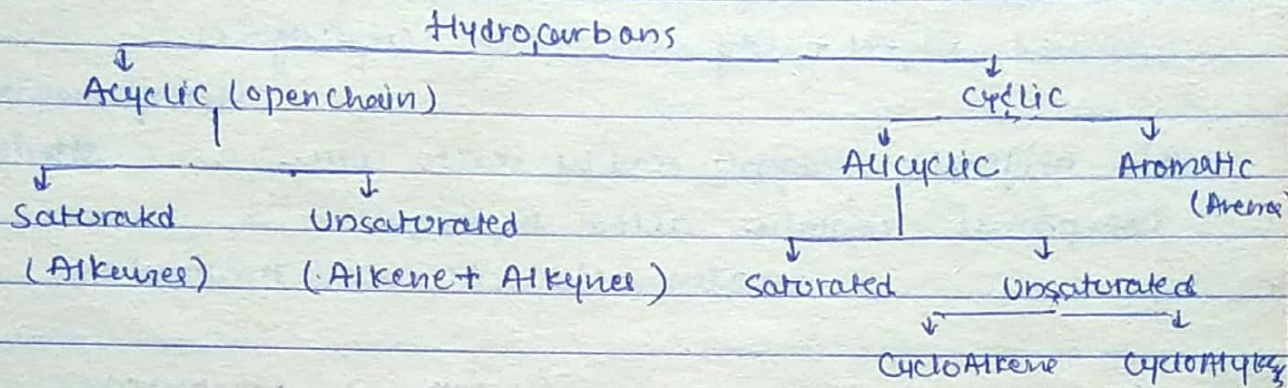
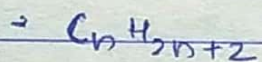


-; HYDROCARBONS ;-

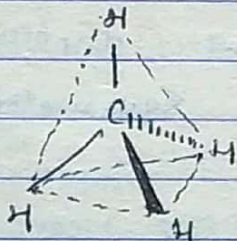
A. Classification of Hydrocarbons :-



B. Alkanes: (Paraffins)



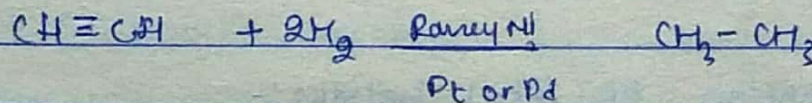
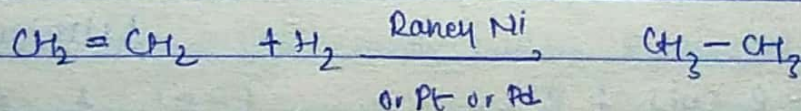
- Structure :- (C-C) - sp^3 -hybridised
- Tetrahedral



(Fischer projection formulae)

→ Methods of preparation :-

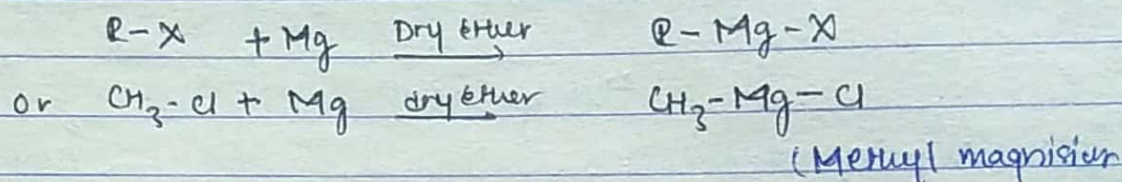
a) From unsaturated hydrocarbons :-



(Sabatier and Sanderson's reduction reaction)

b) From Alkyl halides :-

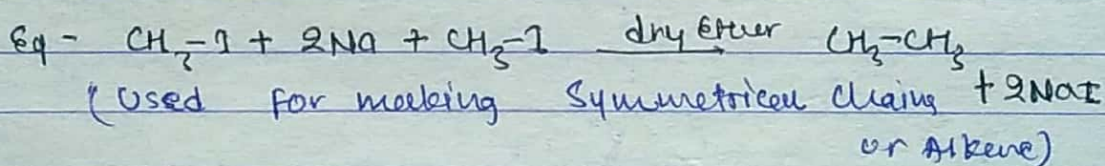
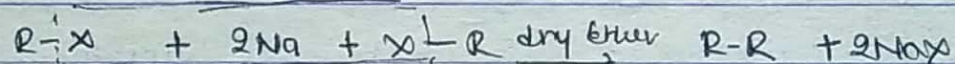
- By Grignard's reagent :-



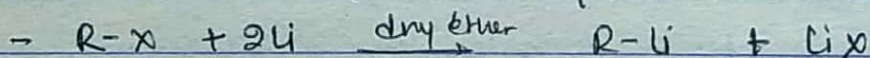
this Grignard's reagent readily reacts with compounds contain active hydrogen.
(water, acid, Alcohols, Ammonia)



- Wurtz reaction :-



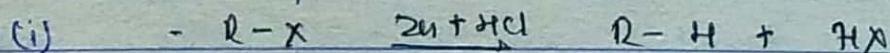
- Corey-House reaction :- (for unsymmetrical Alkane)

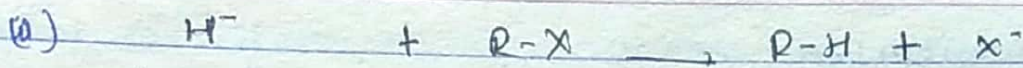


(Lithium dialkyl copper)



- Reduction of Alkyl halides :-



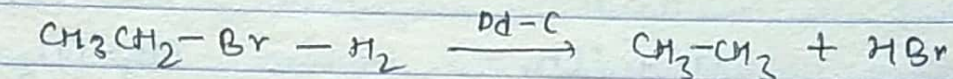


(From $LiAlH_4$)

($LiAlH_4$ used for reducing 1° & 2° Alkyl halide)

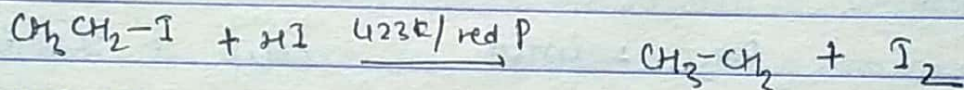
($NaBH_4$ reduces 2° & 3° Alkyl halide)

(ii)



± Catalytic hydrogenolysis.

(iii)

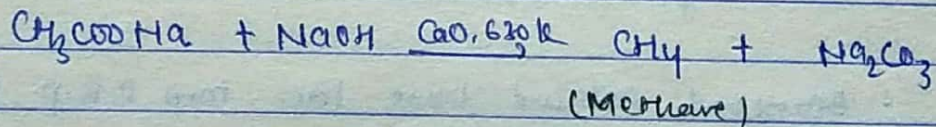
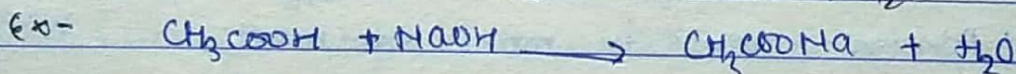
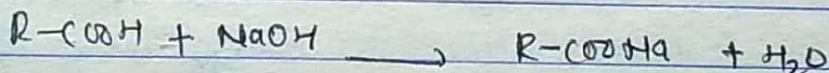


(red phosphorus used to remove iodine formed,



c). From carboxylic acids:-

(i) Decarboxylation:- removal of CO_2 molecule.

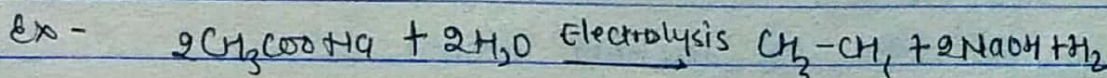


(Produces one less carbon atom Alkane)

(ii) Kolbe's Electrolytic process:-

when a conc. aq. soln of

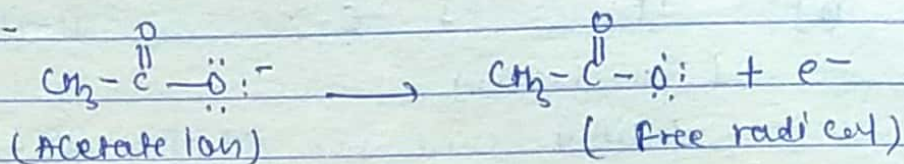
Na or K salts electrolysed.



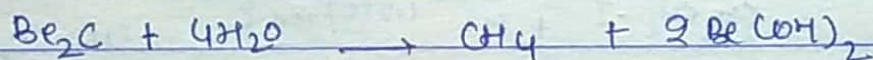
(sodi. ethanoate)

+ $2O_2$

- Mechanism:-



d) By Action of water on beryllium:- (and Aluminium Carbide)



★ Physical properties:-

(i) Boiling points :-
 $\text{C}_1 - \text{C}_4$ - gas
 $\text{C}_5 - \text{C}_{17}$ - liquids
 $\text{C}_{18} - \dots$ - Colourless

• As on increase in molecular mass waxy solids the magnitude of van der waals forces".

• Branched Alkane have low m.p & B.p than correspondingly n-Alkane, this branching tends to approach spherical shape. The surface area decreases the van der waal forces acting. Between their molecules become weaker.

(ii) Melting point:- As same as B.p. it increases on increase in Carbon content or No. of Carbon atoms.

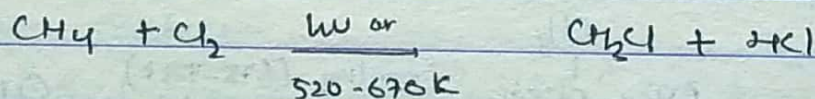
"Alkane with even no. of C-atoms, are more symmetrical than alkane with odd no. of C-atom, so it pack closely in crystal lattice".

(iii) Solubility :- follows rules 'Like dissolves like'. As Alkanes are non-polar so insoluble in solvents such as water, Alcohol etc. but dissolve in Benzene.

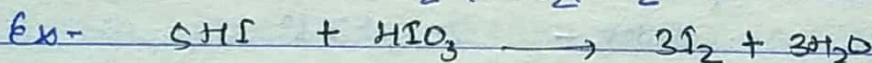
* Chemical reactions :-

(i) Substitution reaction :- in which a H-atom of hydrocarbon is replaced by an atom or group of atom.

• Halogenation of Alkanes :-



Order :- $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

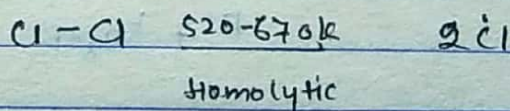


(~~strong~~ acid-oxidising agent)

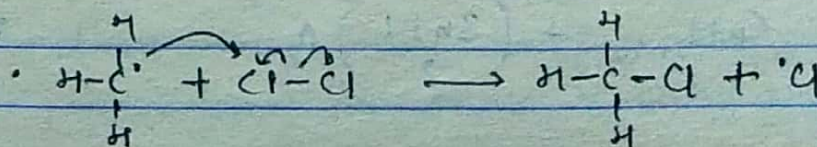
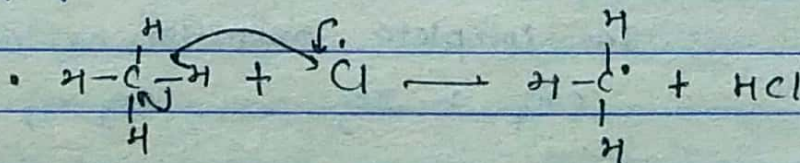
(HNO_3 or H_2O_2 also act as oxidising agent)

→ Mechanism :-

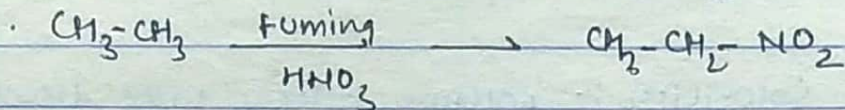
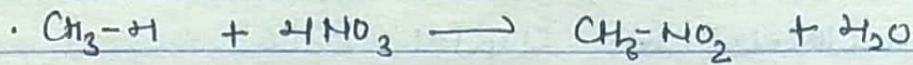
(a) Chain initiation :-



(b) Propagation :-

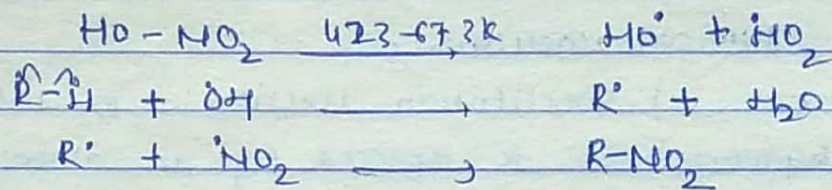


• NITRATION :- Replacement of H-atom with $-NO_2$ group.

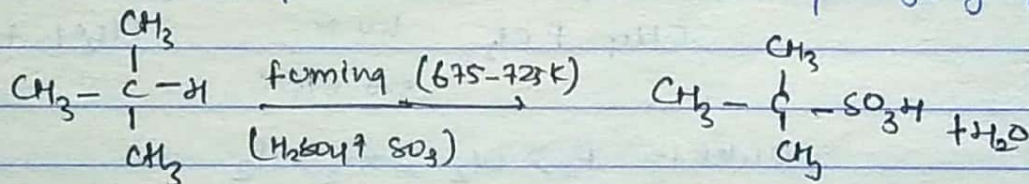


Order - $3^\circ > 2^\circ > 1^\circ$
(of hydrogens)

→ Mechanism :-

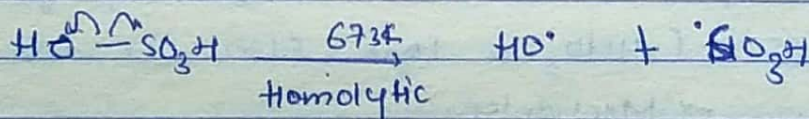


• Sulphonation :- Replacement of H-atom by $-SO_3H$ group



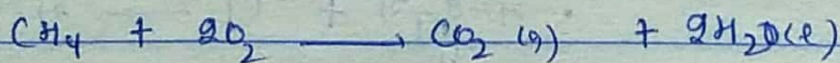
Order - $2^\circ > 2^\circ > 1^\circ$

→ Mechanism :-

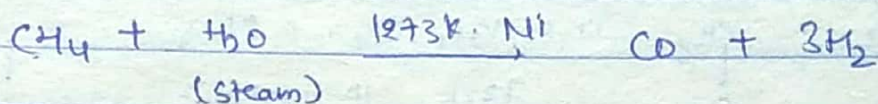


• Oxidation :-

(a) complete oxidation or combustion -

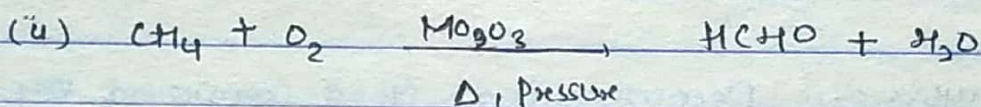
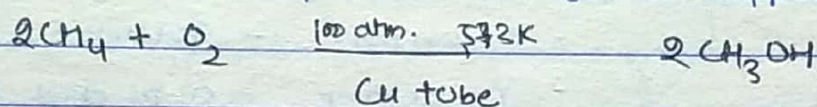


(b) Incomplete combustion -

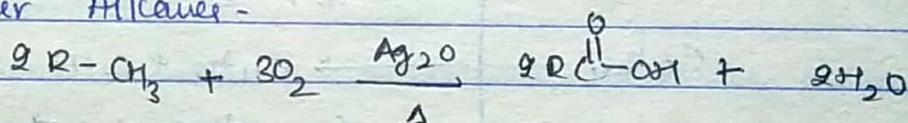


(c) Catalytic oxidation -

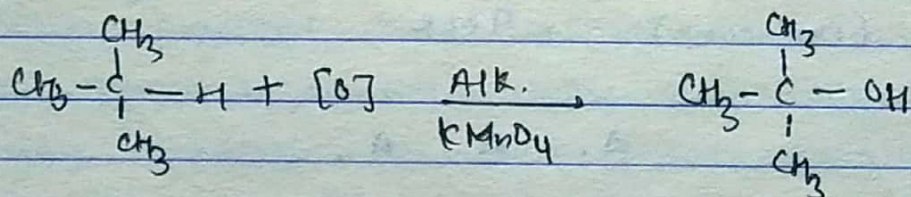
(i) when mixture of methane of oxy at a pressure of 100 atm. is passed through a copper tube (step)



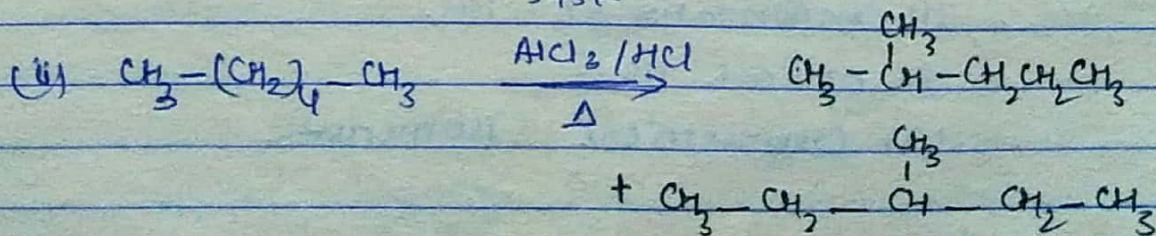
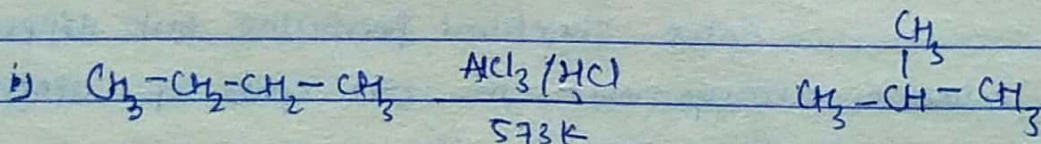
(iii) Higher Alkanes -



(iv) No effect of KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ on Alkanes.
BUT can oxidise 3° Alkanes.



• Isomerization:-



• Conformations of Alkanes :-

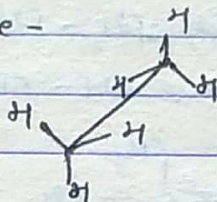
As due to the rotation b/w the C-C single σ -Bond the C-atom can rotate about its axis. So there is infinite NO. of Arrangement.

Ex - conformations of Ethane -

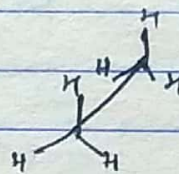
(i) Fischer's 2-D projection.

(ii) Newmann projection.

(iii) Sawhorse -



(staggered)



(eclipsed)

• Relative Stability :-

As in staggered form the distance b/w the electron clouds of σ -bonded H-atoms is more so, there is less repulsion b/w atom.

In eclipsed form these are nearer so a energy produced by torsional strain.

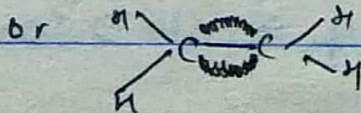
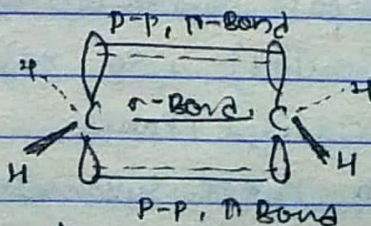
" So staggered is more stable than eclipsed."

• The energy difference b/w both conformations is 12.5 kJ mol^{-1} called 'Energy Barrier'.

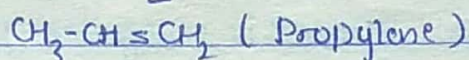
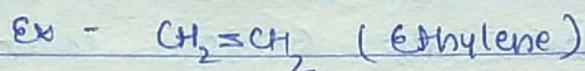
Q. A. Q.

A. Alkenes :- Olefins.

Structure -

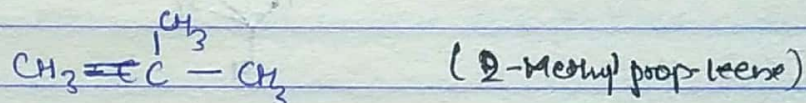
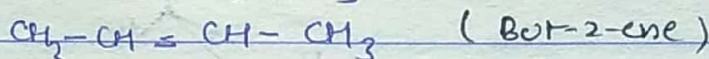
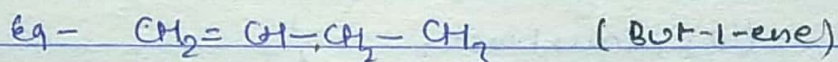


→ Nomenclature :- (C_nH_{2n})



→ Isomerism of Alkene -

(a) Structural :-

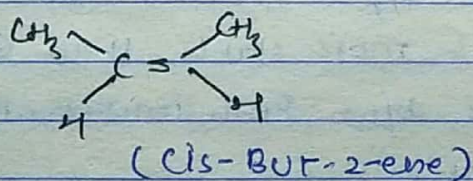


(b) Geometrical -

As there is one σ and one π bond. π -Bond is formed by sideways overlapping of p-orbitals. This restricted the rotation of (C-C) Bond.

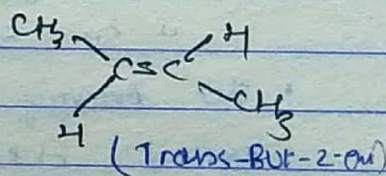
At the same time they form two isomers -

- cis :-



(B.P. 277K)

- Trans -



(B.P. - 274K)

→ Properties :-

(i) As the dipole moment of cis - (0.85D) and Trans is zero (cancelled), so cis is more polar than Trans.

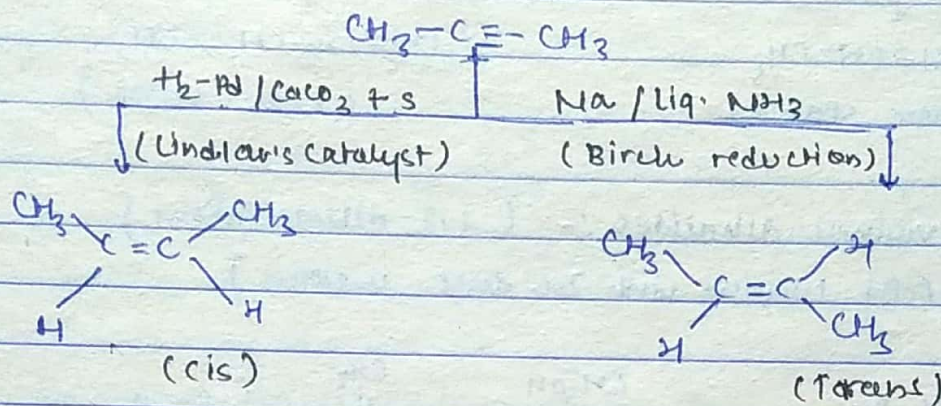
" B.P - cis > Trans.

(ii) As due to more symmetry, mp - Trans > cis.

(iii) more polar more solubility - cis > Trans.

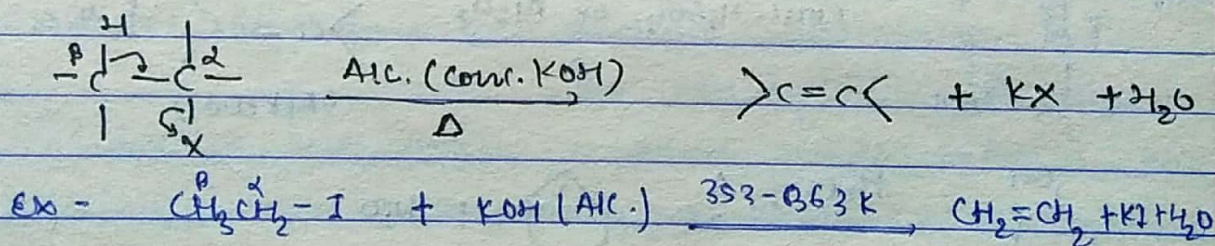
★ General methods of preparation :-

(i) By partial reduction of Alkynes :-
(Catalytic hydrogenation)



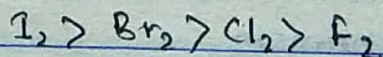
(ii) From Alkyl halides or haloalkenes :-

(Dehydrohalogenation - Alkyl halide on heating with a strong base, conc. Alcoholic KOH.)

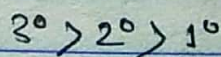


(This is a β -Elimination reaction)

• Ease of dehydrohalogenation -

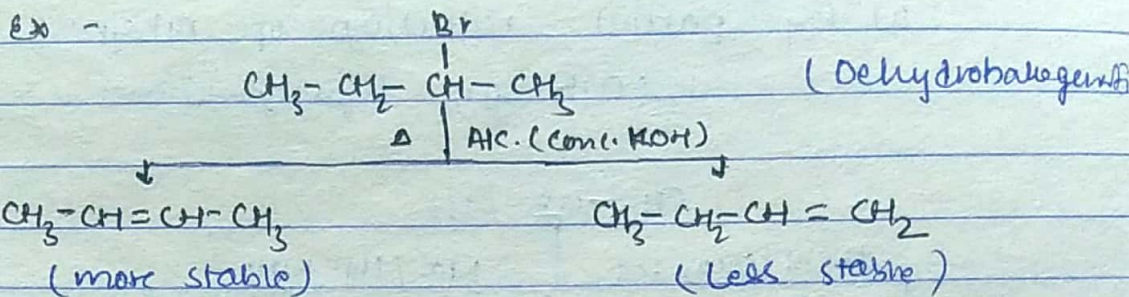


• For same halide diff. Alkyl group -

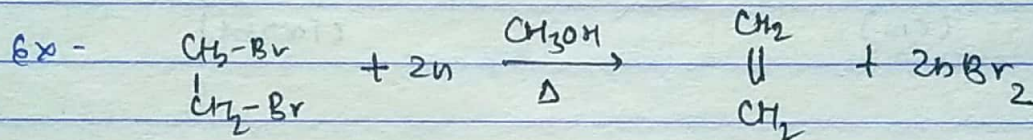


• Saytzeff rule :- when there is a formation of Alkene take place Always more substituted Alkene predominated or formed.

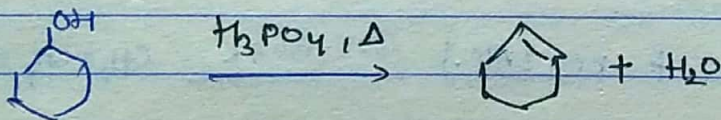
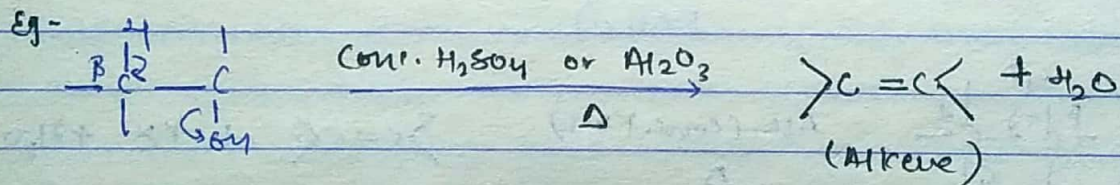
when there is two β -hydrogen on any side the α -ata,



(iii) From vicinal dihalides :- (1,2-dihaloalkane)
(By heating with Zn dust method)



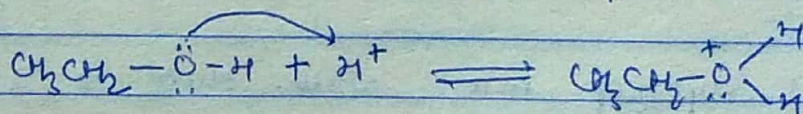
(iv) From monohydric Alcohols or Alkanols :-
(Only that containing β -hydrogen)



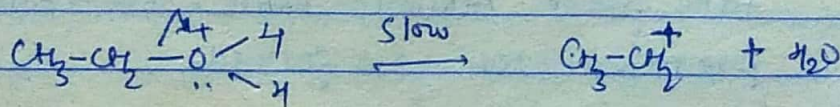
• order of dehydration - $3^\circ > 2^\circ > 1^\circ$
(follow Saytzeff rule)

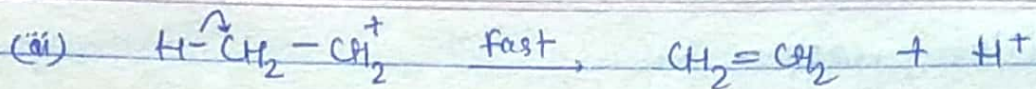
→ Mechanism

(i) Alcohol being Lewis acid accepts a proton.



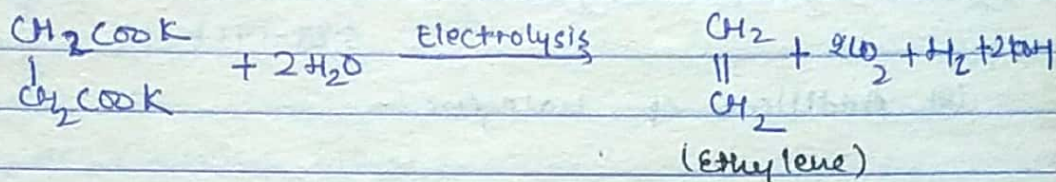
(ii)





(v) From sodium and potassium salts of saturated dicarboxylic acid :-

• Kolbe's Electrolytic reaction :-



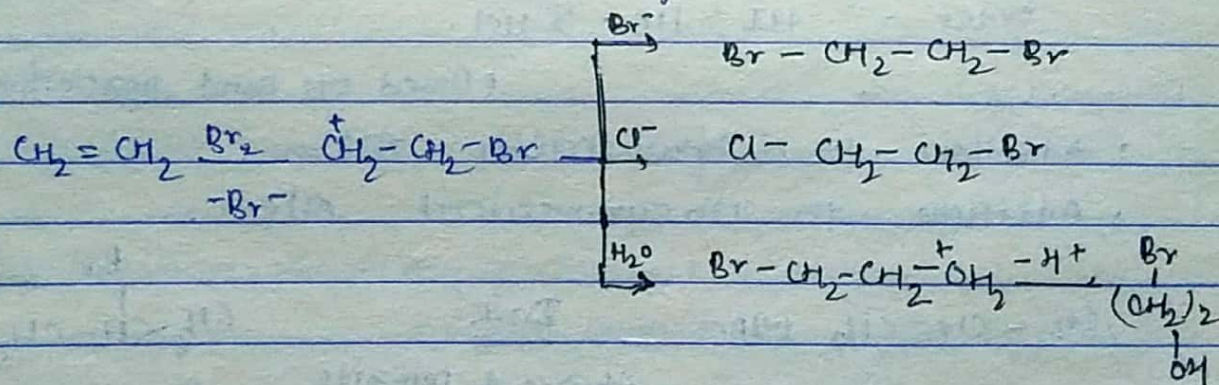
★ Physical properties :-

- (i) Colourless and odourless.
- (ii) Only ethene have pleasant smell.
- (iii) All are insoluble in water, but fairly soluble in non-polar solvents.

→ Alkenes undergoes Electrophilic substitution :-

(or Electrophilic Addition)

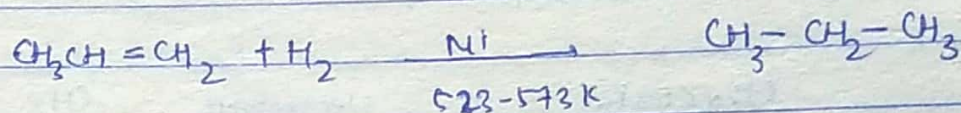
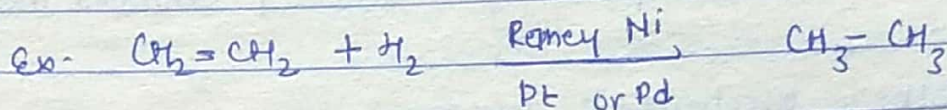
As due to one weak π -bond (251 kJ mol^{-1}) is broken and two strong σ -bond ($2 \times 248 = 496 \text{ kJ mol}^{-1}$)



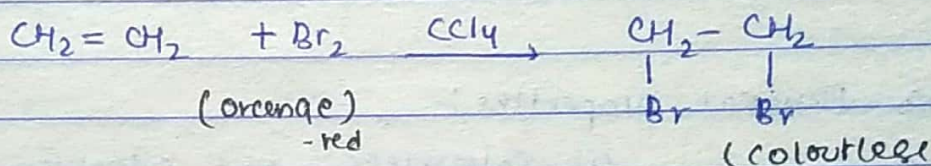
★ Chemical reactions of Alkenes :-

I. Addition reactions:-

(1) Addition of Dihydrogen:-



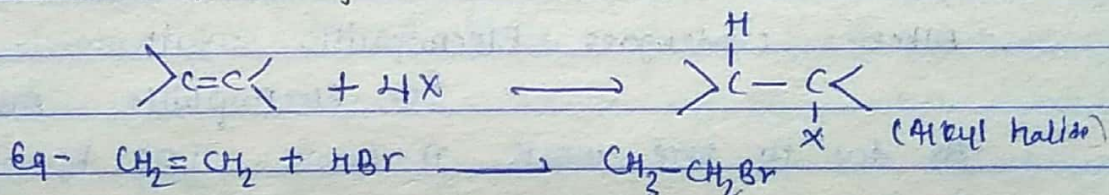
(2) Addition of halogens:-



(This is used for testing unsaturation)

order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

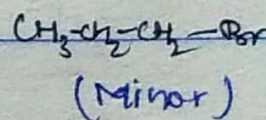
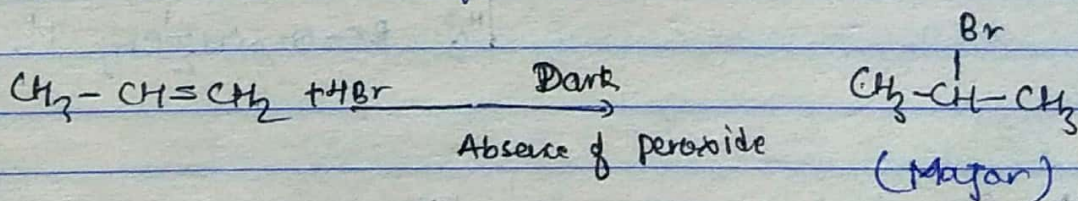
(3) Addition of halogen halides:-



order - $\text{HI} > \text{HBr} > \text{HCl}$.

(Based on Bond dissociation En)

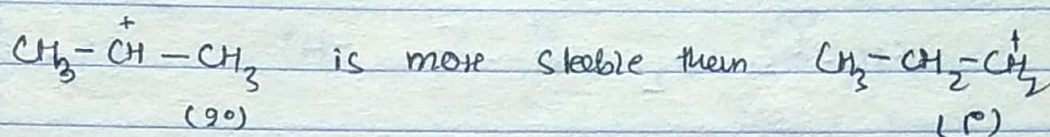
- Addition to a symmetrical Alkene.
- Addition to unsymmetrical Alkene.



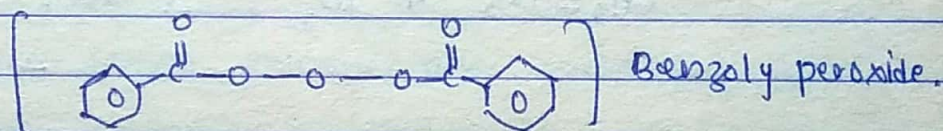
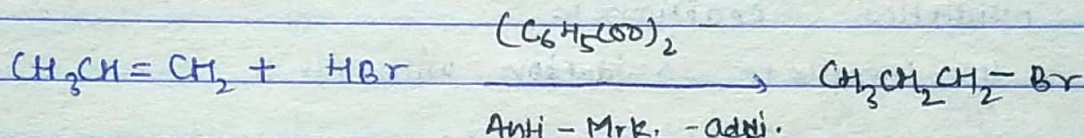
(By Markovnikov rule)

- Markonikov rule :- the halogen atom goes to the carbon atom which has less No. of H-atom

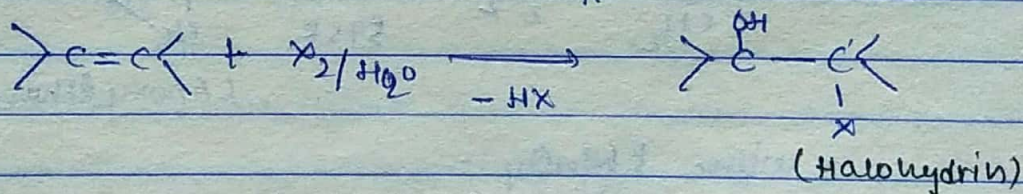
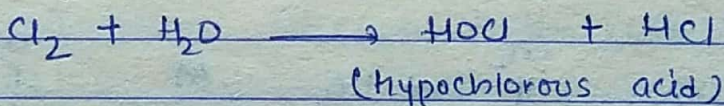
(As due to that the carbocation formed are 2° or 1° ,



- Peroxide or Kharasch effect :-



- (4) Addition of hypohalous acid :-



Order: $\text{HOCl} > \text{HOBr} > \text{HOI}$

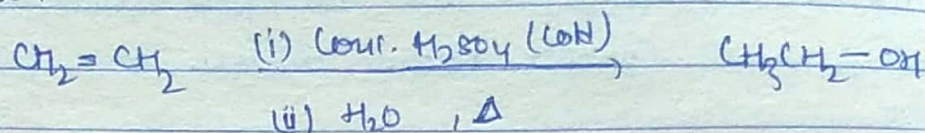
- (5) Addition of H_2SO_4 - Indirect hydration

(Cold, conc. H_2SO_4 added to Alkenes)

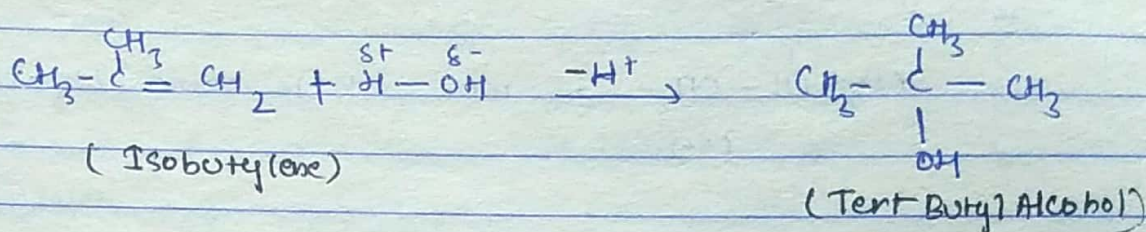


(Ethyl hydrogen sulphate)

- Importance :-

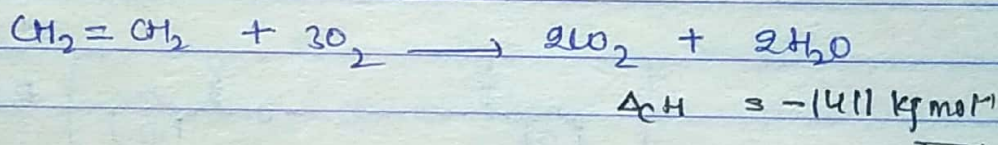


(6) Addition of H₂O - Direct hydration :-



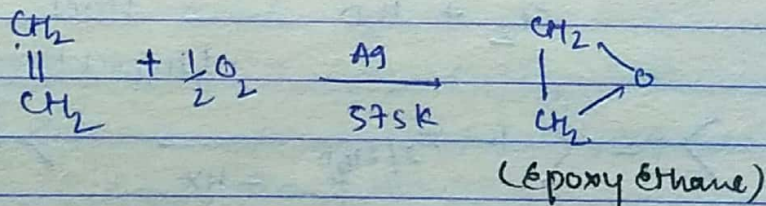
II. Oxidation reactions :-

(1) Complete oxidation with Air :-



(2) Controlled oxidation with oxi. agent :-

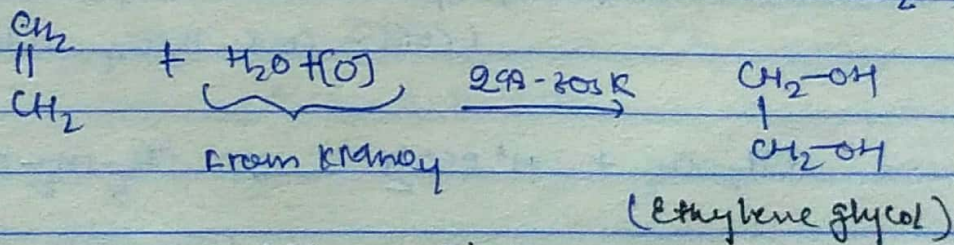
• with oxygen



• with KMnO₄ :-

(i) with cold dilute neutral or alkaline KMnO₄

- hydroxylation -

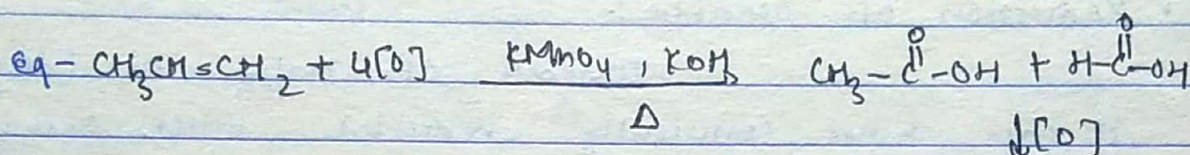
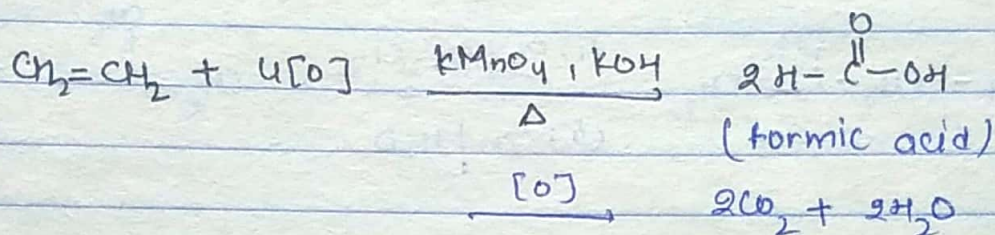


(During this pink colour of KMnO₄ - Discharged .

Brown ppt of MnO₂ formed .

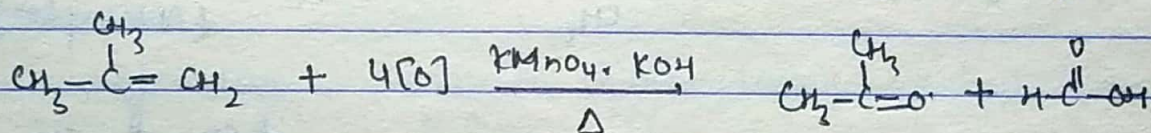
- This is used as test for unsaturation - Baeyer's test!

(ii) with hot KMnO_4 soln :-



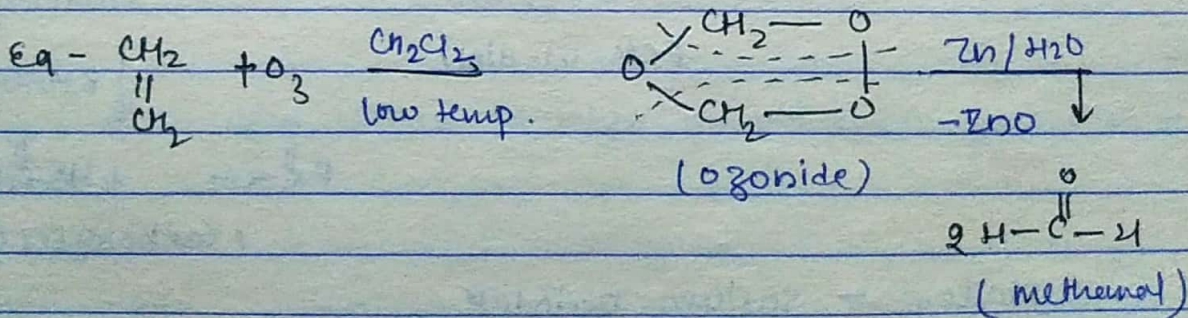
(n-Alkenes form -carboxylic $\text{CO}_2 + \text{H}_2\text{O}$ acids)

(Isobutylene form ketone and Carboxylic acid)



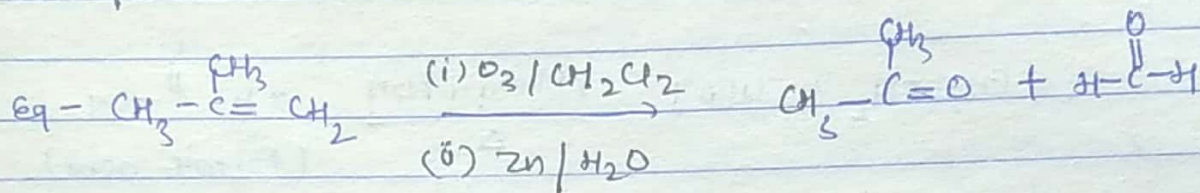
- With Terminal Alkene Both formed.
- with Non-Terminal Alkene Carboxylic acid forms

(iii) Oxidation with ozone :-



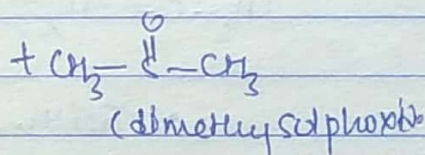
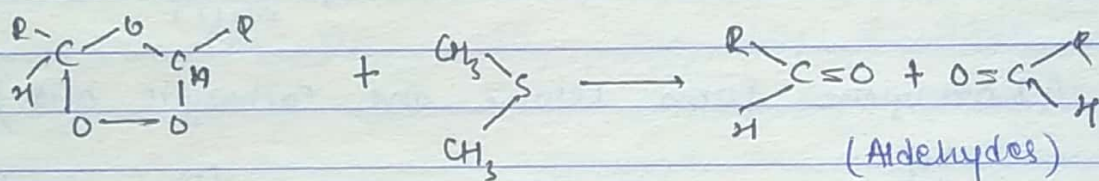
- when propene used, Both ethanal and methanal formed.

- when n-Alkenes used only Aldehydes formed.
- when iso or Neo Alkenes used, Ketone + Aldehyde Both formed.



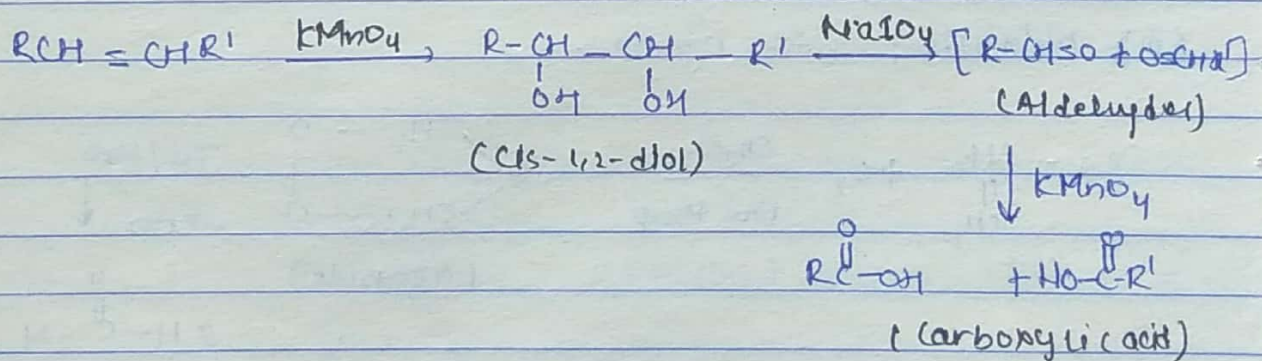
- Reduction of ozonides:-

Instead of Zn/H₂O or (H₂/Pd) it can more conveniently reduced with (CH₃)₂S - dimethyl sulphide.



- Lemieux reagent:-

for oxidation of Alkenes.

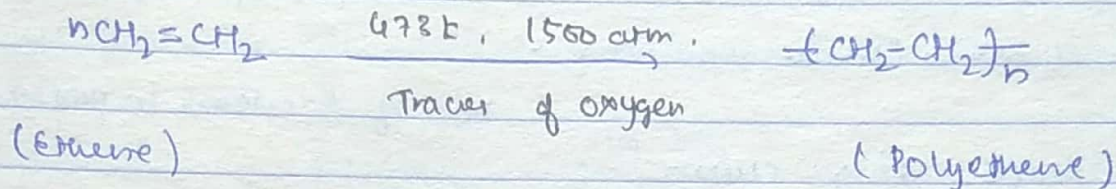


→ NaIO₄ - Sodium periodate

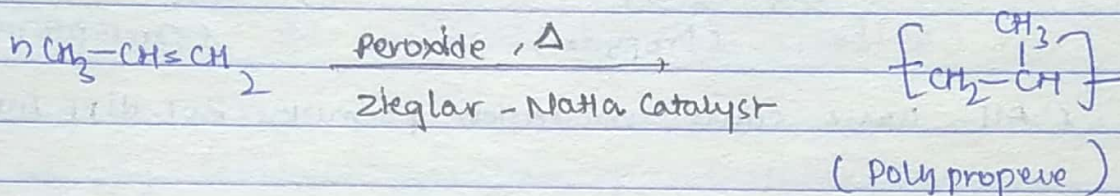
called 'Lemieux reagent'

★ Polymerization reactions :-

(i) Ethene :-



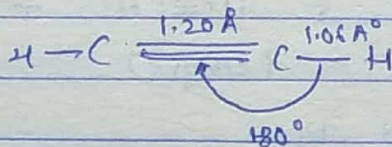
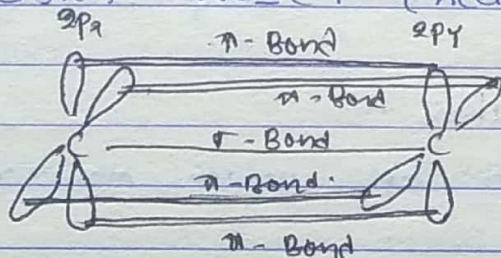
(ii) Propene -



★ ★ ★

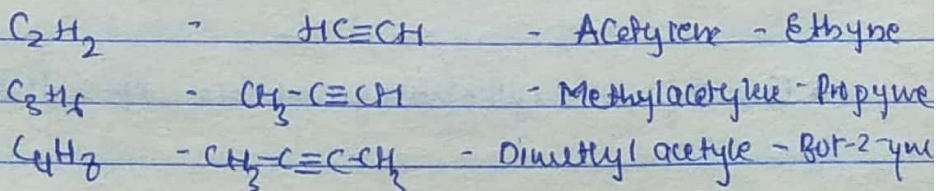
★ Alkynes :-

• Structure :- $\text{HC}\equiv\text{CH}$ (Acetylene) - sp -hybridised.



• Due to its linear structure do not show geometrical iso.

• Nomenclature :-



• Isomerism in Alkynes :-

(i) Position isomerism -

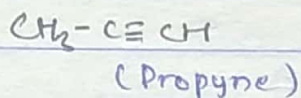
Position of triple Bond.

(ii) Chain isomerism -

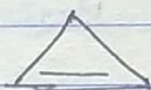
NO. of C-atoms in parent chain.

(iii) Ring chains -

Alkyne show this with cycloalkene.



or

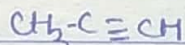


(Cyclopropane)

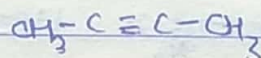
(All have same molecular formulae But diff Arrangement)

• Classification of Alkynes :-

(i) Terminal -

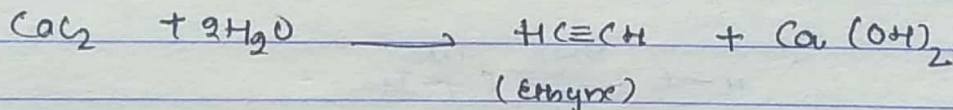


(ii) Non-Terminal -

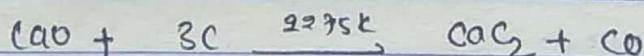
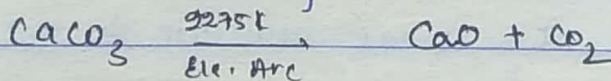


• Methods of preparation :-

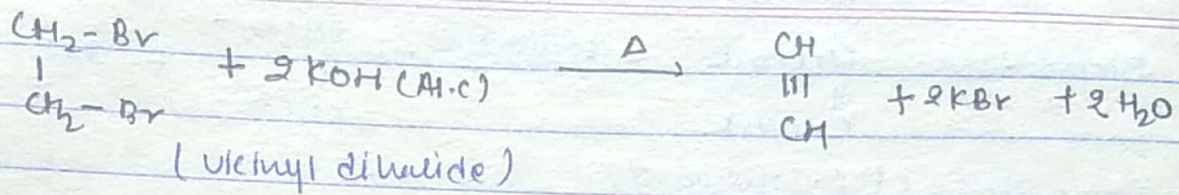
→ (i) By Action of water on Calcium Carbide :-



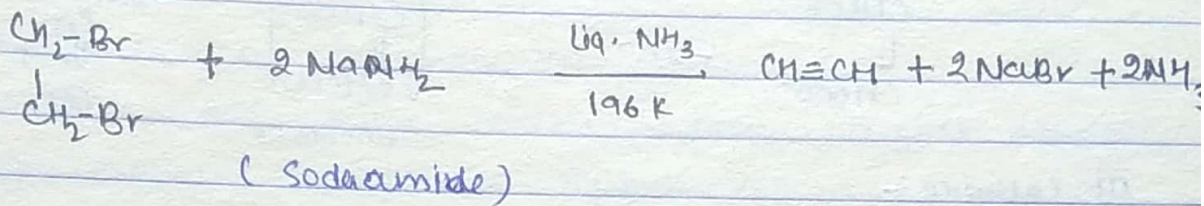
- CaC_2 manufactured by



→ (ii) By dehydrohalogenation of dihaloalkanes.



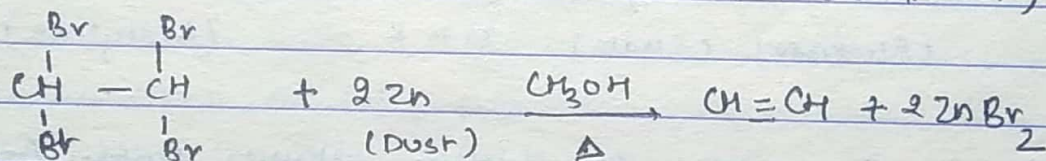
In place of Alc. KOH, liquid Amm. can also be used.



(Also can be prepared by gemdihalide)

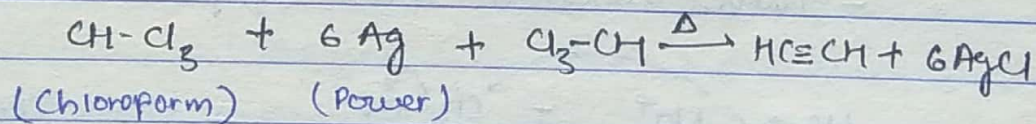
→ (ii) By dehydrohalogenation of Tetrahalides:-

(Tetra haloalkenes)



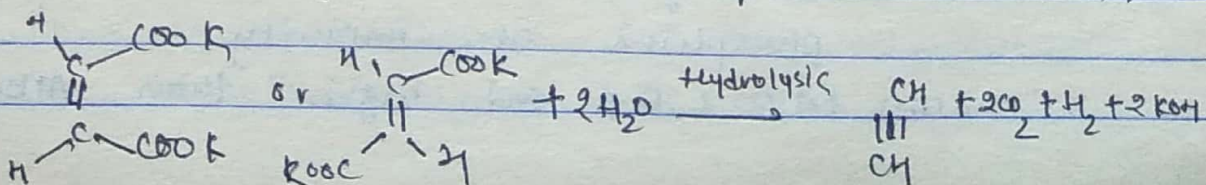
(1,1,2,2-Tetra Bromoethane)

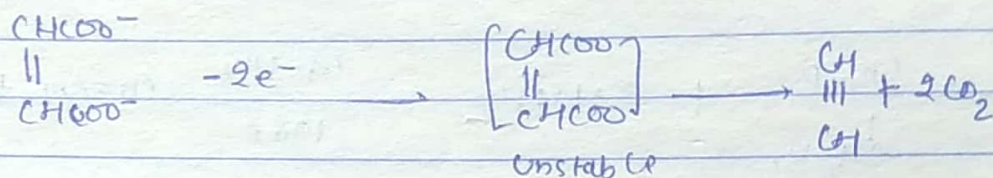
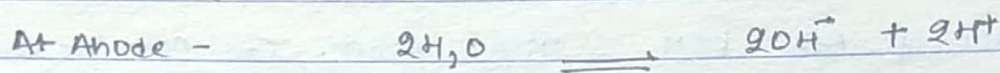
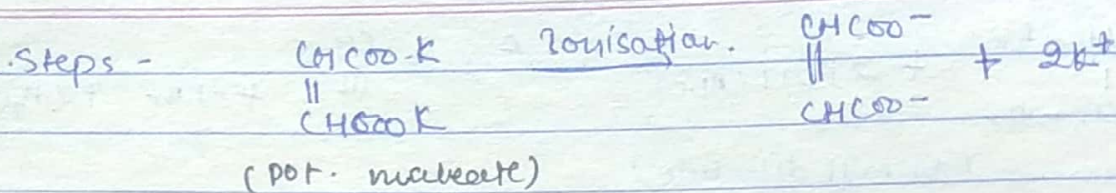
→ (iii) Dehalogenation of haloforms:-



→ (iv) Kolbe's Electrolytic reactions:-

(By Electrolysis of Conc. soln of sodium & potassium salts of maleic acid)

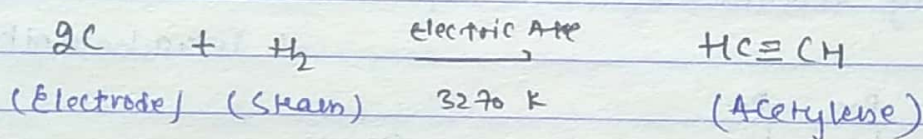




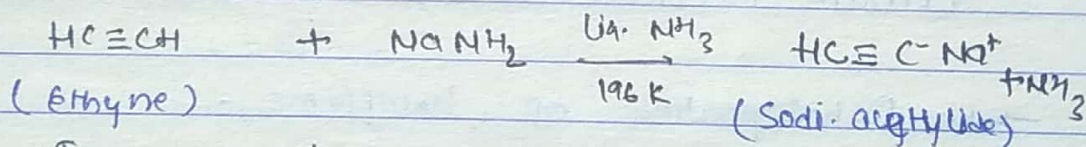
At Cathode -



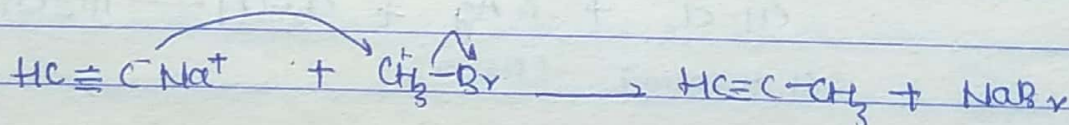
→ (vi) Berthelot synthesis - from Carbon & Hydrogen :-



→ (vii) Synthesis of higher alkynes from Acetylenes :-



- Then reaction with Alkyl halide -



* Physical properties :-

(i) These are colourless, odourless, acetylenic

- As garlic smell due to presence of phosphine as impurity

(ii) M.P & B.P and higher than Alkene.

- As due to (linear structure form or more closely bonded).

(iii) Being non-polar insoluble in water but slightly in non-polar solvent as (Benzene, CCl_4)

★ Reactivity of Alkynes vs Alkenes :-

Alkenes are more reactive than Alkynes toward electrophilic addition reaction.

(i) Due to greater s.ch of sp-hybridised C-atom it held more tightly the π -electrons.

(ii) Due to the cylindrical nature of π -electron cloud in Alkynes, they are more delocalised.

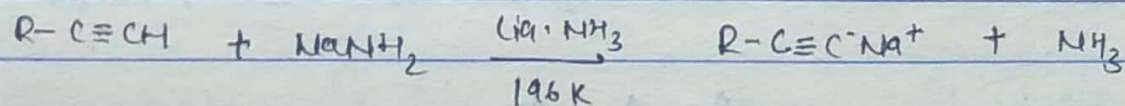
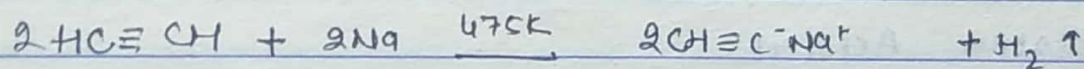
★ Chemical reactions of Alkynes :-

(i) Acidic character of Alkynes :-

The hydrogen attached to Alkynes are more acidic than of Alkene and Alkane, 'Acetylenic hydrogen are acidic in nature'.

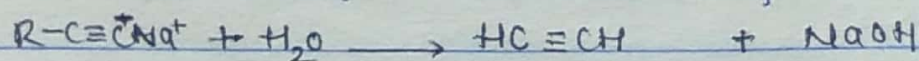
• Formation of Alkali metal Acetylides :-

(Ethyne and other terminal Alkynes)

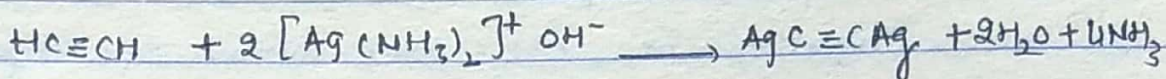


(Rise loses its hydrogen and forms stable carbanion)

• H_2O is more stronger acid than Alkynes :-



- Formation of heavy metal Acetylides :-
(H⁺ also replaced by Cu⁺ Ag⁺ ions)



(Tollen's reagent)

(white ppt.)

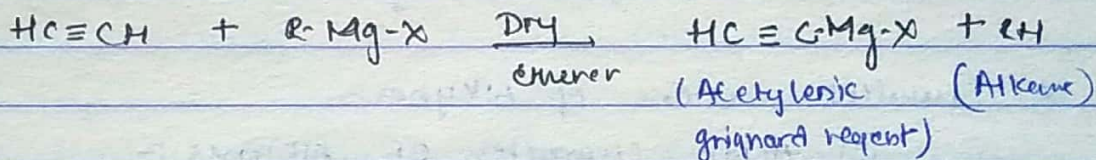
- Ammonical Silver Nitrate soln.

(when amm. cuprous chloride soln used - Red ppt.)

- Stronger Acids than H₂O.

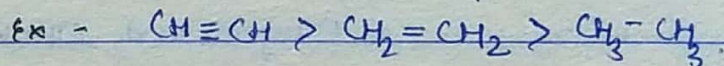


- Formation of Alkynyl Grignard reagent :-

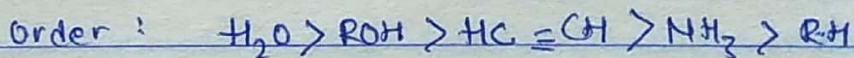


{ These reactions used to distinguish b/w terminal & non-terminal alkynes. }

- Electronegativity order: $\text{sp} > \text{sp}^2 > \text{sp}^3$



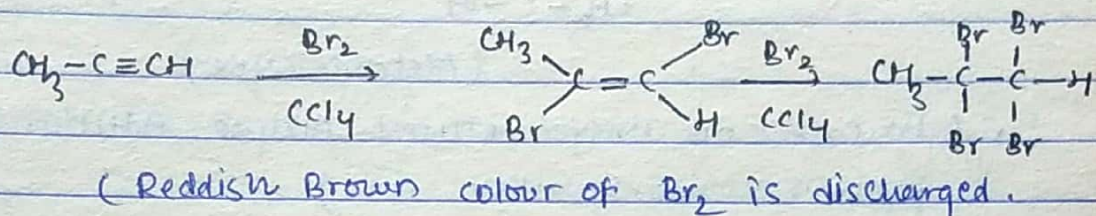
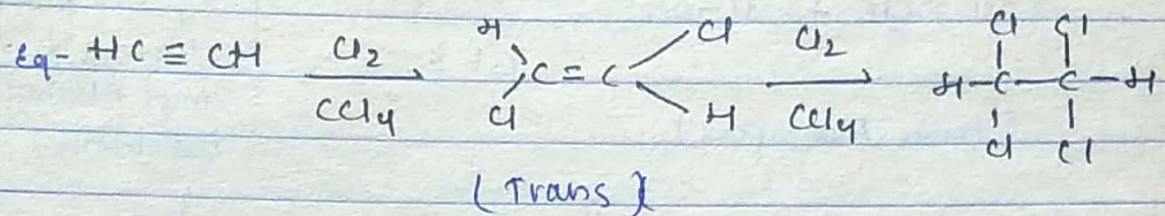
- Relative Acidities :-



★ ★ ★

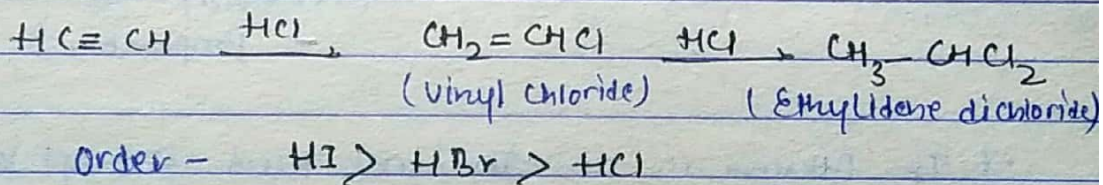
(II). Electrophilic Addition reactions:-

(i) Addition of Halogens:-



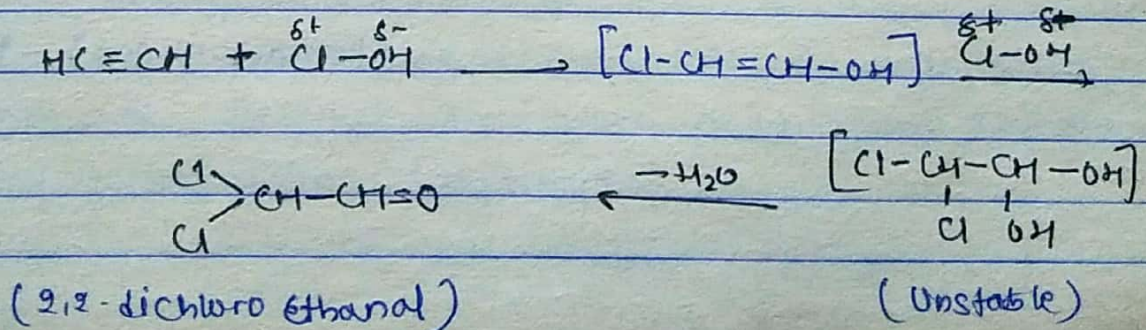
• Order of reactivity :- $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$

(ii) Addition of halogen halides:-



Stability \rightarrow (1° Carbocation $<$ 2° Carbocation)

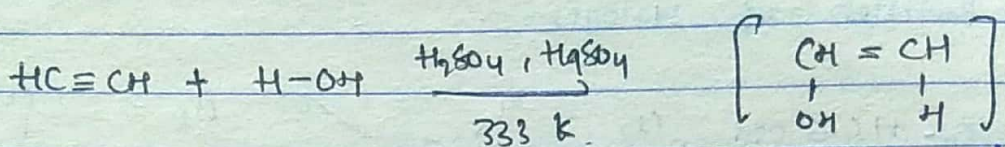
(iii) Addition of Elements of hypohalous acid:-



Reactivity toward Electrophilic Substitution:-

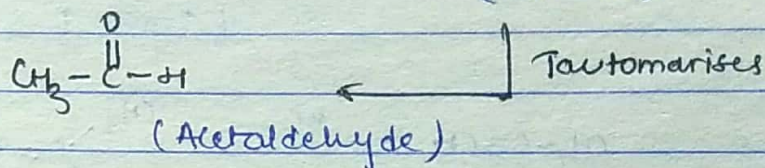
Alkenes > Alkynes.

(iv) Addition of H_2O - Hydration -

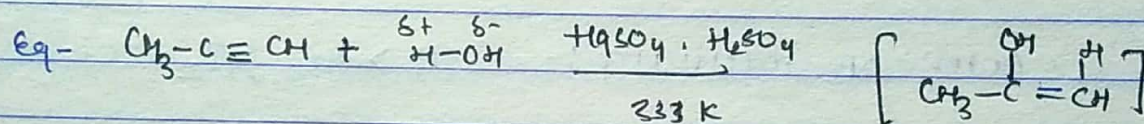


(Form Aldehydes)

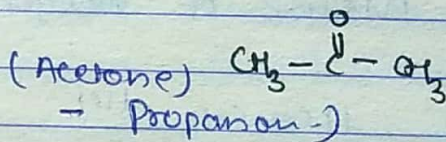
(Vinyl Alcohol)
(Unstable)



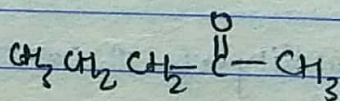
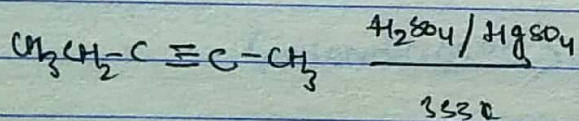
• (in case of unsymmetrical Alkyne Addition of $-OH$ group follows Markovnikov rule)



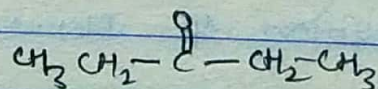
Tautomerises ↓



• (If Alkyne is non-terminal then Methyl ketone predominates)



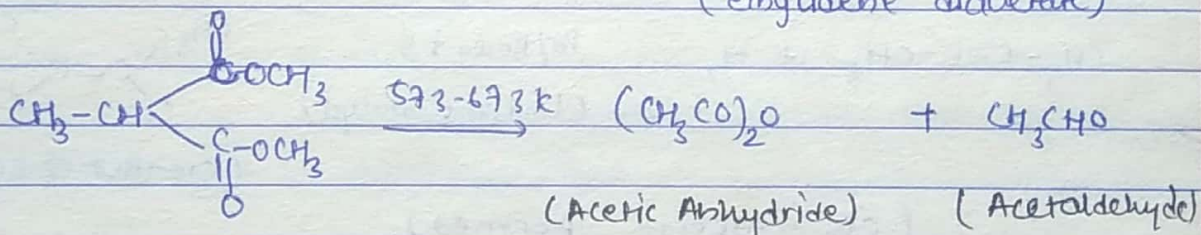
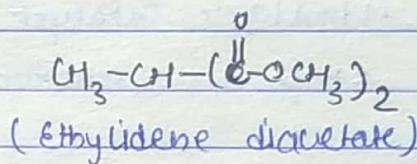
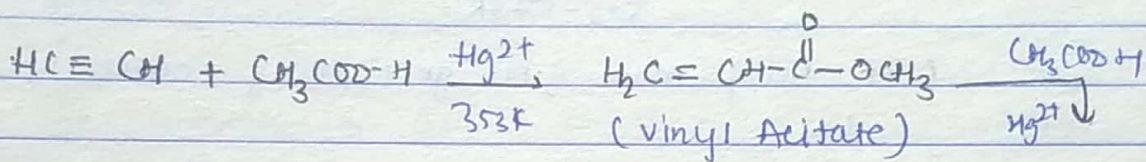
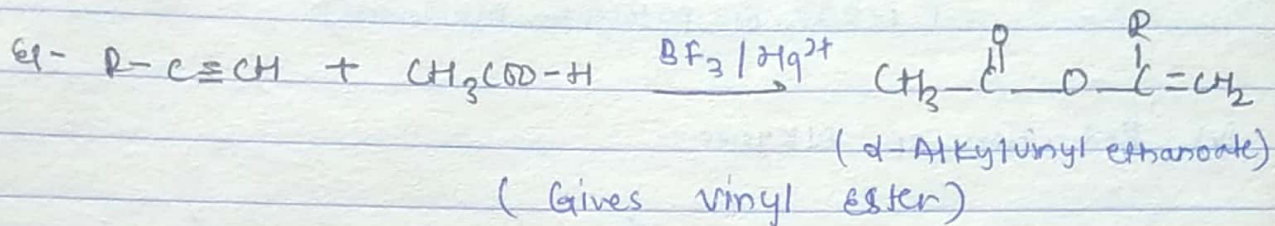
(Pentan-2-one) - Major



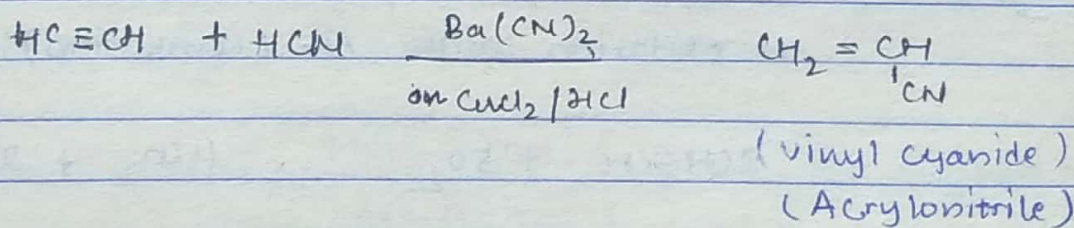
(Pentan-3-one) - Minor

(v) Addition of Carboxylic Acids :-

(In presence of Lewis Acid)



(vi) Addition of Hydrogen Cyanide



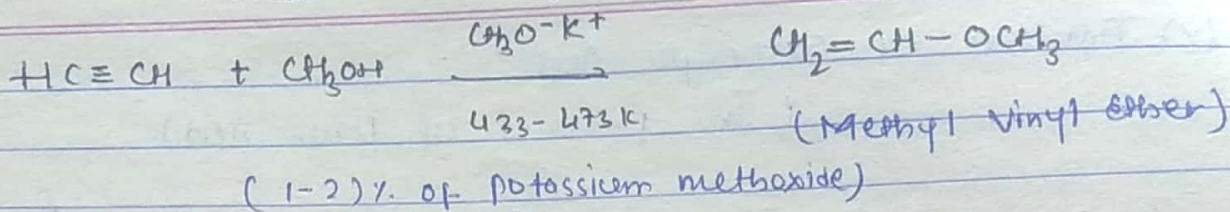
(III). Nucleophilic reactions :-

As due to more E.N., sp-hybridised C-atom of Alkynes are more predominant than Alkene for nucleophilic substitution.

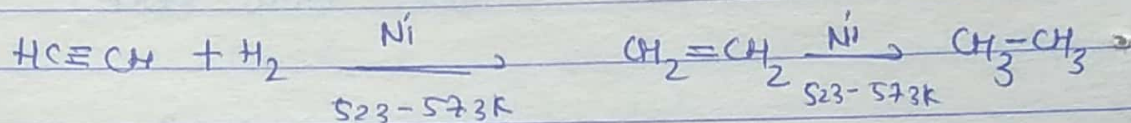
• Birch reduction used for non-terminal Alkynes

(Na or Li in liq. NH_3 , 196-200 K)

• Trans Alkene formed.

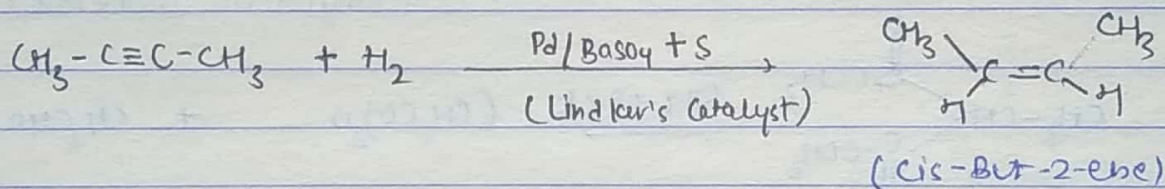


iv) Reduction of Alkynes :-



(It being more s.n. gets easily reduced)

• Lindlar's Catalyst: (Pd/BaSO₄ + S or quinoline) used to stop the reaction at specific state to form Alkene.



(Cis - Alkene formed)

v) Oxidation reactions of Alkynes :-

(i) oxidation with Air (Combustion) :-



(ii) Oxi. with cold dil. potassium permanganet :-

(Alkynes oxidised by Alkaline KMnO_4 to α -dicarbonyl

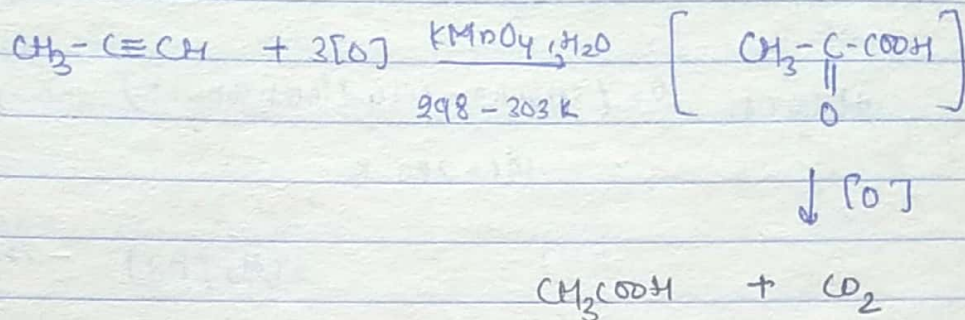
• In case of terminal Alkyne (comp.)

- $\equiv\text{CH}$ oxidise to $-\text{COOH}$

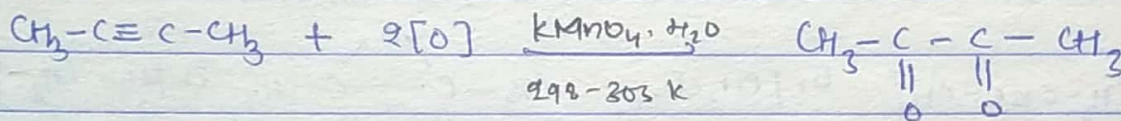
• For Non-Terminated Alkyne -

- $\equiv\text{C}-\text{R}$ oxidised to $-\text{C}(=\text{O})-\text{R}$

Eq- Terminal-



Non-Terminal-



- Pink colour of KMnO_4 discharged and a brown ppt. of MnO_2 formed.

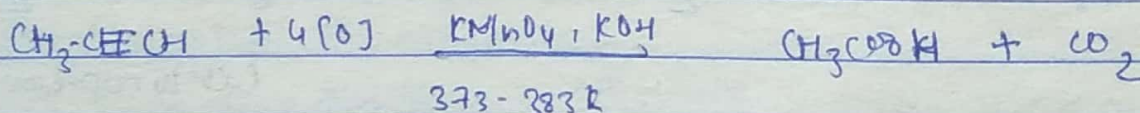
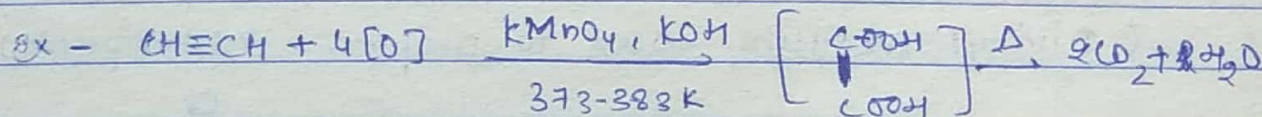
This reaction used as test for unsaturation - Bayer's Test.

(3). Oxi. with Hot KMnO_4 :-

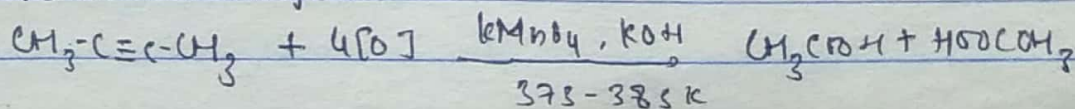
($\text{C}\equiv\text{C}$, Bond cleavage)

$\equiv\text{CH}$, is oxidised to CO_2 and H_2O

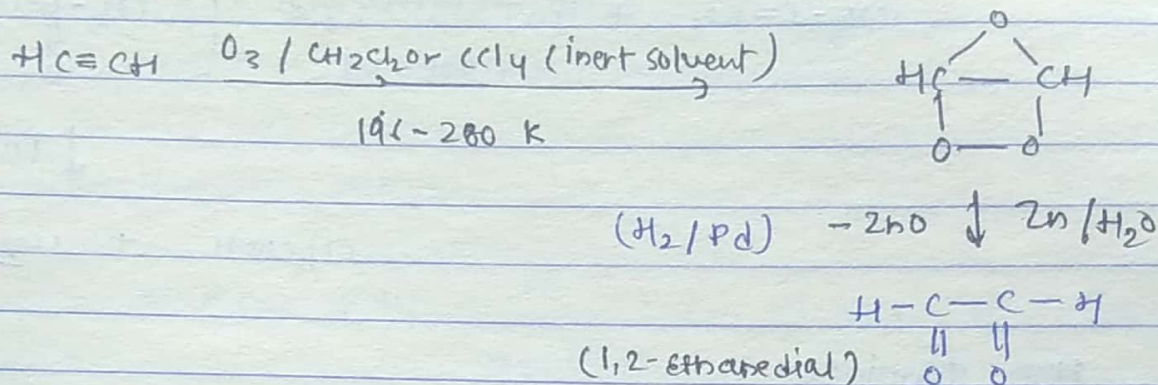
$\equiv\text{CR}$ is oxidised to RCOOH .



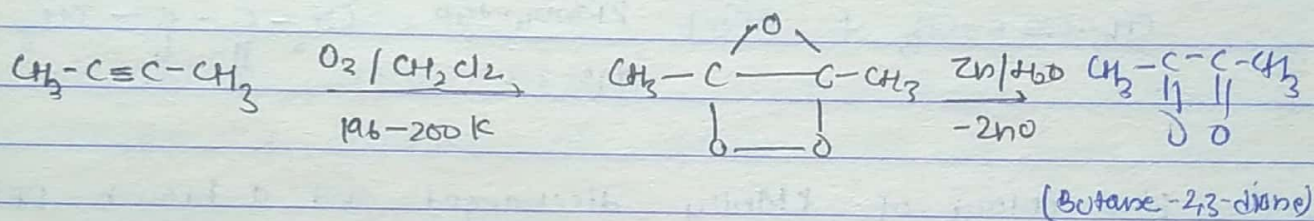
• Non Terminal Alkyne:-



(u) oxi. with ozone :-

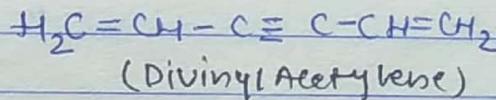
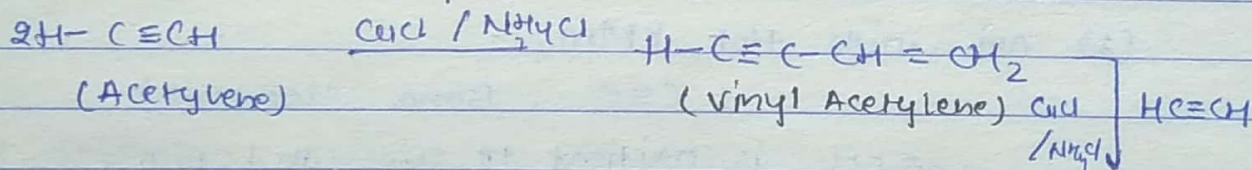


For Non Terminal :-

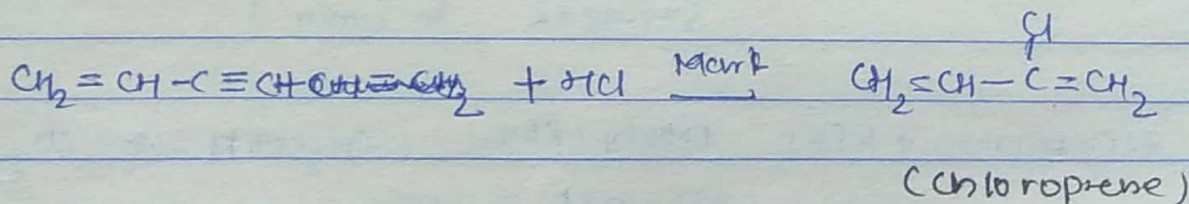


vii) Polymerization reaction of Alkynes :-

(a) Linear polymerisation :-

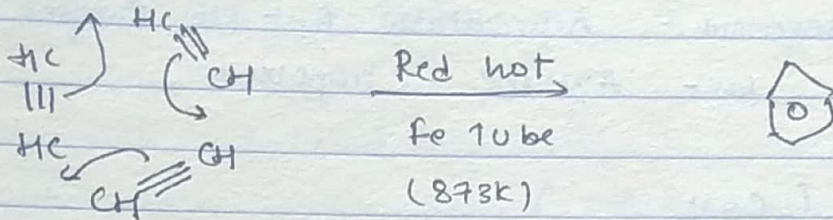


(Divinyl Acetylene used to prepare Chloroprene)

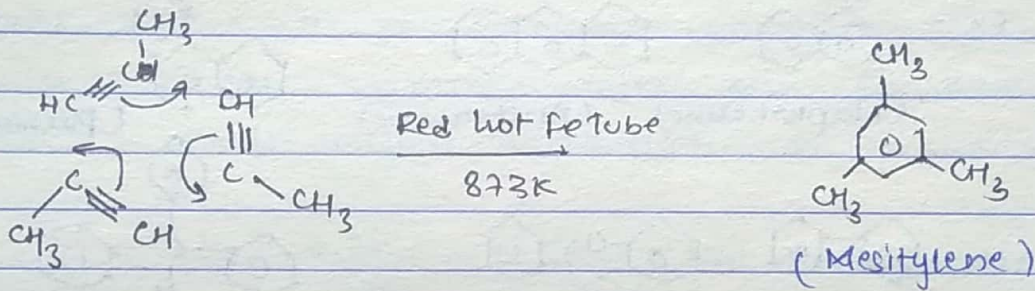


(B) Cyclic polymerization:-

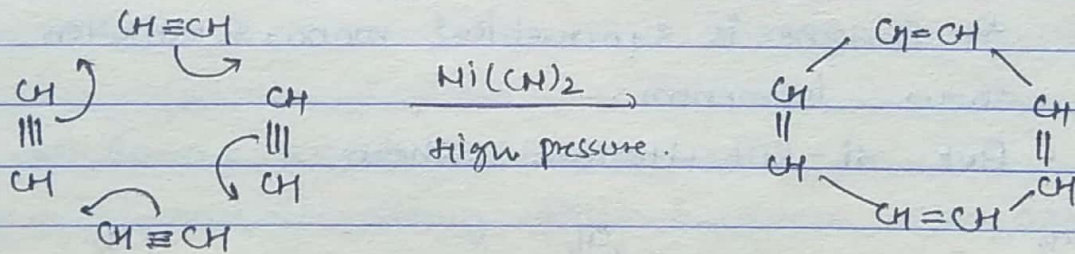
(i) Ethyne passed through red hot iron tube at 873K, it trimerises to give benzene.



• Propyne :-



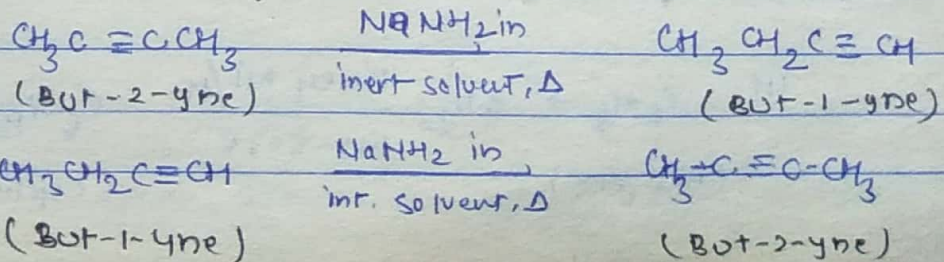
(ii)



(4 ethyne)

(cycloocta-1,3,5,7-Tetraene)

vii) Isomerization of Alkynes:-



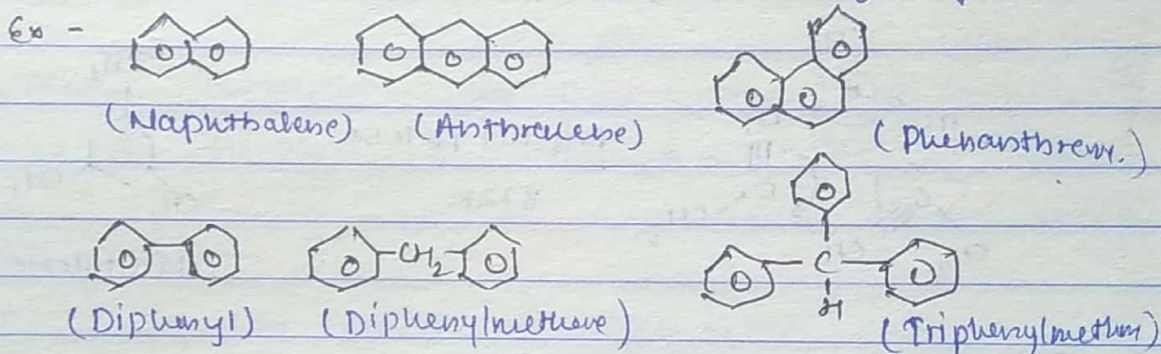
- [ARENES] -

A. Aromatic hydrocarbon:-

- Benzeneoid :- hydrocarbons that contain Benzene ring.
 - Non-Benzeneoid :- Aromatic but No Benzene ring.
- Ex - Azulene, tropolene

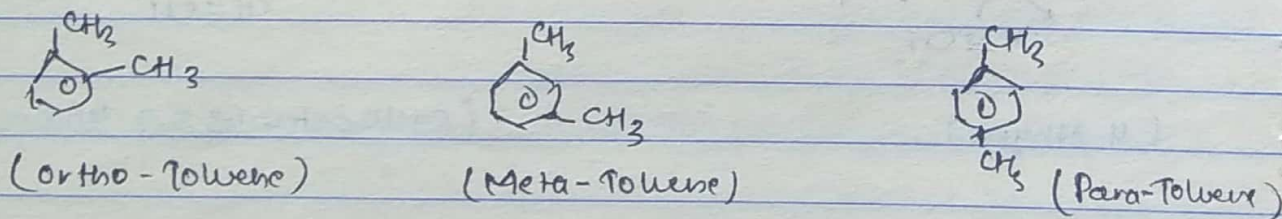
→ Classification :- (C_nH_{2n-6m})

$\left\{ \begin{array}{l} n \text{ is NO. of C-atoms} \\ m \text{ is NO. of rings} \end{array} \right\}$

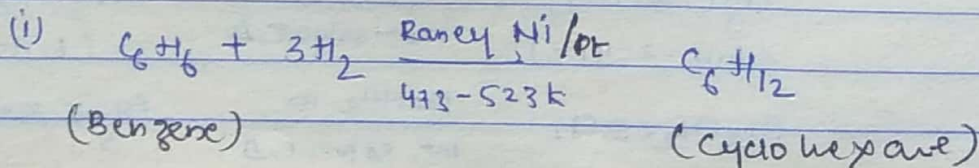


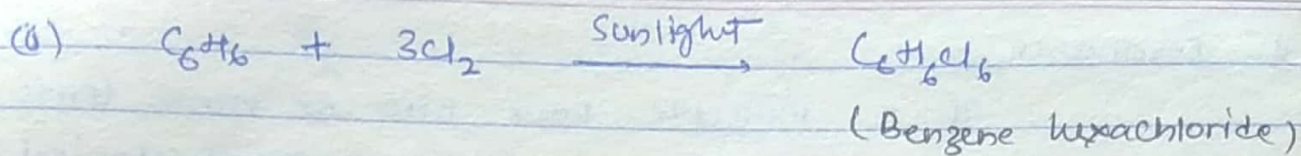
→ Isomerism :-

- As Benzene is symmetrical mono-substitution, do not show isomerism.
- But di-substitution show :-

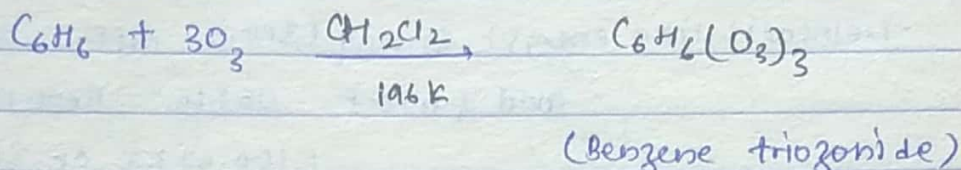


→ Structure of Benzene :- (C_6H_6)





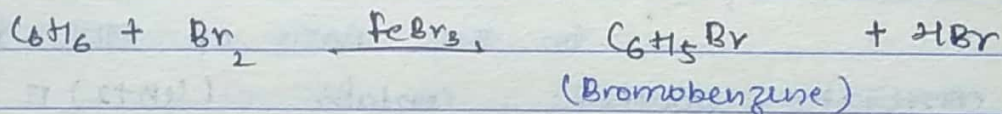
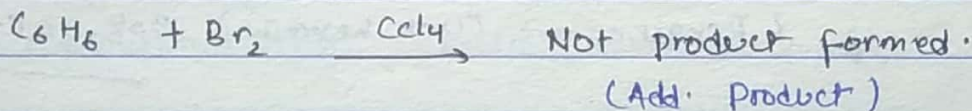
(ii) forms Triozonide with O_3



• Benzene behaves as a saturated compound :-

(i) Undergoes substitution rather than addition :-

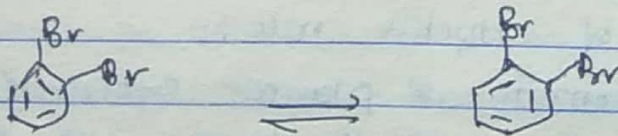
- It doesn't decolourise Br_2 in solⁿ of "CCl₄".



(ii) Benzene is oxi. resistant :-

- It slowly oxidised even when oxidising agents, as Chromic acid, $KMnO_4$ and form CO_2 & H_2O , when these used.

• According to Kekule the position of double bonds are not fixed. It oscillates.



(These two structures are in dynamic equ.)

• As Benzene is symmetrical - Its dipole moment is 0

* Resonance :-

If a molecule, have two or more Lewis structures, diff. in position not relative position - 'Canonical structures'.

• Delocalisation energy :- Energy (Int.) diff. b/w resonance hybrid and of most stable Resonance Structure.
(150.62 KJ or 36.0 Kcal) / mol

• Heat of hydrogenation :- The amount of heat evolved when one mole of an unsaturated comp. hydrogenated (in presence of catalyst)

(Benzene \rightarrow Cyclohexane) 208.36 KJ mol⁻¹

* Aromaticity or Huckle rule :-

On the Basis of MOT, If cyclic conjugated polyenes contain $(4n+2)$ π -electrons and completely delocalised. All such comp. are "Aromatic".
(n = 0, 1, 2, 3, ...)

rules for Aromaticity :- (i) should have cyclic cloud of delocalised π -electrons.

(ii) Ring should be planar, as it allow cyclic overlap of p-orbital.

(iii) should contain $(4n+2)$ π electrons.

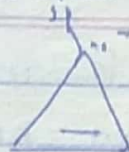
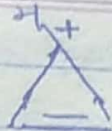
\rightarrow Applications of Huckle rule :-

(For Aromatic, a planar system (cyclic) should have, 2, 6, 10, 14, 18 etc. π -electron)

• Only having a single cyclic π -electron cloud.

(i) monocyclic system :- (Homocyclic)

Ex -



Cyclopropenyl cation

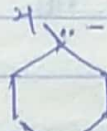
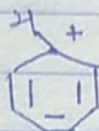
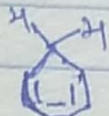
Cyclopropenyl anion

- 2 π - electron

4 π - electron

(Aromatic)

(Non-Aromatic)



(6 π - electron)

(6 π - electrons)

(8 π - electrons)

Not spread in all over ring.

Spread over the ring

(Non-Aromatic)

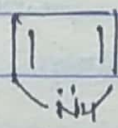
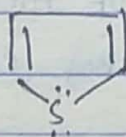
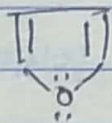
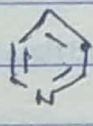
(Aromatic)

(Non-Aromatic)

Cycloheptatrienyl (cation & anion)

(ii) Heterocyclic comp. (Heterocyclic) :-

(Contains other than C-atom also)



(Pyridine)

(Furan)

(Thiophene)

(Pyrrole)

All have 6 π -electrons, delocalised so All are 'Aromatic'.

"As in pyridine, each of five sp²-hybridised, and N-atom have p-orbital perp. to plane, each C-atom produces one π -electron, form cyclic 6 π -electron cloud but the lone pair on N-atom present in

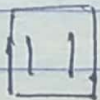
sp^2 -orbital, which is in plane of ring so do not contribute towards Aromatic sextet.

And for other, in cases of furan, thiophene and pyrrole one of the two lone pairs contribute in plane of ring.

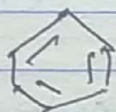
• "Hence All are Aromatic in nature".

• Annulenes :- These are completely conjugated monocyclic polyenes containing even No. of C-atom -

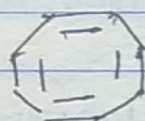
• Formulae - $(CH=CH)_n$, $n = 2, 3, 4, 5, \dots$



[4]-Annulene
(Cyclobutadiene)



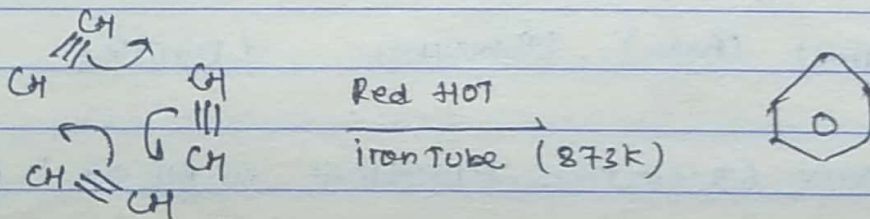
[6]-Annulene
(Benzene)



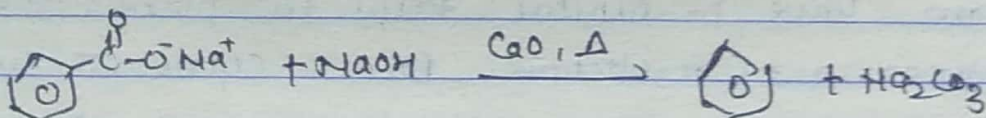
[8]-Annulene
(Cyclooctatetraene)

★ Methods of preparation of Arenes :-

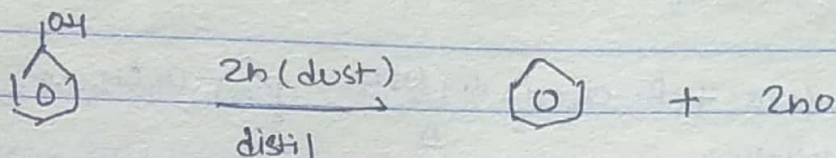
(i) From Ethyne By cyclic polymerization :-



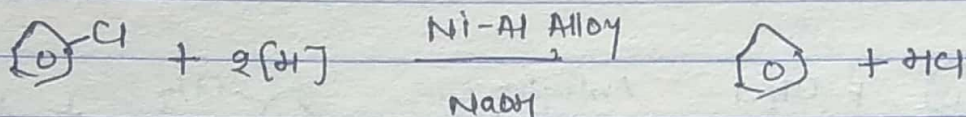
(ii) From Sodium Benzoate by decarboxylation with CaO - Li



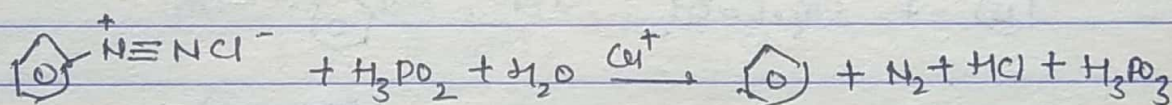
(iii) From phenol by reduction with Zn dust :-



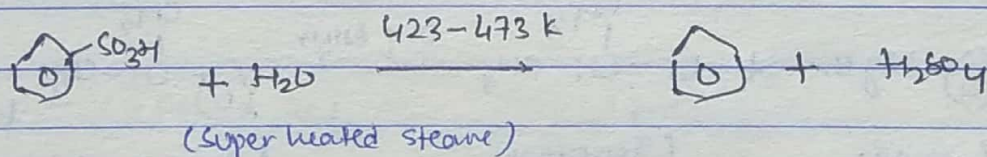
(iv) from Chlorobenzene by reduction with Ni-Al Alloy / NaBH₄ :-



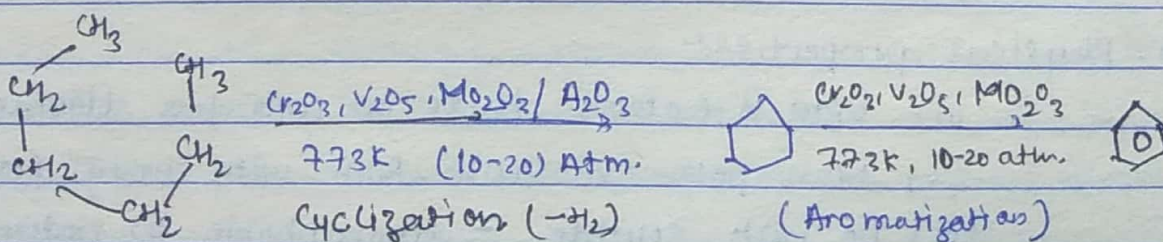
(v) From Benzene diazonium chloride by Reduction with hypophosphorus acid (H₃PO₂) in presence of Cu⁺ ion :-



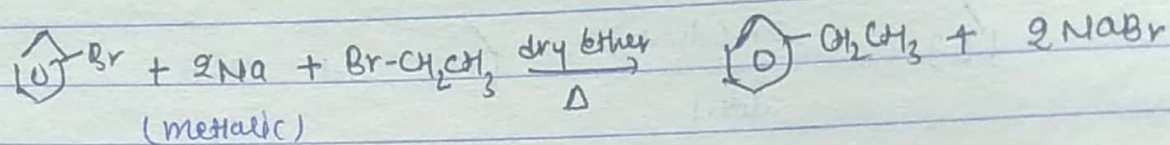
(vi) from Benzene sulphonic acid by heated with superheated steam :-



(vii) from n-hexane or n-heptane :-

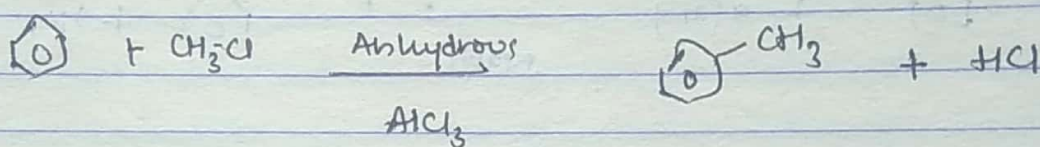


vii) Wurtz-Fittig reaction:-

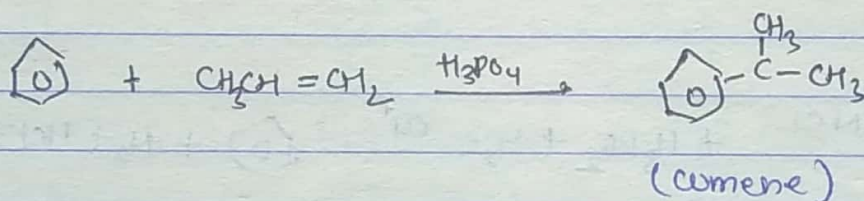


viii) Friedel-Crafts reaction:-

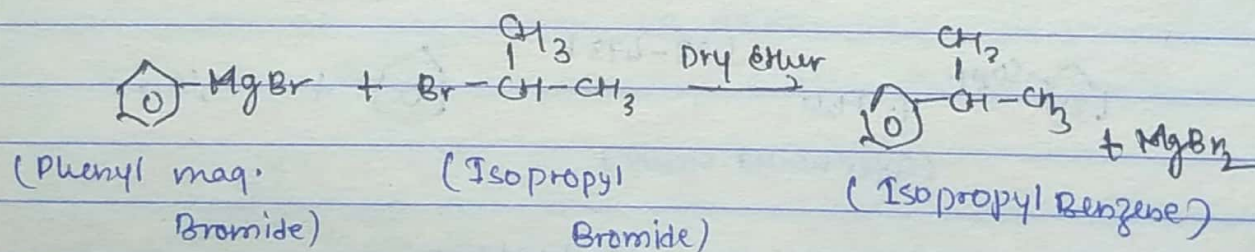
(Benzene react with Alkyl halide in presence of Lewis acid)



- Alcohols Also used in place of Haloalkene.
- Also Carried with Alkenes.



ix) From Grignard reagent:-



A. Physical properties:-

- Upto 8-carbons these are colourless liquids
- Non-polar molecule, Burn with sooty flames.
- Do not soluble - Hydrophobic in nature.
- m.p increase with increase in molar mass. in o,m,

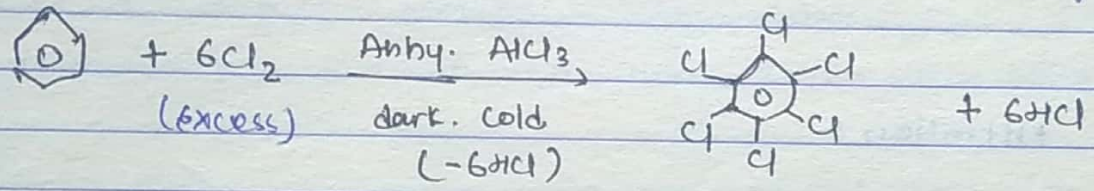
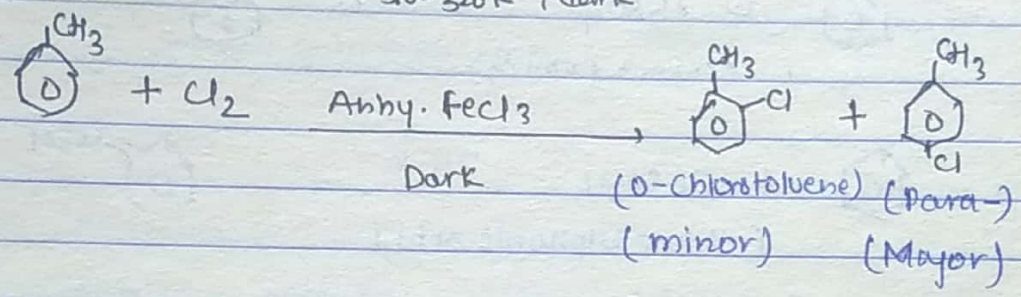
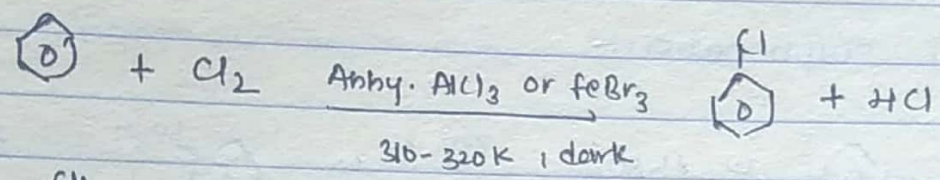
p-xylene. p have highest m.p. Due to symmetry.

Alkenes < Alkynes < Alkenes < Alkyne - Reactivity, order,
 (As due to delocalization of π -Electrons - Extra stability.

4. Chemical reactions of Aromatics:-

(I) Substitution or replacement reactions:-

(1) Halogenation:-



• Lewis acid carry the halogen to aromatic hydrocarbon, "halogen carriers".

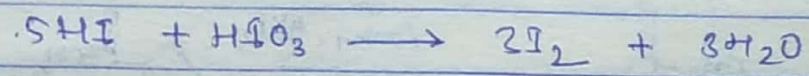
(Chlorobenzene is formed when Benzene is treated with chlorine in presence of iron)

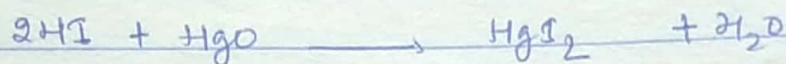


• Direct iodination:-

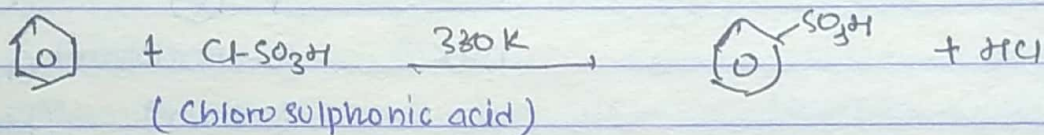
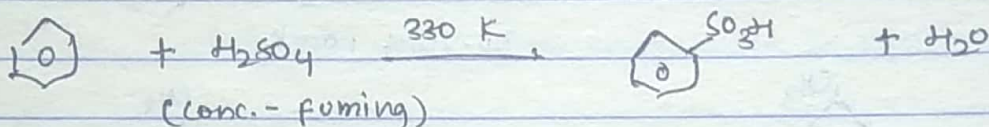


this HI produced, reduces the Aryl iodide back to Arom
 → The oxidising agent; oxidise the HI produced to Iodine to HgI_2 , thus reaction proceed in forward direction.

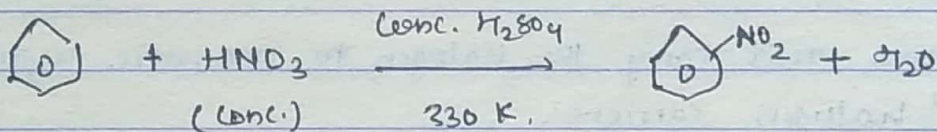




(ii) Sulphonation:-

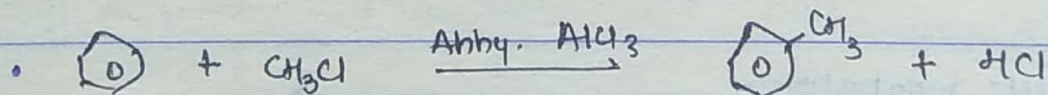


(iii) Nitration:-

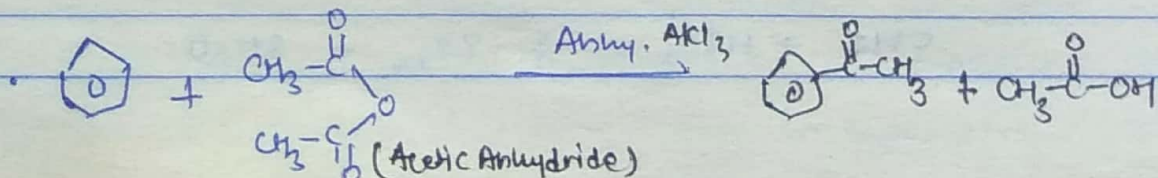
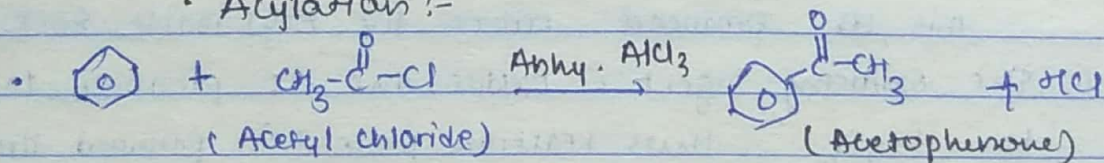


(iv) Friedel-Crafts reaction:-

• Alkylation:-



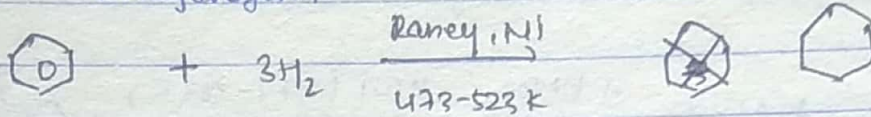
• Acylation:-



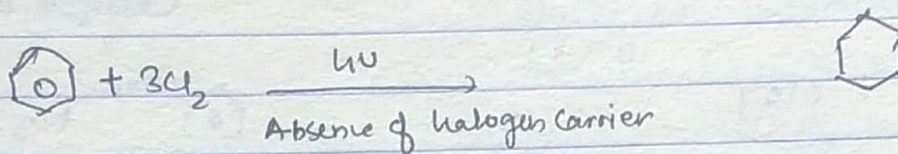
- presence of halogen carrier + Dark \rightarrow Substitution reacⁿ
- Absence of halogen carrier + sunlight \rightarrow Addition reacⁿ.

(II) Addition Reaction:-

- Dihydrogen:-



- Halogen:-



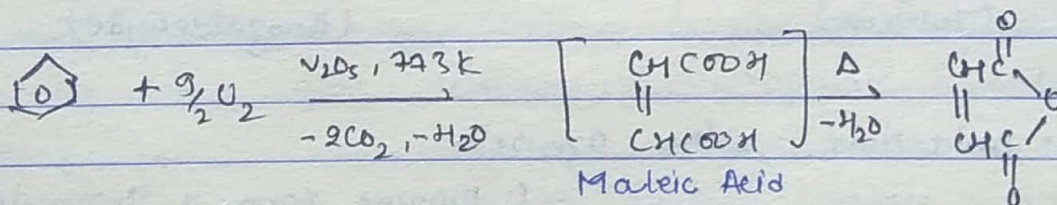
(III) Oxidation Reaction:-

- Complete oxidation - combustion
(On burning, give CO_2 + H_2O with yellow sooty flame)



($\Delta H^\circ_{\text{c}} = -3600 \text{ kJ mol}^{-1}$)

- Controlled oxidation with Air:-



Maleic Acid

(Maleic Anhydride)

- with Alkaline KMnO_4 :-
- Cold dil. KMnO_4 do not oxidises Aromes, (Baeyer's reagent)
this reaction used to distinguish b/w Aromes
and Alkynes and Alkenes.

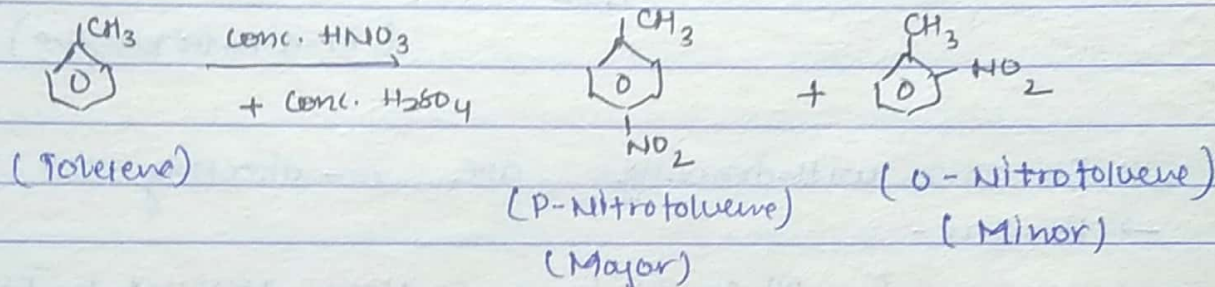
(See the Mechanisms at 13/62)

★ Directive influence of substituents and their effect on reactivity :-

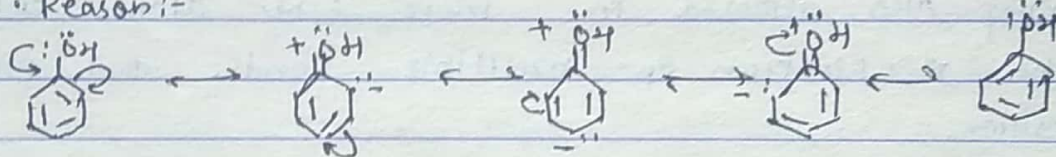
(i) O, p - directing group :-

Directs the incoming group to o, p.

Ex- $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{C}_6\text{H}_5$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OH}$, $-\text{OCH}_3$,
 $-\text{NH}_2$, $-\text{NHCH}_3$, $-\text{N}(\text{CH}_2)_2$, $-\text{NHCOCH}_3$.



Reason :-

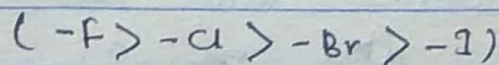
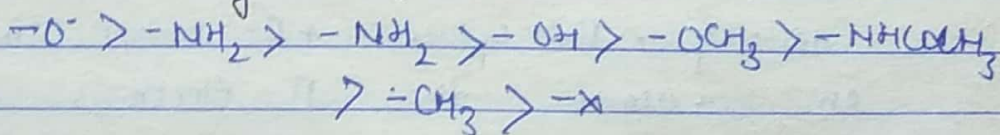


(As Electron density is high at o, p position.)

As these groups increase electron density in benzene ring thus the ring gets activated, so electrophilic substitution is easy.

These groups also called 'Electron donating group'.

Order of electron donating ability :-



• EWG - Activates the ring.

• EDG - Deactivates the ring.

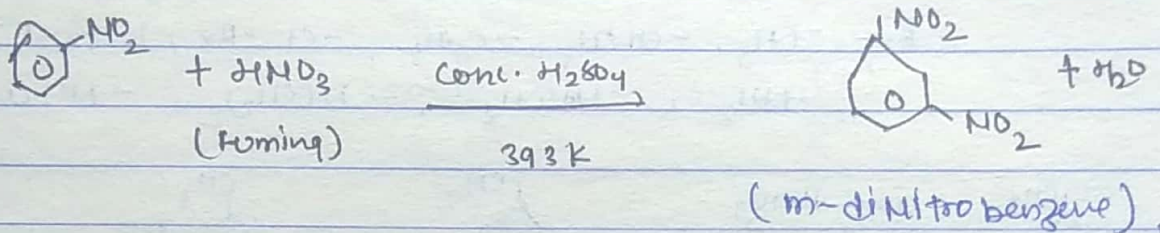
(Halogens deactivates the ring - $-I$ - Effect)

(ii) Meta - Directing group:-

which directs the incoming group

to m- position.

Ex - $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $-\text{CF}_2$, $-\text{CHO}$, $-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$
 $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$ etc.



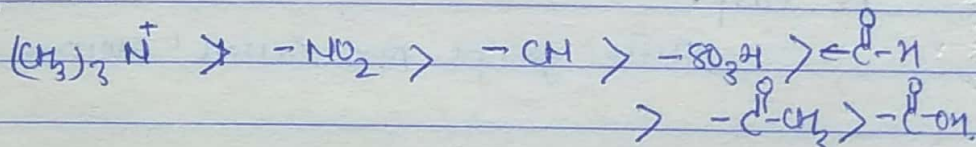
• Electron withdrawings are m-directing.

→ Reason -

As All groups have C-atom attached to Benzene ring ALSO attached to more E.N. atom, which pulls the π -electron of multiple bonds. and from nuclear position.

The decrease is much more at o, p not at meta. Now the electron density is high at m-position, so electrophile will attack at m-position.

• EWG's ability order:-



• Halogens show $-I$ - Effect and decrease the electron density. BUT by the $+R$ - Effect the lone pairs on X-atom the π -electrons comes in conjugation and the electron density increases at o, p - positions.

(Halogens are deactivating BUT o/p - directing group)