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Chapter - 7

Hydrocarbons

Compounds having

- Compounds having carbon and hydrogen only are called hydrocarbons.
- They are the major source of fuel.

Alkanes

1. The hydrocarbons containing carbon single bond carbon and carbon single bond hydrogen are called alkanes and the general formula for alkanes is ~~CnH2n+2~~ C_nH_{2n+2}

2. Alkanes possess change isomerism in their compounds.

Methods Of Preparation

1. From Alkenes or Alkynes (Unsaturated hydrocarbons =or≡)

- ~~At~~ Alkanes can be prepared by hydrogination of unsaturated hydrocarbons in the presence of Ni/Pd/Pt at 50 Kelvin temp.

$$H_2C = CH_2 + H_2 \xrightarrow{Ni/Pd/Pt} CH_3 - CH_3$$

ethene → ethane

$$CH_3 - CH = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$$

$$CH \equiv CH + H_2 \xrightarrow{Ni} CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$$

$$\text{Veg Oil} + H_2 \xrightarrow{Ni} \text{Veg ghee}$$

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2. From Alkylhydes

• By Reduction

Alkylhydes can be reduced to alkanes by any of these reducing agents :- ~~Zn~~

$$R-X+2[H] \xrightarrow[Zn+dil\,HCl\ /\ NaOH]{Zn+CH_3COOH} R-H+HX$$

$$CH_3-Cl+2[H] \xrightarrow{Zn+CH_3COOH} CH_4+HCl$$

☆. Wurtz's Reaction

In this Reaction alkylhyde reacts with sodium in the presence of dry ether to form higher alkanes.

$$CH_3-Cl+2Na+Cl-CH_3 \xrightarrow{dry\ ether} CH_3-CH_3+2NaCl$$

$$C_2H_5-Cl+2Na+Cl-C_2H_5 \xrightarrow{dry\ ether} C_2H_5-C_2H_5+2NaCl$$

→ Unsymmetrical alkanes cannot be prepared by this reaction

→ Methane (CH_4) cannot be prepared by this reaction.

⇒

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☆ Grignard Reagent

- Alkyhalide reacts with magnesium metal to form Grignard Reagent.
- Grignard Reagent formed is decomposed by water to form alkanes

$$R-X + Mg \longrightarrow \underset{\text{Covalent}}{R-Mg} \underset{\text{Ionic}}{-X}$$

$$R-Mg-X + HOH \longrightarrow \underset{\text{Alkanes}}{R-H}$$

$$CH_3-Mg-Br + HOH \longrightarrow CH_4$$

$$C_2H_5-Mg-Br + HOC_2H_5 \longrightarrow C_2H_6$$

* ~~For~~ preparation from Aldehydes & Ketones

1. Clemmensen Reduction:- In this Reaction Carbonil compounds Reacts with Zinc Amalgam and concentrate HCl to form corresponding Alkanes.

$$CH_3-\overset{O}{\overset{\|}{C}}-H + 4[H] \xrightarrow{Zn-Hg + Conc.\ HCl} CH_3-CH_3 + H_2O$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 4[H] \xrightarrow{Zn-Hg + Conc.\ HCl} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

2. Wolff Kischner Reduction:- This reaction is carried o
in the presence of a highly boiling solvent like ethylen
glycol & takes place in two steps

$$CH_3-\underset{H}{\overset{|}{C}}=O + H_2N-NH_2 \xrightarrow{-H_2O} CH_3-CH=N-NH_2 \xrightarrow{-N_2} CH_3-CH_3 + N_2 \uparrow$$

Hydrazine

Ethyl gly.

(g)

☆ Preparation from Carboxylic acid

(A) Decarboxylation Reaction:- It is the reaction in which
↓ Remove CO_2 gas
Carbon dioxide is removed from an
organic compound

2. NaOH + CaO mixture also known as soda lime
is used for this purpose.

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{Soda lime}]{NaOH+CaO} R-H + CO_2$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaOH+CaO} CH_4 + CO_2$$

The alkane formed in this reaction has 1 less carbo
than corresponding acid.

(B) Kolbe Electrolysis Reaction:- Sodium or patassium salt of
↓ to break
monocarboxylic acid is electrolysed to form alka

$$2CH_3COONa + 2H_2O \xrightarrow{\text{Electrolysis}} \cancel{CH_3-CH_3 + 2NaOH} \; CH_3-CH_3 + 2NaOH + H_2 + 2CO_2$$

→ Mechanism of Kolbe Electrolysis Rxn:-

$CH_3COO^-Na^+$

→ Anode → $2CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ —Removal of e⁻→ $2CH_3-\overset{O}{\overset{\|}{C}}-O$ → Decarboxylation → $2CH_3^{\cdot} + 2CO_2\uparrow$

(oxid)

Electrolysis

② $CH_3^{\cdot} + CH_3^{\cdot} \rightarrow CH_3-CH_3$

cathode → $Na^+ + e^- \longrightarrow Na$

$\downarrow 2H_2O$

$2NaOH + H_2$

→ Physical properties:-

1. ~~Lower~~ Physical state:- Lower members C_1 to C_4 are colourless ~~odder~~ odourless gases
2. C_5 to C_{17} are colourless liquid.
3. Higher alkanes are wax like solid.

Boiling point:-

1. Boiling point is the temperature at which vapour pressure = atmospheric pressure.
2. Alkanes have lower boiling point but the boiling point increases on increasing molecular mass.
3. Boiling point increases on increasing surface area or decreasing branches.
4. Alkanes are insoluble in water but ~~its~~ soluble in organic solvent (Benzene, ether, etc.)

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→ Chemical properties:-

1. Substitution reactions:- One or more hydrogen and atoms of alkanes can be replaced by halogens, this reaction is called Halogination Rxn and takes place in the presence of sunlight.

$$CH_4 + Cl_2 \xrightarrow[-HCl]{h\nu} CH_3-Cl + Cl_2 \xrightarrow[-HCl]{h\nu} CH_2-Cl_2 + Cl_2$$

$$\xrightarrow[-HCl]{h\nu} CHCl_3 + Cl_2 \xrightarrow[-HCl]{h\nu} CCl_4$$

→ F_2, I_2
↳ Reversible
↓
Violent / Exothermic

Nitration - It involves the replacement of NO_2 group by hydrogen with conc. HNO_3

$$\underset{\text{n-Hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow{\text{Conc. } HNO_3} CH_3-(CH_2)_4-CH_2-NO_2$$

Oxidation Reaction

Complete → CO_2
Incomplete → $CO, C \rightarrow$ Black

The important oxidation Reaction of alkenes are of two types:-
1. Complete oxidation
2. Incomplete oxidation

$$C_nH_{2n} + 2 + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1)H_2O + \text{heat}$$

$$\text{ex: } CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{Heat}$$

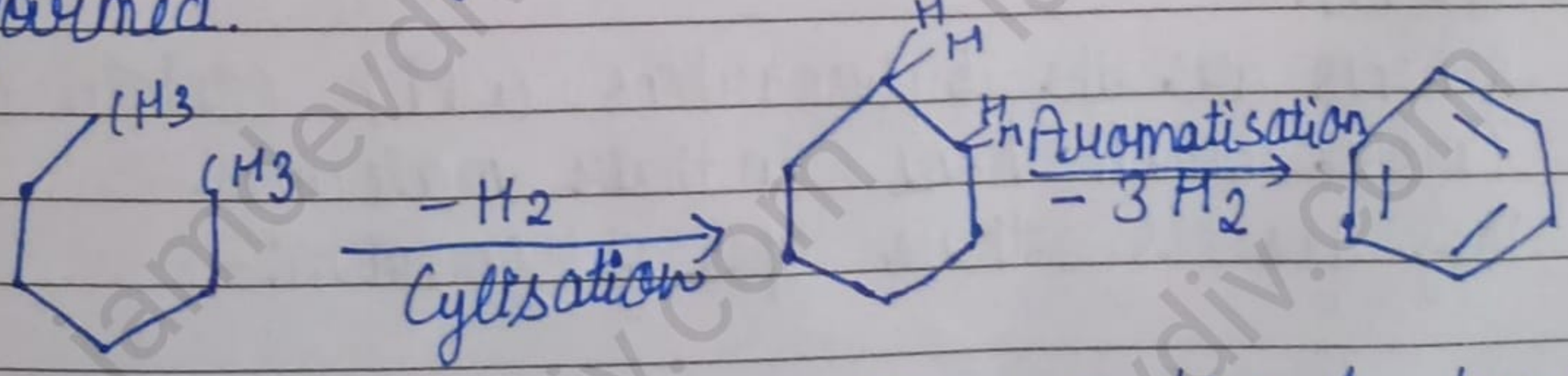
→ Incomplete oxidation - ~~Just~~ This reaction is carried out in limited supply of air to yeum carbon monoxide or Carbon black

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

→ Isomerisation :- In this rxn straight chain alkanes are converted to branched chain in presence of Anhydrous $AlCl_3 + HCl$

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

→ Aromatisation rxn:- Alkanes having six or more carbon under certain condition of temperature and pressure Cr_2O_3/V_2O_5 supported on alumina gel corresponding aromatic hydrocarbons are formed.



→ Pyrolysis :- In this rxn bigger molecules break resulting in the formation of smaller molecules

Ex:-
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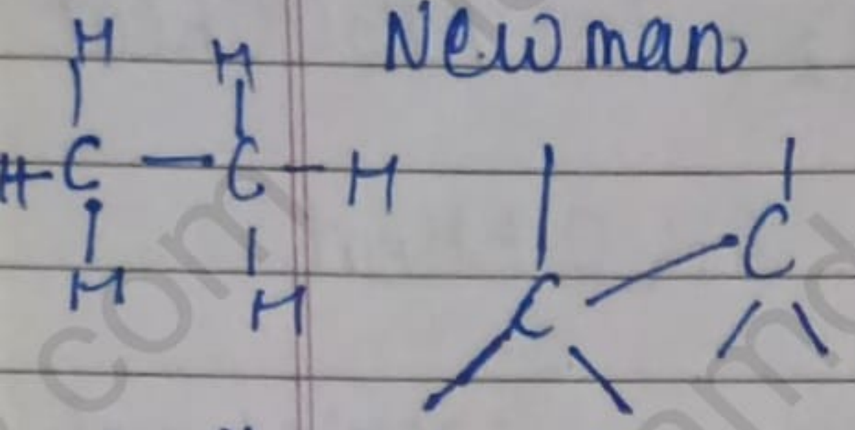
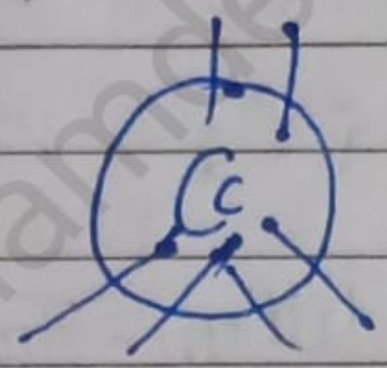
Newman



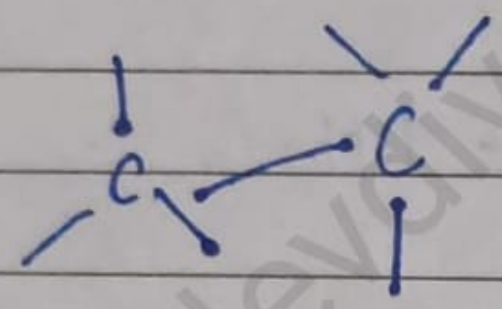
Eclipsed

~~Newman~~

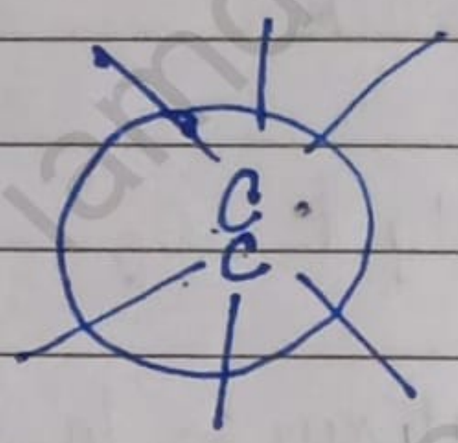


Eclipsed

Saw horse



Staggered



Staggered

~~Conformations of Ethane~~
~~Conformation~~

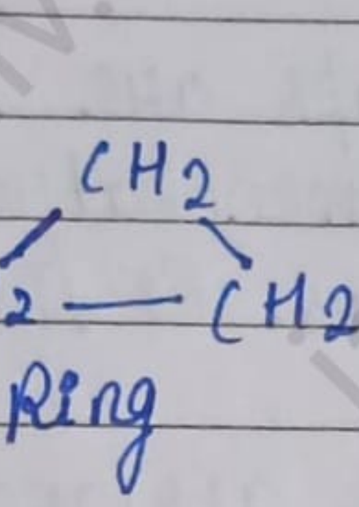
Saw horse projection is more stable. the staggered form of ethane is more stable than that of Eclipsed form it is due to the maximum difference between two bulky groups (hydrogen) and angle between them is torsion angle.

→ Alkenes:-

Alkenes are the hydrocarbons which contain carbon-carbon double bond in their molecules.
They possess three types of Isomerism:-

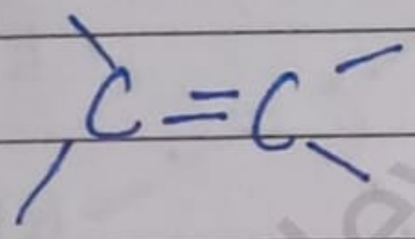
- Chain
- positional
- Ring-Chain Isomerism

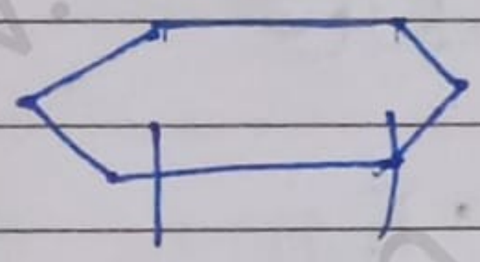
$CH_3-CH=CH_2$
propp-1-ene
chain



Ring

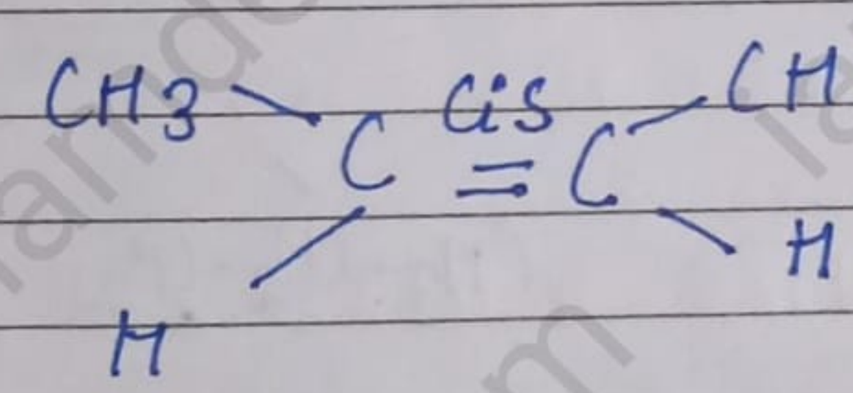
(4) Geometrical Isomerism:- There should be frozen rotation two adjacent carbon in the molecule

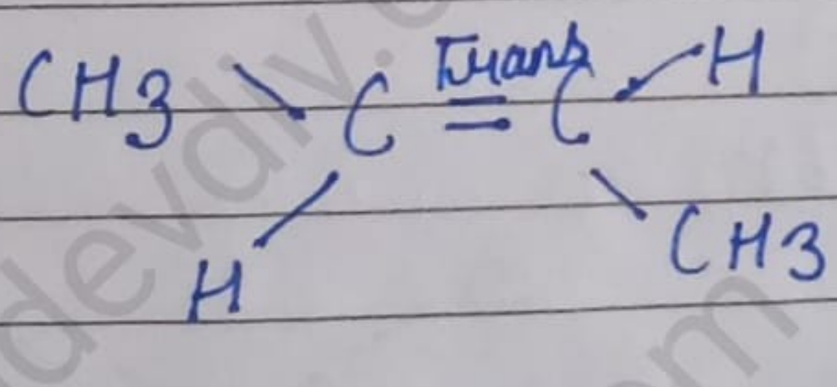
formula:- 

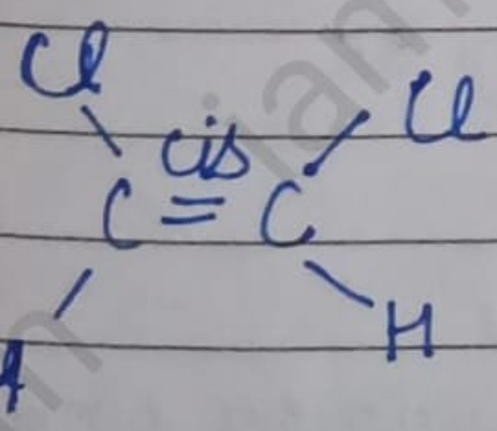


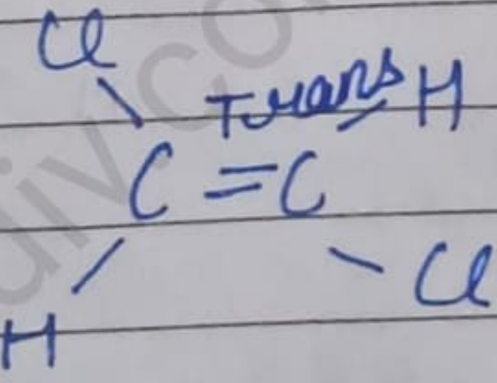
They can be further divided into two types:-

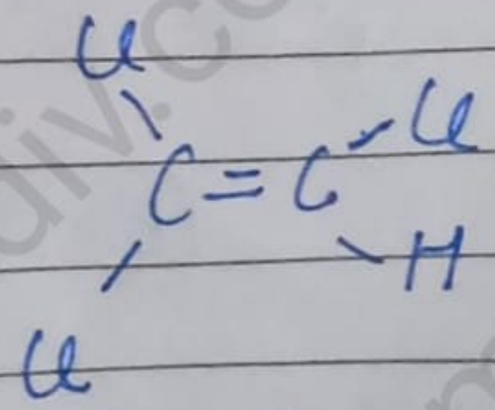
1. Cis
2. Trans









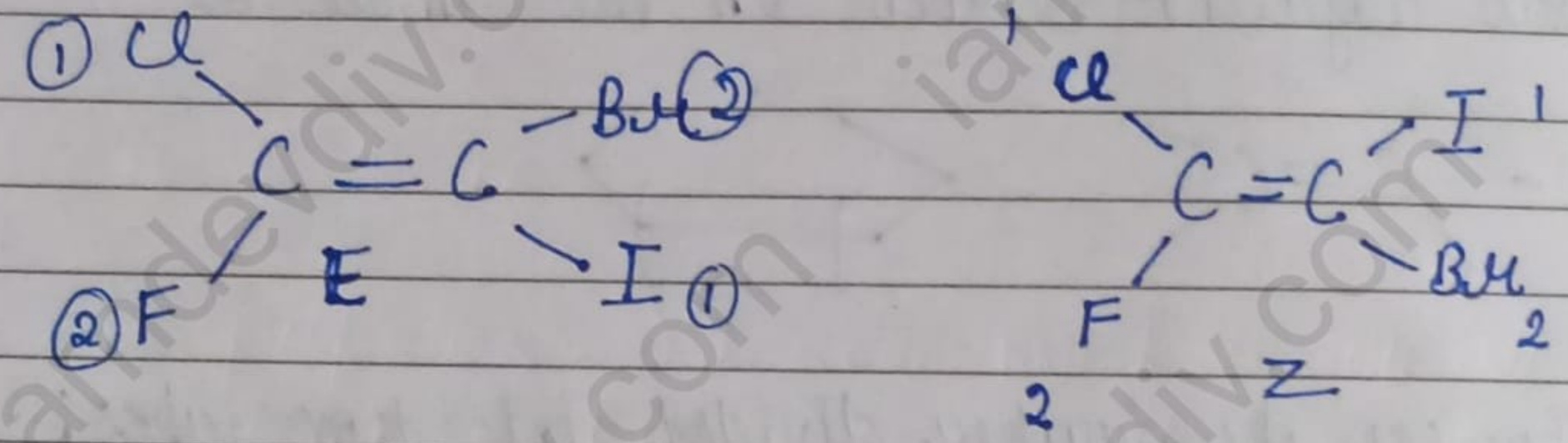


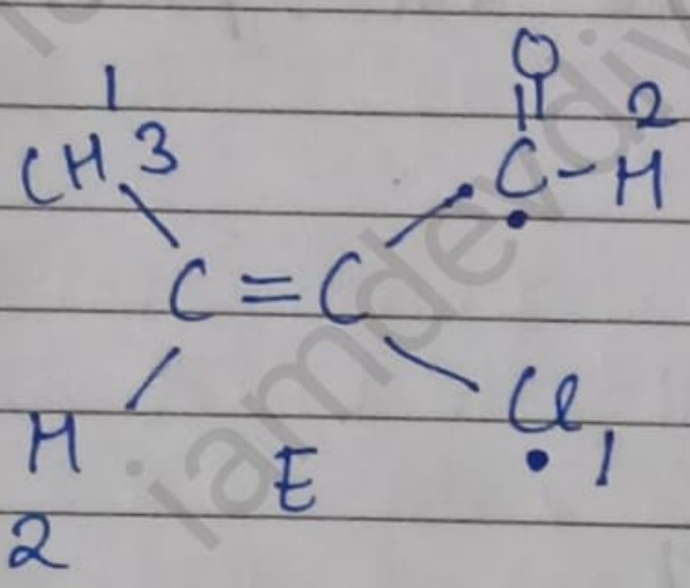
Neither cis/trans same grp.

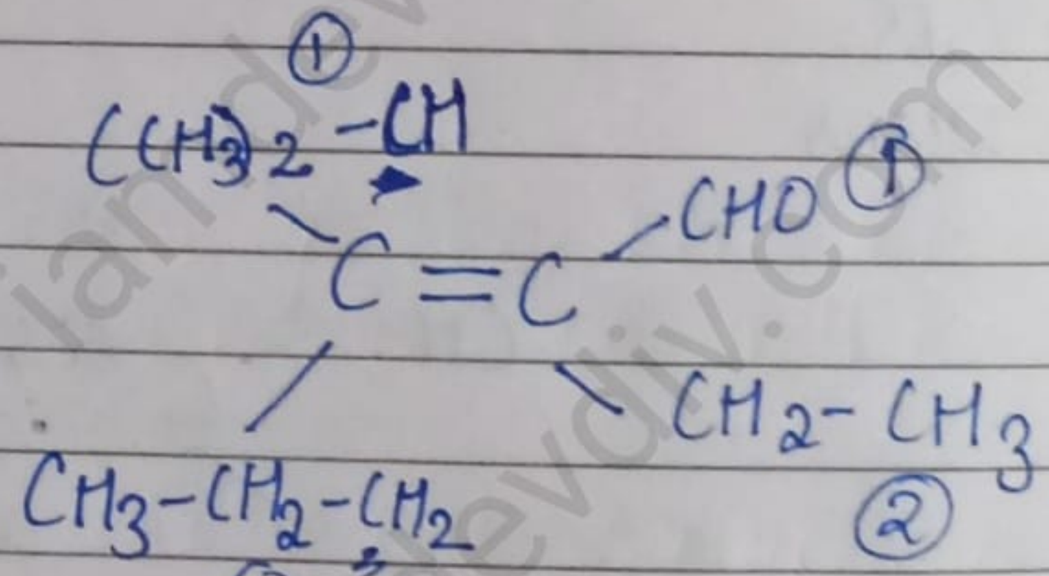
~~In case of~~

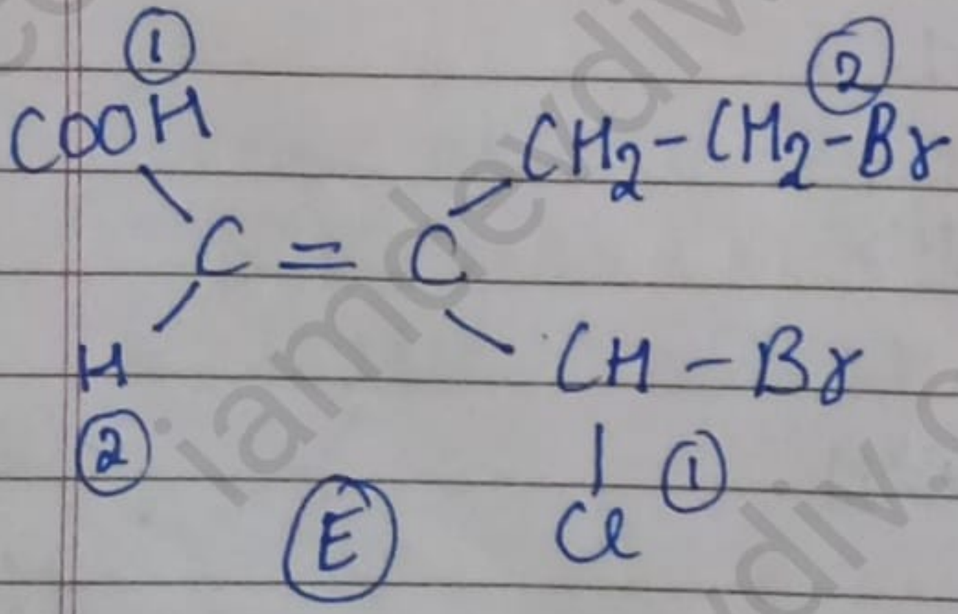
→ When all the groups are different around double bond E/Z Nomenclature will be assigned in place of ~~Cis Trans~~. Cis/Trans.

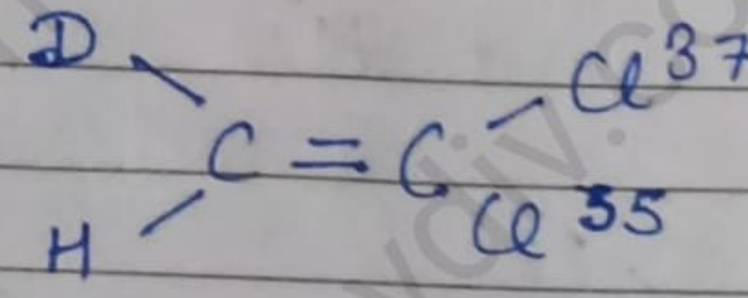
→ Higher priority is assigned to the atom (directly attached) of higher Atomic No.











In case of same atomic no. higher priority should be assigned according to atomic mass

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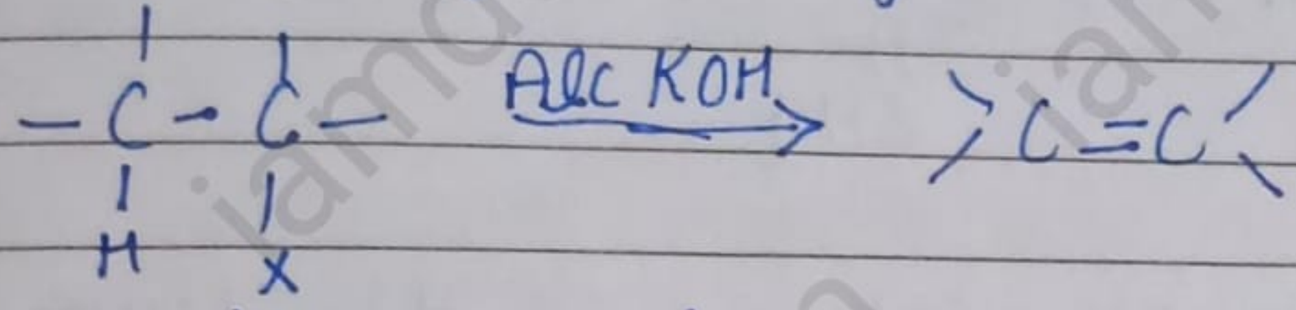
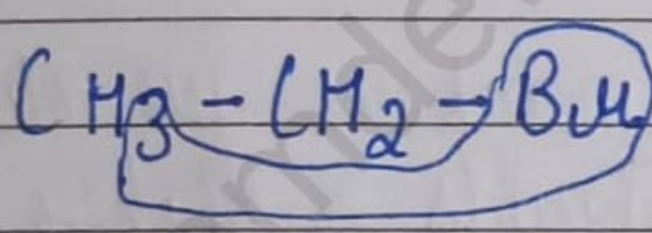
Preparation of Alkenes

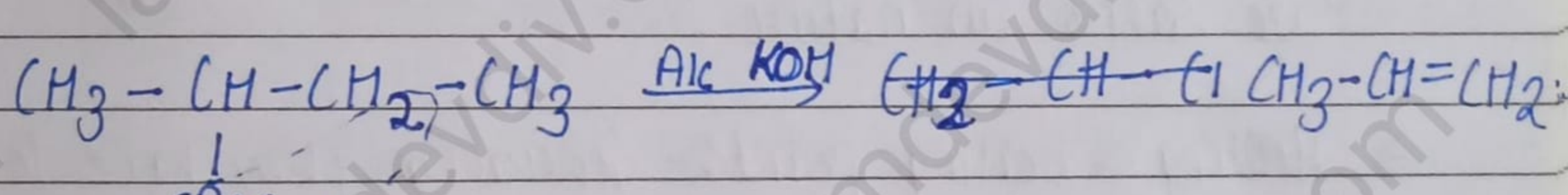
1. ~~Preparation of alkene~~ from Alkyl halides



Dehydrohalogenation

from alkylhalides alkenes are formed by β elimination rxn.



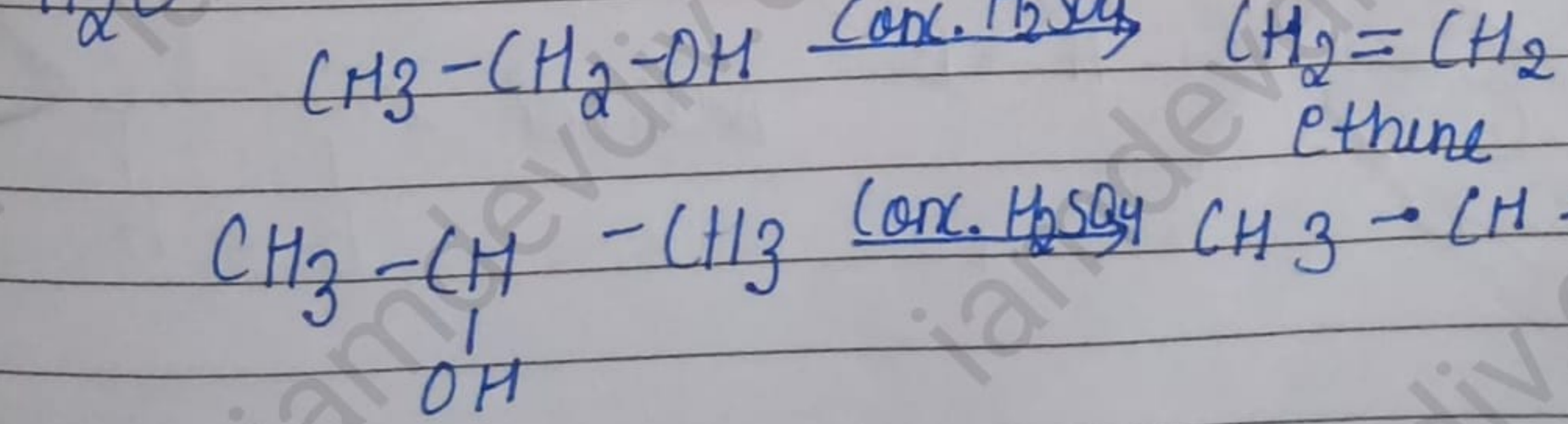


Saytzeff Rule:-

During Elimination hydrogen will go from the carbon which has lesser no. of hydrogen

→ Dehydration of Alcohol :-

Dehydration of Alcohol produce Alkene by the elimination of H_2O



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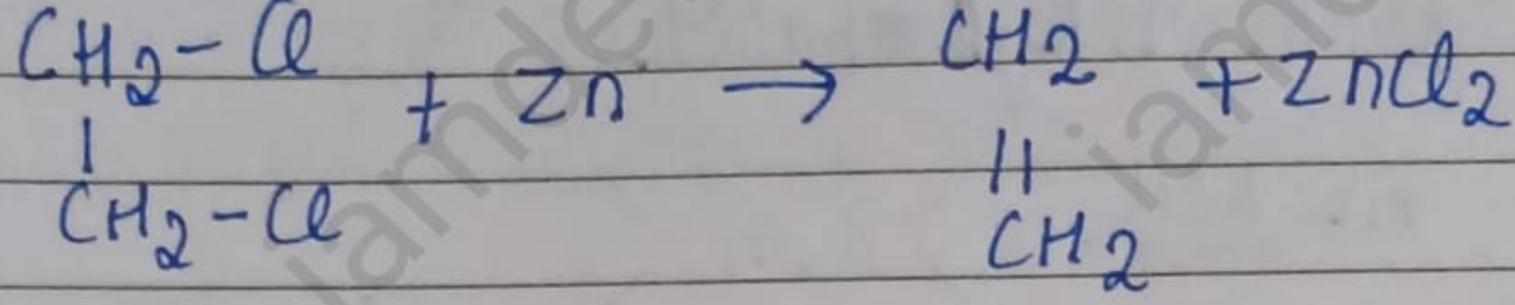
Preparation from Vicinal di halide:-



This reaction is carried out in the presence of zinc dust (methyl alcohol (CH_3OH))

properties of Alkene

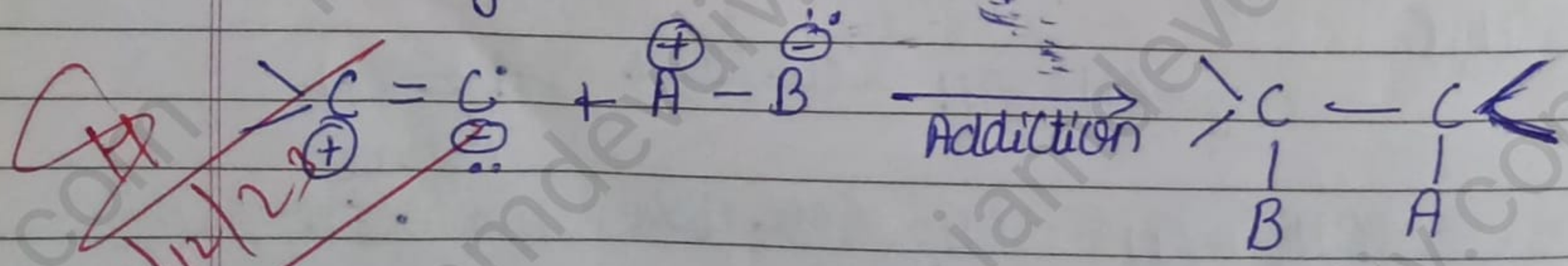
→ Physical properties:- i) Lower members are colourless gases, ~~carbon~~ $C_5 - C_{15}$ are liquids & higher members are solid in natur

→ Melting & boiling point:- Generally they have lower M.P. & B.P. and it increases on increase in the molecular mass

→ ~~In~~ Solubility - Insoluble in water but soluble in organic solvents

Chemical properties

~~Chem~~ Alkenes generally undergo addition rxn in which attacking molecule adds to the double bond to form addition product



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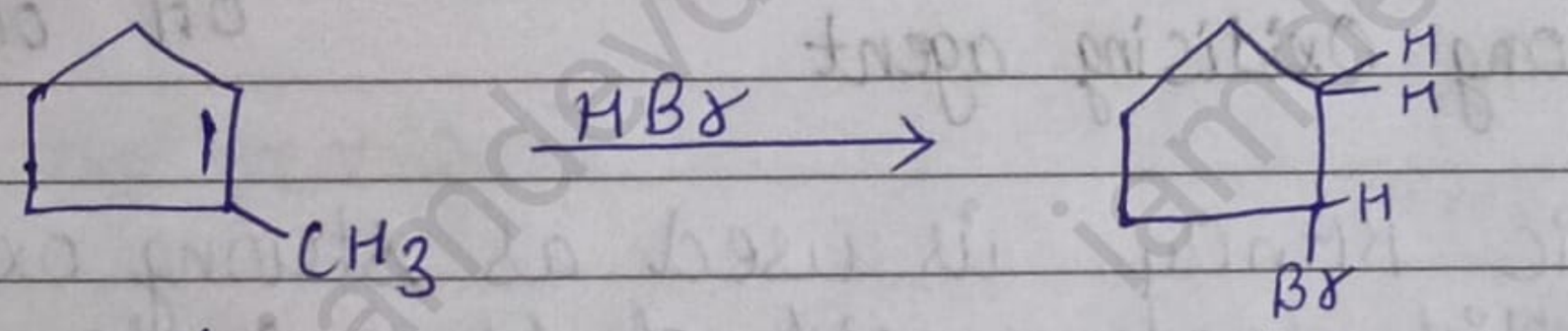
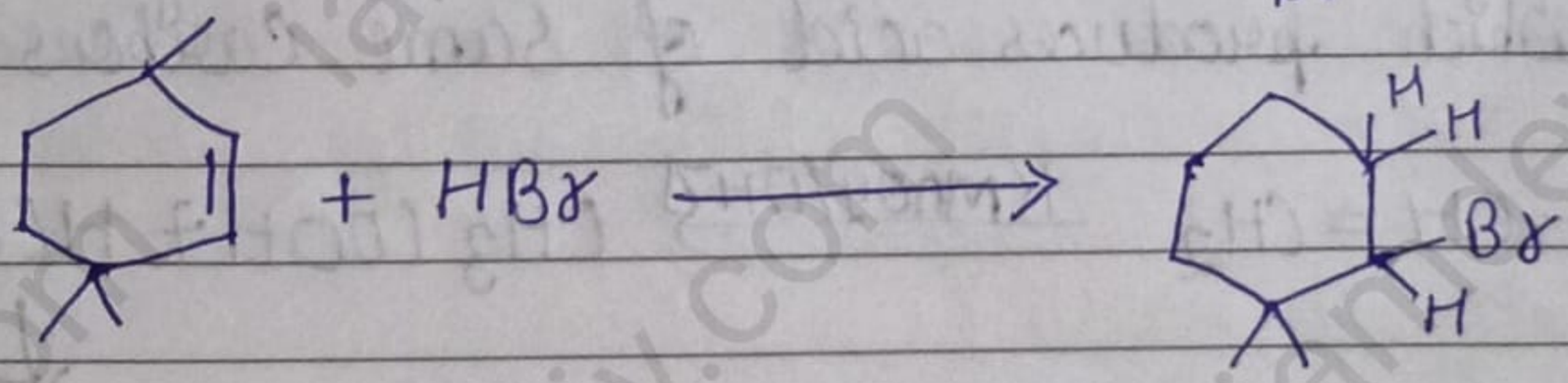
Addition of Halogen acid

$$CH_2=CH_2 + HBr \longrightarrow CH_3-CH_2-Br$$

$$CH_3-CH=CH_2 + \overset{\oplus}{H}\overset{\ominus}{Br} \longrightarrow CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

In case of unsymmetrical Alkene
The addition follows Markonikov's Rule which states that negative part of the species will go to the carbon having lesser no. of hydrogen





⇒ But in case of peroxide the addition follows Anti Markonikov's Rule

$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-Br$$

Addition of water

$$CH_2=CH_2 + \underset{H^+\ OH^-}{H_2O} \longrightarrow CH_3-CH_2-OH$$

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$CH_3-CH=CH_2 + H_2O \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

Oxidation Reactions

→ Oxidation with mild oxiclising agents

$KMnO_4/OH^-$ is a mild oxidising agent which produces diols.

$$CH_2=CH_2 + H_2O + [O] \xrightarrow{KMnO_4/OH^-} \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$$

$$CH_3-CH=CH_2 \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$$

→ with strong Oxidising agent

Hot basic $KMnO_4$ is used as strong oxiclising agent which produces acid of same carbons

$$CH_3-CH=CH_2 \xrightarrow{KMnO_4/OH^-\uparrow} CH_3COOH + HCOOH \xrightarrow{\downarrow\Delta} H_2O + CO_2$$

$$CH_3-CH=CH-CH_3 \xrightarrow{KMnO_4/\Delta/OH^-} 2\,CH_3COOH$$

⇒ But in case of 2° Carbon Ketone is formed

⇒ ~~Ozonolysis~~ Ozonolysis :- In this rxn alkenes directly converts to carbonal compounds (Aldehydes or Ketones)

$$CH_3-CH=CH-CH_3 \xrightarrow[\text{② } Zn, H_2O]{\text{① } O_3, CCl_4} 2\,CH_3-CHO$$

ethanal

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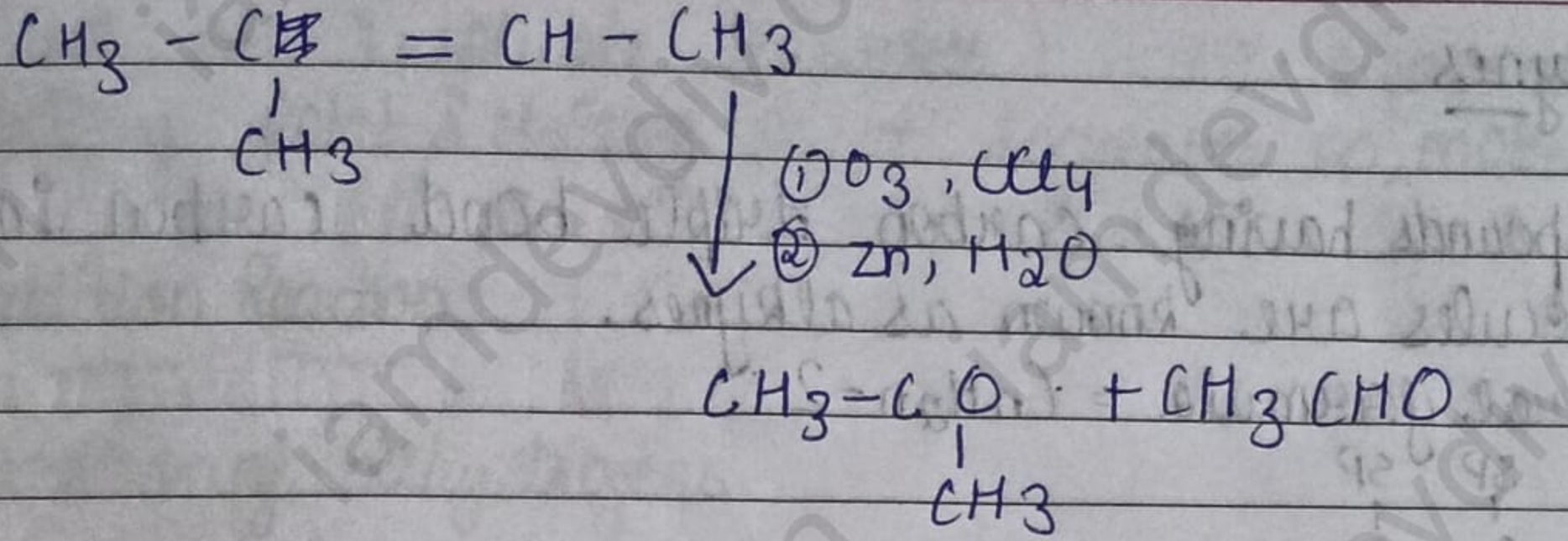

Ques- An alkene produces ethanal & pentan-3-one Ozonolysis write with the IUPAC name & Structural formula?

Ethanal / pentan-3-one

$CH_3 - CH = O$ / $O = C(-CH_2 - CH_3)(-CH_2 - CH_3)$

3-ethyl pent-2-ene → $CH_3 - CH = C(-CH_2 - CH_3) - CH_2 - CH_3$

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Alkynes

Compounds having carbon triple bond carbon in there molecules are known as alkynes.

General formula = C_nH_{2n-2}

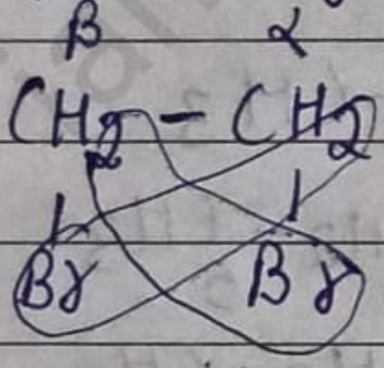
$\overset{SP}{|}\quad\overset{SP}{|}$

Ex:- $H-C\equiv C-H$

Ethyne

Methods of preparation

1. Dehydrohalogenation of ~~mi~~ vicinal di halide



$\xrightarrow[-HBr]{Alc\ (KOH)}$ $HC\equiv CH$

~~treatement~~
vicinal di halide ~~concrement~~ with alc. KOH undergo β elimination RXN in which alkynes are formed

2. Farom Calcium Carbide (CaC_2)

Calcium Carbide reacts with water to form Calcium hydroxide and ethyne

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

properties:-

Physical properties -

1. Lower members are gaseous, then liquid & higher members are solid in nature

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2. These are insoluble in water
3. Boiling point & Melting point increases on increasing molecular mass

Addition Reaction

1. Addition of dehydrogens

$$CH \equiv CH + H_2 \xrightarrow{Ni} H_2C = CH_2 + H_2$$

$$\downarrow Ni$$

$$CH_3 - CH_3$$

Ethane

2. Addition of halogens

$$H-C \equiv C-H + Cl_2 \longrightarrow H-C(Cl) = C(Cl)-H + Cl_2 \downarrow$$

$$H-C(Cl)(Cl)-C(Cl)(Cl)-H$$

3. Addition of halogen acid

$$H-C \equiv C-H + H^{\oplus}-Cl^{\ominus} \longrightarrow H_2C = C(Cl)-H$$

$$+ H^{\oplus}Cl^{\ominus}$$

$$\downarrow$$

$$H_3C-C(Cl)-H$$

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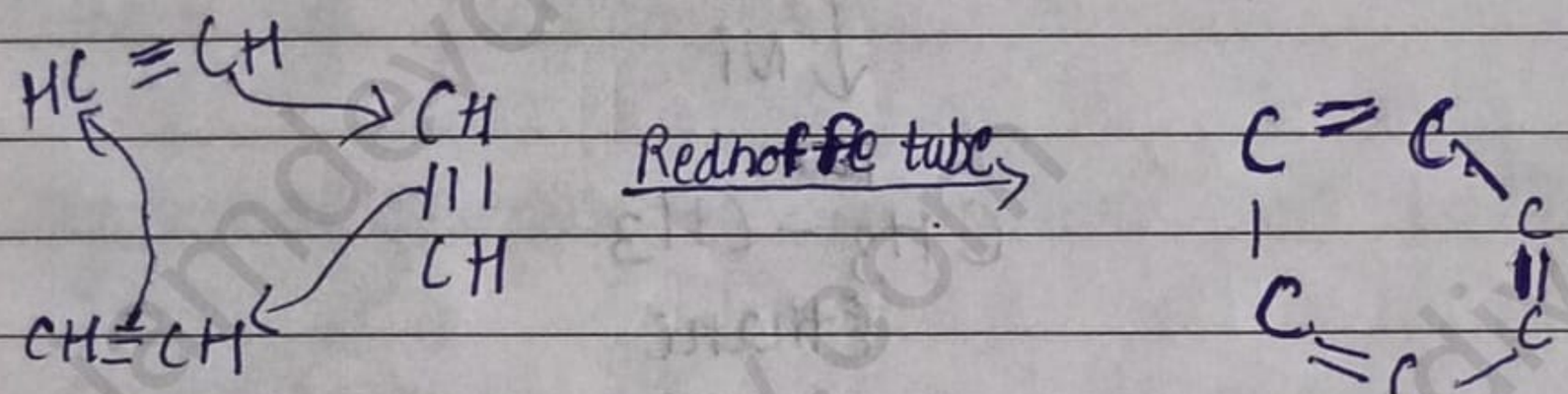
4. Addition of water

$$H-C\equiv C-H + H^{\oplus}-OH^{\ominus} \longrightarrow H_2C=C-H \xrightleftharpoons{\text{Tatomerism}} H_3C-C-H$$

(OH: Enol; Ethenol; Keto; Ethenal)

Tautomerism

Cyclic Polymerisation Reaction



Acidic nature of Alkynes (Terminal Alkynes)

Acidic character of Terminal Alkynes can be explained on the basis of hybridisation of ≡ bonded carbon atom which is sp hybridised & has 50% S character so these are quite electro-ve in nature & the electrons get displaced to the more electrone carbon atoms release the H^+ ions hence it is weakly acidic in nature

$H-C\equiv C-H \rightarrow H^{\oplus}$ (sp, sp)

$H-C\equiv C^{\ominus}$

$=EN\uparrow - Stability\uparrow$

5% + 5% = 100

50%

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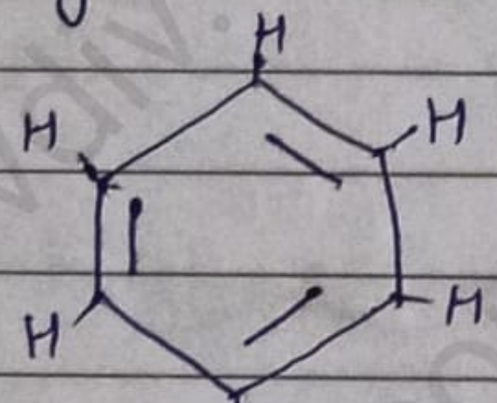
Aromatic Hydrocarbons

Aromatic compounds must ~~have~~ follow these conditions:

1. They should be cyclic in nature.
2. They must be planar (sp^2 hybridisation)
3. They should have conjugated system alternative $-$ & $=$ bond
4. They should follow Huckel's Rule $\Rightarrow (4n+2)\pi e^-$

$n = 0, 1, 2, 3 \cdots \infty$

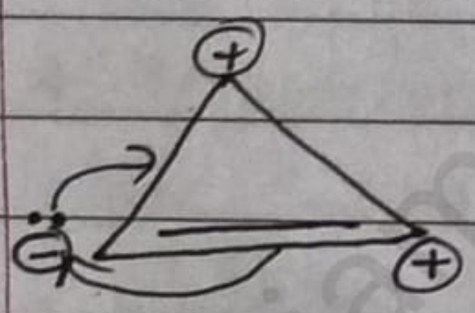
$2, 6, 10, 14, 18$



Aromatic

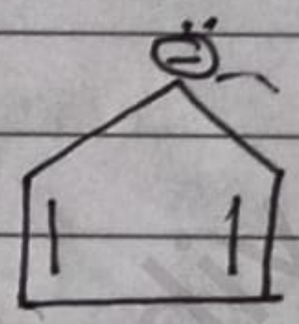
$6\pi e^-$

a)



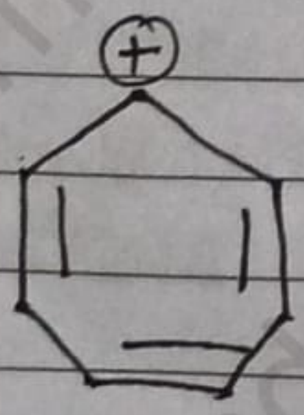
$2\pi e^-$

(b)

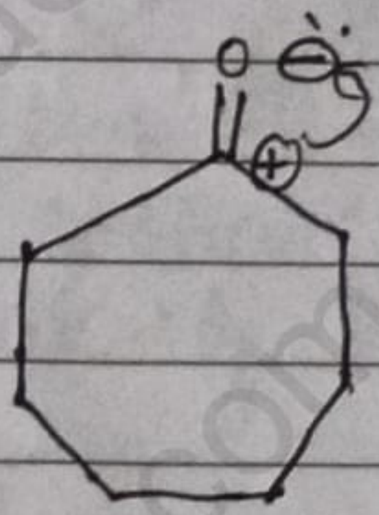


$6\pi e^-$

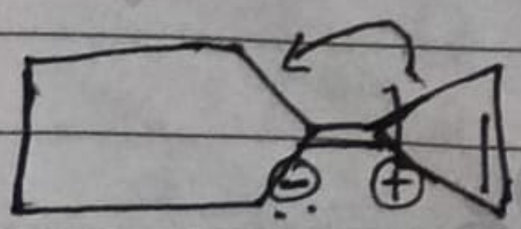
c)



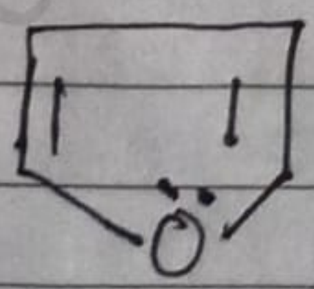
(d)



e)



(f)



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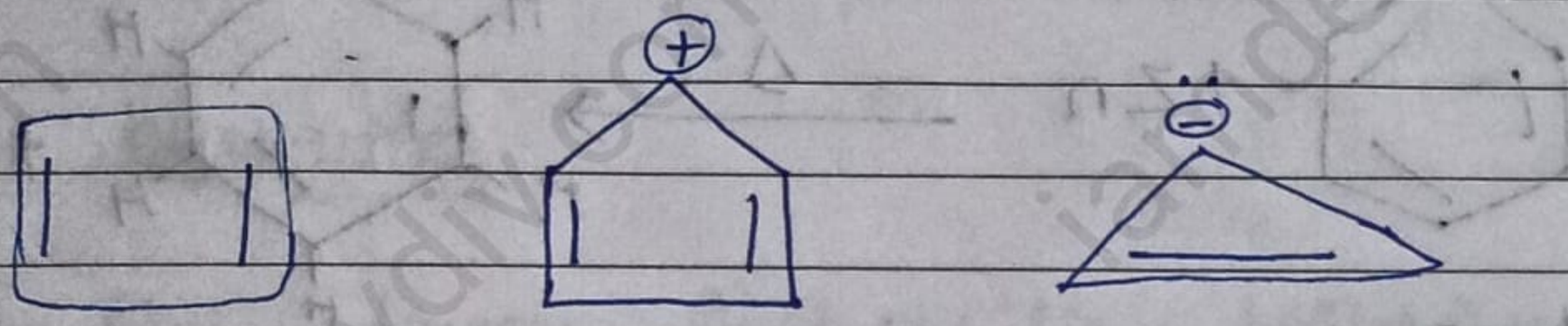
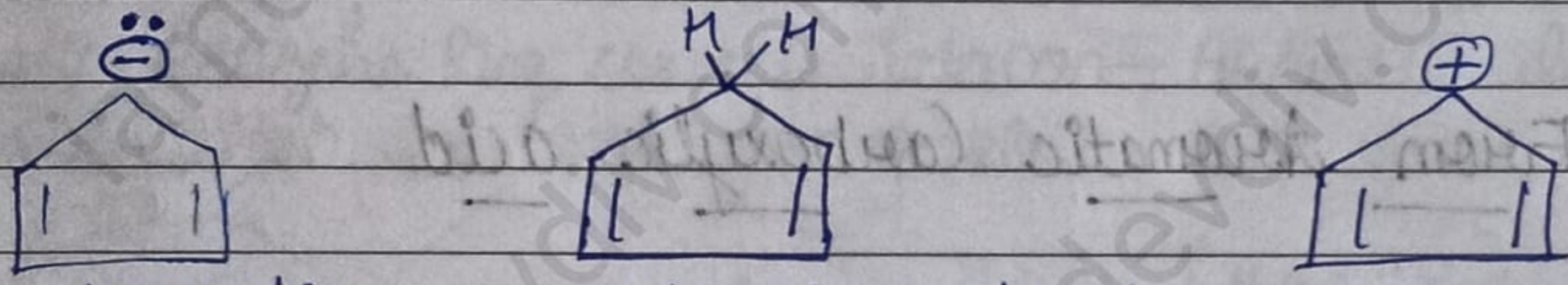
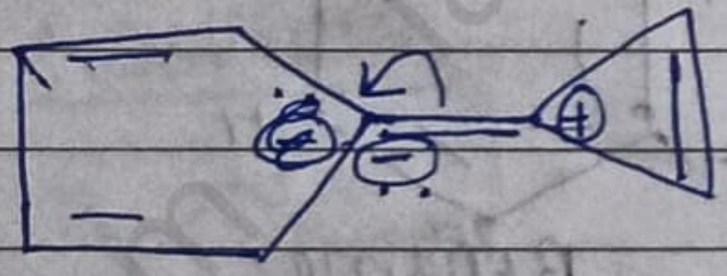
Concept of Anti-Aromaticity

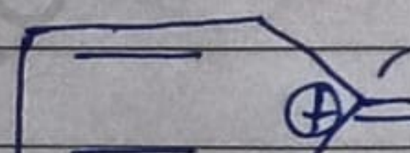
1. Cyclic
2. planar
3. Conjugation
4. $4n\pi e^-$

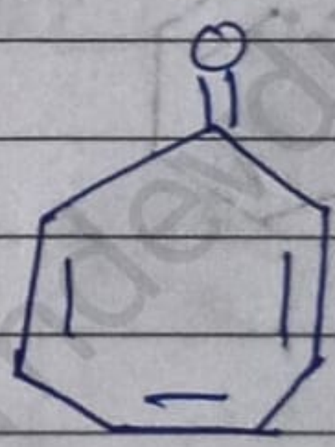


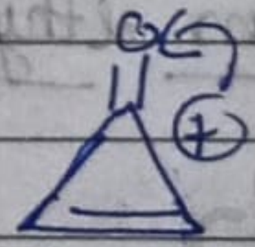


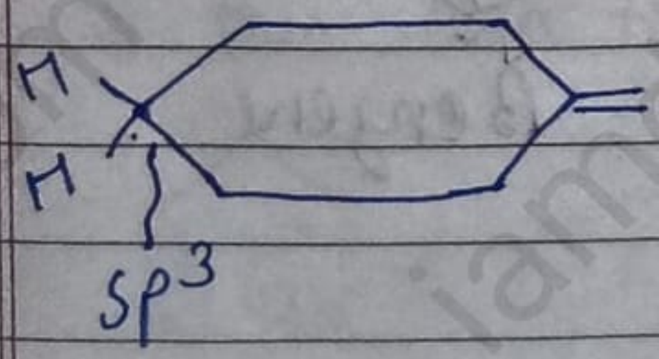
Stability → Aromatic > Non-Aromatic > Anti-Aromatic

a)  Aro.

b)  Anti Aro.

c)  → Aromatic

d)  Aromatic

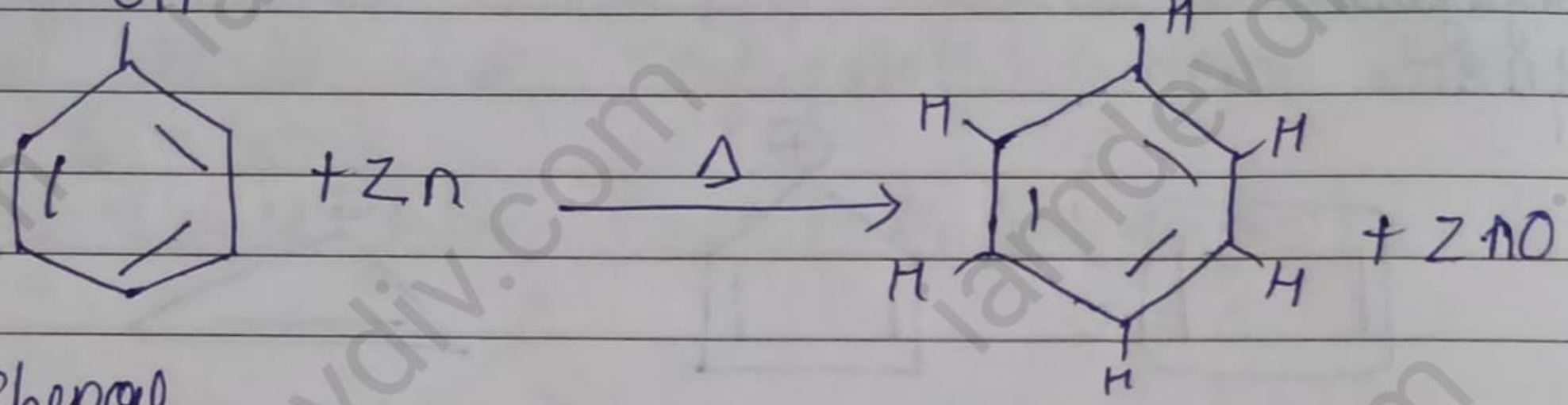
e)  → Non-Aromatic

Date ___/___/_____

Saathi

Methods of preparation of Benzene:-

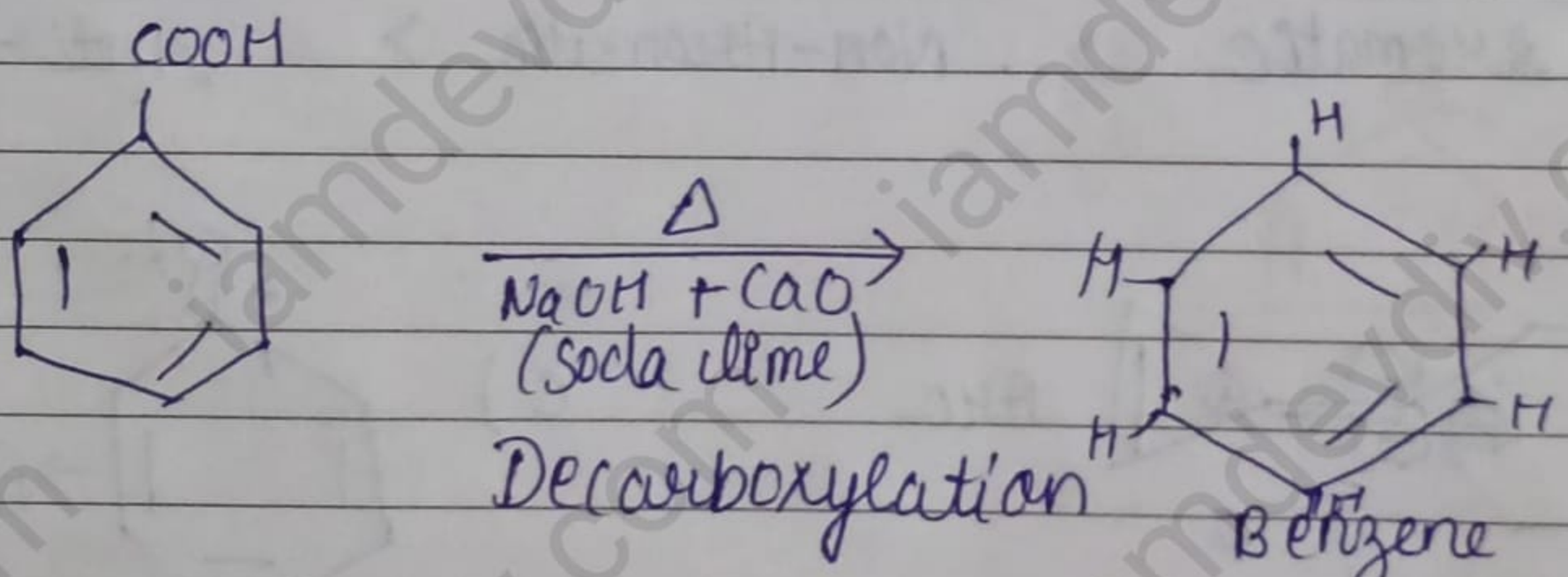
Phenol can be converted into Benzene with the reaction of heated zinc dust



Phenol

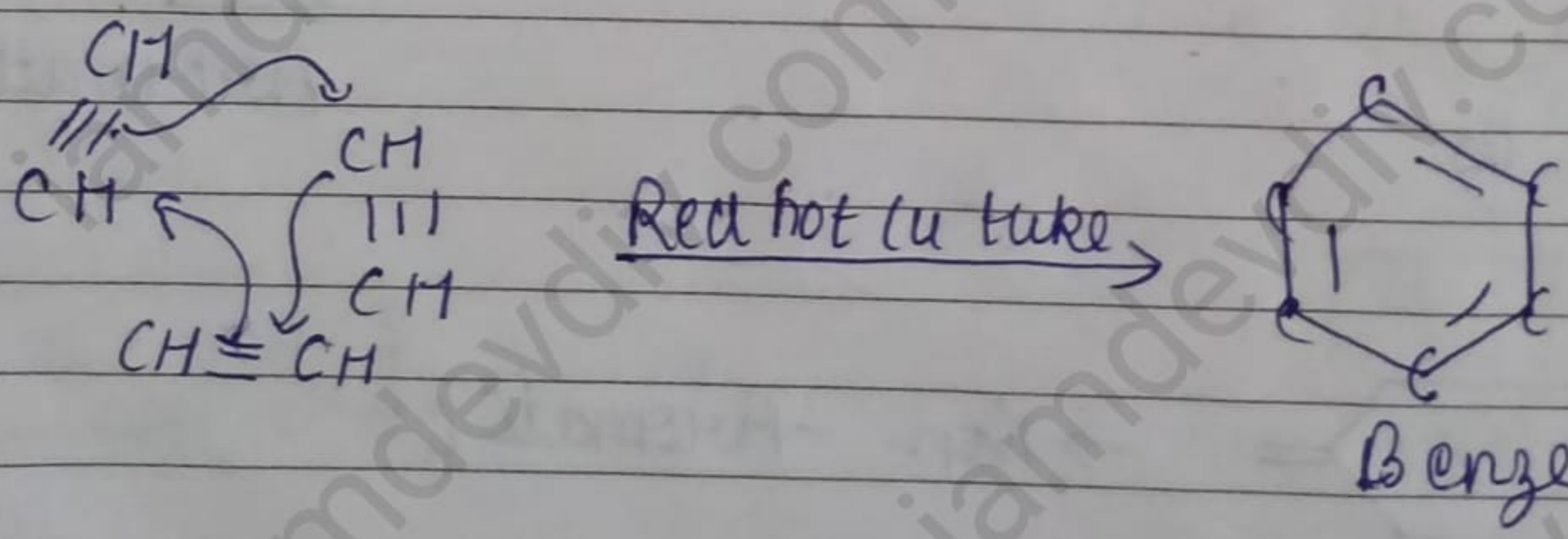
Benzene

From Aromatic Carboxylic acid



Benzene

From Ethyne



Benzene

Date ___ / ___ / _____

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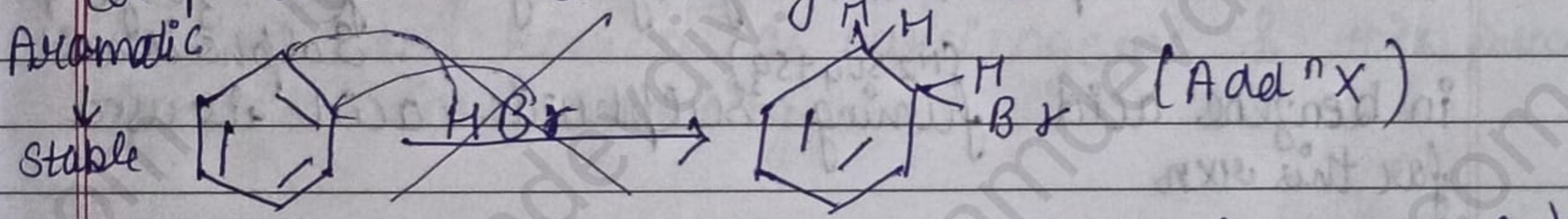
→ Properties of Benzene or other Aromatic compound Physical properties

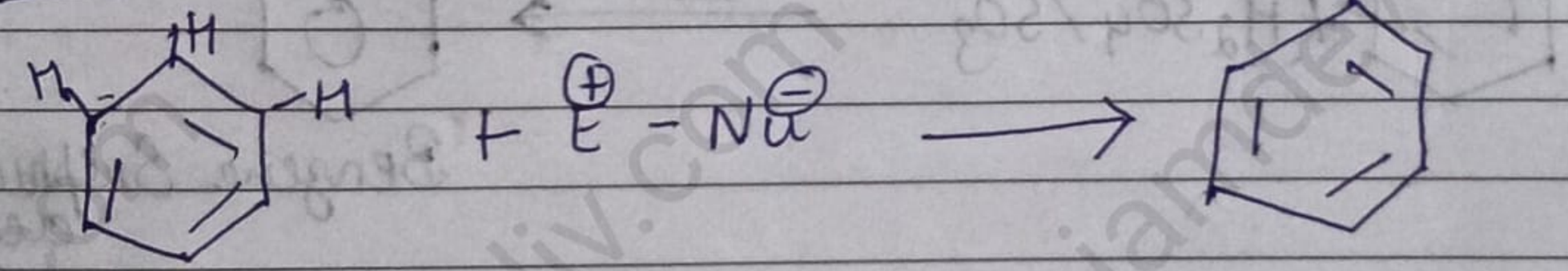
- Benzene is a colourless liquid which does not dissolve in water.
- Aromatic compounds have characteristic smell, napthelene balls are used in a preservation of cloth.

Chemical properties

Benzene Ring undergoes Electrophilic substitution rxn (ESR) ie. it does not give Addition Rxn because in addition Rxn Aromatic Benzene Ring converts into non-Aromatic less stable compound which is not favourable



Substitution



Electrophilic substitution Rxn

1. Halogenation :- In the presence of Lewis acid like ($FeCl_3$ or $AlCl_3$) benzene react with halogen to give Chloro benzene & this rxn takes place in the absence of light.

Date __/__/____

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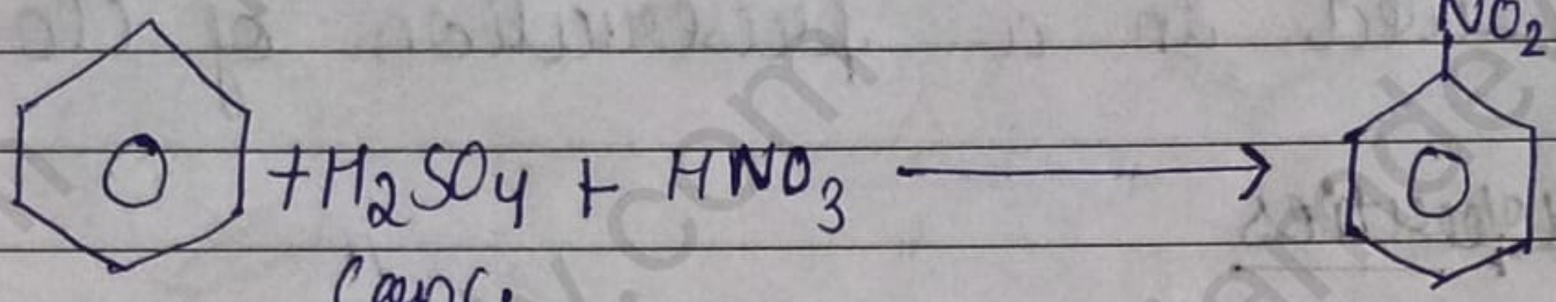
Nitration

A mixture of Conc. $HNO_3 + H_2SO_4$ is known as nitrating mixture & it provides $NO_2^{\oplus}$ ions ~~NIT~~ for the reaction.

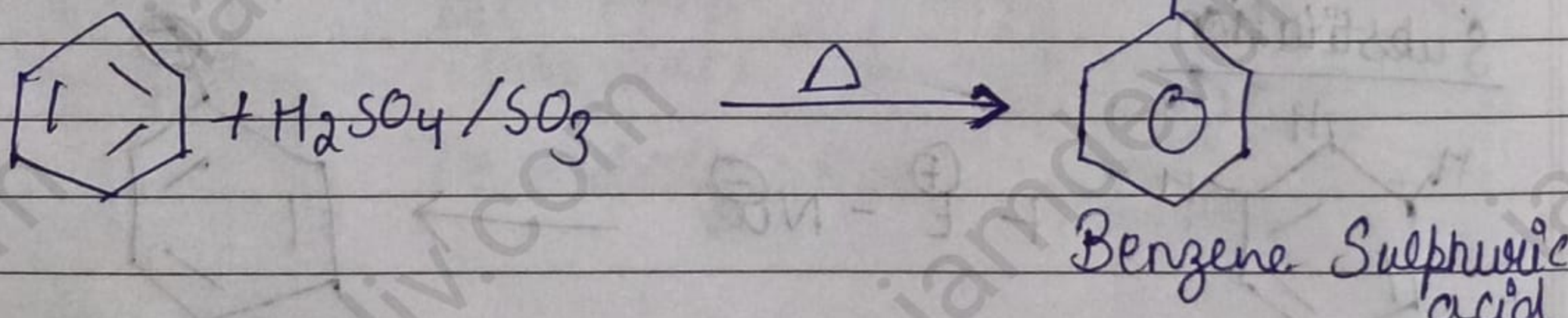


Sulfphoration

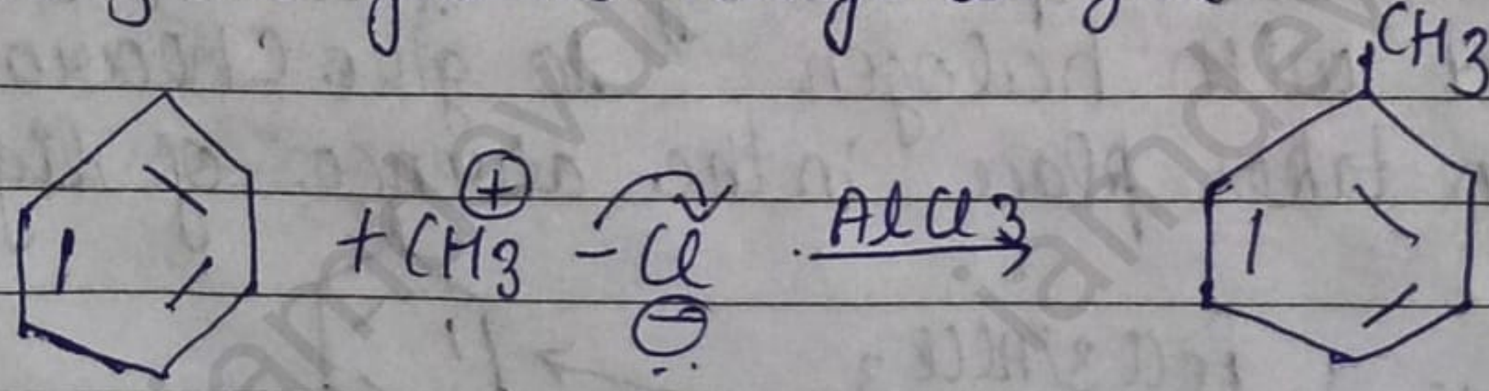
It is the replacement of hydrogen by $-SO_3H$ group

Salphonic acid

in benzene acid. ($H_2SO_4 + SO_3$) fuming Sulphuric acid is used for this rxn.



☆ Friedel Craft Alkylation Rxn:- When benzene is treated with Alkylehalide in the presence of $AlCl_3$ it forms Alkyl benzene



Methyl Benzene (Toluene)

Saathi

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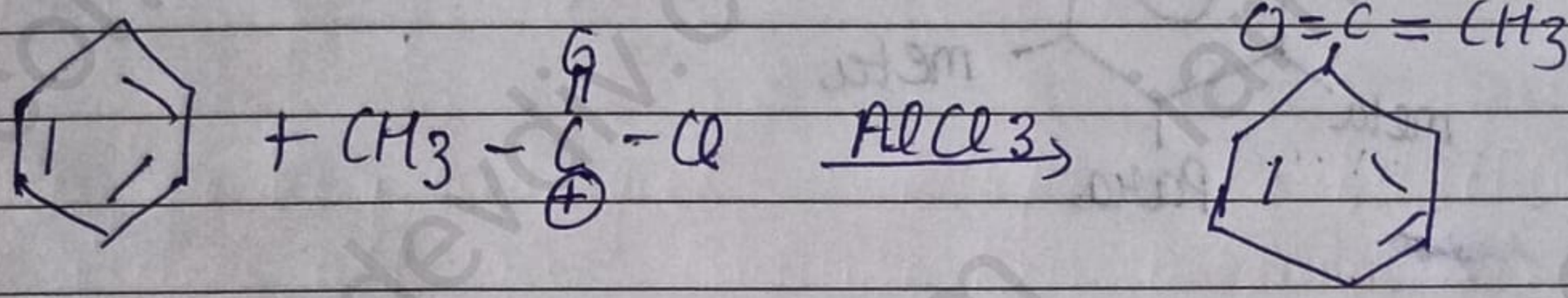
This rxn takes place by formation of carbocation intermediate & the order of stability of carbocation is $3^{\circ} > 2^{\circ} > 1^{\circ}$

Friedel craft Alkylation Rxn:-



→ Carcinogenacity & Toxicity:- Compounds that can cause cancer are known as carcinogenic & this phenomenon is called carcinogenacity.

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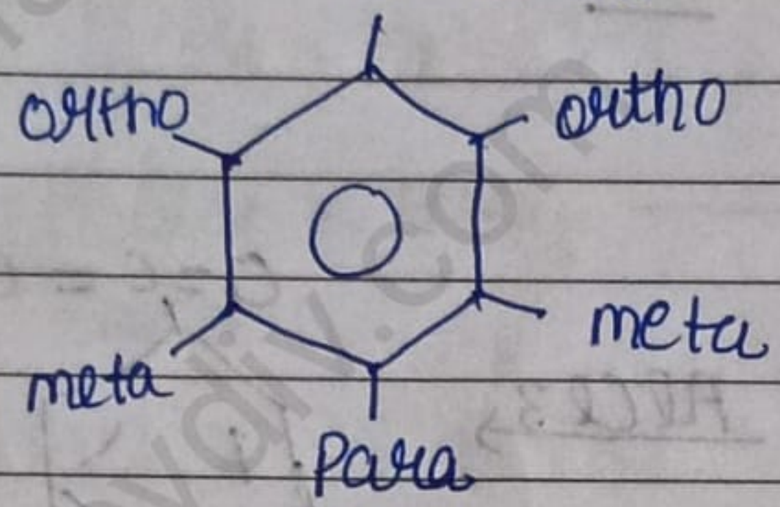
Directive influence of functional group in mono-substituted benzene

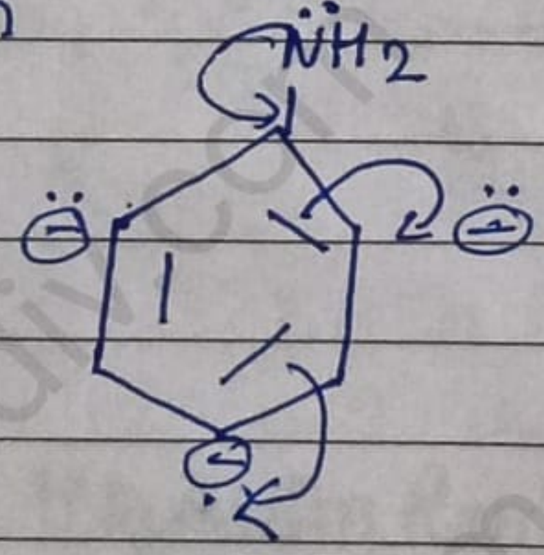
The mono substituted benzene has three positions



The group attached to benzene can be classified into two categories:-

1. +R → ⟸ Identification :- having lp or -ve charge

- +R is ortho para directive because the electron density is higher on these positions as compared to meta position



2. -R :- Identification :- having +ve charge or EN atom bonded with multiple bond

- In -R the meta products are formed because the meta position has higher electron density as compared to Ortho para so electrophile attacks on Meta position

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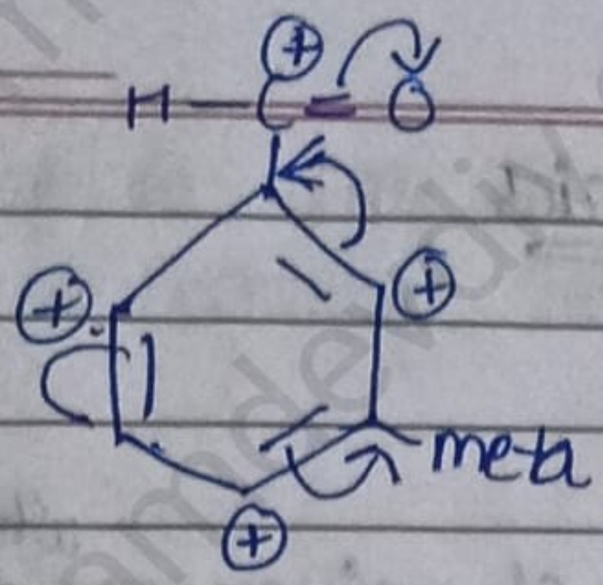

+R is op
+R is meta