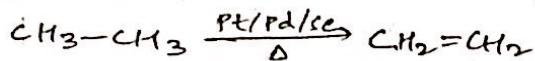


ALKENES:-

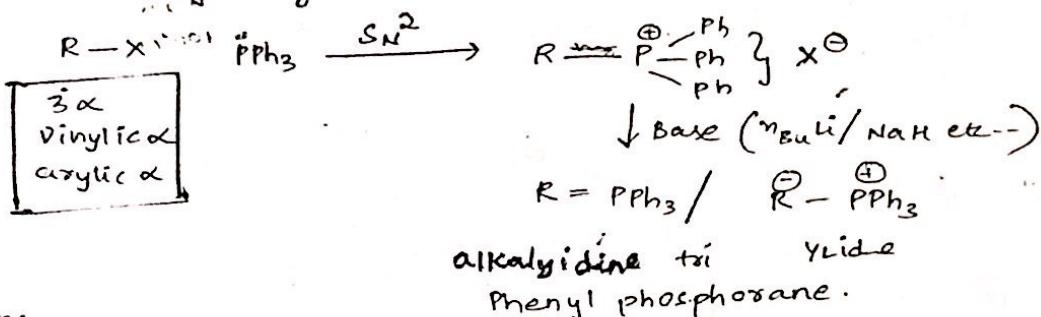
Preparations:

Dehydrogenation:

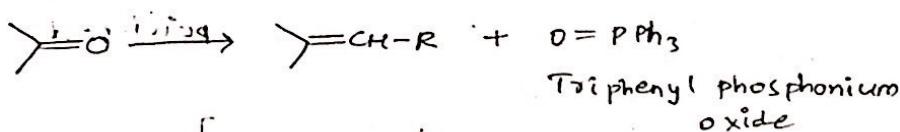
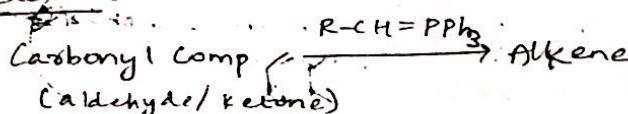


Wittig reaction:-

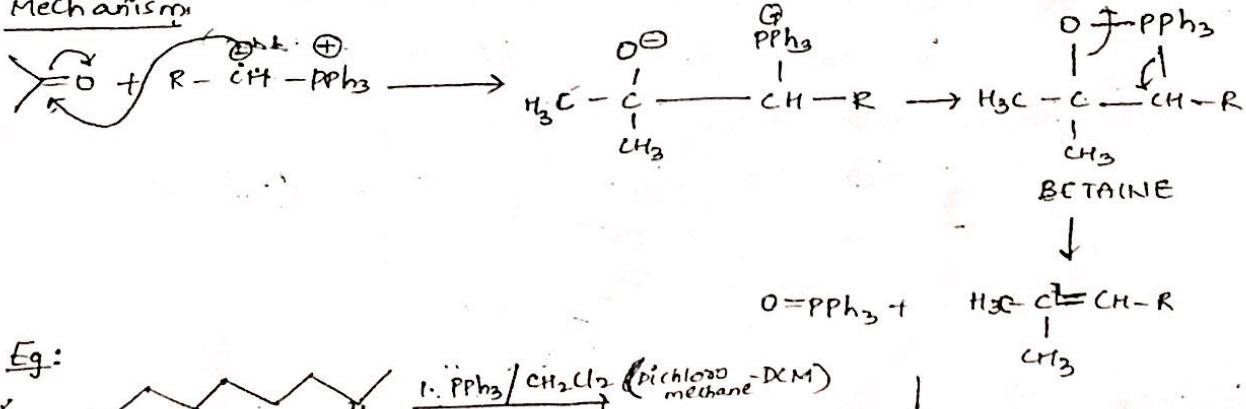
→ Prep. of Wittig reagent:



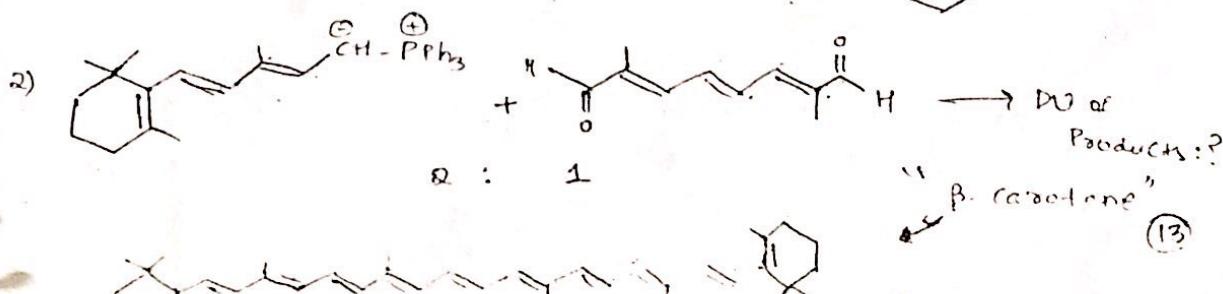
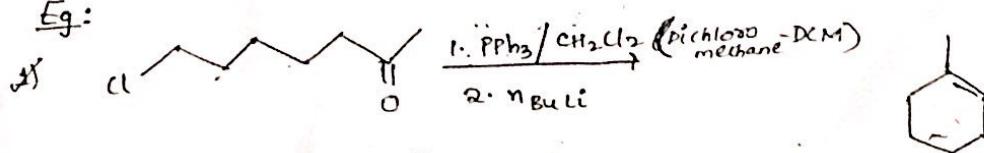
Reaction:



Mechanism:



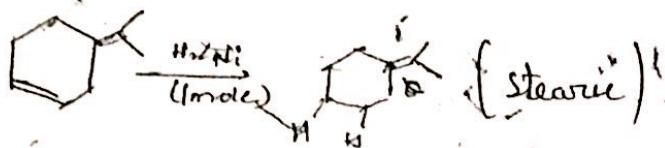
Eg:



→ After some time, they enhance the speed of production. That particular period is called Induction.

Period:

(8)

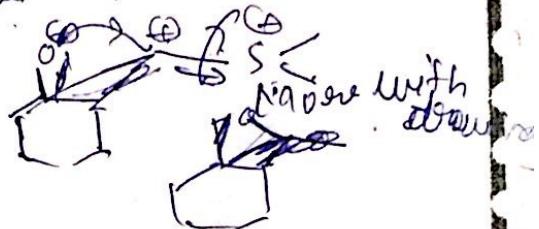
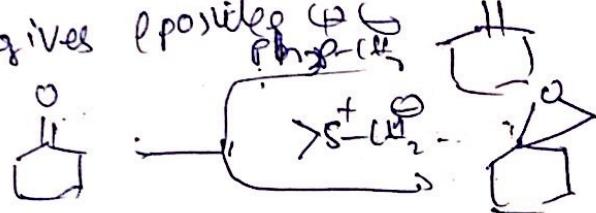


P_2/Ni

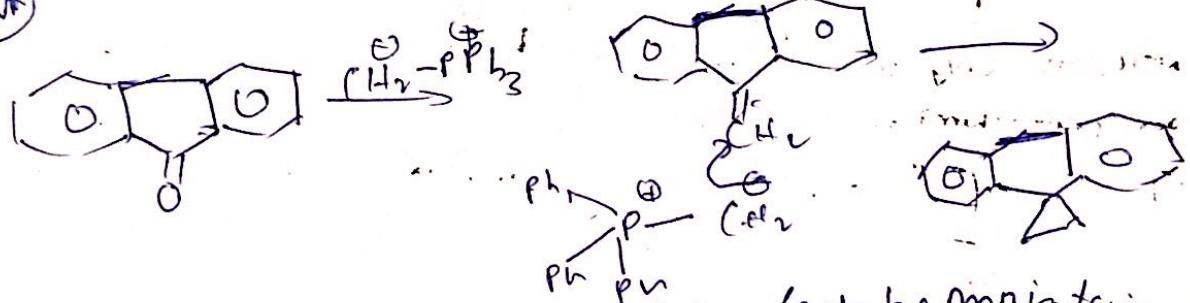


Phosphorous lides forms alkenes & sulphurylides

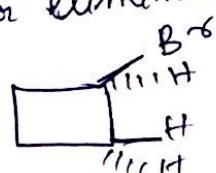
gives epoxide



(N)



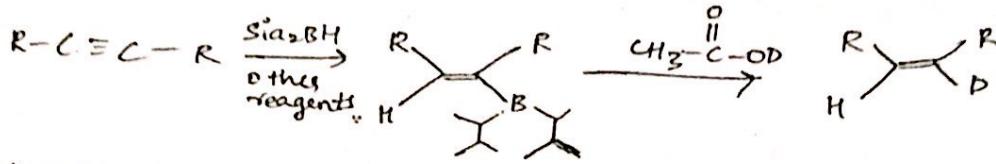
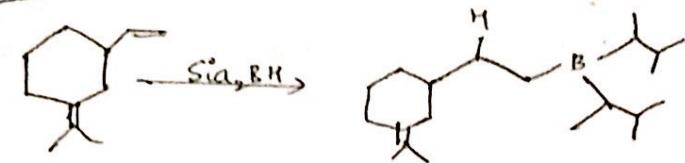
→ For elimination 0° or 180° angle to be maintained



180° not possible so syn elimination

→ Antielimination → Good in SE_6 but not possible in SE_4

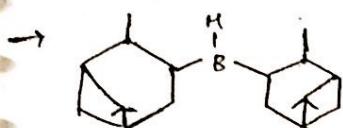
Advantage of $\text{Si}(\text{BH})_3$:



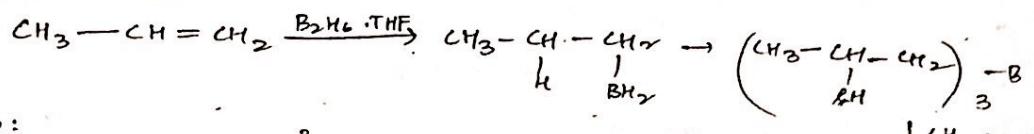
Other reagents:

→ $\text{B}_2\text{H}_6 \cdot \text{THF}$ (Not good) (N^* only accepts)

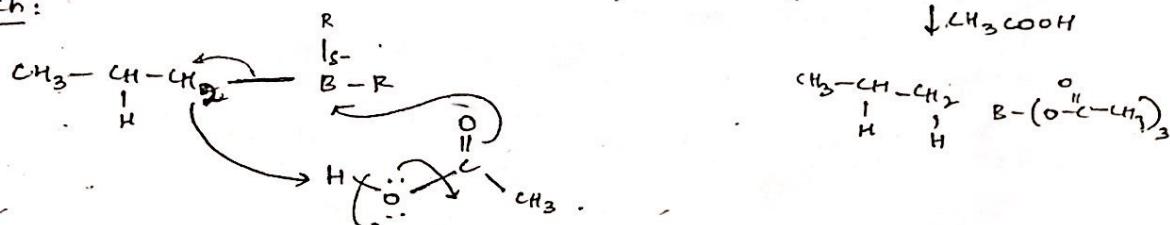
→ Catalytic Borane (



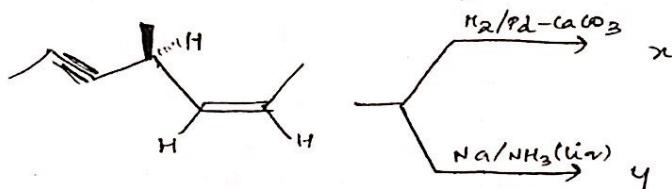
(N^*) Acatalysis reaction proceeds through cyclic 6-membered ring transition state.



Mech:



B)

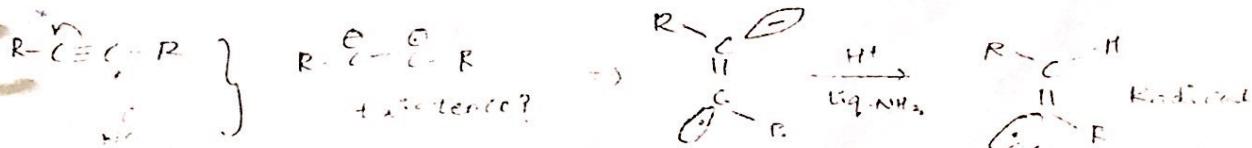


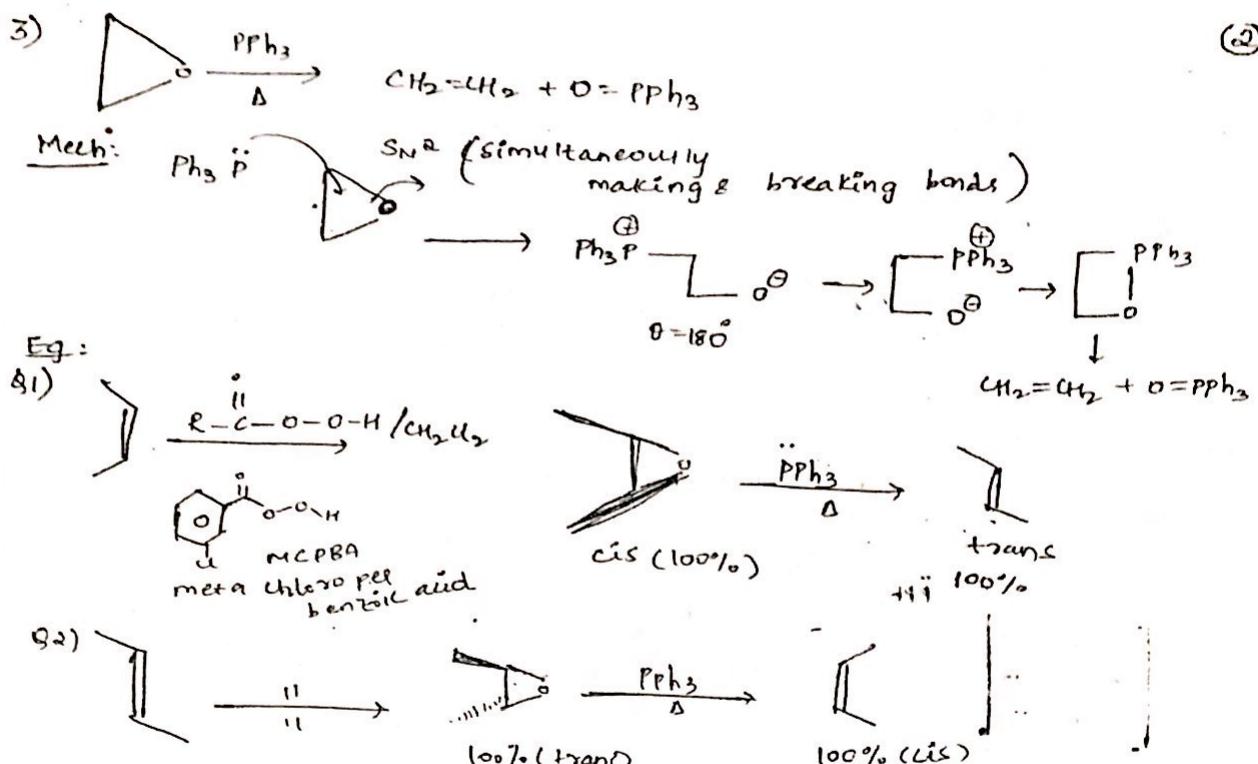
→ ~~BY~~ BIRCH REDUCTION:

source $\leftarrow \text{Na}/\text{NH}_3 \text{ (liq)}$ \rightarrow source of proton
of e^- $\text{Li}/\text{R-OH}$ (N^*)

→ it is failed to convert terminal alkynes to alkanes

→ Due to high s character, internal alkynes accept H^+ radical anion.





4) Catalytic hydrogenation:-

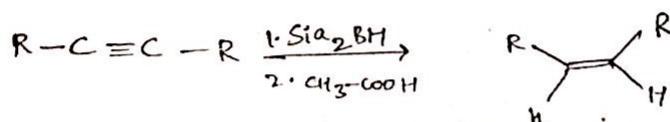
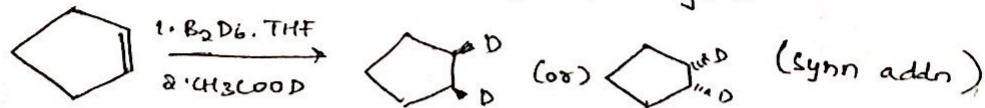
Reagents (1) Lindlar's catalyst. $\left(\text{H}_2/\text{Pd}-\text{BaSO}_4 + \text{Quinoline + Sulphur} \right)$
 $\text{Pd}-\text{CaCO}_3 + \text{C}_6\text{H}_5\text{N}_3$

→ After adding reagent to metal, metal gets poisoned and its activity decreased.

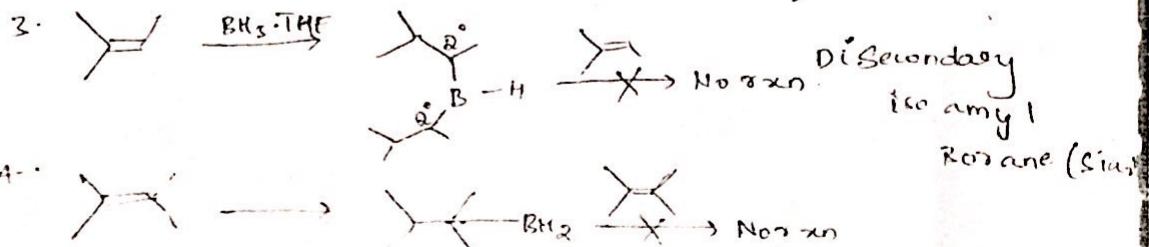
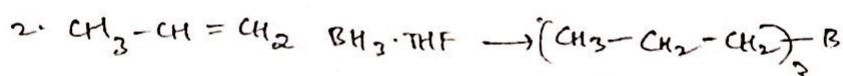
(2) Ni_2B (DiNickel Boride) / [P-2 catalyst]

yne → ene $\cancel{\rightarrow}$ alne (syn phase addn)

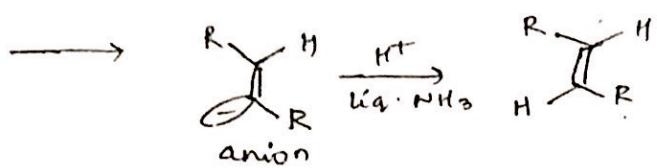
(3) Hydroboration followed by acetalysis.



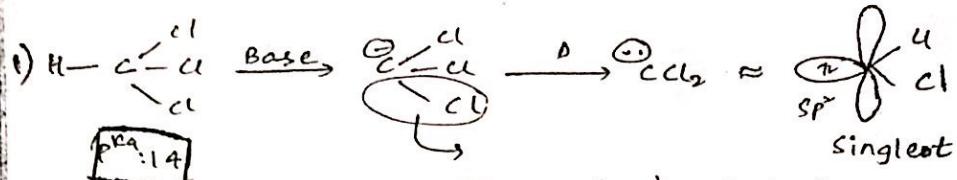
Mechanism:



(4)

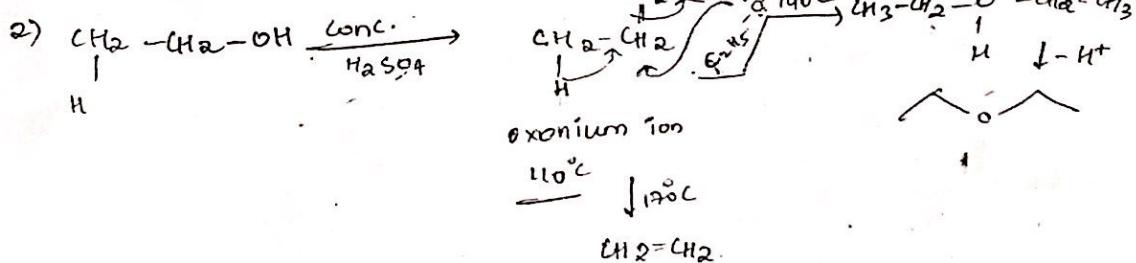
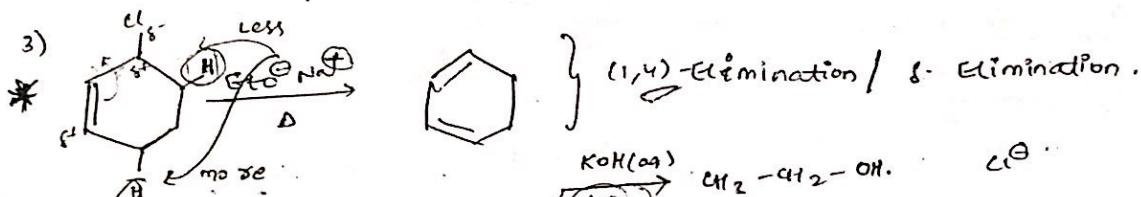
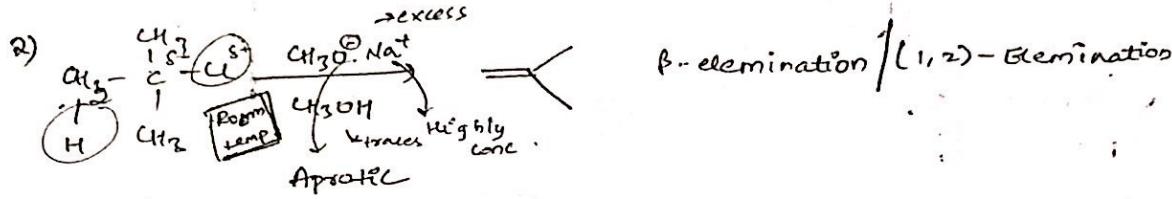


ELEMINATION REACTIONS:



α -elimination (or) (1,1)-elimination.

→ both the atoms are departing from same atom.



→ low temp. favours substitution, high temp. favours elimination.

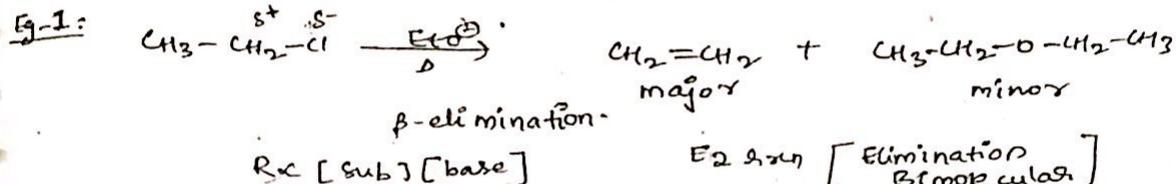
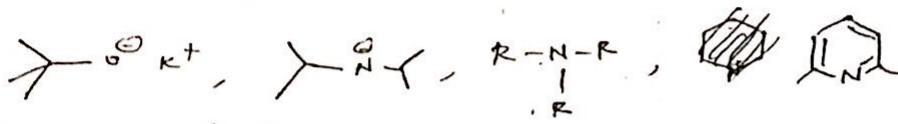
Expl:- $\Delta G = \Delta H - T\Delta S$

→ Entropy is more for elimination (Generally products are more than substitution).

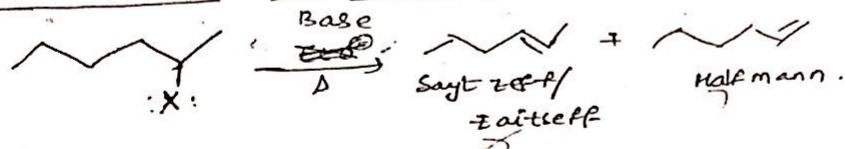
• If you rise temp. elimination become much more favoured.

Demyldeo halogenation:

② Reagents: NH_3 ,  , alc. KOH , EtO^- , $\text{R}-\text{C}\equiv\text{C}^-$, $\text{R}-\text{MgX}$ etc.
which are sterically free.



2) ORIENTATION OF π-bond:-



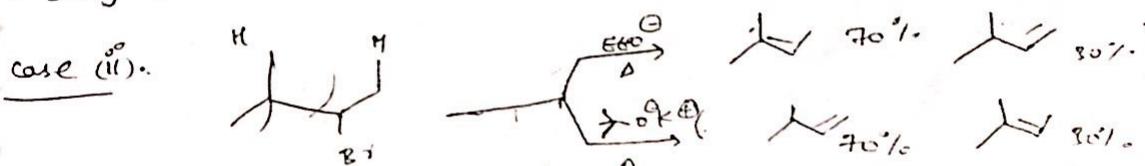
case(i):

leaving group ability / Elemental effect (Nucleofugacity)
 Base: MeO^-

-I:	81%	79%, 19%
-Br:	72%	28%
-Cl:	67%	33%
-F:	30%	70%

Expl:

- if leaving group is good, it immediately attains the transition state.
- stable trans. state forms major product
- if leaving group is poor, reluctant to attain trans. state, proceeds through partial carbocation character.
- only if base is sterically free.



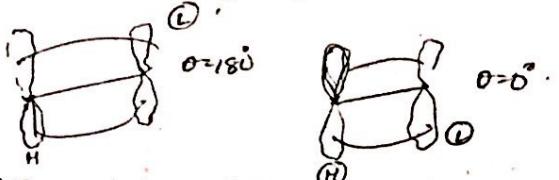
PRIMARY TERTIARY ALKENES & EXP. (REGIOSELECTIVITY)

ORIENTATION DURING E-2 REACTIONS: (ELIMINATION)

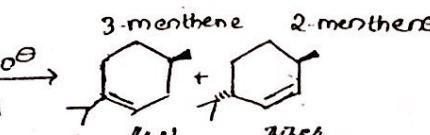
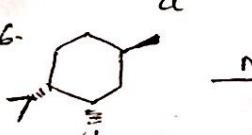
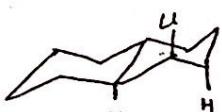
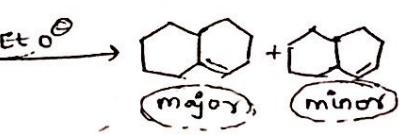
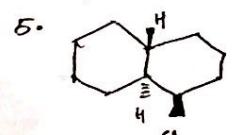
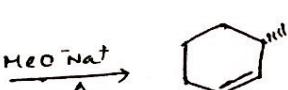
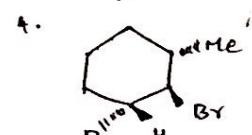
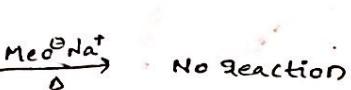
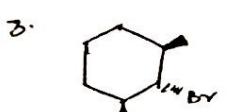
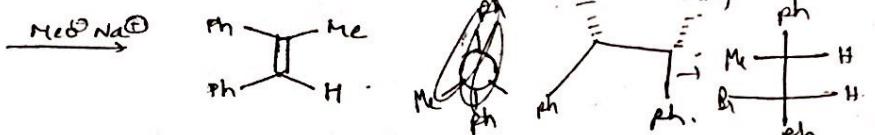
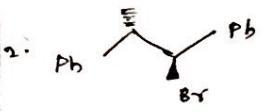
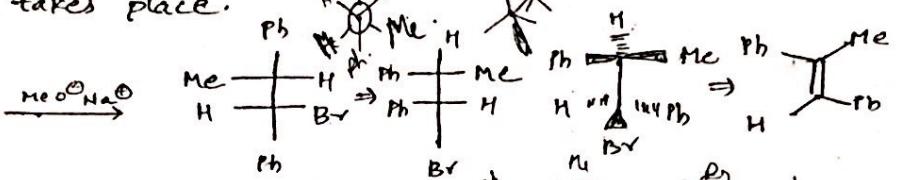
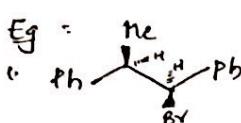
(6)

→ E-2 reaction proceeds through transition state and establish new π -bond therefore departing groups should maintain either $\theta = 180^\circ$ / $\theta = 0^\circ$.

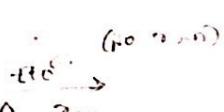
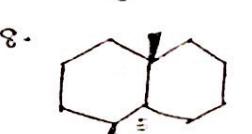
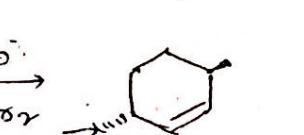
L-leaving group:

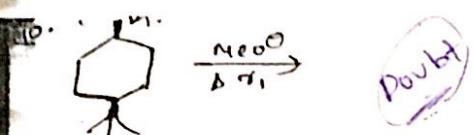


→ In sterically free system, anti periplanar elimination is more favour, whereas as in rigid systems, syn periplanar elimination takes place.

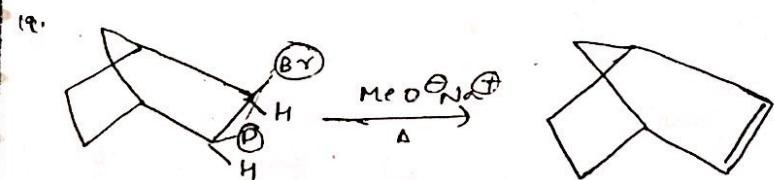
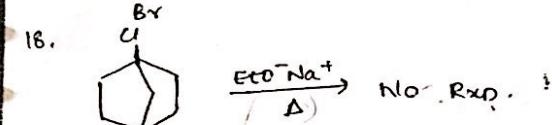
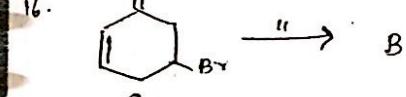
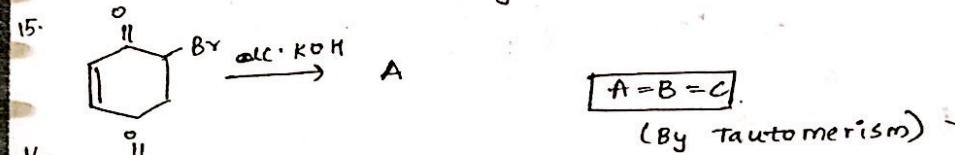
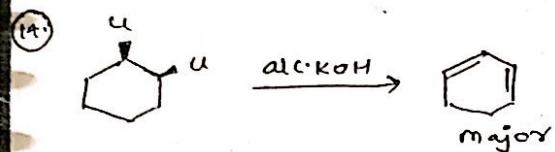
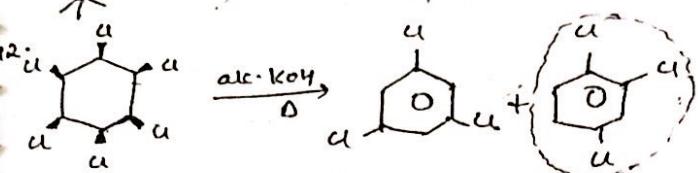
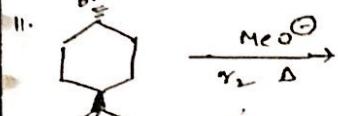


$$\frac{\tau_1}{\tau_2} \approx 250$$





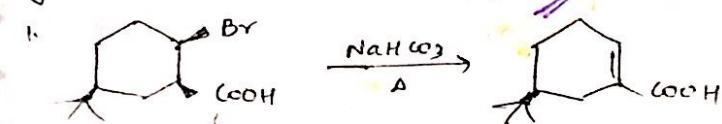
$\gamma_1 > \gamma_2$



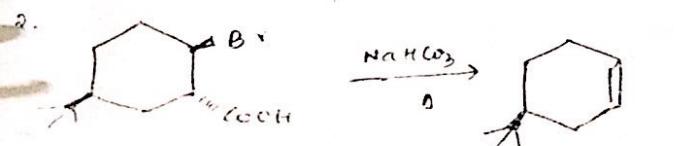
(E-2) Rigid system
synn periplanar
elimination takes place

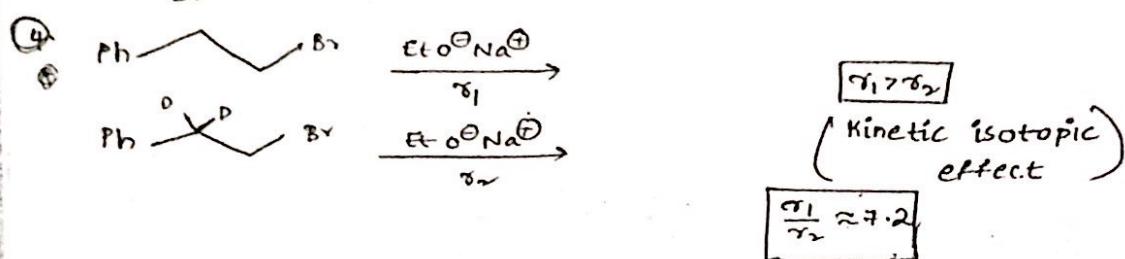
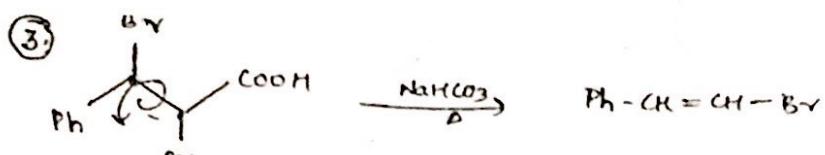
→ During dehydrohalogenation, C-C of halogen, (loss of CO_2) decarboxylation is more spontaneous.

Eg:



~~Loss of CO_2 when dihydral angle is 0° and no loss when it is 180°~~

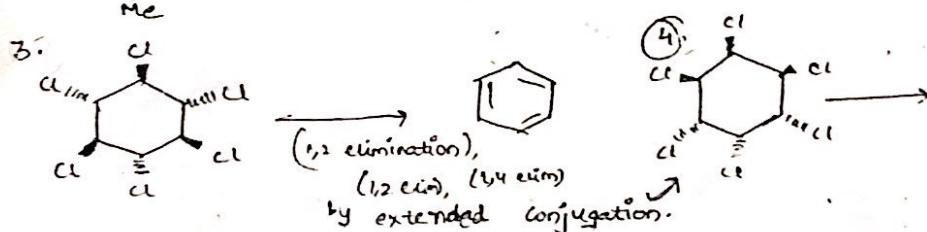
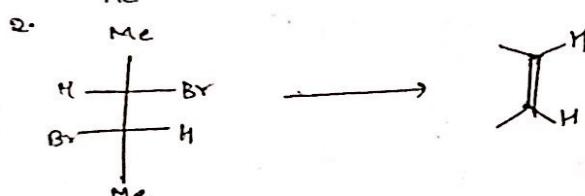
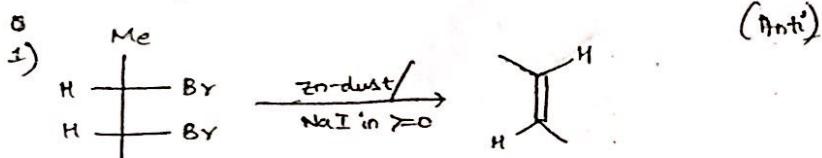
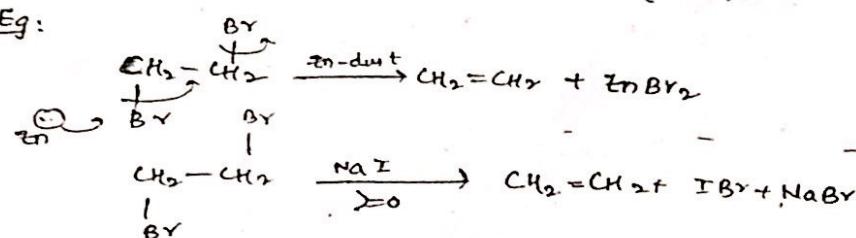




DE-HALOGENATION :-

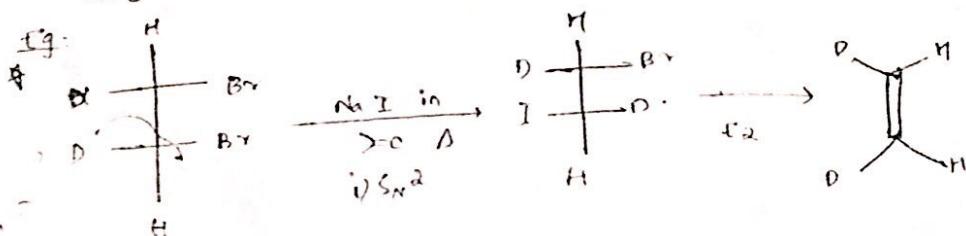
Reagents: Zn-dust / Na-I in acetone (≥ 0)

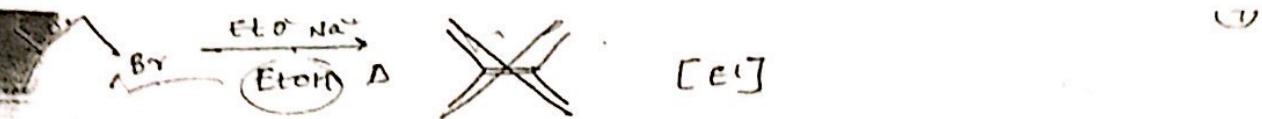
Eg:



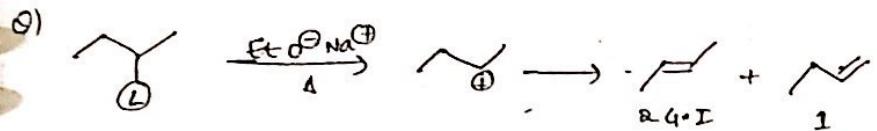
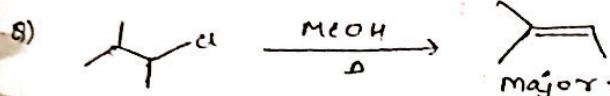
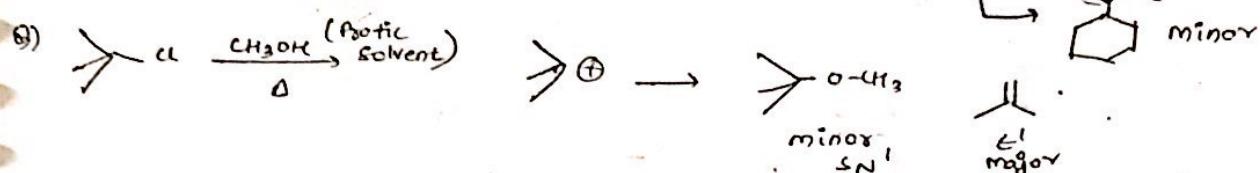
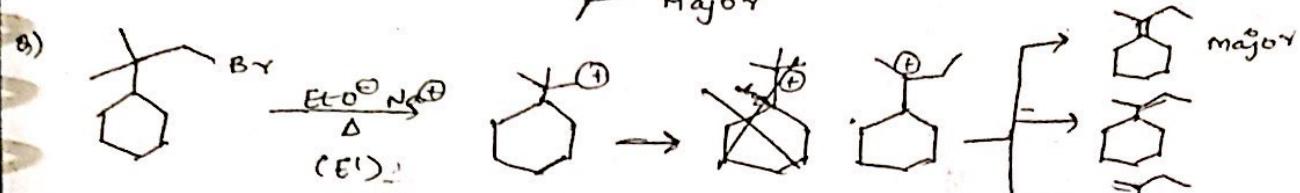
NOTE: NaI in acetone is a very good nucleophile. I⁻ is a very strong base. It can readily replace Cl⁻ and Br⁻ (2nd year NCERT)

∴ In Dihalide, if atleast one of the halide site is primary, before elimination, substitution takes place at one side.



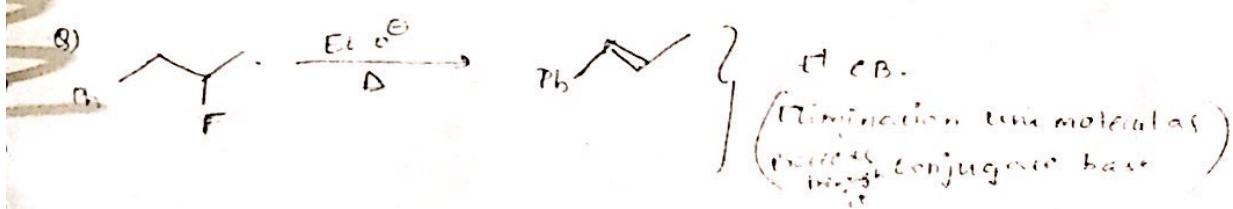


→ In highly concentrated base, we are expected E-2 reaction, if there is no β -proton, expected reaction. But despite that E-1 reaction promotes with traces of solvent.



-Br :	72%	81%	Path: (E2)
-F :	30%	70%	+ NH ₂ ClO.
-SMe ₂ :	26%	74%	H-CN ≈ 10
-NMe ₂ :	5%	95%	

→ Strong acids conjugate bases are good leaving groups.

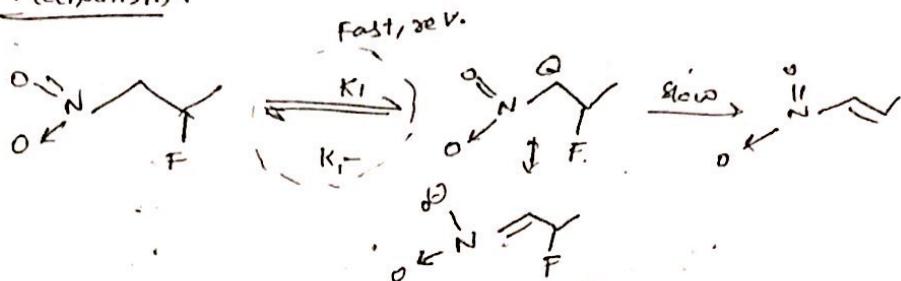




(1d)

-Cond'n: poor leaving group and carbocation stabilising grp
box (E1 CB)

Mechanism:



Rate law:

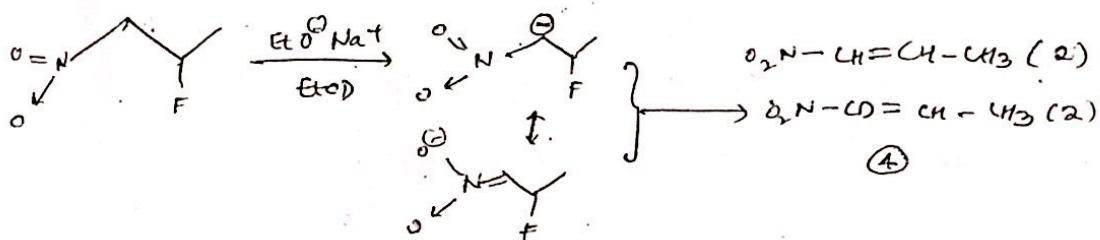
Rate $\propto [\text{C} \cdot \text{B}]^{\frac{1}{2}}$ unimolecular

$\propto [\text{substrate}][\text{Base}]$

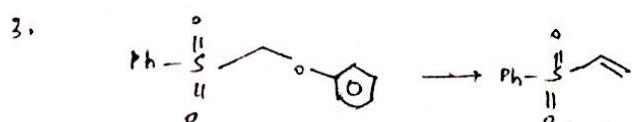
\Rightarrow pseudo first order (Follows 2nd order kinetics)

and shows: * Reverse Kinetic Isotopic Effect (or)

Solvent kinetic isotopic effect.

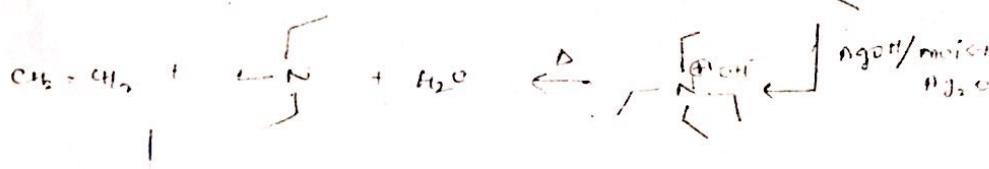
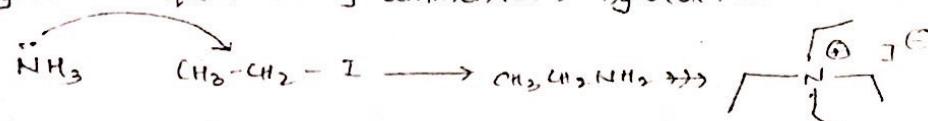


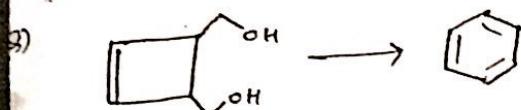
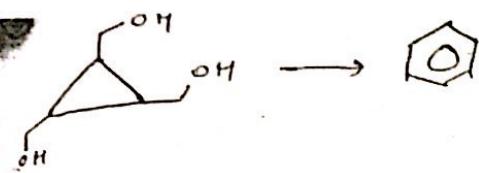
Other Examples:-



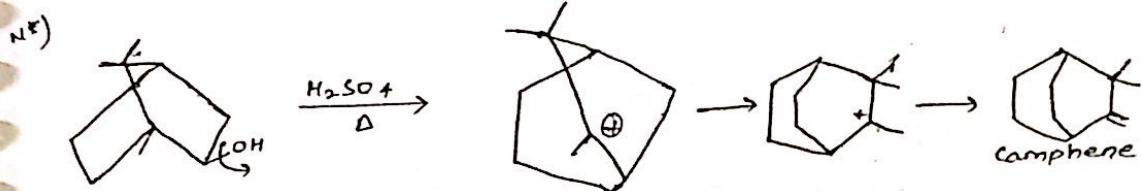
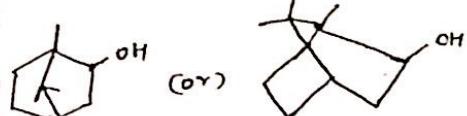
Hofmann-degradation:

\rightarrow Pyrolysis of quaternary ammonium hydroxide

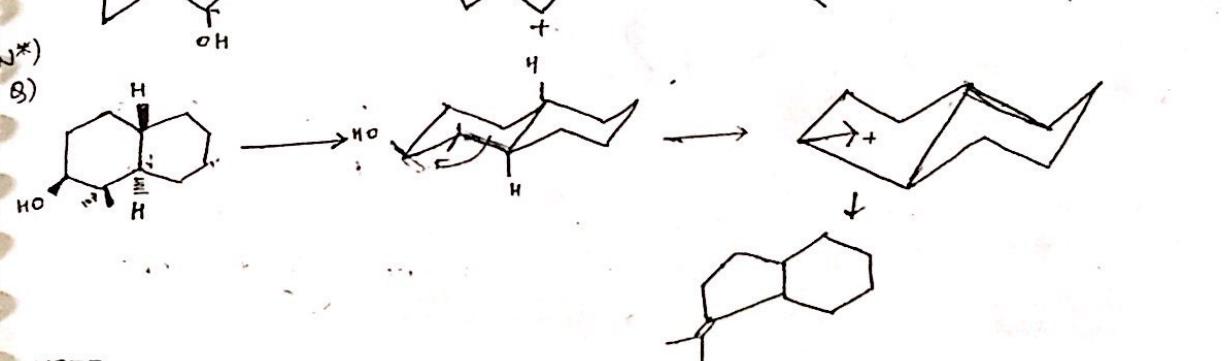




Koboraneol:



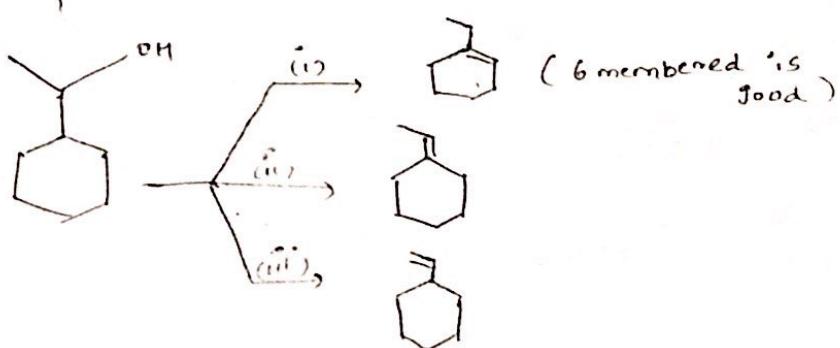
Campheniol: (Not in JEE)



NOTE:

- Conc. H_2SO_4 , H_3PO_4 , & Al_2O_3 favours E_i path.
- ⇒ Rearrangements are most common.
- $Al_2O_3 \cdot PY$ gives dehydration product without rearrangement (Seitzeff)
- TiO_2 gives halfmann product without rearrangement

Eg:

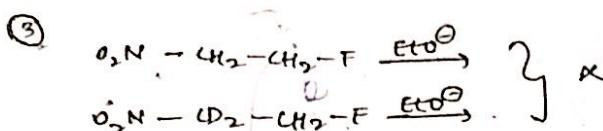
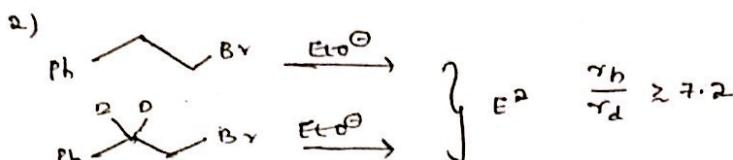
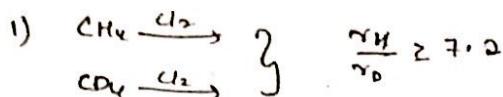


PRIMARY KINETIC ISOTOPIC EFFECT:

(6)

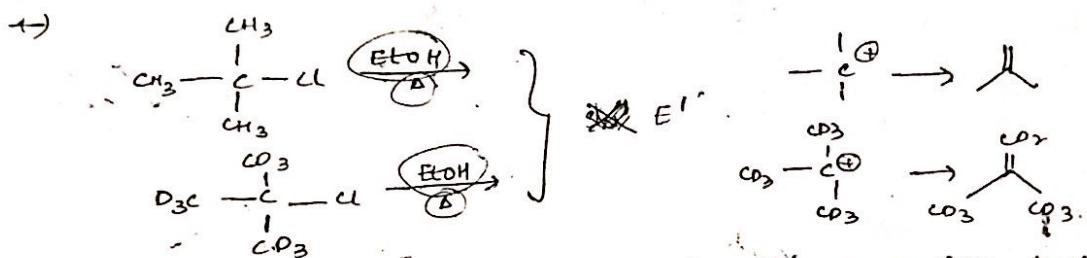
→ Cleavage of isotopic bond involved in RDS step by which more difference is observed in the rates. (approximately ≥ 7)

Eg:



It is E_{1CB} reaction → does not show isotopic effect.

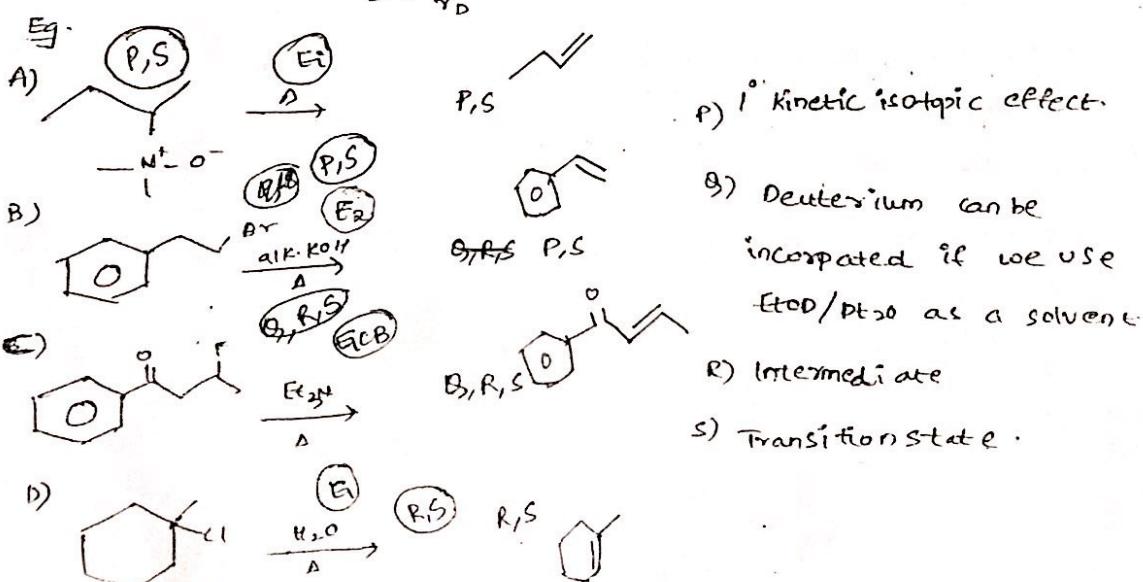
Doubt: It shows solvent isotopic effect (Not isotopic effect)



→ Isotopes aren't involved towards its formation, but in fast step, cleavage of isotopic bond is involved.

∴ E₁ reactions are called secondary isotopic kinetic effect

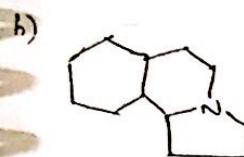
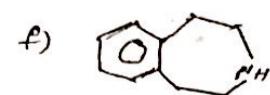
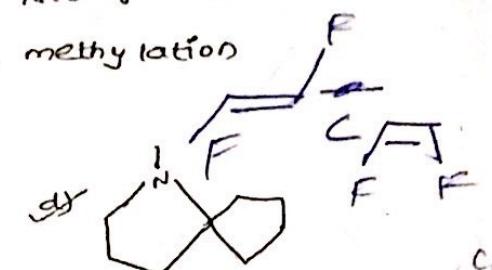
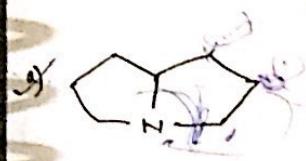
$$3 > \frac{r_H}{r_D} > 0$$



(17)

a) Li/Δ (zinc dust)b) NaZ in C_2O_4 c) Na in Et_2O d) Mg in Et_2O (Grignard)

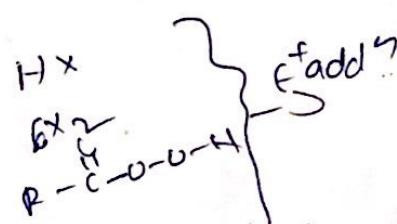
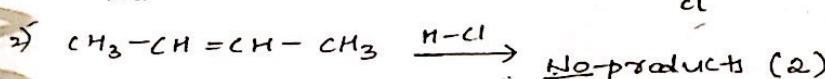
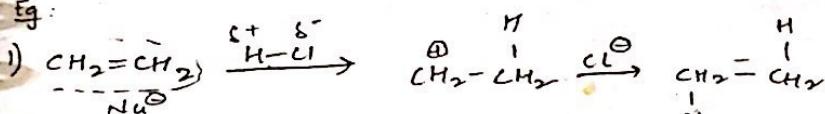
N*) In how many of the following molecules Nitrogen is completely departed during exhaustive methylation followed by Hoffmann elimination.



PROPERTIES OF ALKENES:

1) ADDITION OF HX :

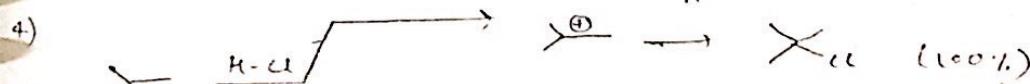
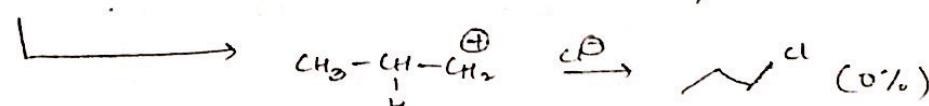
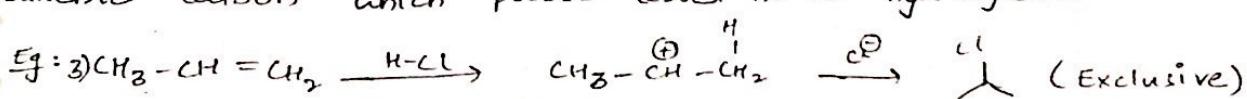
Eg:

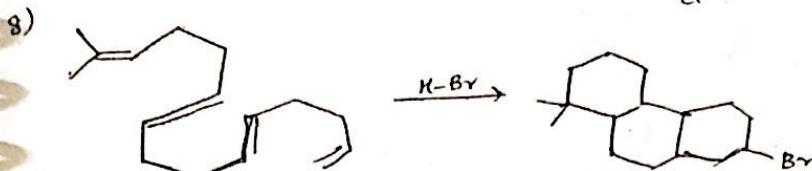
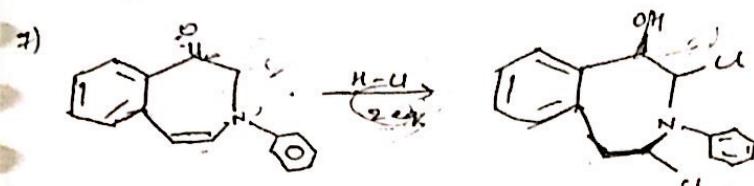
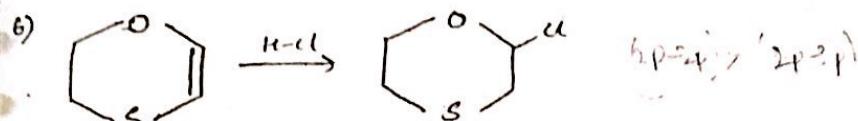
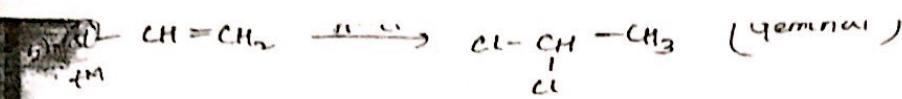


impt
 Therefore Nu^- more
 If no character more
 geometrical then more reactive

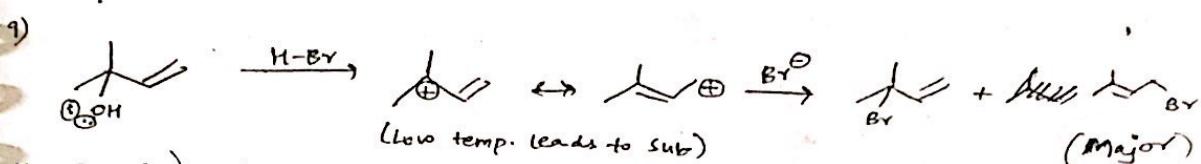
Markovnikov's:-

→ From the reagent, negative counter part is added to alkenic carbon which posses lesser no-of hydrogens.





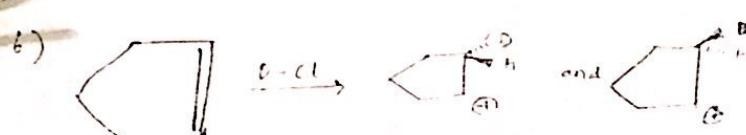
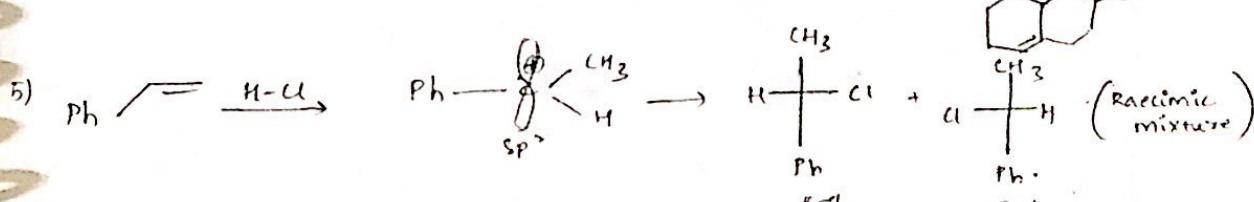
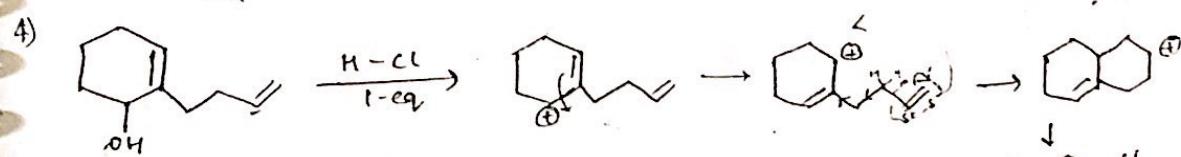
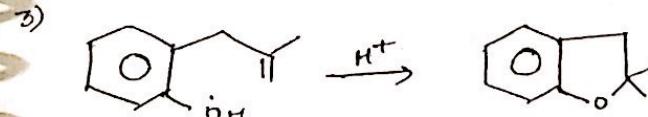
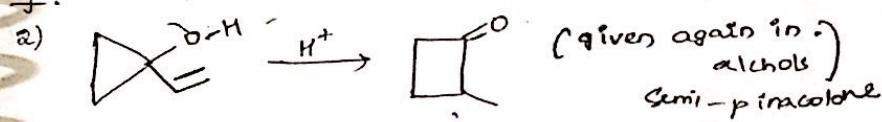
No. of carbocations formed: ④



→ Protination of LP > Protination of π -bond. and the most imp. is which forms stable carbocation.

- Give imp. for product stability if rxn is carried out at more than 0°C .
- Give imp. for intermediate stability if reaction is carried out less than 0°C .

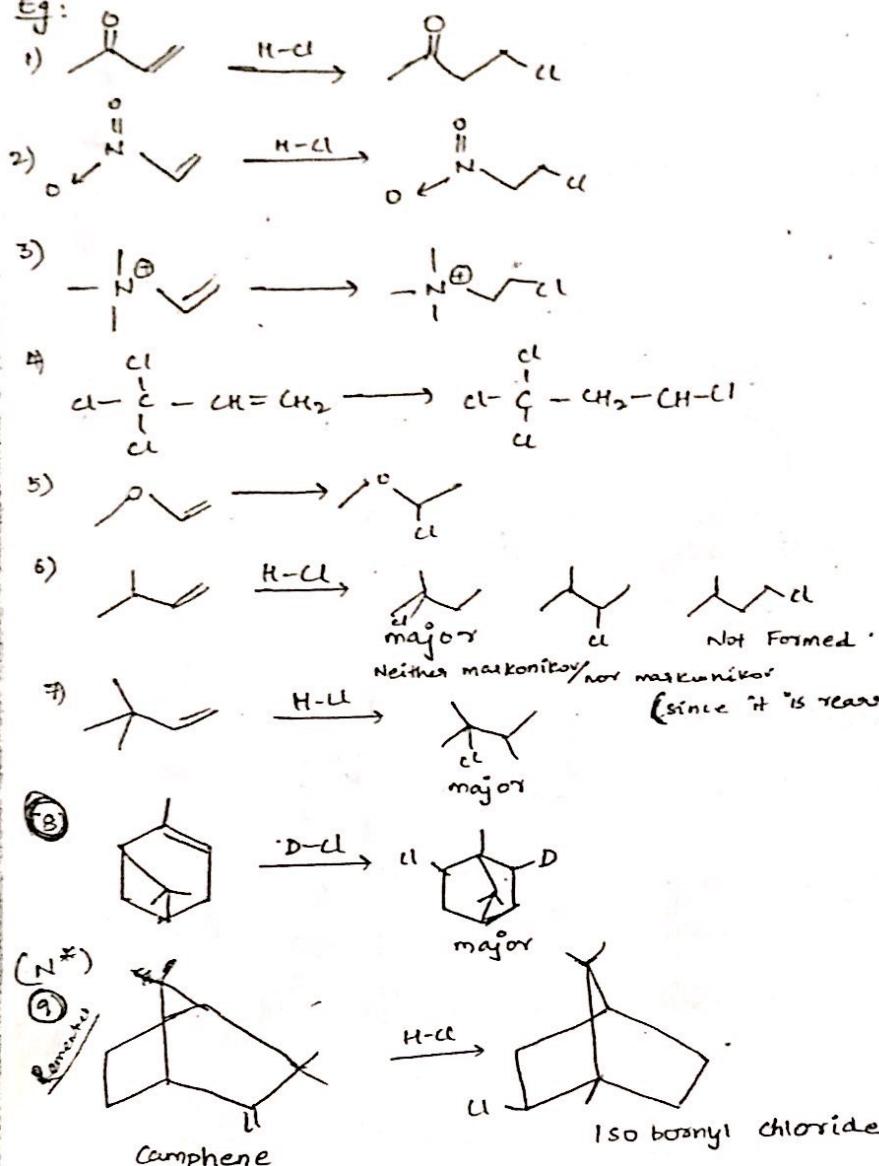
Eg.:



→ If both the carbons in alkene have substituent, it gives 2 products but if only one carbon is having substituent, it gives only one product.

(18)

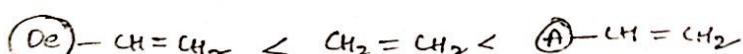
Eg:



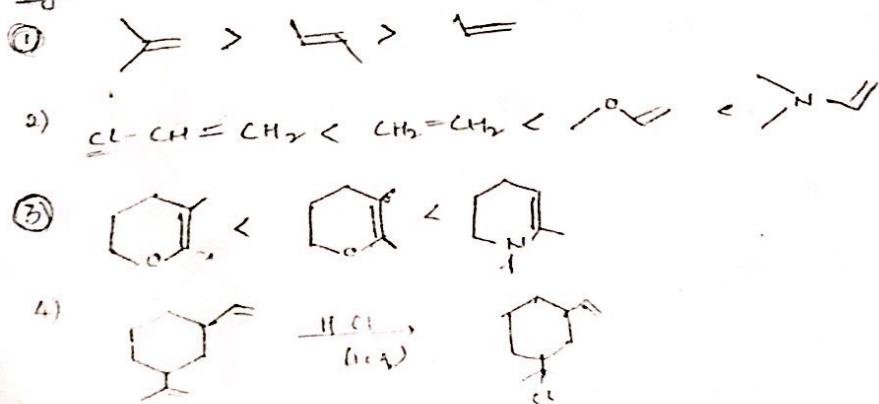
REACTIVITY:-

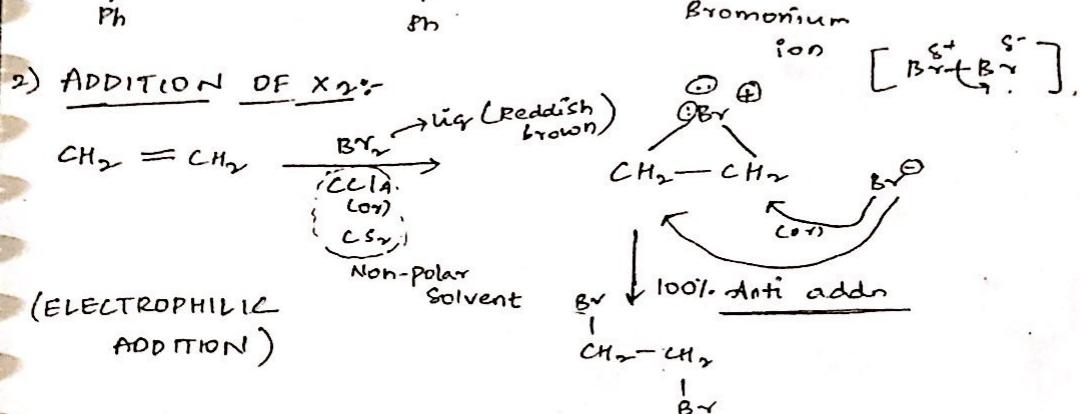
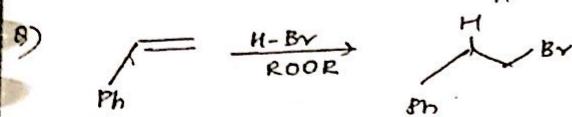
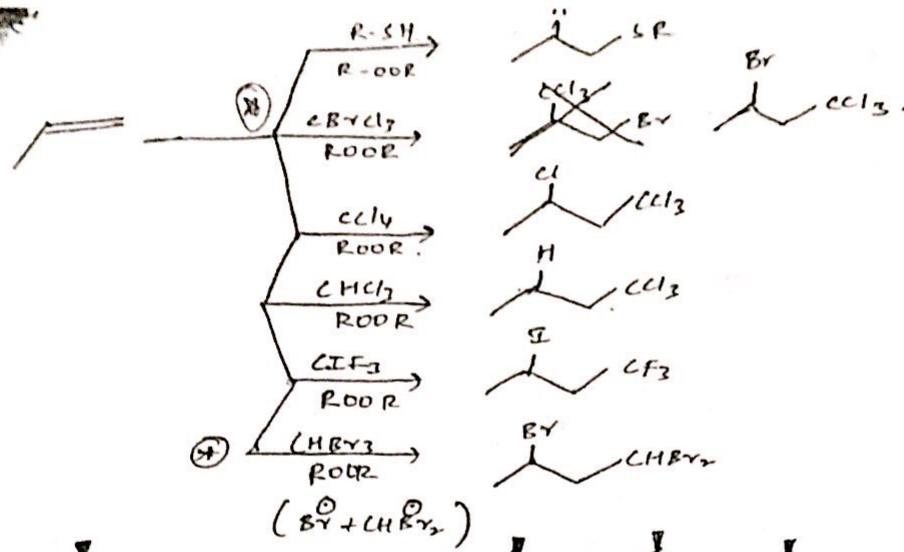
de-deactivating

+A - Activating



Eg:





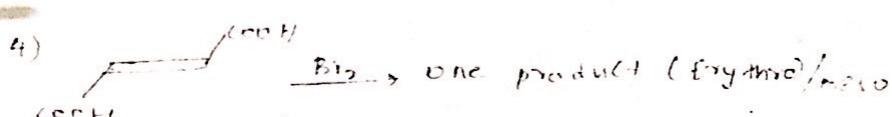
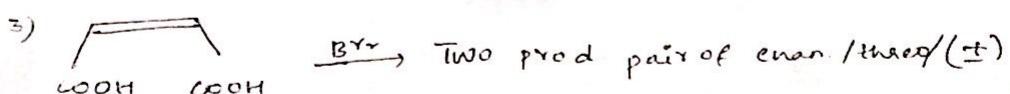
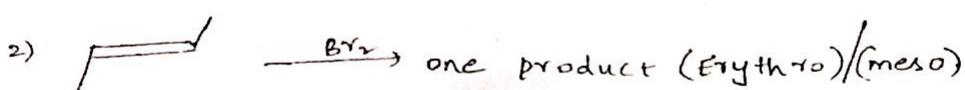
ADVANTAGE:

→ To detect unsaturation like $\text{C=C}/\text{C}\equiv\text{C}/\text{Alkene}$ present in a compound.

Reported: Red. Brown \rightarrow Colourless.

π -bond decolorises bromine.

Eg.





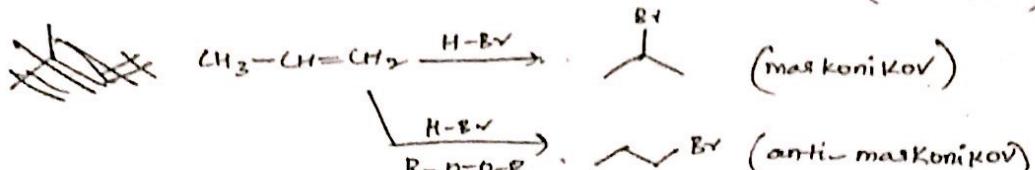
(D is more repellent)

Q1

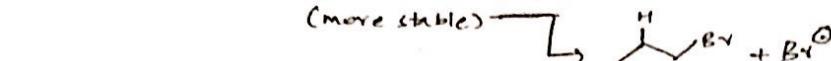
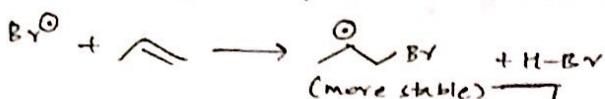
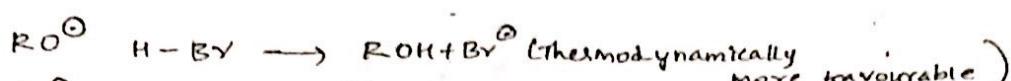
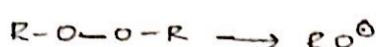
major

Addition of H-X in presence of peroxides:- (Kharasch effect)

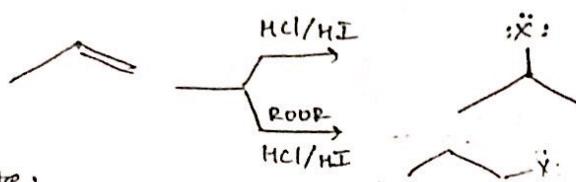
1)



Mechanism:-



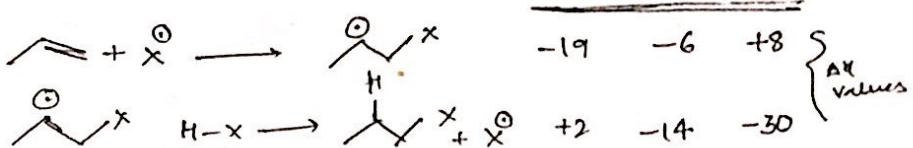
2)



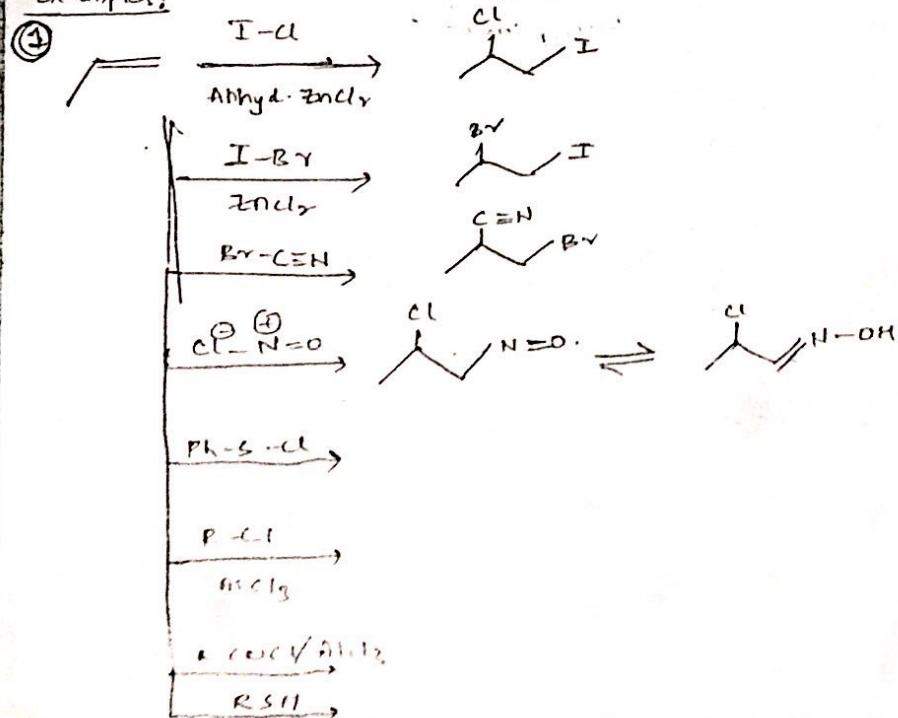
Note:

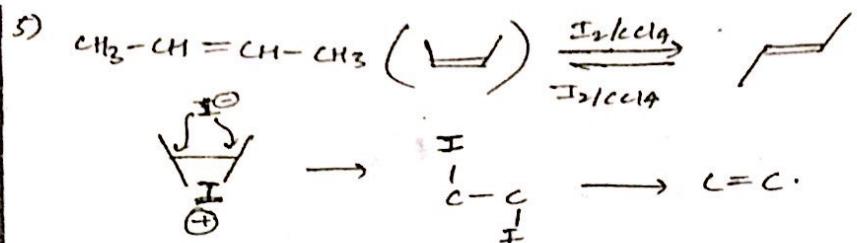
→ Peroxide effect is not observed in case of H-Cl and H-I
means it is electrophilic addn

CRUCIAL STEPS:-



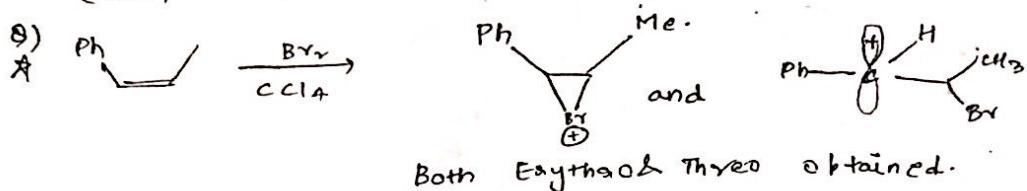
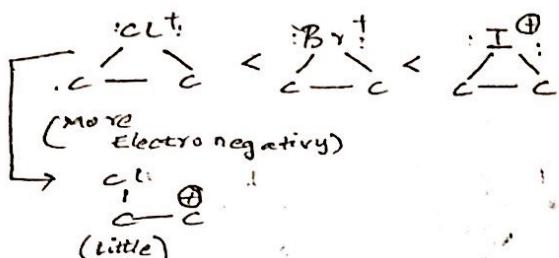
Example:-



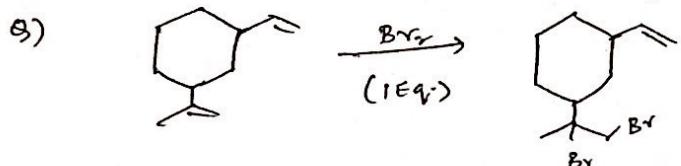
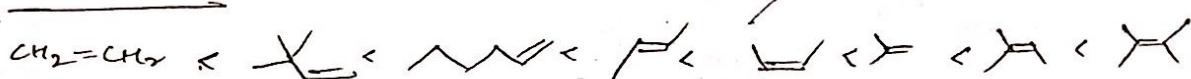


2 Iodines cannot stay
on adj. carbon atoms

Stability:



REACTIVITY:

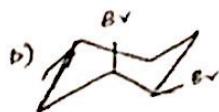
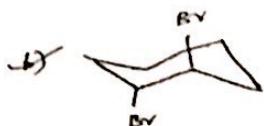
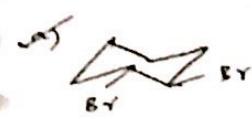


8) Which is/are gives pair of diastereomers?
(on addn of Br_2/CCl_4)

- (A)
- (B)
- (C)
- (D)
- (E)



Product is (are)

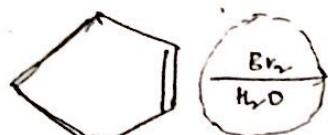


Q)



No. of tetrabromo prod: ③

Q)



* NO H^+

* Step (1):



* Step (2):

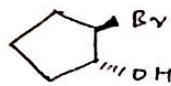
Hint: From alkyl halide

(Nucleophilicity) : (P.P.S) : $I^- > Br^- > Cl^-$

Polar protic solvents



→



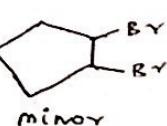
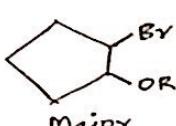
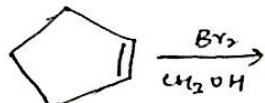
and

minor

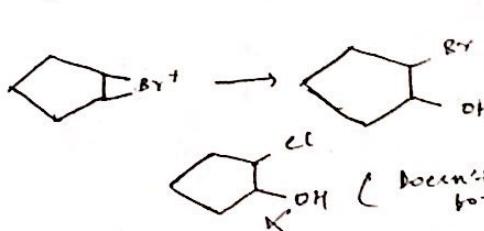
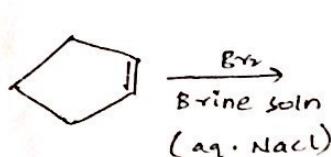
Major

(High conc. of H_2O)

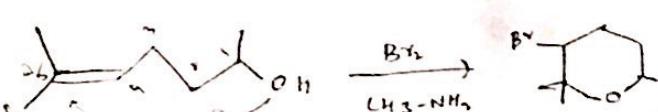
Q)



Q)

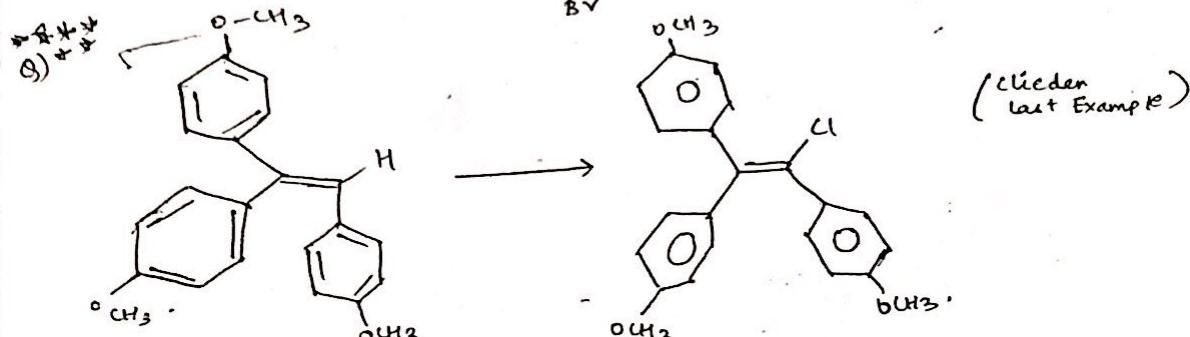
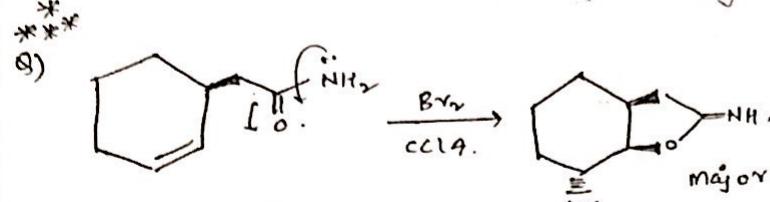
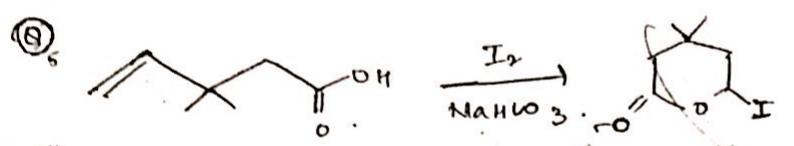
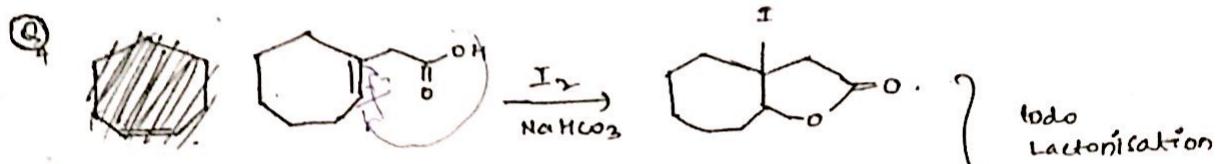


Q)

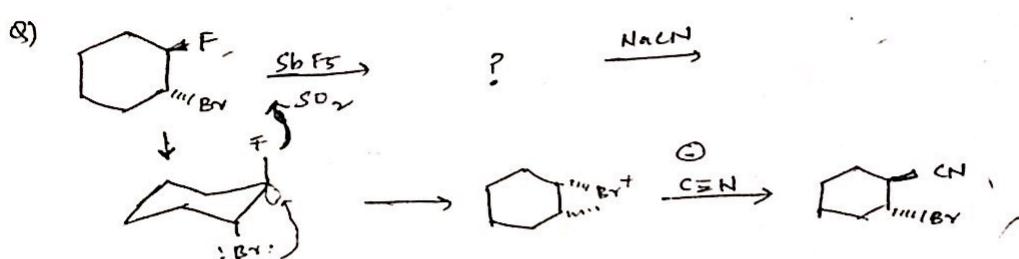


Q)





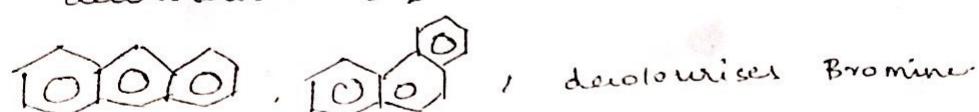
EVIDENCE FOR HALONIUM ION:

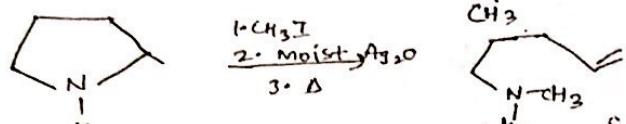
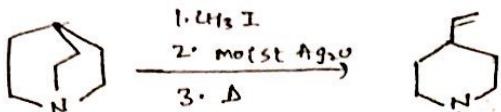
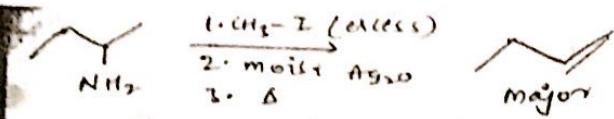


NOTE:

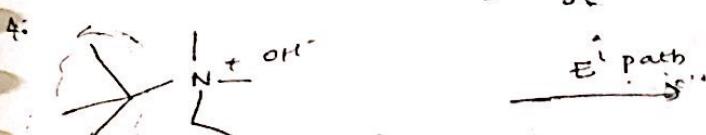
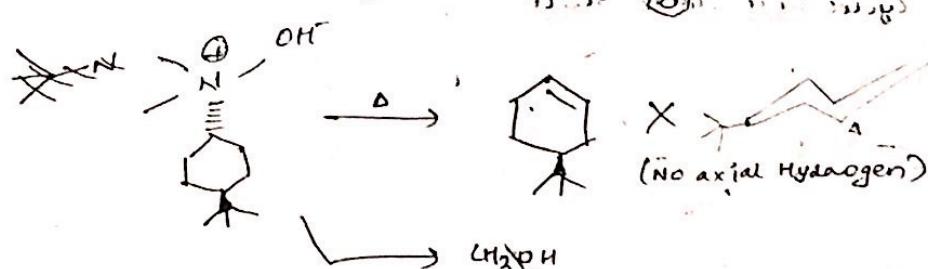
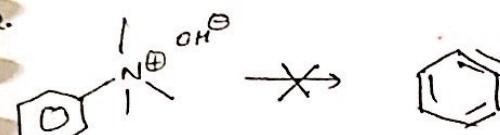
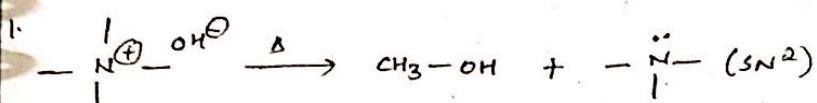


decolourise Br₂. whereas as cyclo propane (Δ),





Fact:



Highly hindered
groups are present.

\rightarrow Reaction proceeds through E^\ddagger path. OH^- will take proton from methyl, that CH_2^+ takes. Hydrogen adds makes cyclic 5 membered ring transition state.



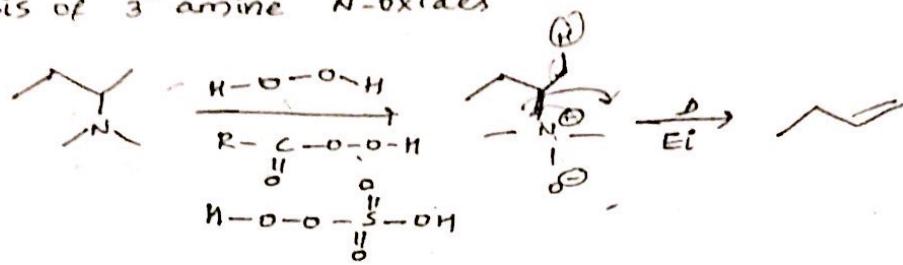
intra molecular
elimination.

Cope Elimination:

(12)

→ Pyrolysis of 3° amine N-oxides

Eg: 1.



→ (Ei)

→ Expected Hoffmann elimination

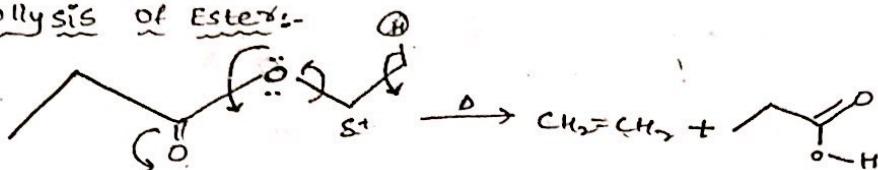
→ Proceeds through 5-membered transition state.

→ Synn periplanar

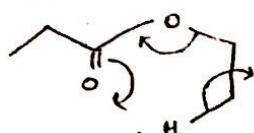
2.



Pyrolysis of Esters:



Mechanism:



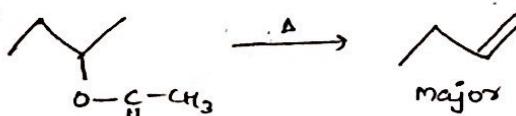
→ Ei

→ Synn-elimination

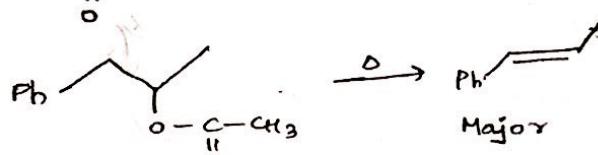
→ 6 membered cyclic Transition state

→ Hoffmann orientation

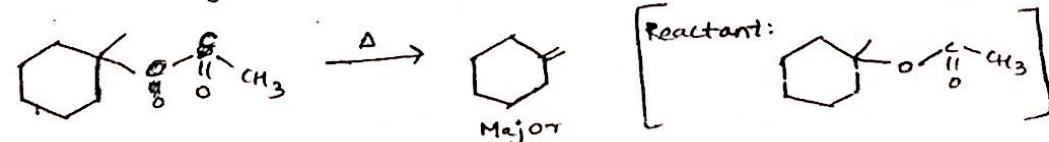
B1)



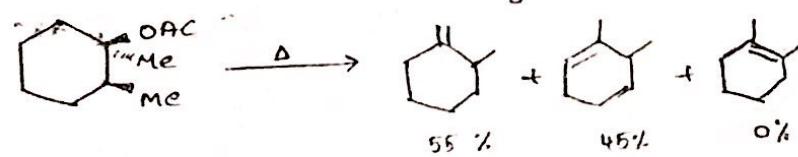
B2)



B3)

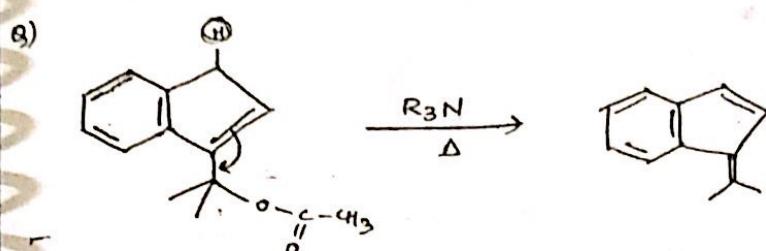
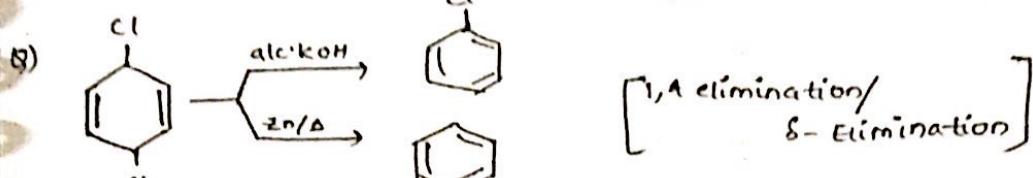
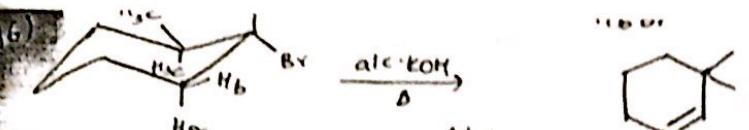


B4)



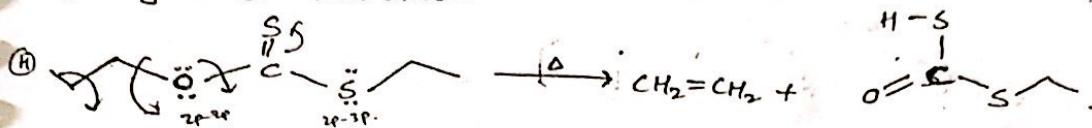
B5)





CHUGAWE ELIMINATION:-

→ Pyrolysis of xanthate.



→ E_i

→ G.T.S#

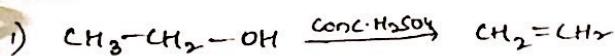
→ Generally halfmann orientation

→ syn elimination.

DEHYDRATION:

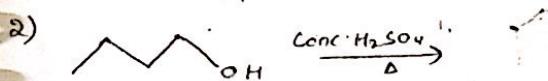
- Reagents:-
- 1) Conc. H₂SO₄
 - 2) H₃PO₄
 - 3) Al₂O₃
 - 4) Al₂O₃ · Py (Pyridine)
 - 5) ThO₂
 - 6) POCl₃ · Py
 - 7) KHSO₄

Eg-1:

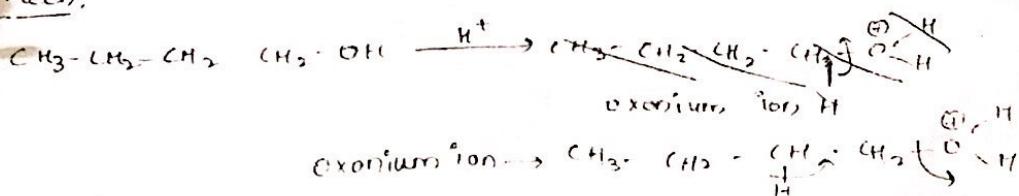


Path: E₂

Temperature: 170°C

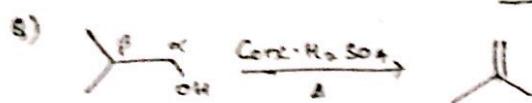
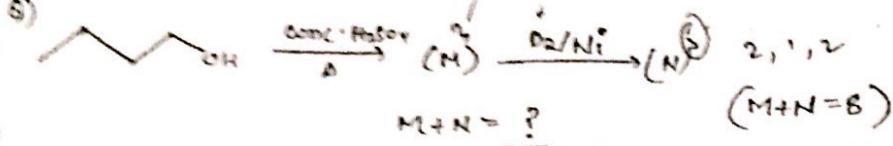


Mech:



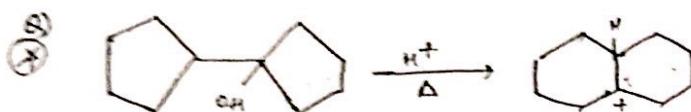


→ E2 path followed by Rearrangement

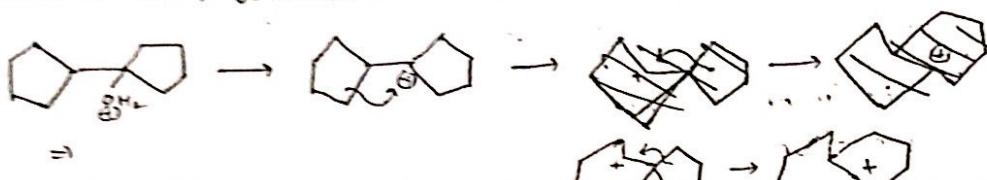


Intermediates

Oxonium ion, nearly carbocation, no-of intermediates: 30111.09
rearranged Carbocation. no-of TS: 4

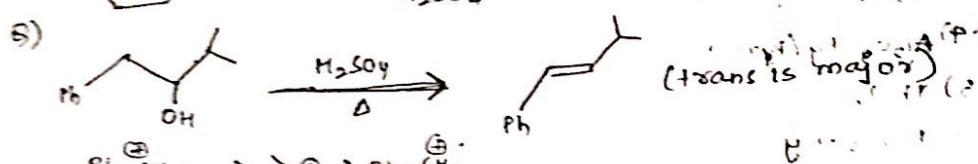
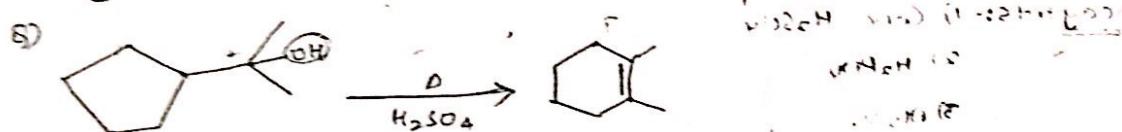


→ oxonium ion, formation of Carbo Cation.

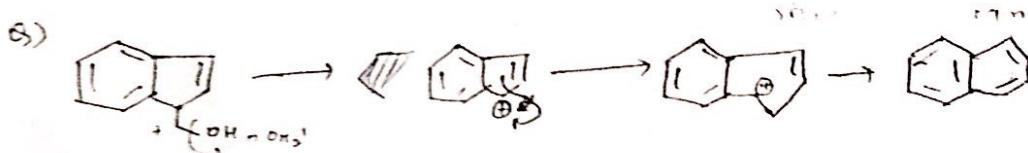


Intermediates: 4

T.S.: 6

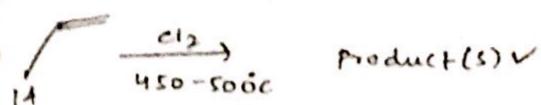


$\text{E}^{\oplus} = \text{Alcohol}$



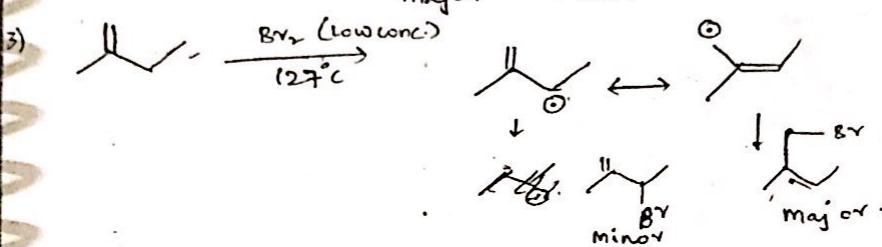
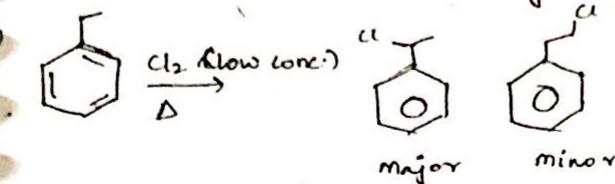
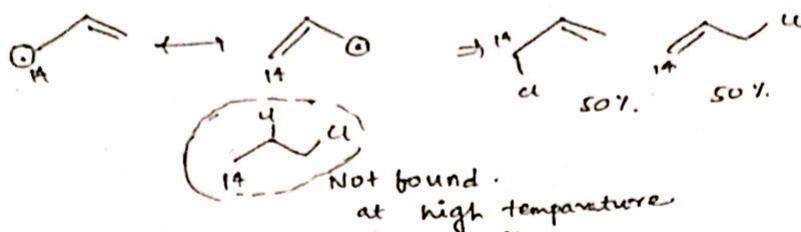
25'

Reactions at High temperature: (Free-radical substitution)



→ High temperature facilitates radical mechanism.

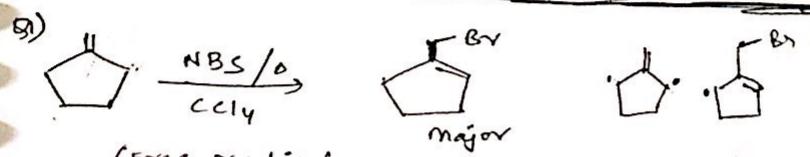
Rate: Benzylic & allylic $> 3 > 2 > 1$.



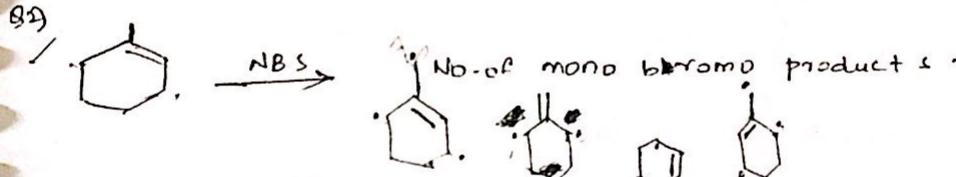
NOTE:

→ Selectively to conduct reaction, only at allylic and benzylic positions

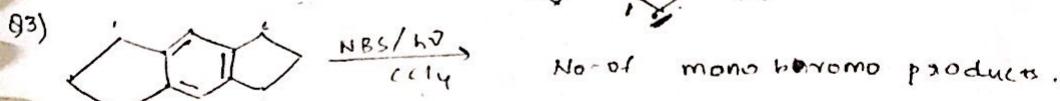
Best Reagents: NCS (*n*-chloro succinimide)
NBS (*n*-Bn Bromo succinimide)



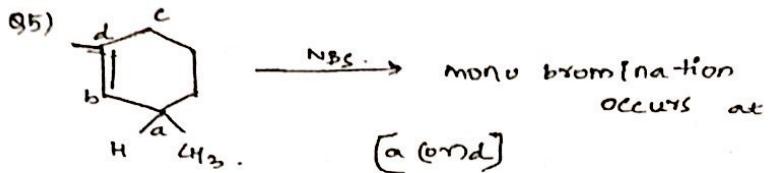
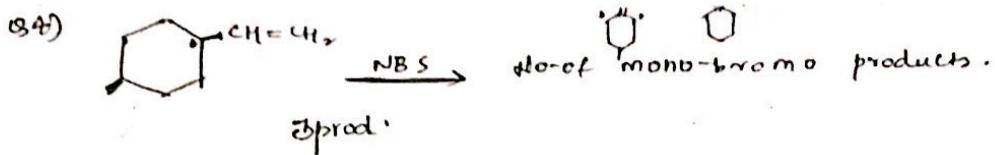
(Free-radical substitution)



⑤



⑥

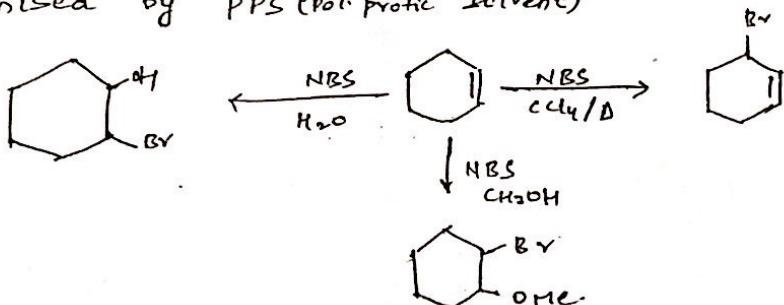


NOTE:

→ NBS reactions are free-radical substitution.

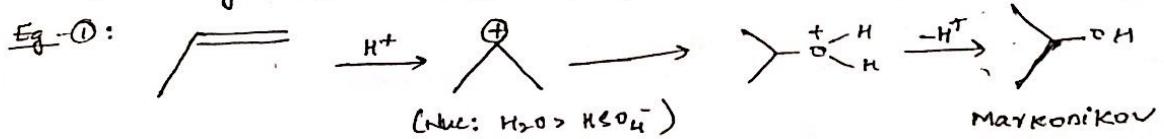
→ NBS if we carry out in presence of polar-protic solvent, halo hydration formation takes place predominantly by electrophilic addn.

→ Since, NBS develops molecule bromine (Br_2) which is ionised by PPS (polar protic solvent)

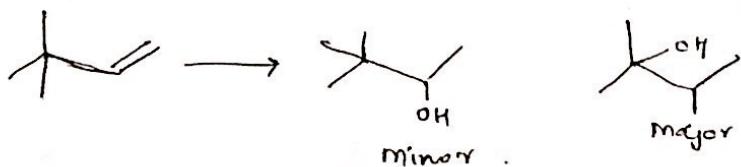


ADDITION OF WATER :-

i) By using H_3O^+ (or) dil. H_2SO_4

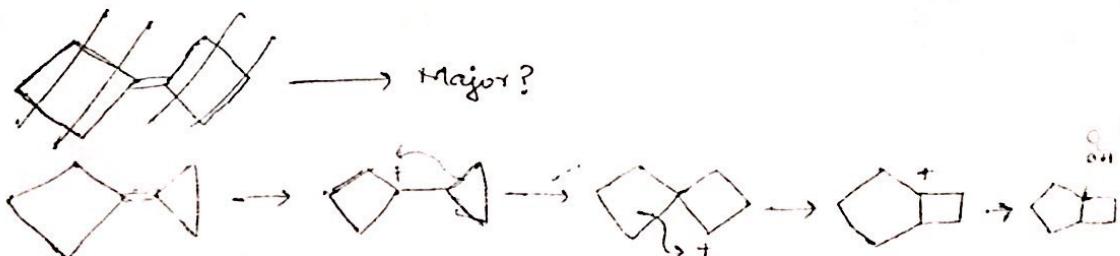


Eg - ②:



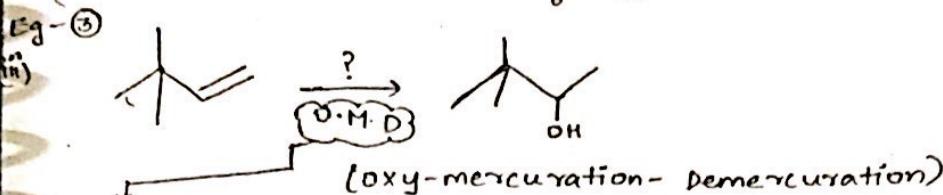
No. of intermediates in formation of major product: ③

Eg - ③:



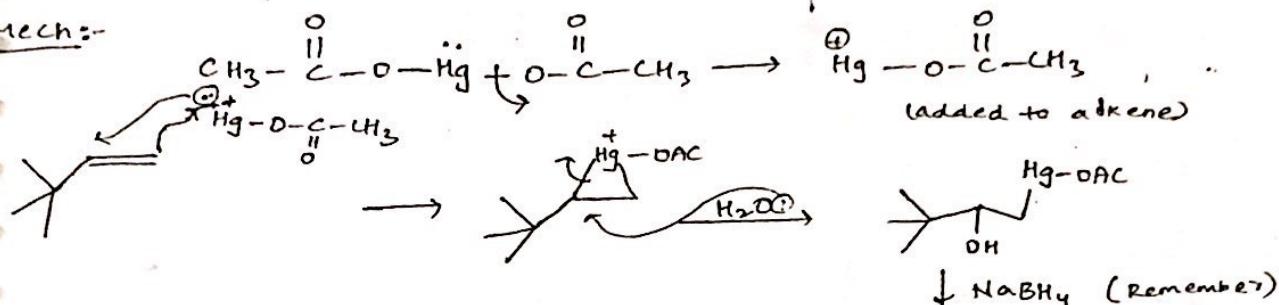
By using conc. H_2SO_4 (only at *vic*)
to prevent dehydration

(2)

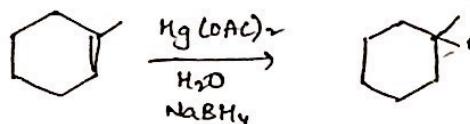


- 1) $Hg(OAc)_2$
- 2) H_2O
- 3) $NaBH_4$

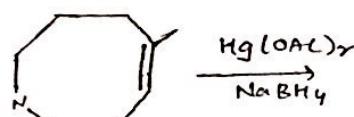
Mech:-



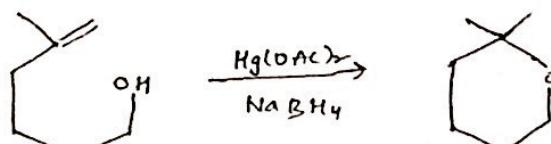
Eg-①:



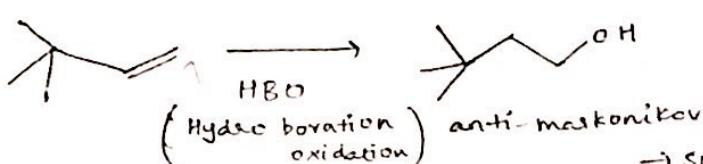
Eg-②:



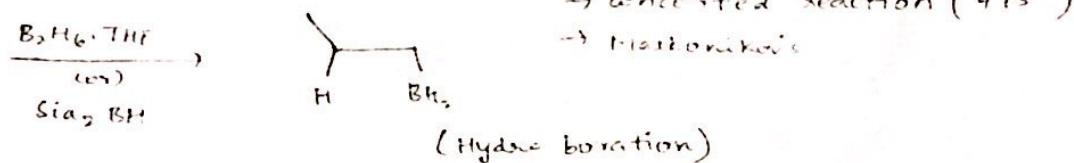
Eg-③:

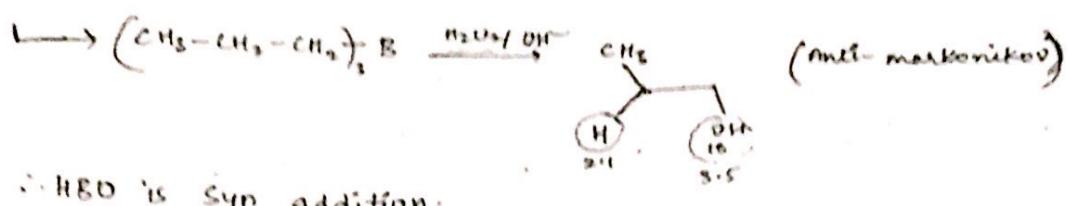


Eg-④:

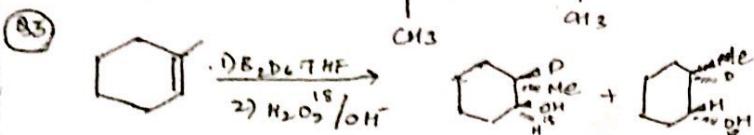
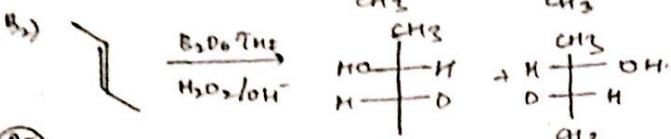
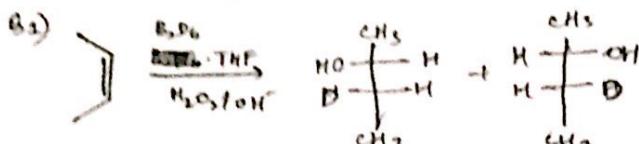


Eg-⑤:



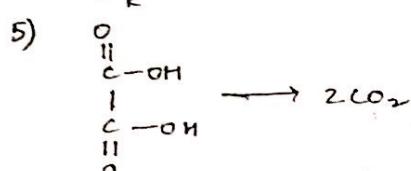
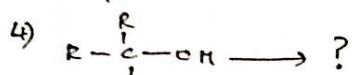
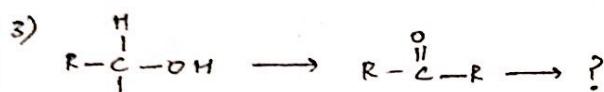
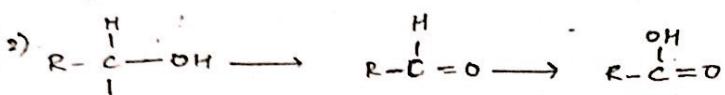
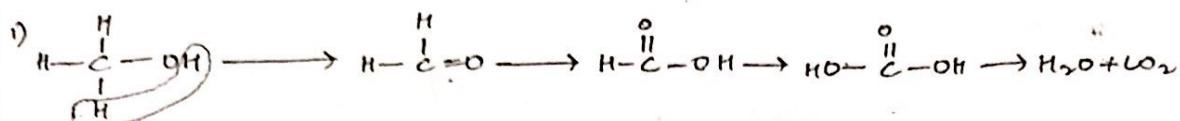


$\therefore H_2O_2$ is Syn addition.



(Q4)

Hint from alcohols:



(Q4)(ii)

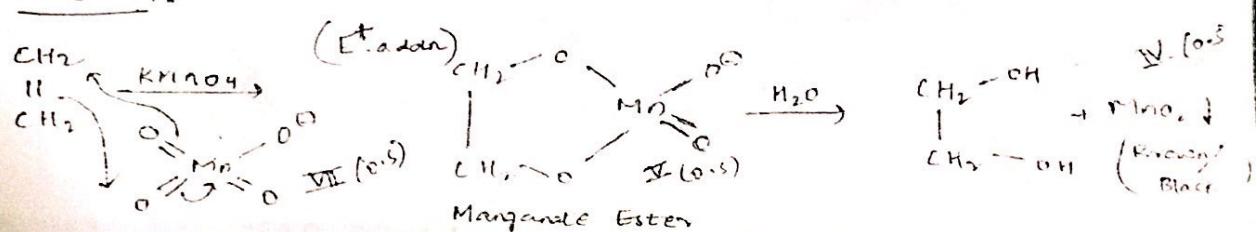
(i) Cold dil alkyl KMnO₄: (Purple) (Bayer's Reagent)

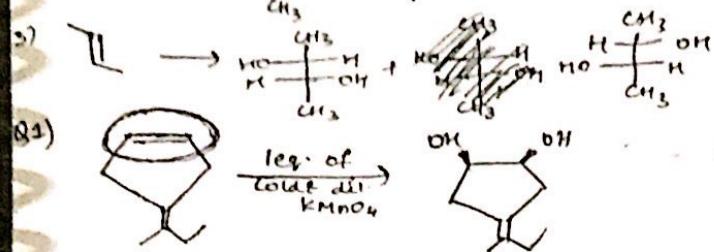
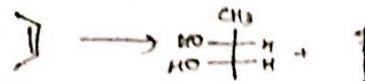
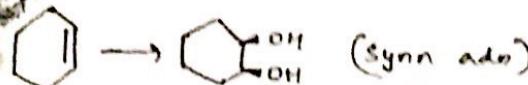
→ Bayer's reagent is used to detect unsaturations like

$\text{C}=\text{C}/\text{C}\equiv\text{C}/\text{C}=\text{C}-\text{C}=\text{C}$ etc... in the lab.

Report: πe^- decolorises purple colour of $KMnO_4$.

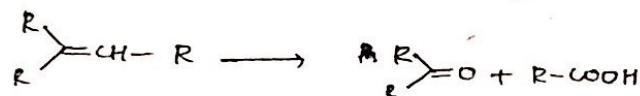
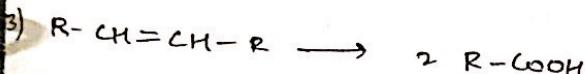
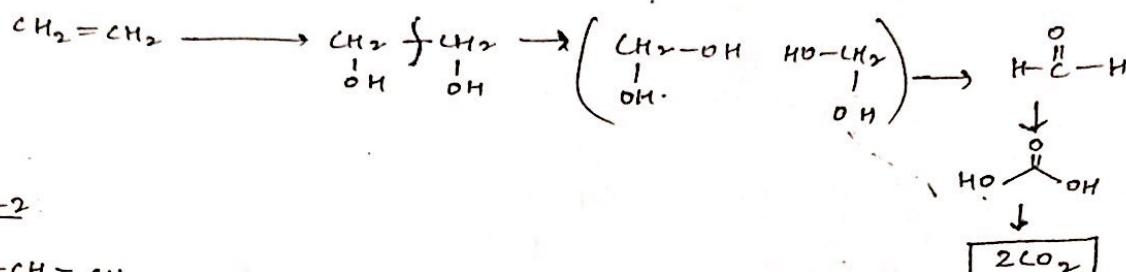
Reaction:



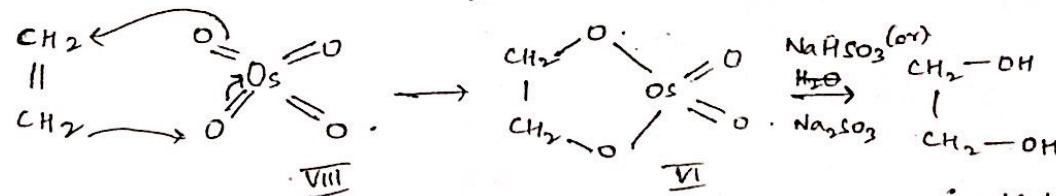


Reason: manganese ester selectively reforms at free π -bond
 \rightarrow upper bond is done for electrophilic addition.
 \rightarrow sterically free π -bond $>$ Hindered π -bond (Preference)
(Circled π -bond)

(iv) Warm $KMnO_4$ / hot $KMnO_4$:



(v) OSO_4 : (Cosmium Tetraoxide)



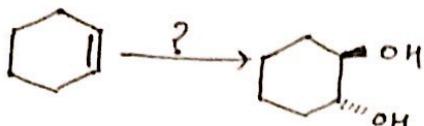
cis diol
(syn phase)
addn

\rightarrow Hydrolysis is carried out in presence of
slightly basic medium to prevent " H_2OSO_4 "
(byproduct) since it is toxic gas.

Preferable reagent: OSO_4 (Industry)

\downarrow
other functional
groups are not affected

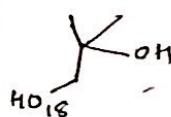
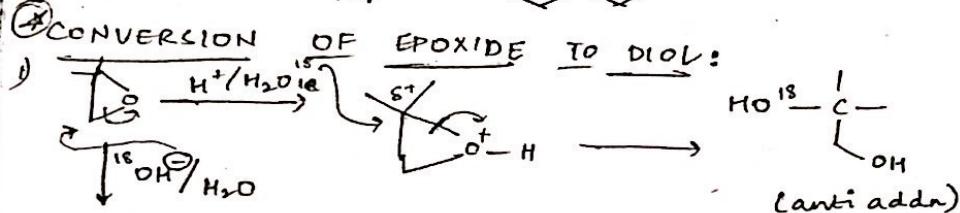
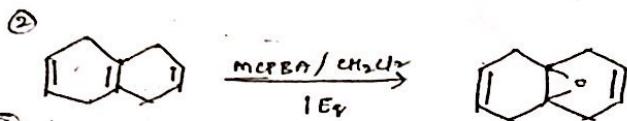
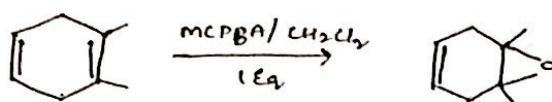
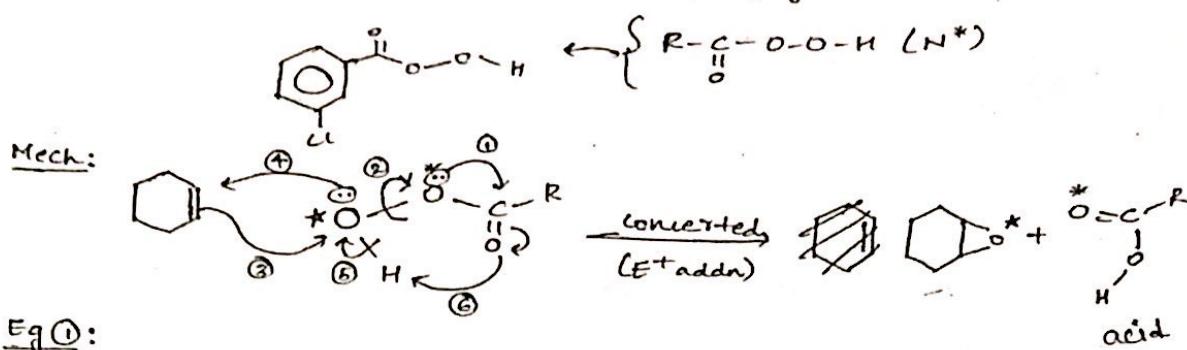
(iv)



(60)

- ① Epoxidation
- ② Hydrolysis

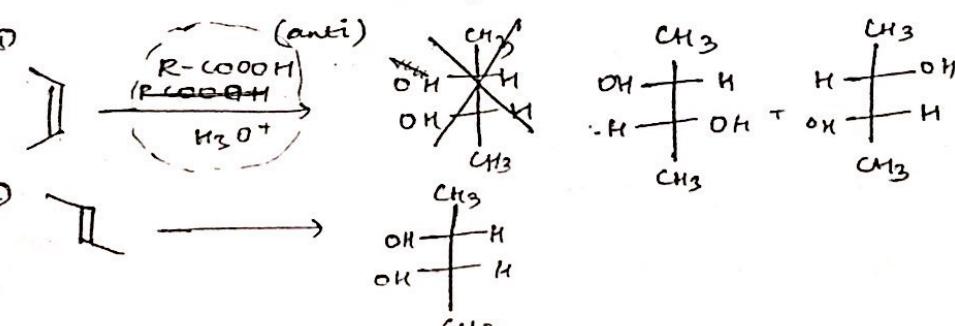
Reagents used for epoxidation: $\frac{1}{2} \text{O}_2/\text{Ag}$ (JEE MAIN)



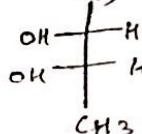
→ In acidic medium, cleavage occurs at hindered side.

→ In basic medium, cleavage occurs at Free side.

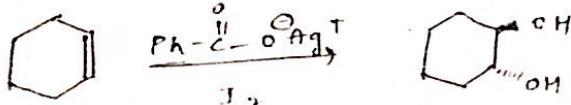
Eg - ①



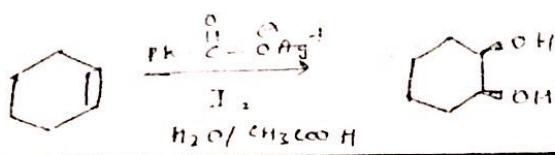
②

 N^{**}

(v) Prevost reaction:-



(vi) Woodward:

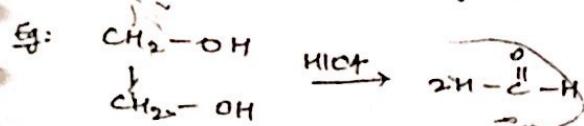


NOTE:- (✓)

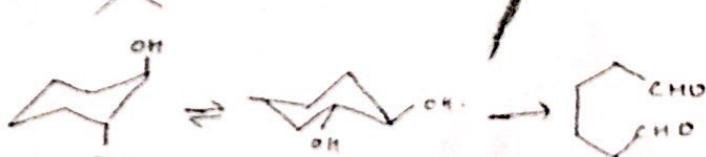
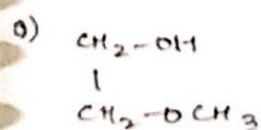
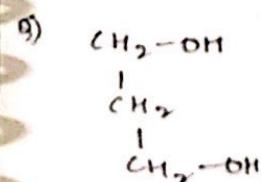
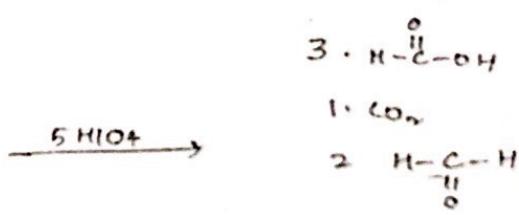
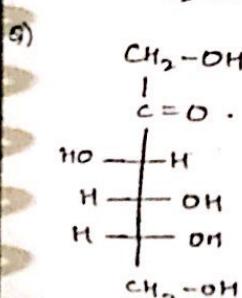
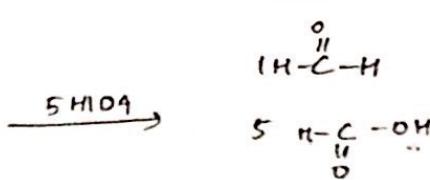
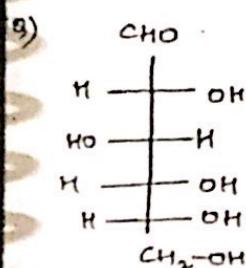
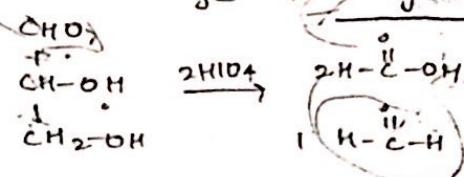
Extra syllabus from di-ol chapter:

i. Reaction with Periodic acid. ($\text{HIO}_4/\text{HIO}_4 \cdot 2\text{H}_2\text{O}/\text{NaIO}_4$)

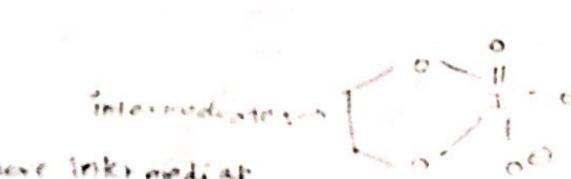
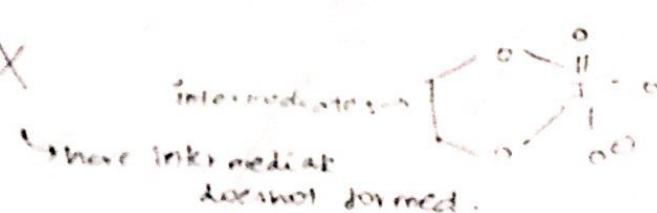
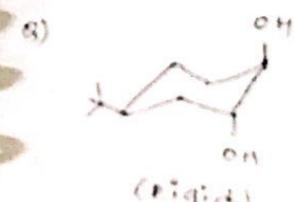
Function: i) Oxidative cleavage of $1,2\text{-dol}$ (vicinal diol)

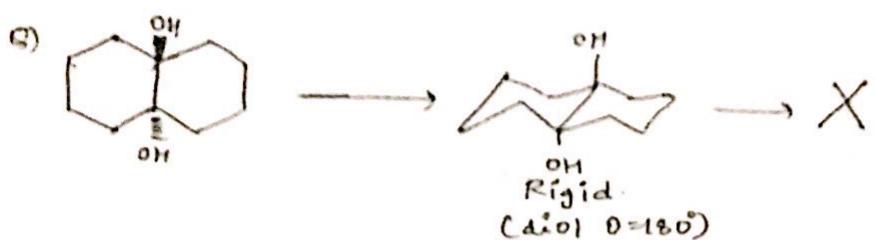


ii) Oxidative cleavage of α -hydroxy Carbonyl Compound.



(due to strained ring (3-membered))

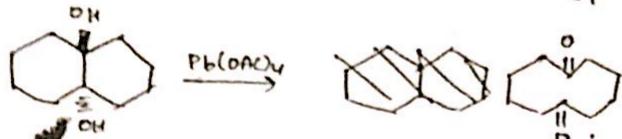




(52)

NOTE:

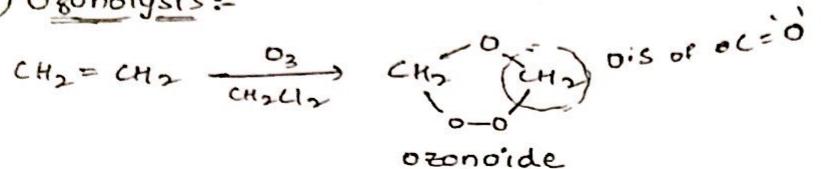
→ $\text{Pb}(\text{OAc})_4$ will cleave all type of 1,2 diols.



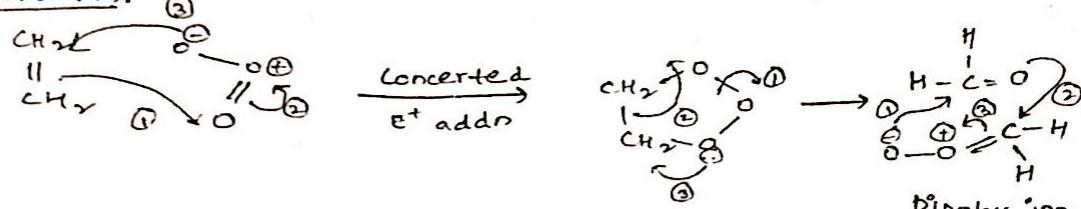
2. Lumex-Johnson Reagent :- (Mix. of OSO_4 & NaIO_4)



5) Ozonolysis:

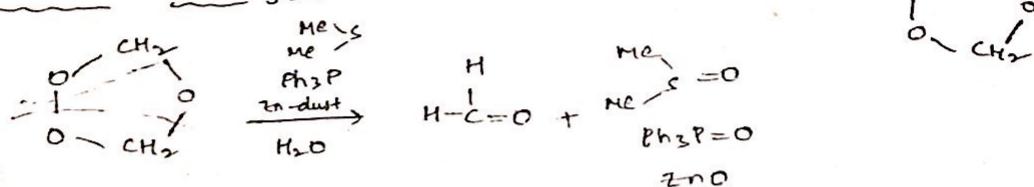


Mechanism:

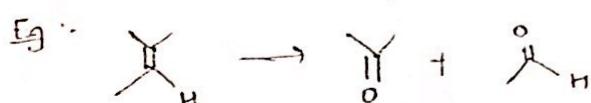
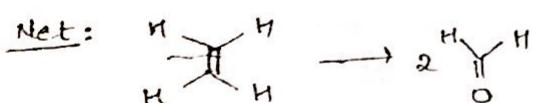


case in:

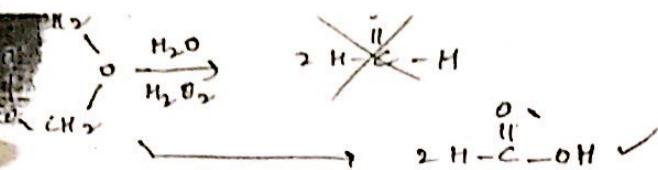
Reductive Ozonolysis:



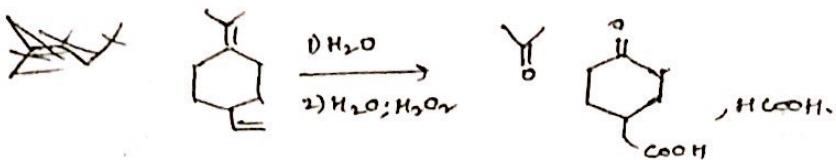
→ among the above 3; DMS (di methyl sulphide) is best bcz it's low B.P (can be easily separated)



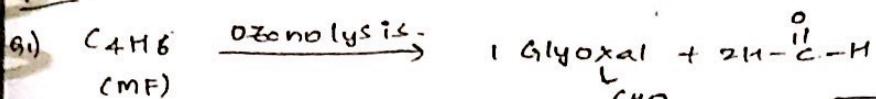
Case in: oxidative ozonolysis:



Net:

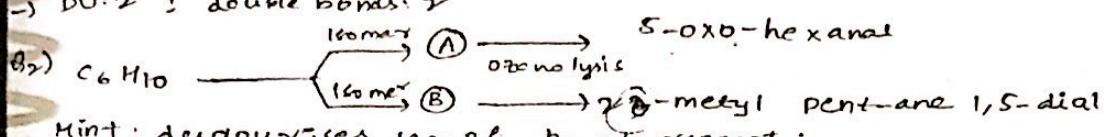


Net:



Hint: Decolorise \rightarrow eq. Br₂

\rightarrow DU: 2 : double bonds: 2

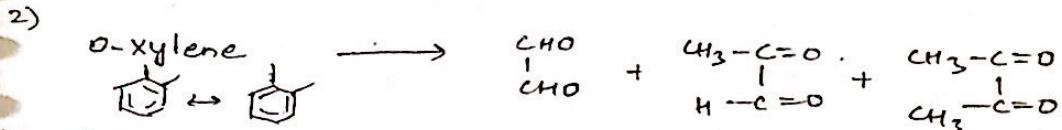
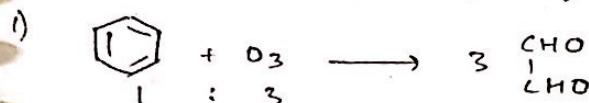
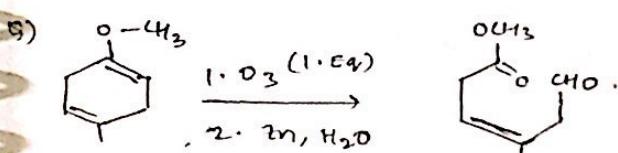
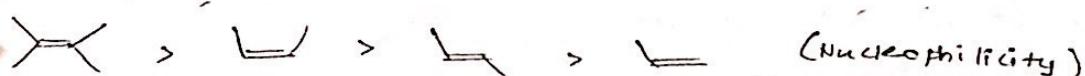


Hint: decolorises eq. of Bayer's reagent.

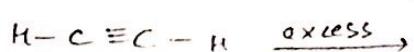
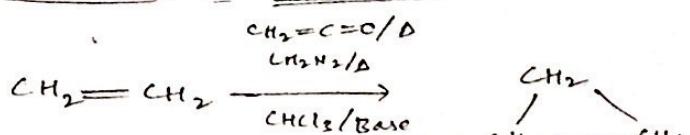
DU: 2



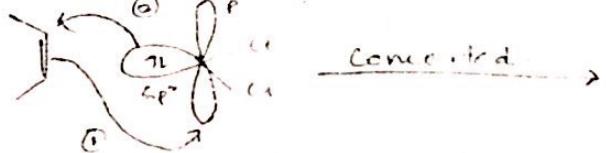
\rightarrow Under extreme conditions, Benzene undergoes ozonolysis

Reactivity:

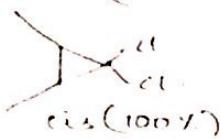
6) ADDITION OF CARBENE:-

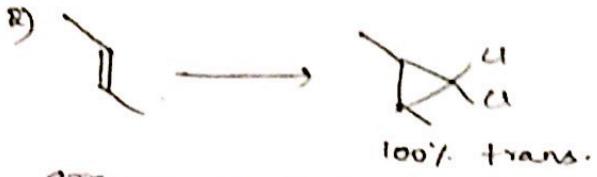


Mech: Case (i): vinyl singlet carbene (Proceeds through carbonion) (for exam)



Conc. Ind. \rightarrow





STEREO SPECIFIC REACTIONS:-

→ 2 different stereo isomers of the same compound involved in same type of reactions separately produces different stereo-chemical products.

Eg: Addn of Singlet Carbene to 2-Butene
 " " Bromine " " "
 catalytic deuteration " 2-butene.

STEREO SELECTIVE REACTIONS:

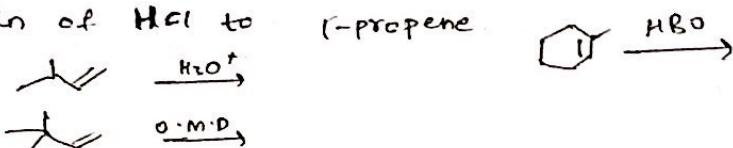
→ Stereo chemical product is obtained either major (or) exclusively.

Eg: 1. Lindlar's catalyst on 2-butene-butyne
 2. Birch reduction of 2-butene
 3. All stereo specific reactions.

REGIO-SELECTIVE:

→ Among the expected 2(or)more structural isomeric products one is formed major (or) exclusively.

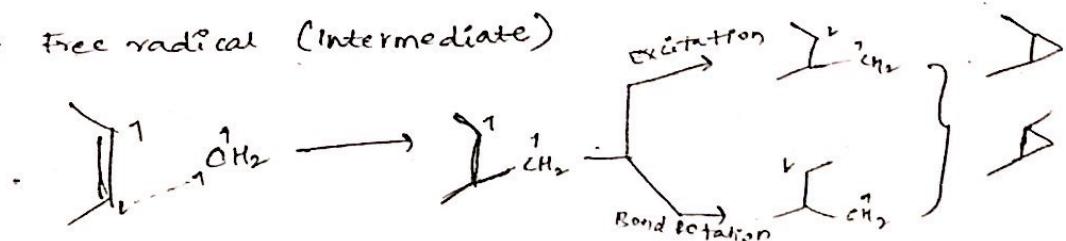
Eg: addn of HCl to (-)propene



Case(ii): w.r.t to triplet carbene.

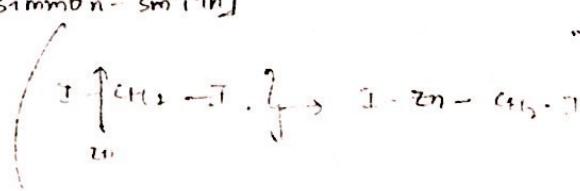
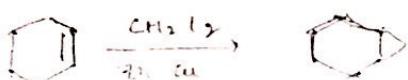
Path: free radical (intermediate)

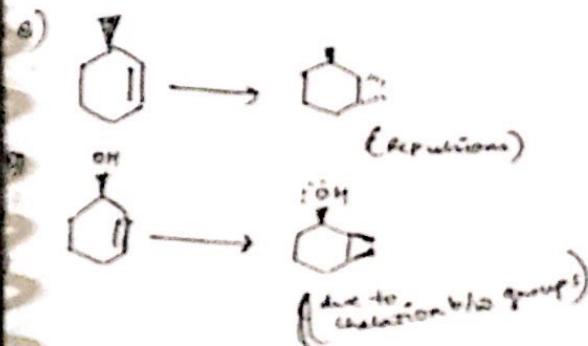
Eg:



(NOT a stereo specific reaction)

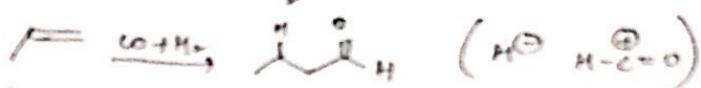
7) ADDITION OF CARBONIDE :- [Simmon-Smith]





b) OXO-PROCESS: $[\text{Co}_2(\text{CO})_8]$

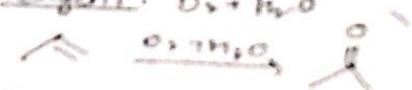
Reagent: $\text{CO} + \text{H}_2$



(Hydro formylation according to markonikov rule)

c) WACKER'S PROCESS: (catalyst: PdCl_2 , CuCl_2)

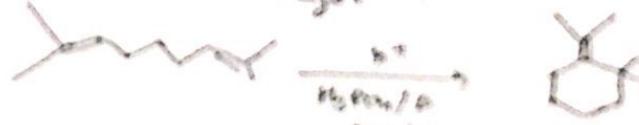
Reagent: $\text{O}_2 + \text{H}_2\text{O}$



d) DIMERISATION OF ALKENES:



Major



PROPERTIES OF SOLUBLE OXIDES (SOLN)

1) Alkene \rightarrow Alcohol

2) Benzene \rightarrow Carbonyl



3) Carbonyl \rightarrow α,β -diketone

