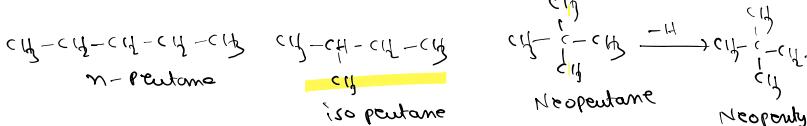
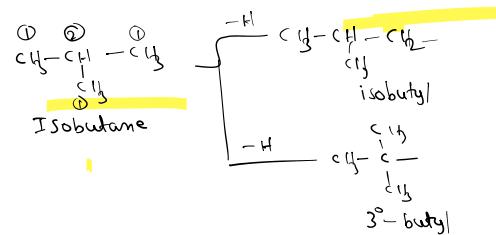
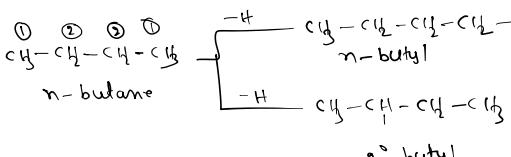
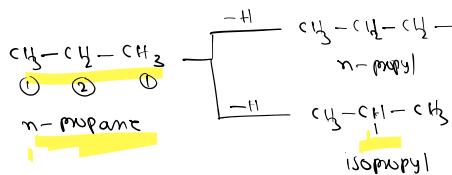
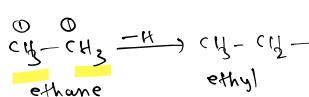
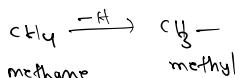
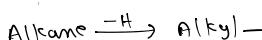
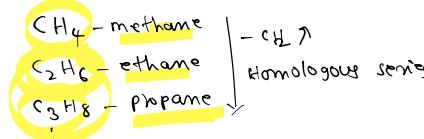
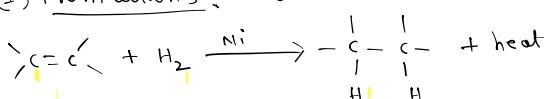


* Alkanes $\text{f C}_n\text{H}_{2n+2}$



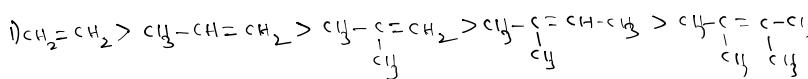
* Preparations of alkanes

(I) From alkenes :— Hydrogenation - Sabatier-Sondreyen's reaction

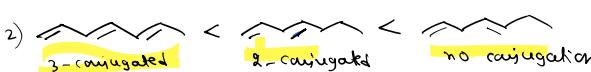


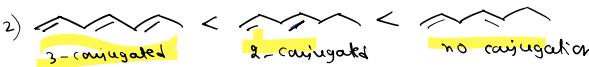
$$\Delta H_{\text{hydrogenation}} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{Hyperconjugation}} \propto \frac{1}{\text{conjugation}}$$

DH hydrogenation of



no. of α -H \uparrow , H-C \uparrow , stability \uparrow , rate of hydrogenation \downarrow



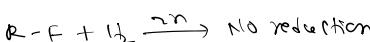
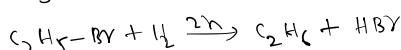
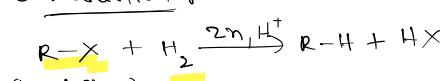


Note for

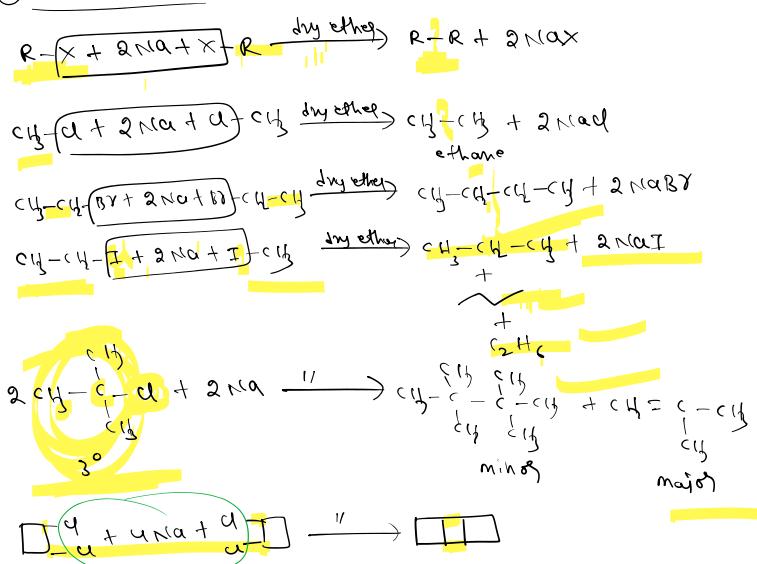
- ① methane can't be prepared
- ② C-H bond formation takes place

(II) From alkynes :-

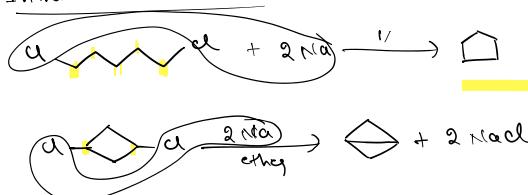
① Reduction to



② Wurtz reaction :

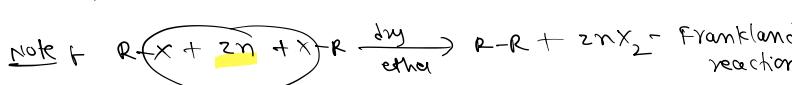


Intramolecular Wurtz G



draw backs

- ① CH_4 can't be prepared
- ② unfavourable for the prep. of unsymmetrical (i.e. odd numbered) alkanes
- ③ 3° -alkyl halides undergo elimination to produce alkenes or may form instead of alkanes (rarely)



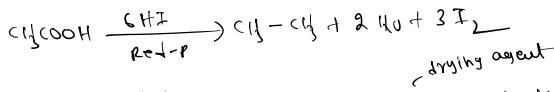
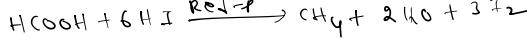
(III) From carboxylic acids :-

① Reduction to

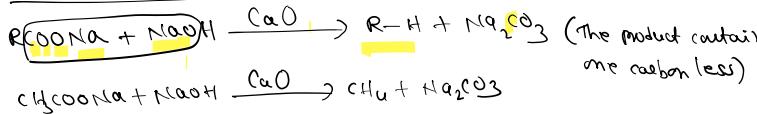


This can be given by alcohols also. But they require only 2-moles of HI

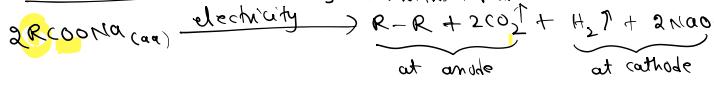




② De-carboxylation :- $\text{NaOH} + \text{CaO} = \text{soda-lime}$



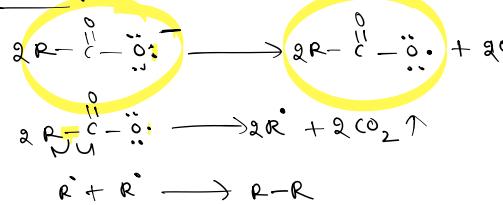
③ Kolbe's electrolysis :- sodium/potassium salts of carboxylic acids in aqueous undergo electrolysis to produce alkane at anode.



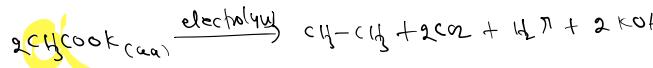
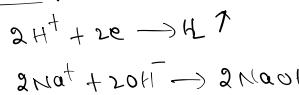
mech f



Anode f



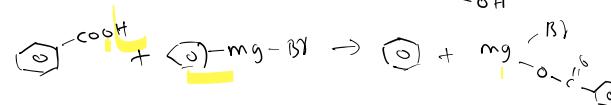
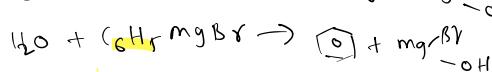
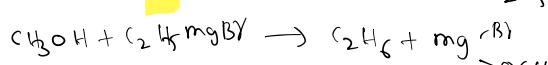
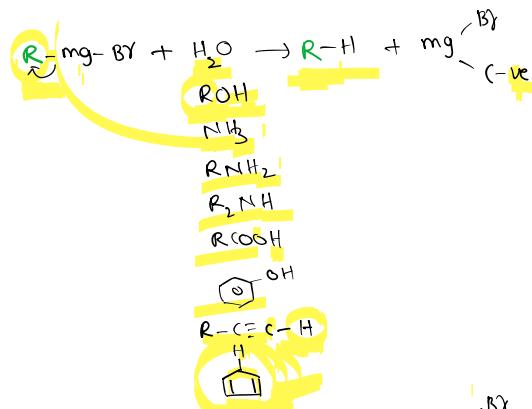
cathode f



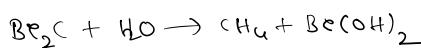
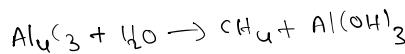
Note +) Cu can't be prepared

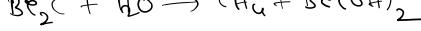
2) unfavourable to produce unsymmetrical alkane

(IV) From Grignard reagent (b)



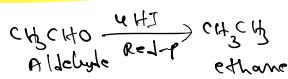
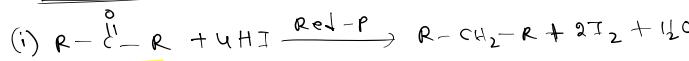
(v) From carbides v



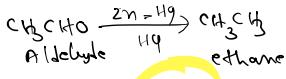
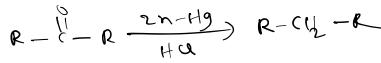


(VI) From carbonyl compounds

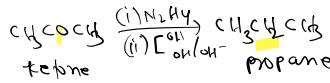
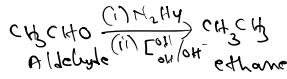
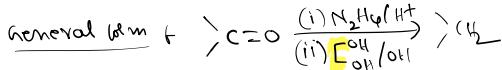
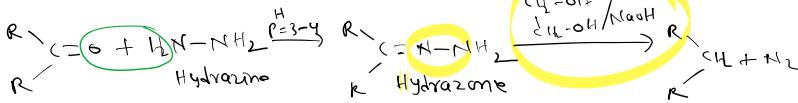
① Reduction :-



(ii) clemenson reduction :-



(iii) wulff-kishner reduction



Properties of alkanes

physical ↗

- ① Non polar
 - ② Insoluble in water. But, soluble in organic solvent
 - ③ Have very less m.p & b.p
 - ④ Alkanes upto C_4 are gases, C_5-C_{17} - liquids, C_{18+} - solids.
 - ⑤ \propto $\frac{1}{\text{molecular weight}}$

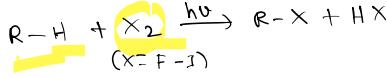
⑤ m.p & b.p \propto molecular weight $\propto \frac{1}{\text{Branching}}$

Egg m.p & b.p of $\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--}$

Branching \Rightarrow
compounds will become more spherical
surface area \downarrow
M.P & B.P \downarrow

chemical properties

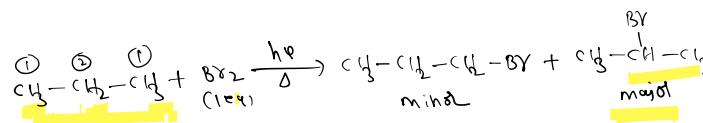
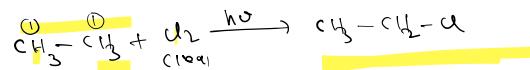
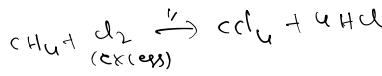
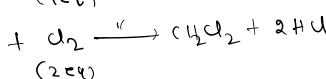
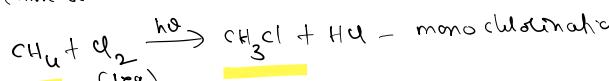
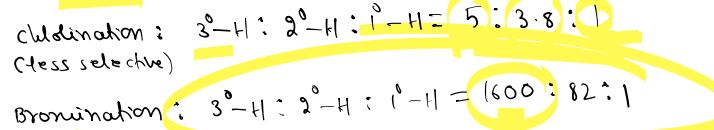
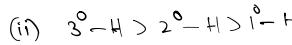
① Halogenation :



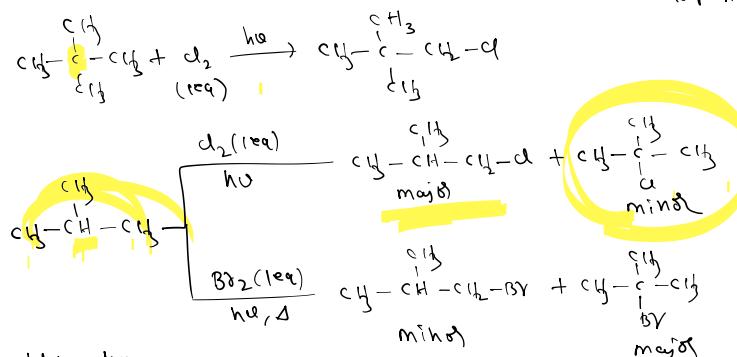
Reactivity

- $$(1) F_2 >>> d_2 > Bx_2 > I_2$$

$$(iii) \quad 3^{\circ} - H > 2^{\circ} - H > 1^{\circ} - H$$



No. of monohalogenation structural isomers = no. of sets of equivalent carbons (where substitution is possible)



chlorination

Total no. of 1^o-H in substrate = 9

Total replaceability factor of $1^o-H = 9 \times 1 = 9$

Total no. of 3^o-H in substrate = 1

Total replaceability factor of $3^o-H = 1 \times 5 = 5$

$\gamma.$ of 1^o -chloride = $\frac{9}{14} \times 100 =$

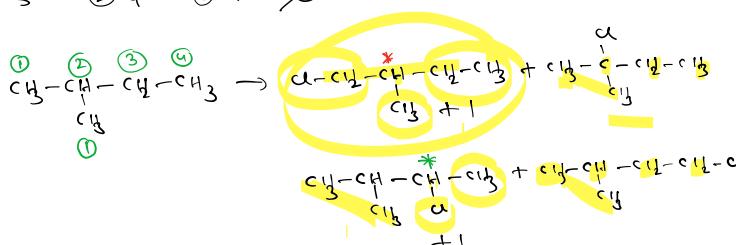
$\gamma.$ of 3^o -chloride = $\frac{5}{14} \times 100 =$

* which of the following compounds will produce highest no. of mono halogenated structural isomers?



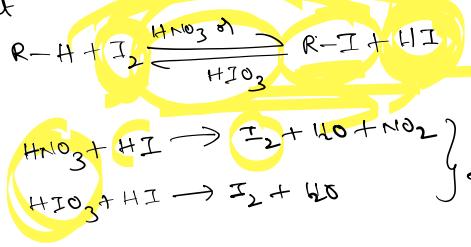
* Find the no. of isomers possible (including stereo isomers) on monochlorination of isopentane is —

- ① 3 ② 4 ③ 5 ④ 6



Iodination of alkanes is reversible. The oxidizing agents like I_2 , Br_2 , ClO_4^- etc., increase the yield of alkyl iodide

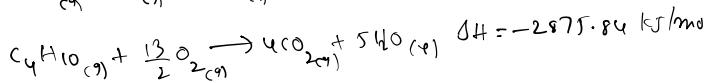
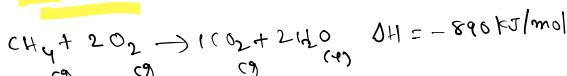
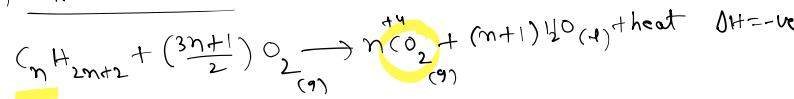
Iodination of alkanes is reversible. The oxidising agents like HNO_3 & HIO_3 can be used to increase the yield of alkyl iodide product.



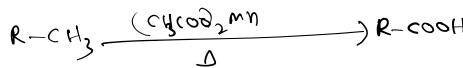
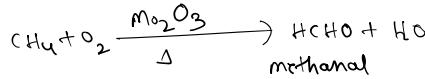
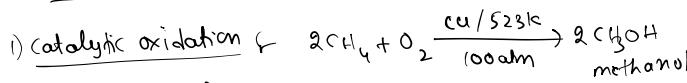
shift the above equilibrium right side by removing HI and producing I_2

② Oxidation ↗

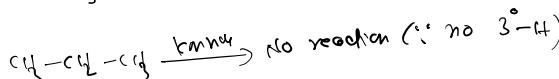
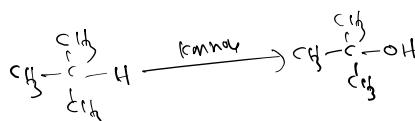
(i) complete oxidation ↗ combustion



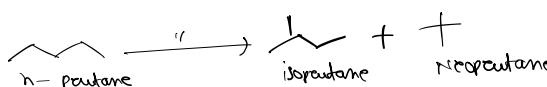
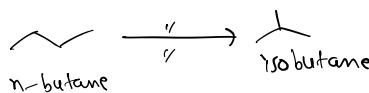
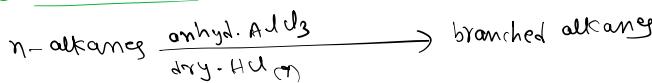
(ii) controlled oxidation ↗



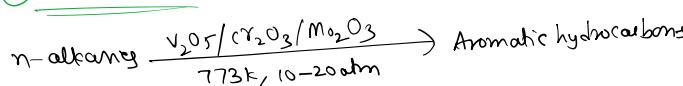
2) with oxidising agents ↗ this is very difficult since alkanes are resistant towards oxidising agent. only KMnO₄ can oxidise alkanes having 3°-H into alcohol

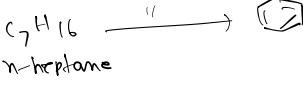


③ Isomerisation ↗

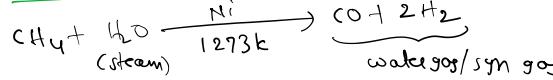


④ Aromatisation ↗

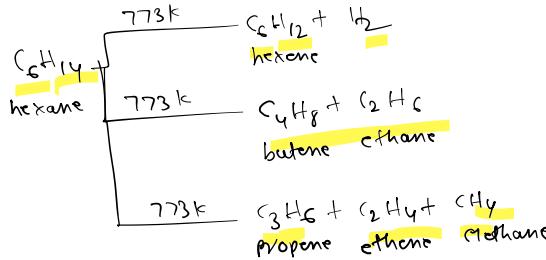




⑤ Reaction with steam

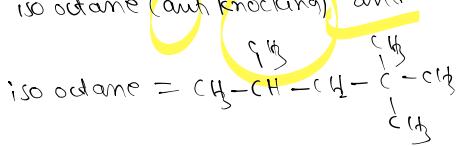


⑥ Pyrolysis of

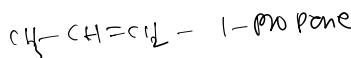
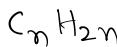


Quality of petrol is expressed in terms of octane number which indicates % of iso-octane in the mixture of

iso-octane (anti-knocking) and iso-heptane (knocking)

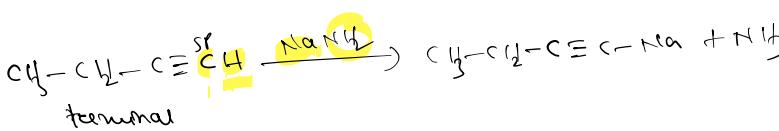
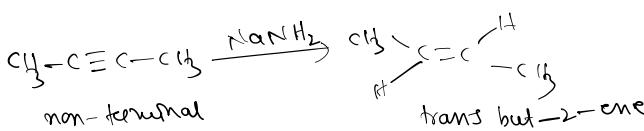
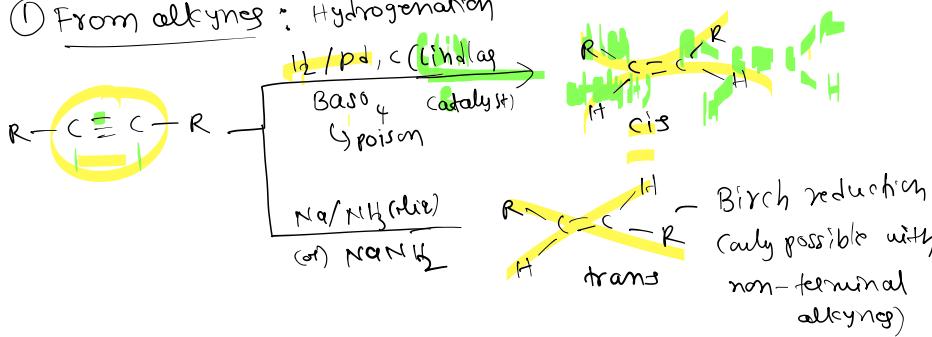


* Alkenes :



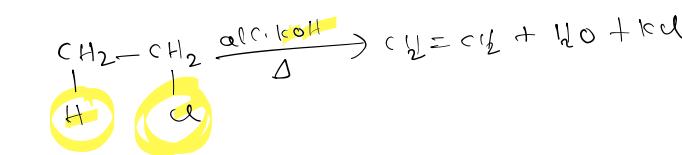
Preparation :

① From alkynes : Hydrogenation

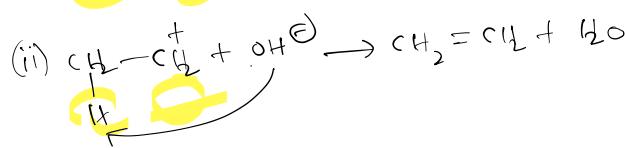
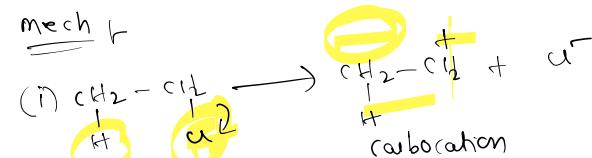


② From alkyl halides : alkyl halide on dehydrohalogenation

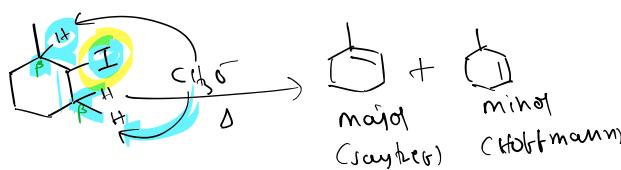
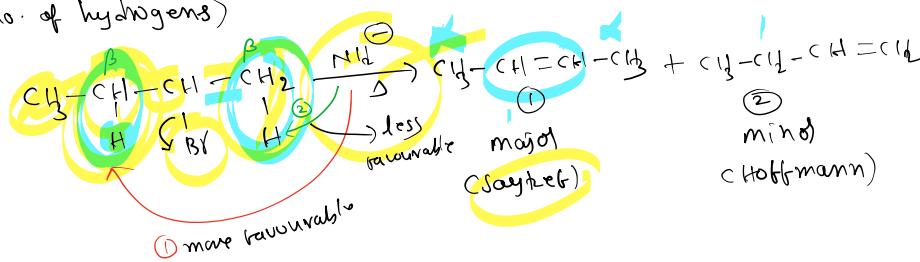
② From alkyl halides: alkyl halide on dehydrohalogenation via β -elimination in the presence of strong bases like $\text{NH}_2^-(\text{NaNH}_2)$, alc. KOH (RO^-) at high temp. produce alkenes.



mech ↗

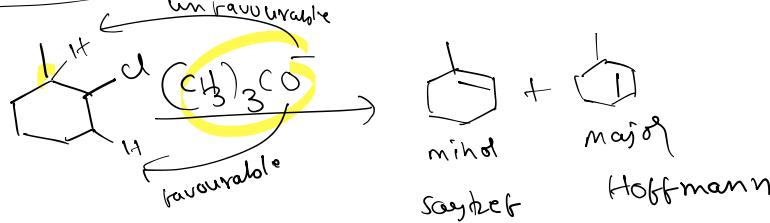


In case of unsymmetrical alkyl halides, saytzev (Zaitsev) alkene will be major which is formed by the removal of proton from more substituted β -carbon (i.e. β -carbon having less no. of hydrogens).

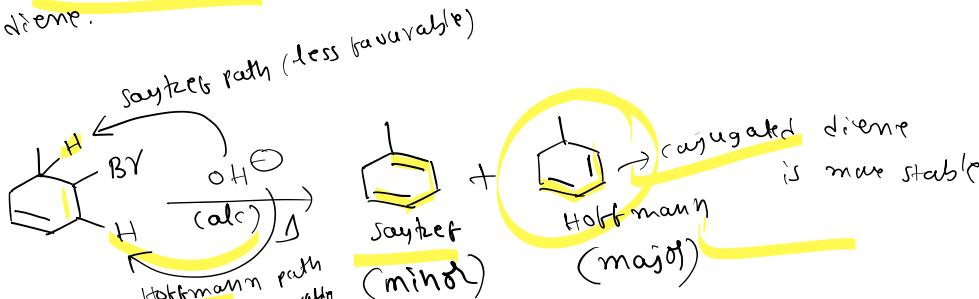


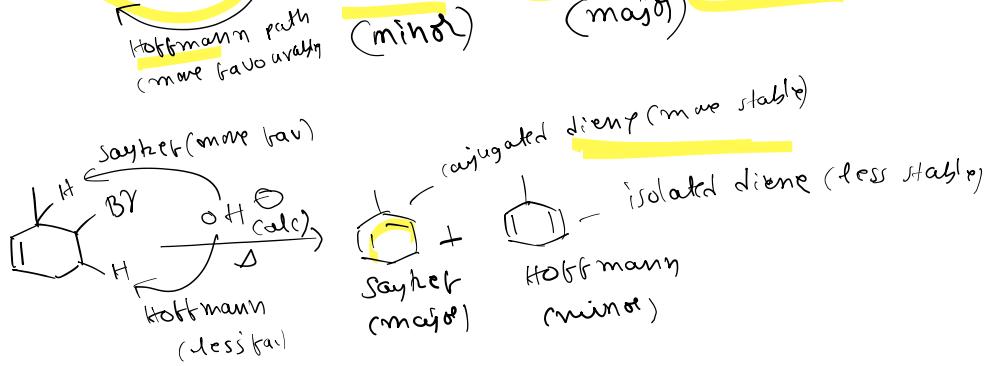
In the following three cases, Hoffmann alkene will be major.

Case - (i) f when bulky base is used

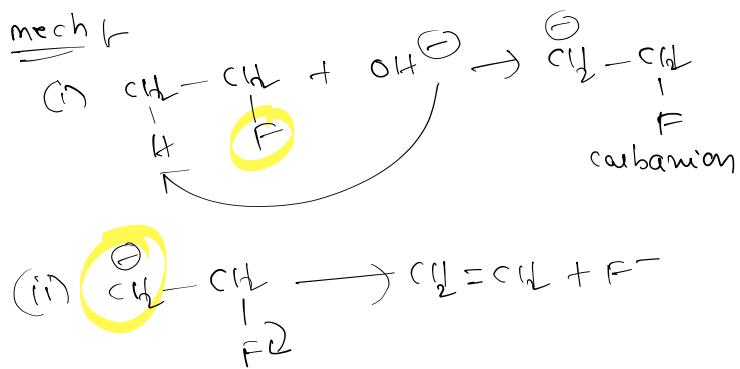
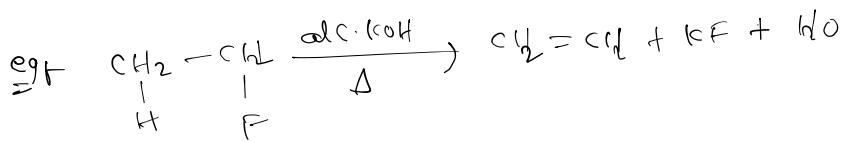


Case - (ii) f where there is a chance to get conjugated diene.

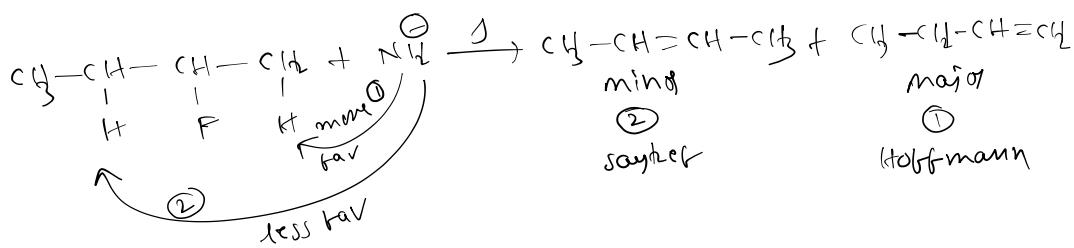




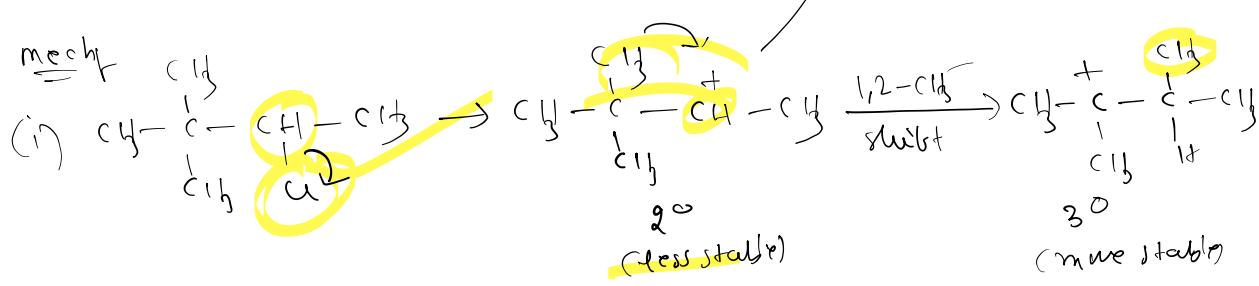
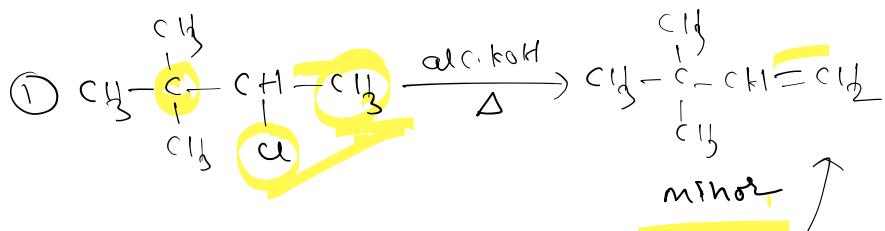
(iii) when alkyl fluorides are taken, reaction mechanism will change since, fluorine is poor leaving group.

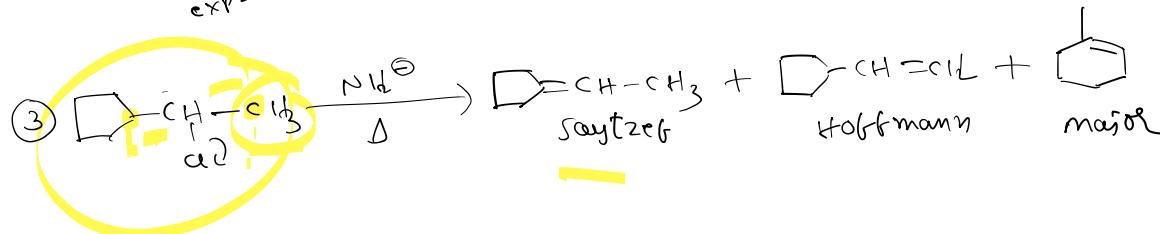
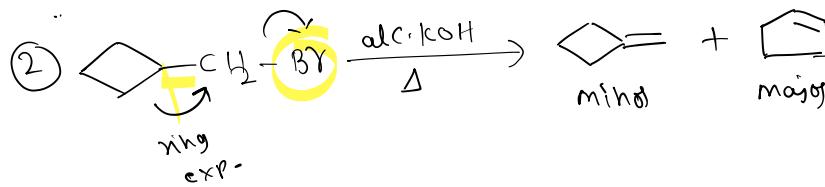
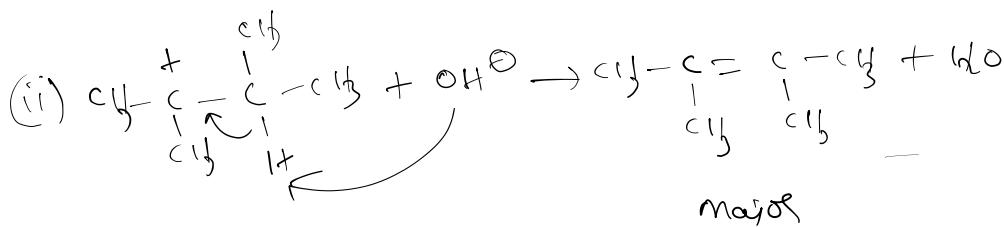


lower degree carbamions are more stable. Hence, base will attack on proton of less substituted β -carbon. so, Hoffmann alkene will be major

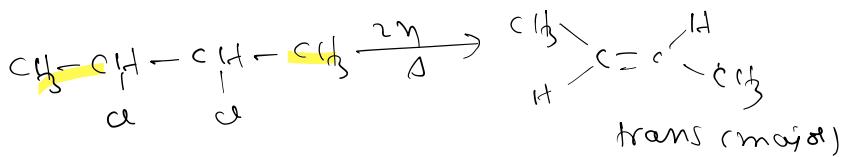
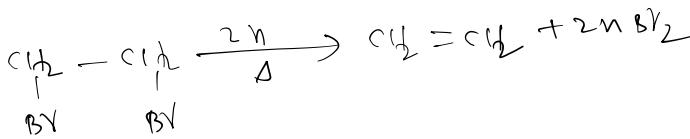
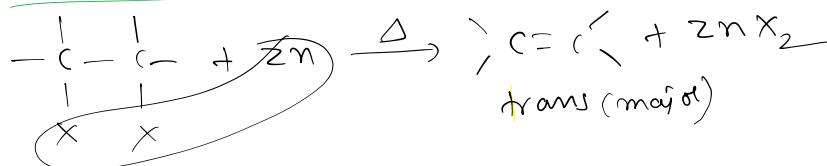


Carbocation rearrangements

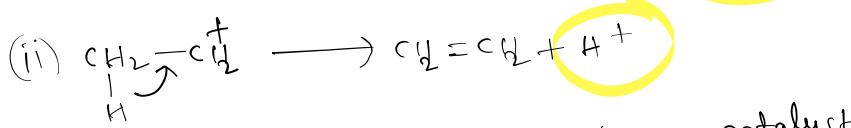
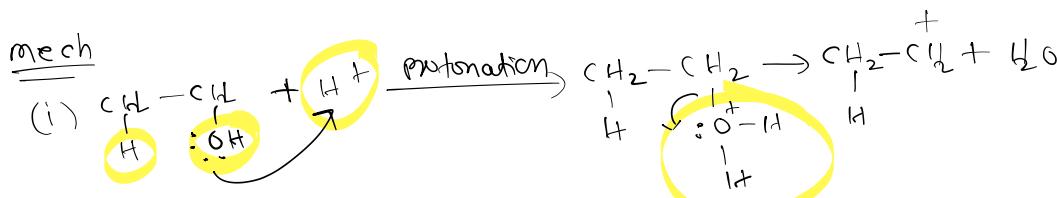




③ De-halogenation :-

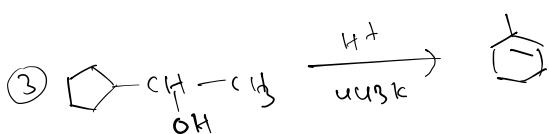
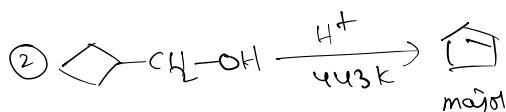
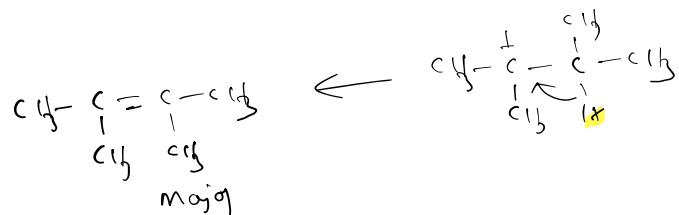
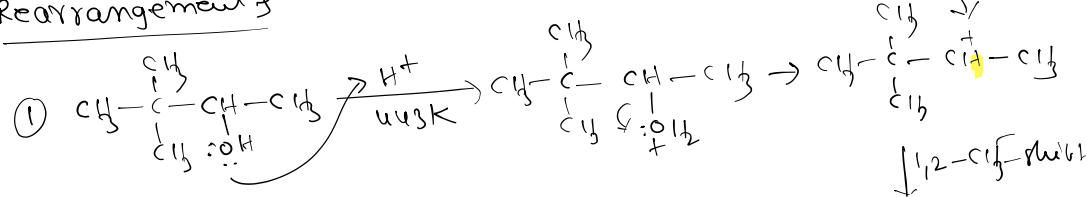


④ De-hydration :- Alcohols on β -elimination in the presence of conc. H_2SO_4 /conc. KHSO_4 produce alkene



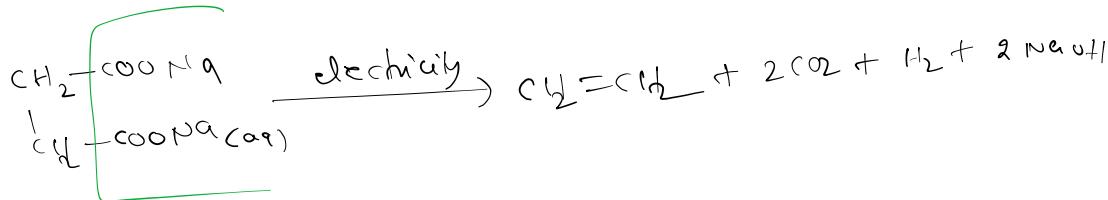
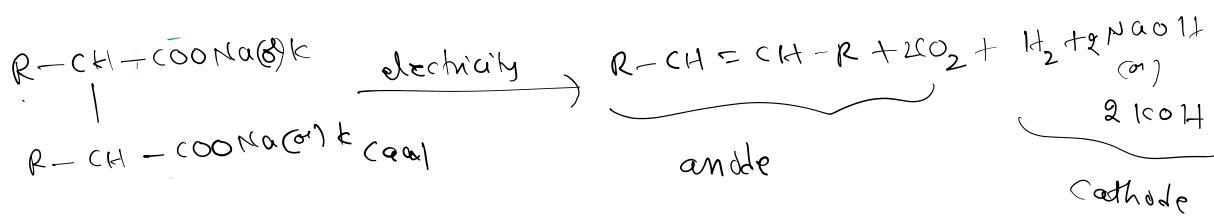
Note:- In this reaction, acid will act as a catalyst

Rearrangement



④ Kolbe's electrolysis of sodium/potassium salts of dicarboxylic acid

in aq. medium on electrolysis produce alkenes at anode



Physical properties

Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size i.e., every -CH₂ group added increases boiling point by 20–30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds.

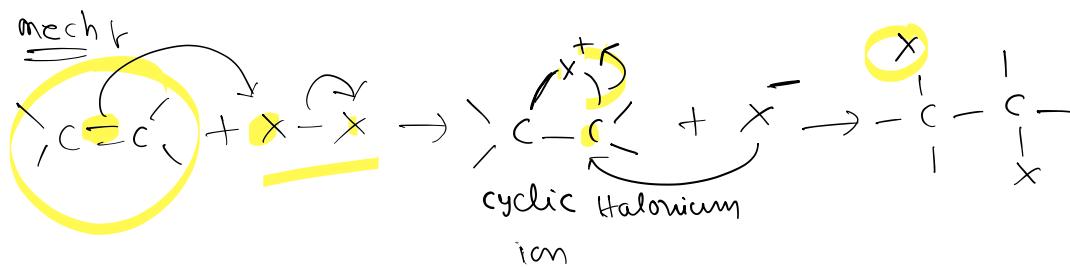
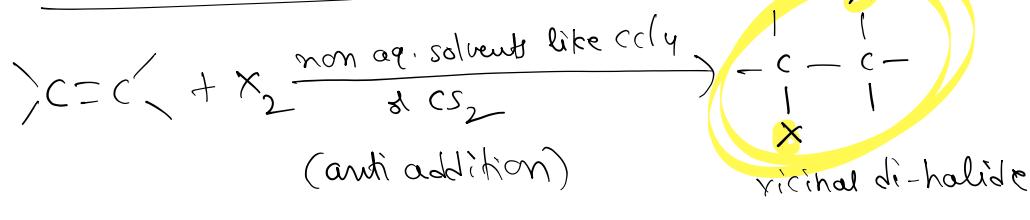
* Chemical properties Alkenes will mainly show addition reactions and substitution reactions.

Addition reactions :

① Addition of halogens ()

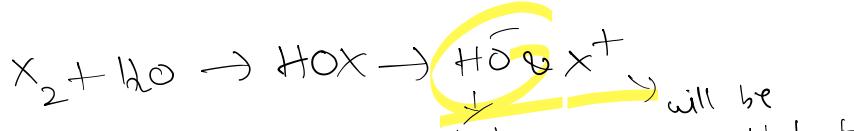
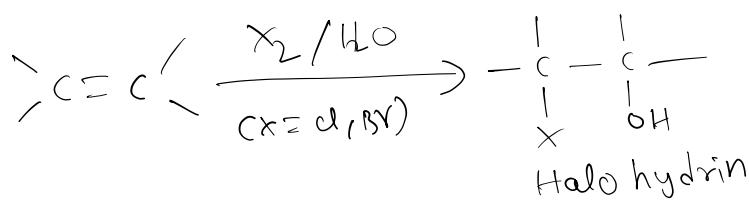
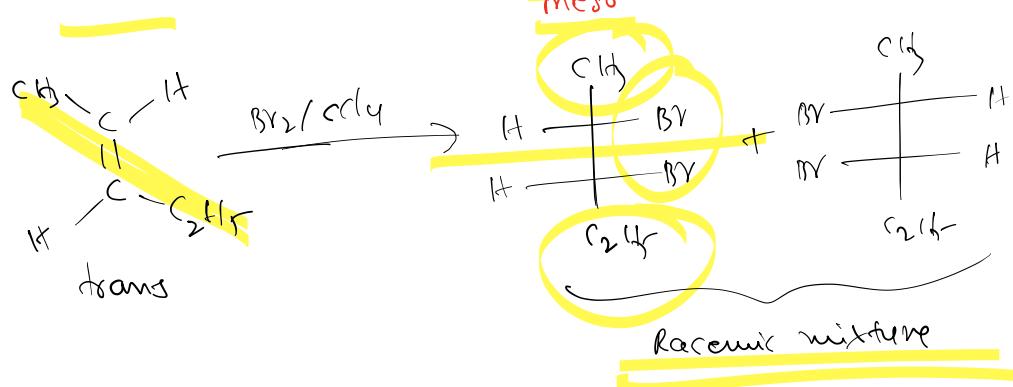
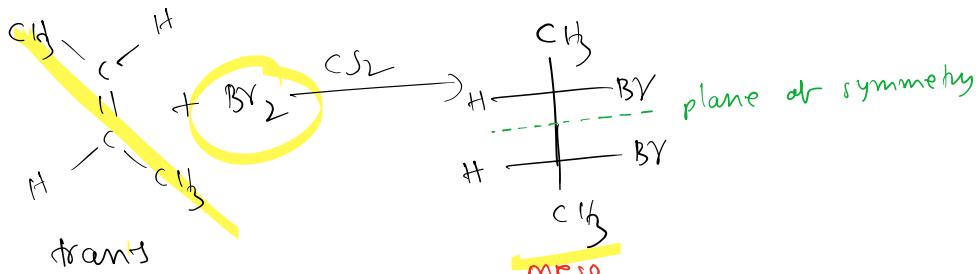
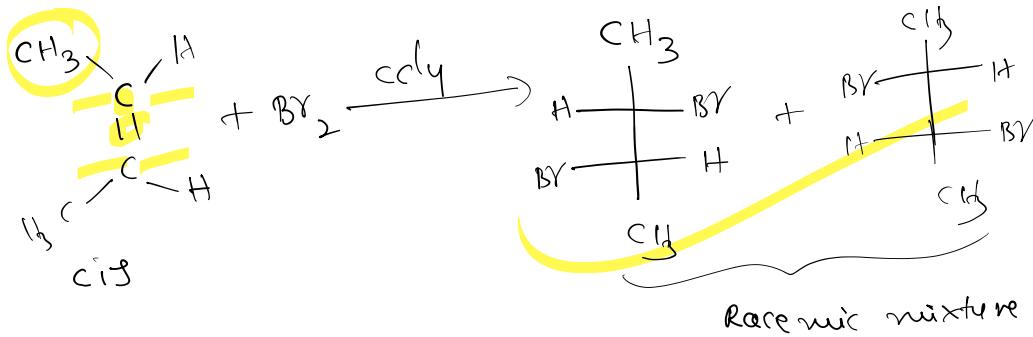
in aq. solvents like CCl₄

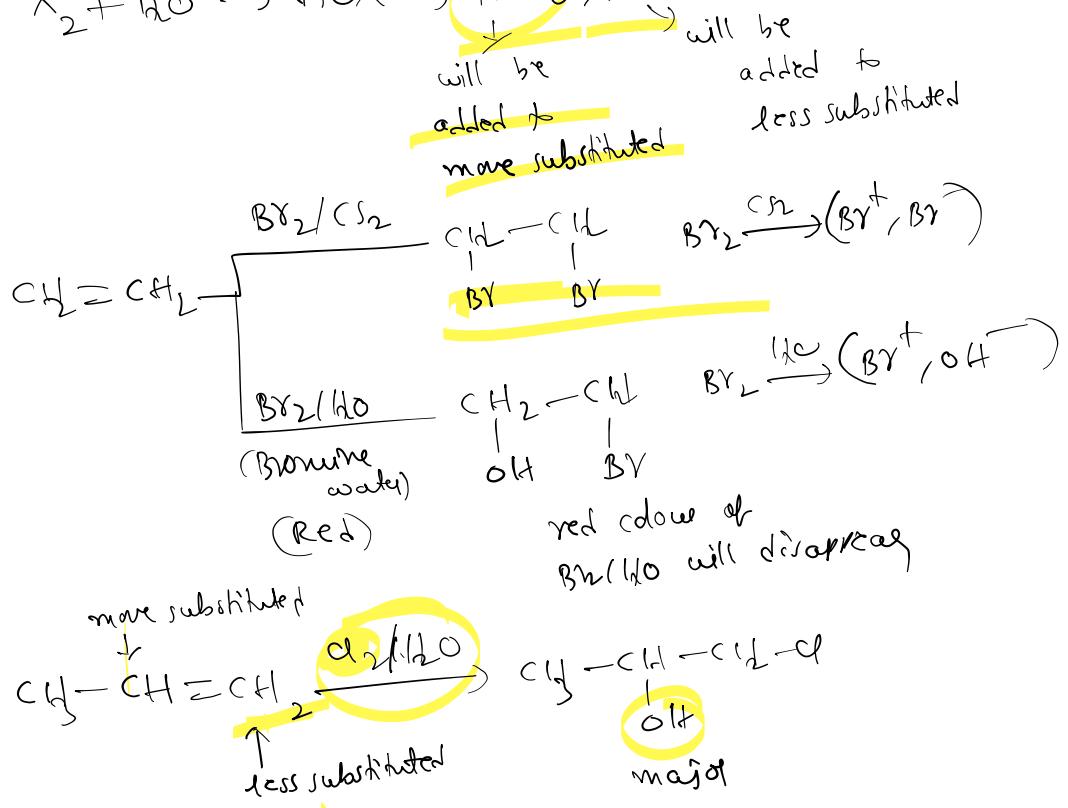




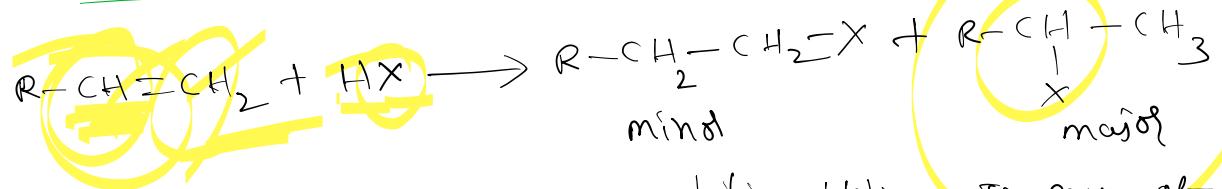
cis-alkene anti addition \rightarrow Racemic mixture (CAR)

trans-alkene anti addition \rightarrow meso compound * (TAM)
 (*) when there is a plane of symmetry

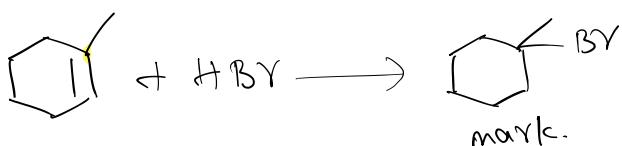
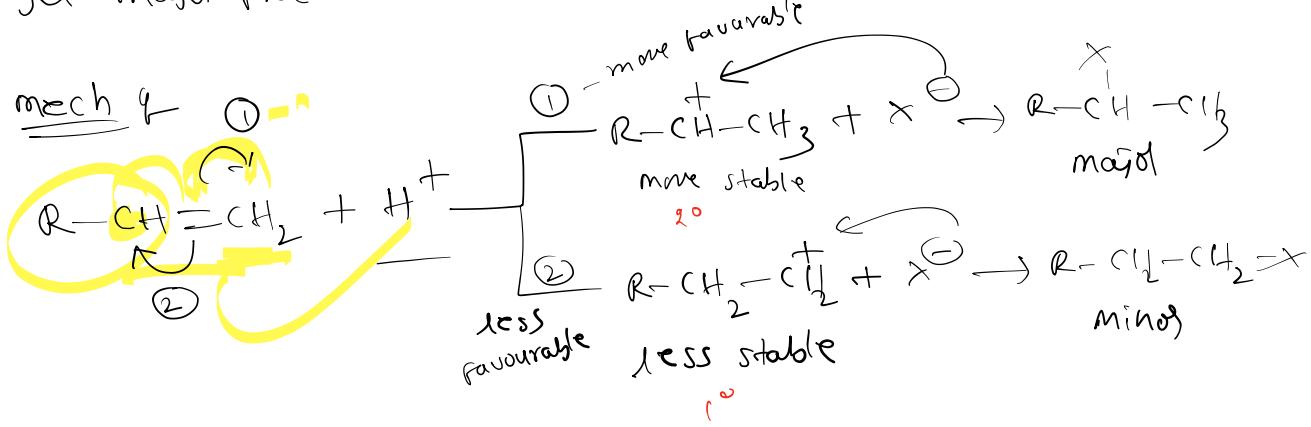




② Addition of HX :-

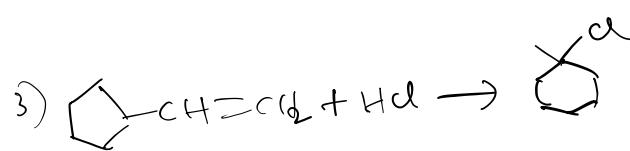
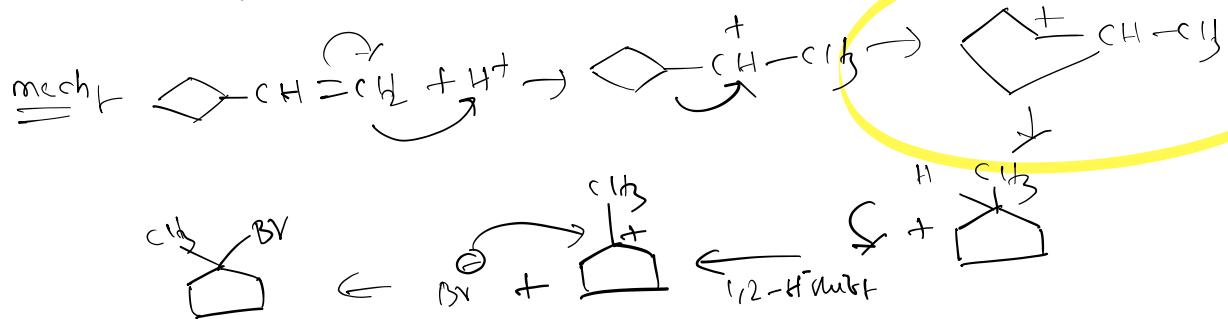
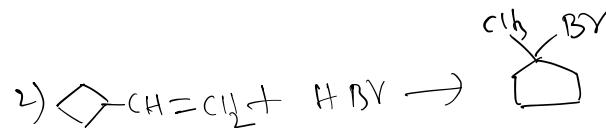
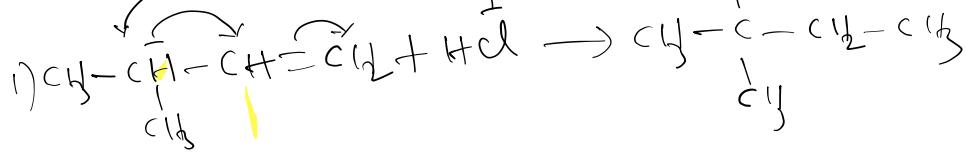


The above will come under electrophilic addition. In case of unsymmetrical alkenes, add X^- to more substituted carbon to get major product. This is also called Markovnikov's addition.

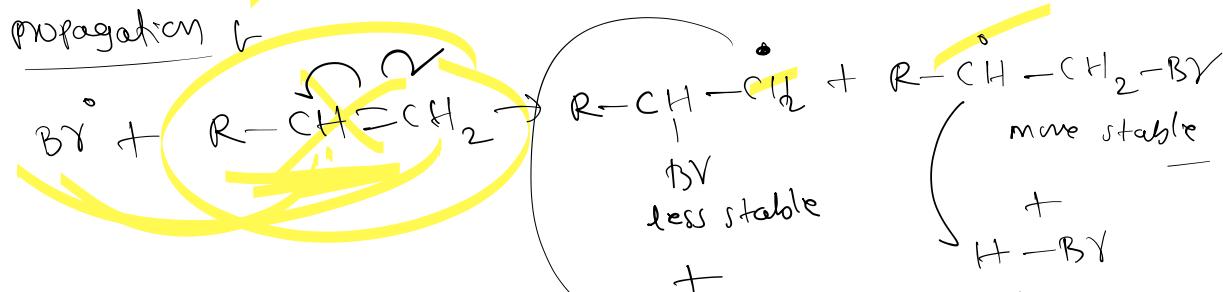
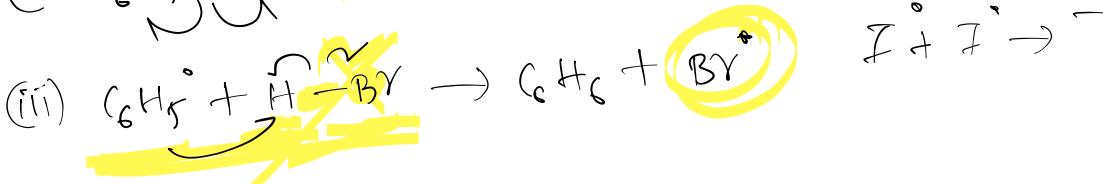
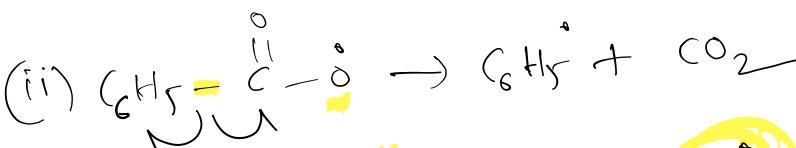
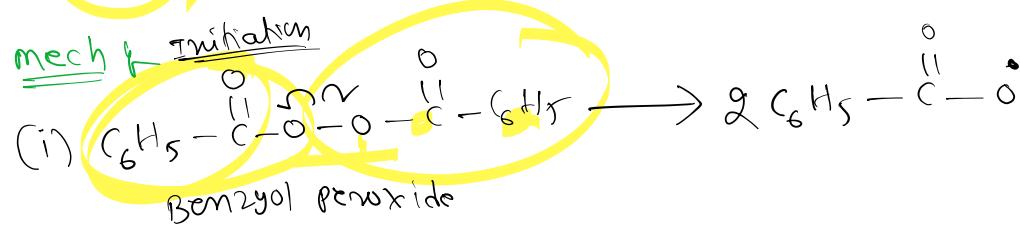
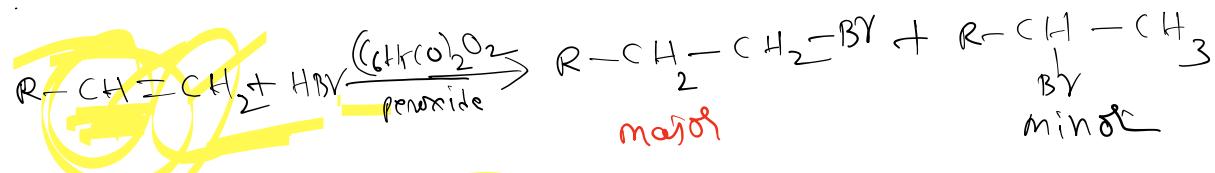


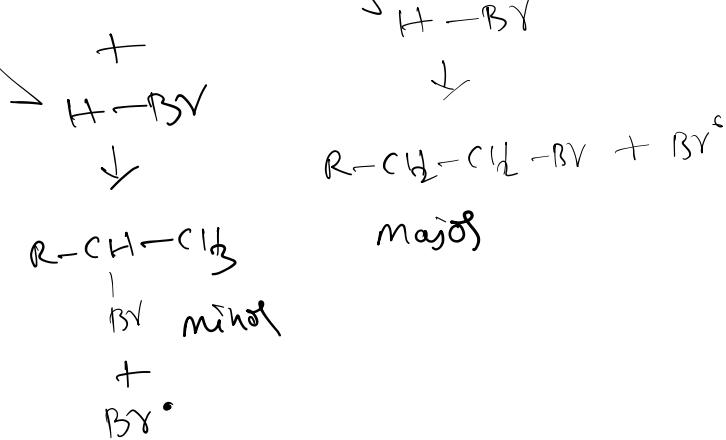
Rerrangements



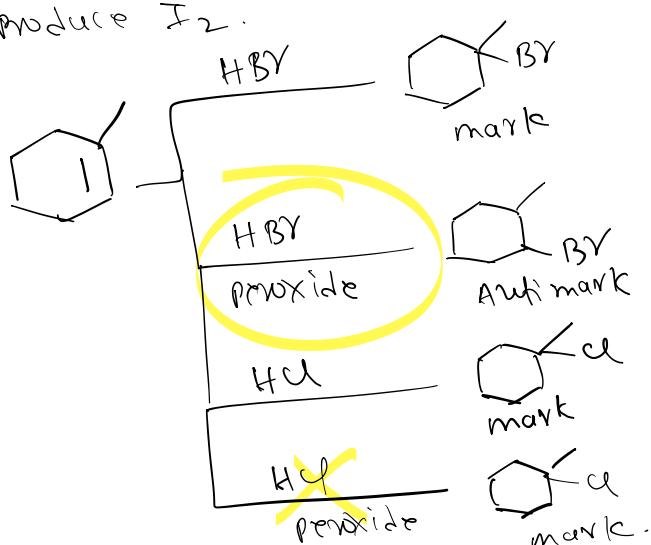


Addition of HBr in the presence of peroxide like Benzoyl peroxide, hydrogen peroxide etc. will follow free radical addition in which bromine will be attached to less substituted carbon. This is due to peroxide (Kharasch) effect. This addition is also called anti markovnikov's addition

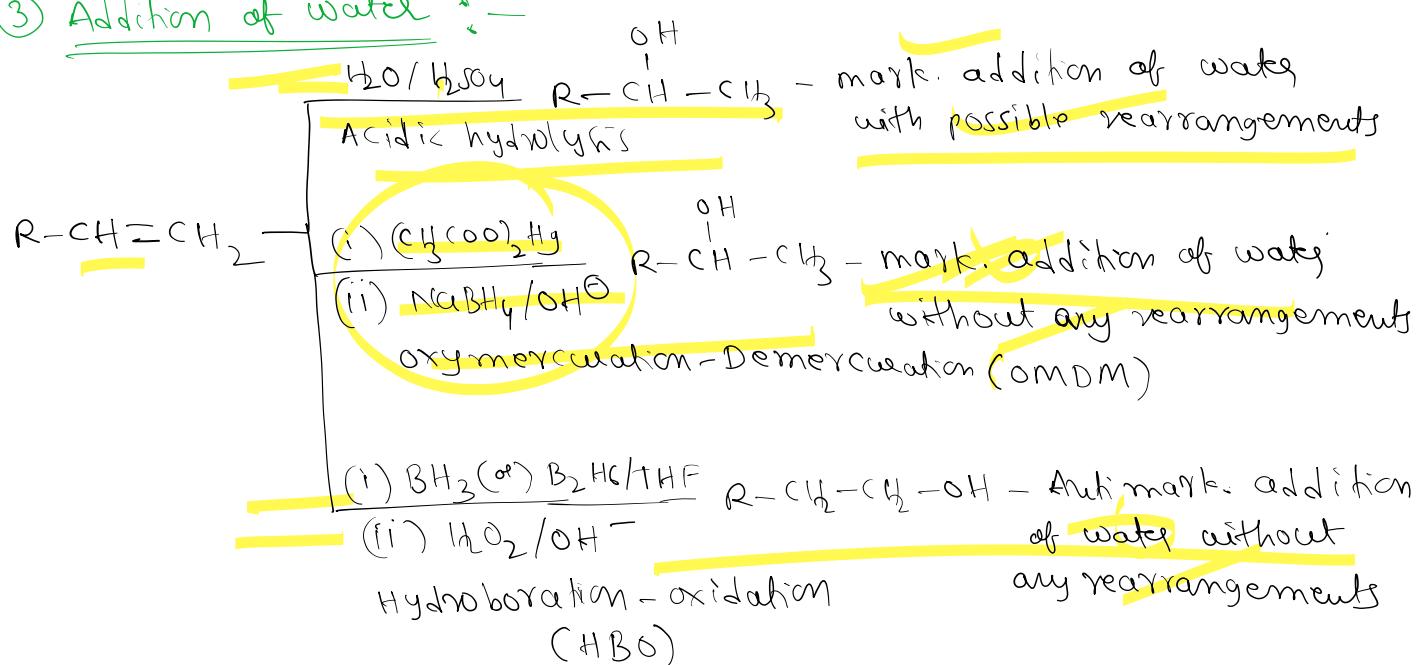




Note 8
 Peroxide effect is not possible with HCl and HF. Since, H-Cl bond breaking is difficult, I⁻ produced will react with itself to produce I₂.



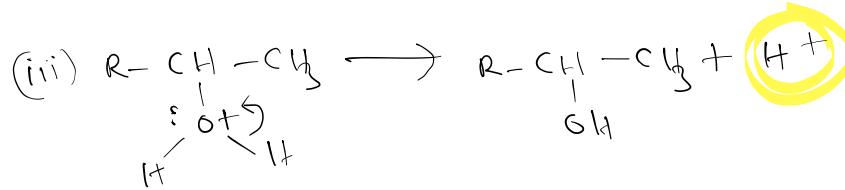
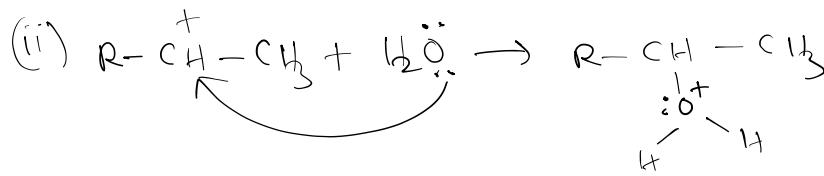
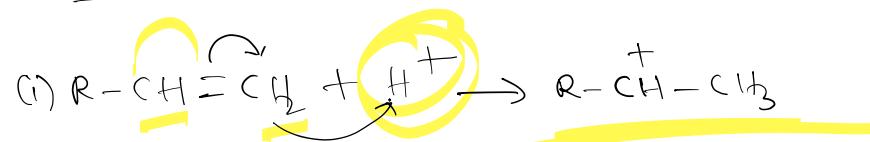
③ Addition of water :-



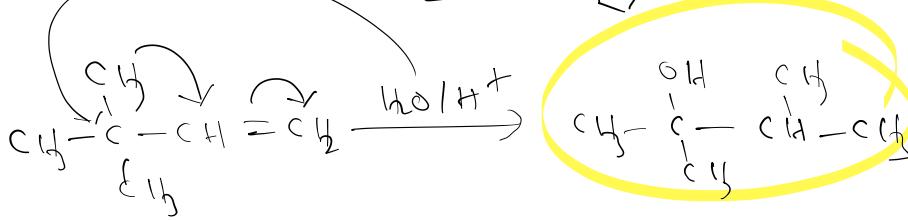
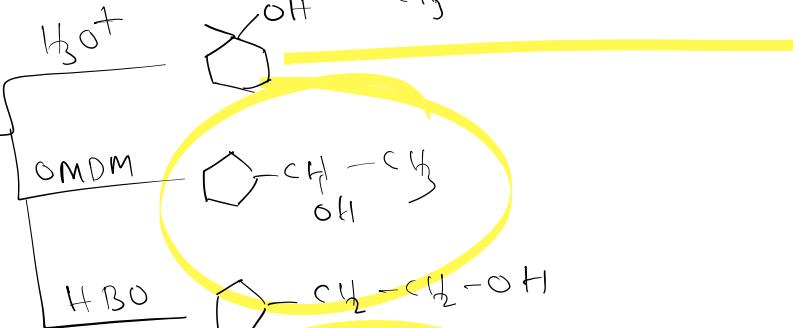
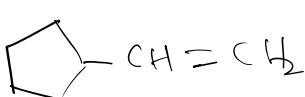
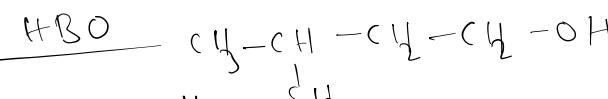
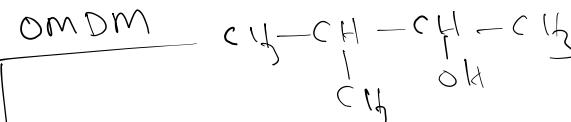
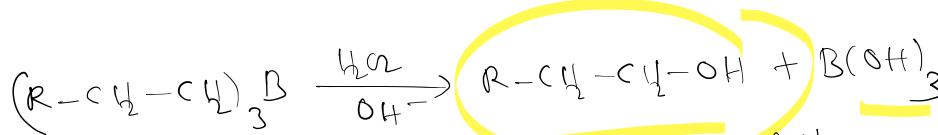
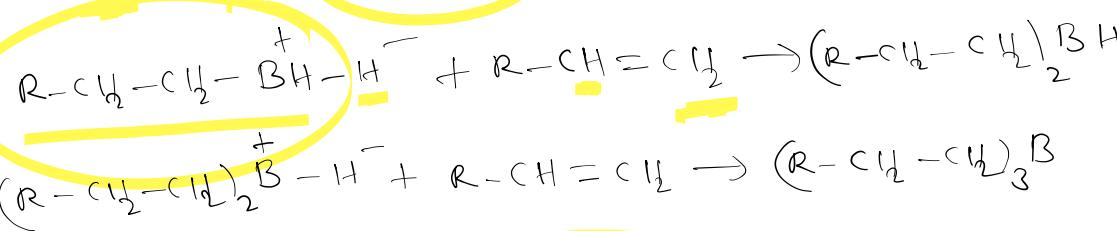
mech.

① Acidic hydrolysis :-

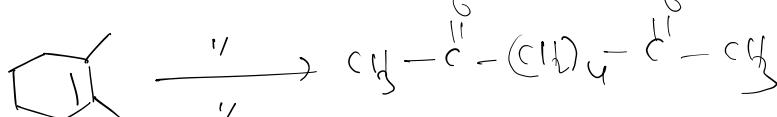
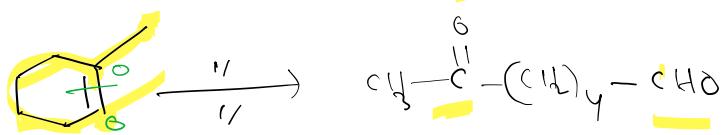
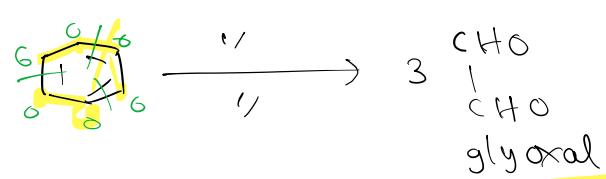
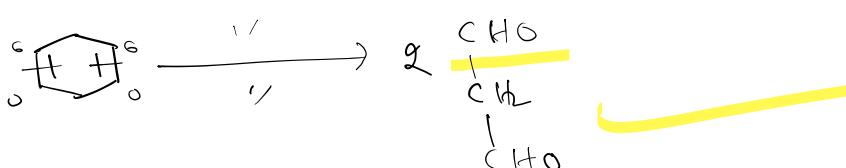
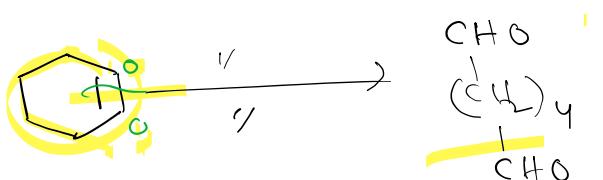
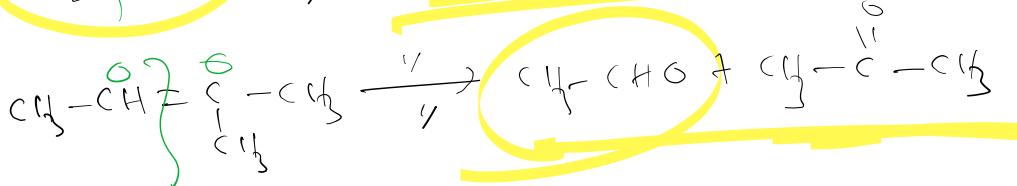
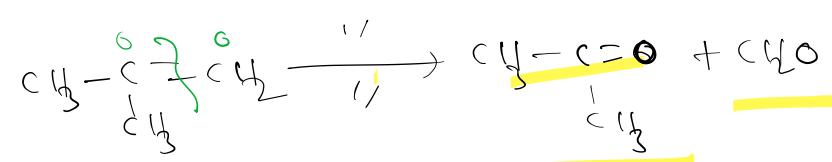
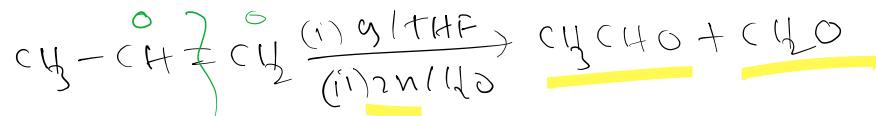
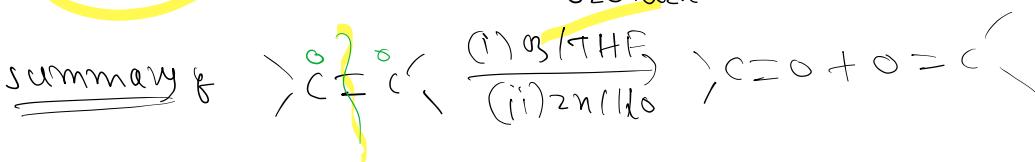
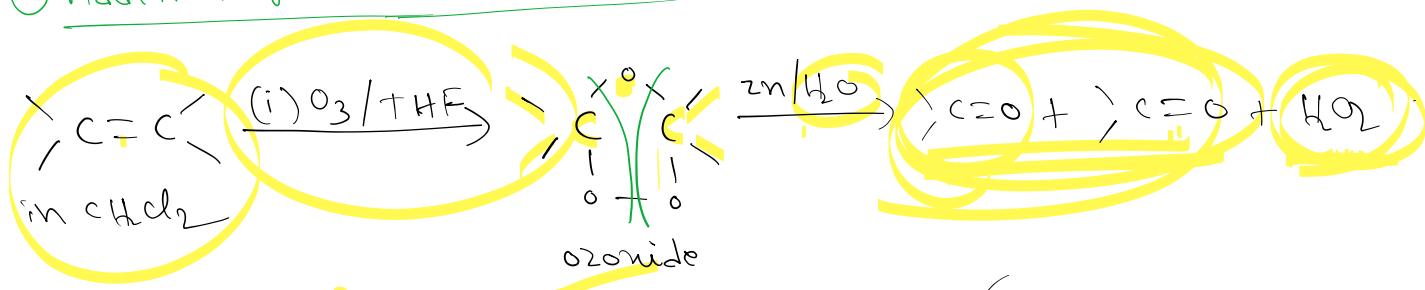
① Acrylic acid esters



② HBO

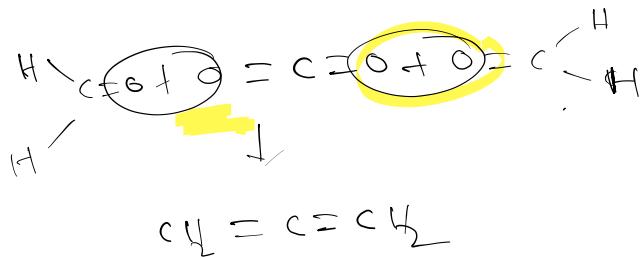
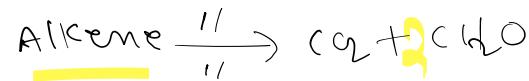
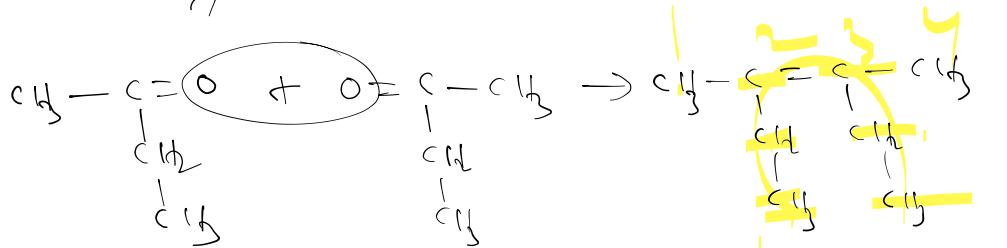
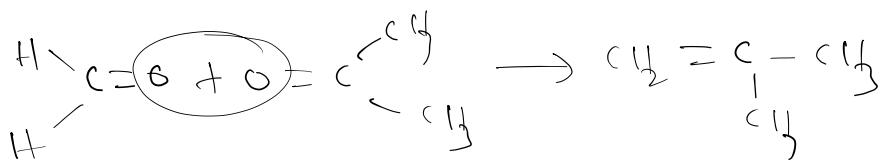
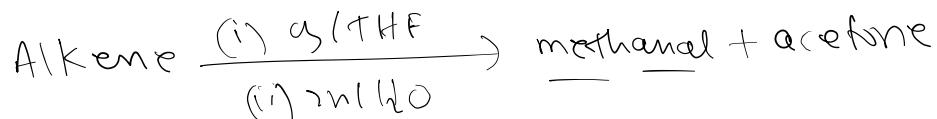
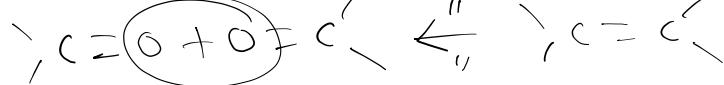


④ Addition of ozone - ozonolysis :

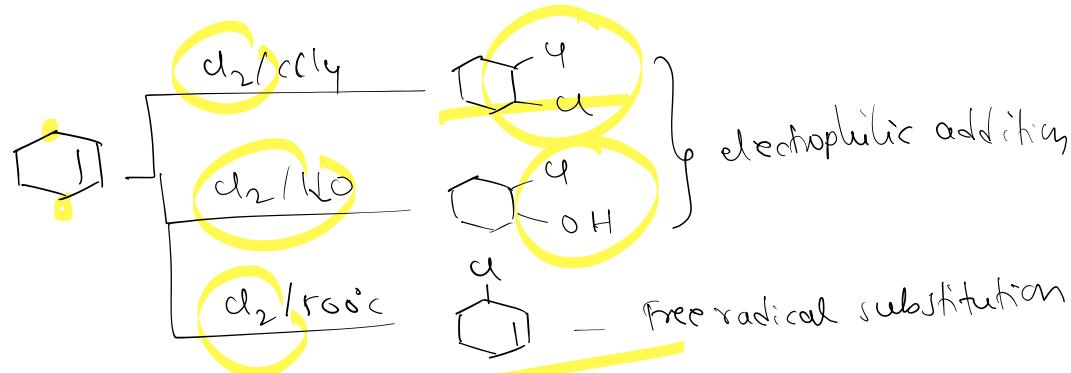
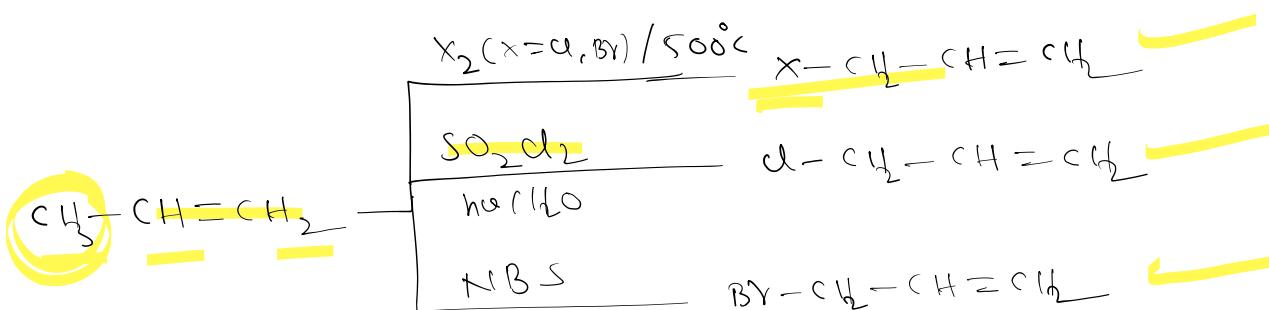


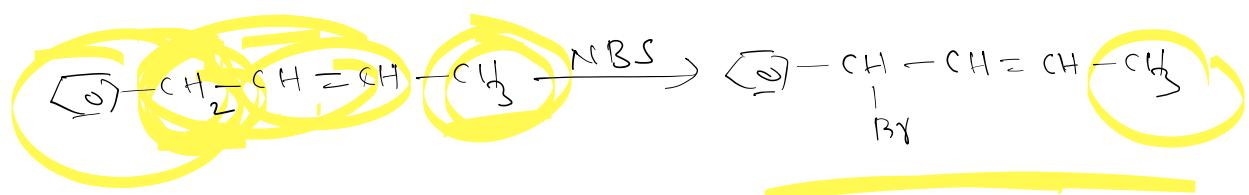
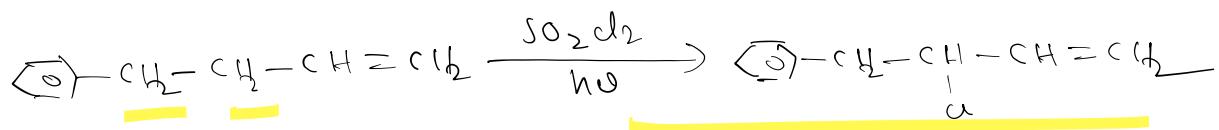
Retro q





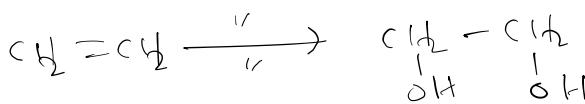
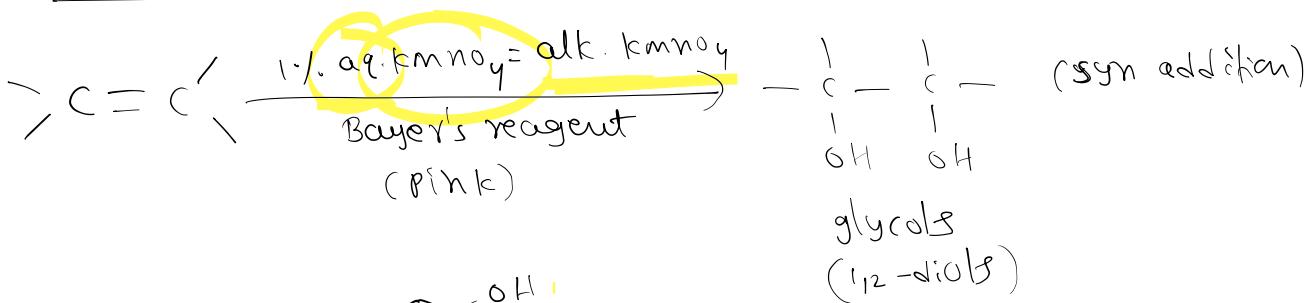
* substitutions of alkenes & Alkenes mainly undergo free radical substitutions which are highly favourable at allyl/benzyl positions





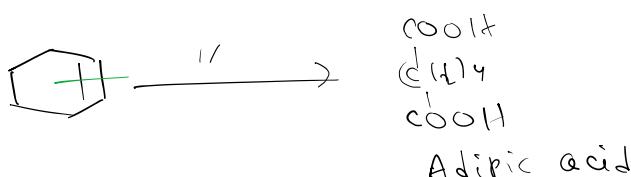
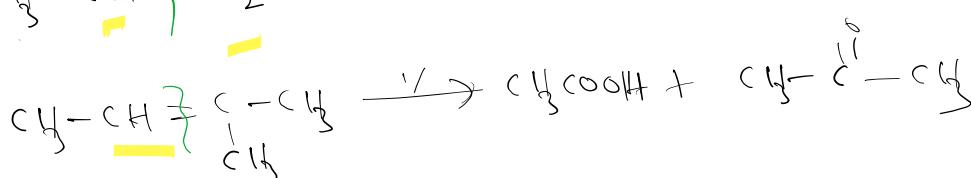
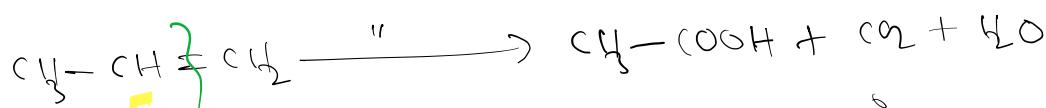
* Oxidation of alkenes

① Basic medium



In this reaction, alkene will de-colourise pink colour of KMnO₄

② Acidic medium & KMnO4/H⁺ or K₂C₂O₇/H⁺

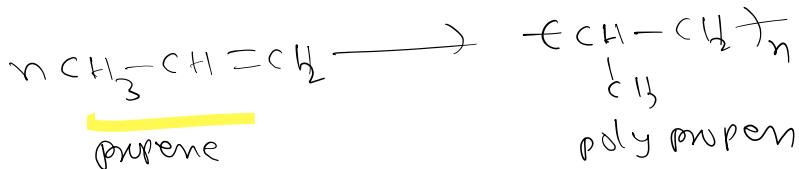


In this type of oxidation, alkene will split along double bond and each doubly bonded carbon oxidised as follows:

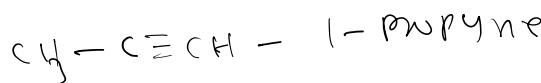
+ substituted (i.e. contain two

- (i) If doubly bonded carbon is not substituted (i.e. contain two hydrogens) then it will be oxidised to $\text{CO}_2 + \text{H}_2\text{O}$
- (ii) If doubly bonded carbon is partially substituted (i.e. contain only one hydrogen) then it will be oxidised to $-\text{COOH}$.
- (iii) If doubly bonded carbon is fully substituted (i.e. no hydrogen) then it will be oxidised to $>\text{C}=\text{O}$ (ketone)

* Polymerisation :-

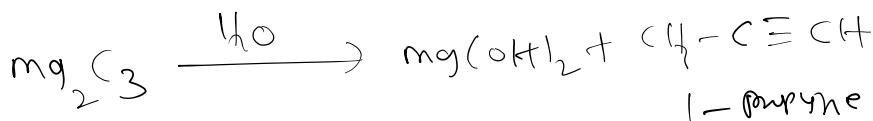
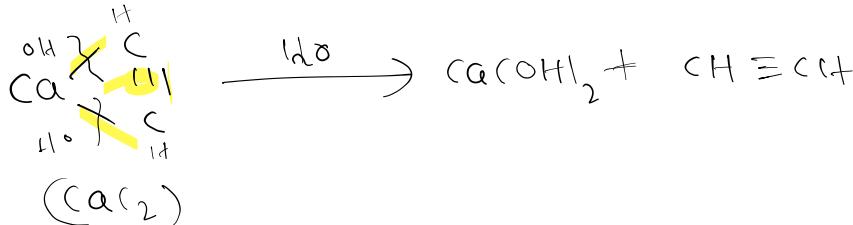


* Alkyne :- $\text{C}_n\text{H}_{2n-2}$

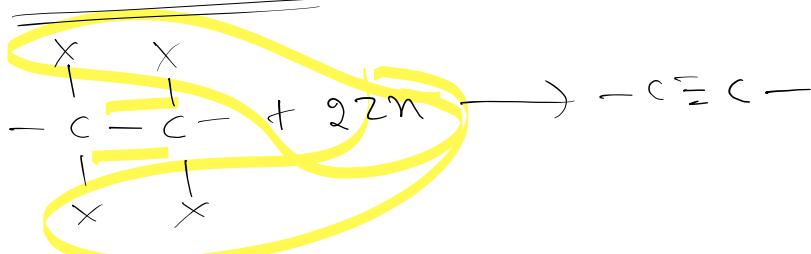


Prep :-

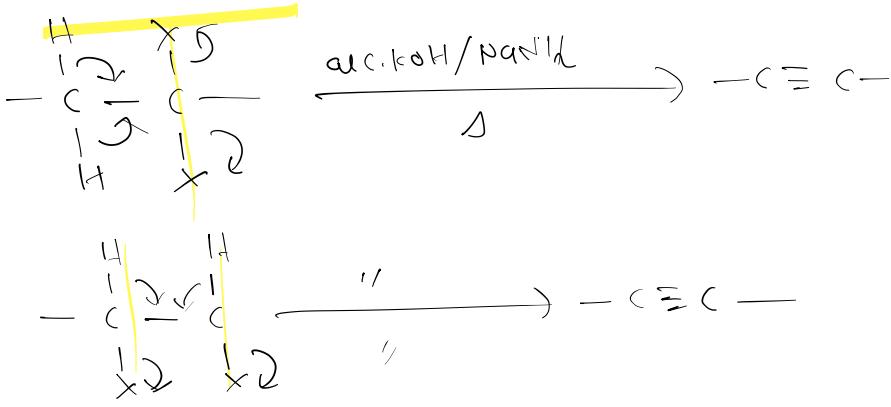
① From carbides :-



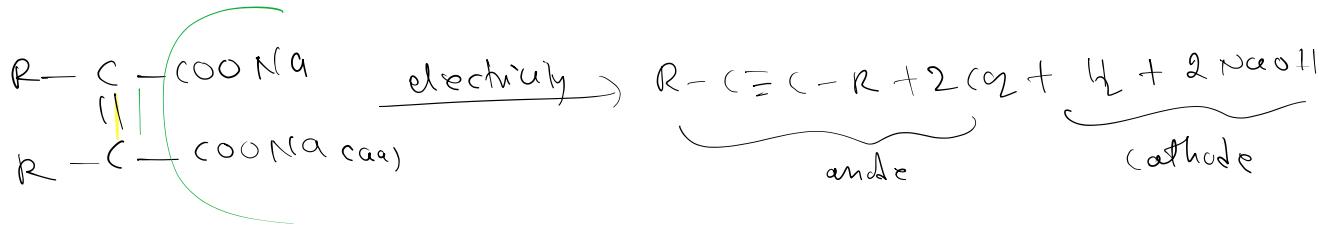
② De-halogenation :-



③ Dehydrohalogenation

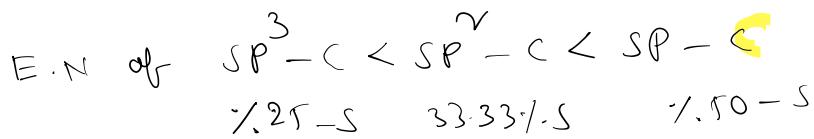


④ Kolbe's electrolysis &

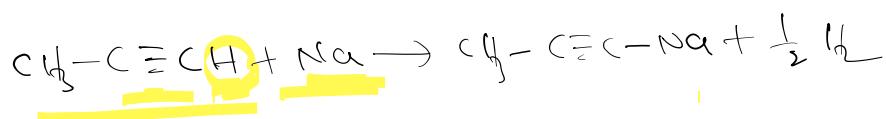
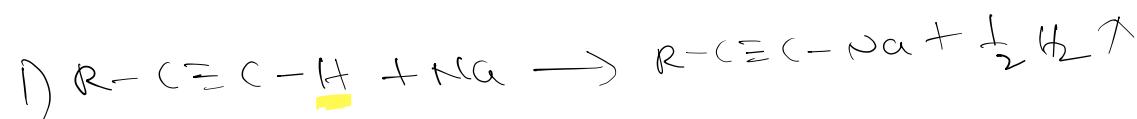


* properties

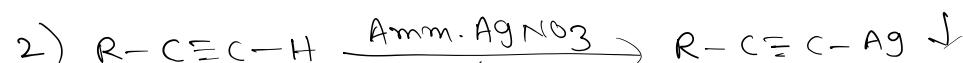
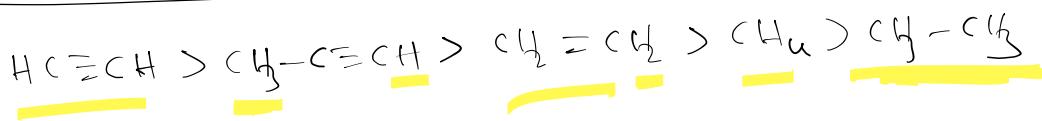
① Acidic nature

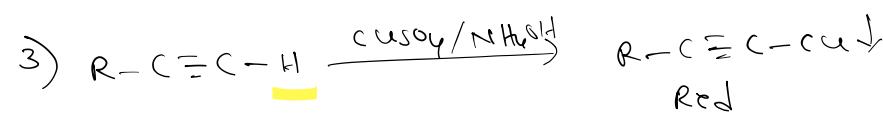
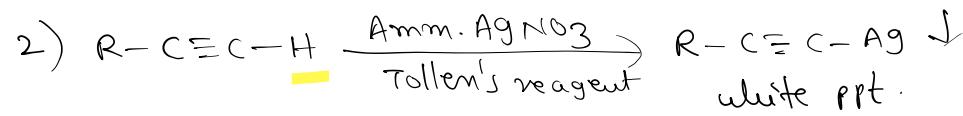


∴ Hydrogen attached to sp-carbon (triply bonded) will show slight acidic character. The following reactions will prove that



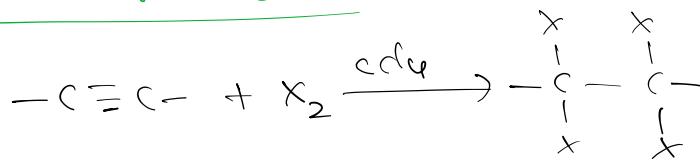
Acidic strength of cgs



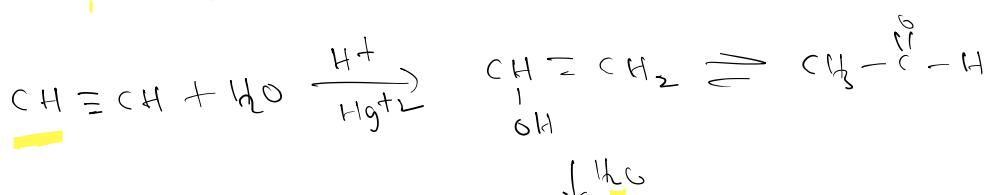
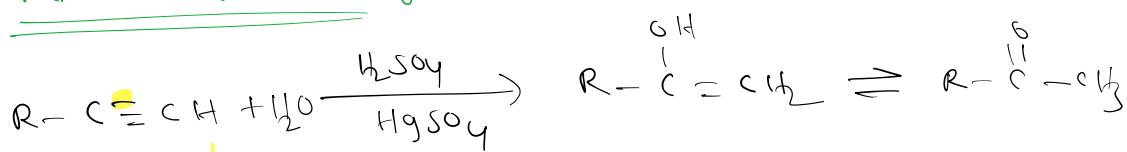


Alkynes are not strong enough acidic to react with NaOH

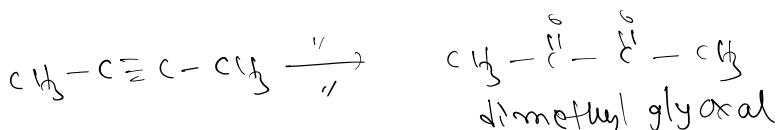
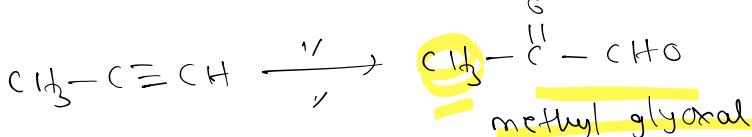
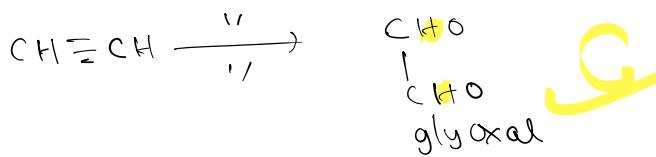
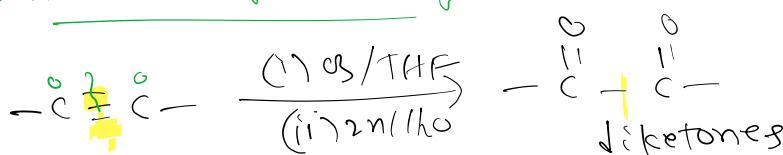
② Addition of halogens ↴



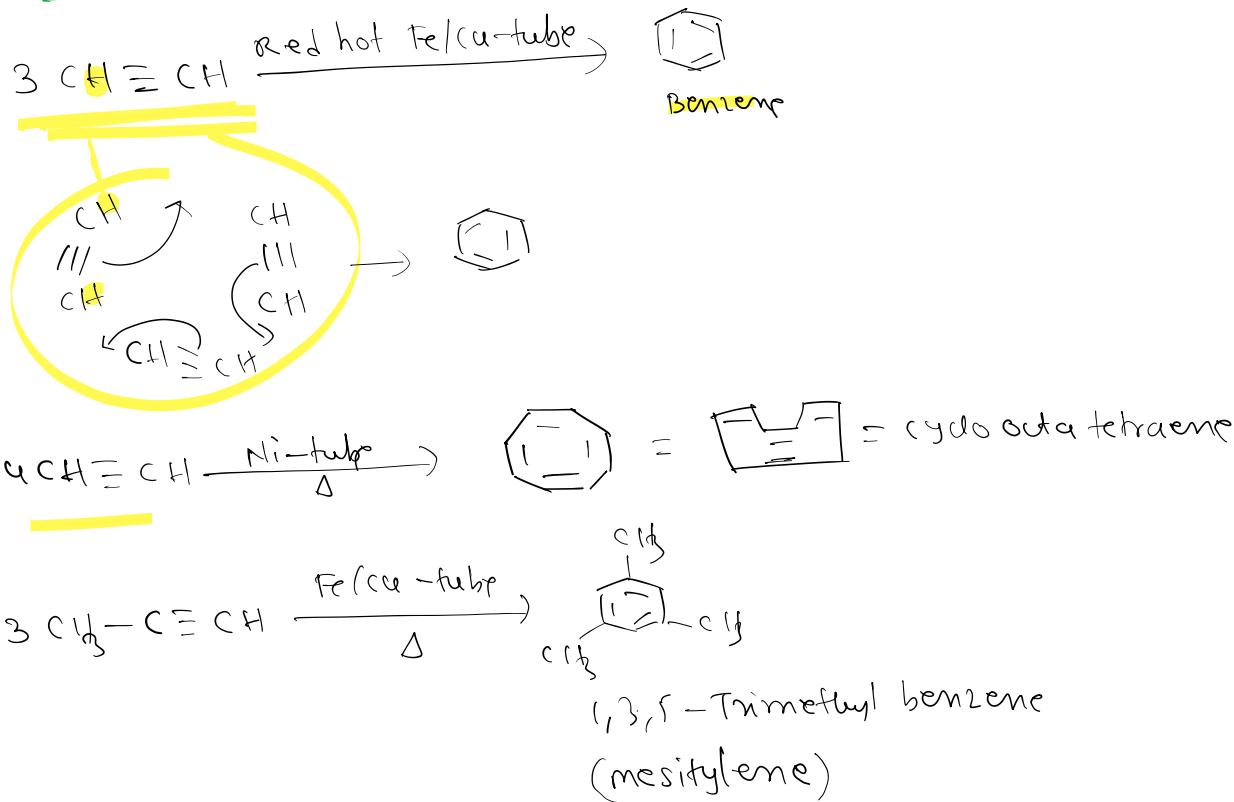
③ Addition of water ↴



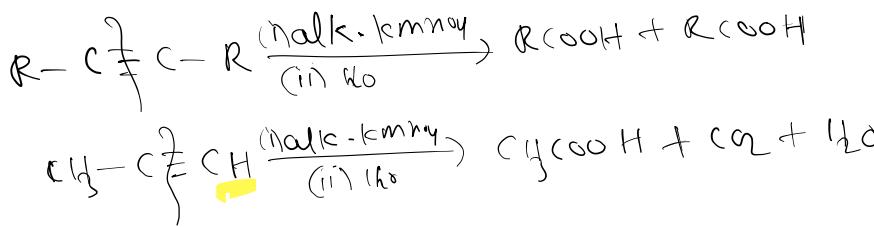
④ Addition of ozone ↴



⑤ Polymerisation of



⑥ Oxidation of



* Benzene of

$$\% \text{C} = 92.3$$

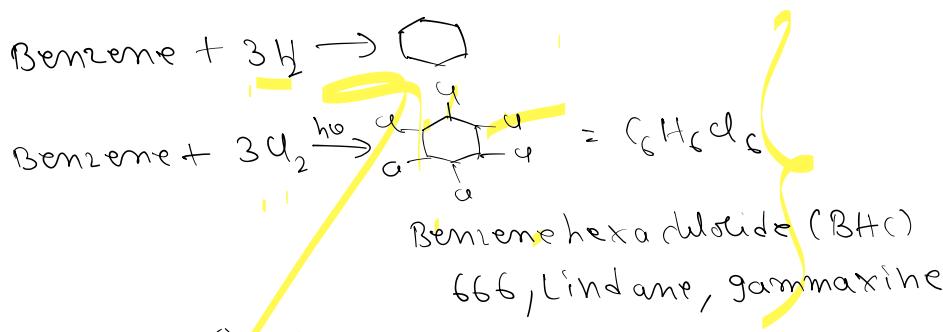
$$\% \text{H} = 7.7$$

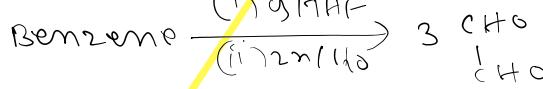
$$\text{EF} = \text{CH}, \text{EW} = 12 + 1 = 13$$

$$\text{VD} = 39$$

$$\text{MW} = 2 \times 39 = 78$$

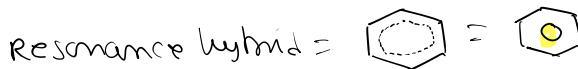
$$\text{MF} = (\text{CH}) \times \frac{78}{13} = \text{C}_6\text{H}_6$$



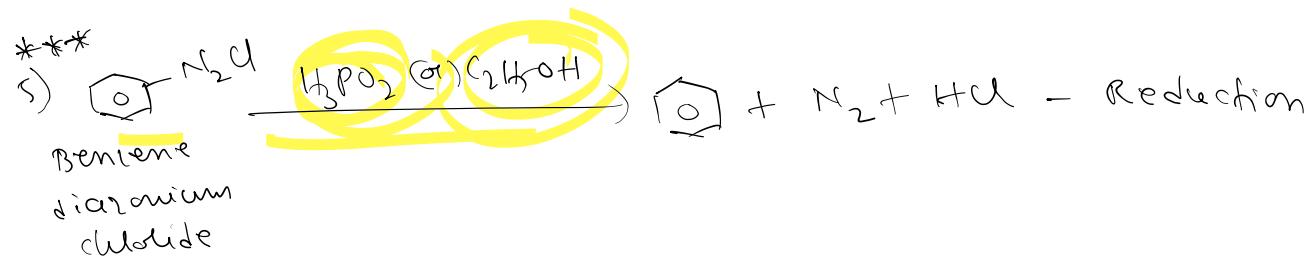
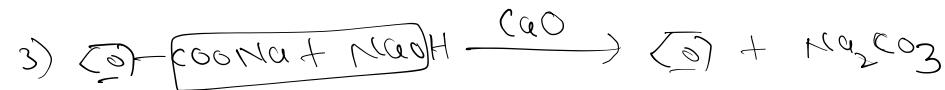
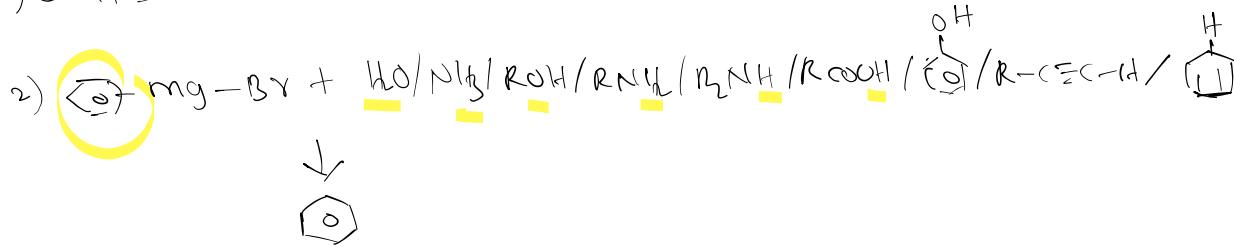
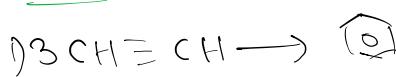


 = Kekulé structure

But, benzene will not decolorise $\text{Br}_2/\text{H}_2\text{O}$ and pink colour of alk. KMnO₄



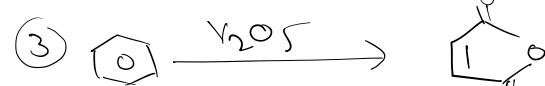
PREP &



Properties &

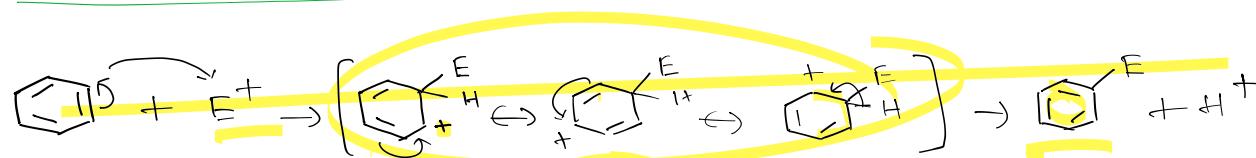
① pleasant smelling liquid

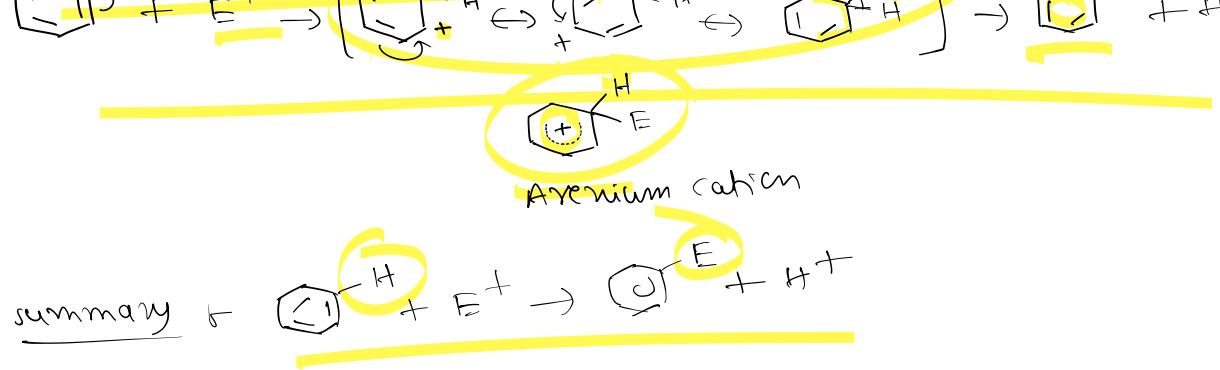
② insoluble in water



maleic anhydride

Electrophilic substitution (EAS or S_E) of Benzene :-





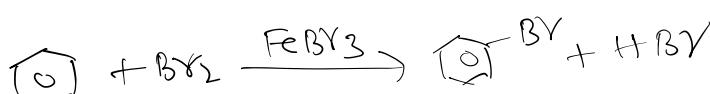
① Halogenation



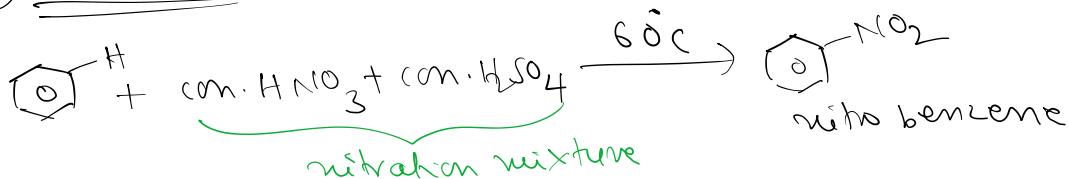
$$X_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2$$

lewis acids = anhyd. AlX_3 , FeX_3

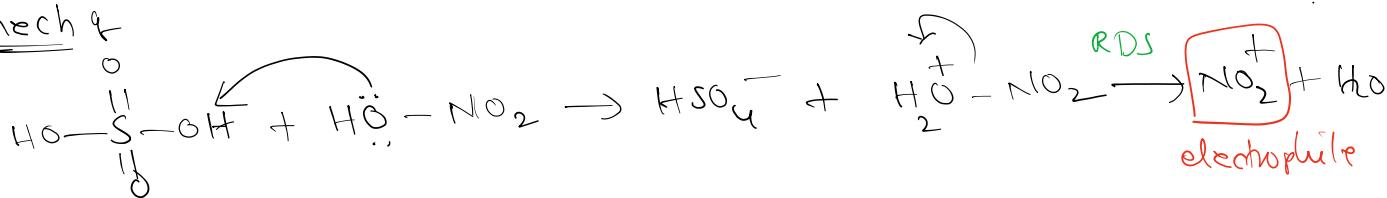
mech



② Nitration

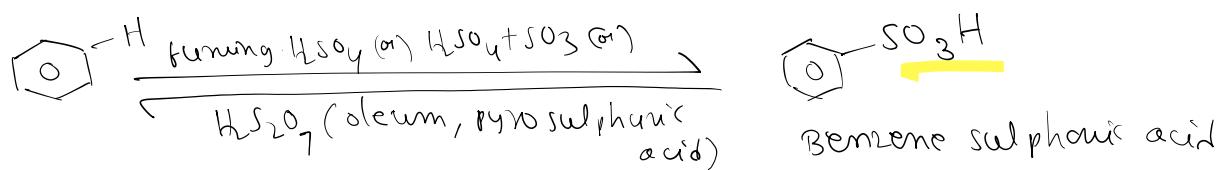


mech

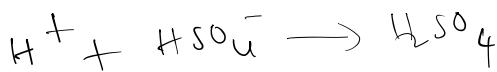
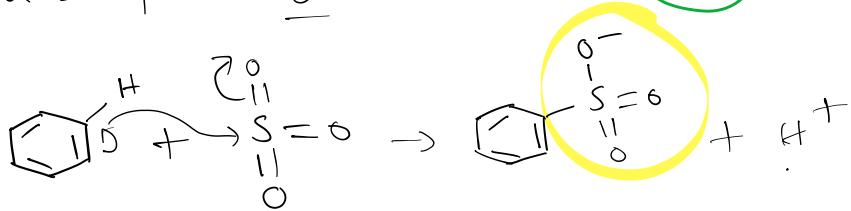




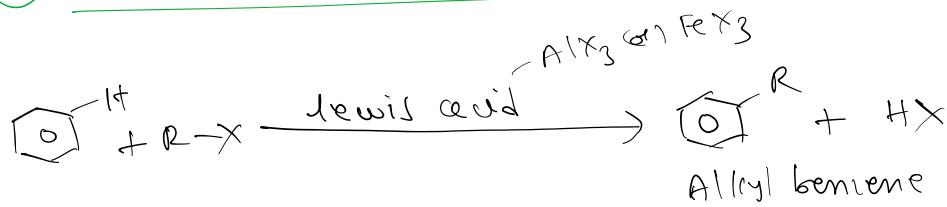
(3) sulphonation



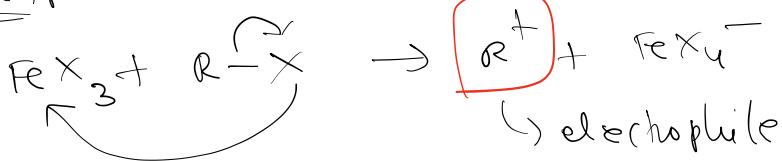
mech of

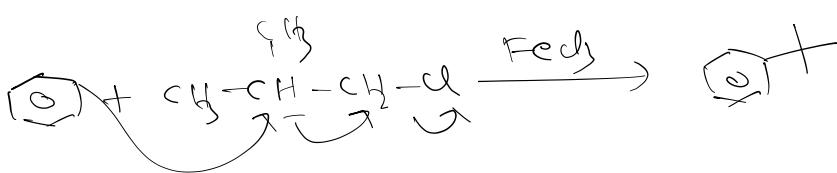
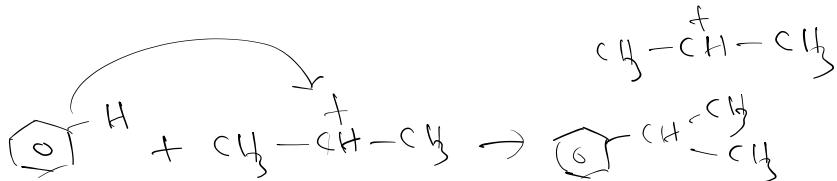
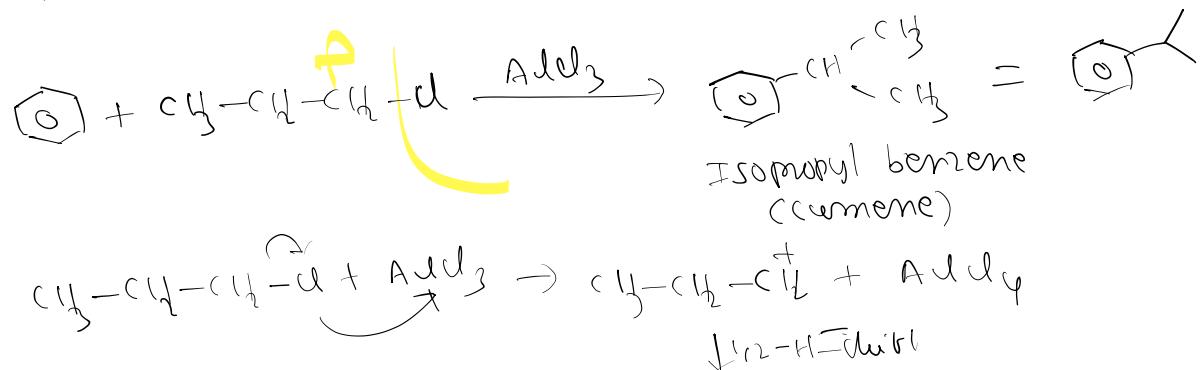


(4) Friedel-Crafts alkylation/acetylation



mech

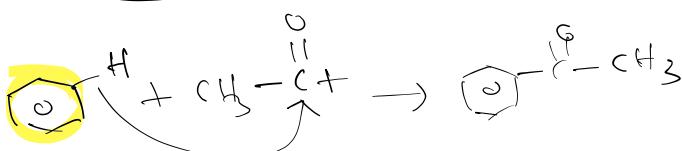
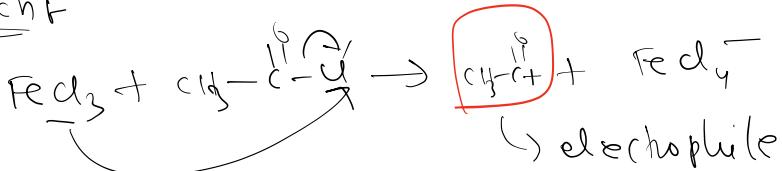




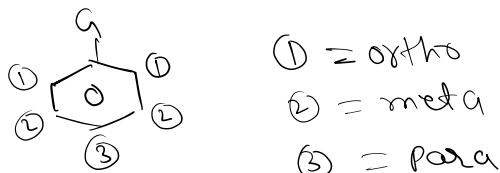
Acetylation of benzene



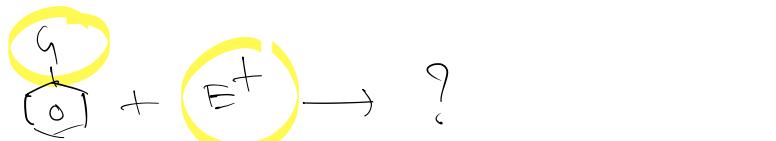
mech



S_E in monosubstituted benzene



- ① = ortho
- ② = meta
- ③ = para



The position of E^+ will be decided by the nature of group G .

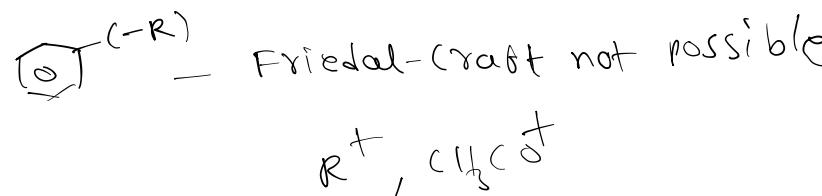
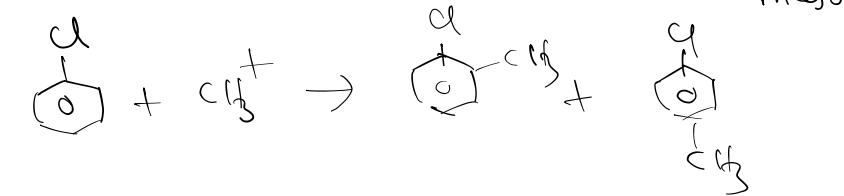
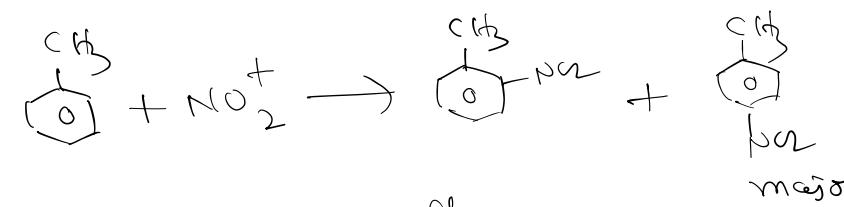
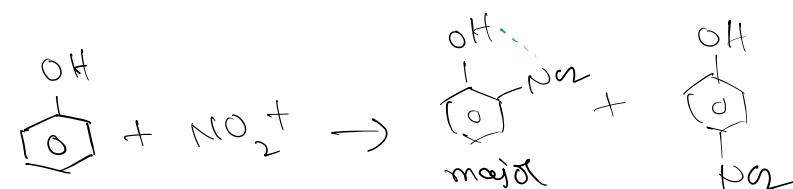
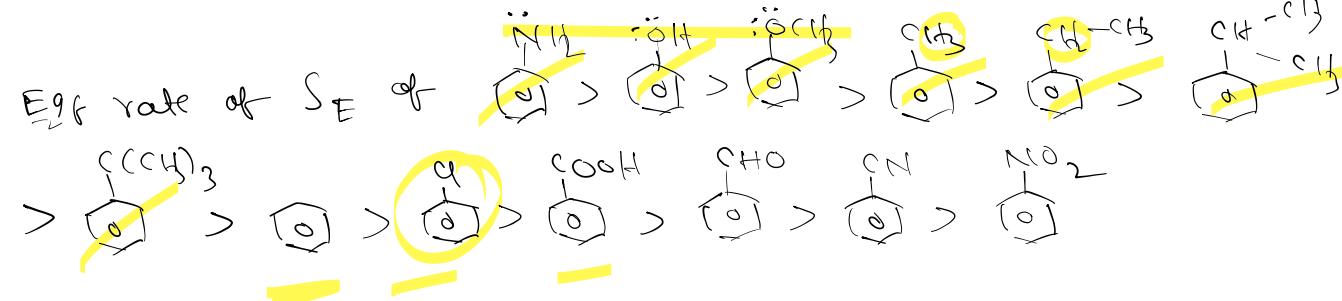
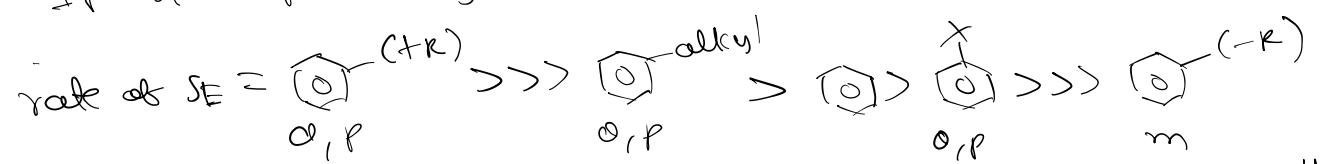
* G = substituent

The position or

If $\alpha = +R = \text{strong activating}^* = \sigma, p\text{-directing}$
 $(^*x = \text{weak deactivation})$

If $\alpha = \text{alkyl group} = \text{hyperconjugation} = \text{weak activation} = \sigma, p\text{-directing}$

If $\alpha = -R = \text{strong deactivating} = m\text{-directing}$

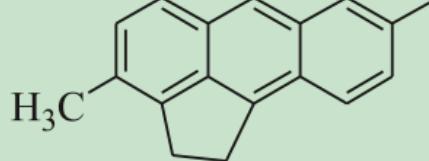


polycyclic aromatic compounds are carcinogens

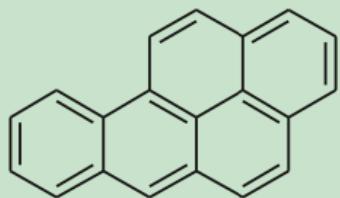




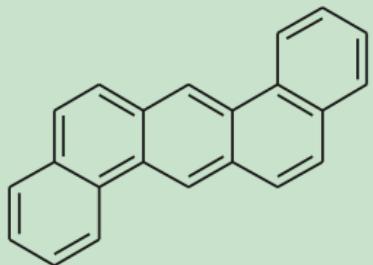
1,2-Benzanthracene



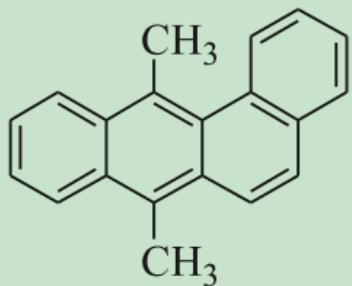
3-Methylcholanthrene



1,2-Benzpyrene



1,2,5,6-Dibenzanthracene



9,10-Dimethyl-1,2-benzanthracene