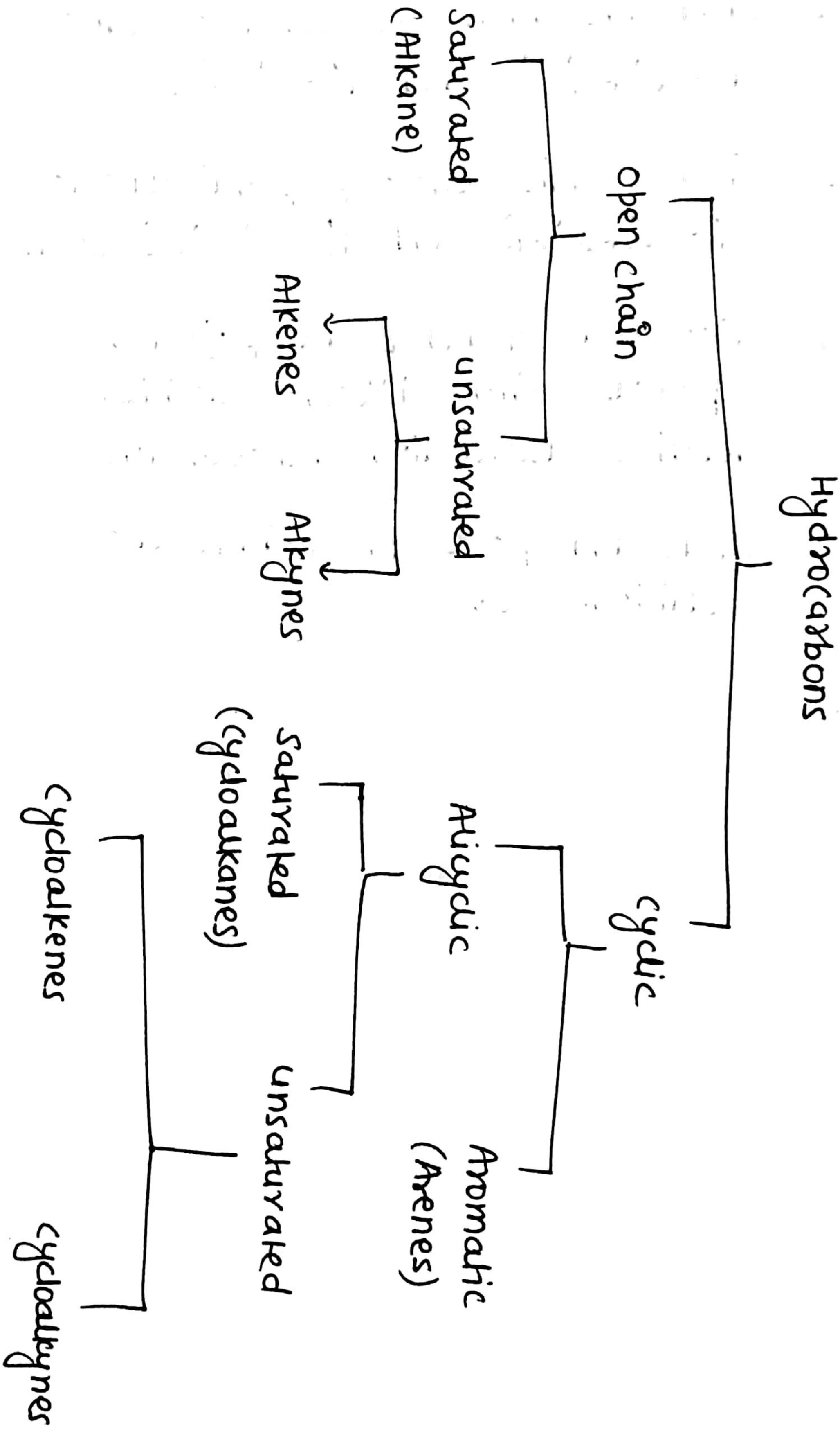
HYDROCARBON

The simplest organic compounds containing carbon and hydrogen only are called hydrocarbons.



Alkanes (C_nH_{2n+2})

① Preparation

→ from unsaturated hydrocarbons

$$CH_2=CH_2 + H_2 \xrightarrow[\text{or Pd}]{\text{Ni}} CH_3-CH_3$$

this Rx^n is used to prepare Vanaspati Ghee from edible vegetable oils.

→ Wurtz Reaction

$$R-\boxed{X + 2Na + X}-R \xrightarrow[\text{ether}]{\text{Dry}} R-R + 2NaX$$

$$CH_3-\boxed{Cl + 2Na + Cl}-CH_3 \xrightarrow[\text{ether}]{\text{Dry}} CH_3-CH_3 + 2NaCl.$$

→ It doubles the no of carbon atom in the chain.

→ Used to prepare an even no of Carbon atoms chain.

limitation of wurtz

→ Cannot be used to prepare odd no of carbon atom chain. E.g

$$CH_3-Cl + 2Na + CH_3CH_2Cl \longrightarrow$$

There are 3 possibilities

(i) Two molecules of CH_3-Cl can React with each other

$$CH_3Cl + 2Na + Cl-CH_3 \xrightarrow[\text{ether}]{\text{Dry}} CH_3-CH_3 + 2NaX$$

(ethane)

(ii) Two molecules of CH_3CH_2Cl can react with each other.

$$CH_3CH_2Cl + 2Na + CH_3CH_2Cl \xrightarrow[\text{ether}]{\text{Dry}} CH_3-CH_2CH_2CH_3 + 2NaCl$$

(Butane)

(iii) molecule of CH_3Cl can react with molecule of CH_3CH_2Cl.

$$CH_3Cl + Na + CH_3CH_2Cl \xrightarrow[\text{ether}]{\text{Dry}} CH_3CH_2CH_3 + 2NaCl$$

(propane)

So Here we are getting mixture of three alkanes i.e ethane, propane & butane. The boiling points of these alkanes are very close and hence they can not be separated by even fractional distillation.

Hence wurtz Rx^n is not used to prepare a carbon chain containing odd no of carbon atoms.

Role of Dry ether in wurtz Rx^n

Wurtz Reaction is carried out with sodium metal which is highly reactive, hence we need to select a solvent which will not react with sodium metal. Thus ether becomes the best choice. Dry ether is a very good solvent and provide medium for the Rx^n.

→ **Decarboxylation Rx^n** (Removal of COOH Group) (CO_2)

$$R-COOH + NaOH \longrightarrow R-COONa + H_2O$$

$$R-COONa + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$

E.g $$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

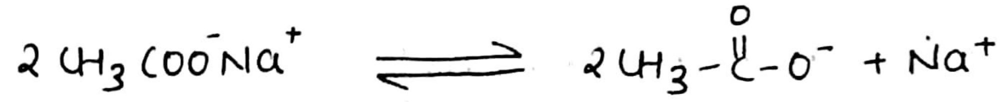
(NaOH + CaO) is known as soda lime.

→ **Kolbe's electroytic method**

$$2RCOONa + H_2O \xrightarrow{Current} R-R + NaOH + H_2 + CO_2$$

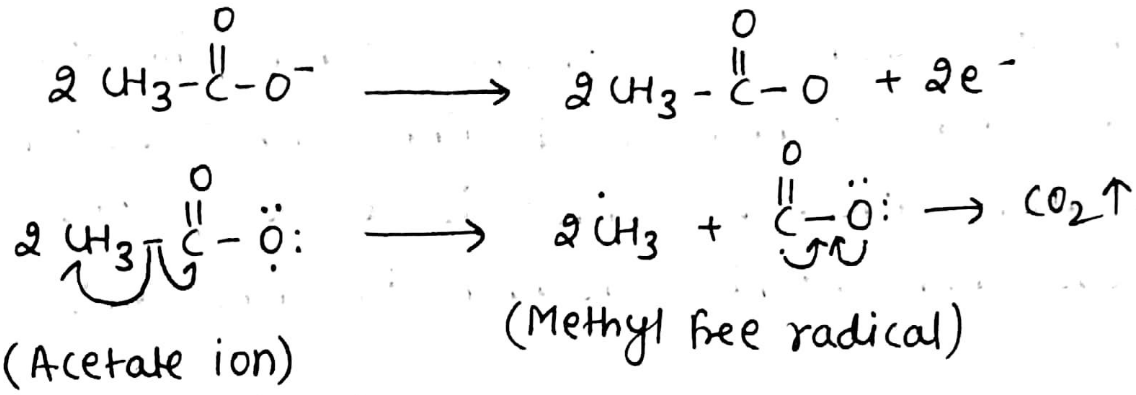
E.g $$2CH_3COONa + H_2O \xrightarrow{Current} CH_3-CH_3 + NaOH + H_2 + CO_2$$

Mechanism:-

i) 

$$2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{O}{\overset{\|}{C}}-O^- + Na^+$$

At anode:-



$$2CH_3-\overset{O}{\overset{\|}{C}}-O^- \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-\dot{O} + 2e^-$$

$$\underset{\text{(Acetate ion)}}{2CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}:} \longrightarrow \underset{\text{(Methyl free radical)}}{2\dot{C}H_3} + \overset{O}{\overset{\|}{C}}-\ddot{O}: \rightarrow CO_2\uparrow$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

At cathode:-

$$H_2O + e^- \longrightarrow OH^- + \dot{H}$$

$$2\dot{H} \longrightarrow H_2\uparrow$$

Limitation:- methane can not be prepared.

→ This Rxn can not be used to prepare carbon chain of odd no of Carbon atoms.

② Physical Properties of alkanes

$$\boxed{\text{No. of Carbon atom} \propto \text{boiling point}}$$

If two compound contain same no C-atom then

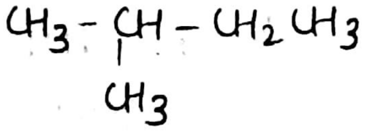
$$\boxed{\text{Boiling point} \propto \frac{1}{\text{no of side chain}}}$$

Q Arrange them in ↑ order of their boiling point.

(i) pentane , Isopentane , Neopentane.

① pentane → $CH_3CH_2CH_2CH_2CH_3$ (No Branch)

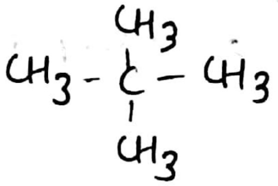
Isopentane →



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2CH_3$

(1 Branch)

neopentane →



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

(2 Branch)

so Boiling point order will be

neopentane < isopentane < pentane.

Chemical Properties of alkane

① Chlorination

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} CHCl_3 + HCl$$

(chloro form)

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

Mechanism:-

→ It follows free radical mechanism which involves 3 steps.

① Initation

$$Cl-Cl \xrightarrow{h\nu} 2\dot{Cl}$$

② chain Propogation

$$CH_3-H + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$$

× $[\dot{C}H_3Cl + \dot{Cl}-Cl \longrightarrow$

$$\dot{C}H_3 + Cl-Cl \longrightarrow CH_3Cl + \dot{Cl}$$

③ **Chain termination**

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

$$\dot{C}H_3 + \dot{Cl} \longrightarrow CH_3Cl$$

② **Combustion**

① Complete combustion

$$CH_4 + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

② Incomplete combustion

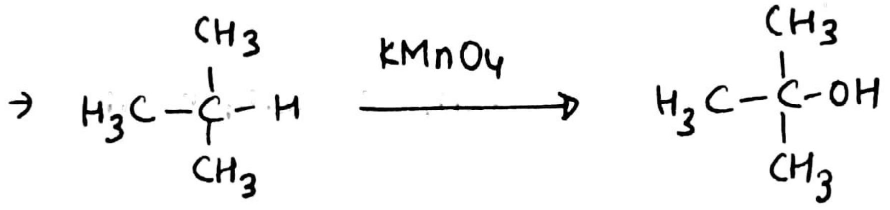
$$CH_4 + O_2 \xrightarrow[\text{Limited air}]{\text{absence or}} \underset{\text{(carbon Black)}}{C(s)} + 2H_2O$$

③ **Controlled ~~combustion~~ oxidation**

→ $$CH_4 + O_2 \xrightarrow[\text{100 atm}]{Cu/523K} \underset{\text{(Methanol)}}{CH_3OH}$$

→ $$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} \underset{\text{(Methanal)}}{HCHO} + H_2O$$

→ $$CH_3CH_3 + O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} CH_3COOH$$



→ $$H_3C-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-H \xrightarrow{KMnO_4} H_3C-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

④ Isomerisation

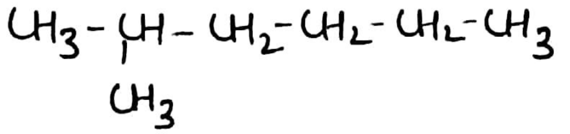
$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anh. } AlCl_3} \text{Isomer of Hexane}$$

(Hexane)

⑤ Aromatization

$$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow[\substack{773K \\ 10\text{-}20atm}]{V_2O_5 / Cr_2O_3}$$

(Hexane) (Benzene)



$$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2-CH_2-CH_2-CH_3 \xrightarrow[773K]{V_2O_5}$$

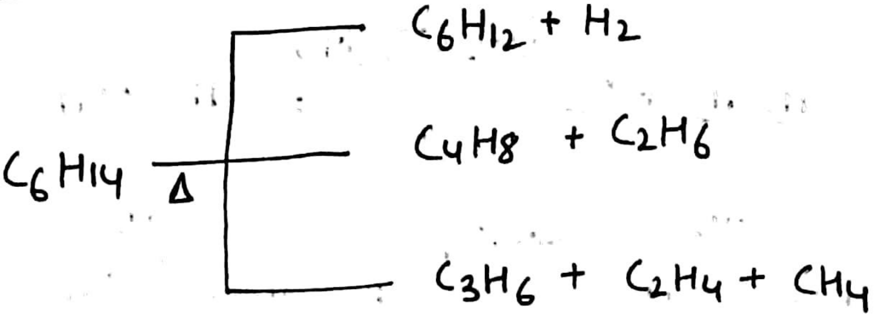
(2-Methyl hexane) (Toulene)

⑥ Reaction with steam

$$CH_4 + H_2O \xrightarrow[Ni]{\Delta} CO + 3H_2$$

This method is used for industrail preparation of dihydrogen gas.

⑦ Pyrolysis (Cracking)



$$C_6H_{14} \xrightarrow{\Delta} C_6H_{12} + H_2$$

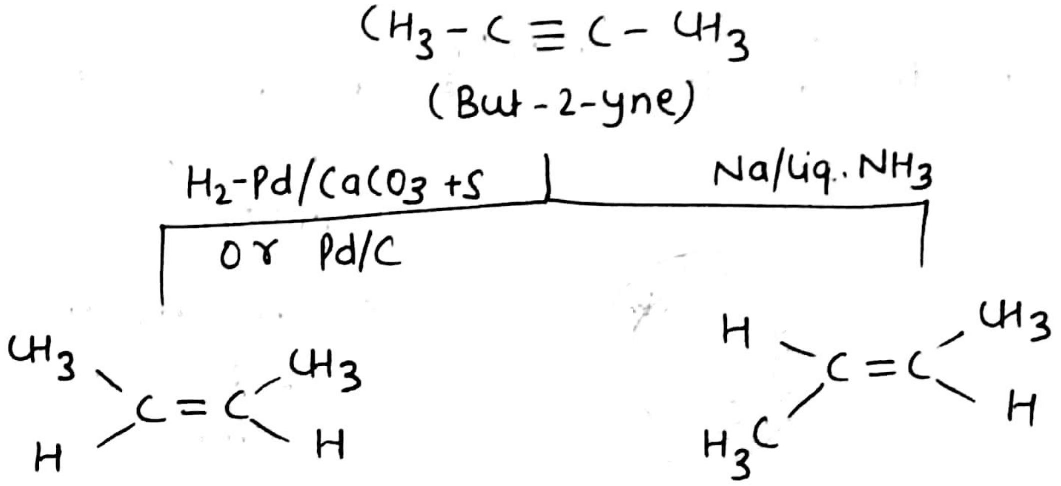
$$C_6H_{14} \xrightarrow{\Delta} C_4H_8 + C_2H_6$$

$$C_6H_{14} \xrightarrow{\Delta} C_3H_6 + C_2H_4 + CH_4$$

Alkene (C_nH_{2n})

Preparation

① from alkynes



cis-But-2-ene

trans-But-2-ene

② from alkyl halides (β-elimination Rx^n)

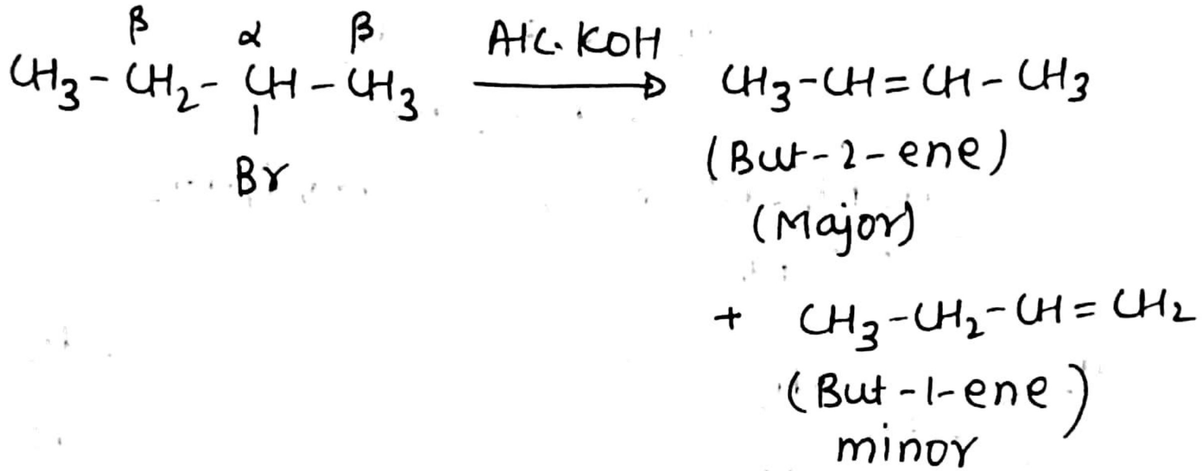
$$\overset{\beta}{CH_3}\,\overset{\alpha}{CH_2}-Br \xrightarrow{alc.\ KOH} CH_2=CH_2 + HBr$$

from α-carbon there is a removal of Halogen atom & from β-carbon there is a removal of Hydrogen atom.

→ This Rx^n is also known as dehydrohalogenation.

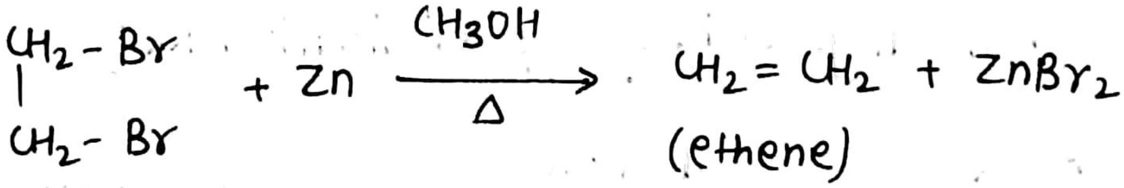
Saytzeff rule :- when there are 2-β carbon then removal of Hydrogen takes place from that β carbon which contains lesser no of hydrogen atoms.

E.g



$$\overset{\beta}{CH_3}-CH_2-\underset{|\atop Br}{\overset{\alpha}{CH}}-\overset{\beta}{CH_3} \xrightarrow{Alc.\,KOH} \underset{\text{(But-2-ene) (Major)}}{CH_3-CH=CH-CH_3} + \underset{\text{(But-1-ene) minor}}{CH_3-CH_2-CH=CH_2}$$

③ From vicinal dihalides



$$\begin{matrix} CH_2-Br \\ | \\ CH_2-Br \end{matrix} + Zn \xrightarrow[\Delta]{CH_3OH} \underset{\text{(ethene)}}{CH_2=CH_2} + ZnBr_2$$

④ from alcohols (Dehydration)

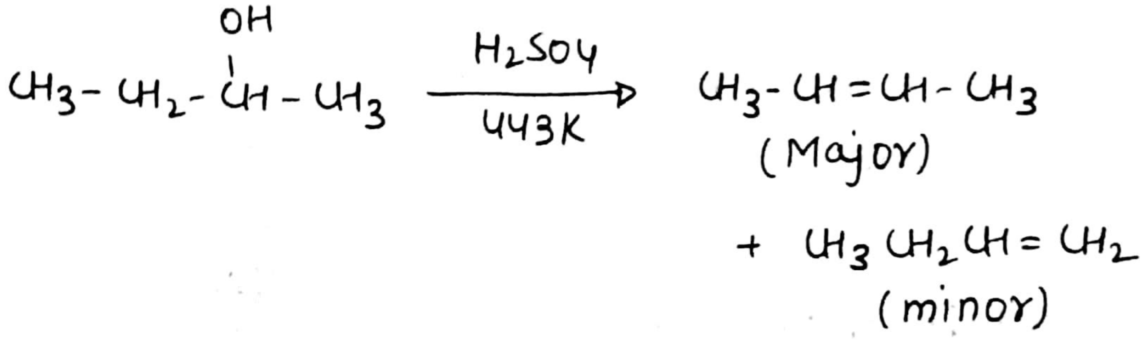
Dehydration :- Removal of H_2O.

$$CH_3CH_2OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2$$

→ Remove OH from α-Carbon and H from β carbon.

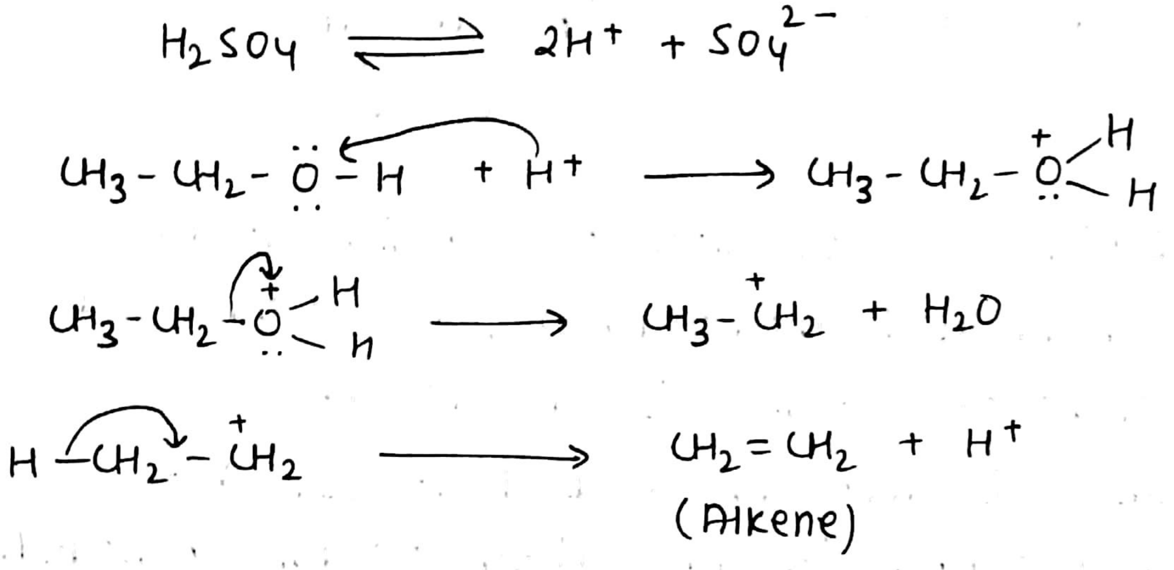
→ If there are more than one β-Carbon then follow Saytzeff rule.

E.g



$$CH_3-CH_2-\overset{OH}{CH}-CH_3 \xrightarrow[443K]{H_2SO_4} CH_3-CH=CH-CH_3 \text{ (Major)} + CH_3CH_2CH=CH_2 \text{ (minor)}$$

Mechanism: -



$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{+}{O}H_2$$

$$CH_3-CH_2-\overset{+}{O}H_2 \longrightarrow CH_3-\overset{+}{C}H_2 + H_2O$$

$$H-CH_2-\overset{+}{C}H_2 \longrightarrow CH_2=CH_2 + H^+$$

(Alkene)

Chemical Properties of Alkenes

① Addition of H_2

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

(ethene) (ethane)

② Addition of Halogens

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}}$$

★ During the addition of bromine to the unsaturated hydrocarbons, the orange red colour of bromine is discharged.

Hence this Rxn can be used to test for unsaturation in the given organic compound.

③ Addition of Hydrogen halide (HX)

$$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2Br$$

Markovnikov's Rule :- Halogen atom goes to that double bonded carbon atom which contain lesser no. of hydrogen.

E.g $CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + CH_3-CH_2-CH_2Br$

(major) (minor)

Mechanism: -

$$HBr \longrightarrow H^+ + Br^-$$

$$\underset{②}{CH_3-CH}=\underset{①}{CH_2} + H^+ \longrightarrow$$

There ~~is~~ are two cases

i) when double bond is shifted to ① carbon.

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

(2° carbocation)

(ii) when double bond is shifted to ② carbon.

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

(1° degree carbocation)

we know that 2° carbocation is more stable than 1°. So further attacks will take place on 2° carbocation.

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

(2-Bromo propane)

④ Addition of HX in presence of peroxide

anti-markovnikov's Rule / kharasch effect :-

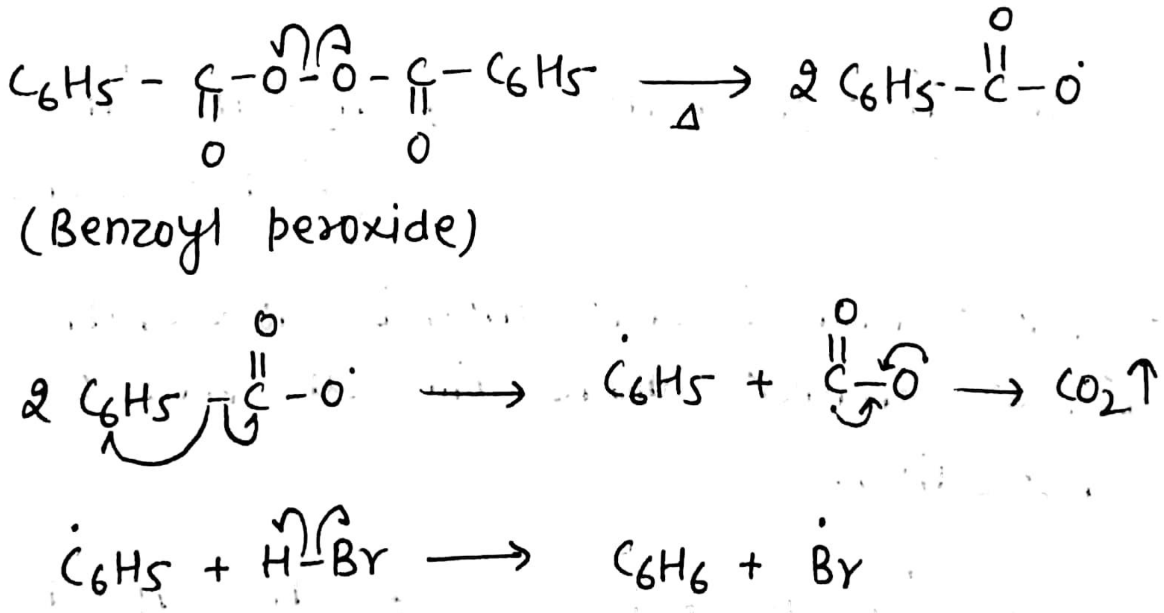
Halogen atom goes to that double bonded carbon atom which contains more no of hydrogen. atoms.

E.g $CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-CH_2-CH_2Br$ (major)

$+ CH_3-\underset{\cancel{CH_3}Br}{\underset{|}{CH}}-CH_3$ (minor)

Mechanism:- (free radical mechanism)

① Initation



$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow[\Delta]{} 2\,C_6H_5-\overset{\overset{O}{\|}}{C}-\dot{O}$$

(Benzoyl peroxide)

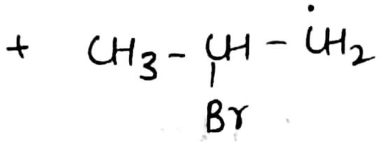
$$2\,C_6H_5-\overset{\overset{O}{\|}}{C}-\dot{O} \longrightarrow \dot{C}_6H_5 + \overset{\overset{O}{\|}}{\dot{C}}-\dot{O} \longrightarrow CO_2\uparrow$$

$$\dot{C}_6H_5 + H-Br \longrightarrow C_6H_6 + \dot{B}r$$

2) Propogation

$CH_3-CH=CH_2 + \dot{B}r \longrightarrow CH_3-\dot{C}H-CH_2Br$

(2° degree)



$+ CH_3-\underset{Br}{\underset{|}{CH}}-\dot{C}H_2$

(1° degree)

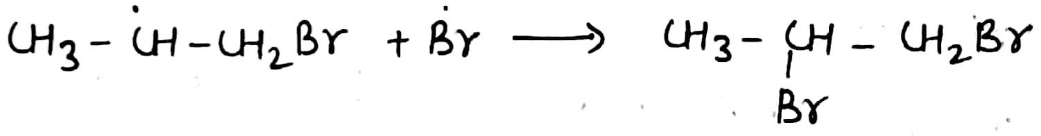
we know that 2° radical is more stable.

$CH_3-\dot{C}H-CH_2Br + H-Br \rightarrow CH_3-CH_2-CH_2Br + \dot{B}r$

(Bromopropane)

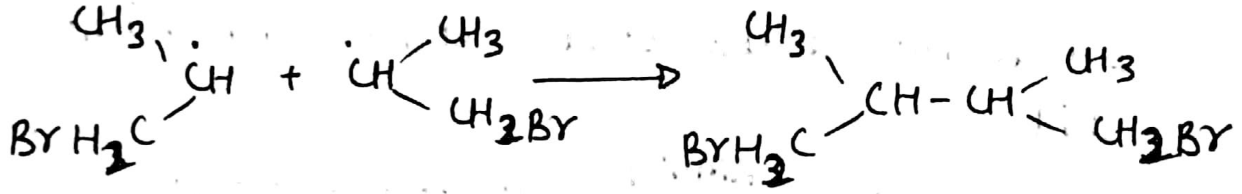
3) Termination

$\dot{B}r + \dot{B}r \longrightarrow Br_2$

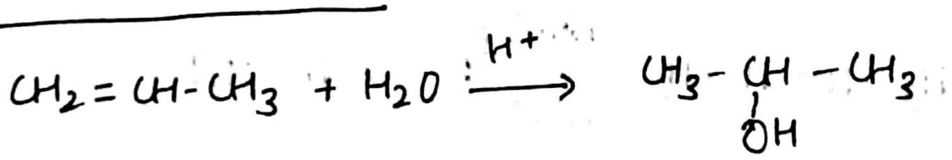


$CH_3-\dot{C}H-CH_2Br + \dot{B}r \longrightarrow CH_3-\underset{Br}{\underset{|}{CH}}-CH_2Br$

(1,2-Dibromo propane)



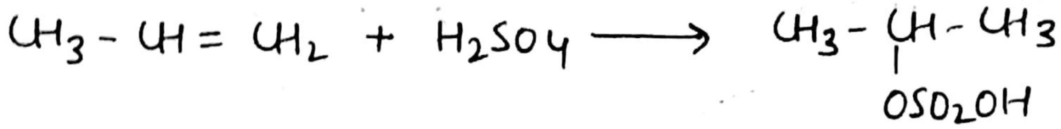
⑤ Addition of water



$CH_2=CH-CH_3 + H_2O \xrightarrow{H^+} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$

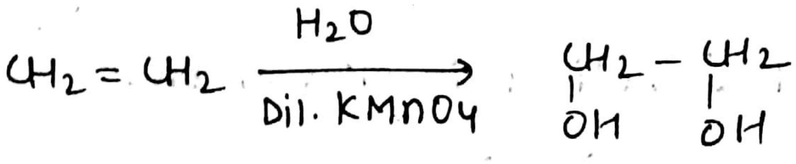
Add OH & H acc. to Markovnikov's rule.

⑥ Addition of H_2SO_4



$$CH_3-CH=CH_2 + H_2SO_4 \longrightarrow CH_3-\underset{\displaystyle OSO_2OH}{\underset{|}{CH}}-CH_3$$

⑦ oxidation



$$CH_2=CH_2 \xrightarrow[\text{Dil. } KMnO_4]{H_2O} \underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

(Glycol).

- ★ During this Reaction the pink colour of $KMnO_4$ sol^n is discharged and a brown ppt is obtained. Hence this Rx^n can be used to test unsaturation in the organic compound.
- ★ $KMnO_4$ is known as Baeyer's Reagent.

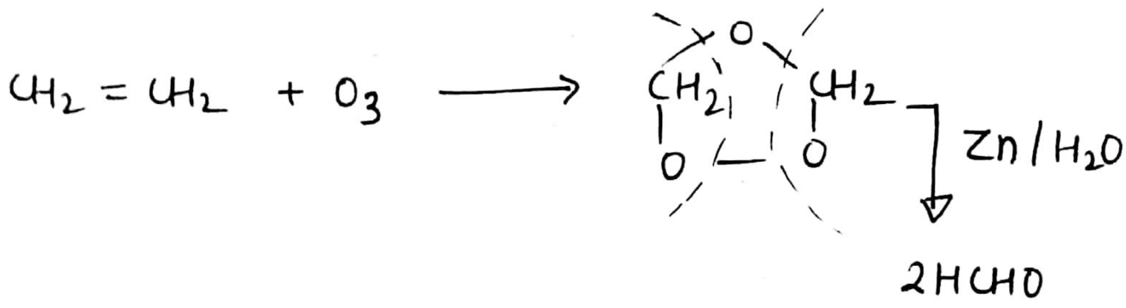
Oxidation with Hot $KMnO_4$

→ Break the double bond & converts them into acid

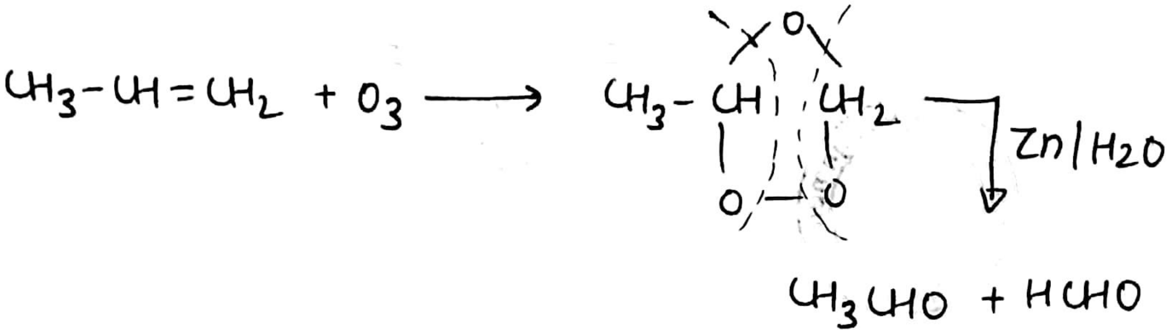
$$CH_3-CH=CH_2 \xrightarrow[KOH]{KMnO_4} CH_3COOH + HCOOH$$

$$CH_3-CH=CH-CH_3 \xrightarrow[KOH]{KMnO_4} 2CH_3COOH$$

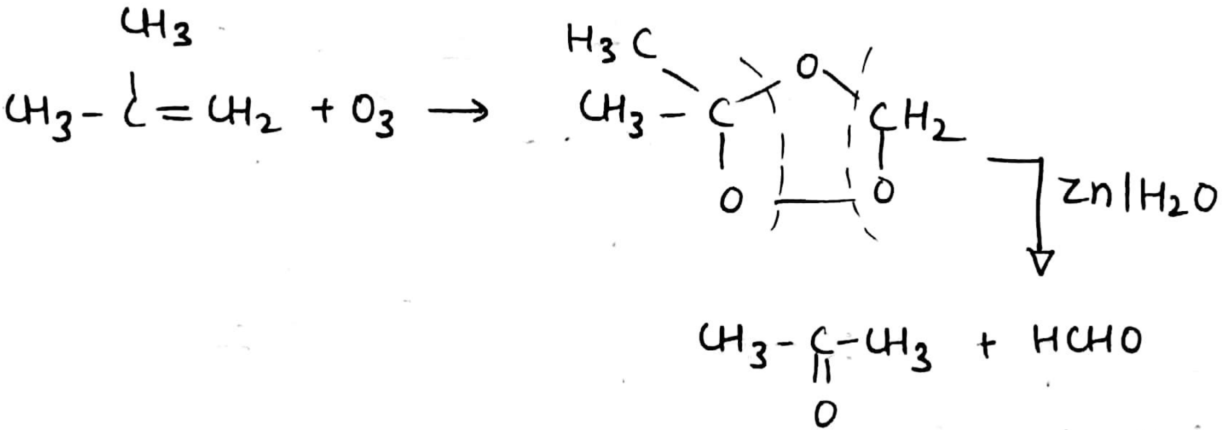
⑧ Ozonolysis (Addition of ozone)



(methanal)

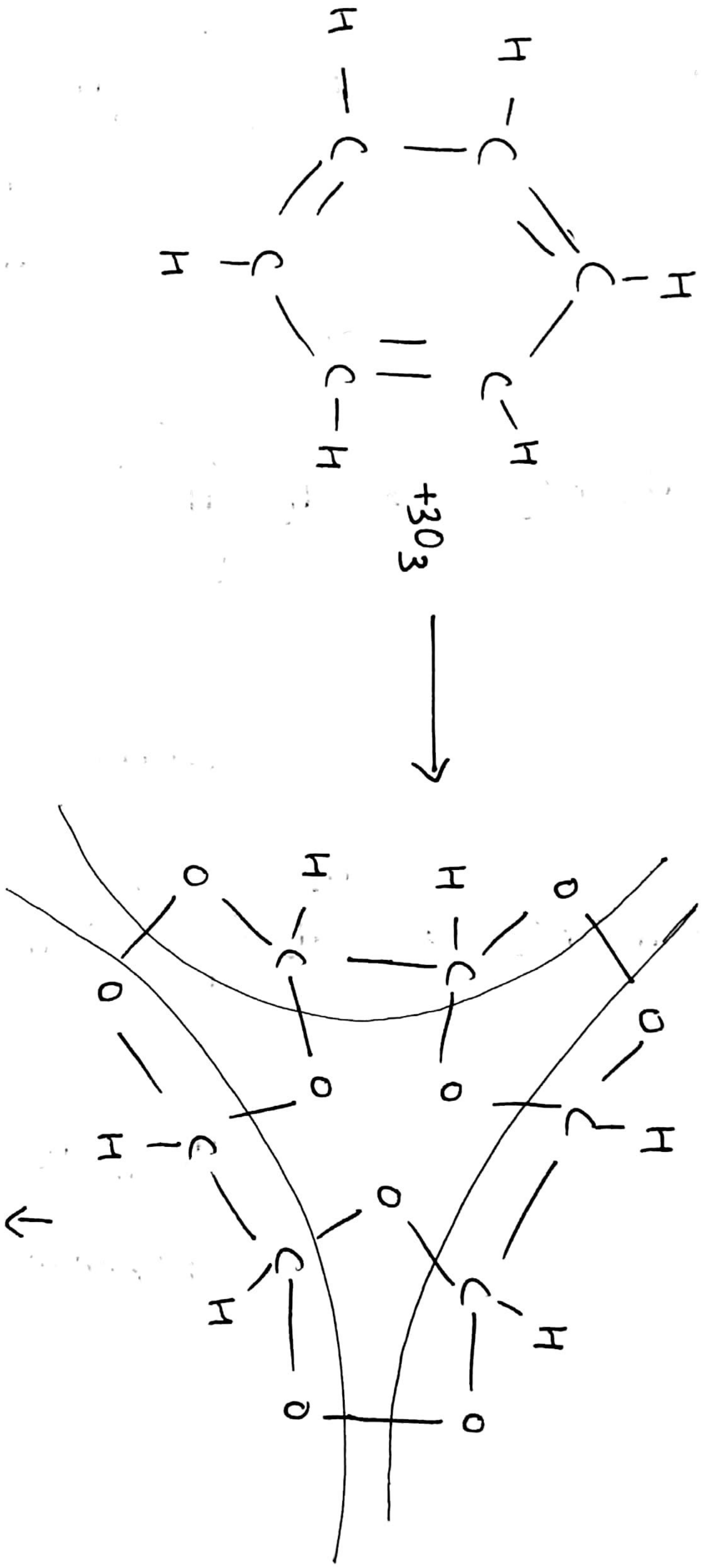


(Ethanal) (methanal)



(Propanone) (methanal)

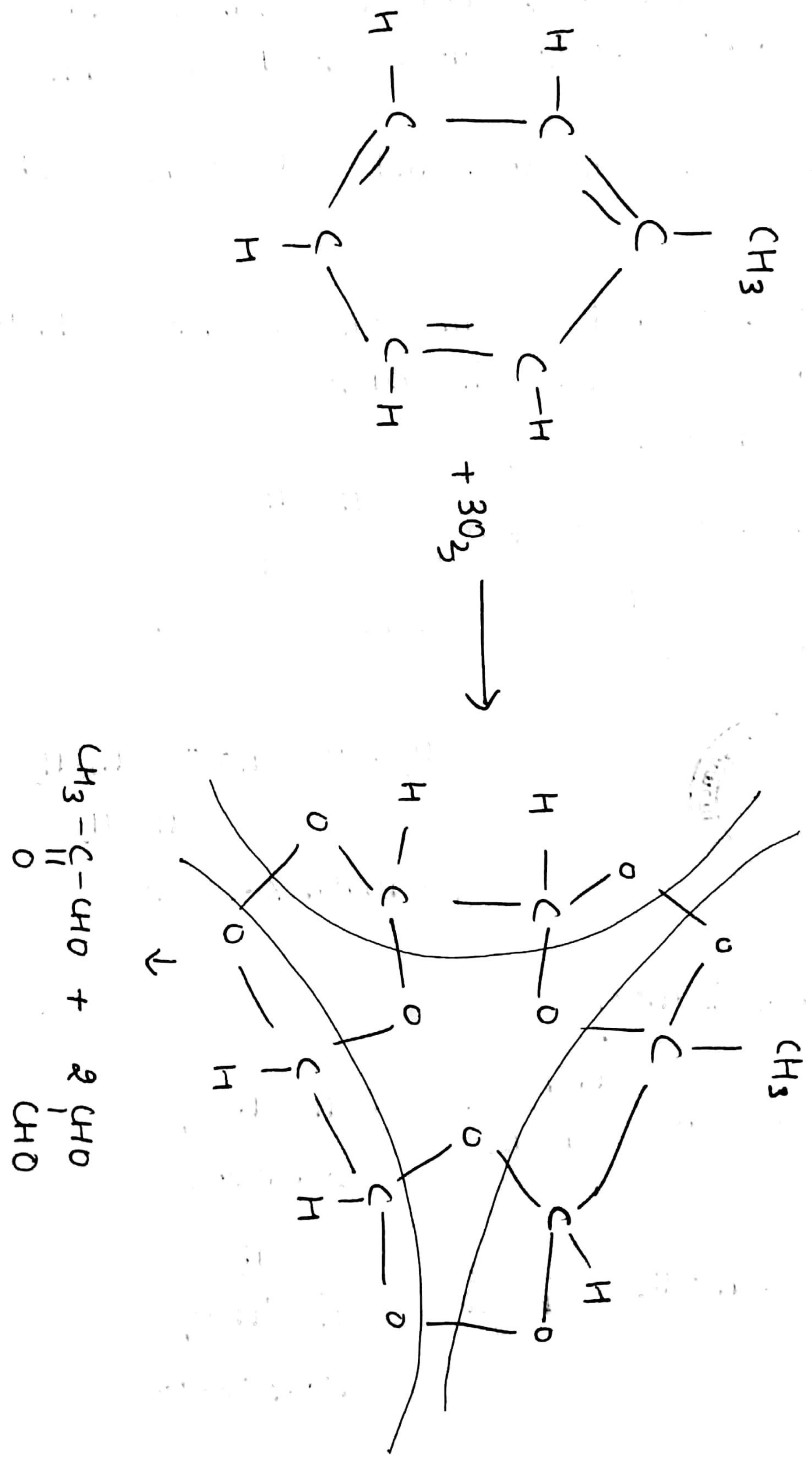
ozonolysis of Benzene



3- $\begin{matrix} CHO \\ | \\ CHO \end{matrix}$

(Ethane-1,2-dial)

Ozonolysis of Toulene



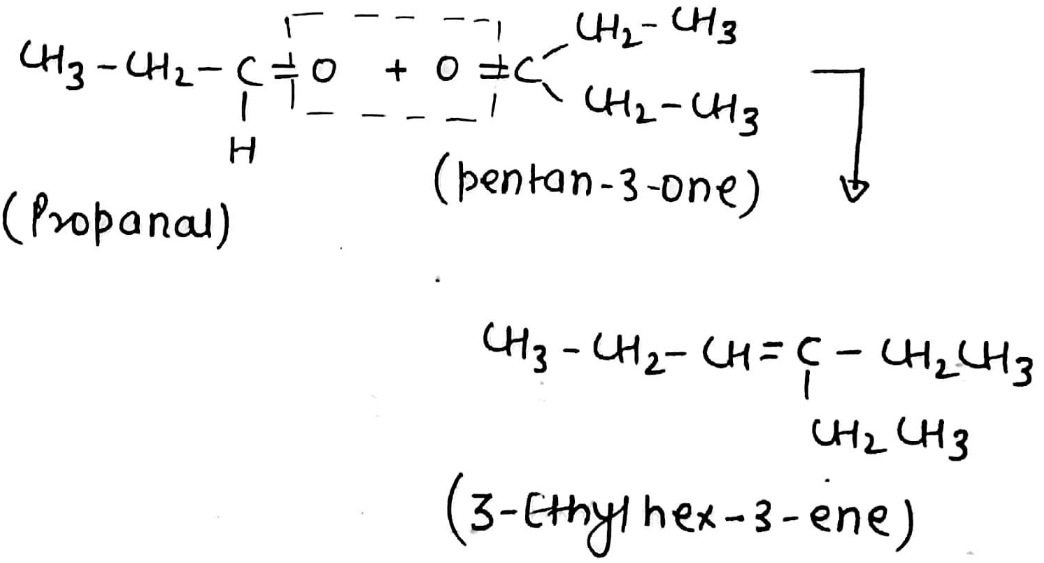
$CH_3-\underset{\underset{O}{\|}}{C}-CHO + 2\begin{array}{c}CHO\\|\\CHO\end{array}$

How to ~~Rea~~ write Reactant from the given products of ozonolysis

→ Draw structure of products in such a way that their oxygen atom should face each other.

→ Replace oxygen atom and add double bond there.

E.g Propanal and pentan-3-one are the products of ozonolysis. write name & structure of the alkene.



$CH_3-CH_2-CH=O + O=C(CH_2-CH_3)_2$

(Propanal) (pentan-3-one)

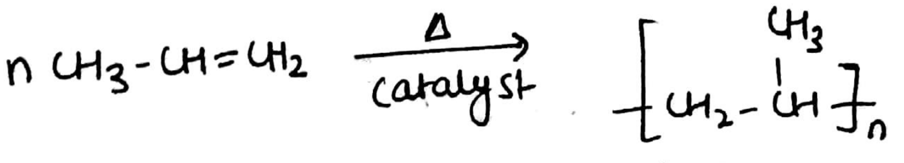
$CH_3-CH_2-CH=C(CH_2CH_3)-CH_2CH_3$

(3-Ethyl hex-3-ene)

⑨ Polymerisation

$n\ CH_2=CH_2 \xrightarrow[\text{catalyst}]{473K} +CH_2-CH_2+_n$

(polyethene)



$n\ CH_3-CH=CH_2 \xrightarrow[\text{catalyst}]{\Delta} [CH_2-CH(CH_3)]_n$

(polypropene)

Alkynes (C_nH_{2n-2})

① Preparation

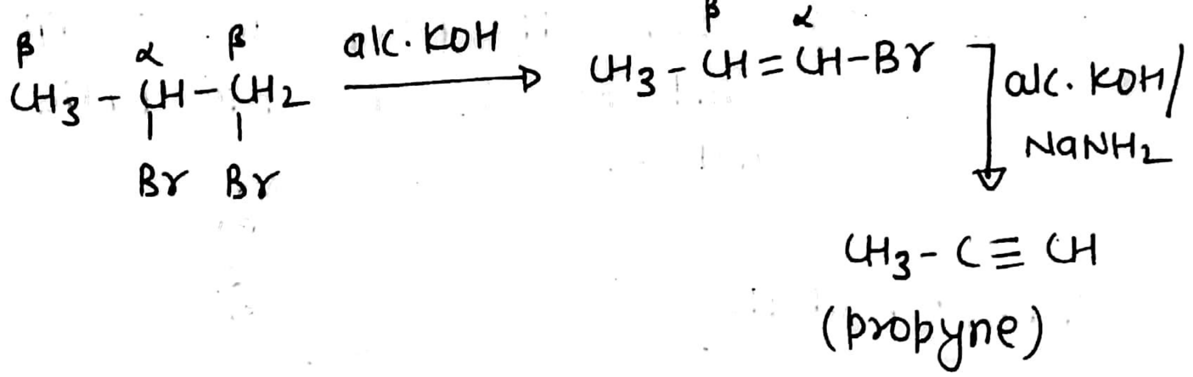
① from calcium carbide

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

$$CaO + 3C \longrightarrow CaC_2 + CO\uparrow$$

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{(Ethyne)}}{CH\equiv CH}$$

② from vicinal dihalides



$$\overset{\beta'}{CH_3}-\underset{Br}{\overset{\alpha}{CH}}-\underset{Br}{\overset{\beta}{CH_2}} \xrightarrow{alc.\,KOH} CH_3-\overset{\beta}{CH}=\overset{\alpha}{CH}-Br \xrightarrow{alc.\,KOH/\,NaNH_2} \underset{\text{(propyne)}}{CH_3-C\equiv CH}$$

chemical Properties of alkynes

① Acidic nature of alkyne

$$CH\equiv CH + Na \longrightarrow HC\equiv C^{-}Na^{+} + \frac{1}{2}H_2\uparrow$$

almost all metal Reacts with acid and produce H_2 gas. Since alkyne is also producing H_2 with Reactive metal, hence it is acidic in nature.

Q Arrange them in ↑ order of acidic nature

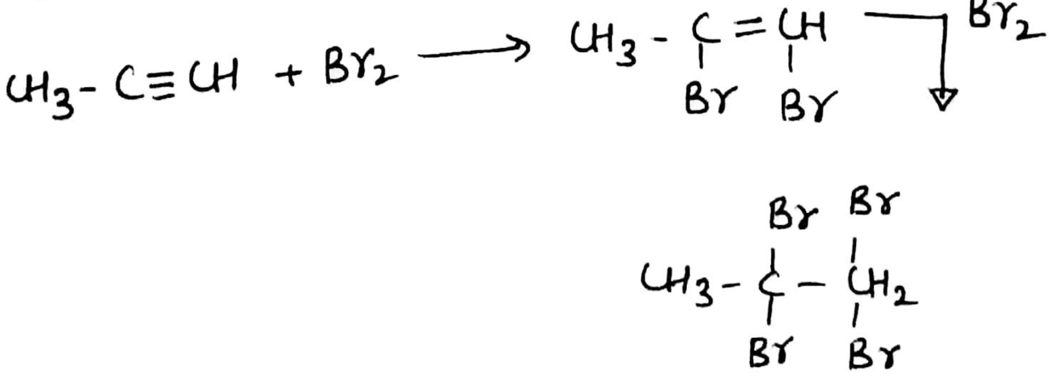
i) $CH\equiv CH$ (ii) $CH_3-C\equiv CH$ (iii) $CH_3-C\equiv C-CH_3$

A (3) <(2) < (1) Since CH_3 group has +I effect and +I decreases the acidic nature.

② Addition of H_2

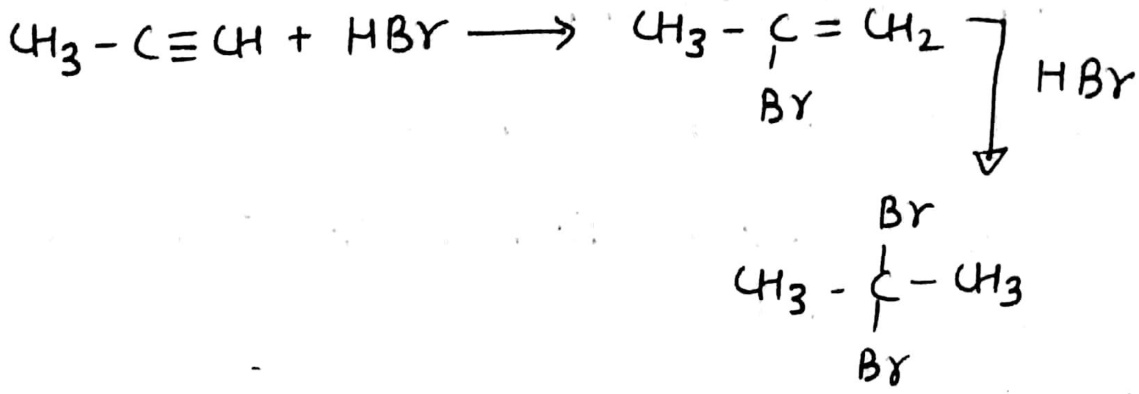
$$CH\equiv CH \xrightarrow{H_2/Ni} CH_2=CH_2 \xrightarrow{Ni/H_2} CH_3-CH_3$$

③ Addition of Halogen



$$CH_3-C\equiv CH + Br_2 \longrightarrow CH_3-\underset{Br}{C}=\underset{Br}{CH} \xrightarrow{Br_2} CH_3-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{CH_2}}$$

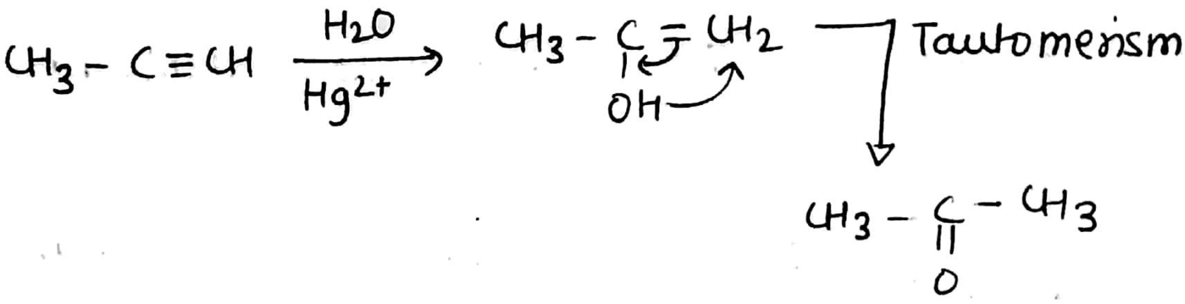
④ Addition of HX



$$CH_3-C\equiv CH + HBr \longrightarrow CH_3-\underset{Br}{C}=CH_2 \xrightarrow{HBr} CH_3-\overset{Br}{\underset{Br}{C}}-CH_3$$

(Geminal dihalide)

⑤ Addition of water

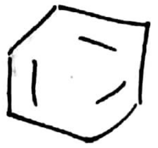


$$CH_3-C\equiv CH \xrightarrow[Hg^{2+}]{H_2O} CH_3-\underset{OH}{C}=CH_2 \xrightarrow{\text{Tautomerism}} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

(propanone)

⑥ Polymerisation

$$3\ CH\equiv CH \xrightarrow[873K]{\text{Red hot Fe}}$$



(Ethyne)

Aromatic hydrocarbons

condition for Aromaticity

① Structure should be planar.

② Complete delocalisation of the π electrons in the ring.

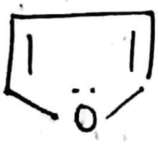
③ Structure should contain $(4n+2)\pi$ electrons where $n = 0, 1, 2 ---$ (known as Hükel rule)

Q Which of the following compounds are aromatic

(i)

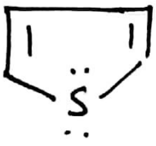
$\pi e^- \Rightarrow 6 \Rightarrow (4(1)+2)$ Hence aromatic

(ii)



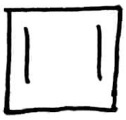
$\pi e^- \Rightarrow 6 \Rightarrow (4(1)+2)$ Hence aromatic

(iii)



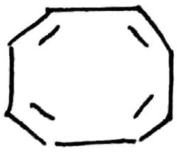
$\pi e^- \Rightarrow 6 \Rightarrow (4(1)+2)$ Hence aromatic

(iv)

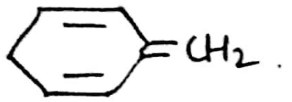


$\pi e^- \Rightarrow 4$ not aromatic

(v)



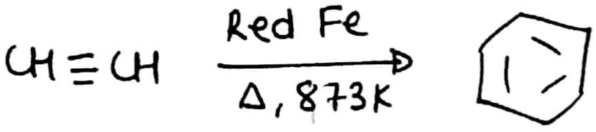
$\pi e^- \Rightarrow 8$ not aromatic

(vi)  not aromatic (missing of conjugation)

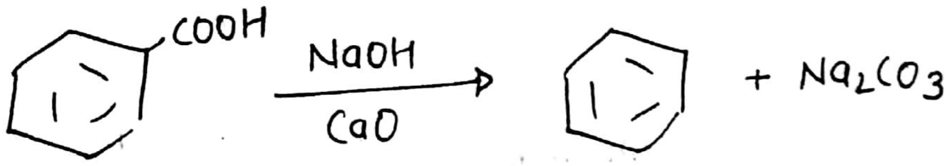
(vii)  not aromatic (missing conjugation)

Preparation of Benzene

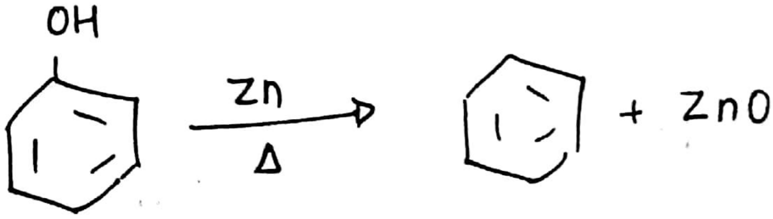
① Polymerisation of ethyne



② from Decarboxylation of benzoic acid



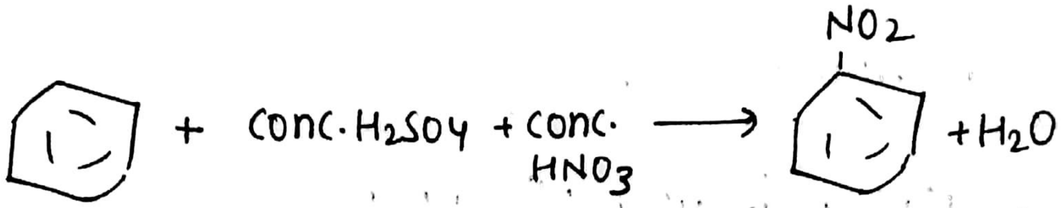
③ from phenol



Chemical Properties of Benzene

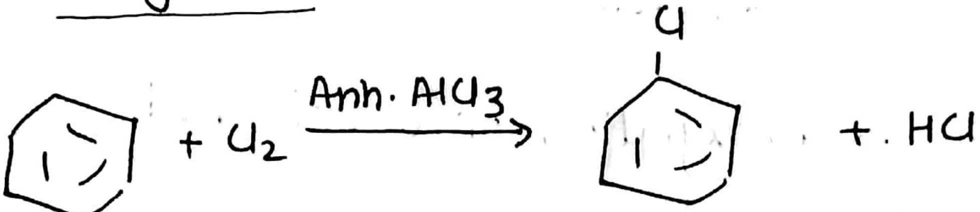
① Electrophilic substitution Rx^n

① Nitration

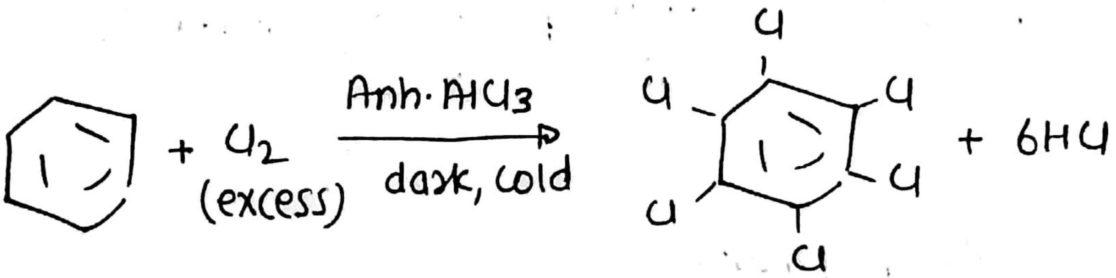


(nitrobenzene)

② Halogenation

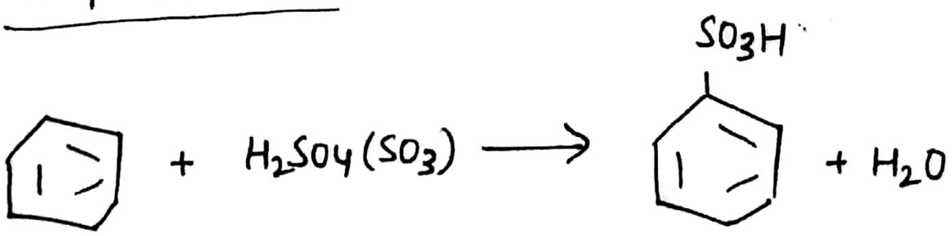


(Chlorobenzene)



(Hexa chlorobenzene)

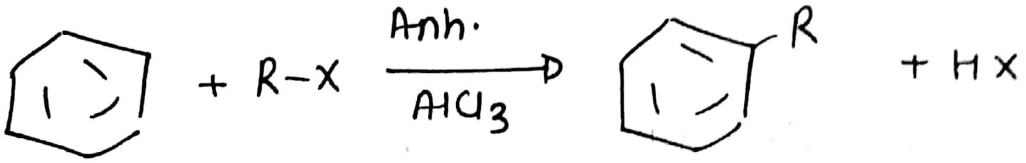
③ Sulphonation



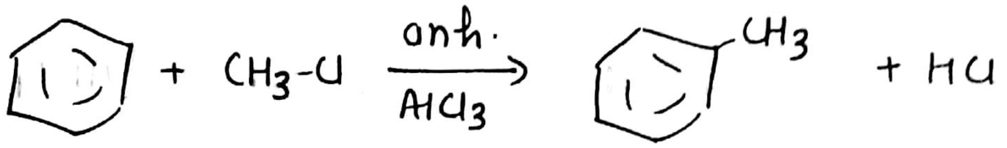
(Benzene sulphonic acid)

④ Friedel Crafts Rxⁿ

① Alkylation

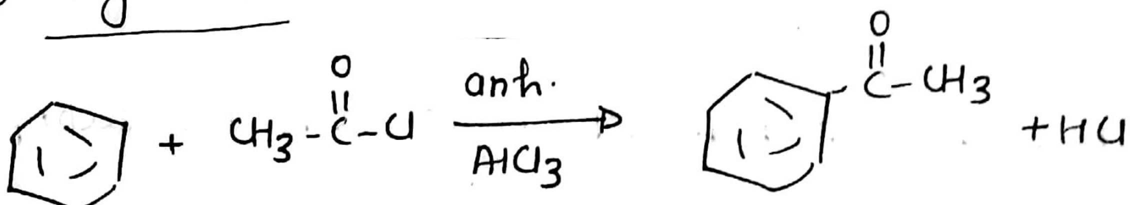


E.g

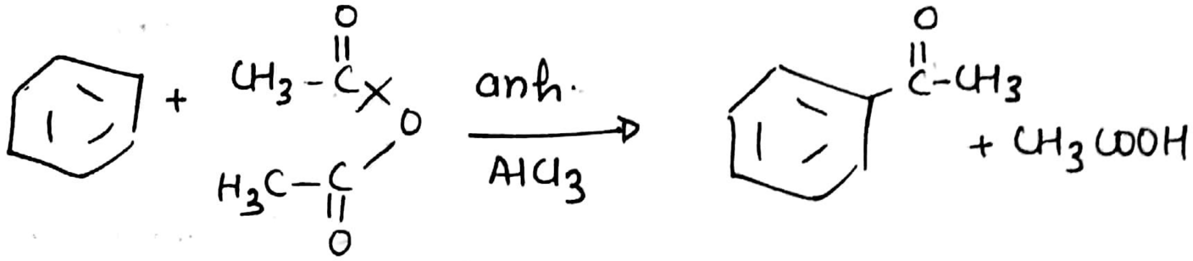


(Towlene)

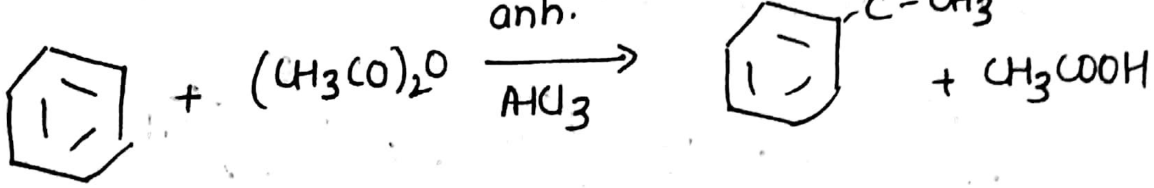
② Acylation



(Acetophenone)



(acetic anhydride)



Mechanism of Electrophilic substitution

① Generation of electrophile (E^+)

② Formation of Carbocation intermediate

③ Removal of proton (H^+)

① Generation of electrophile (E^+)

→ $Cl-Cl + AlCl_3 \longrightarrow \overset{+}{Cl} + [AlCl_4]^-$

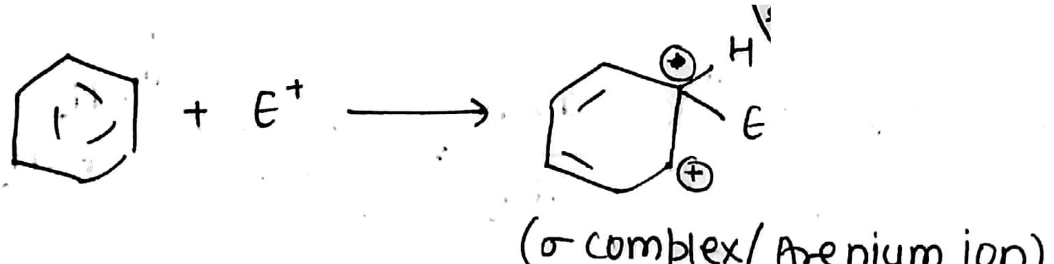
→ $CH_3-Cl + AlCl_3 \longrightarrow \overset{+}{C}H_3 + [AlCl_4]^-$

→ 

$CH_3-\underset{\underset{O}{\|}}{C}-Cl + AlCl_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{\overset{+}{C}} + [AlCl_4]^-$

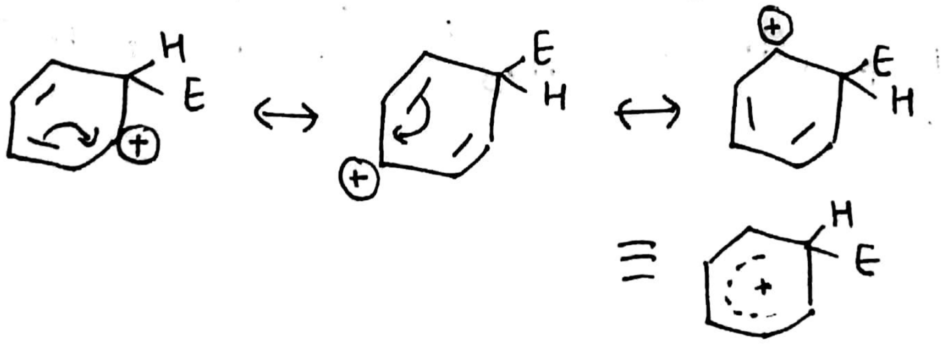
Here role of anh. $AlCl_3$ is to generate electrophile.

② Formation of Carbocation

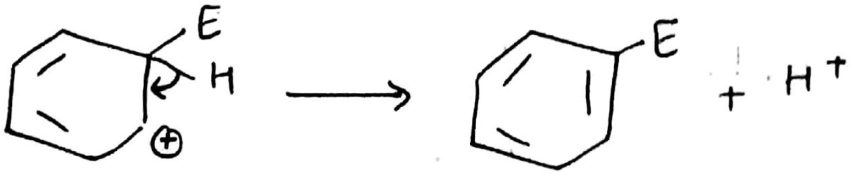


(σ complex/ Arenium ion)

Arenium ion gets stabilised by resonance.

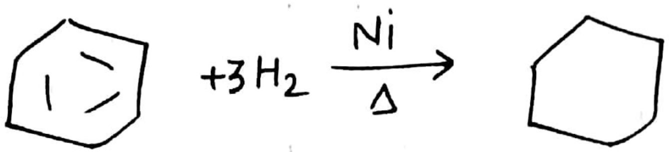


③ Removal of proton (H^+)



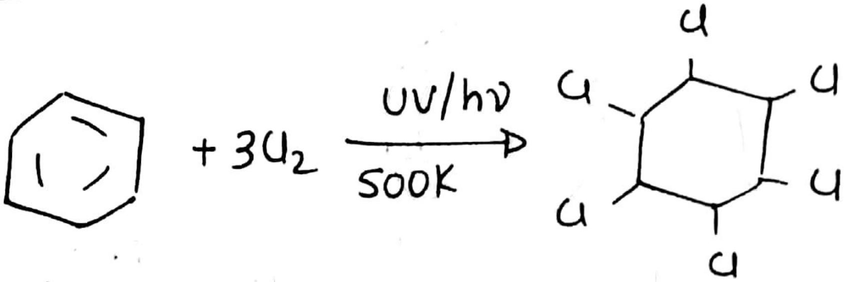
Addition Reaction

① Addition of H_2



(Benzene) (cyclohexane)

② Addition of Cl_2



(Benzene Hexa chloride)
(BHC)

Combustion of Benzene

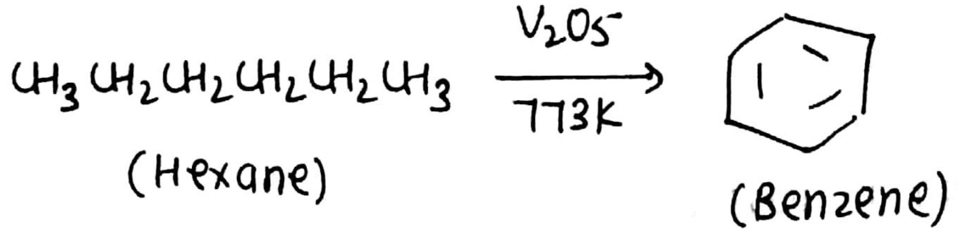
$$C_6H_6 + \frac{15}{2}O_2 \xrightarrow[\Delta]{} 6CO_2 + 3H_2O$$

Q Convert following into benzene

(i) hexane ii) ethene (iii) ethyne

(iv) ethanoic acid.

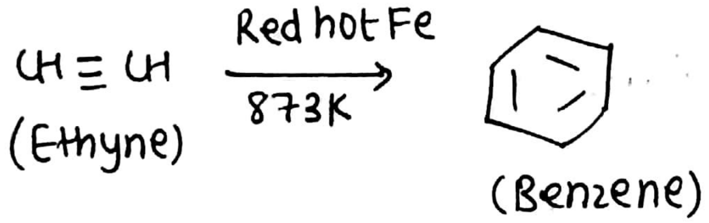
A (i)



$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow[773K]{V_2O_5}$

(Hexane) (Benzene)

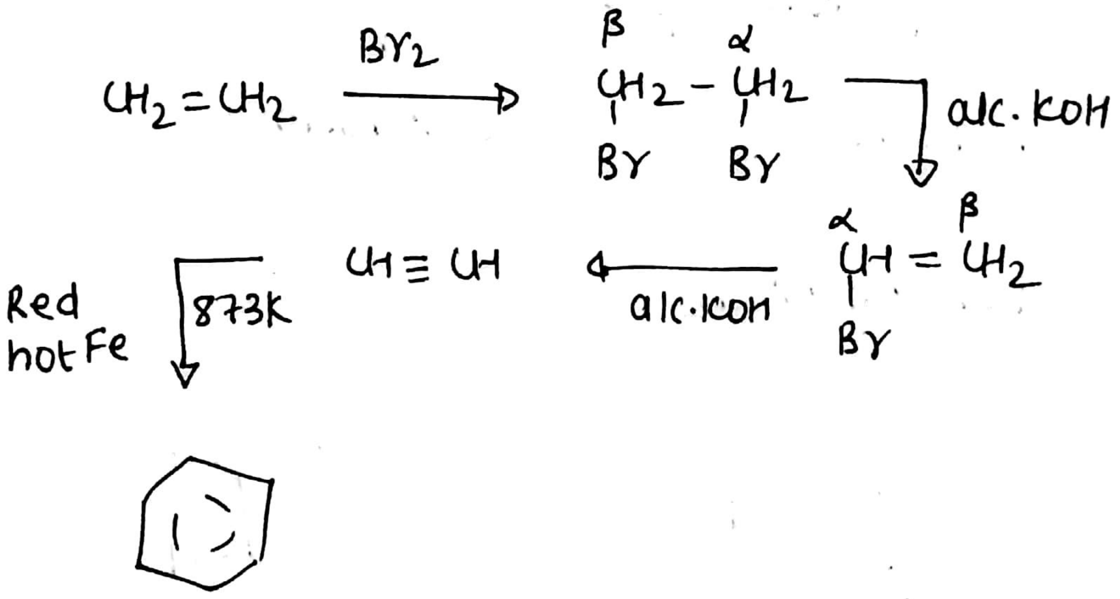
(iii)



$CH \equiv CH \xrightarrow[873K]{\text{Red hot Fe}}$

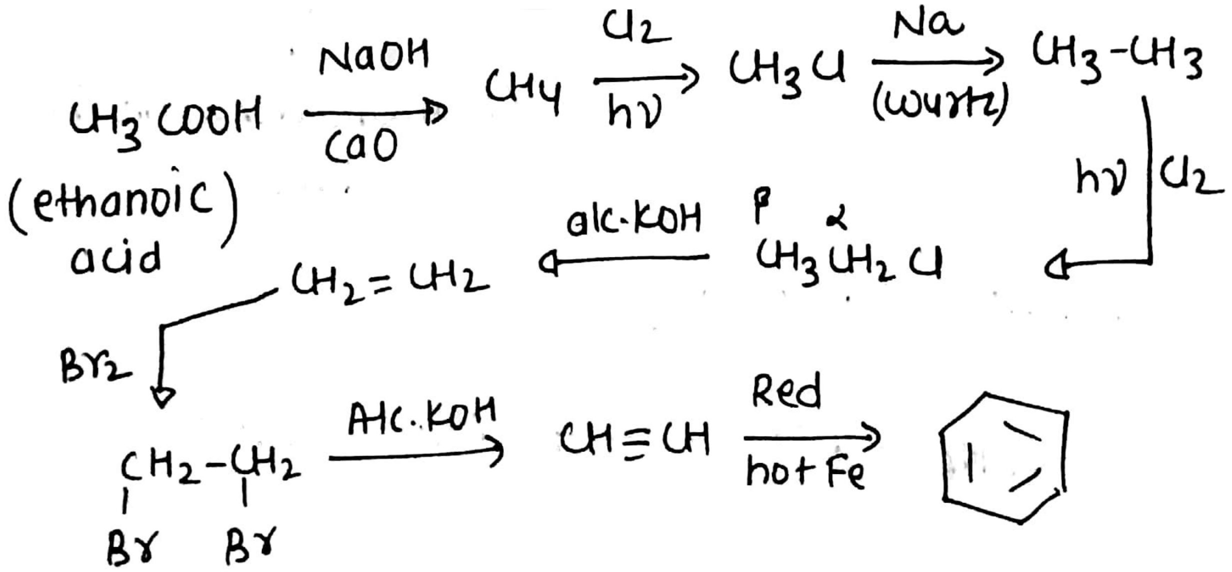
(Ethyne) (Benzene)

(ii)



$CH_2=CH_2 \xrightarrow{Br_2} \overset{\beta}{C}H_2(Br)-\overset{\alpha}{C}H_2(Br) \xrightarrow{\text{alc. KOH}} \overset{\alpha}{C}H(Br)=\overset{\beta}{C}H_2 \xrightarrow{\text{alc.KOH}} CH \equiv CH \xrightarrow[873K]{\text{Red hot Fe}}$

(iv)



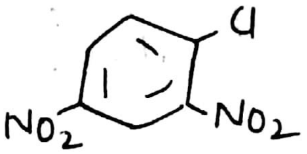
$CH_3COOH \xrightarrow[CaO]{NaOH} CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[(Wurtz)]{Na} CH_3-CH_3 \xrightarrow{h\nu, Cl_2} \overset{\beta}{C}H_3\overset{\alpha}{C}H_2Cl \xrightarrow{\text{alc-KOH}} CH_2=CH_2 \xrightarrow{Br_2} CH_2(Br)-CH_2(Br) \xrightarrow{\text{Alc. KOH}} CH \equiv CH \xrightarrow[\text{hot Fe}]{\text{Red}}$

(ethanoic acid)

Q Arrange the following set in order of their decreasing reactivity with an electrophile E^+

(i) chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene

①



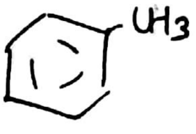
②

③

Intermediate is carbocation and we know that -I effect decreases the stability of carbocation. (NO_2 has -I effect).

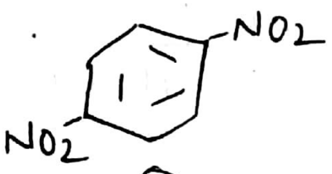
So order is :- ① > ③ > ②

(ii) Towene, $p-CH_3-C_6H_4-NO_2$, $p-NO_2-C_6H_4-NO_2$



①

②



③

Since NO_2 has -I effect. Hence order will be

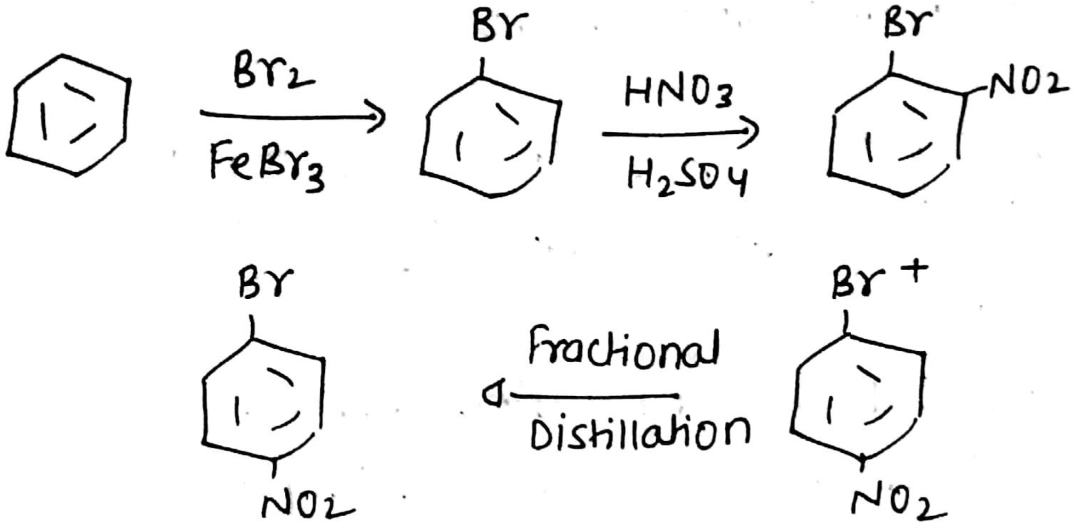
① > ② > ③.

Q. Convert Benzene into

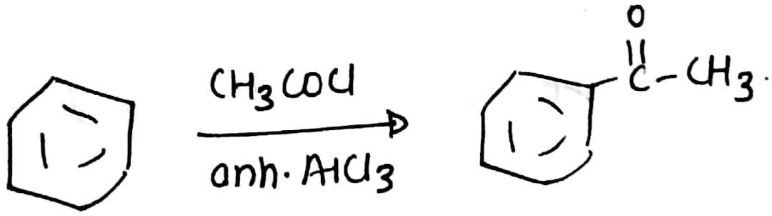
(i) p-nitro bromo benzene (ii) acetophenone

(iii) m-nitro chloro benzene (iv) p-nitro toluene

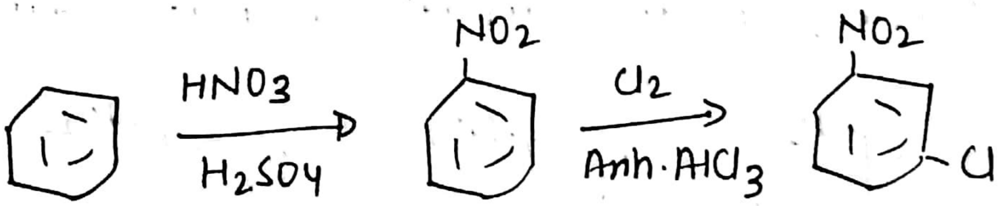
A (i)



(ii)



(iii)



(iv)