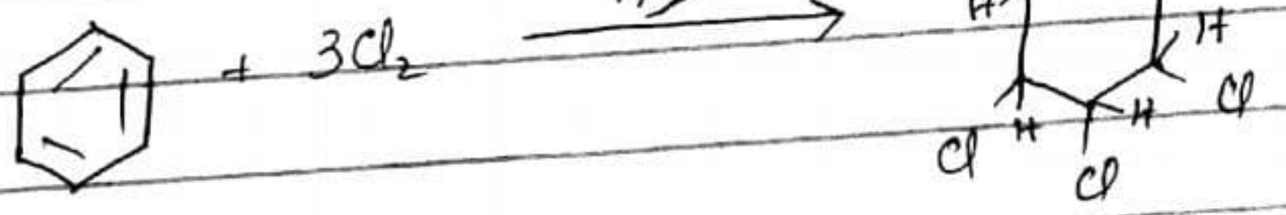
(ii) 

Disubstituted Product

This experiment is showing that all carbons in benzene are at identical position having same reactivity.

(iii) 

This experiment is showing that benzene has 3 double bonds.

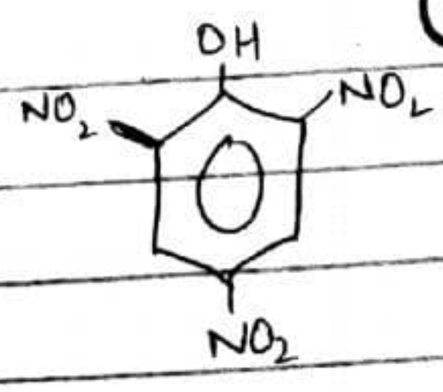
(iv) 

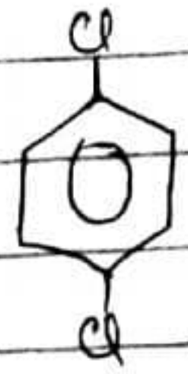
This experiment is showing that benzene has 3 alternate double & single bonds.

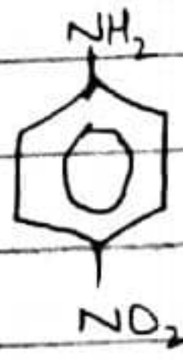
(b)

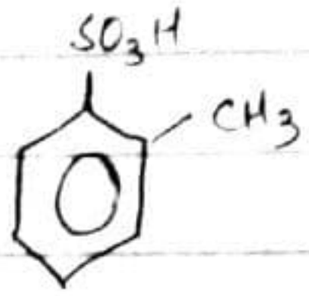
See the topic "MOT of benzene".

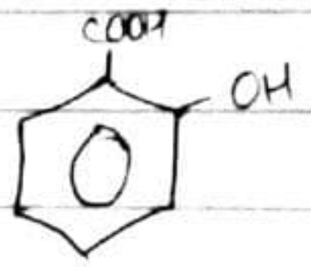
Question : 07

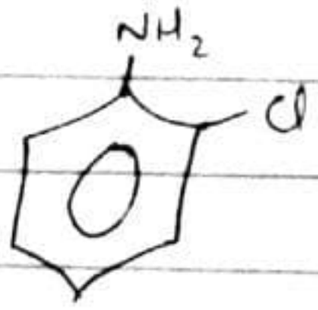
a) 

b) 

c) 

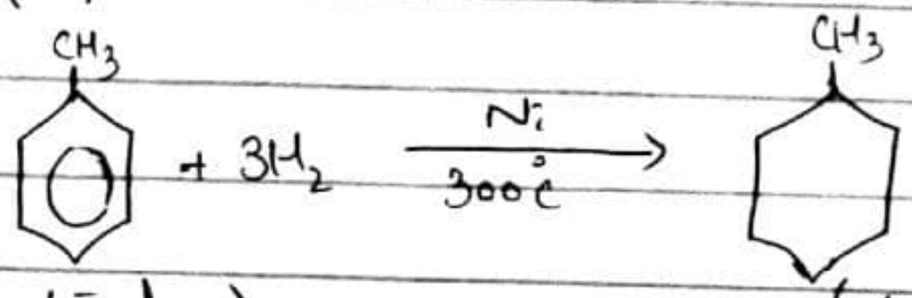
d) 

e) 

f) 

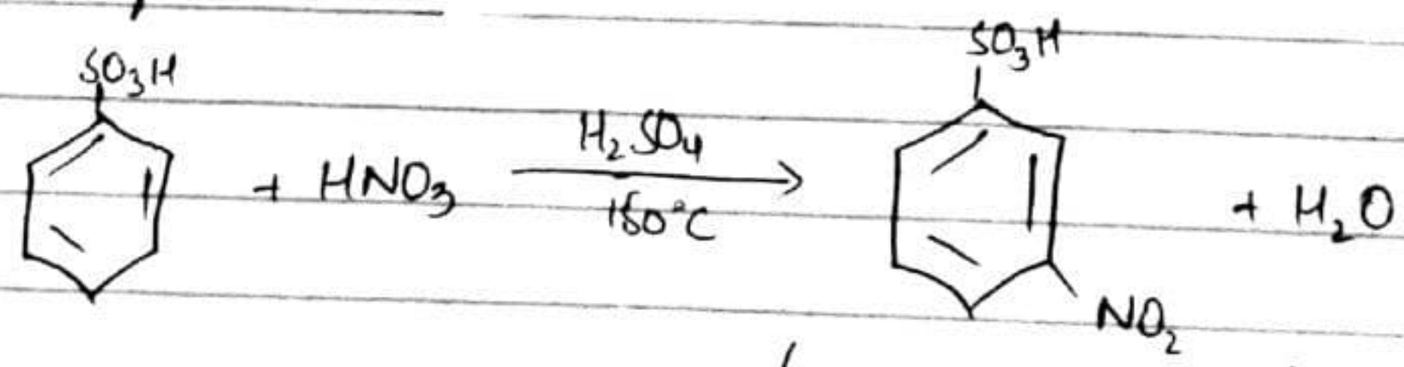
Question : 08

(a)



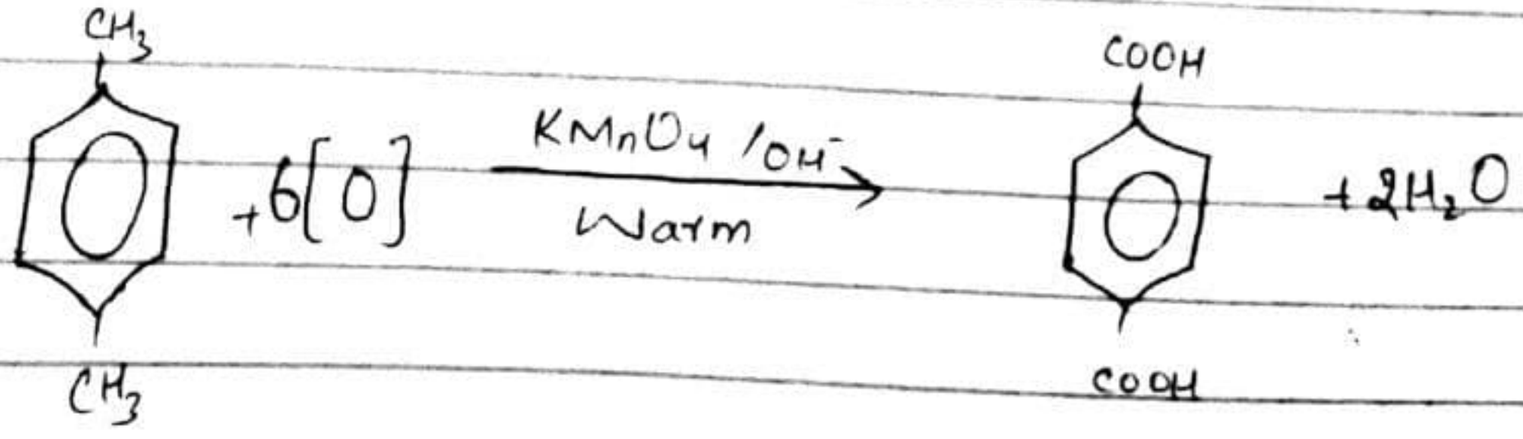
(Toulene) (Methyl cyclohexane)

(b)

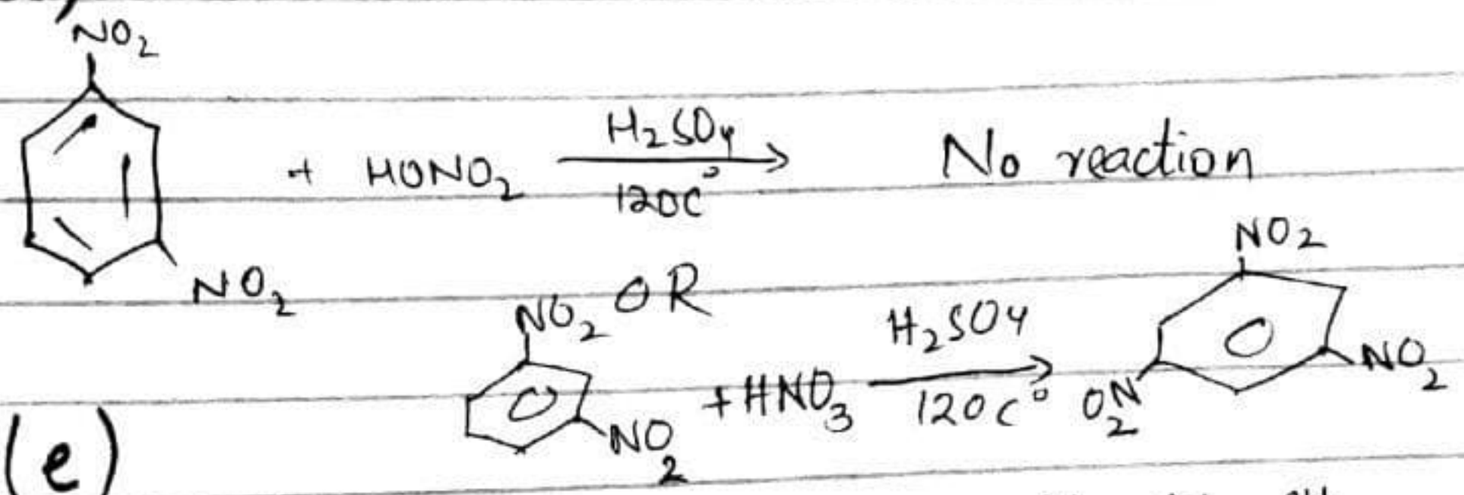


(m - Nitrobenzene sulphonic acid)

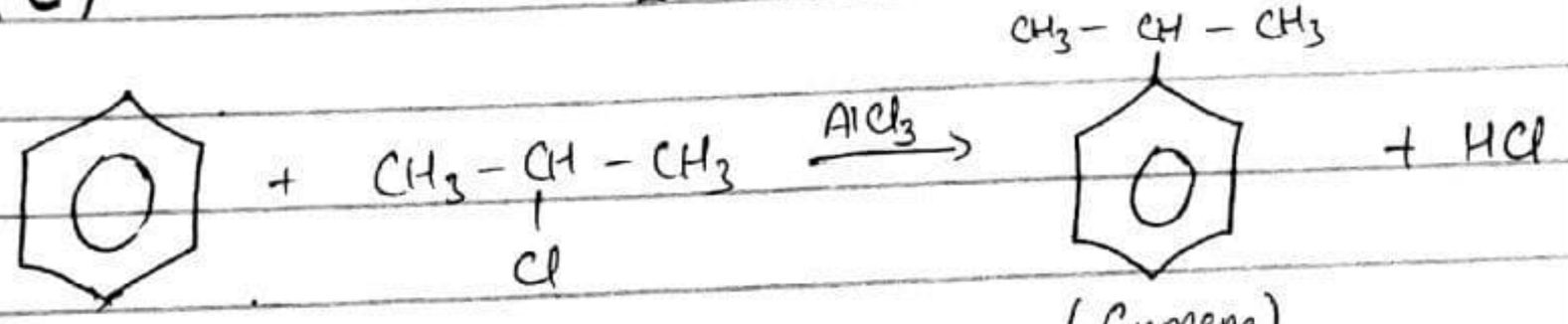
(c)



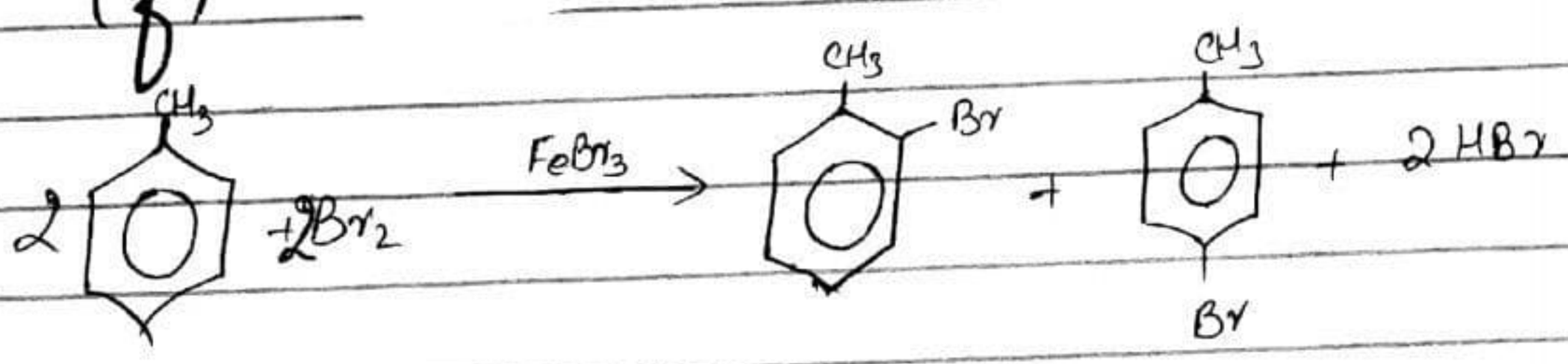
(d)



(e)



(f)



Question : 09

(a)

1,3 - Dibromobenzene

(b)

1,2 - Dimethylbenzene

(c)

1,2,3 - Trimethylbenzene

(d)

1 - Bromo - 3 - Chloro - 5 - Nitrobenzene

(e)

4 - Nitrobenzoic acid

(f)

3 - Chlorophenol