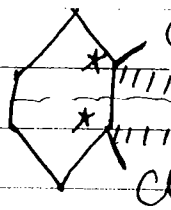
Isomerism → some good examples from DDP.

Q1. 

MESO = (1)
O.I = (2)
Total S.I. = (3)

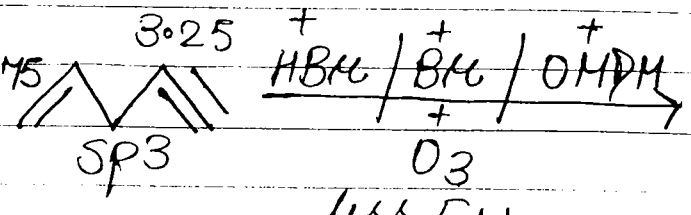
*** → If after one interchange then symm. possible then consider the compound as symmetrical.

Hint → POS/COS → given form

chiral / achiral → 3 group rotation

SI/OI/GI → one interchange

Structure → positional, functional, chain

Q2. 

(=>≡)

Ni / Pd / Pt
H2
→ less steric

(≡ > =)

Application of Isomerism

Photohalogenation

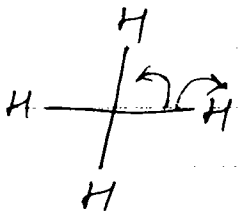
$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + H-Cl$$

Mechanism → ⇄ Free radical substitution
|| || chain rea^n.

Initiation → $:\ddot{Cl}-\ddot{Cl}: \xrightarrow{h\nu} :\ddot{Cl}^{\bullet} + Cl^{\bullet}$

weak bond — 7e — 7e

Propagation →

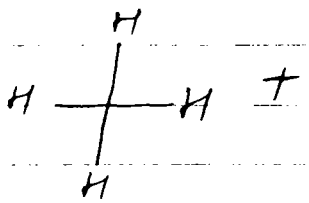


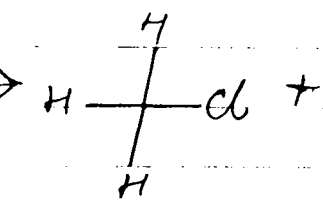
$+ Cl^{\bullet} \longrightarrow CH_3^{\bullet} + H-Cl$

7e 7e

$CH_3^{\bullet} + Cl-Cl \longrightarrow CH_3-Cl + Cl^{\bullet}$

7e 7e

Net → 

$+ Cl_2 \xrightarrow{Cl^{\bullet} \text{ and } CH_3^{\bullet}}$ 

$+ H-Cl$

Termination →

$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow$ CH_3-Cl
$Cl-Cl$
CH_3-CH_3 side product

Identify Product.

Sub. $\xrightarrow[Cl_2]{h\nu}$ H replace by halogen.

(A) $CH_4 + Br_2 \rightarrow CH_3-Br + HBr$

(B) $CH_3-CH_3 + Cl_2 \longrightarrow CH_3-CH_2-Cl + HCl$

(C) $CH_4 + Cl_2$ (excess) $\rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

*** (D) $CH_3CH_3 + Cl_2$ (ex.) $\rightarrow$ { CH_3CH_2Cl CH_3CHCl_2 / CH_3CCl_3 $Cl-CH_2-CCl_3$ / $HCCl_2-CCl_3$ CCl_3-CCl_3 }

9 Product

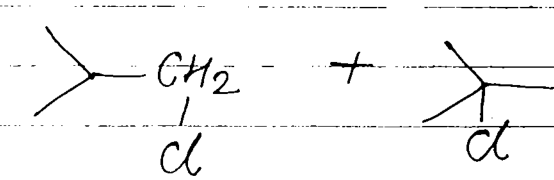
geminal

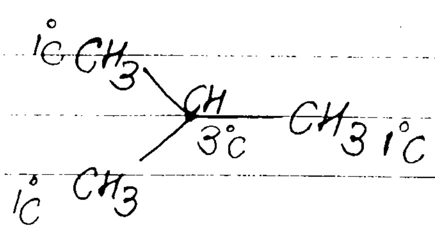
$CH_2(Cl)-CH_2(Cl)$ $CH(Cl)(Cl)-CH_2(Cl)$

$CH(Cl)(Cl)-CH(Cl)(Cl)$

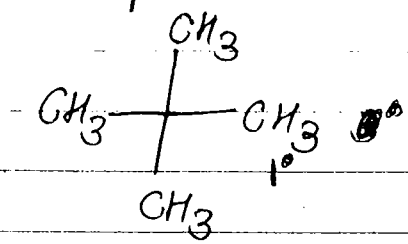
vicinal

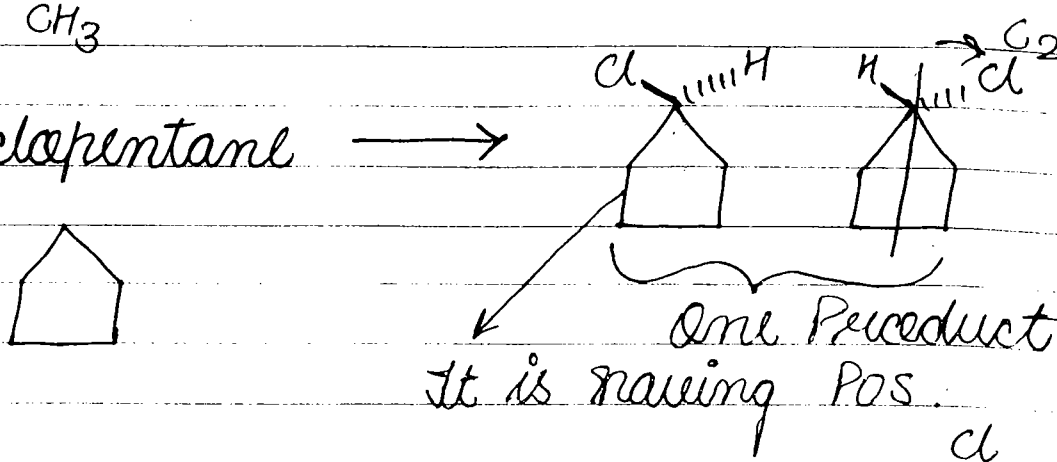
(E) Isobutane ⟶





M.C.P / mono chlorination Product

(F) Neopentane $\xrightarrow[Cl_2]{h\nu}$ 

(G) cyclopentane $\longrightarrow$ 

One Product

It is having POS.

(H) $CH_3-CH_2-CH_2-CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2\underset{*}{CH}(Cl)-CH_3$

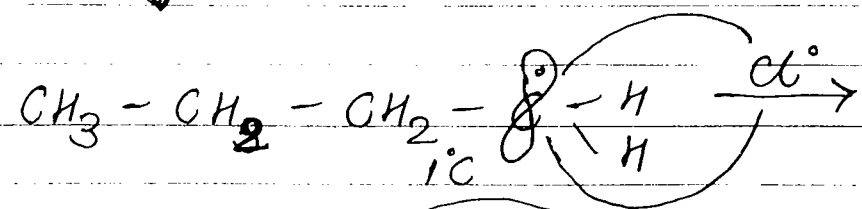
Butane

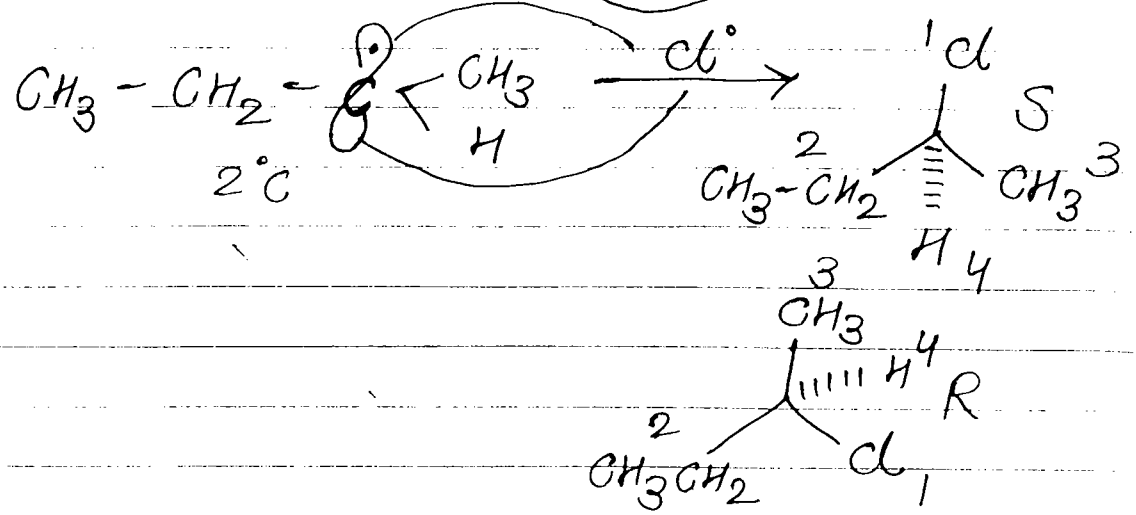
Mechanism Cl°

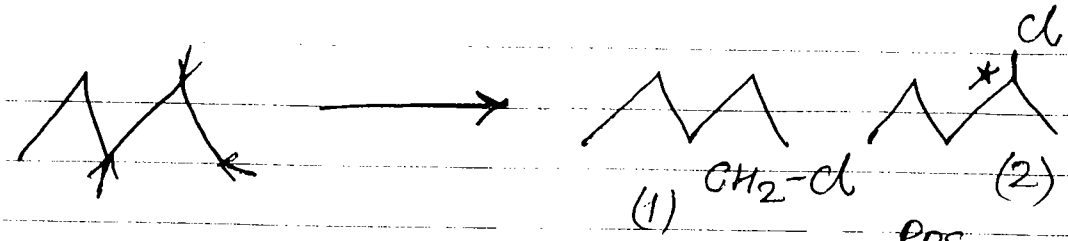
New chiral center

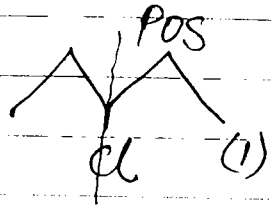
$2' = 2 \rightleftarrows R, S$

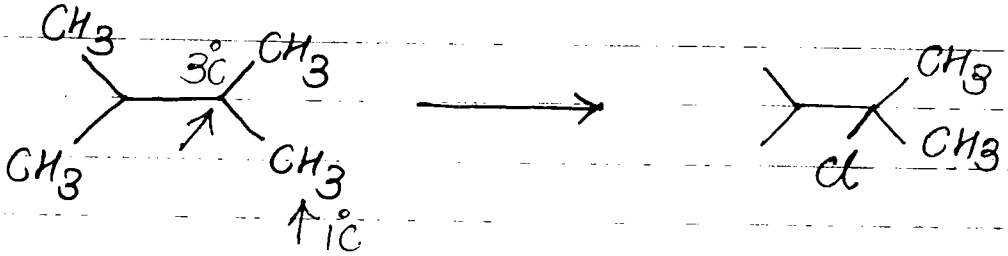
3 M.C.P.

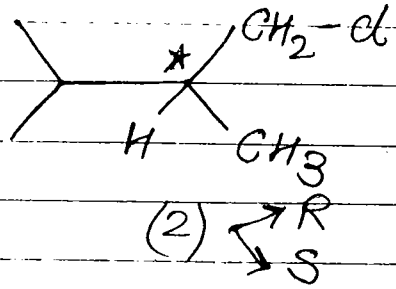


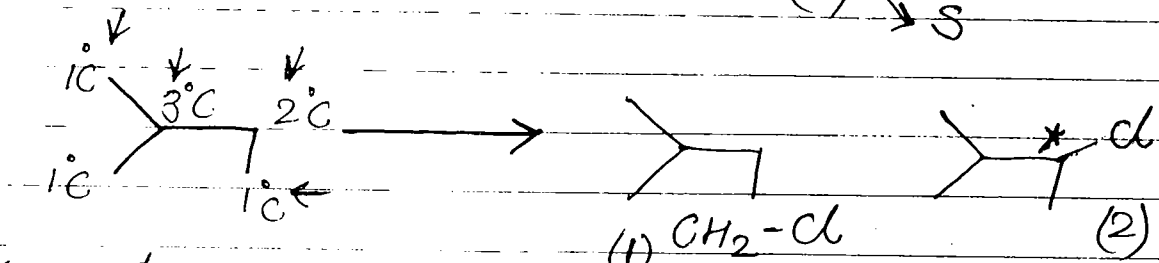


(I) 

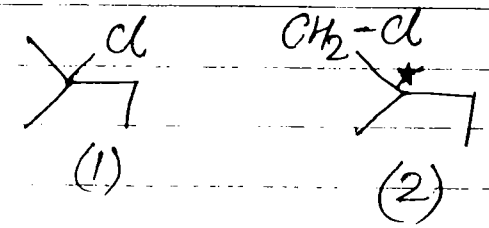
4 M.C.P. 

(J) 

3 M.C.P. 

(K) 

Isopentane



(A) no. of structural Product 4

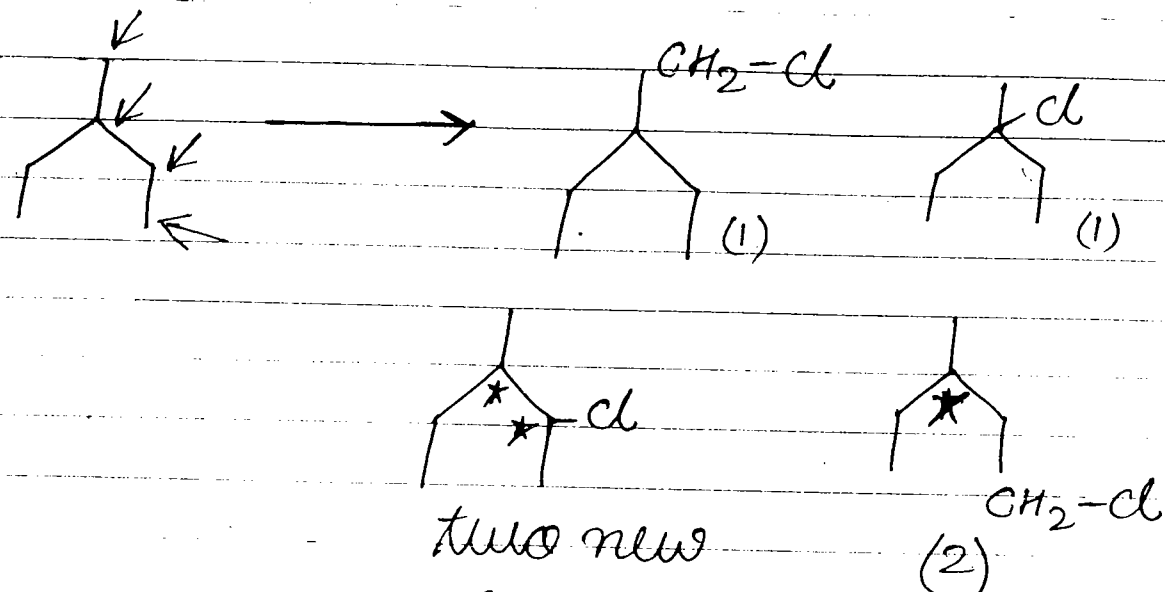
(B) no. of Product (Including stereo.) 6

(C) chiral Product 4

(d) distillation Product = Total - Cha. Pair

6 - 2 Pair = 4

(K)



two new C.C-

$2^2 = 4$

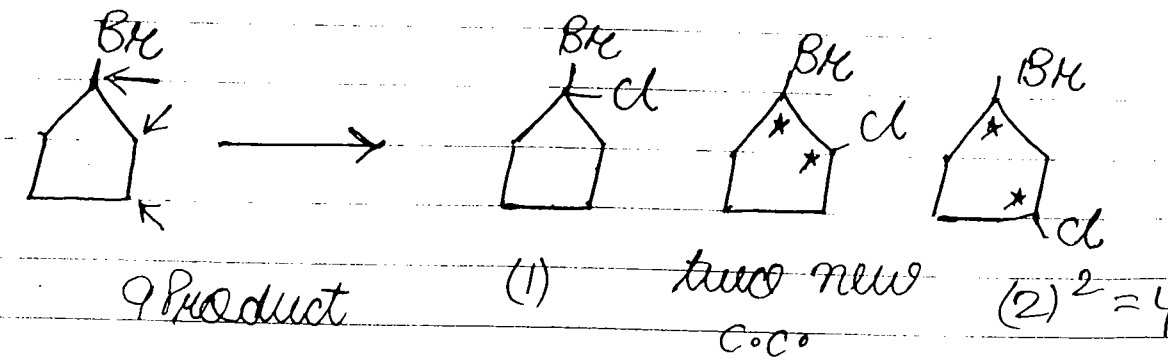
(A) 4

(B) 8

(C) 6

(D) 8 - 3 Pair = 5

(M)

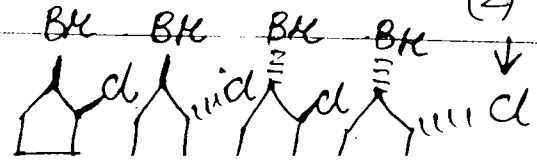


9 Product

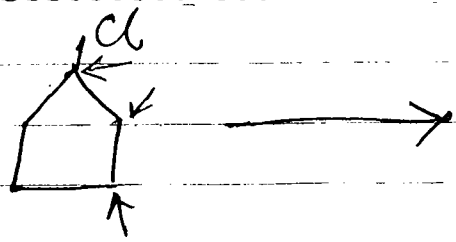
two new C.C.

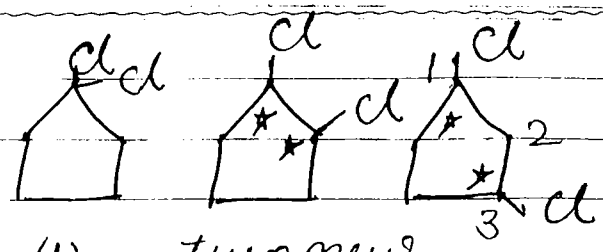
$(2)^2 = 4$

$(2)^2 = 4$



(N)



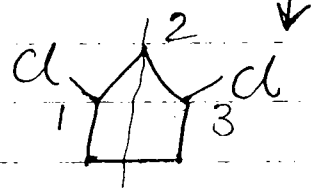


(1) two new C·C symmetry

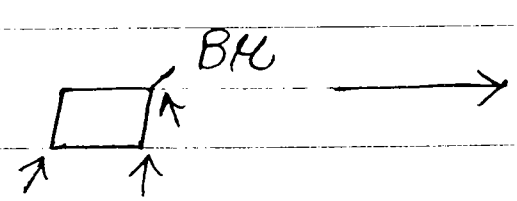
(3) Sym-metry

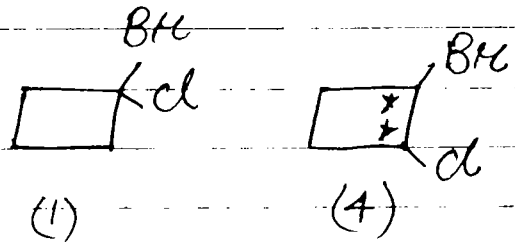
(3)

7 Product

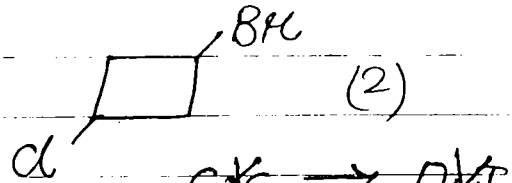


(0)





(1) (4)

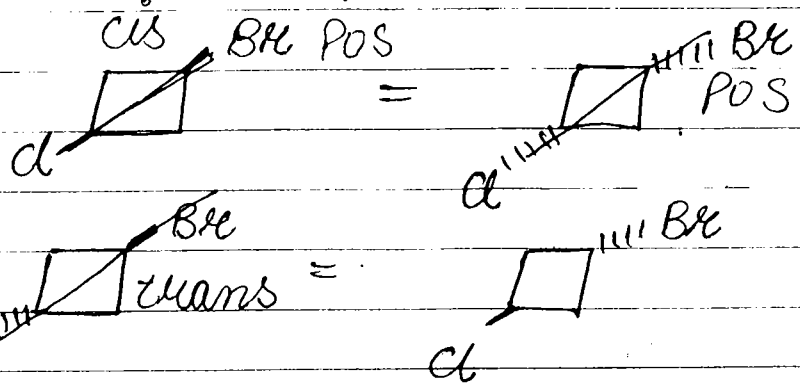


(2)

C≠C → O≠C

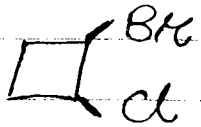
Ring → G·I·

7 Product



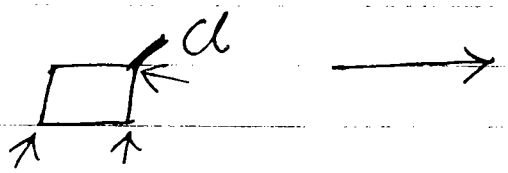
(a) 3

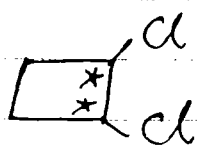
(b) 7

(c) chiral 4 → 

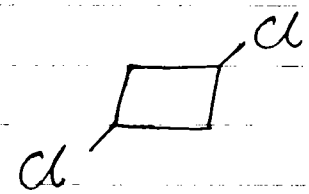
POSx
COSx

(d) 7 - 2ena. pair
RR/SS
RS/SR
= 5

(P) 

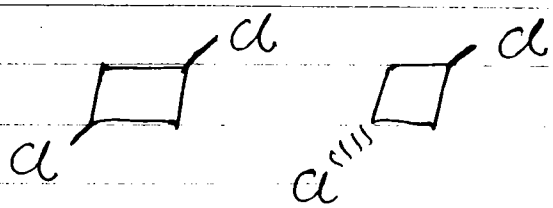
(1)


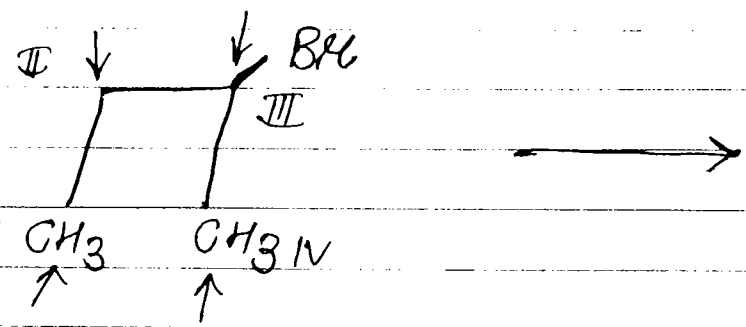
symmetrical
(3)



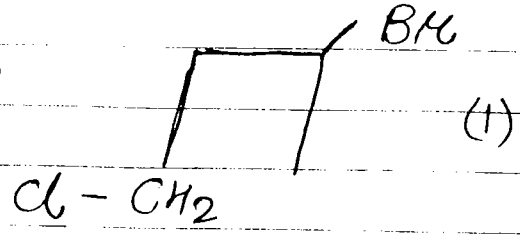
C·C → NO
ring → G·I·

6 Product

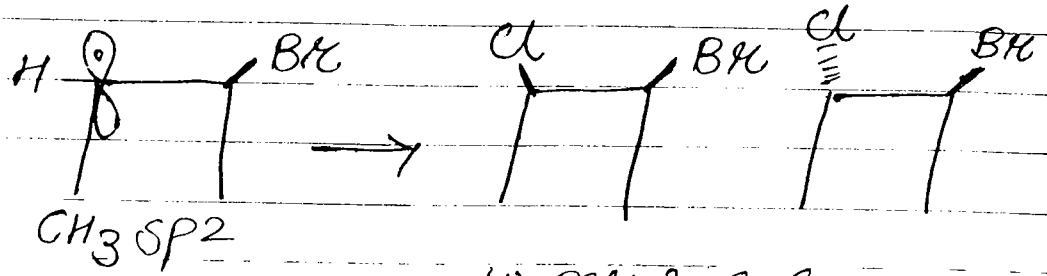
(2)


(8) 

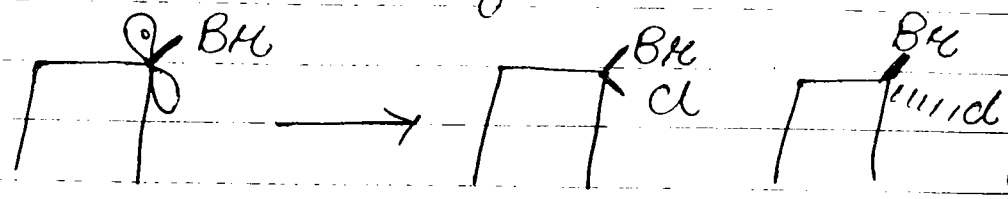
2R- bromo butane

I → 

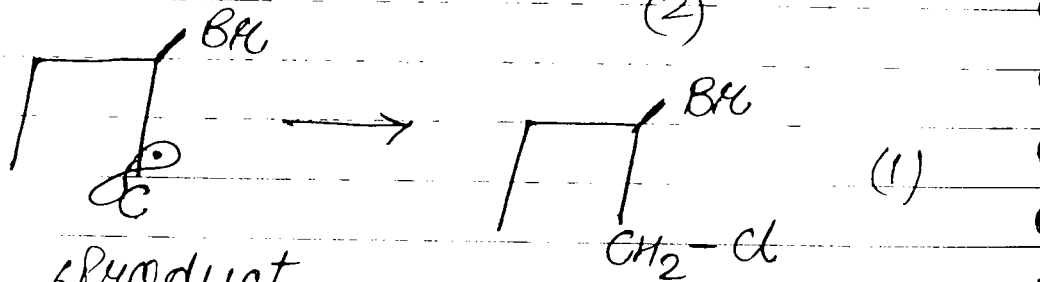
(1)

II → 

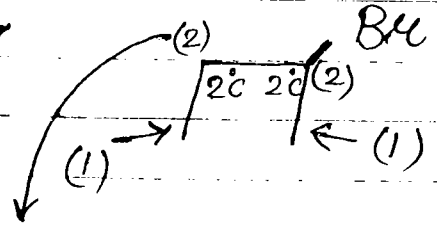
(1) new C·C formed = (2)

III → 

(2)

IV → 

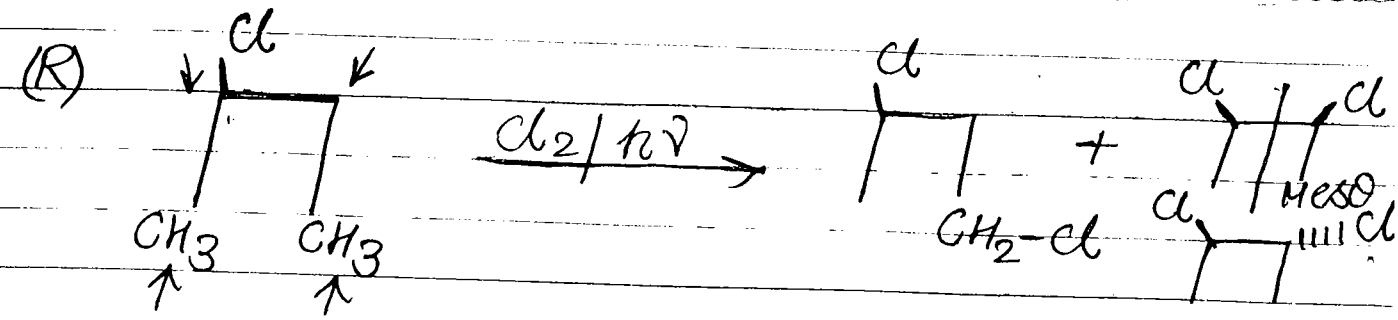
(1)

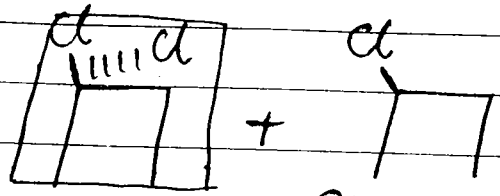
Hint → 

wedge-dash

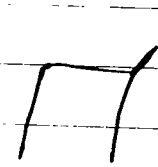
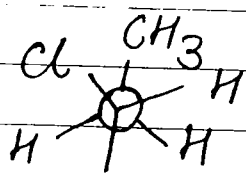
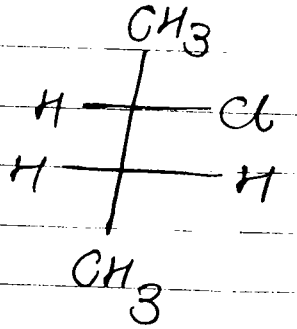
→ If reaction take place out of C·C then configuration do not change.

→ If reax. take place on chiral center then two form possible if intermediate is sp^2.

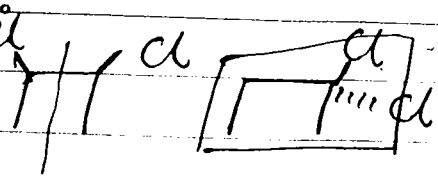


2-R chloro butane +  +

5 Product < Achiral (2) → geminal meso
chiral (3)

(S)  OR  OR 

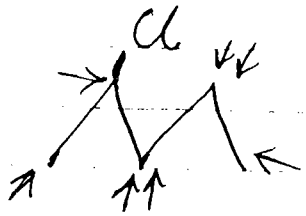
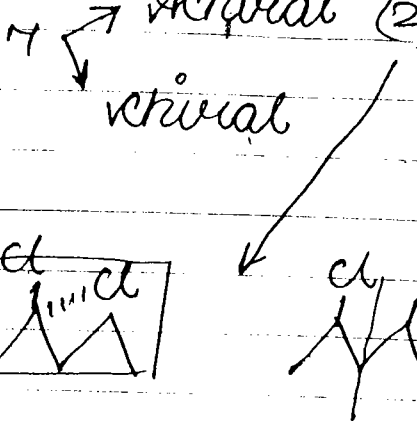
Ena are having same physical and chemical properties.

(5) < 2 chiral
3 chiral 

(T) Racemic R- chloro butane

R+S = 5+5 = 10 - 2 Achiral / 2 Repeat

= 8

(4)  $\xrightarrow{Cl_2/h\nu}$ 

2S- chloropentane

(5) 2R- chloro Pentane 4

(6) Racemic 2- chloro Pentane

$R+S = 4+4-2$ Achiral

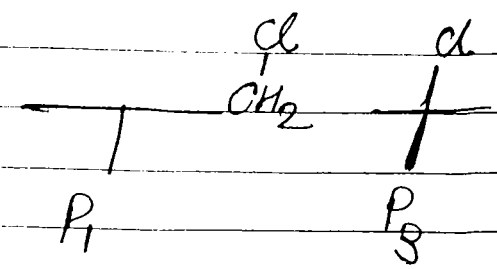
$= 12.$

Q. calculate % of product

Reactivity series (at 20°C)	$1^\circ H$	:	$2^\circ H$	:	$3^\circ H$
$Cl^\circ \rightarrow$	1	:	3.8	:	4.5
$Br^\circ \rightarrow$	1	:	82	:	1600

$$\frac{P_1}{P_2} = \frac{n_1 \times R_1}{n_2 \times R_2}$$

P_1 → % of product, n_1 → no. of degree of H, R_1 → reactivity

(1) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{Cl_2}$ 

P_1 P_3

$1^\circ H = 9 = n_1$

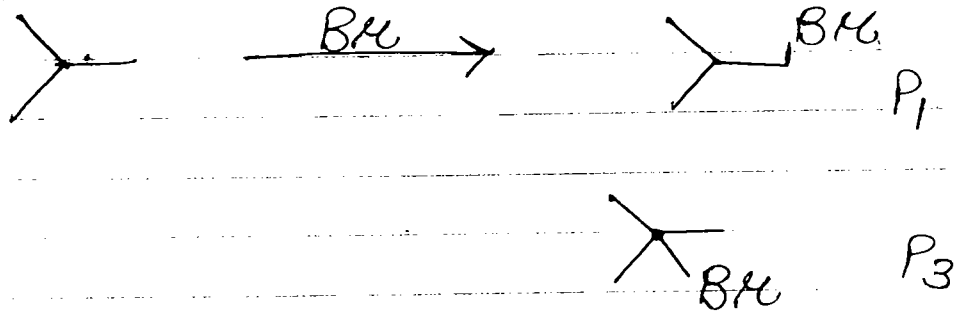
$3^\circ H = 1 = n_3$

$$\frac{P_1}{P_2} = \frac{9 \times 1}{1 \times 4.5} = \frac{9}{4.5} = \frac{2}{1}$$

total $= 2 + 1 = 3$

$$\% P_1 = \frac{2}{3} \times 100 = 66.66\% \quad P_1$$

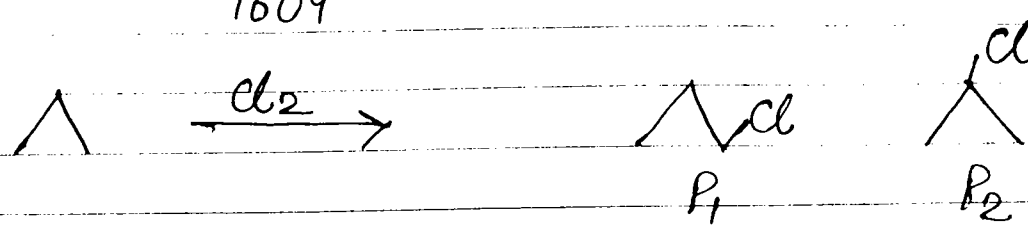
$33.33\% \quad P_2$

(2) 

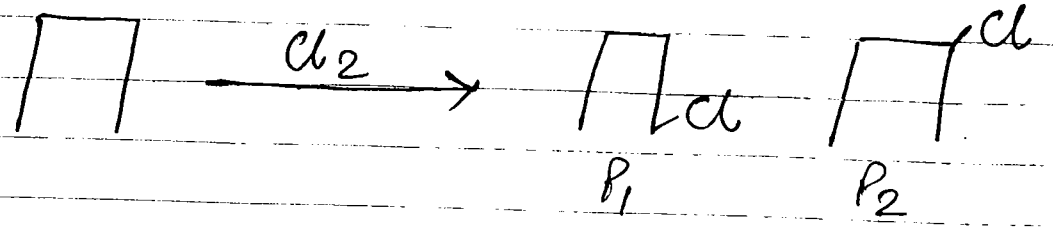
$$\frac{P_1}{P_3} = \frac{9 \times 1}{1 \times 1600} = \frac{9}{1600}$$

Total $= 1609$

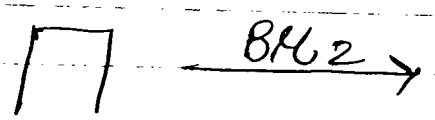
$$\frac{1600}{1609} \times 100 = 99.9\% \quad P_3$$

(3) 

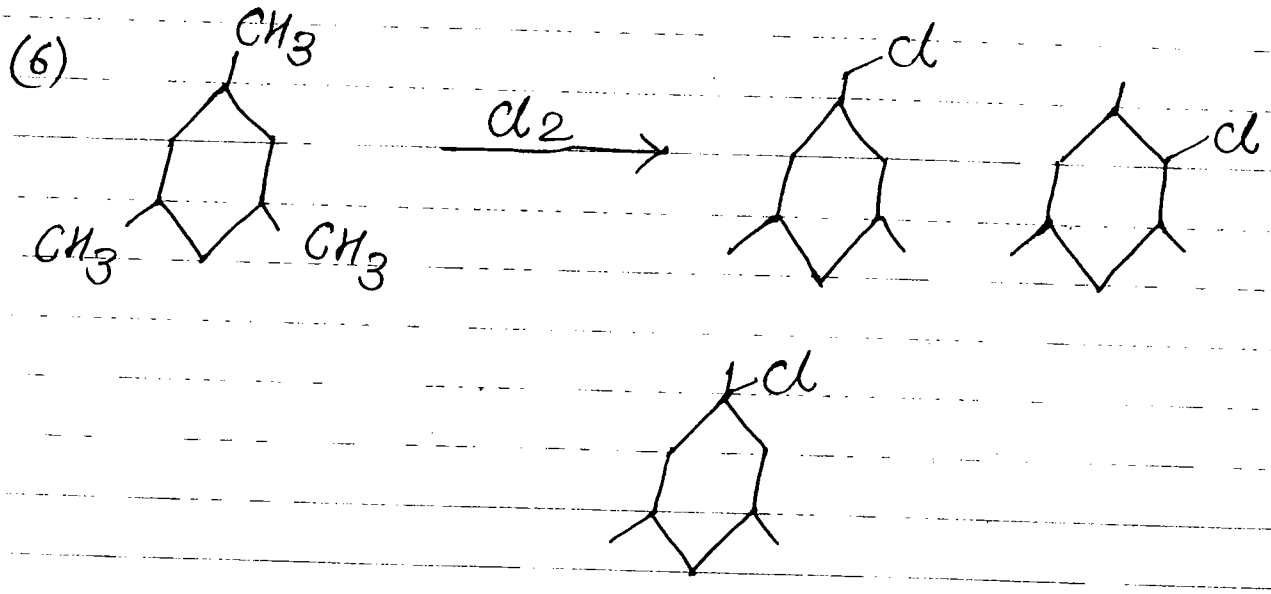
$$\frac{P_1}{P_2} = \frac{6}{2} \times \frac{1}{3.8} = \frac{6}{7.6}$$

(4) 

$$\frac{P_1}{P_2} = \frac{6}{4} \times \frac{1}{3.8}$$

(5) 

$$\frac{P_1}{P_2} = \frac{6}{4} \times \frac{1}{82}$$

(6) 

$P_1 = n_1 \mu_1 = 9 \times 1 = 9$

$P_2 = n_2 \mu_2 = 6 \times 3.8 = 22.8$ major

$P_3 = n_3 \mu_3 = 3 \times 4.5 = 13.5$

Total = 45.3

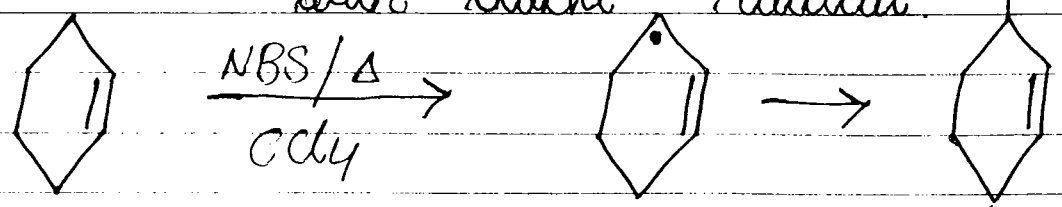
$\therefore$ 45.3 $\longrightarrow$ P_2 22.8

$$100 \longrightarrow \frac{22.8}{45.3} \times 100 = 50\%$$

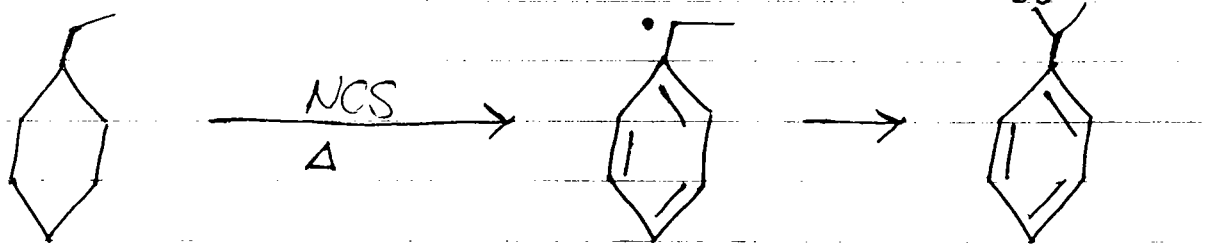
Allylic substitution OR Benzyllic substitution →

Hint → α-H replaced by halogen with stable radical.

(1)

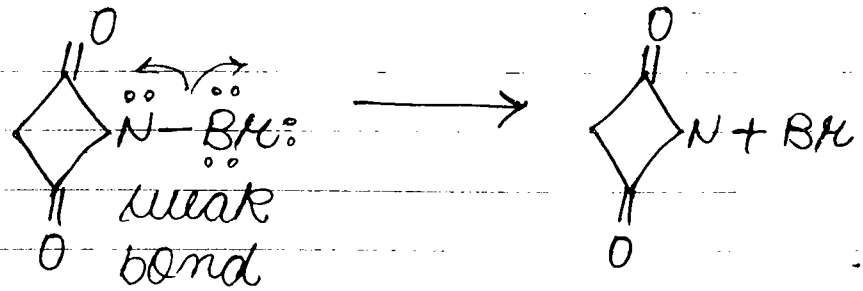


(2)



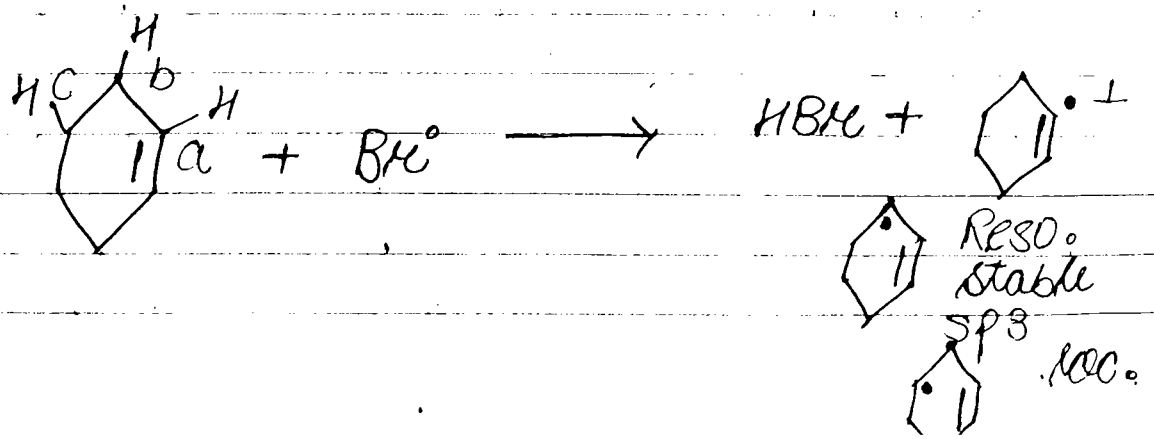
Mechanism → Free radical chain rxn.

Initiation →

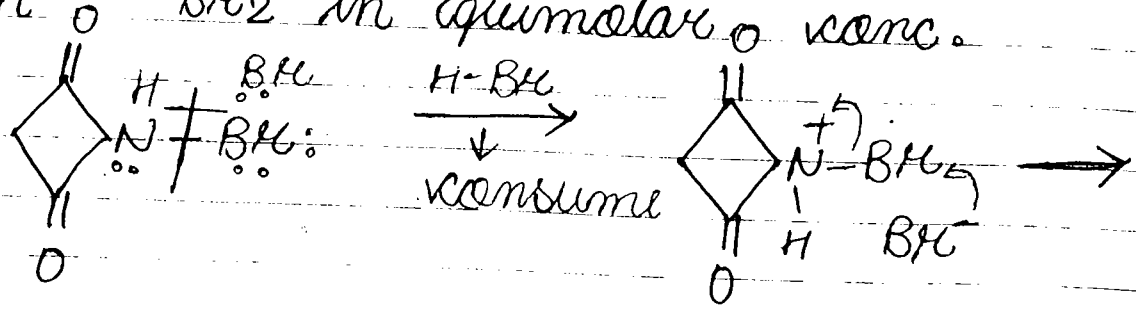


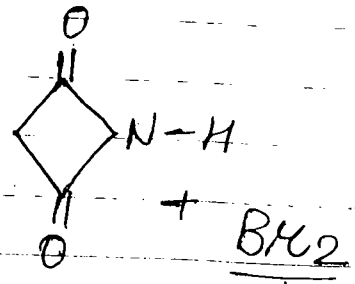
N- Bromo succinimide

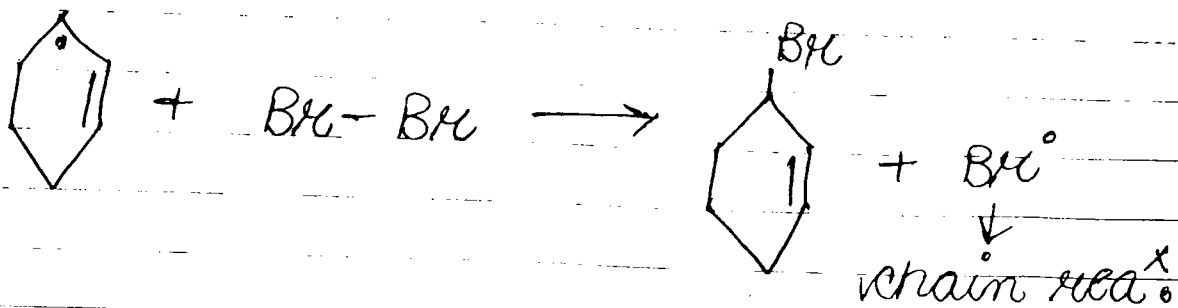
Propagation →



Role of N.B.S → to consume HBr and form Br_2 in equimolar conc.

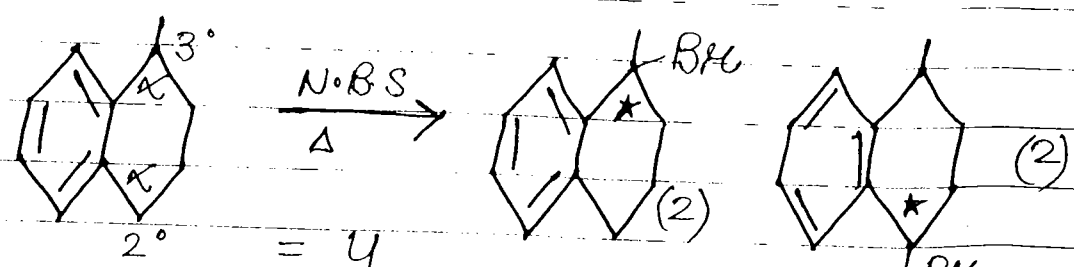






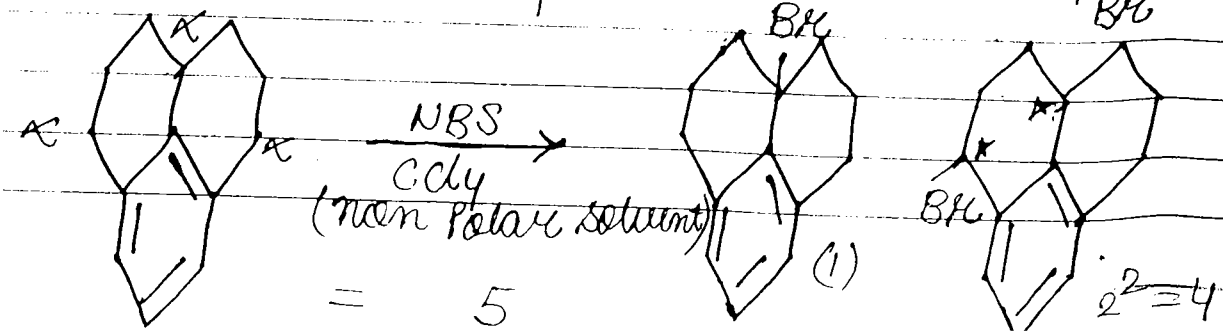
Q1. Identify no. of product.

(1)

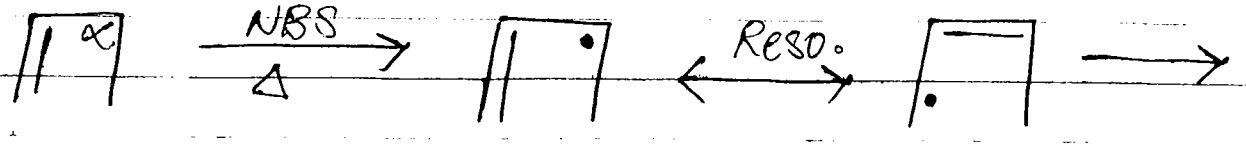


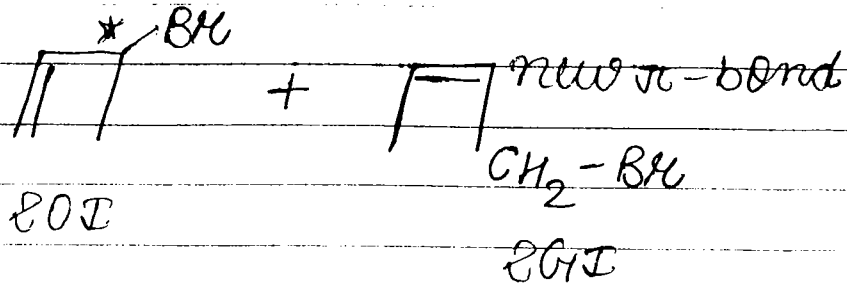
= 4

(2)

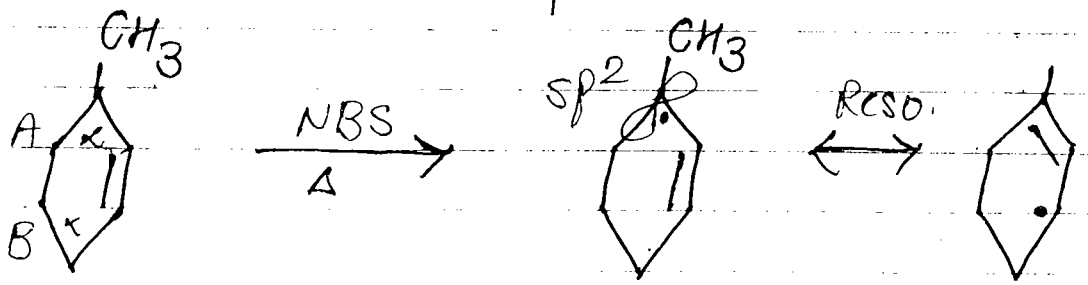


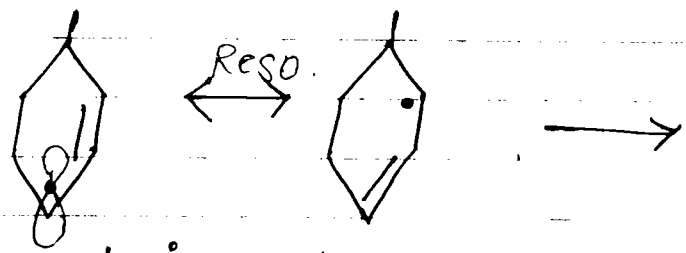
= 5

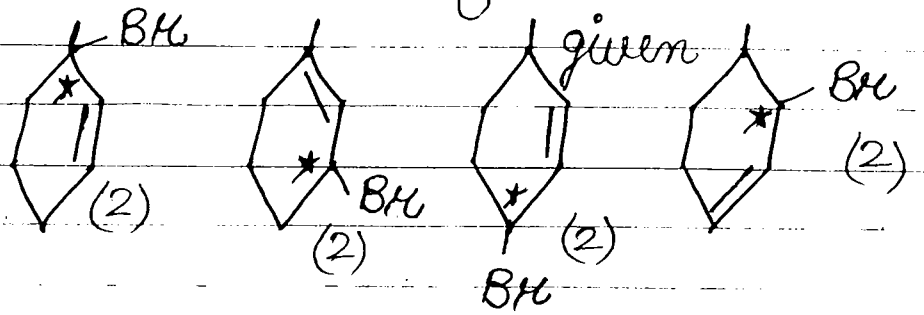
(3) 



= 4

(4) 



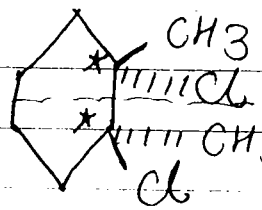


= 8 O.I.

~~6 I.~~

(5) identify major product →

Isomerism → some good examples from DDP.

Q1. 

Meso = (1)

O.I = (2)

Total S.I. = (3)

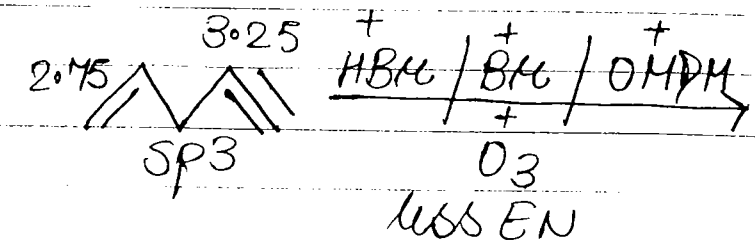
*** → If after one interchange then symm. possible then consider the compound as symmetrical.

Hint → POS/COS → given form

chiral / achiral → 3 group rotation

SI / OI / GI → one interchange

Structure → positional, functional, chain

Q2. 

(=>≡)

Ni / Pd / Pt
H2
→ less steric

(≡ > =)

Application of Isomerism

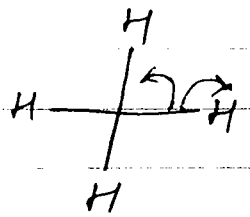
Photohalogenation

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl + H-Cl$$

Mechanism → Free radical substitution
|| || chain rea^{n}.

Initiation → $:\ddot{Cl}-\ddot{Cl}: \xrightarrow{h\nu} :\ddot{Cl}^{\bullet} + Cl^{\bullet}$
weak bond 7e 7e

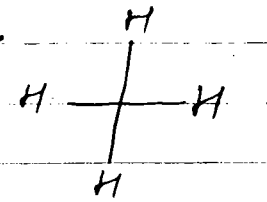
Propagation →



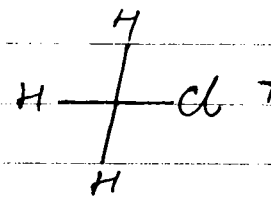
$+ Cl^{\bullet} \longrightarrow CH_3^{\bullet} + H-Cl$
7e 7e

$CH_3^{\bullet} + Cl-Cl \longrightarrow CH_3-Cl + Cl^{\bullet}$
7e 7e

Net →



$+ Cl_2$ Cl• and $CH_3^{\bullet}$ →



$+ H-Cl$

Termination →

$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3-Cl$
$Cl-Cl$
CH_3-CH_3 side product

Identify Product.

Sub. $\xrightarrow[Cl_2]{h\nu}$ H replace by halogen.

(A) $CH_4 + BrCl \longrightarrow CH_3-Br + HBr$

(B) $CH_3-CH_3 + Cl_2 \longrightarrow CH_3-CH_2-Cl + HCl$

(C) $CH_4 + Cl_2$ (excess) $\longrightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

(D) $CH_3CH_3 + Cl_2$ (ex.) $\longrightarrow$ 9 Product

CH_3CH_2Cl CH_3CHCl_2

CH_3CCl_3 $Cl-CH_2-CCl_3$

$HCCl_2-CCl_3$ CCl_3-CCl_3

geminal

CH_2Cl-CH_2Cl $CHCl_2-CH_2Cl$

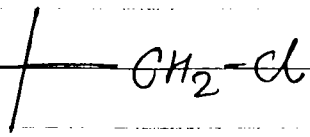
$CHCl_2-CHCl_2$

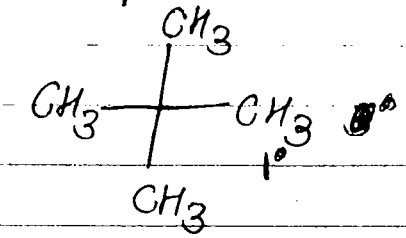
vicinal

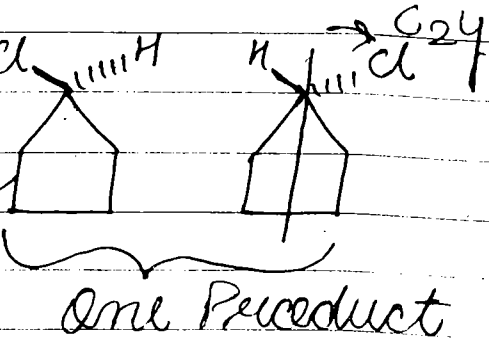
(E) Isobutane $\longrightarrow$ CH_2Cl + Cl

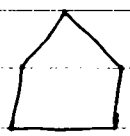
1°C CH_3, 3°C CH, CH_3 1°C, 1°C CH_3

M.C.P / mono chlorination Product

(F) Neopentane $\xrightarrow[Cl_2]{h\nu}$ 



(G) cyclopentane $\longrightarrow$ 



One Product
It is having POS.

(H) $CH_3-CH_2-CH_2-CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2\underset{*}{CH}(Cl)-CH_3$

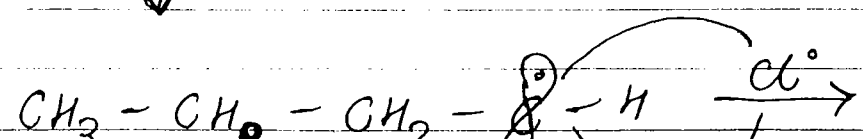
Butane

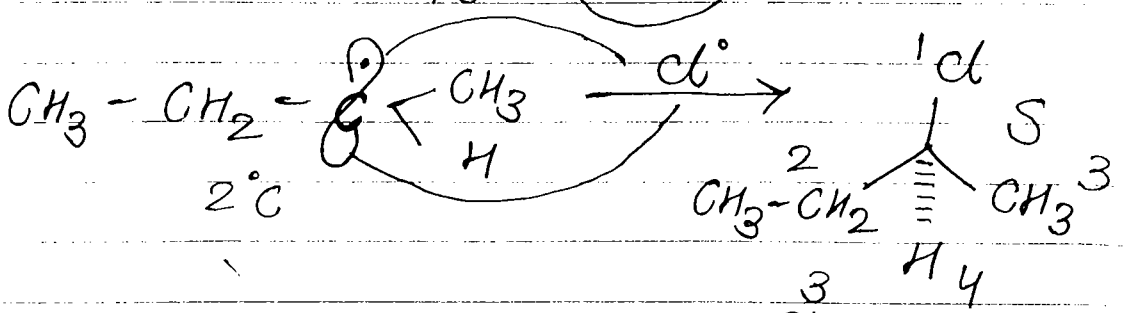
Mechanism: Cl°

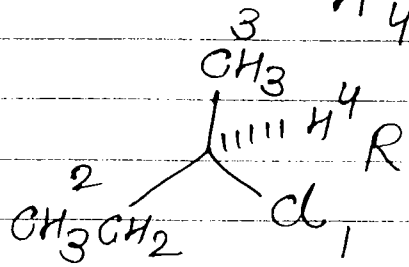
New chiral center

$2' = 2 \rightleftarrows R, S$

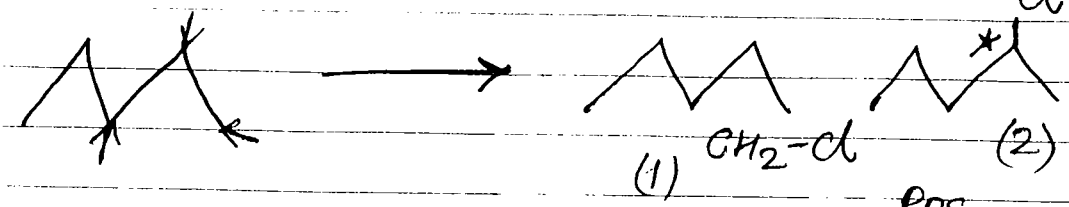
3 M.C.P.



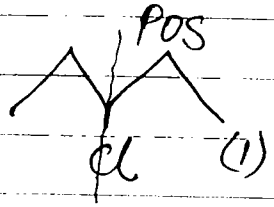




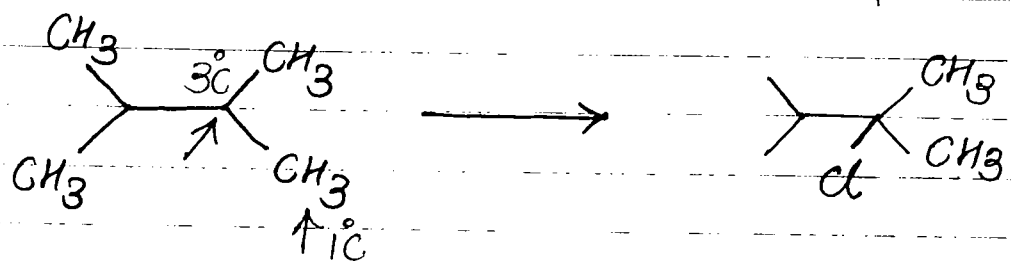
(I)



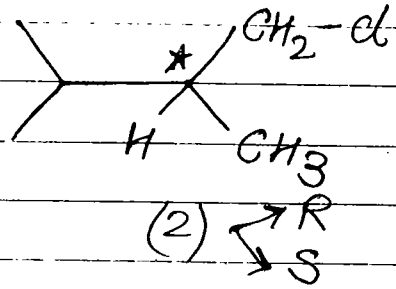
4 M.C.P.



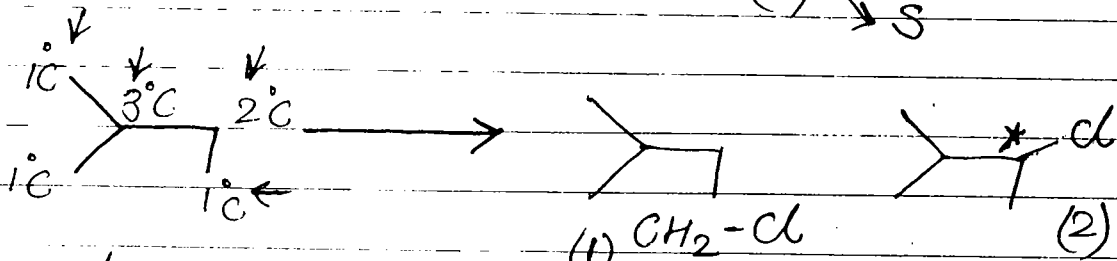
(J)



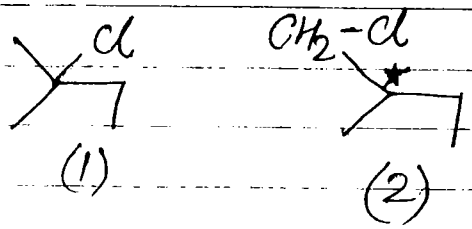
3 M.C.P.



(K)



Isopentane



(A) no. of structural Product 4

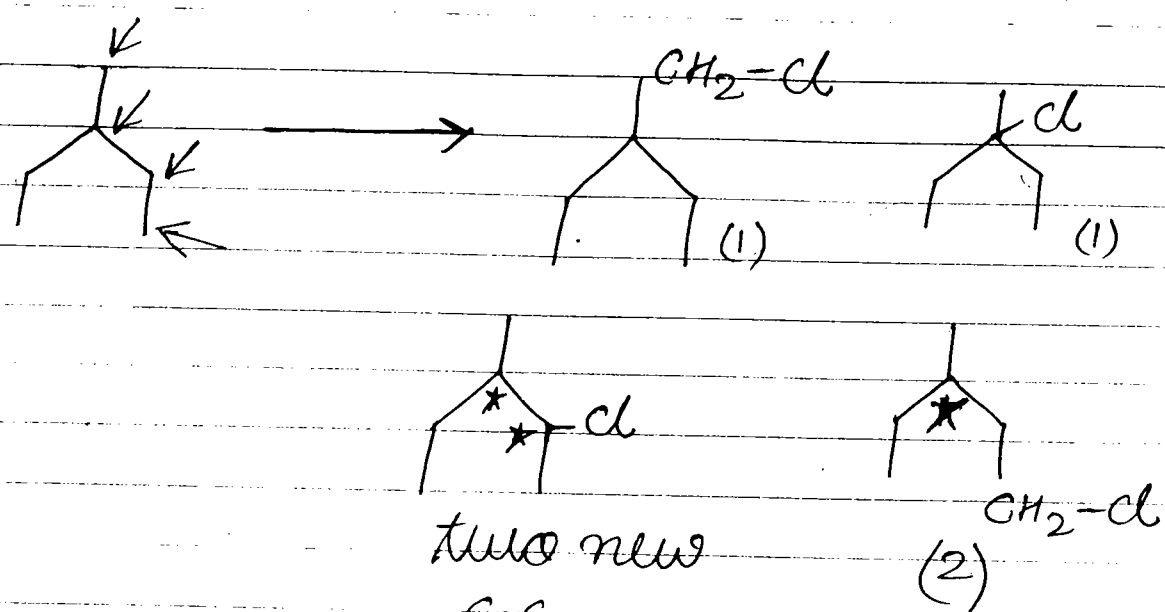
(B) no. of Product (Including stereo.) 6

(C) chiral Product 4

(d) distillation Product = Total - ena. Pair

6 - 2 Pair = 4

(K)



$2^2 = 4$

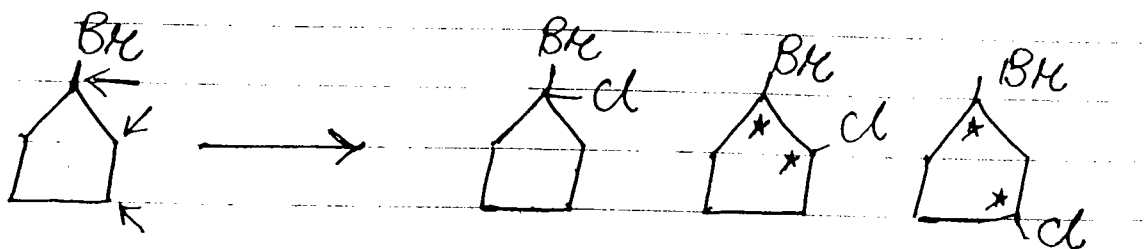
(A) 4

(B) 8

(C) 6

(D) 8 - 3 Pair = 5

(M)



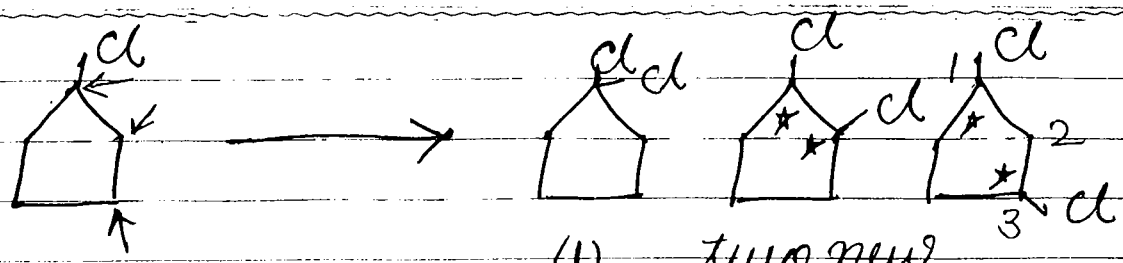
9 Product

$(2)^2 = 4$

BH BH BH BH

Cl Cl Cl Cl

(N)

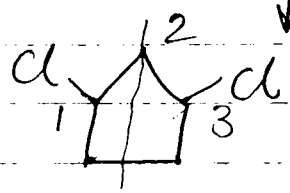


(1) two new C·C symmetry

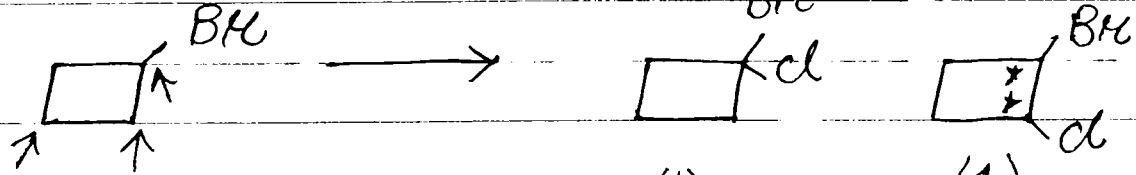
(3) Sym-metry

(3)

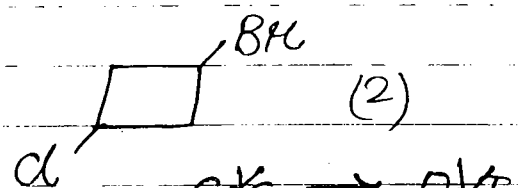
7 Product



(0)



(1) (4)

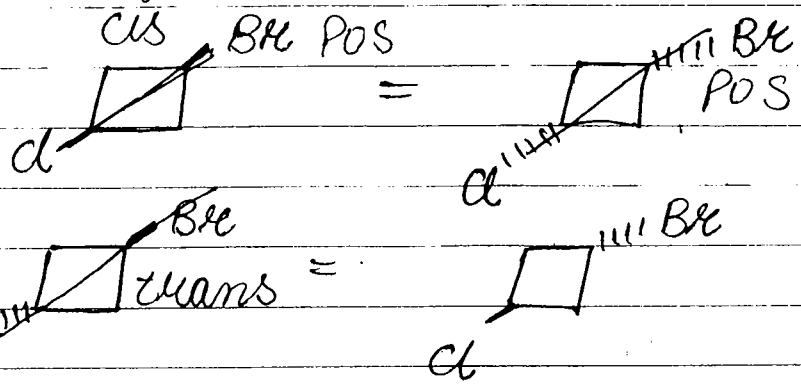


(2)

C≠C → O≠C

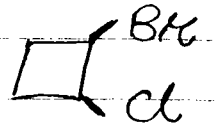
7 Product

Ring → G.I.

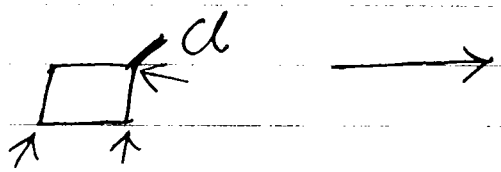


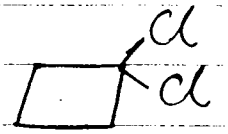
(a) 3

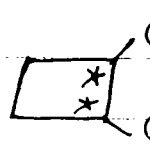
(b) 7

(c) chiral 4 →  POSX COSX

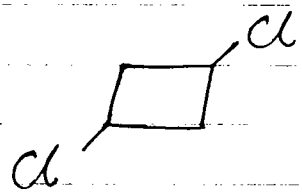
(d) 7 - zero. pair
RR/SS
RS/SR
= 5

(P) 

(1) 

 Symmetrical

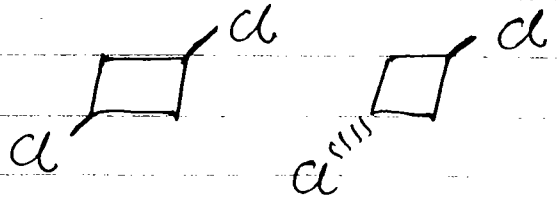
(3)

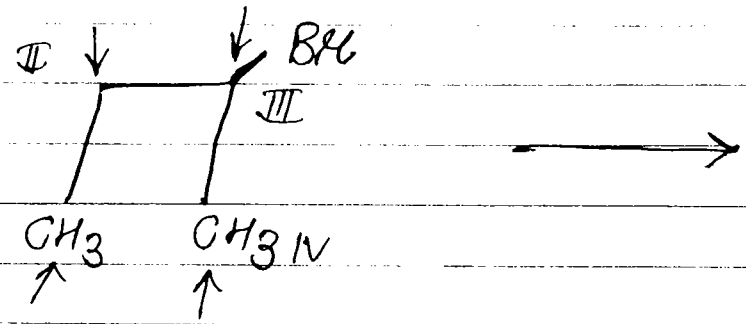


C·C → NO
ring → G·I·

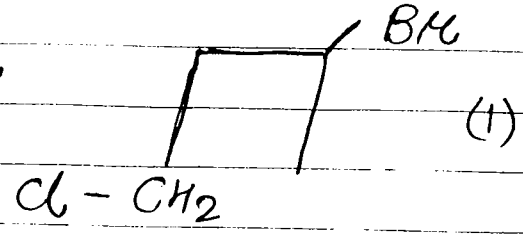
6 Product

(2)

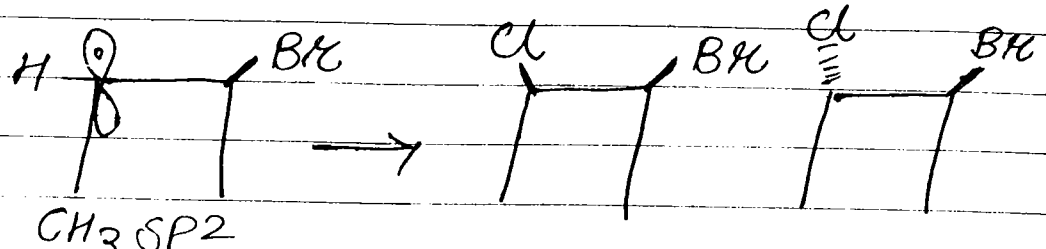


(8) 

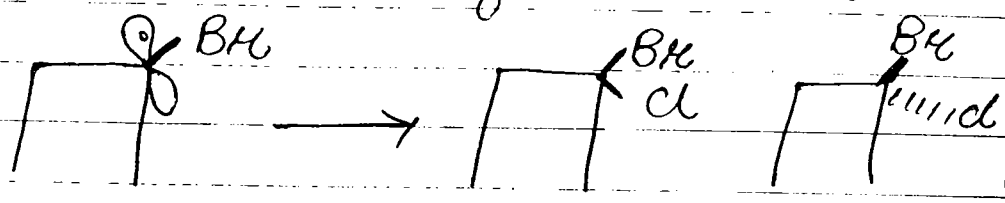
2R- bromo butane

I → 

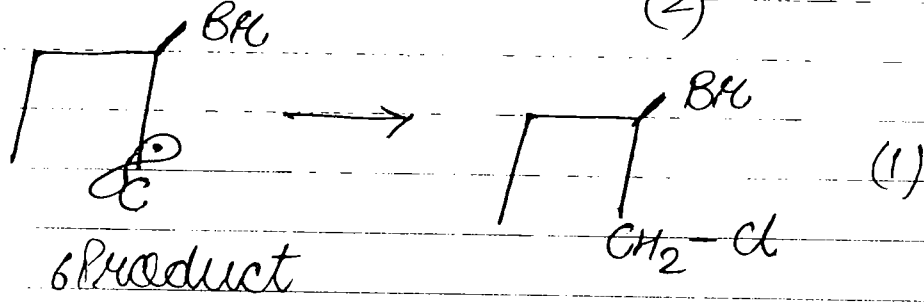
(1)

II → 

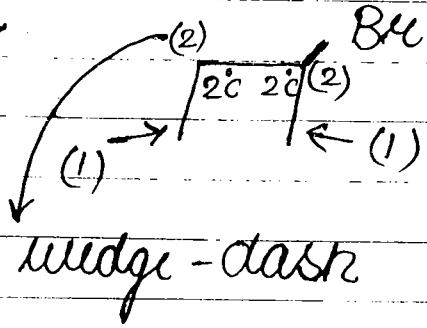
(1) new C·C formed = (2)

III → 

(2)

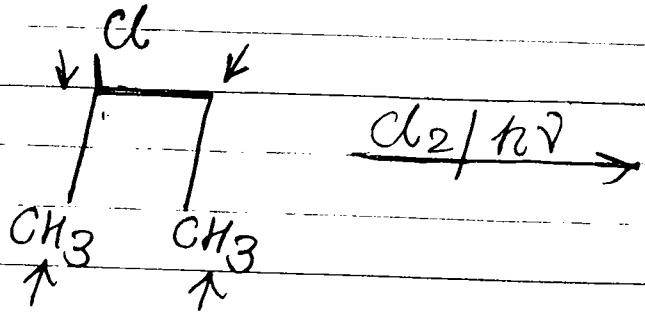
IV → 

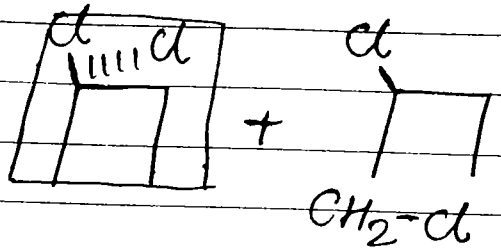
(1)

Hint → 

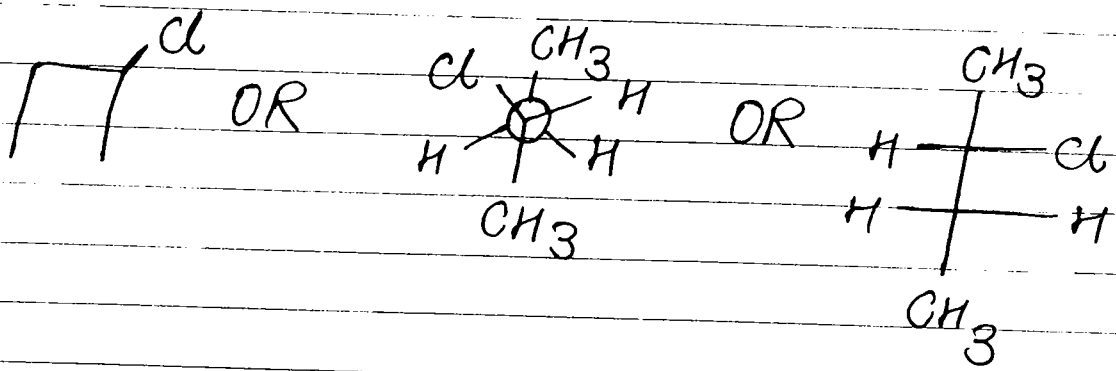
→ If reaction take place out of C·C then configuration do not change.

→ If reax. take place on chiral center then two form possible if intermidiate is sp^2.

(R) 

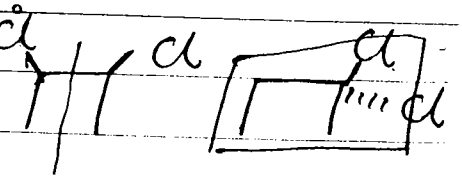
2-R chloro butane +  +

5 Product < Achiral (2) → geminal, meso
chiral (3)

(S) 

Ena are having same physical and chemical properties.

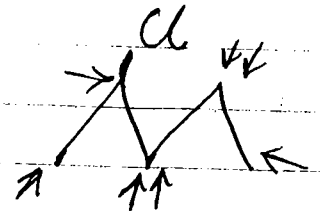
(5) < 2 Achiral
3 chiral



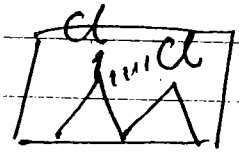
(7) Racemic R- chloro butane

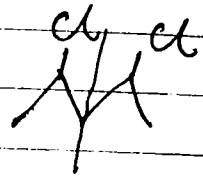
R+S = 5+5 = 10 - 2 Achiral / 2 Repeat

= 8

(iii)  $\xrightarrow{Cl_2/h\nu}$ 4 → Achiral (2), 4 → chiral

2S- chloropentane





(v) 2R- chloro Pentane 4

(iv) Racemic 2- chloro Pentane

$R+S = 4+4-2$ Achiral

$= 12.$

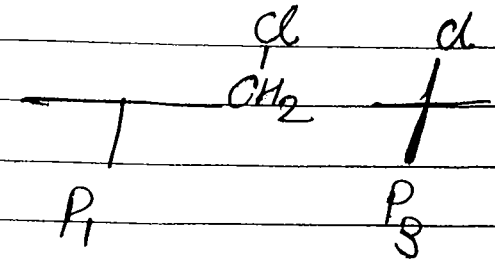
Q. calculate % of product

Reactivity series (at 20°C)

	1°H	2°H	3°H
Cl° →	1	3.8	4.5
Br° →	1	82	1600

$$\frac{P_1}{P_2} = \frac{n_1 \times R_1}{n_2 \times R_2}$$

P_1, P_2 ↓ % of product; n_1, n_2 ↓ no. of degree of H; R_1, R_2 → reactivity

(i) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{CH}}}-CH_3 \xrightarrow{Cl_2}$ 

P_1 P_3

$1^{\circ}H = 9 = n_1$

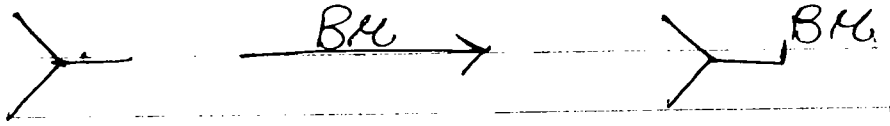
$3^{\circ}H = 1 = n_3$

$$\frac{P_1}{P_2} = \frac{9 \times 1}{1 \times 4.5} = \frac{9}{4.5} = \frac{2}{1}$$

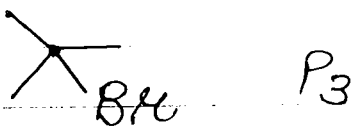
total $= 2 + 1 = 3$

$$\% P_1 = \frac{2}{3} \times 100 = 66.66\% \quad P_1$$

$33.33\% \quad P_2$

(2) 

P_1

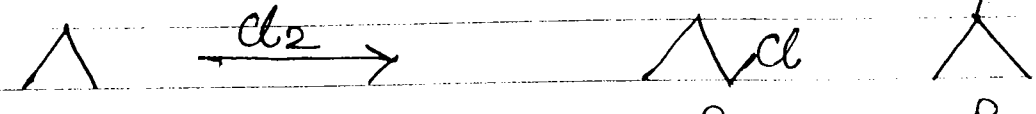


P_3

$$\frac{P_1}{P_3} = \frac{9 \times 1}{1 \times 1600} = \frac{9}{1600}$$

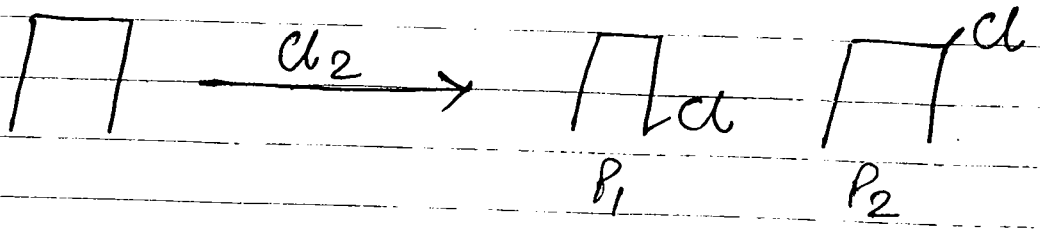
Total $= 1609$

$$\frac{1600}{1609} \times 100 = 99.9\% \quad P_3$$

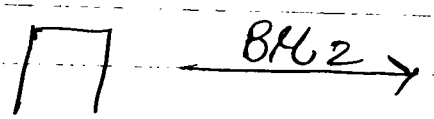
(3) 

P_1 P_2

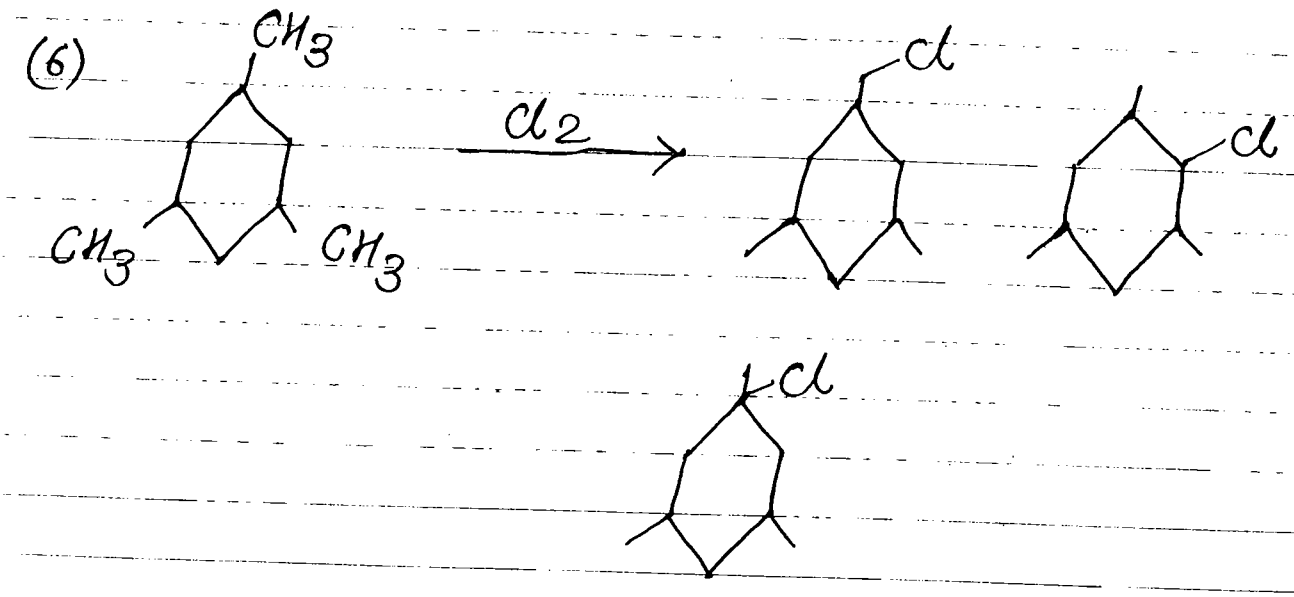
$$\frac{P_1}{P_2} = \frac{6}{2} \times \frac{1}{3.8} = \frac{6}{7.6}$$

(4) 

$$\frac{P_1}{P_2} = \frac{6}{4} \times \frac{1}{3.8}$$

(5) 

$$\frac{P_1}{P_2} = \frac{6}{4} \times \frac{1}{82}$$

(6) 

$P_1 = n_1 M_1 = 9 \times 1 = 9$

$P_2 = n_2 M_2 = 6 \times 3.8 = 22.8$ major

$P_3 = n_3 M_3 = 3 \times 4.5 = 13.5$

Total $= 45.3$

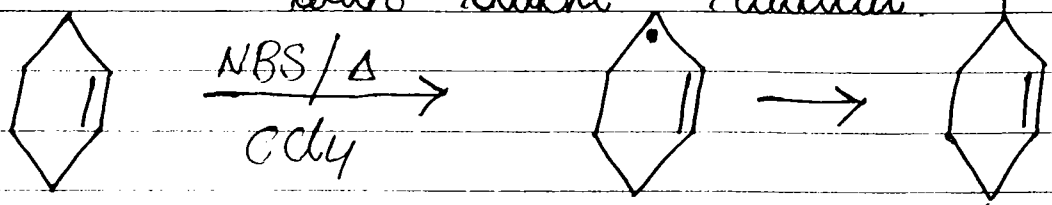
$\therefore$ $45.3 \longrightarrow P_2$ 22.8

$100 \longrightarrow \frac{22.8}{45.3} \times 100 = 50\%$

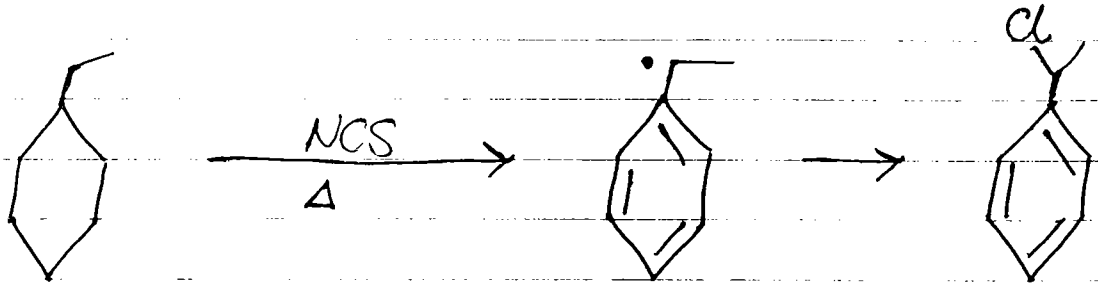
Allylic substitution OR Benzyllic substitution →

Hint → α-H replaced by halogen with stable radical

(1)

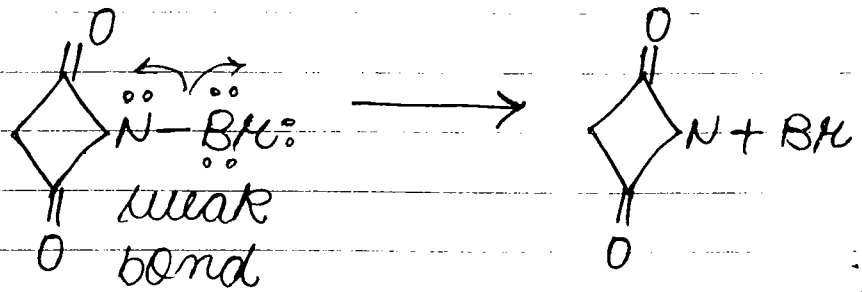


(2)



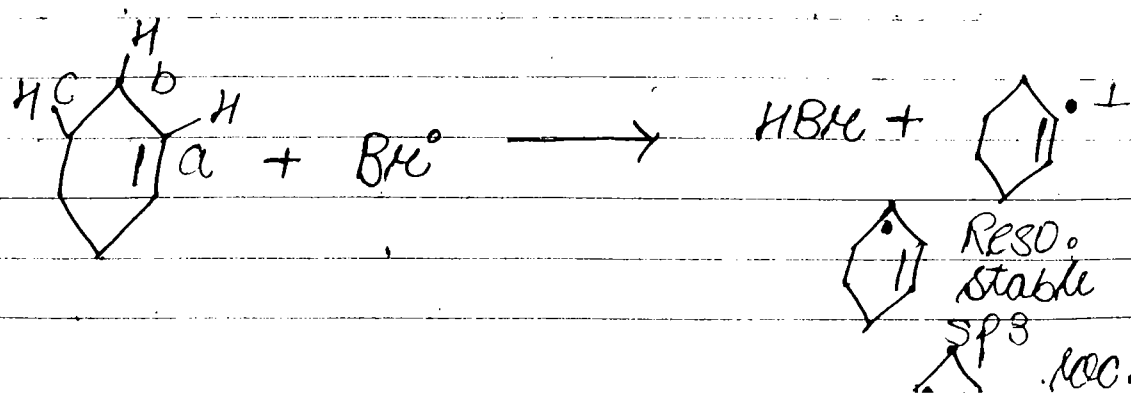
Mechanism → Free radical chain rxn.

Initiation →

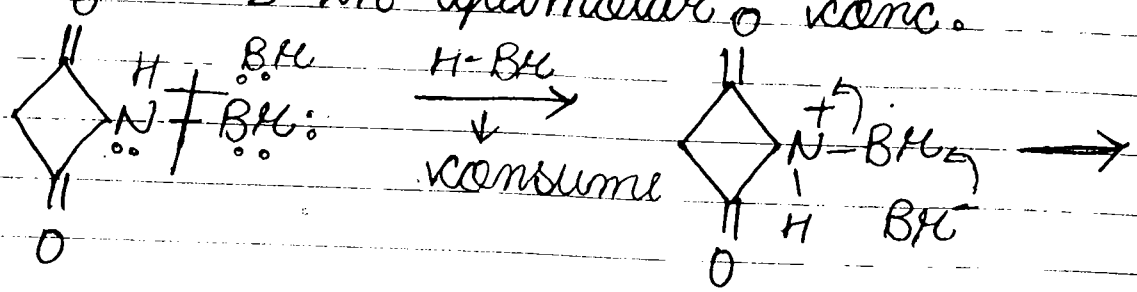


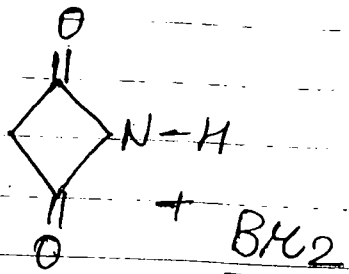
N- Bromo succinimide

Propagation →

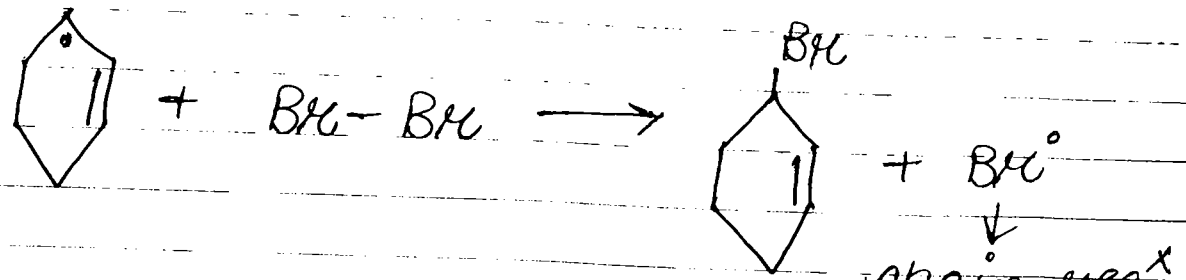


Role of N.B.S → to consume HBr and form Br_2 in equimolar conc.





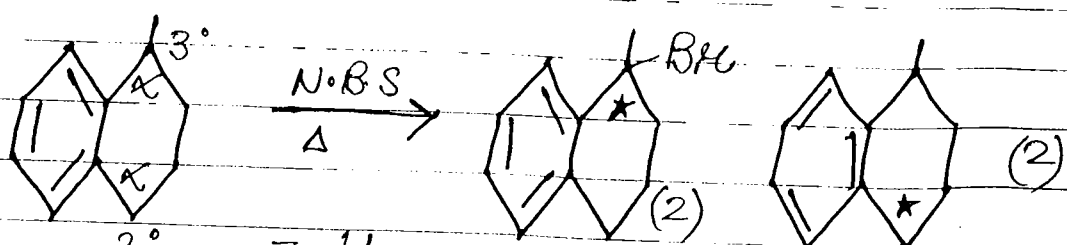
form



chain reaction

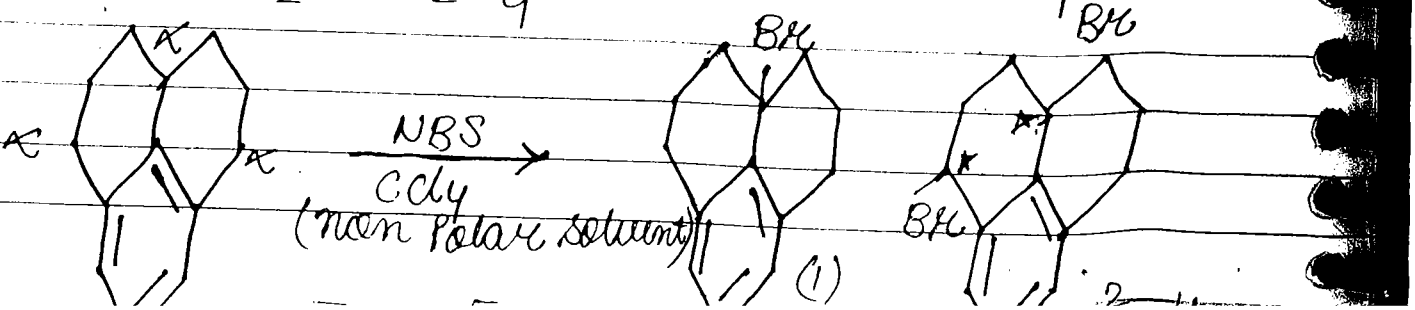
Q1. Identify no. of product.

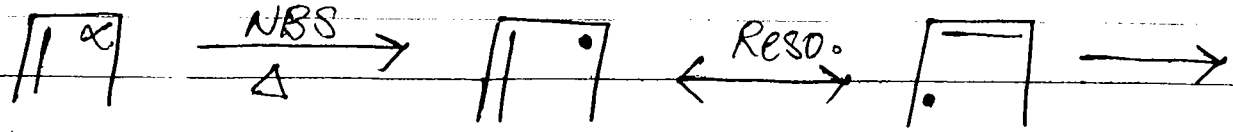
(1)

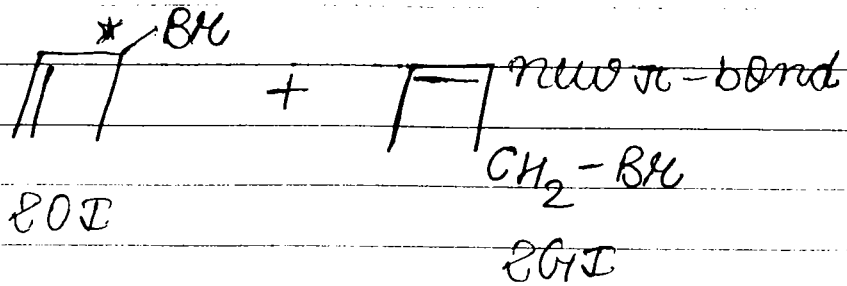


= 4

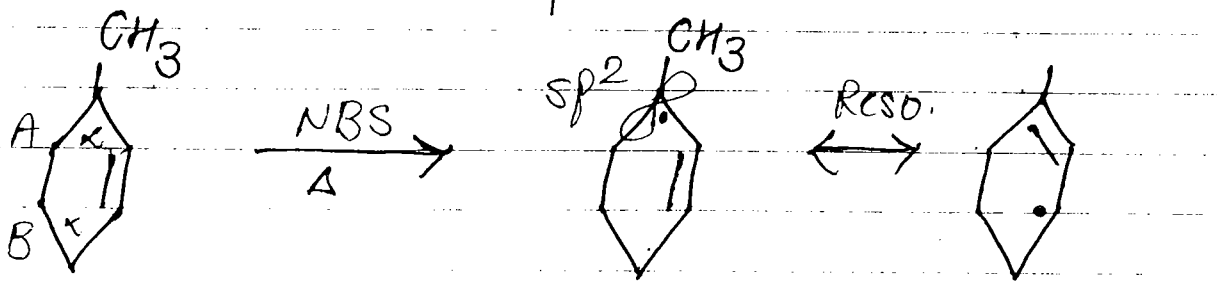
(2)

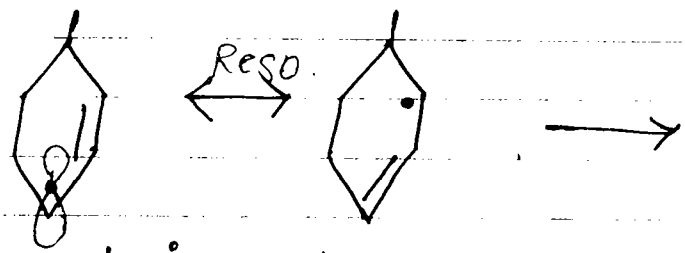


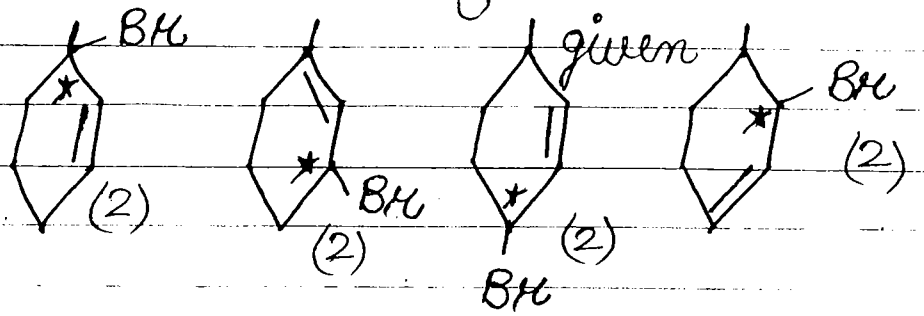
(3) 



= 4

(4) 

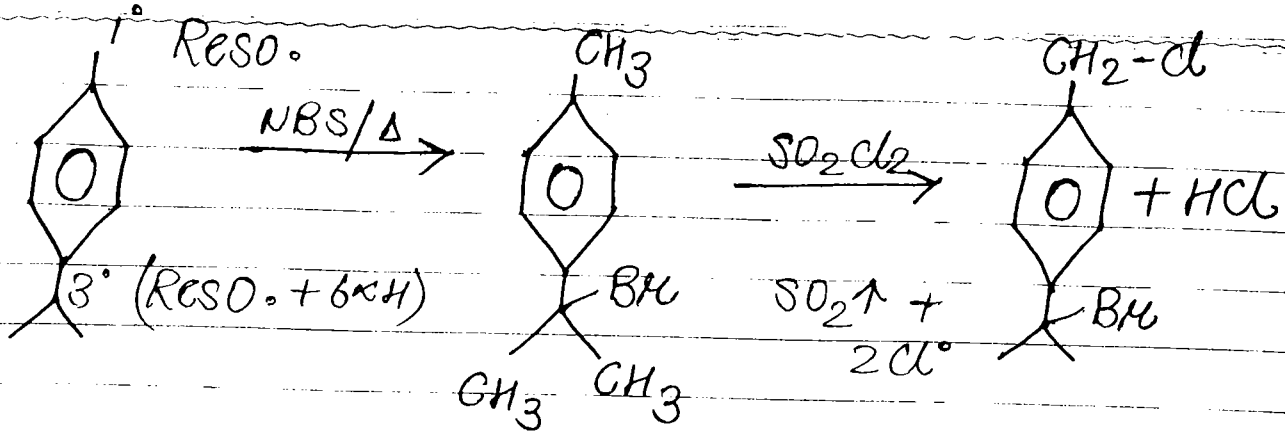




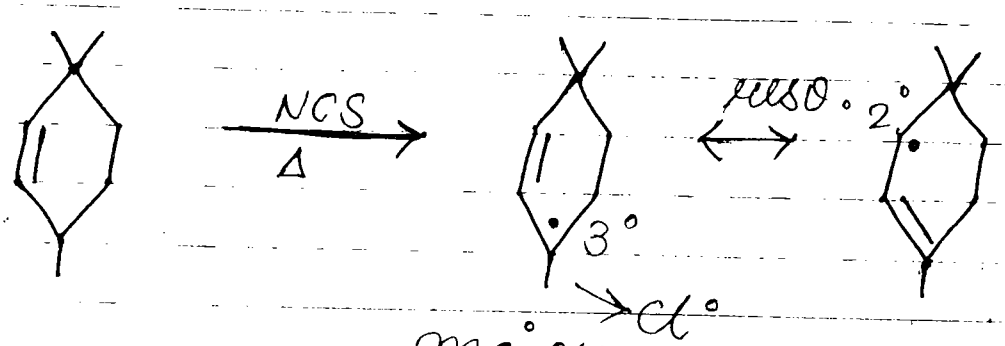
= 8 O.I.

~~6 I.~~

(5) Identify major product →

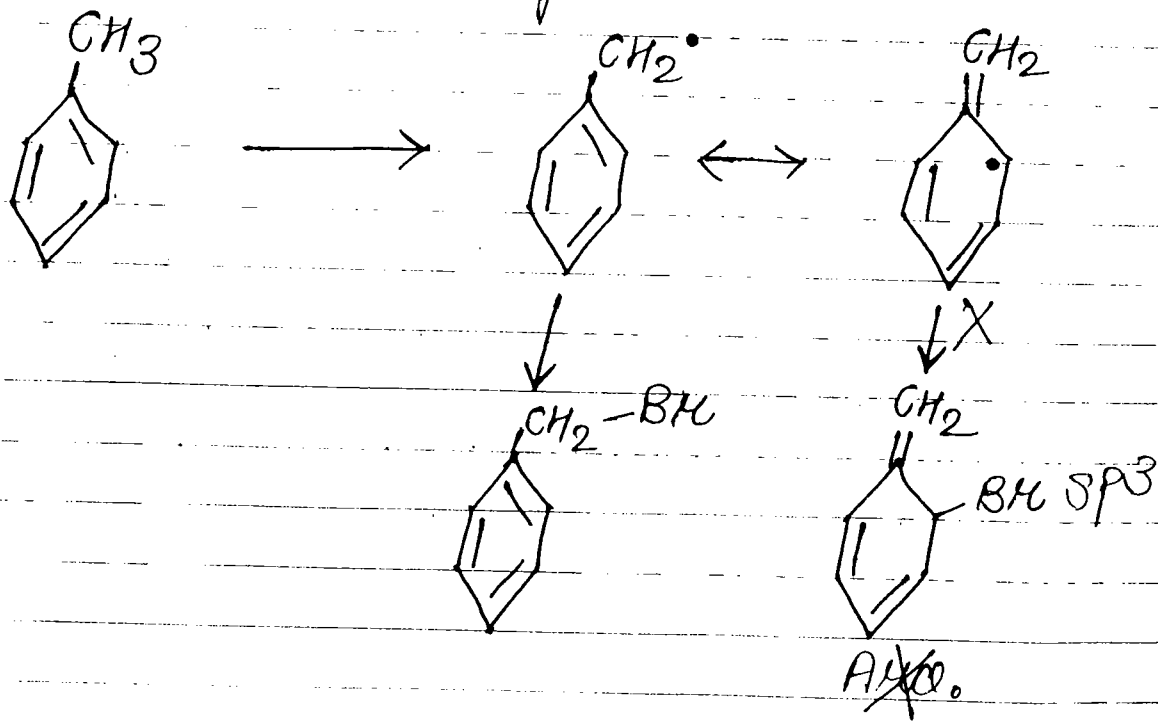


(6)

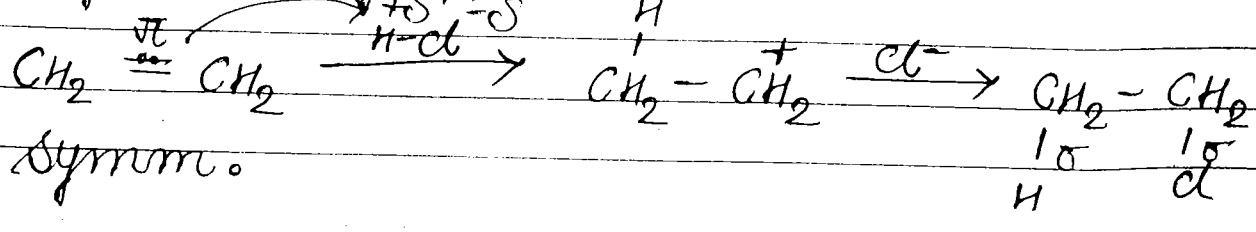


Major

(7)



Hydrohalogenation →



$8e \xrightarrow[\text{slow}]{H^+/E^+} 6e \xrightarrow[\text{fast}]{Cl^-/Nu^-} 8e$

Electrophillic addition

$E^+ \rightarrow$ slow step

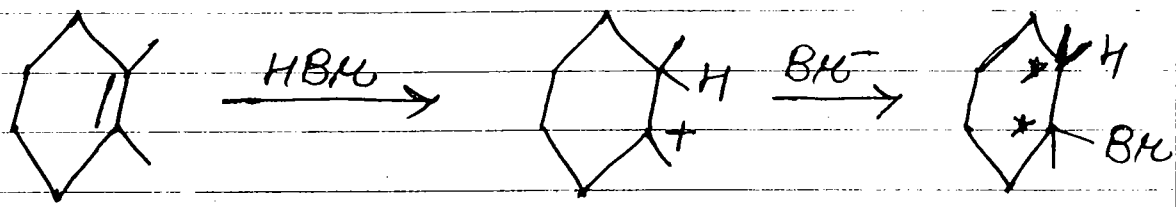
$\pi \rightarrow$ replace by 2σ bond

(1) $CH_3-CH=CH-CH_3 \xrightarrow{H-BH} CH_3-\underset{H}{CH}-\overset{+}{C}H-CH_3$

$\xrightarrow{BH^-} CH_3-\underset{H}{CH}-\overset{*}{\underset{BH}{CH}}-CH_3$

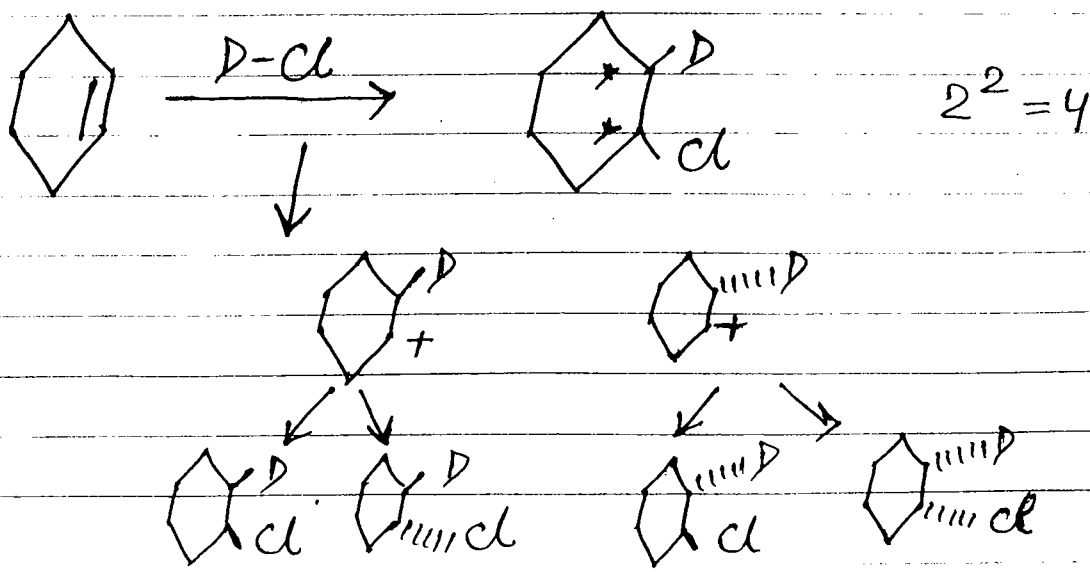
(1) new C·C (2) $\overset{R}{\underset{S}{\leftrightarrows}}$

(2)

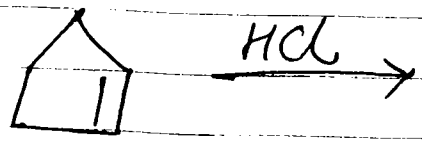
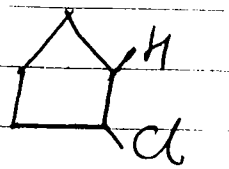


$2^2 = 4$

(3)

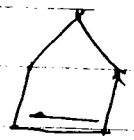


$2^2 = 4$

(4)  

symm. → Zero c.c.

↓

 (1) product

Some facts →

(1) In hydrohalogenation alkene or alkyne react with HX.
(Halogen)

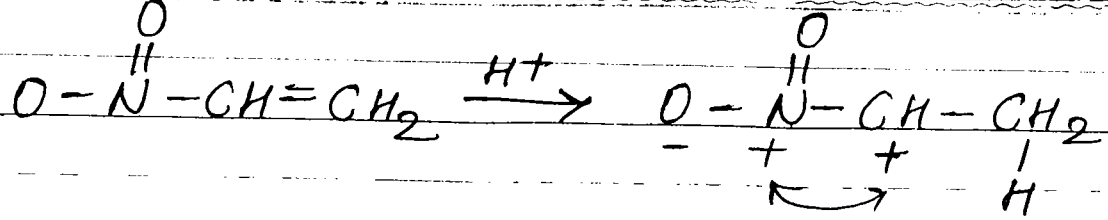
(2) Its a electrophillic addition beco electrophile involve in slow step.

Markovnikove rule →
In unsymm. alkene electrophile add to those alkene carbon which is having more the no. of hydrogen.
(old definition)

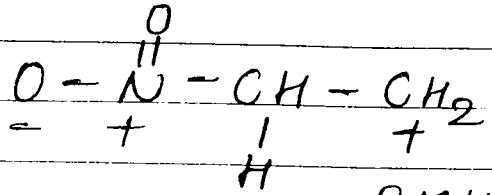
Advance Markovnikove rule →
H+ add to those alkene carbon which give more stable cation.

(1) $CH_3-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{+}{C}H-CH_2H$ 6 H (Stable)

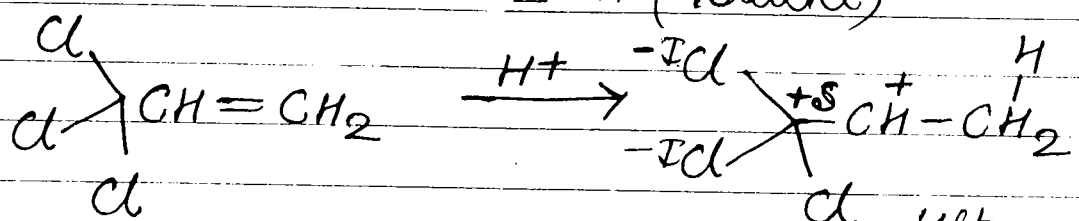
$CH_3-CH(H)-\overset{+}{C}H_2$ 2 H

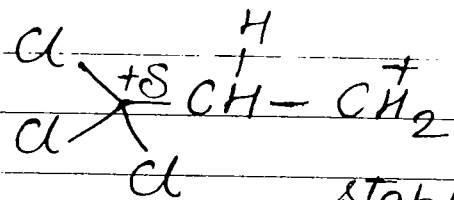
(2) 

mp. + 3°H (unstable)

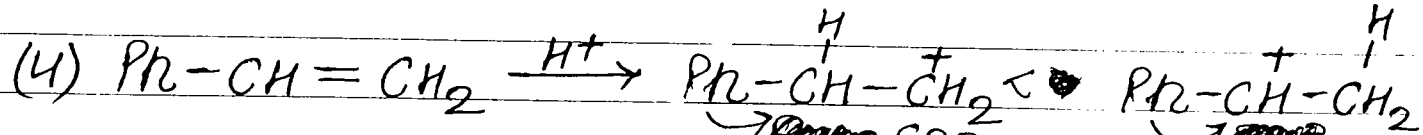


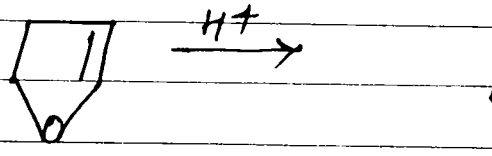
2°H (stable)

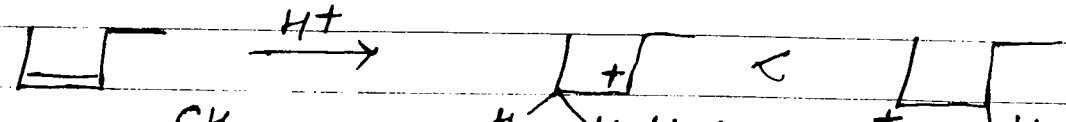
(3) 

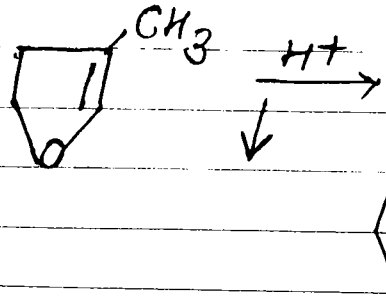


stable

(4) 

(5) 

(6) 

(7) 

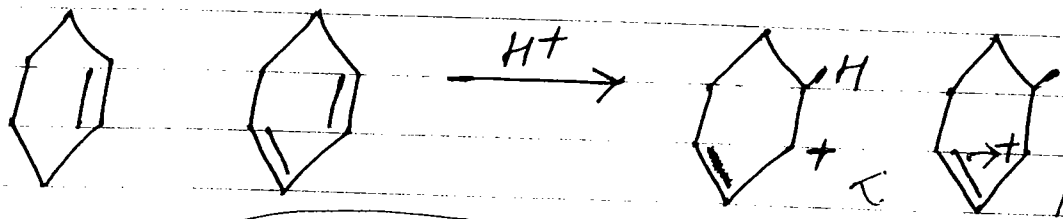
stable

→ If two diff. reactant then more stable cation give more the rate of reaction.

Q1. Identify the rate of reaction.

(1) $Ph-\overset{A}{CH}=CH-Ph$ < $Ph-\overset{B}{C}(Ph)=CH_2$ $\xrightarrow{H^+}$

$Ph-\underset{Sp3}{\overset{H}{\underset{|}{C}}H}-\overset{+}{C}H-Ph$ < $Ph-\overset{+}{\underset{|}{C}}(Ph)-CH_2$ (more reso.)

(2) 

(3) $CH_2=CH_2$ > $HC\equiv CH$ $\xrightarrow{H^+}$

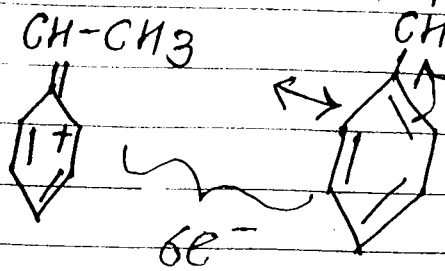
2.75 EN — 3.25 EN

less EN

$CH_2-\overset{+}{C}H_2$ > $HC=\overset{+}{C}H$

3° — Sp2 — No.°

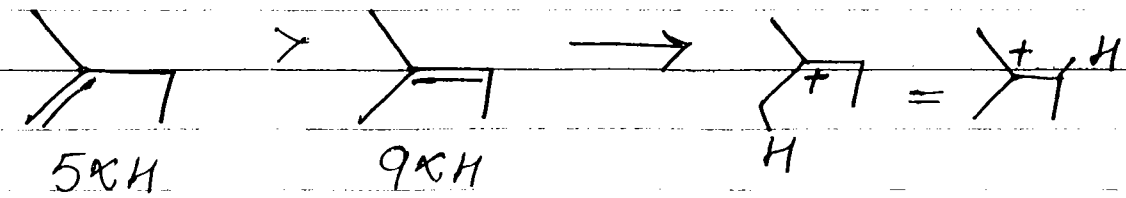
(4) $Ph-CH=CH_2$ < $CH_3O-CH=CH_2$ $\xrightarrow{H^+}$



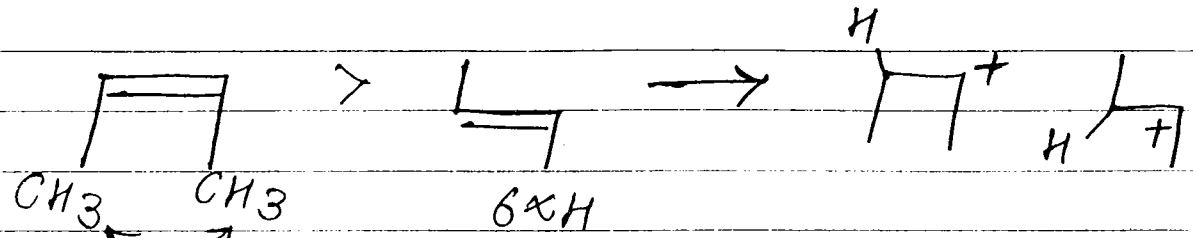
$CH_3\ddot{O}-\overset{+}{C}H-CH_2$ ↔ $CH_3-\overset{+}{O}=CH-CH_2$

8e-

(5)

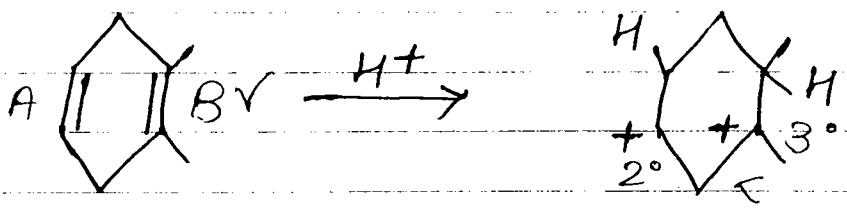


(6)

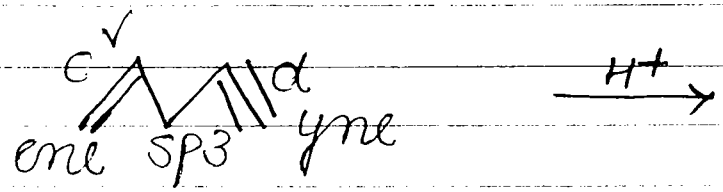


If same cation form then consider unstable alkene for more rate of rea.ˣ

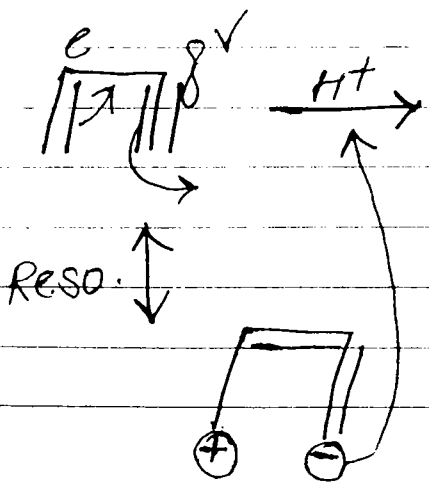
(7)



(8)



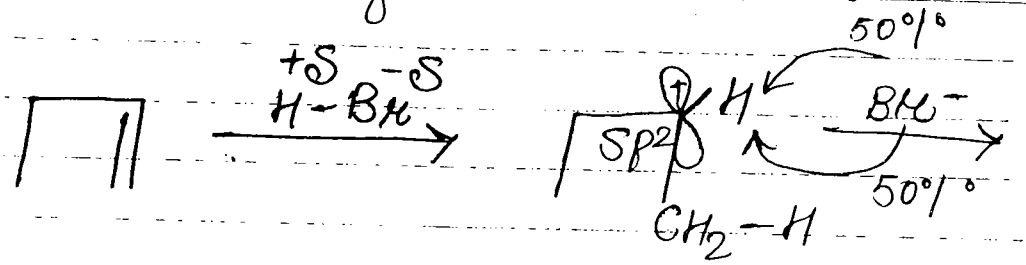
(9)

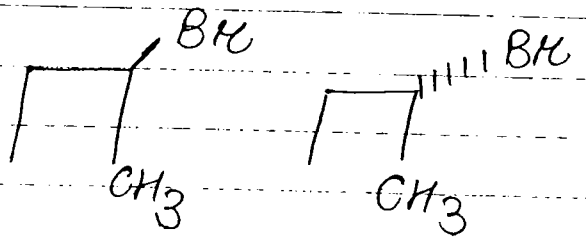


→ In general ene is more reactive than yne but in HSO. yne is ~~more~~ more reactive for electrophile.

→ carbocation is sp^2 hybridized it means nucleophile attacks from both side.

(10)

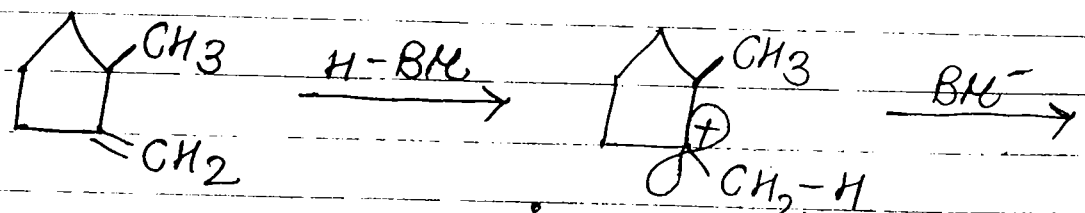


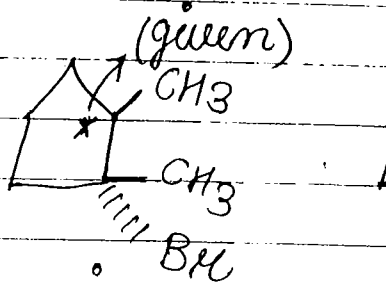


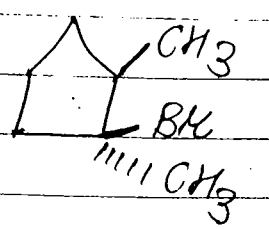
1 new C·C

Racemic mix.

(11)



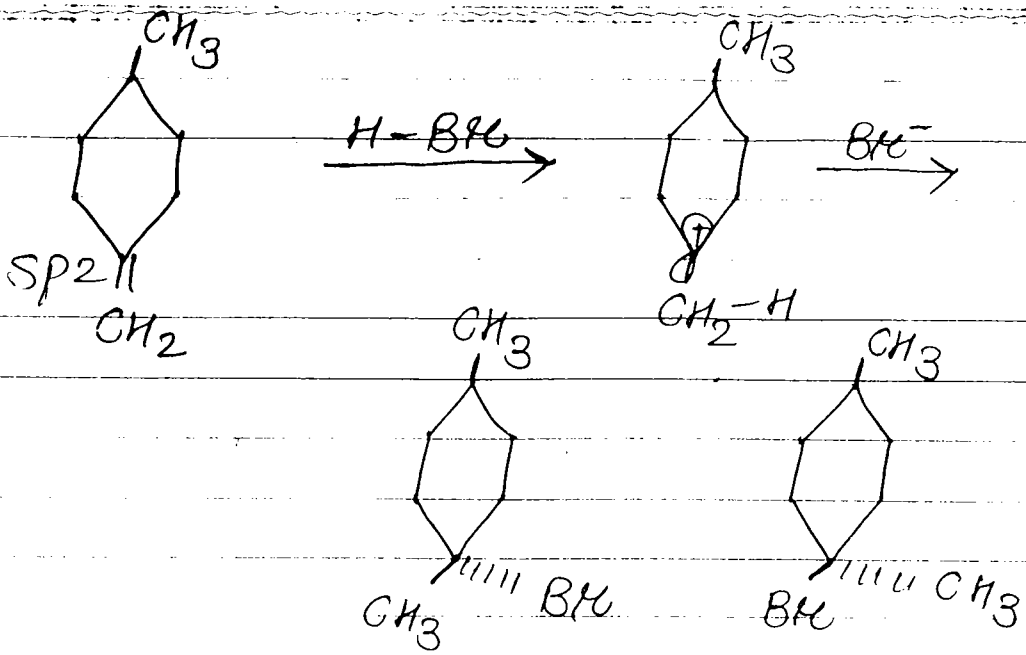




cis trans

Dia.

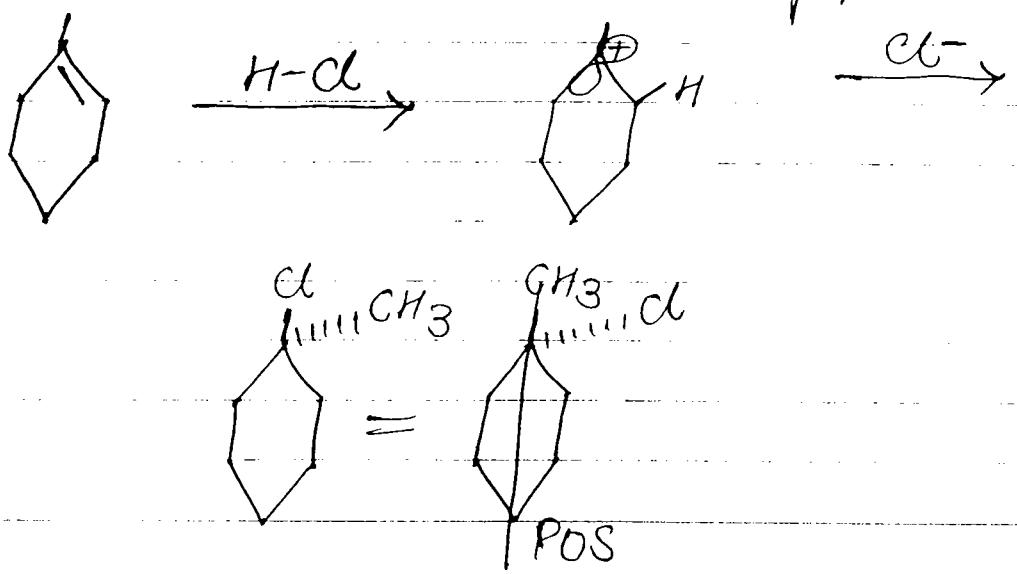
(12)



O.I. = 0 → C≠C

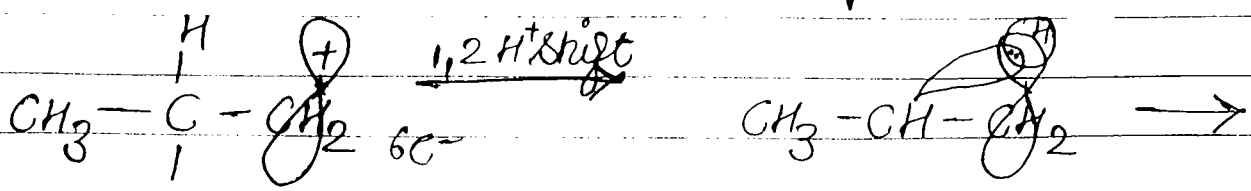
G.I. = 2 ring / dia.

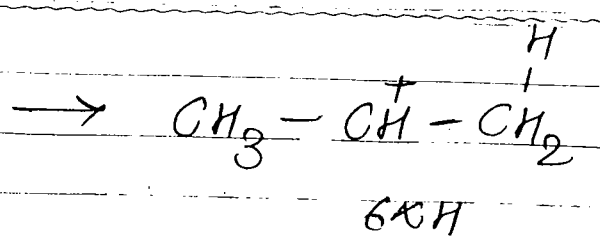
(13)



Identical

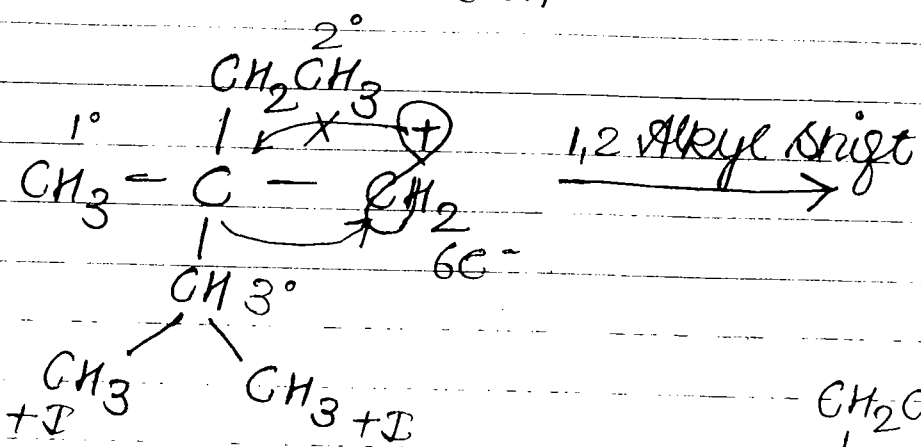
→ carbocation can be rearrange into more stable cation by 1, 2-shift.



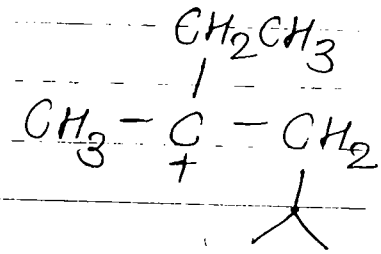


6 α H

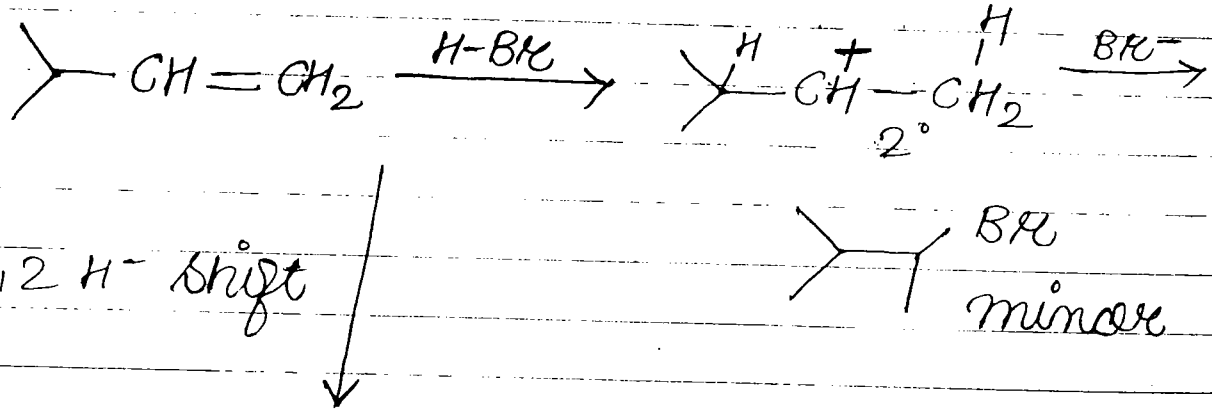
(B)



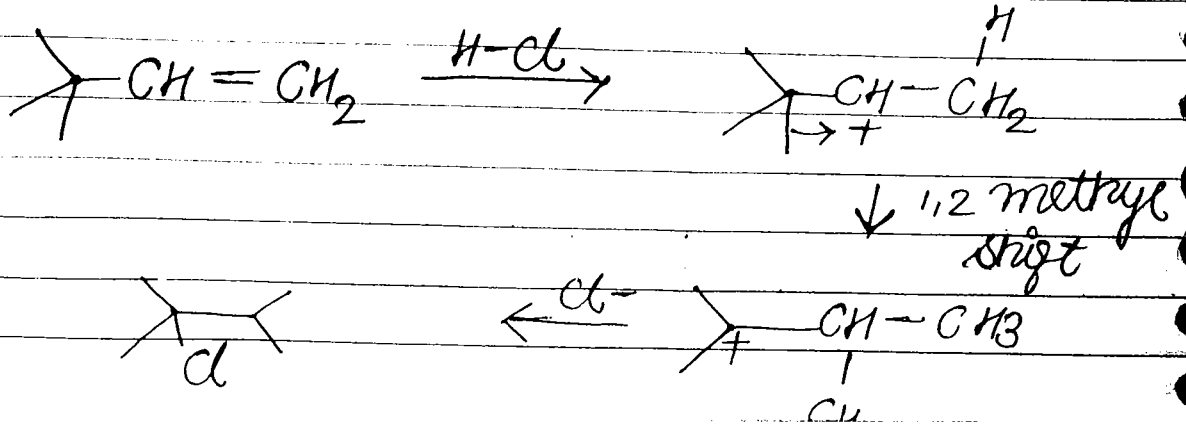
more e⁻ density



(1)



(2)



→ Na^+ and K^+ are not electrophile becoz it can not form covalent bond.

(1) $CH_2 = CH_2 \xrightarrow[8e^- \quad 18e^-]{\overset{+}{Na}Cl / \overset{+}{K}Cl}$ NO rea. ×

cov ✗ bond

$\overset{Na}{\underset{|}{}}$ ✗ $\overset{+}{C}H_2$

$CH_2 - \overset{+}{C}H_2$

(2) $CH_2 = CH_2 \xrightarrow[Na^+ Cl^- (excess)]{H-Br}$ $\overset{H}{|}$ $CH_2 - \overset{+}{C}H_2$

(+S → H–Br; ✗ → Na^+ ; E^+ ✗, Cl^- ↓ Nu^-)

$\xrightarrow{Br^- < Cl^- (excess)}$ $CH_3 - CH_2 - Cl$ (major)

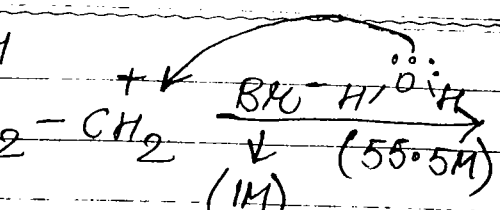
\+

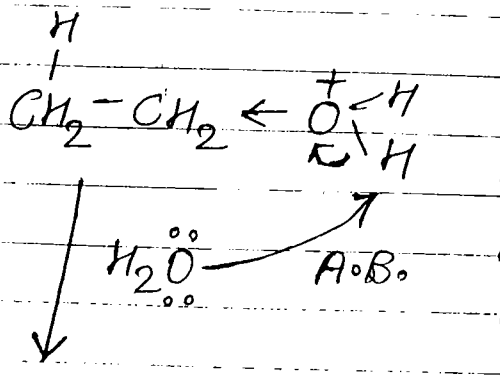
$CH_3 - CH_2 - Br$

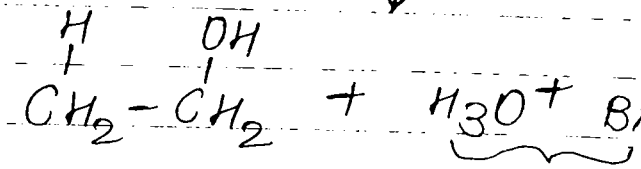
→ If non polar solvent is replaced by polar solvent then end product is changed.

(3) $CH_2 = CH_2 \xrightarrow[CCl_4 \text{ non-Polar}]{H-Br}$ $\overset{H}{|}$ $CH_2 - \overset{+}{C}H_2 \xrightarrow{Br^-}$ $CH_3 - CH_2 - Br$

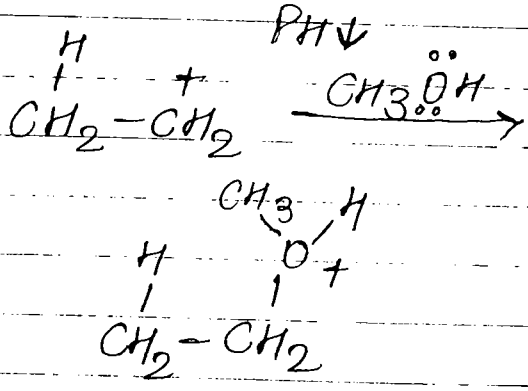
(4) $CH_2 = CH_2 \xrightarrow[H_2O]{H-BH} CH_2-CH_2$ (Polar)



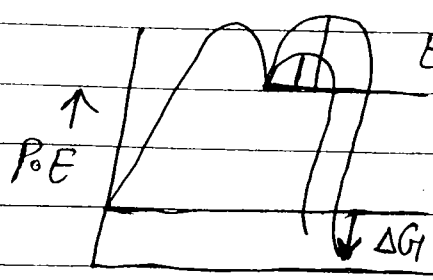


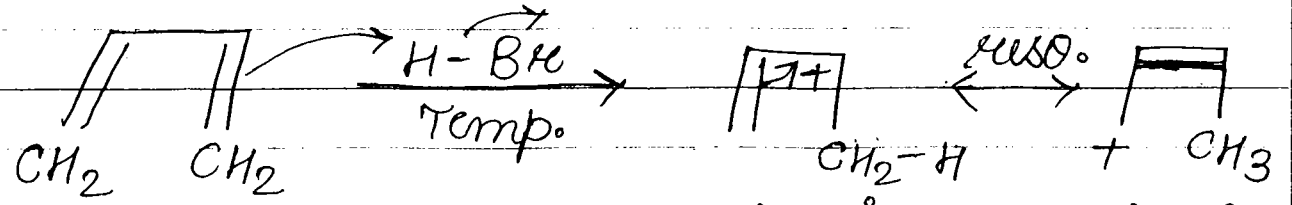


(5) $CH_2 = CH_2 \xrightarrow[CH_3OH]{H-BH}$ (Polar)

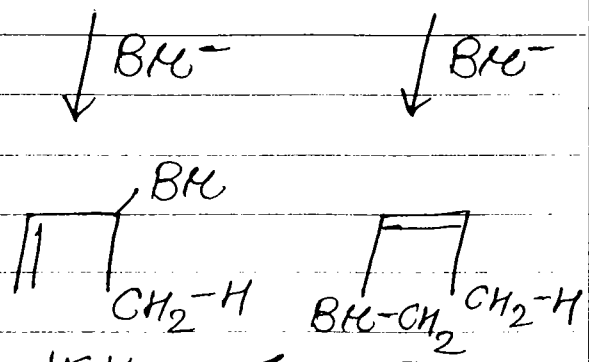


→ In conjugated dyene system major product is decided by temp.





2°cation > 1°cation



1°H < 5°H

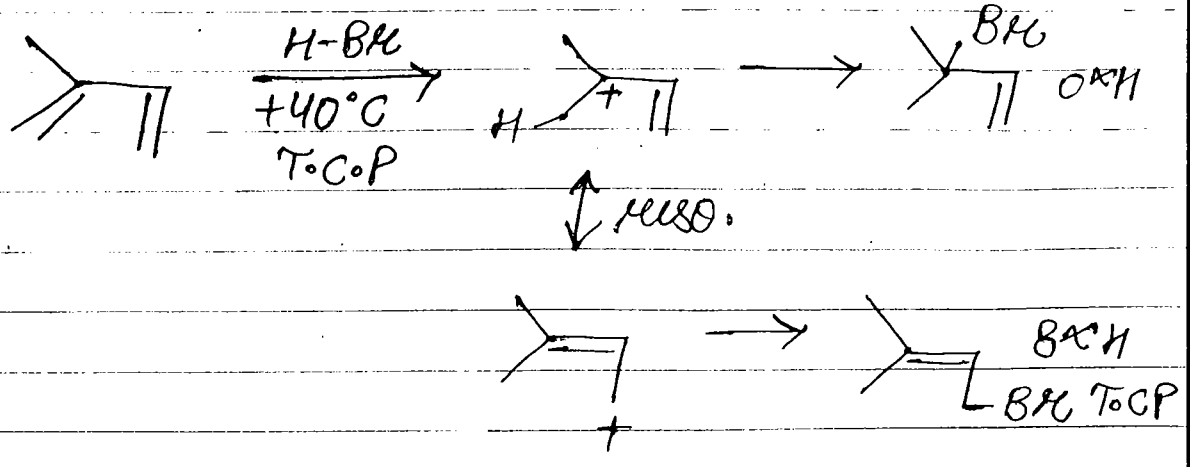
1,2 addition — 1,4-add.

K.C.P — T.C.P

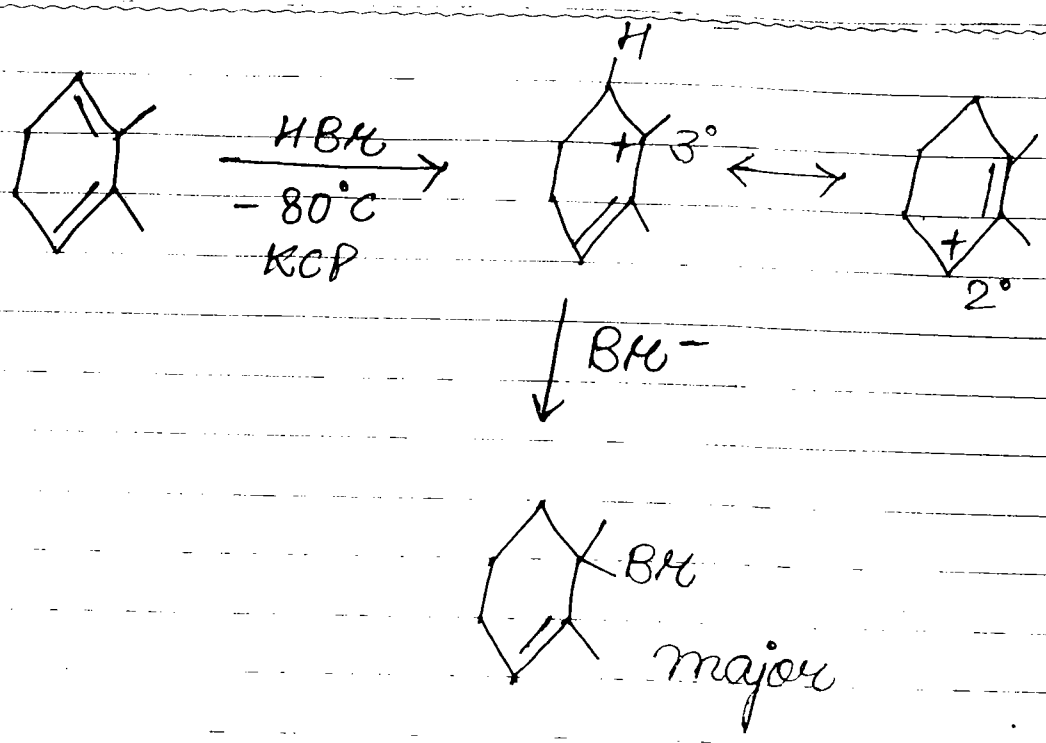
K.C.P / Kinetically control product
low Temp. → −80°C
Stable intermediate

T.C.P / ~~Tenon~~ Thermodynamic control Product
High Temp. → +40°C
Stable product

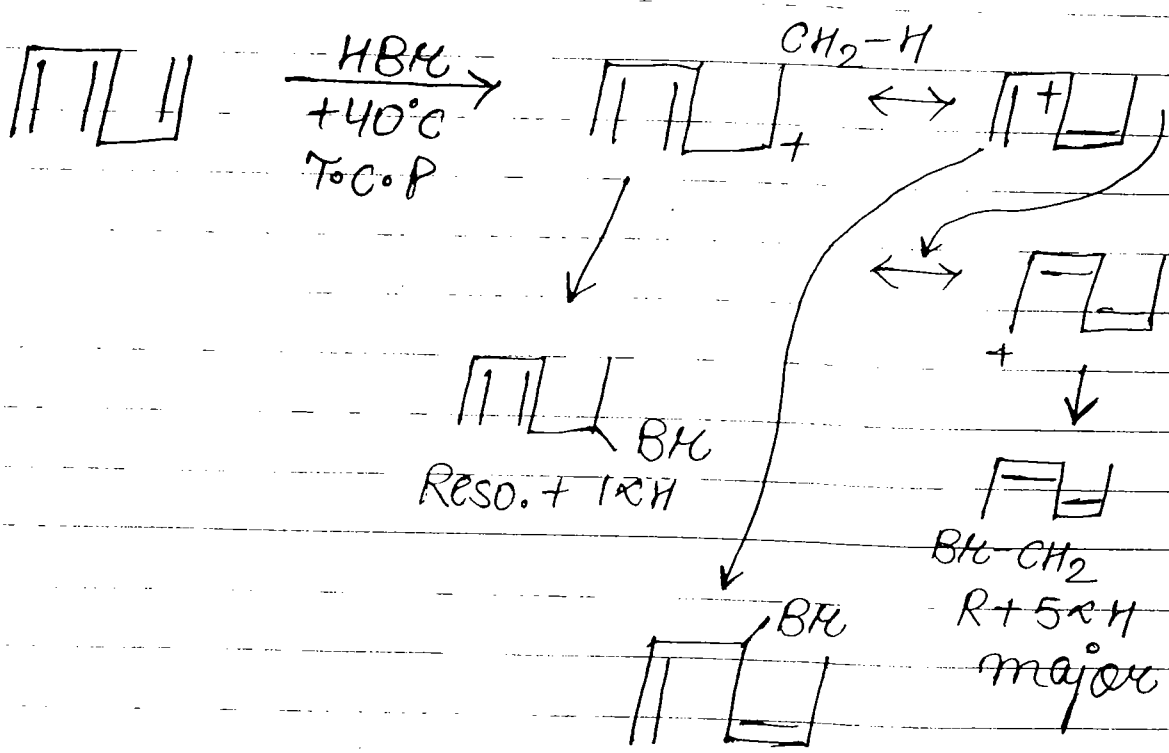
(1)



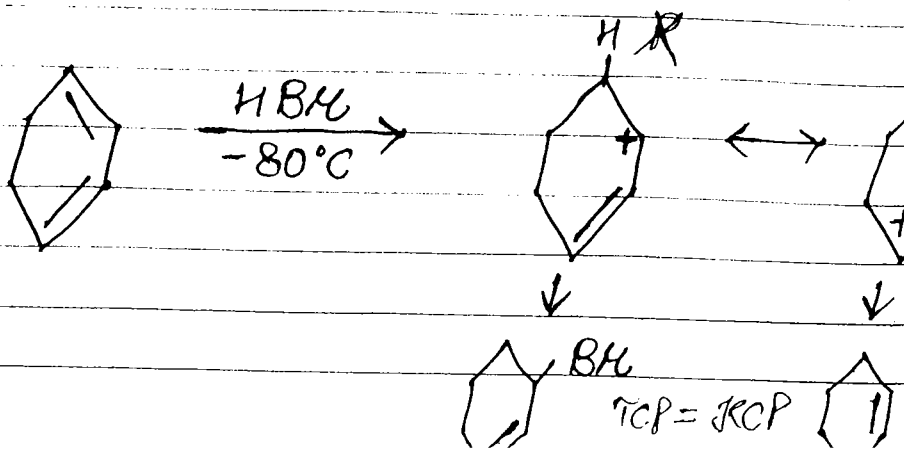
(2)


HBr
−80°C
KCP
H
3°
2°
Br⁻
Br
major

(3)


HBr
+40°C
T.C.P
CH₂−H
Br
Reso. + 1°H
Br
major
Br−CH₂
R + 5°H

(4)


HBr
−80°C
H
R
H
Br
T.C.P = K.C.P

→ Anti- Markownikoff / Kharash / Peroxide effect →

$$CH_3-CH=CH_2 \xrightarrow[R_2O_2/\Delta]{HBr/\text{anti}} CH_3-\underset{}{CH}(H)-CH_2(Br) \; (90\%) \; + \; CH_3-CH(Br)-CH_2(H) \; (10\%)$$

HBr/CCl4, Mark. → $CH_3-CH(Br)-CH_3$ 90% ; $CH_3-CH_2-CH_2Br$ 10%

Mechanism → Free radical chain reaˣ

$$R-\ddot{O}-\ddot{O}-R \xrightarrow{\Delta} R-\ddot{O}^{\bullet} \xrightarrow{HBr} R-O-H + Br^{\circ}$$

rep.

$R-\ddot{O}^{\bullet} \not\rightarrow R-\ddot{O}-Br + H^{\circ}$ (rep.)

Propagation →

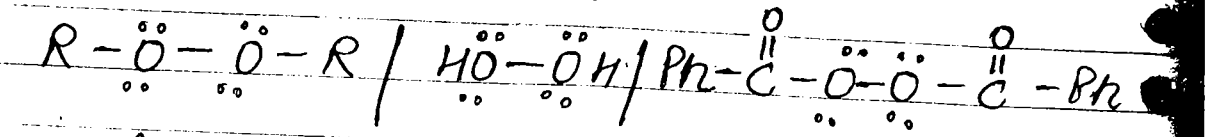
$$CH_3-CH=CH_2 + Br^{\circ} \longrightarrow CH_3-\overset{\circ}{C}H-CH_2Br \; (2°R^{\circ}) \; + \; CH_3-CH(Br)-\overset{\circ}{C}H_2 \; (1°R^{\circ})$$

2nd Step → $CH_3-\overset{\circ}{C}H-CH_2Br + H-Br \longrightarrow CH_3-CH(H)-CH_2Br + Br^{\circ}$

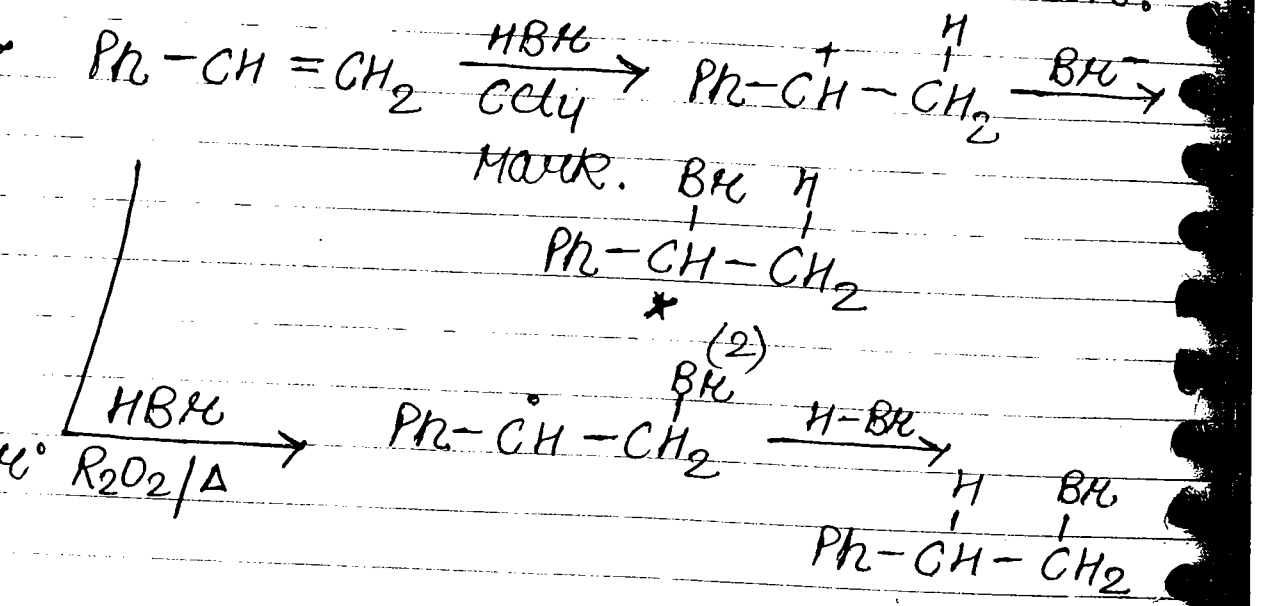
chain

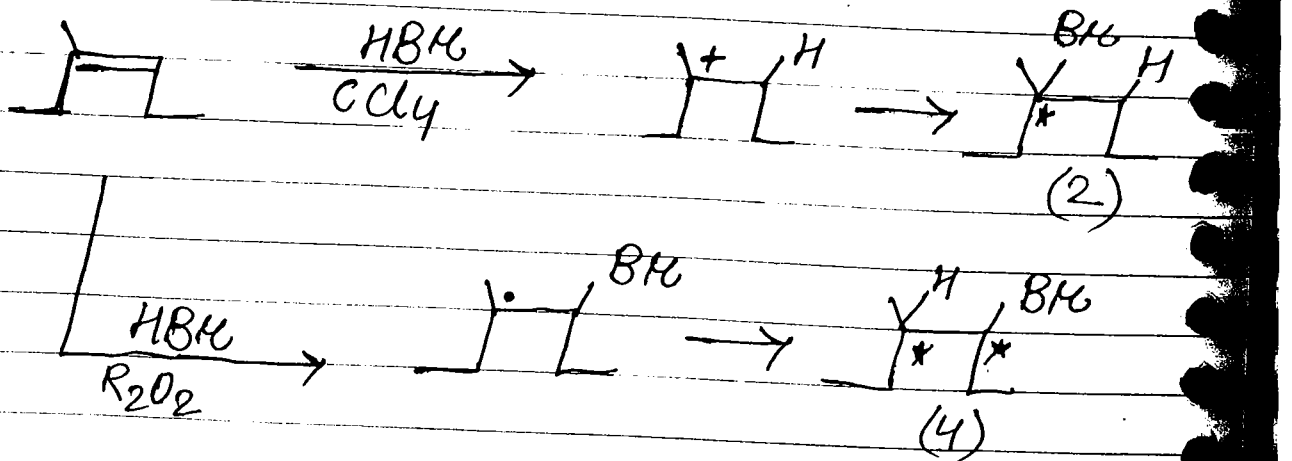
Some facts →

(1) In anti Mark. peroxide is required for the formation of radical.

eg. → 

(2) In anti Mark consider stable radical and in Mark. consider 1° cation.

eg. → 

(2) 

(3) For continuous chain rea.ˣ both propogation step must be exothermic.

(4) Anti Mark. rule is not applicable for HF, HCl and HI becoz one of the propagation step is endothermic.

Point → HI → 1^{st} step] endo.
HF, HCl → 2^{nd} 〃

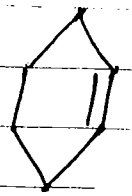
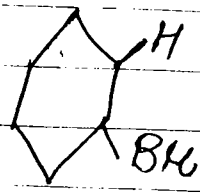
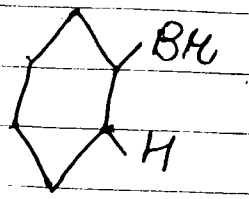
→ $CH_3-CH=CH_2 + F^\circ / Cl^\circ / Br^\circ / I^\circ \xrightarrow{2P\ 3P\ 4P\ 5P} CH_3-\overset{\circ}{C}H-CH_2(F/Cl/Br/I)$ (2P) — I ↓ weak endo

$CH_3-\overset{\circ}{C}H-CH_2(F/Cl/Br) +$ H–F (1S, 2P), H–Cl 3P, H–Br 4P] strong $\xrightarrow{endo}$

Eg. → $Ph-CH=CH_2 \xrightarrow[R_2O_2]{HBr} Ph-\overset{\circ}{C}H-CH_2Br \longrightarrow Ph-CH(H)-CH_2Br$

$\xrightarrow[H_2O_2]{HCl\ (H^+)}$ Mark. $Ph-\overset{+}{C}H-CH_2(H) \longrightarrow Ph-CH(Cl)-CH_2(H)$

(5) Symmetrical alkene, symm. alkyne and vinyl halide give identical product either by Mark. or by anti Mark.

eg. →  $\xrightarrow[HBr/R_2O_2]{HBr/CCl_4}$  = 

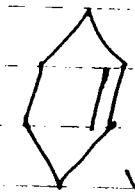
(2) $HC \equiv CH \longrightarrow HC=CH = HC=CH$

(3) $CH_2=CH-Cl \xrightarrow{HBr} CH_2-\overset{+}{C}H+\ddot{Cl}: \longrightarrow CH_2-CH-Cl$

$\xrightarrow[R_2O_2]{HBr}$ $CH_2-\dot{C}H-\ddot{Cl}: + \dot{C}H_2-CH-Cl$ (resonance)

stable

Hint

 $HC \equiv CH$ $CH_2=CH-Cl$

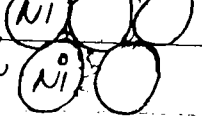
Same Product either by Mark. or anti Mark.

Hydrogenation / catalytic Reduction

$CH_2=CH_2 \xrightarrow[T,P]{Ni/Pd/Pt+H_2} CH_2-CH_2-HOH$

Mech.ⁿ → (1) $CH_2=CH_2$ collision

(2) H-H H-H

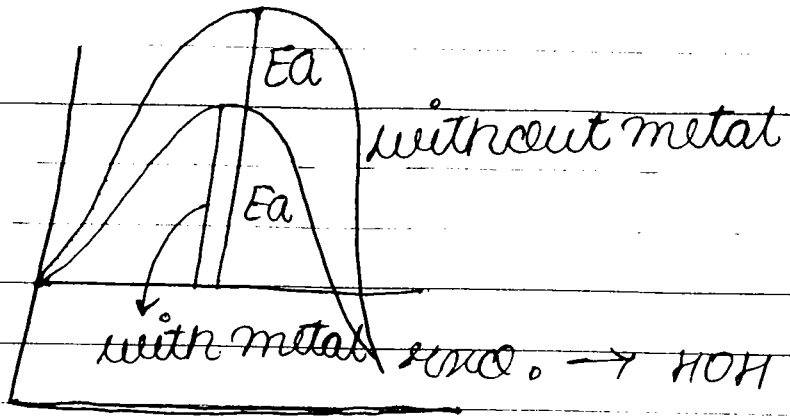
Solid 

↑ syn-add → same

$CH_2=CH_2$

Br / Br

H — H



(1) Hydrogenation is a exo. process and released energy is known as HOH

(1) more π bond ∝ HOH
HOH ∝ unstability
HOH ∝ less steric (for metal)

(2) Hydrogenation is a heterogenous mix.

Heterogenous → gas + solid

exception → Homogenous → wilkinson catalysts $(Ph_3P)_3$

(3) Hydro. is a syn-add because both bond formation from same-side.

(4) Metal behave as a catalysts because it reduce activation energy by providing surface for collision.

(5) Hydro. is a stereo specific rea.*.

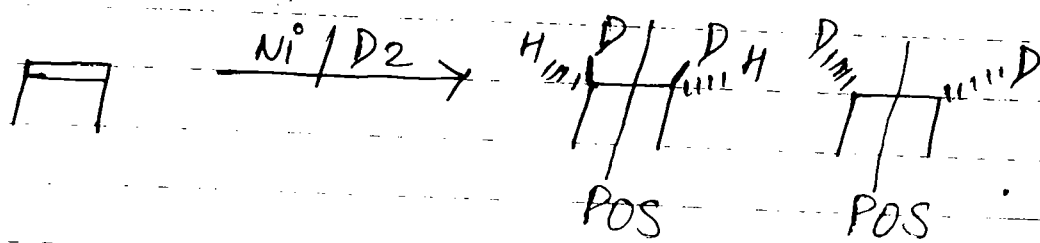
Stereo specific → Cis ⊄ Syn Erythro

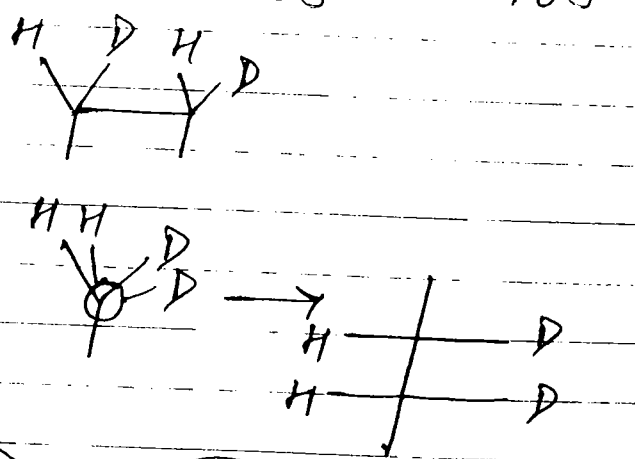
Trans ⊄ Syn Threo

for given only

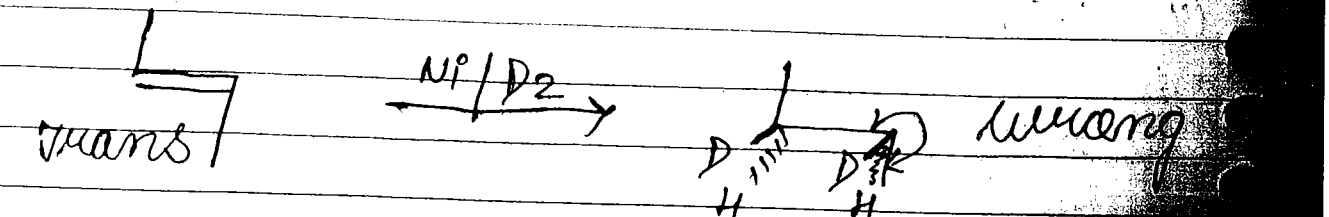
cis —Syn→ erythro

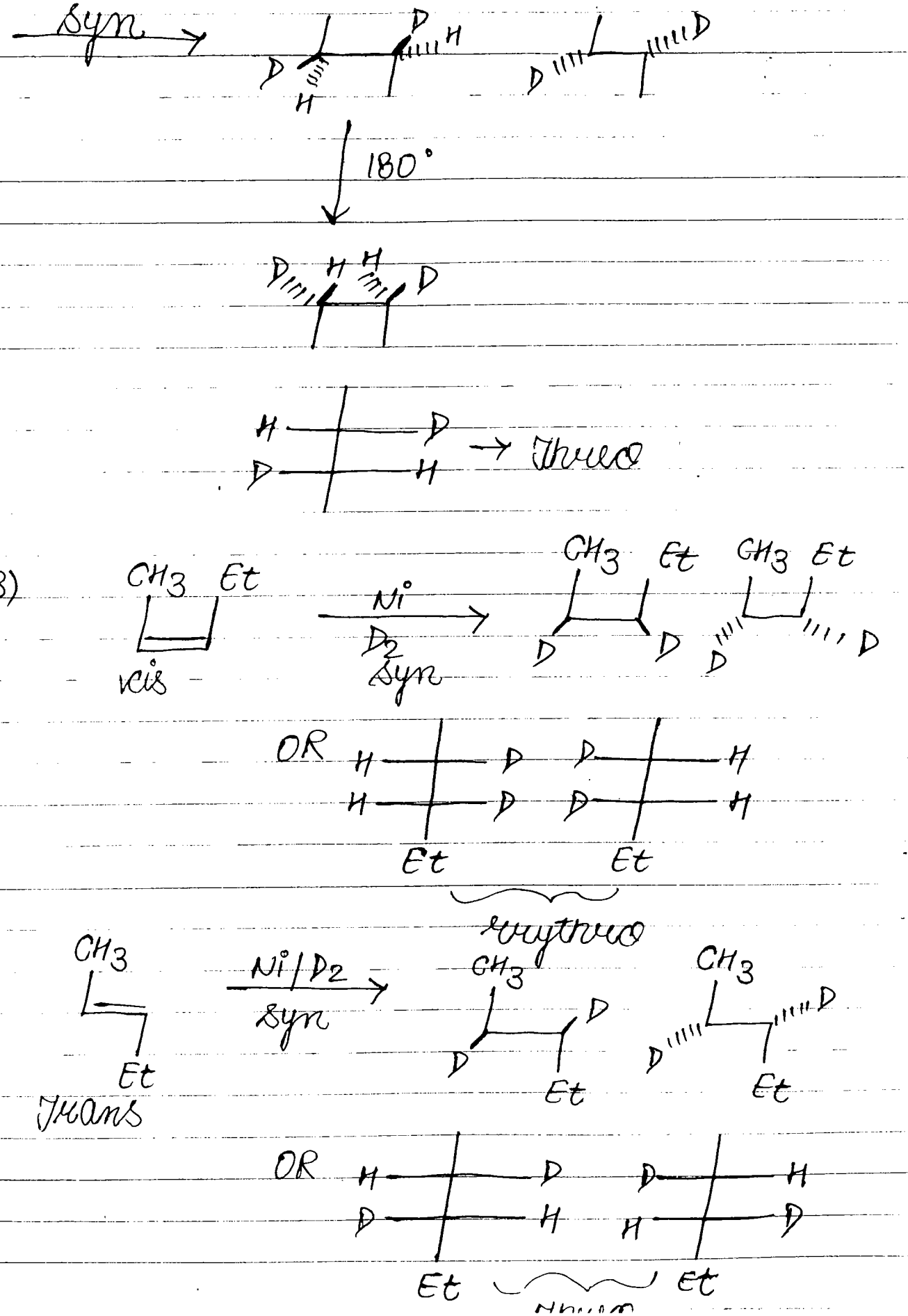
Trans —Syn→ Threo

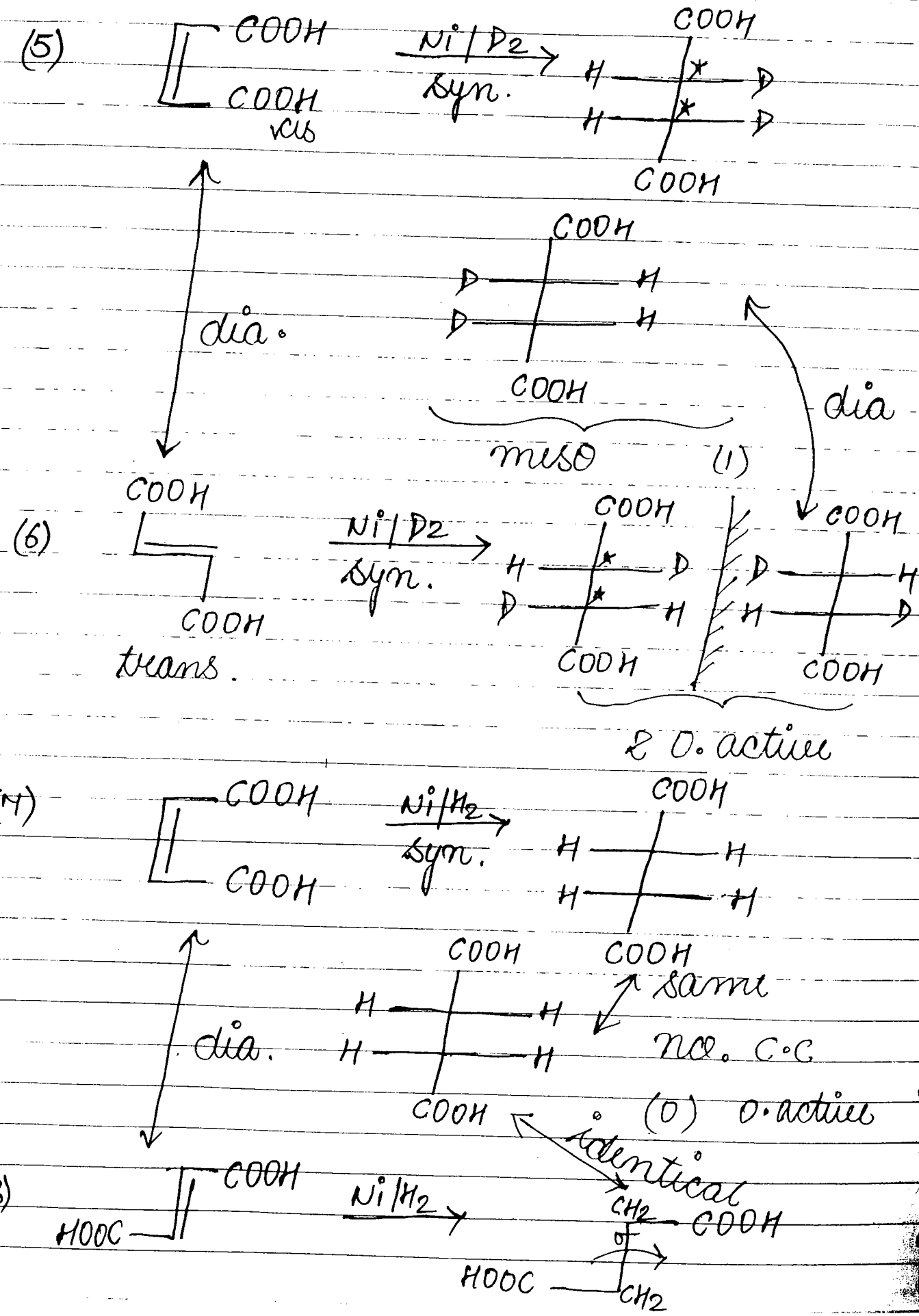
(1) 

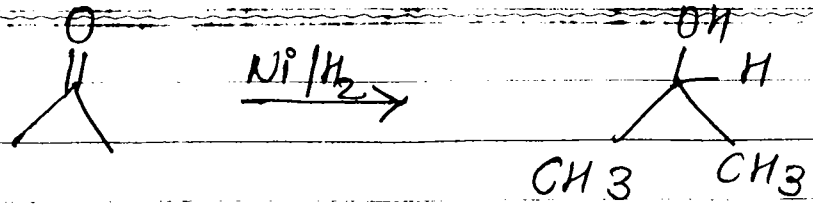


(1) Identical

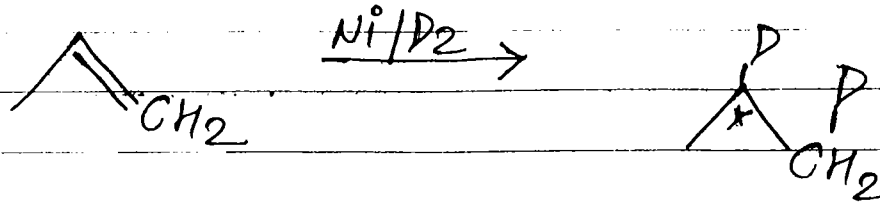
(2) 


Syn
180°
Threo
(3)
CH3 Et
cis
Ni
D2
Syn
OR
Et
Et
erythro
(4)
CH3
Et
trans
Ni/D2
Syn
OR
Et
Et

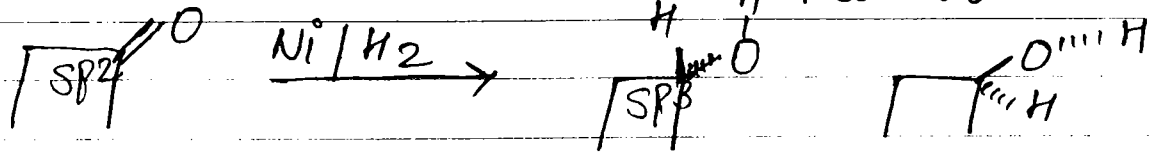

(5)
COOH
COOH
cis
Ni | D2
Syn.
COOH
H
H
D
D
COOH
dia.
COOH
D
D
H
H
COOH
meso
(1)
dia
(6)
COOH
COOH
trans.
Ni | D2
Syn.
COOH
H
D
D
H
COOH
COOH
D
H
H
D
COOH
2 O. active
(7)
COOH
COOH
Ni | H2
Syn.
COOH
H
H
H
H
COOH
dia.
COOH
H
H
H
H
COOH
same
no. C.C
(0) O. active
identical
(8)
COOH
HOOC
Ni | H2
CH2
COOH
HOOC
CH2

(9) 

(1)

(10) 

(2) R ⇄ S isomer

(11) 

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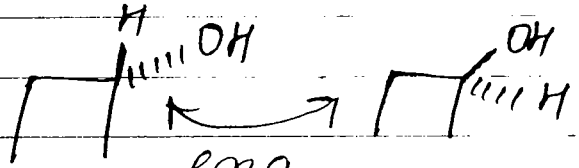
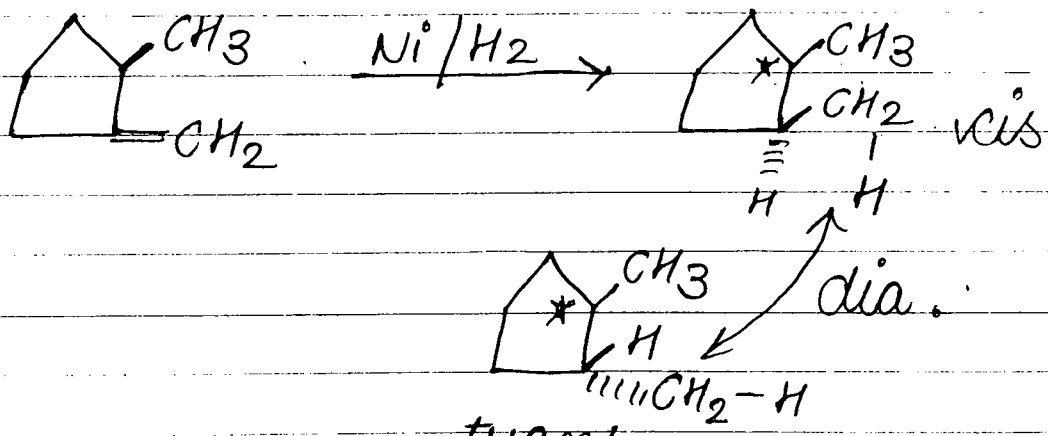
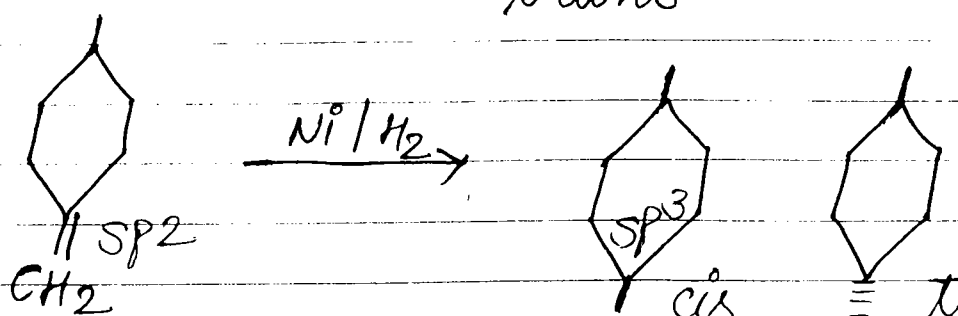


ena.

(12) 

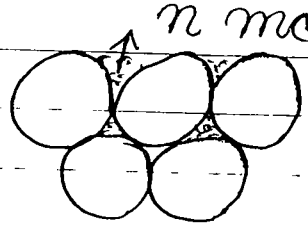
trans

(13) 

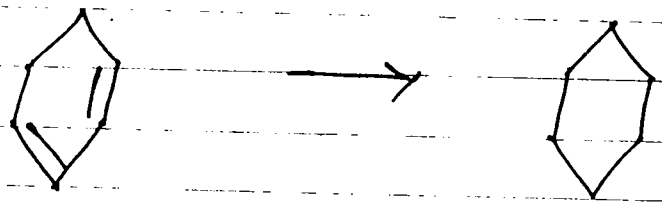
OI ✗
GI (Ring)
dia.

→ In catalytic hydrogenation mole concept can not follow bcoz no. of H_2 are available in void.

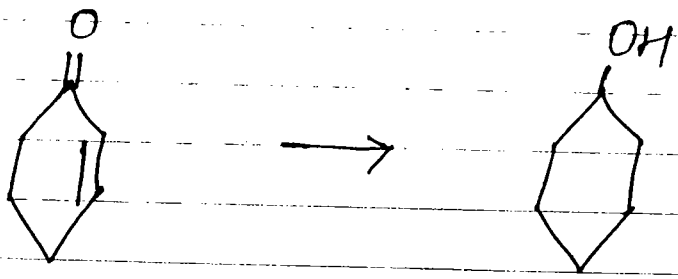
(1) $R-C\equiv C-R \xrightarrow{Ni+H_2\ 25^\circ C} R-CH_2-CH_2-R$



(2)

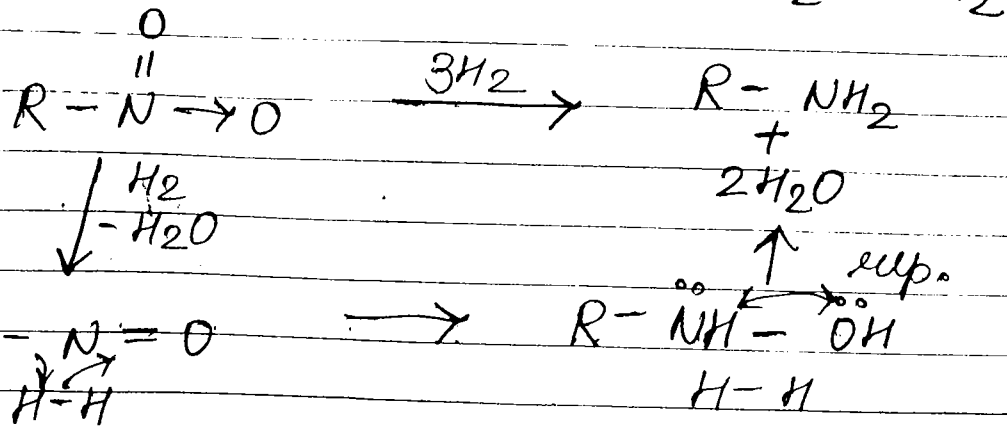


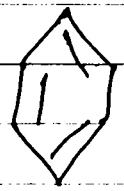
(3)



(4) $R-C\equiv N \longrightarrow R-CH_2-NH_2$

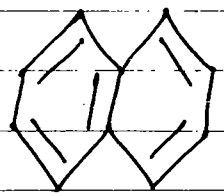
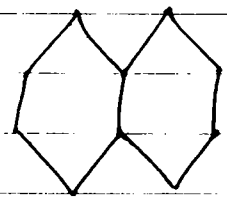
(5)



(6)  $\xrightarrow[25^\circ C]{Ni/H_2}$

$\xrightarrow[(100^\circ C)]{Ni/H_2}$ 

(7)  $\xrightarrow[120^\circ C]{Ni/H_2}$ 

(8)  $\xrightarrow[200^\circ C]{Ni/H_2}$ 

(9) $R-\overset{\overset{O}{\uparrow}}{C}-OR$

(10) $R-\overset{\overset{O}{\uparrow}}{C}-OH$

(11) $R-\overset{\overset{O}{\uparrow}}{C}-NH_2$

$\xrightarrow[25^\circ C]{Ni/H_2}$ NO. Rea.^{x}

→ In Lindlaar catalysts only one mole H_2 is available for reduction bcoz. surface area of metal is reduced by $BaSO_4$

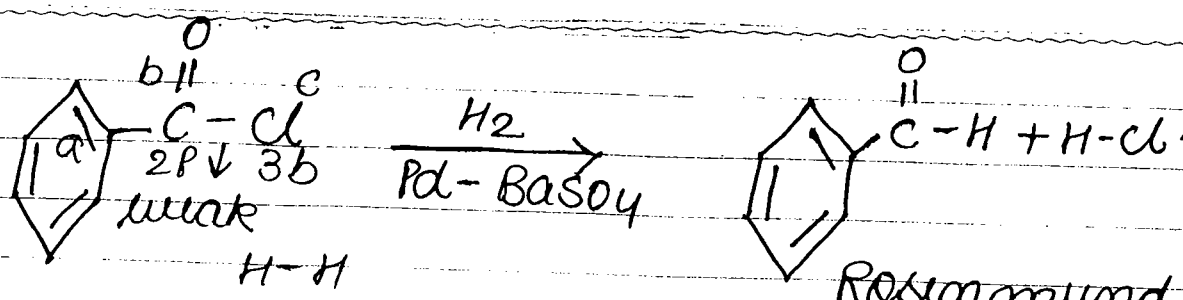
(1) $R-C\equiv C-R \xrightarrow[Pd-BaSO_4]{H_2\ (1\ mole)} \underset{\text{cis}}{R-\underset{H}{C}=\underset{H}{C}-R}$

$H-H$

$H:H$

Syn

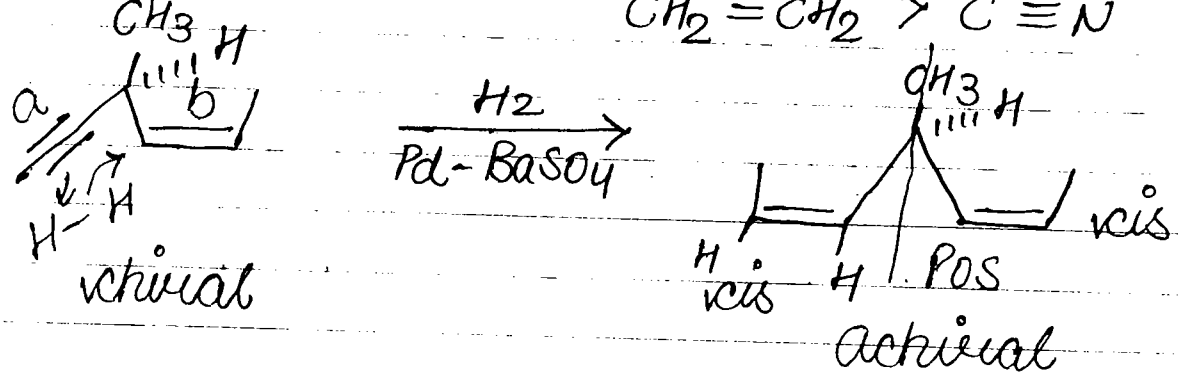
(1)



1 mole → Reactivity order

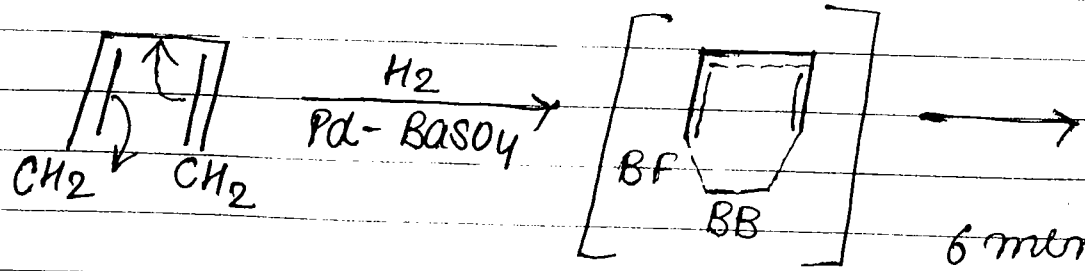
$$C-Cl > -C\equiv CH > -CH=O > CH_2=CH_2 > C\equiv N$$

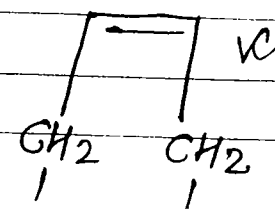
(2)



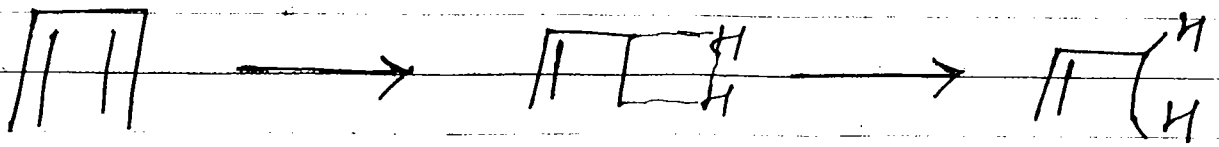
→ In conjugated ~~diene~~ di-ene system 1-4 addition take place with lindlaar catalysts bcoz 6-membered cyclic transition state are more stable than 4 mem. cyclic transition state.

(1)





OR



4 mem. CTS 1,2.

Different Reagent →

(1) $Ni - Al + H_2 \longrightarrow$ Sabatier - Sandurson

(2) $Ni_2B + H_2 \longrightarrow$ P-2 catalysts

(3) $PtO_2 + H_2 \longrightarrow$ Adam catalysts

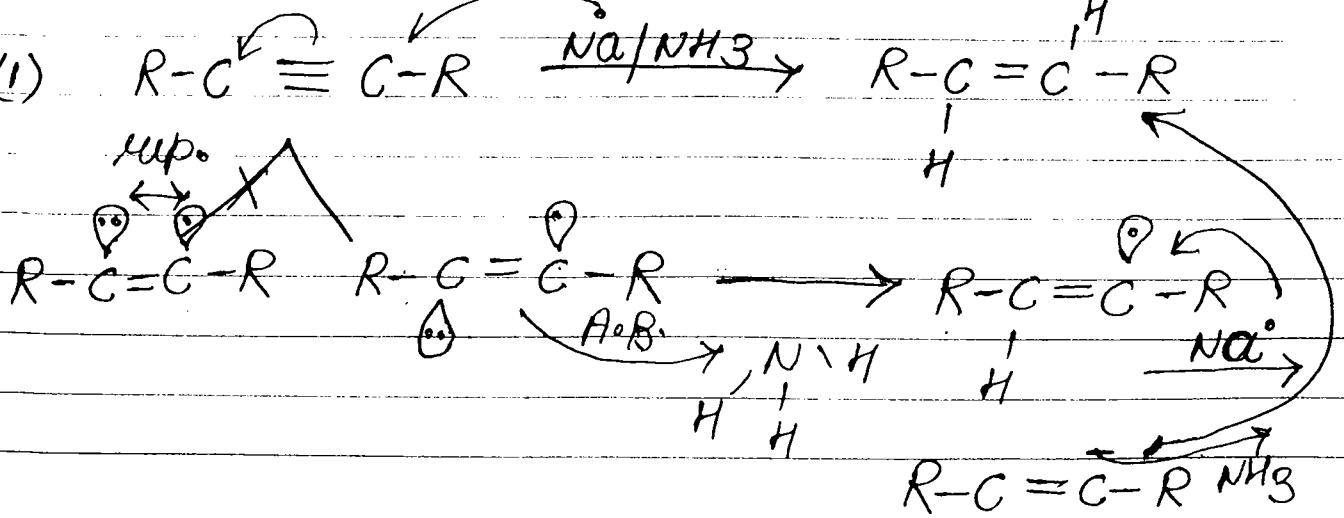
(4) ~~$(PPh_3)_3 RhCl$~~ $(PPh_3P)_3 RbCl \longrightarrow$ Wilkinson

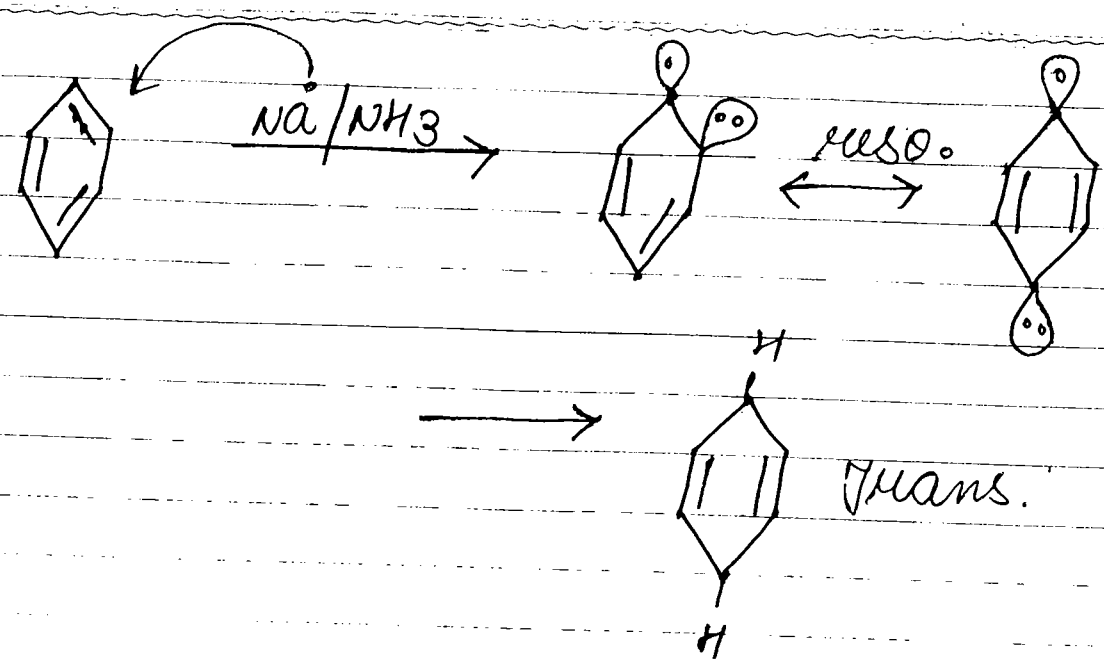
(5) $Na + C_2H_5OH \longrightarrow$ B.B. reduction

(6) $Na + NH_3 \longrightarrow$ Birch reduction

→ In Birch reduction internal alkyne interconvert into trans alkene and benzene interconvert into 1,4 addition due to less e⁻ - e⁻ rep.

(1) $R-C \equiv C-R \xrightarrow{Na/NH_3} R-C(H)=C(H)-R$

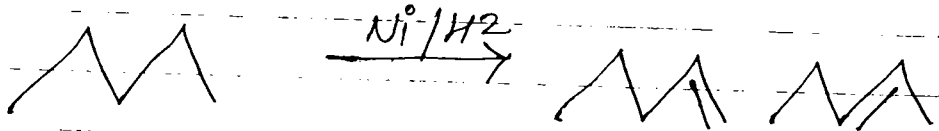


(2) 

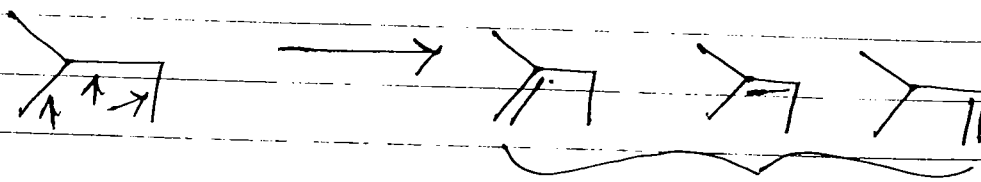
trans.

1,4 add.

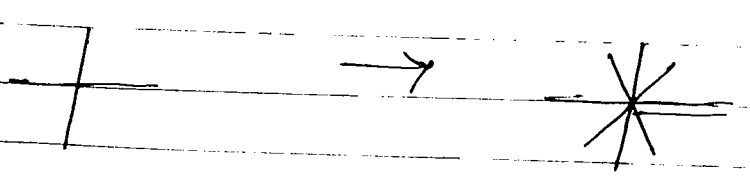
Q1. no. of alkene →

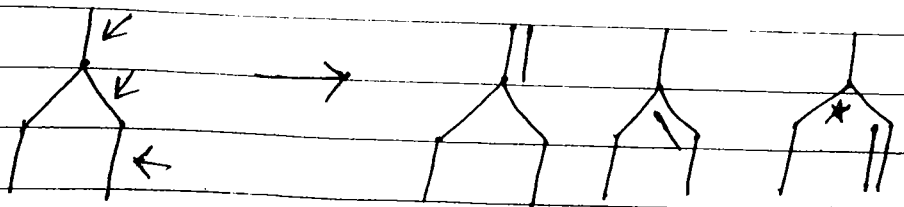
(1) 

(1) (2) G.O.I.

(2) 

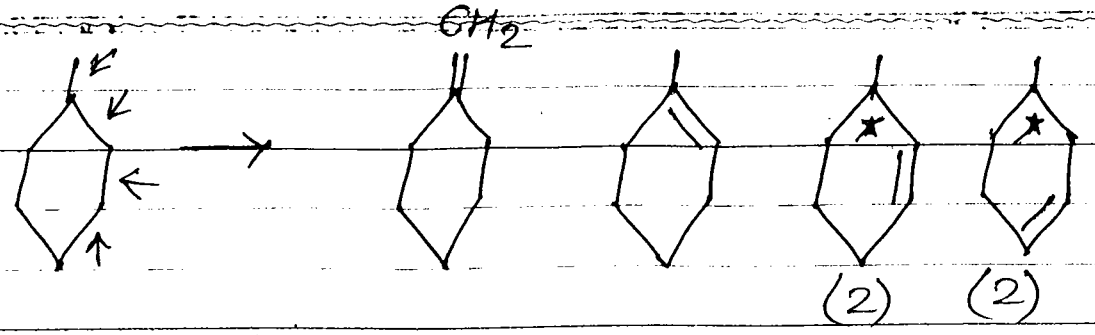
(3) G.O.I.

(3) 

(4) 

(2) G.O.I. (2) O.I.

(5) Ans.

(5) 

G.C. → 6 mem.

Types of cation →

(A) classical cation / C.C →

$$CH_3-CH=CH_2 \xrightarrow[\text{Mark.}]{H^+/D^+/T^+} CH_3-\overset{H/D/T}{\overset{|}{C}}H-CH_2$$

localized

(B) non-classical cation / N.C.C →
(cation + lone pair)

$$CH_3-CH=CH_2 + :\ddot{B}\ddot{r}^+ \longrightarrow$$

$$CH_3-\overset{2^\circ}{\overset{+}{C}}H_2-CH_2 \longleftrightarrow CH_3-\overset{2^\circ}{\underset{+}{C}}H-CH_2 \longleftrightarrow CH_3-\underset{+}{\overset{1^\circ}{C}}H_2-CH_2$$

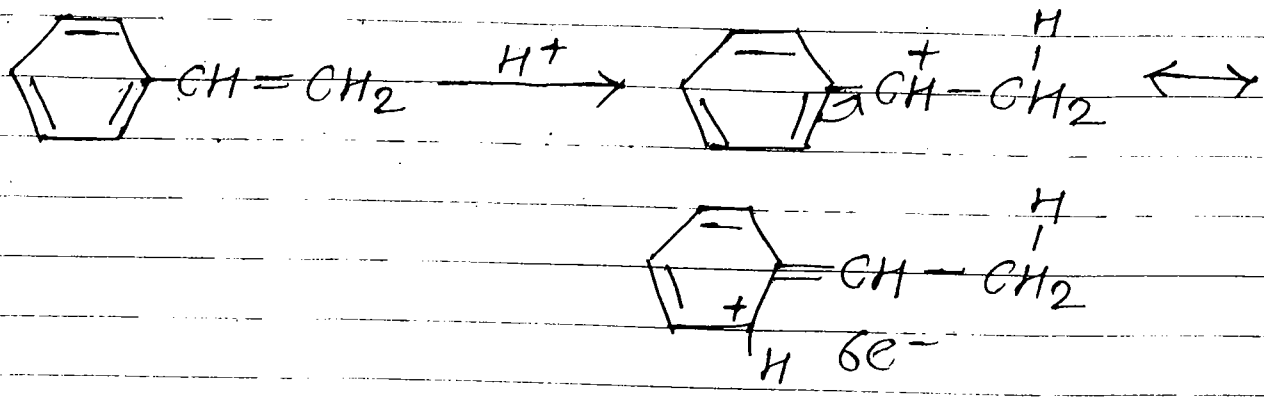
$$CH_3-CH_2-CH_2 \longleftrightarrow CH_3-CH-CH_2 \longleftrightarrow CH_3-CH-CH_2$$

$$CH_3-\overset{+S}{C}H-\overset{+S}{C}H_2 \quad (\text{less bulky}) \rightarrow$$

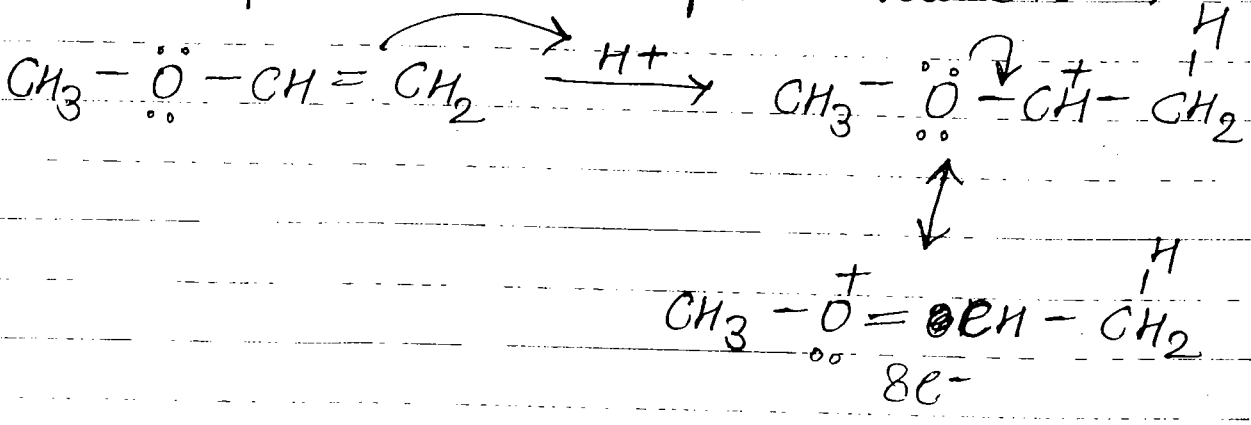
λ_1 > λ_2

weak bond

(C) Resonance stable cation →



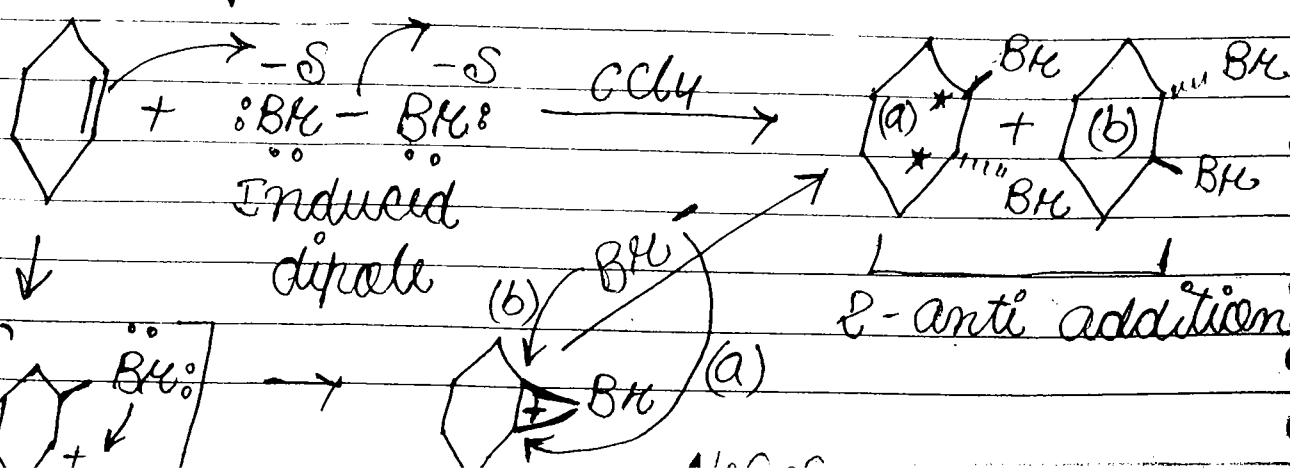
(D) OCC | octate complete cation →

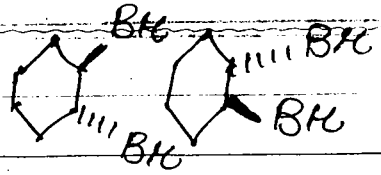


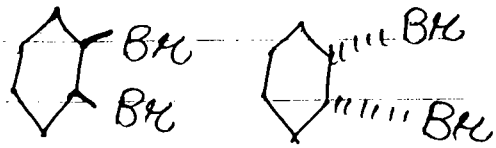
OCC > RSC > NCC > CC

8e⁻ Reso. Reso. + angle strain Loca.

Halogenation →

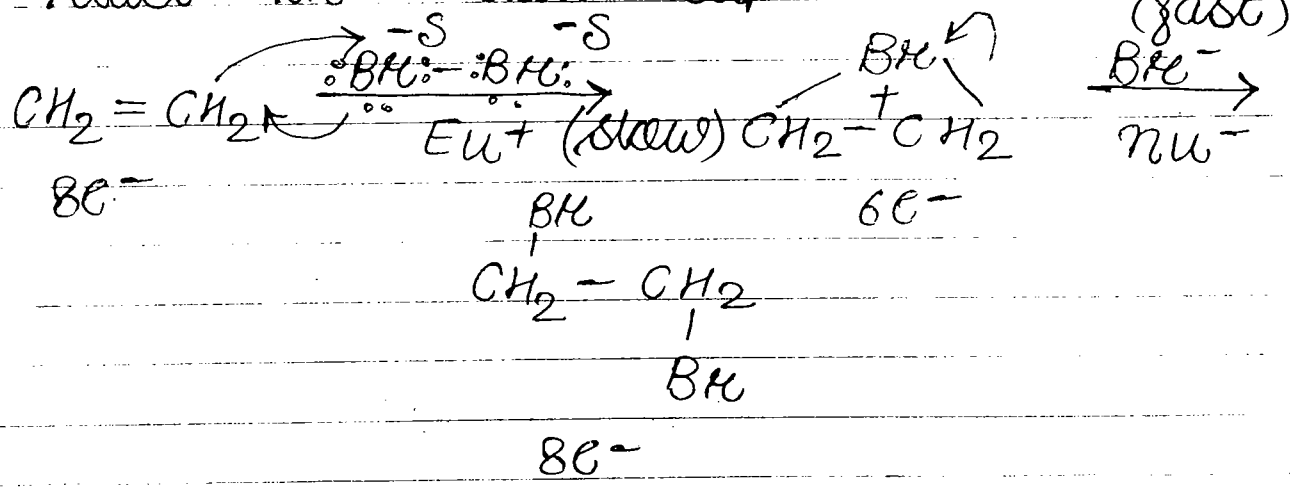


$(2)^2 = 4$ → 2 anti ✓ 

→ 2 syn ✗ 

(1) Halogenation is a anti-addition beca^z formation of N.C.C. OR cyclic bromonium ion (CBI)

(2) Its a electrophilic add. beca^z electrophile react in slow step.



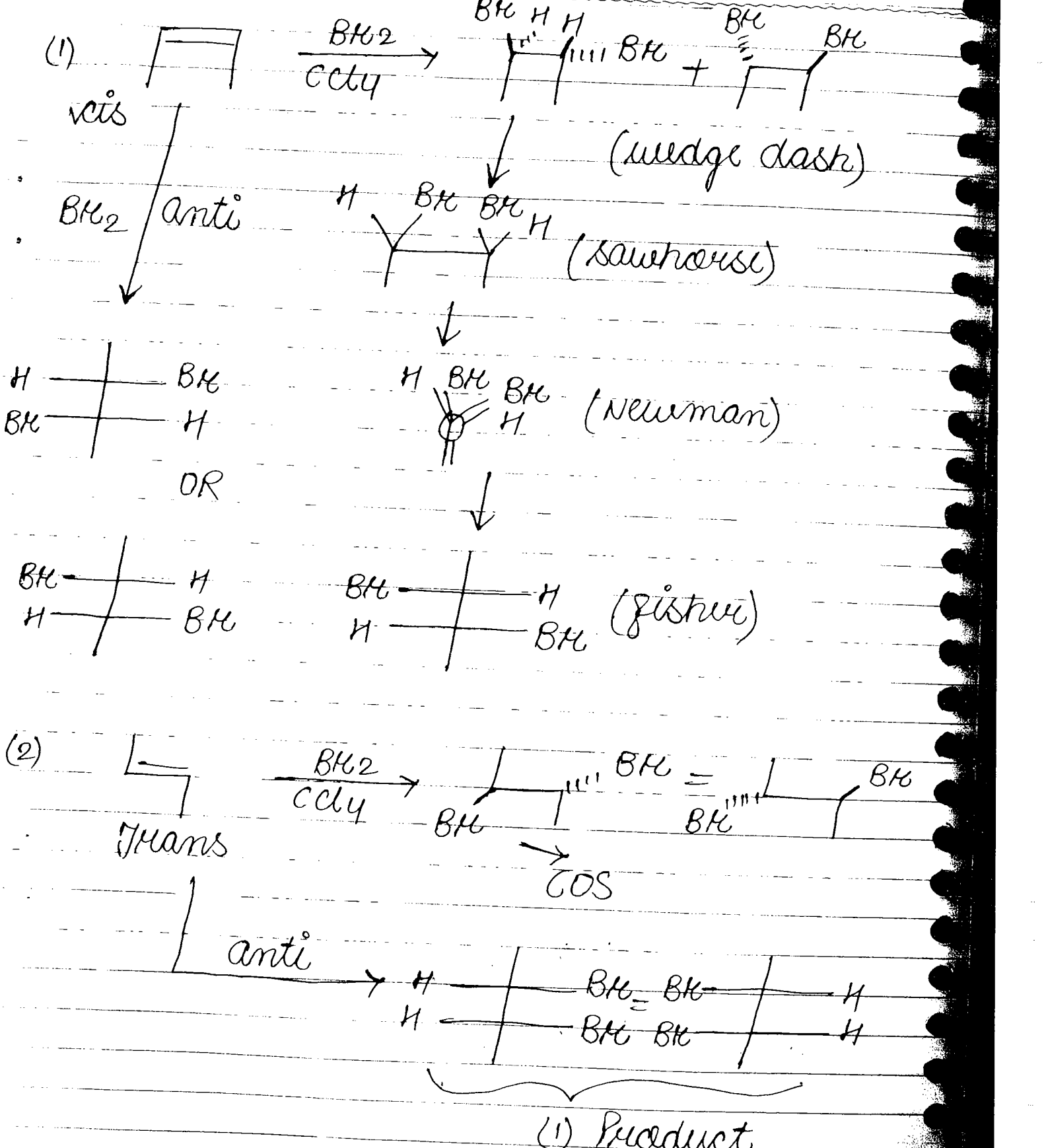
(3) Its a stereo spicific rea.^{x}

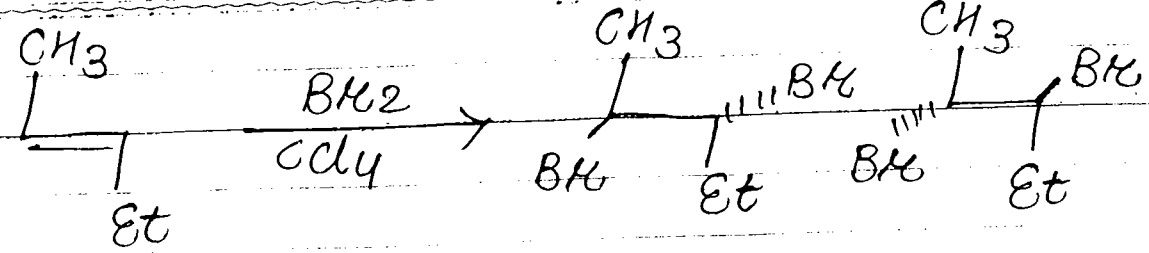
cis $\xrightarrow{anti}$ Threo Cis Anti Threo

Trans $\xrightarrow{anti}$ Erythro Trans Anti Erythro

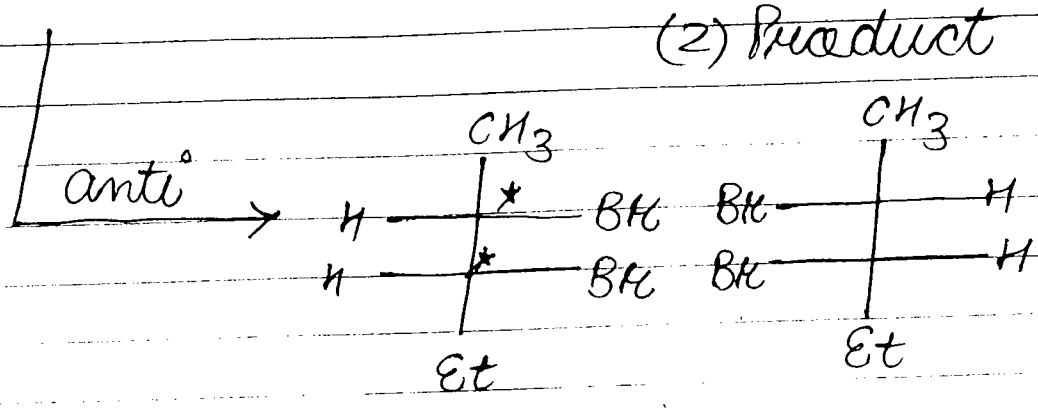
↓

gave pure only

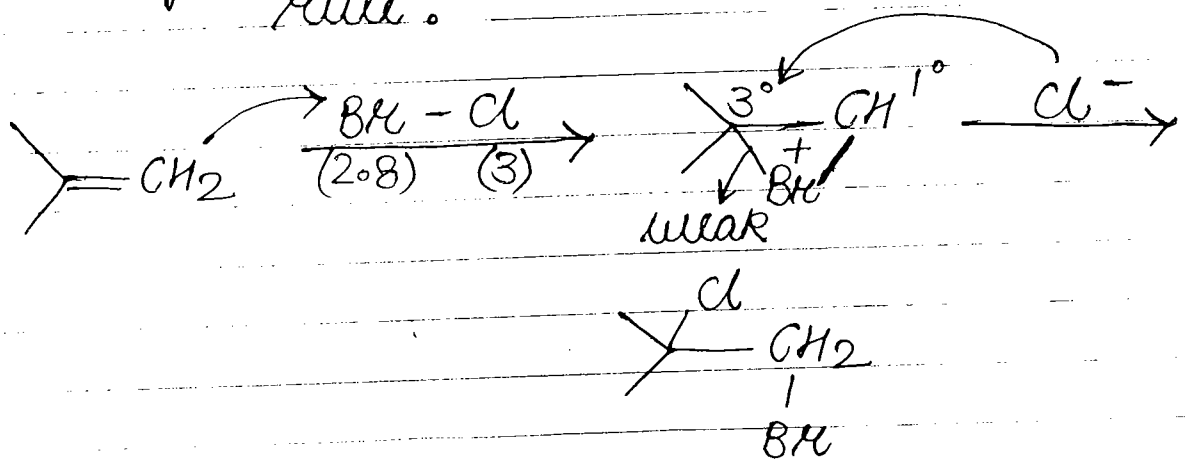

(1)
BH2
CCl4
cis
anti
BH2
(wedge dash)
(sawhorse)
(Newman)
OR
(just like)
(2)
BH2
CCl4
Trans
anti
(1) Product

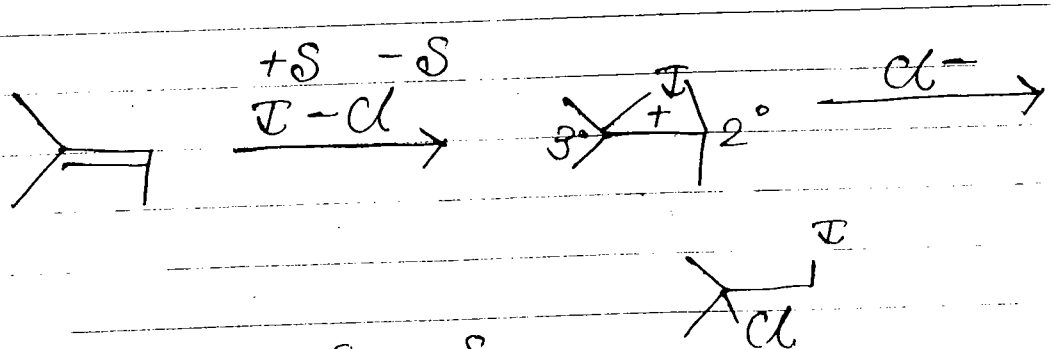
(3) 

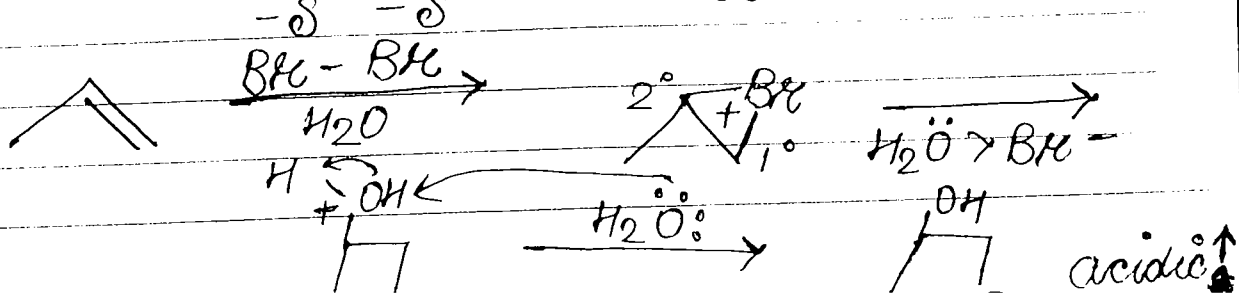
(2) Product



→ Halogenation follows adv. mark. rule.

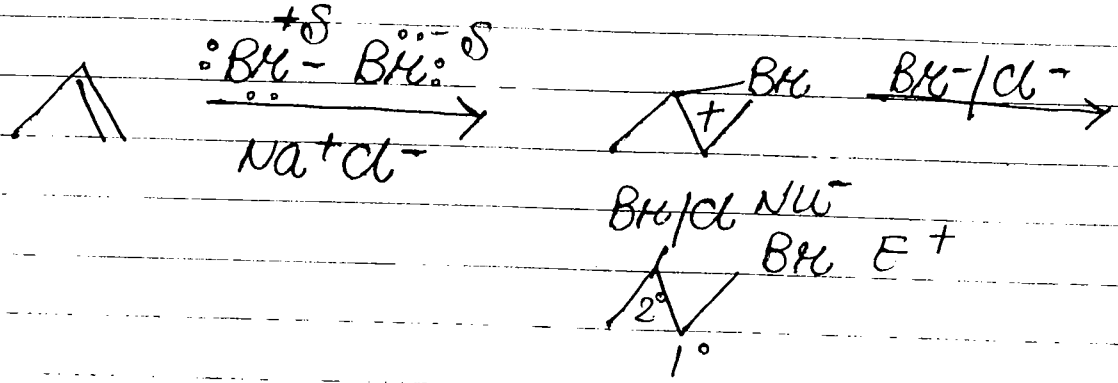
(1) 

(2) 

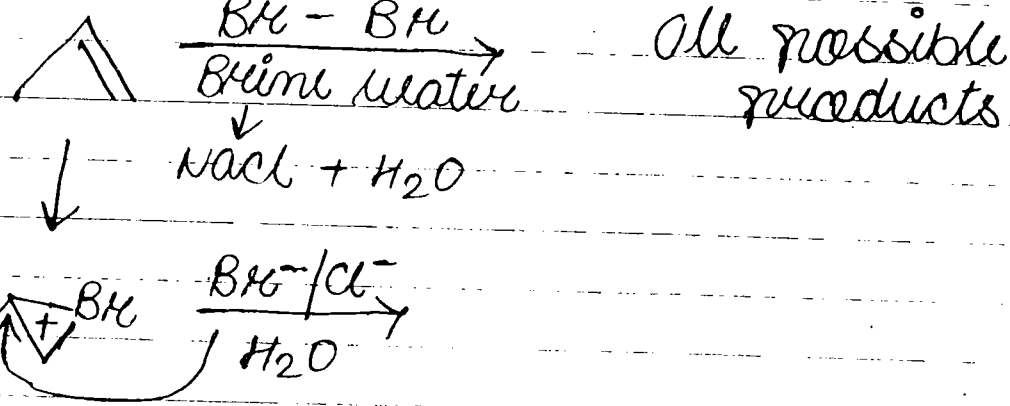
(3) 

→ In unsymm. alkene electrophile attach to less steric carbon.

(1)



(2)



All possible products

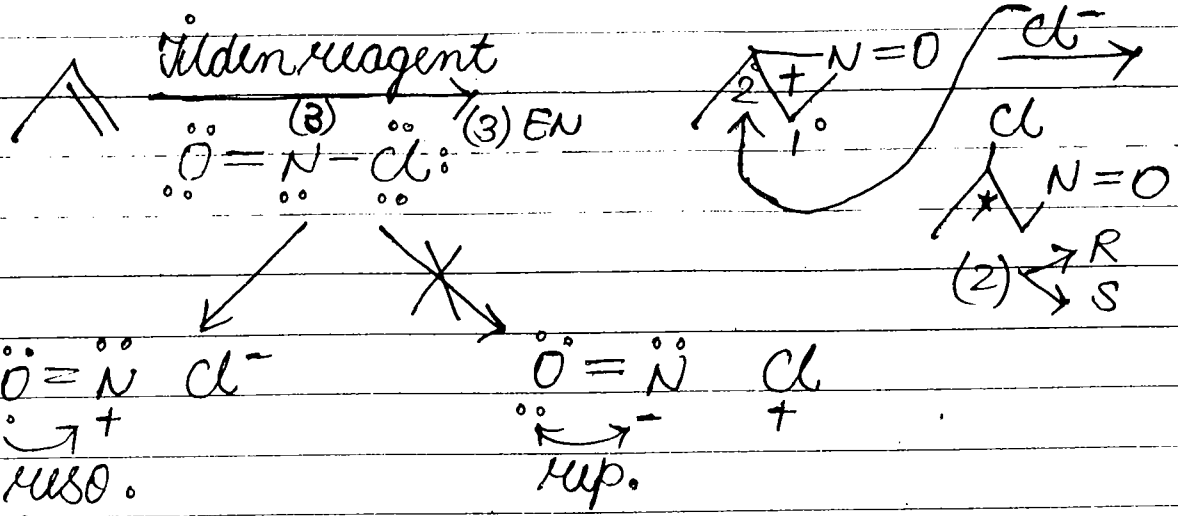
(A) BH, BH (B) BH, OH (C) OH, BH

(D) Cl, BH (E) BH, Cl (F) OH, OH

(3) (A) + (B) —(C)→ OH, BH (2° / 1° (E+))

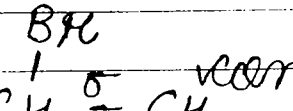
(A) → ; (B) → BH_2 ; (C) → H_2O

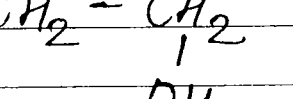
retro synthesis

(4) 

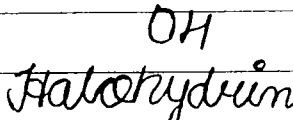
(cation with lone Pair → non classical)

→ Bromine - water is a unsaturation test for alkene, alkyne bcoz its reddish - brown colour after rea.* decolorised

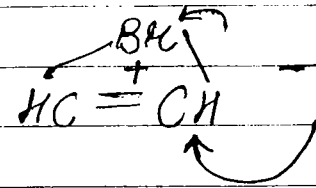
(1) $CH_2 = CH_2 \xrightarrow[\text{reddish-brown}]{Br_2 / H_2O}$  conformation

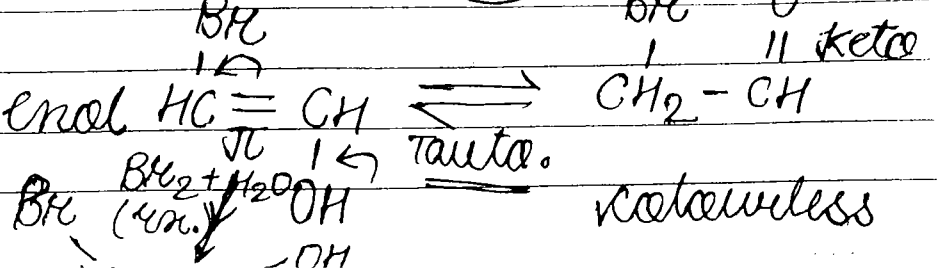


Halohydrin OR



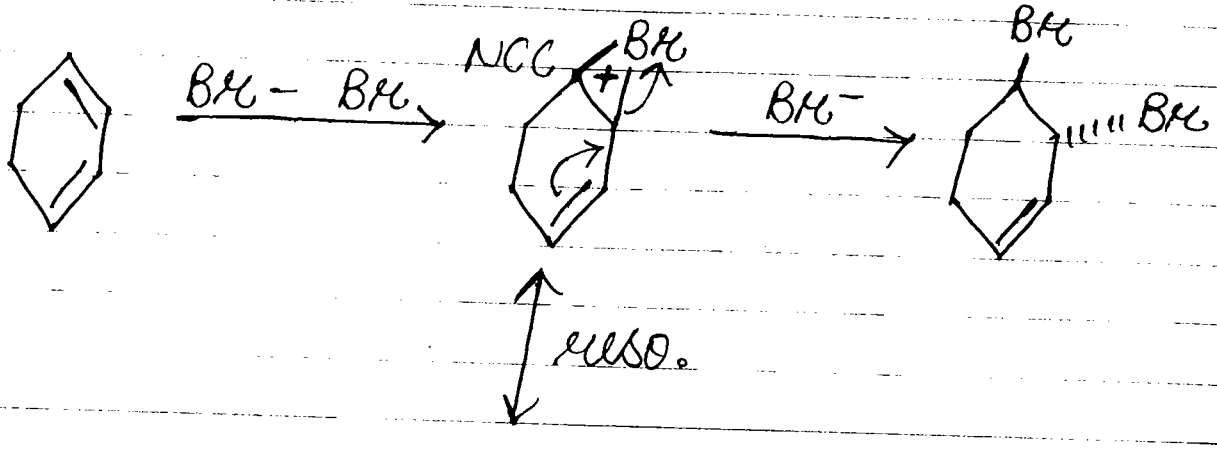
colourless

(2) $HC \equiv CH \xrightarrow[H_2O]{Br-Br}$  $\xrightarrow{-H_2O}$



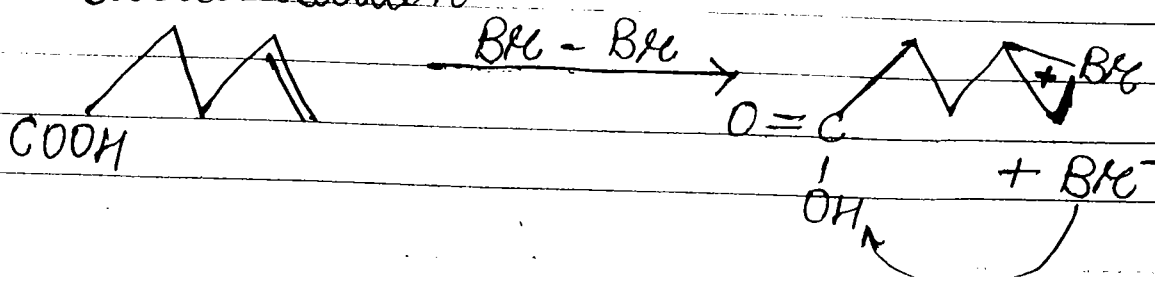
→ conjugate system show syn and anti both type of add. becoz it interconvert into resd. stable cation.

(1)

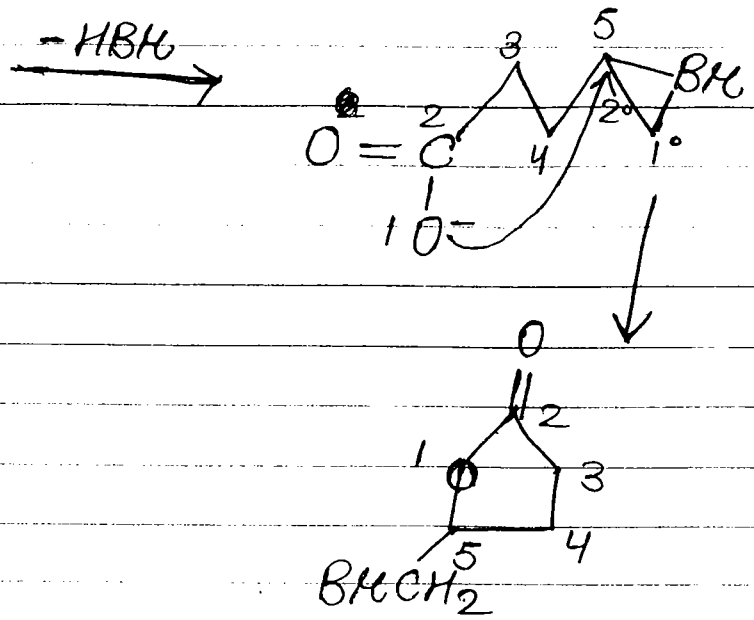


→ If compound is having internal ~~nucleophile~~ nucleophile then ~~cyclisation~~ cyclisation possible.

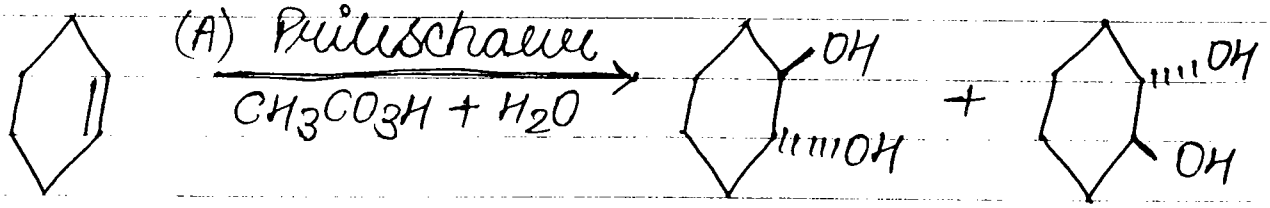
(1) Lactonisation



cyclic amide → lactum



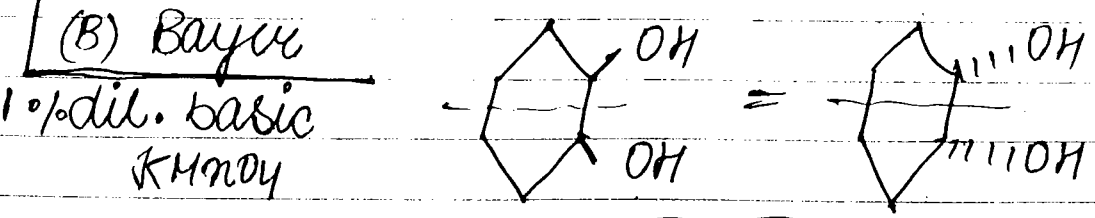
Hydroxylation → Vicinal diol formation



anti add.

↓

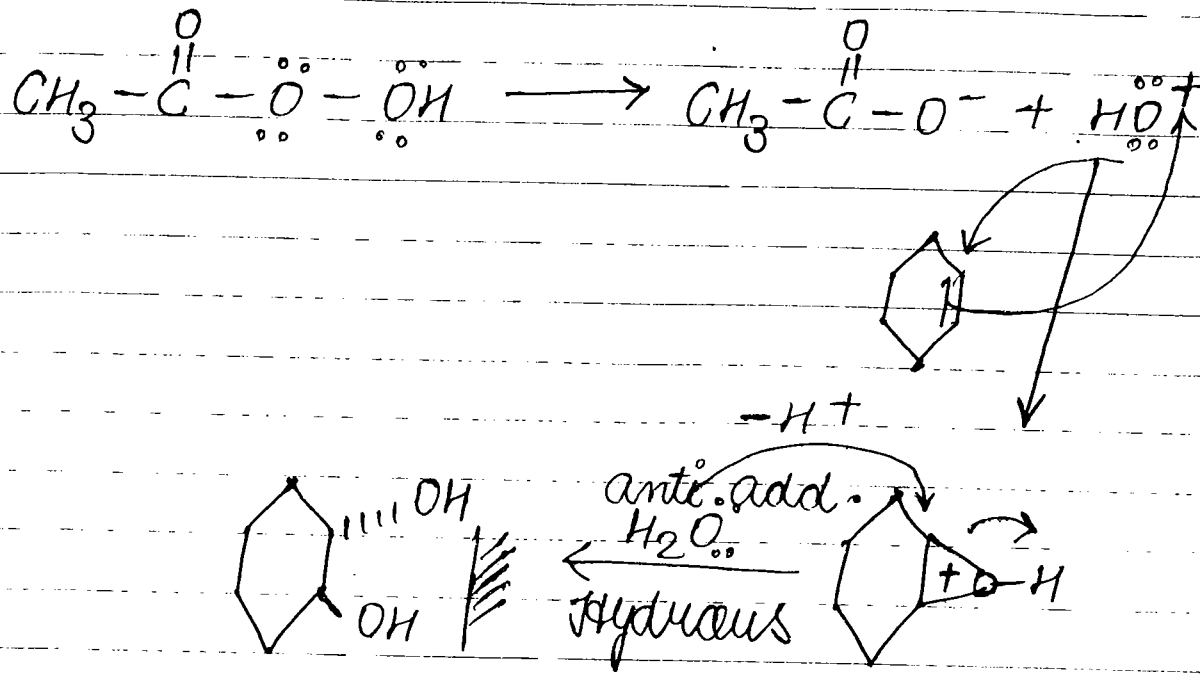
Chiral, optically inactive due to racemic mix.



syn add.

Achiral → optically inactive

Mechⁿ. →



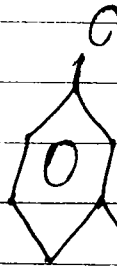
→ In Prileschaeu rea.ˣ diff. peroxyide can be used.

$CH_3-\overset{O}{\overset{\|}{C}}-O-OH$ / Peroxy acetic acid / PAA

Ph-CO_3H / Peroxy benzoic acid / PBA

H_2O_2 / H.P.

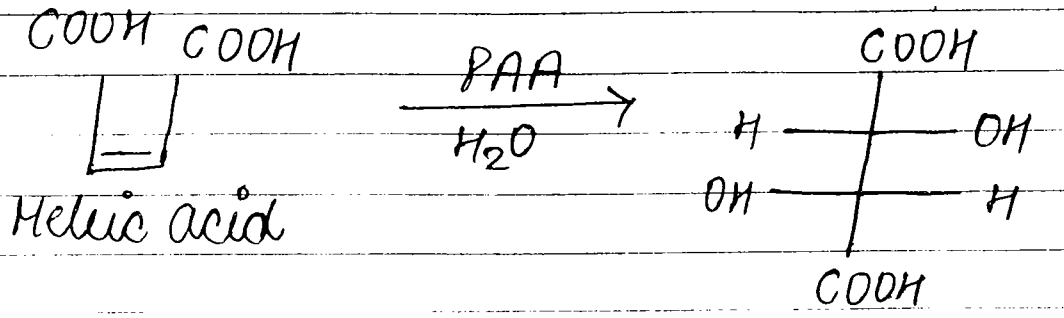
H_2SO_5 / caro acid



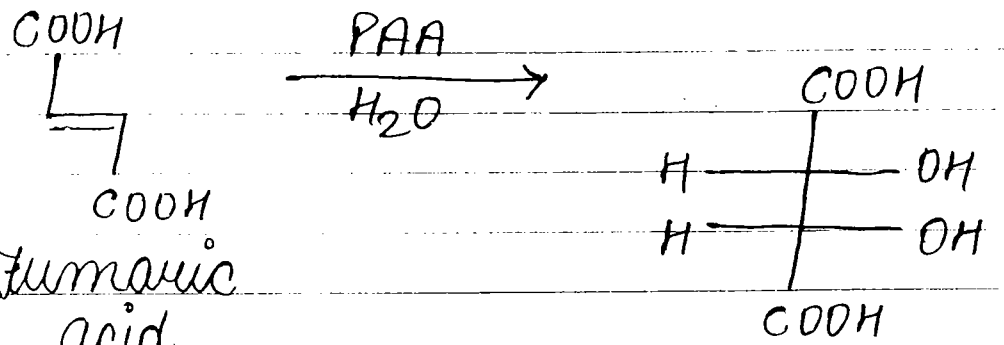
/ meta chloro PBA

→ Its a anti add. it means

CAT and TAE



Melic acid

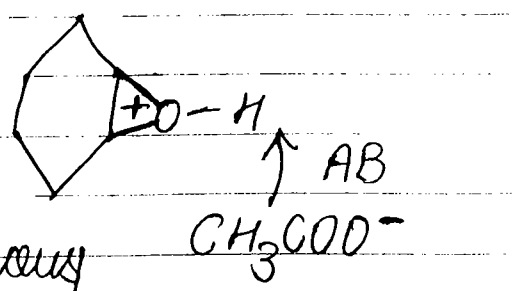


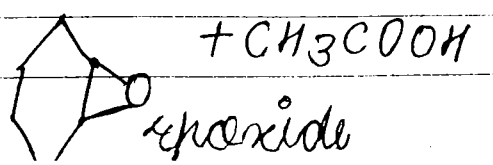
Fumaric acid

Meso tartaric

→ In presence of water (Hydrous) anti add. take place but in unhydrous condition cyclic ether (epoxide) take place.

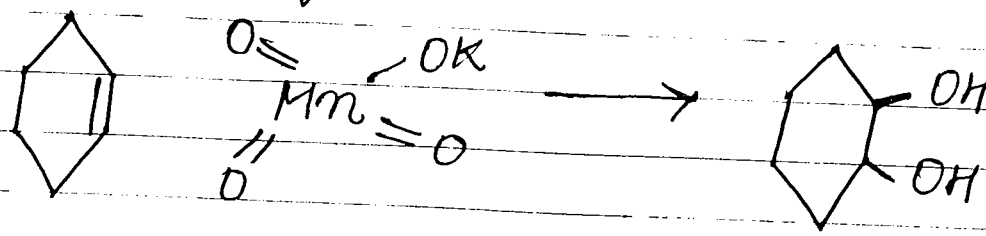
Mechn. →



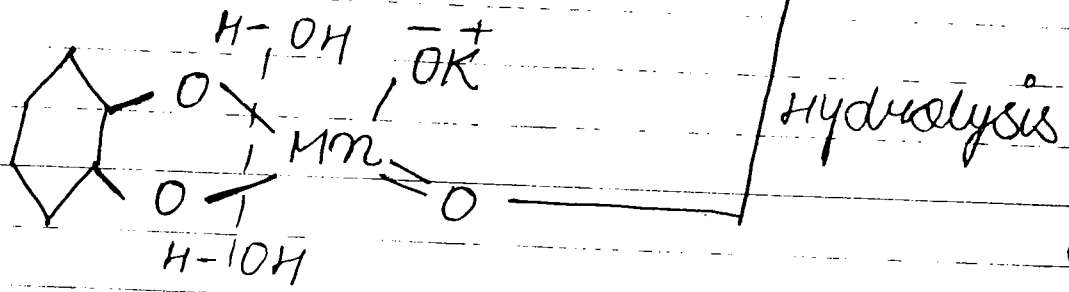


(B) Bayer reagent →

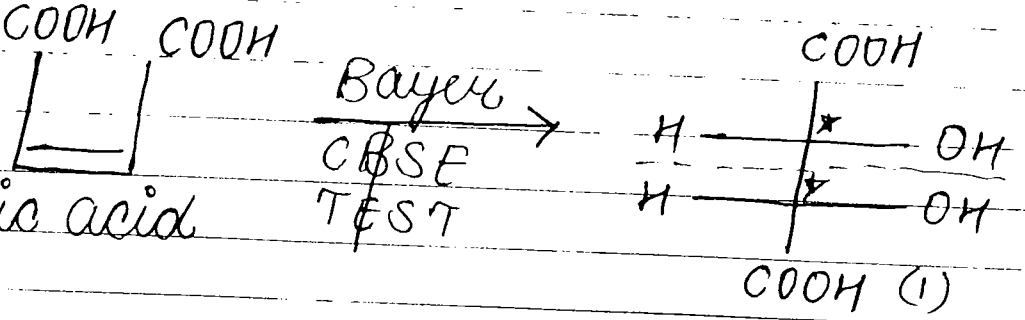
(1)



one-step ⟷ Syn-add



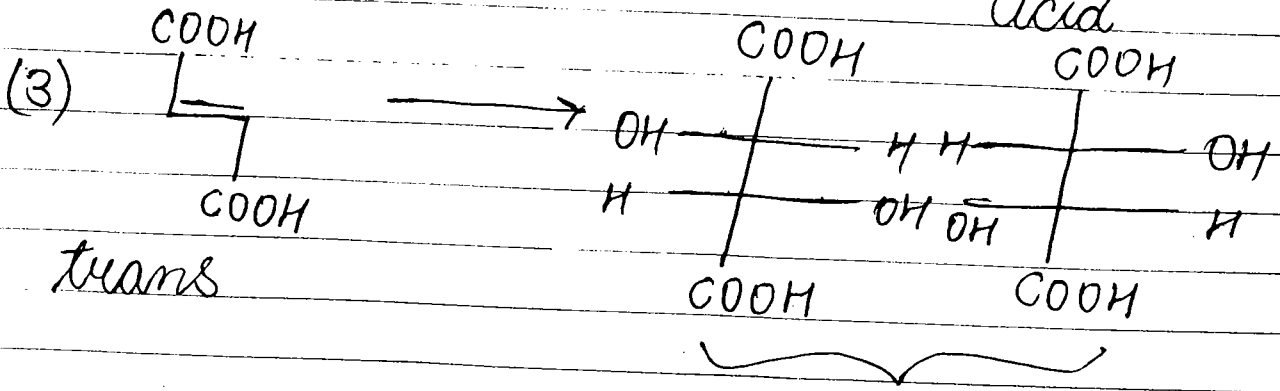
(2)



Meso-tartaric acid

Meleic acid

(3)

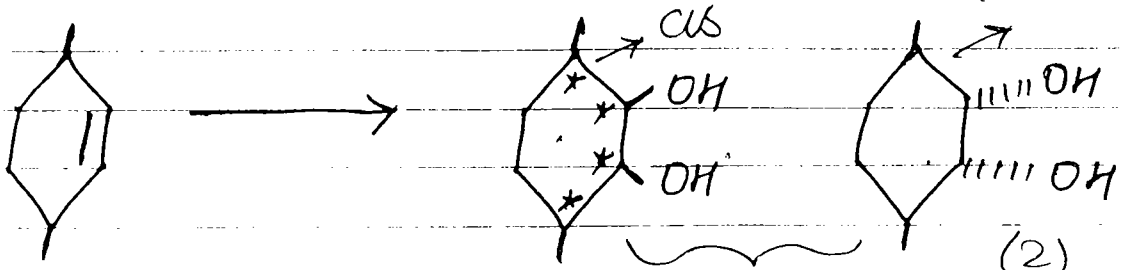


(2)

→ Bayer reagent is a syn-add. becoz its a one step process with cyclic transition state.

→ Its a stereo specific.

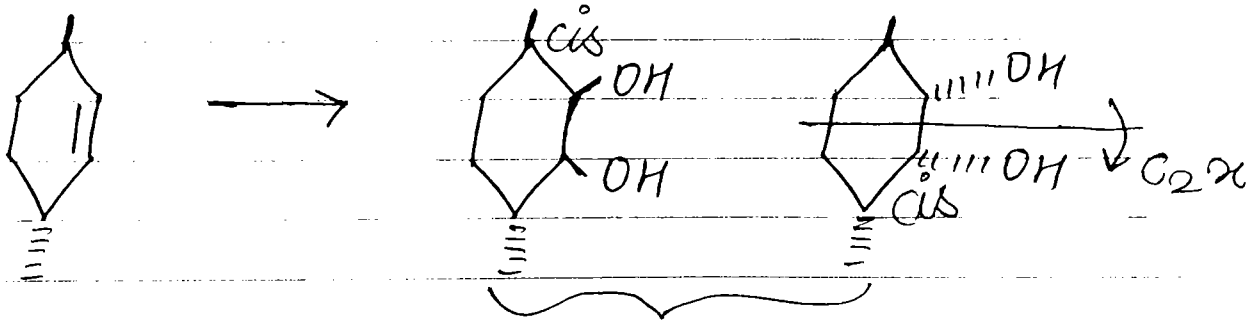
(4)



(2)

dia. ← c-t
ε-threo
2cc – (1) inter

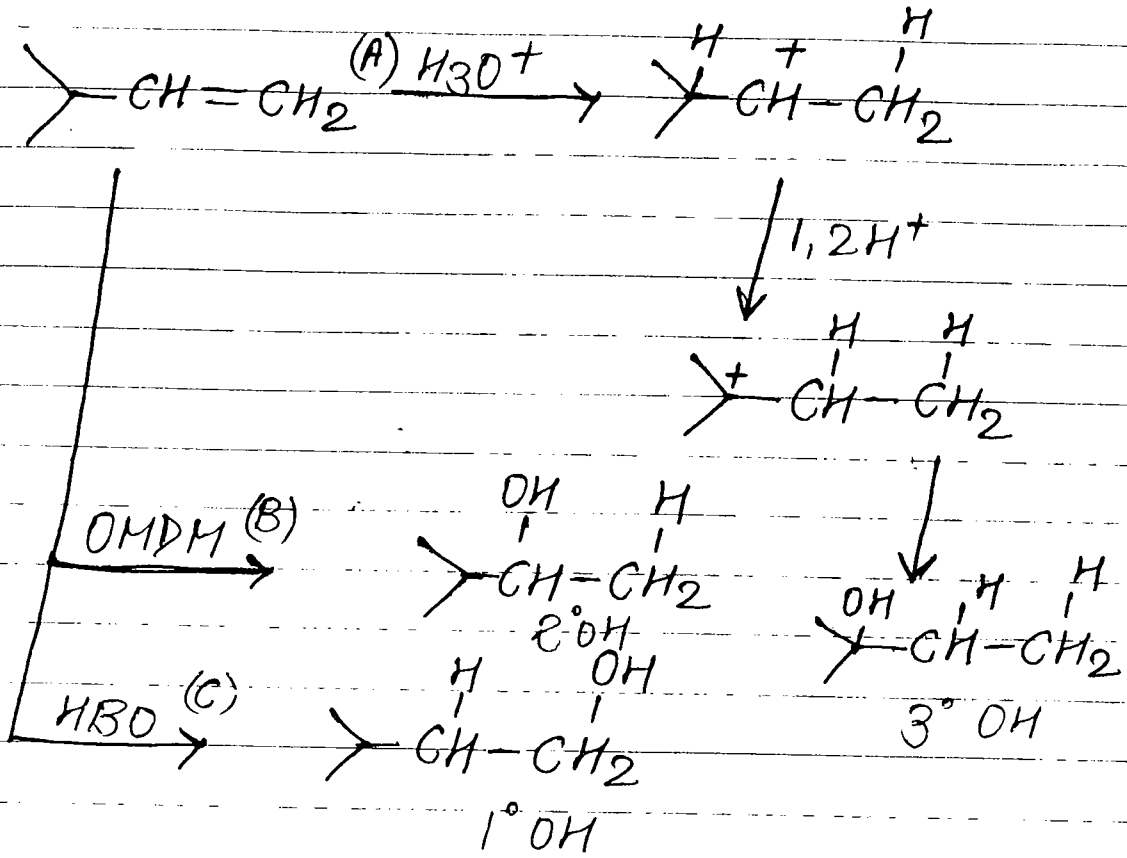
(5)

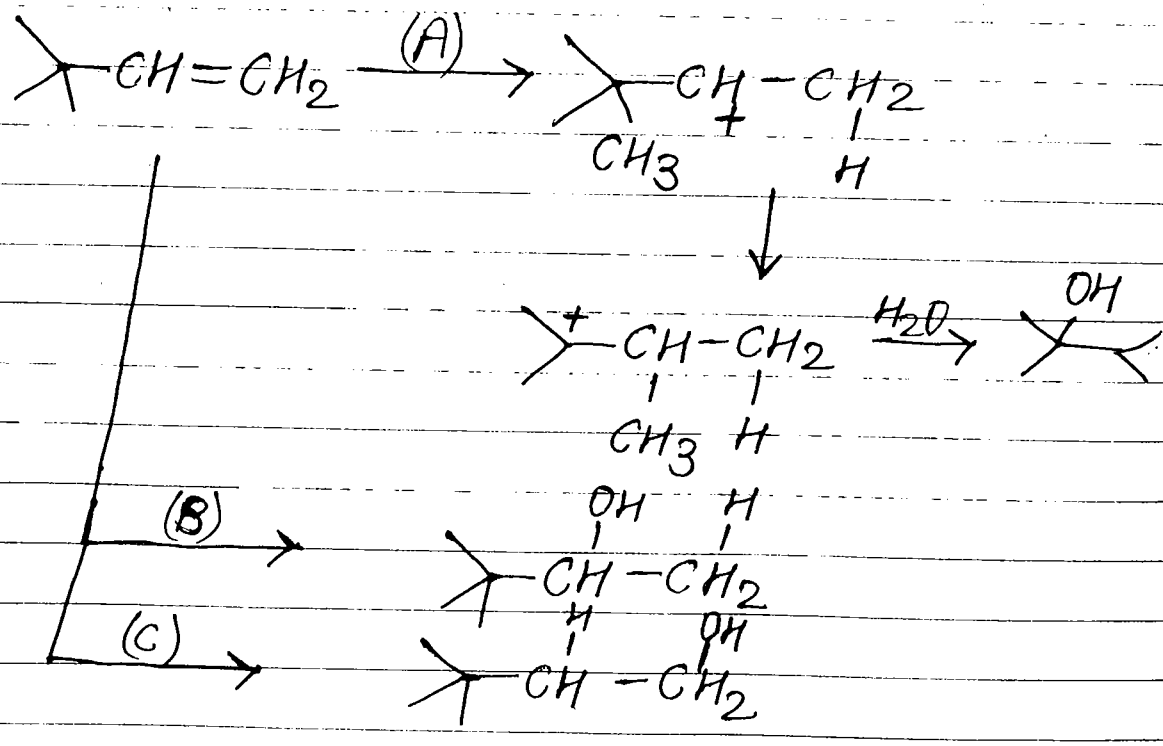


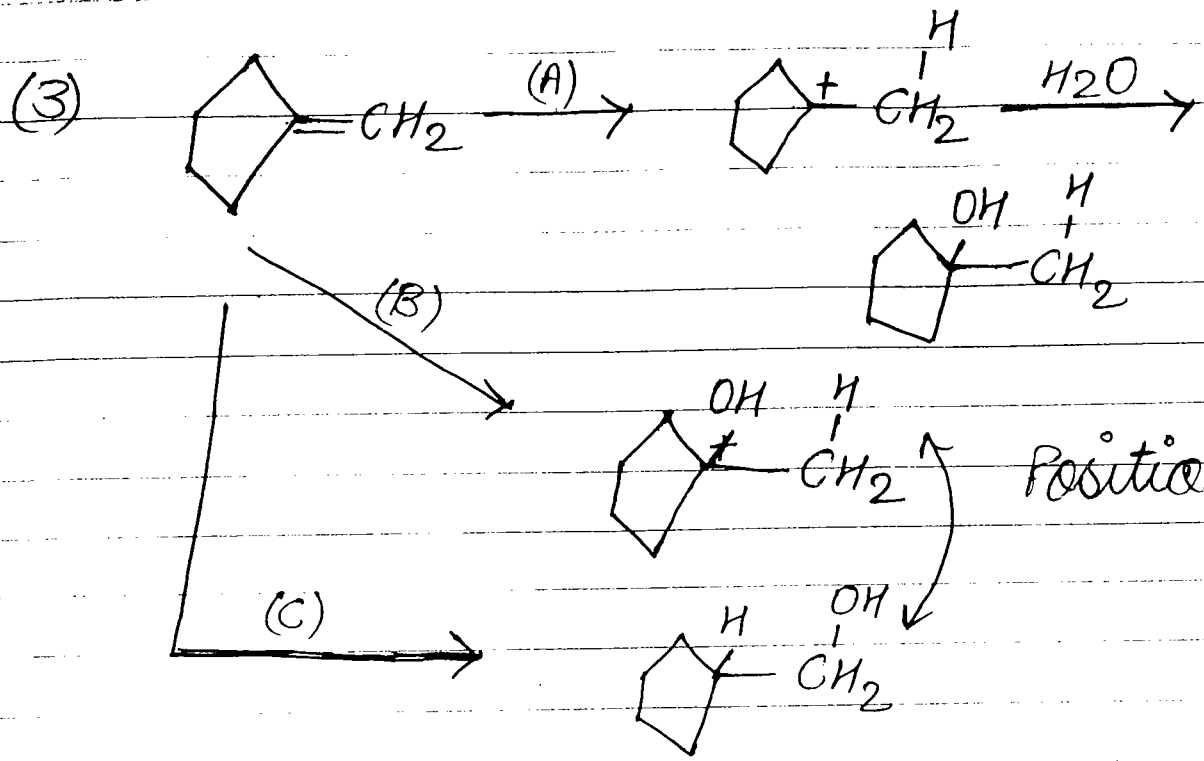
(1) Identical

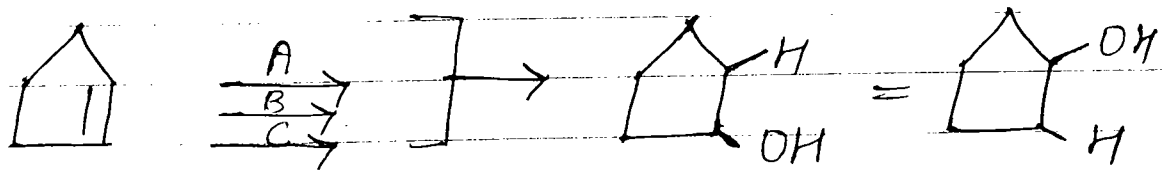
→ OSO_4 give same result like $KMnO_4$.

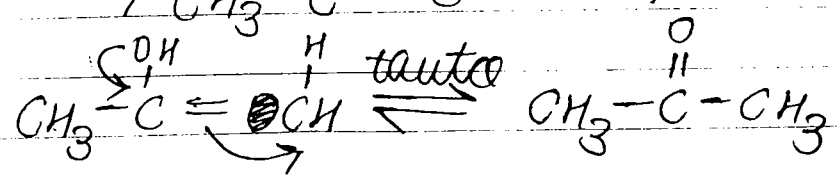
Hydration →
- (A) Dil H_2SO_4 → Mark. rule with shifting
- (B) OMDM → Mark. rule with no shifting
- (C) HBO → anti-Mark. with no shifting

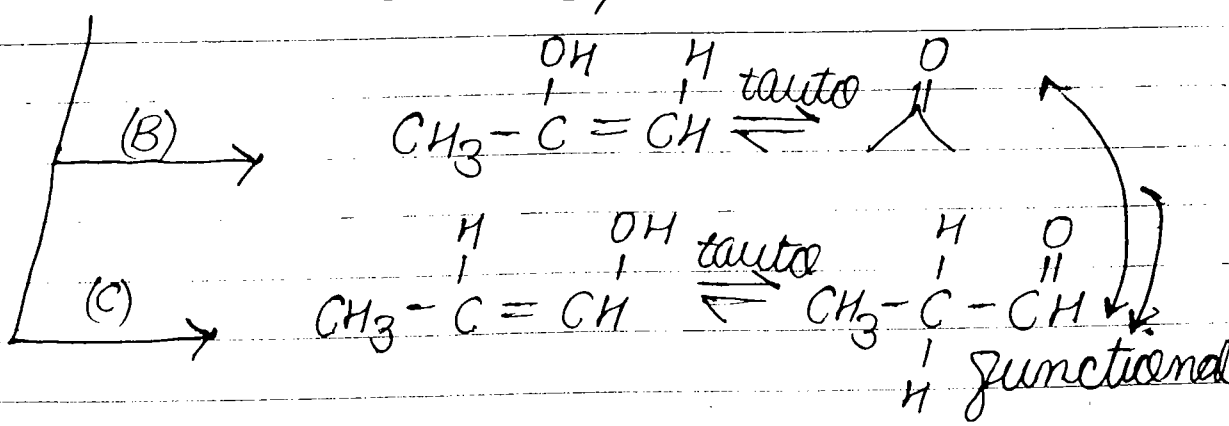
(1) 

(2) 

(3) 

(4) 

(5) $CH_3-C\equiv CH \xrightarrow{(A)} CH_3-\overset{+}{C}=CH \xrightarrow{H_2O}$ 

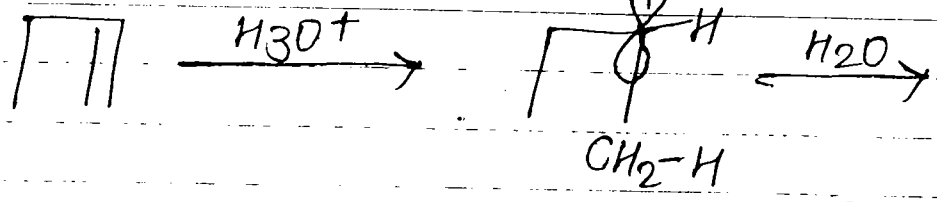


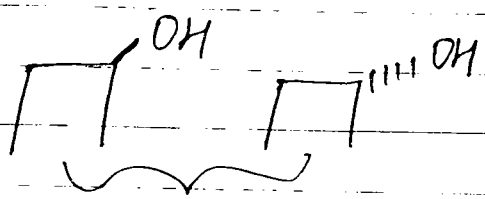
(A) Dil H_2SO_4 / H_3O^+ → Mark. rule with shift due to classical cation.

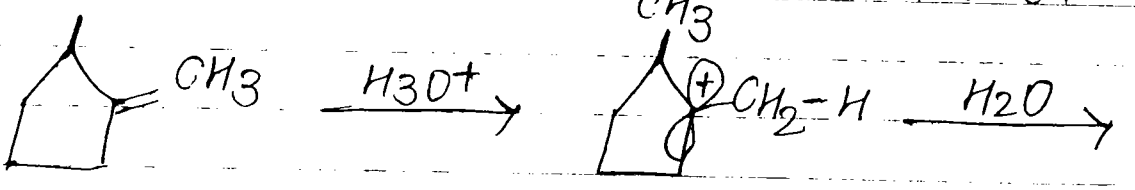
(1) $CH_2 = CH_2 \xrightarrow{dil\ H_2SO_4} CH_2(H)-CH_2^{+} \xrightarrow{H_2O} \text{H-bonding} \xrightarrow{} CH_2(H)-CH_2(OH) + H_3O^+$ stable

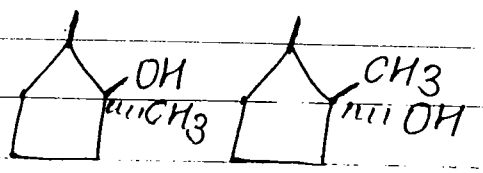
Industrial preparation of ethanol

$CH_2(H)-CH(O\backslash H) \xrightarrow{H_2O} CH_2(H)-CH_2(OH) + H_3O^+$

(2) 



(3) 

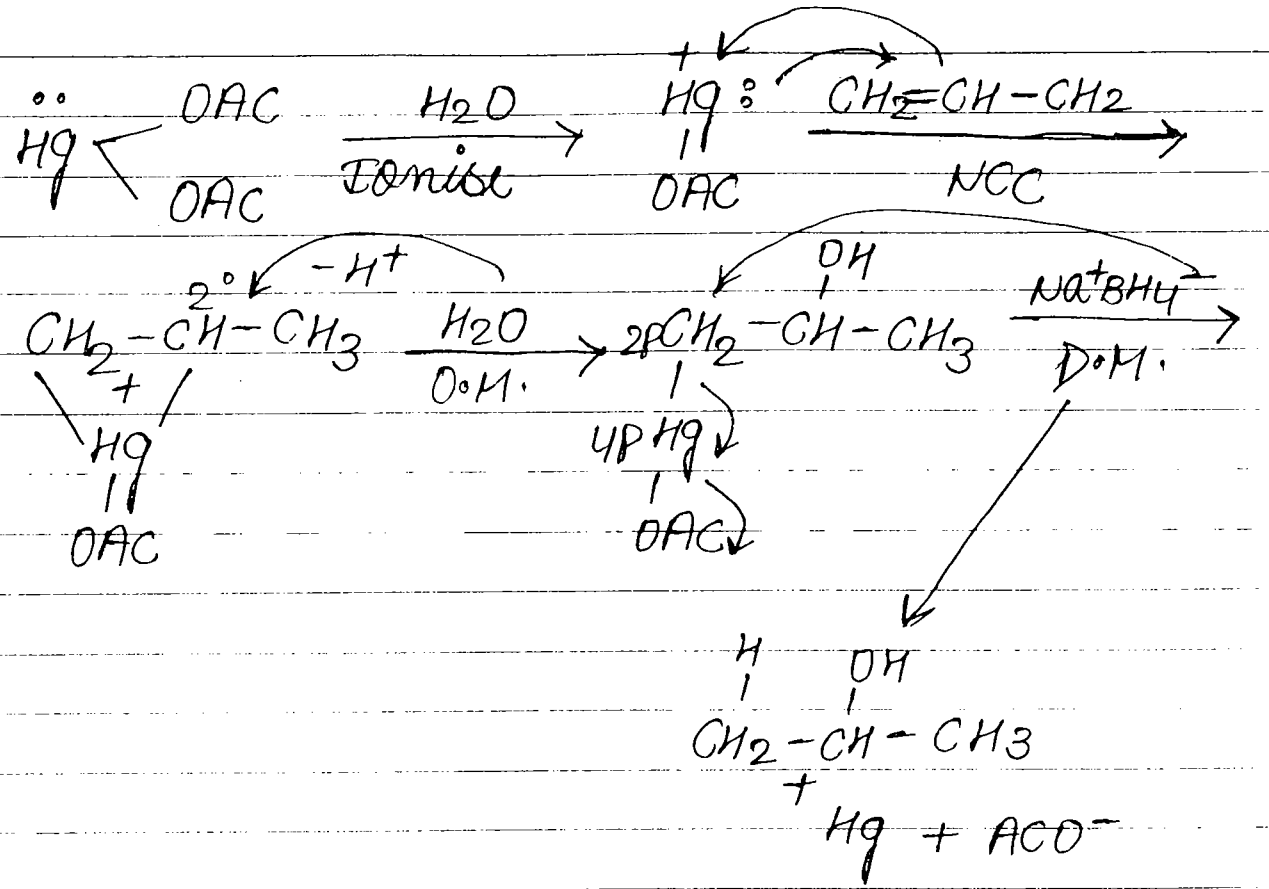


(4) $Ph-CH_2-CH=CH_2 \xrightarrow{H^+} Ph-CH(H)-\overset{+}{C}H-CH_2(H) \longrightarrow Ph-\overset{+}{C}H-CH(H)-CH_2(H) \xrightarrow{H_2O} Ph-\underset{OH}{\overset{*}{C}H}-CH_2-CH_3$

(B) O.M.D.M / Oxy-mercuration De-mercuration

$$CH_3-CH=CH_2 \xrightarrow[(2)\ NaBH_4]{(1)\ Hg(OAc)_2,\ H_2O} CH_3-\underset{OH}{CH}-\underset{H}{CH_2}$$

Mechⁿ. →



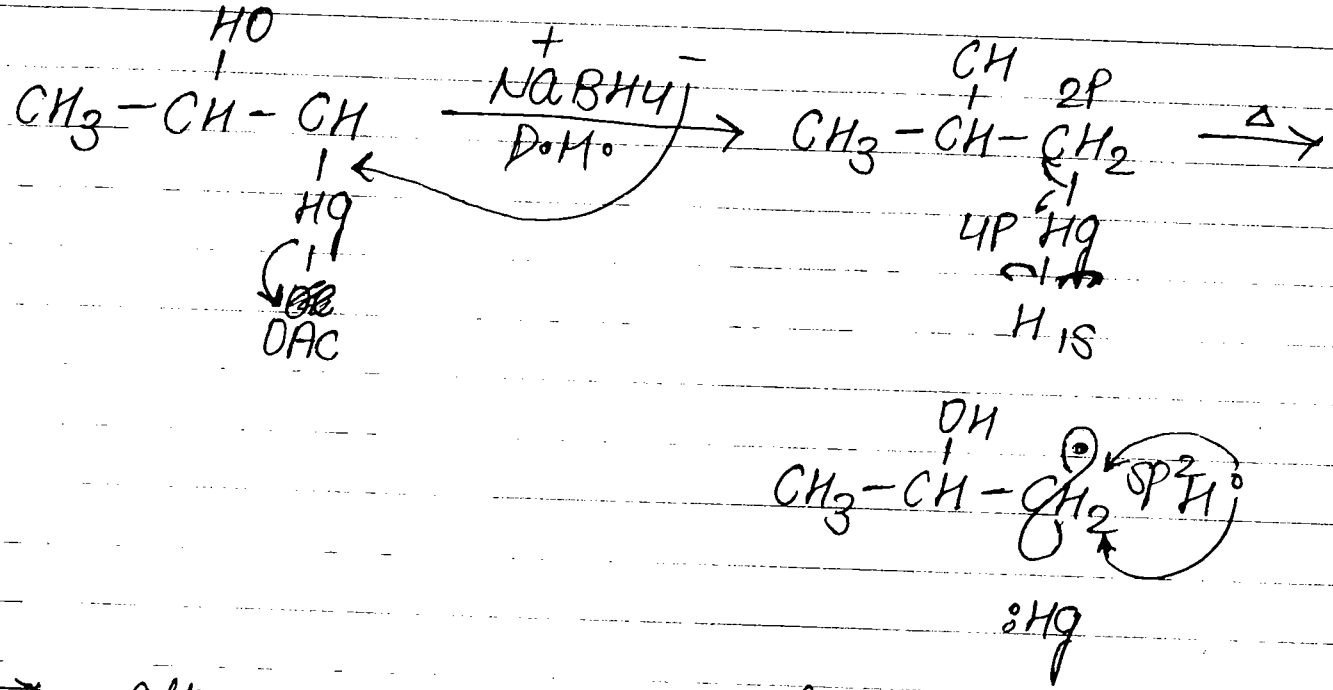
$$CH_2-\underset{OH}{CH}-CH_3 + Hg + ACO^-$$

→ In O.M.D.M. mark. with no shifting due to non-classical cation.

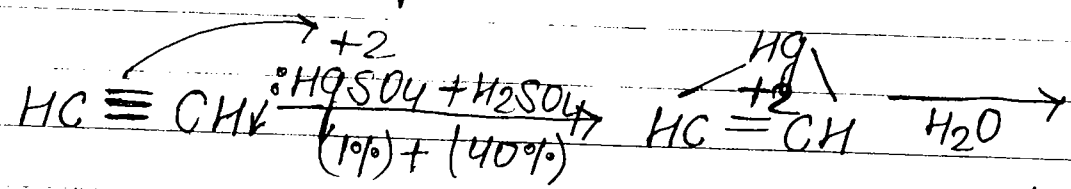
(2) $CH_3-CH=CH_2 \xrightarrow[NaBD_4]{Hg(OAc)_2,\ H_2O\ (Solvent)} CH_3-\underset{OH}{CH}-\underset{D\ \rightarrow\ NaBD_4}{CH_2}$

$$CH_3-\underset{OCH_3}{CH}-\underset{T}{CH_2} \xleftarrow[NaBT_4]{Hg(OAc)_2\ CH_3\ddot{O}H} CH_3-CH=CH_2$$

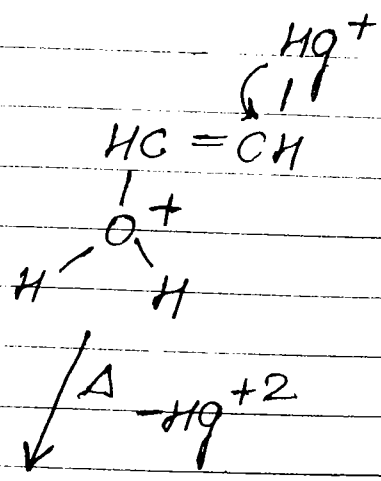
→ In O·M·D·M syn- and anti both add. take place becoz last step is radical mechanism.

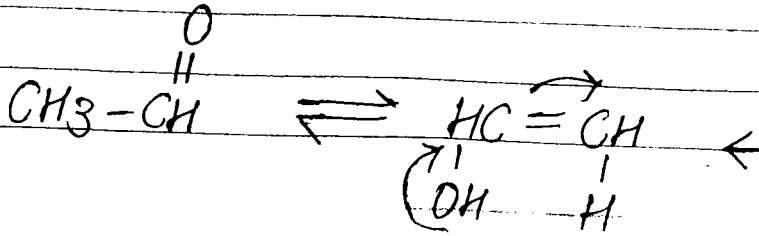


→ alkyne are less reactive so require strong electrophile.



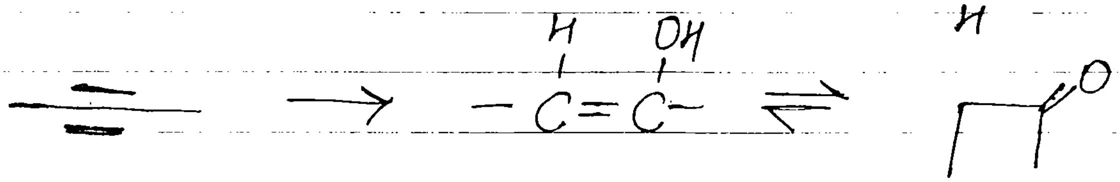
Markovnikov - rule.





(1) $CH_3-C\equiv CH \xrightarrow[H_2SO_4]{Hg^{+2}} CH_3-\overset{OH}{C}=\overset{H}{C}H \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(2) $Ph-C\equiv CH \longrightarrow Ph-\overset{OH}{C}=\overset{H}{C}H \rightleftharpoons Ph-\overset{O}{\overset{\|}{C}}-CH_3$

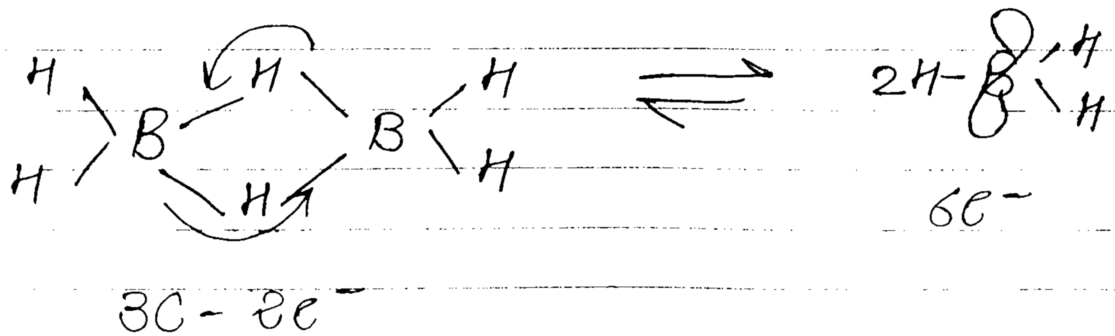
(3) 

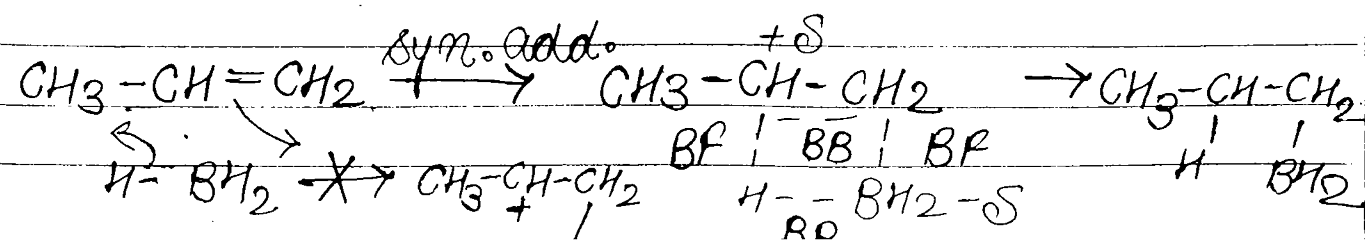
H·B·O / Hydroboration - Oxidation →

$CH_3-CH=CH_2 \xrightarrow[(2)\ H_2O_2/NaOH]{(1)\ B_2H_6} CH_3-\underset{2^\circ}{CH}-\underset{1^\circ}{CH_2}$ ($BH_3 \leftarrow H$, $OH \rightarrow$ Reagent added on CH_2)

Syn - add.

Mechn. →

(1) 

(2) 

(3) $CH_3-CH(H)-CH_2-BH_2 \xrightarrow{2CH_3-CH=CH_2} (CH_3-CH(H)-CH_2)_3-B$

OR R_3B

Reagent (A) $3HO-OH \xrightarrow{\text{Oxidation}} CH_3-CH(H)-CH_2(OH) + B(OH)_3$

(B) $3NH_2-Cl \xrightarrow{\text{Amination}} R-NH_2 + BCl_3$

(C) $3BH-BH \xrightarrow{\text{Bramination}} R-BH + BBH_3$

(d) $3D-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{Reduction}} R-D + B(OAC)_3$

(4) R_3B (6e⁻) $\xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}-D} R_3\overset{-}{B} \leftarrow \overset{+}{O}(D)-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow$

A.B.

$R-D + R_2B-\ddot{O}-\overset{O}{\overset{\|}{C}}-CH_3$

Some facts →

(1) In HBO syn-add take place becoz formation of cyclic transition state.

Syn - add ← $Ni + H_2$
dil. $KMnO_4$
HBO

CBSE
TEST

Anti - add ← $BH_2 + CCl_4$
$BH_2 + H_2O$
$PAA + H_2O$

CAT
TAE

(2) HydroB-- is a Mark. rule but after oxidation its anti - mark.

$CH_3-CH=CH_2 \xrightarrow[\text{Mark.}]{H\cdot B\cdot} CH_3-\underset{H}{\underset{|}{CH}}-\underset{BH_2}{\underset{|}{CH_2}} \xrightarrow[\text{anti}]{H\cdot B\cdot}$

$H-BH_2$

2·1 Nu⁻ — 2 E⁺

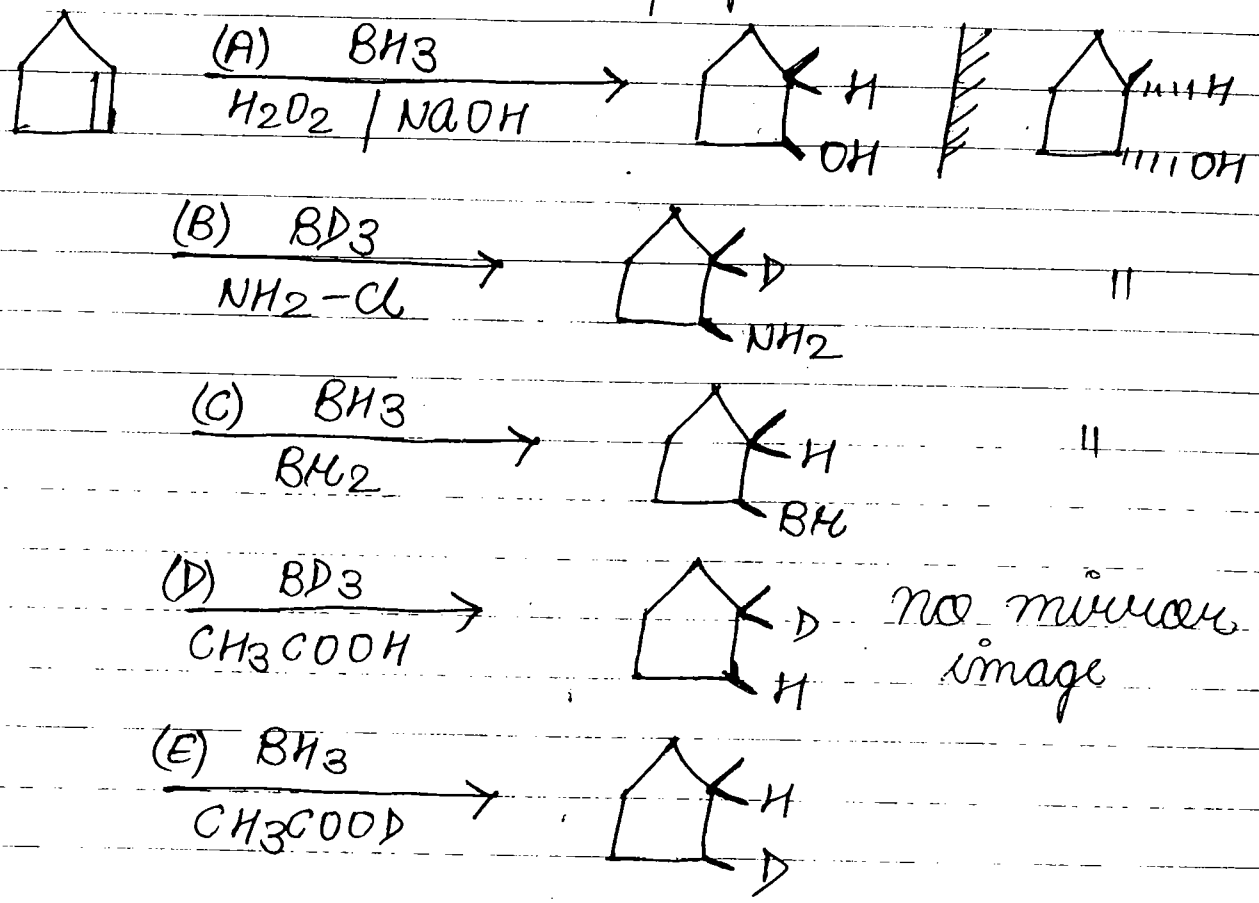
$CH_3-\underset{H}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

2·1 — 3·5

E⁺ — Nu⁻

(3) In HBO diff diff. reagent give diff. product.

HBO → anti mark. / syn addd.



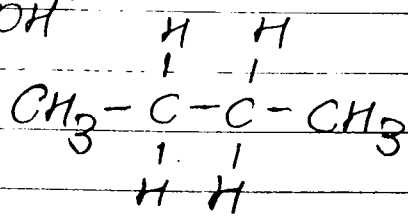
II

II

no mirror image

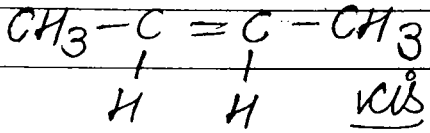
(4) In HBO one mole BH_3 required 3 mole alkene for only one mole we prefer 9-BBN which is react from less steric side.

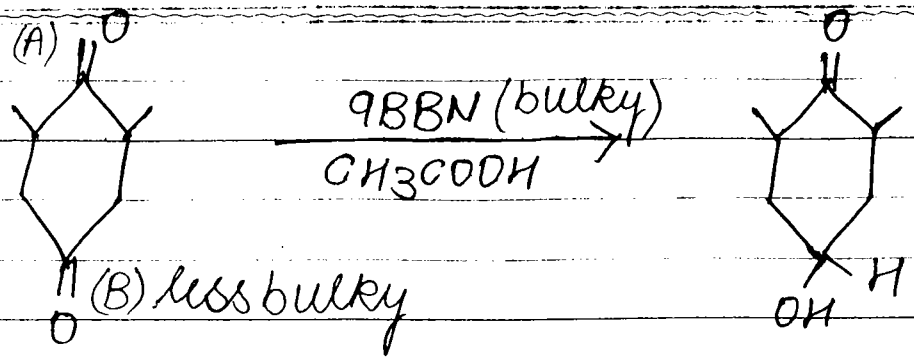
→ $CH_3-C\equiv C-CH_3 \xrightarrow[CH_3COOH]{BH_3}$



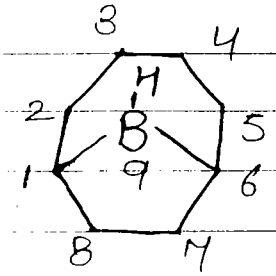
→ $CH_3-C\equiv C-CH_3 \xrightarrow[CH_3COOH]{9BBN}$

H-B





9BBN → 9-boron-bicyclo nonane



Oxidation of Alcohol →

(A) $R-CH_2-OH \xrightarrow[-H_2]{Oxi} R-CH=O \xrightarrow{Oxi} R-COOH$

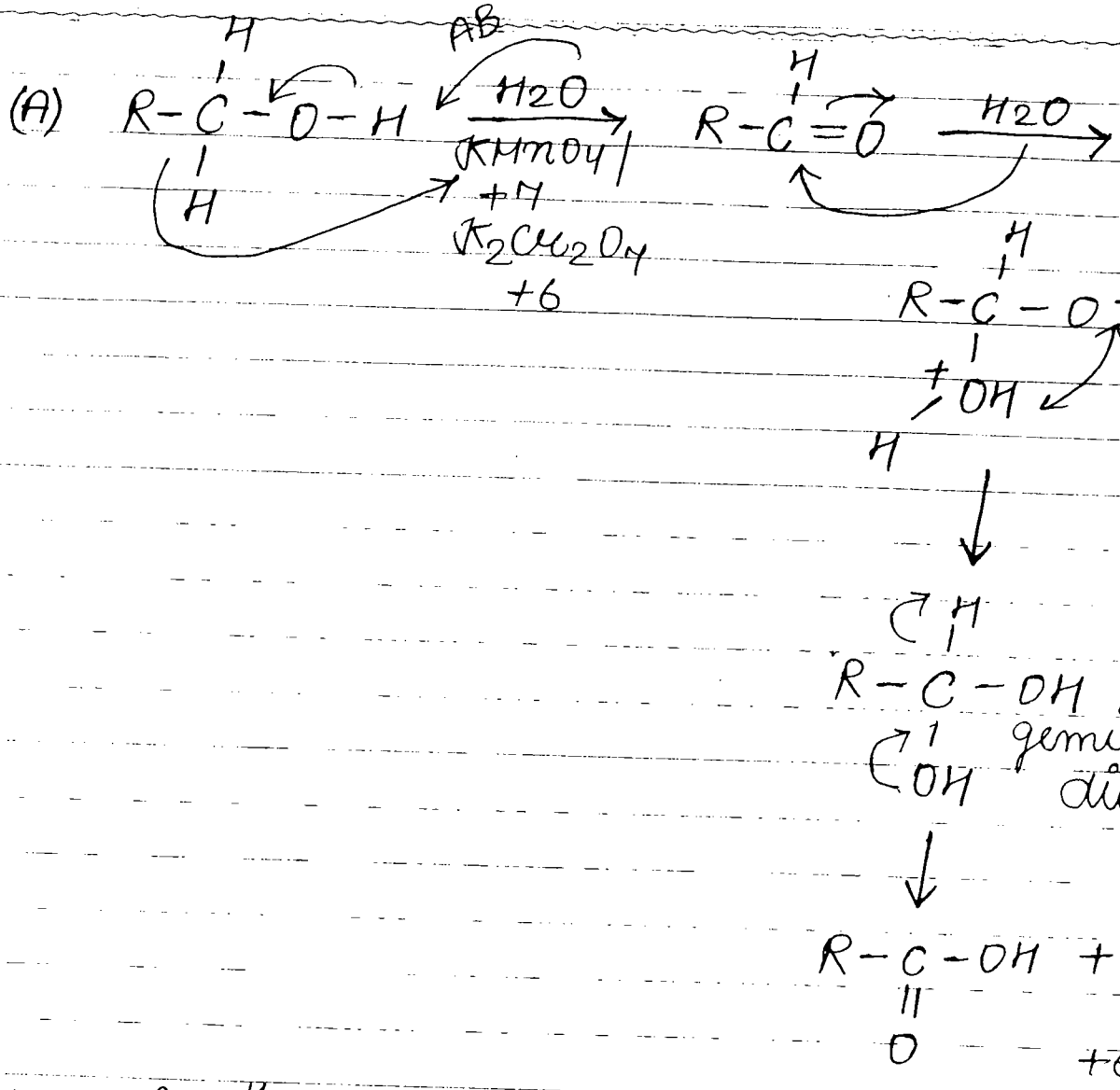
2°H — Aldehyde — acid

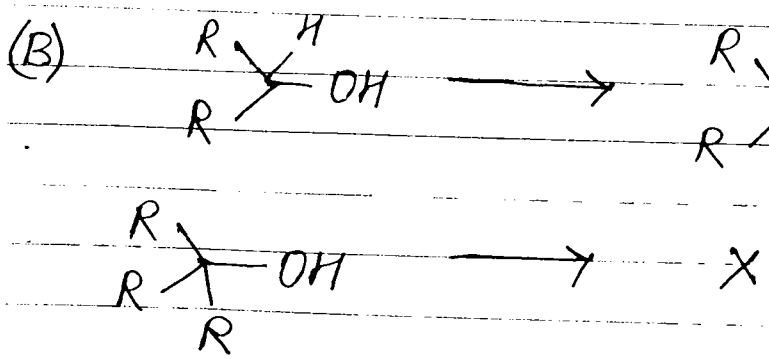
(B) $R_2CH-OH \xrightarrow[-H_2]{Oxi} R_2C=O$ Ketone

1°H

(C) R_3C-OH (0°H) → no oxidation

Mechⁿ. →

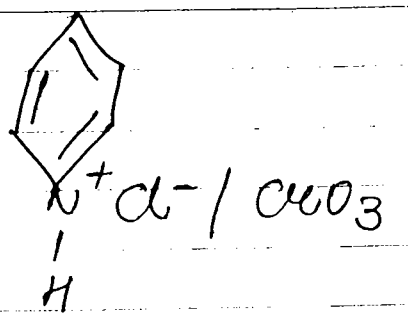
(A) 

(B) 

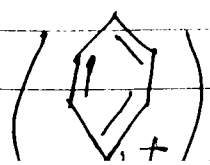
Bad leaving group
non Polar

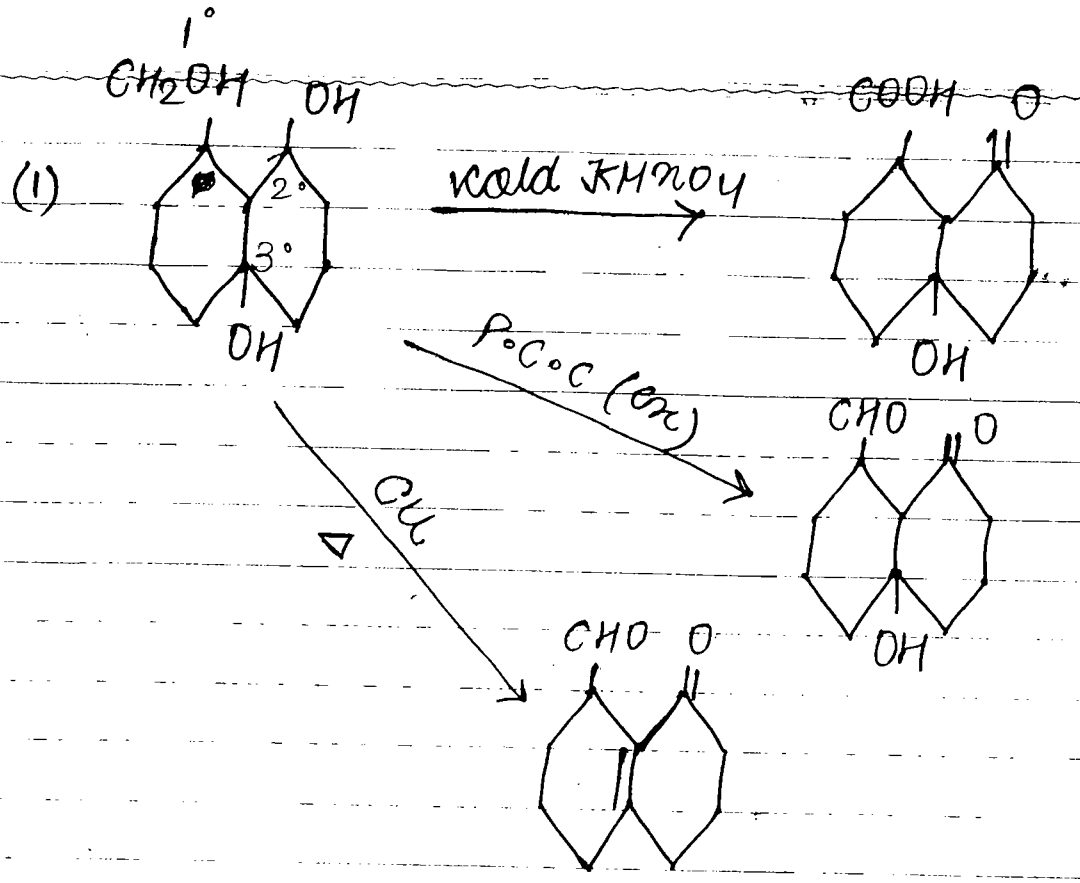
Reagent	>OH	>OH	CH_3CH_2OH
cold $KMnO_4$ (Purple → colourless)	X		
Aq. $K_2Cr_2O_4$ orange-green	X		
$H_2O + CrO_3$ H_2CrO_4	X	>=O	H_2O present CH_3COOH
PCC / collin	X		
PDC / sarrate	X		H_2O absent CH_3CHO
Cu + 450°C	>=CH_2 + H_2O↑ (dehydration)		

P.C.C → Pyridinium chloro chromate



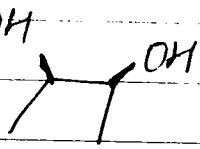
PDC → Pyridinium dichromate

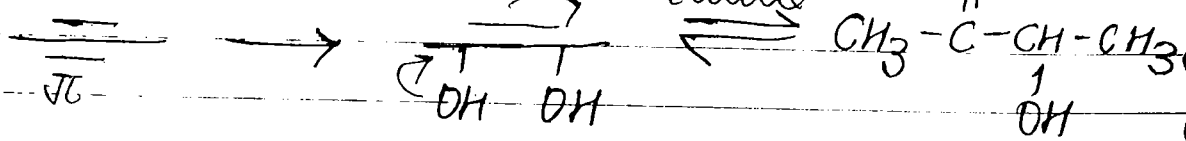




Type of $KMnO_4$ →

(A) Bayer $\xrightarrow{1\%\ dil\ KMnO_4}$ ~~X~~

(1) $\boxed{\pi}$ → 

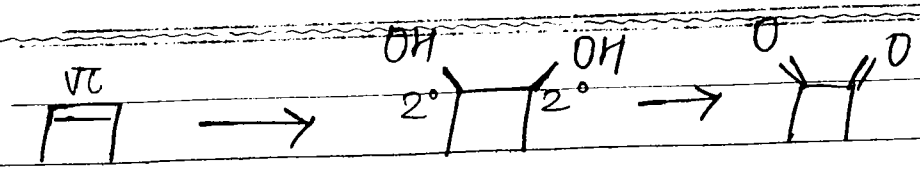
(2) 

(B) cold $KMnO_4$

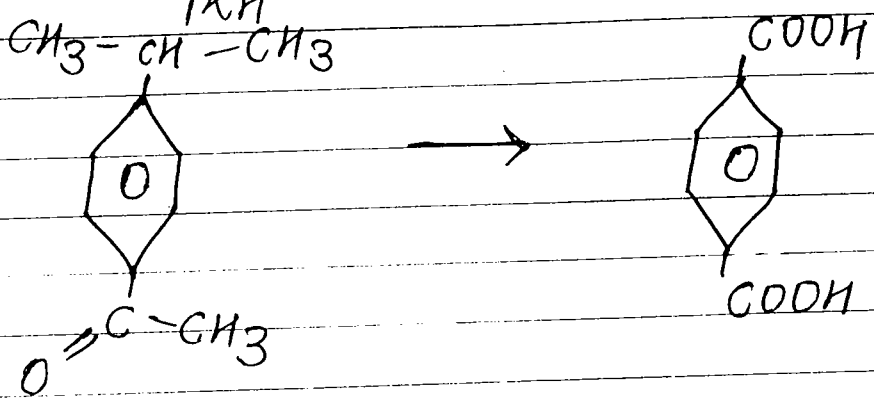
(1) $R-CH_2-OH \rightarrow RCOOH$

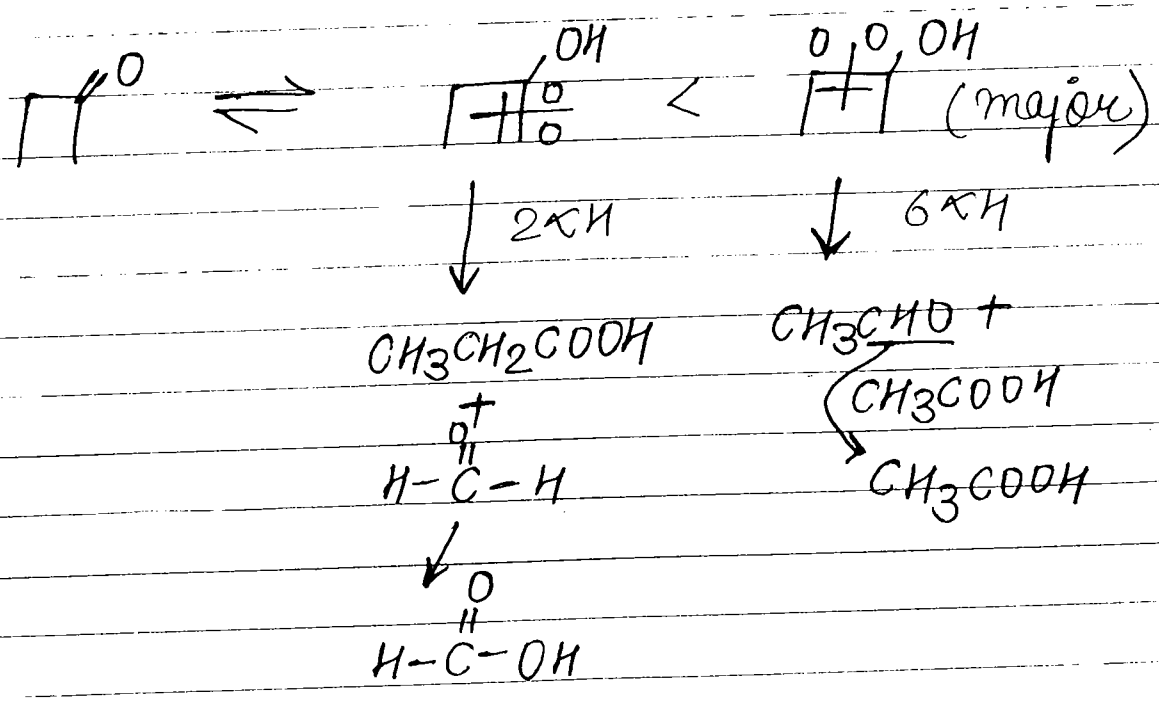
(2) $>OH \rightarrow >C=O$

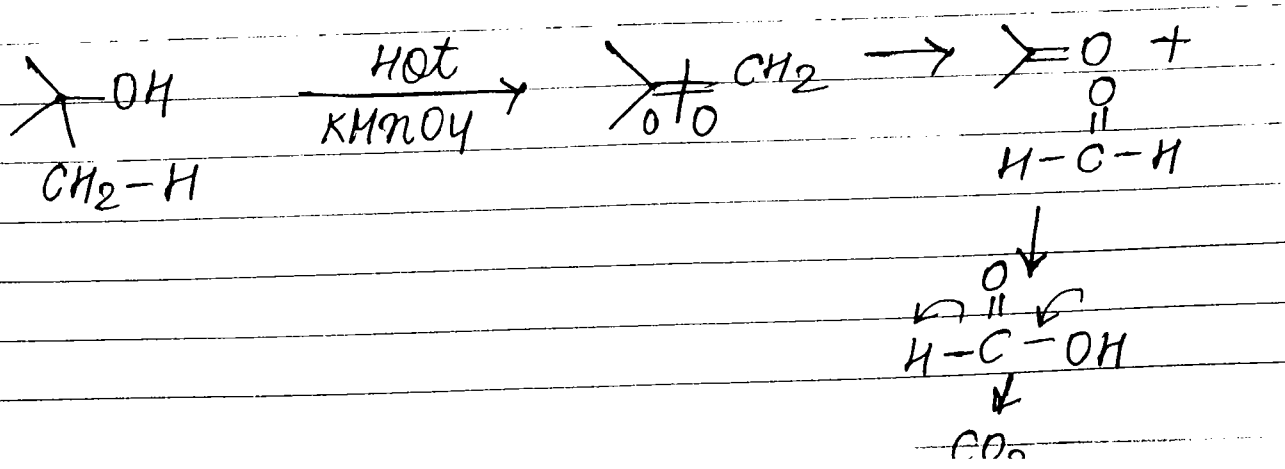
(3) $-OH \rightarrow X$

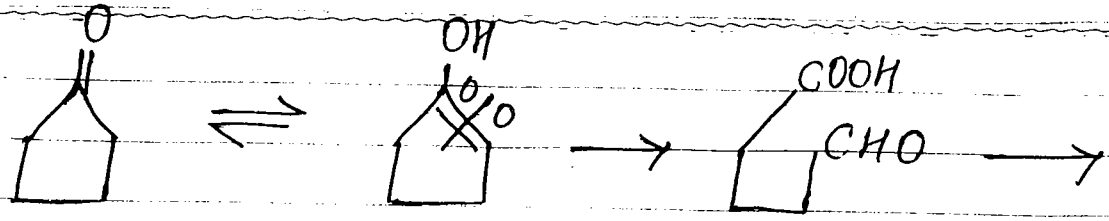
(4) 

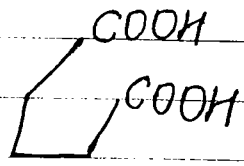
(C) Hot $KMnO_4$ →

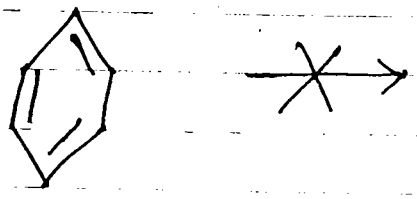
(1) 

(2) 

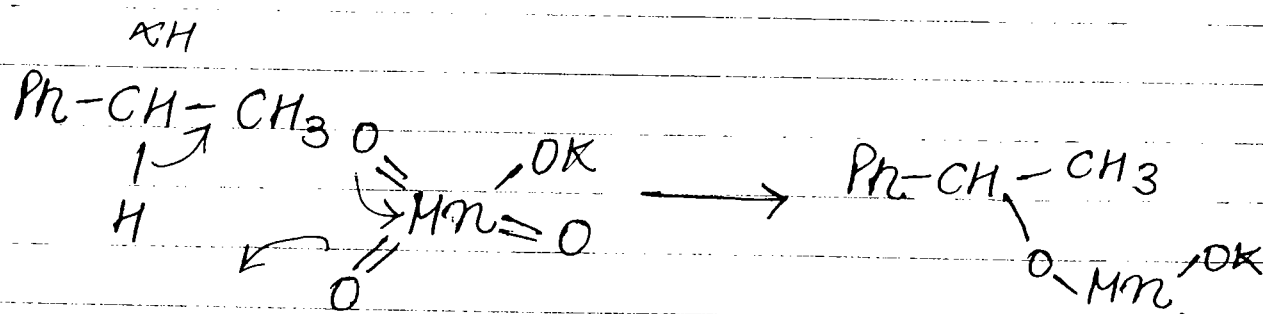
(3) 

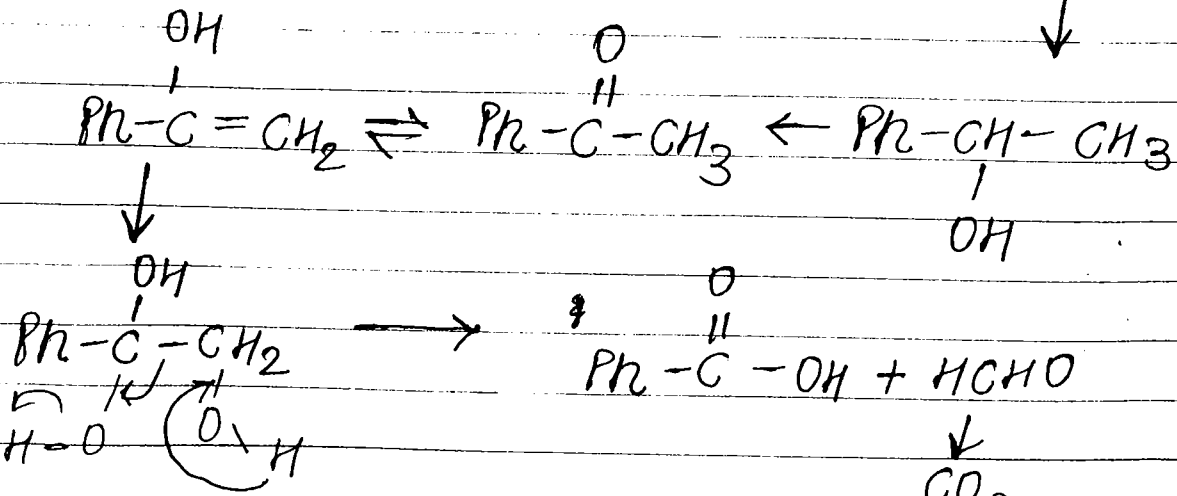
(4) 
O
OH
COOH
CHO


COOH
COOH

(5) 

Mechⁿ. →


Ph-CH-CH3
H
O
OK
Mn=O
O
Ph-CH-CH3
O
Mn
OK
=O
HO


OH
Ph-C=CH2
O
Ph-C-CH3
Ph-CH-CH3
OH
OH
Ph-C-CH2
H-O
O-H
O
Ph-C-OH + HCHO
CO2

Ozonolysis →

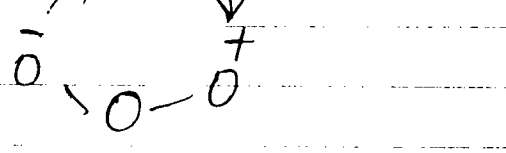
(1) $CH_3-CH=CH-CH_3 \xrightarrow[Zn/H_2O]{O_3}$

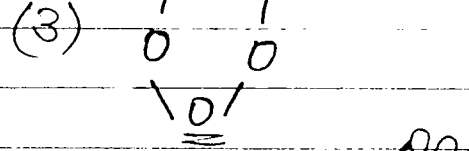
$CH_3-CH=O + O=CH-CH_3$

(2) $CH_3-C\equiv C-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

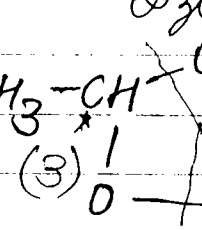
Hint →

$CH_3-\overset{sp^2}{CH}=CH-CH_3 \longrightarrow$ (Molozonide) $CH_3-CH-CH-CH_3 \longrightarrow$ (3)





$(H_2O_2) \leftarrow CH_3\overset{sp^2}{C}HO + CH_3CH=O \xleftarrow{H_2O}$ Ozonide $CH_3-CH-CH-CH_3$ (3)

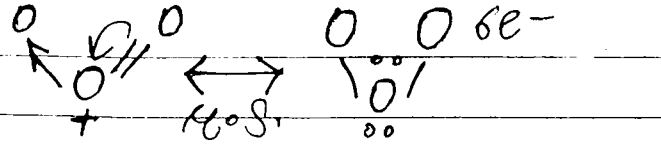


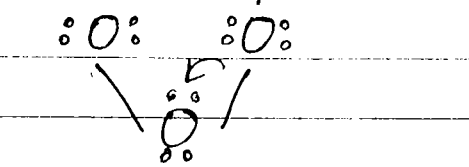
$\downarrow Zn/CH_3SCH_3$

$H_2O + ZnO / ;S=O$

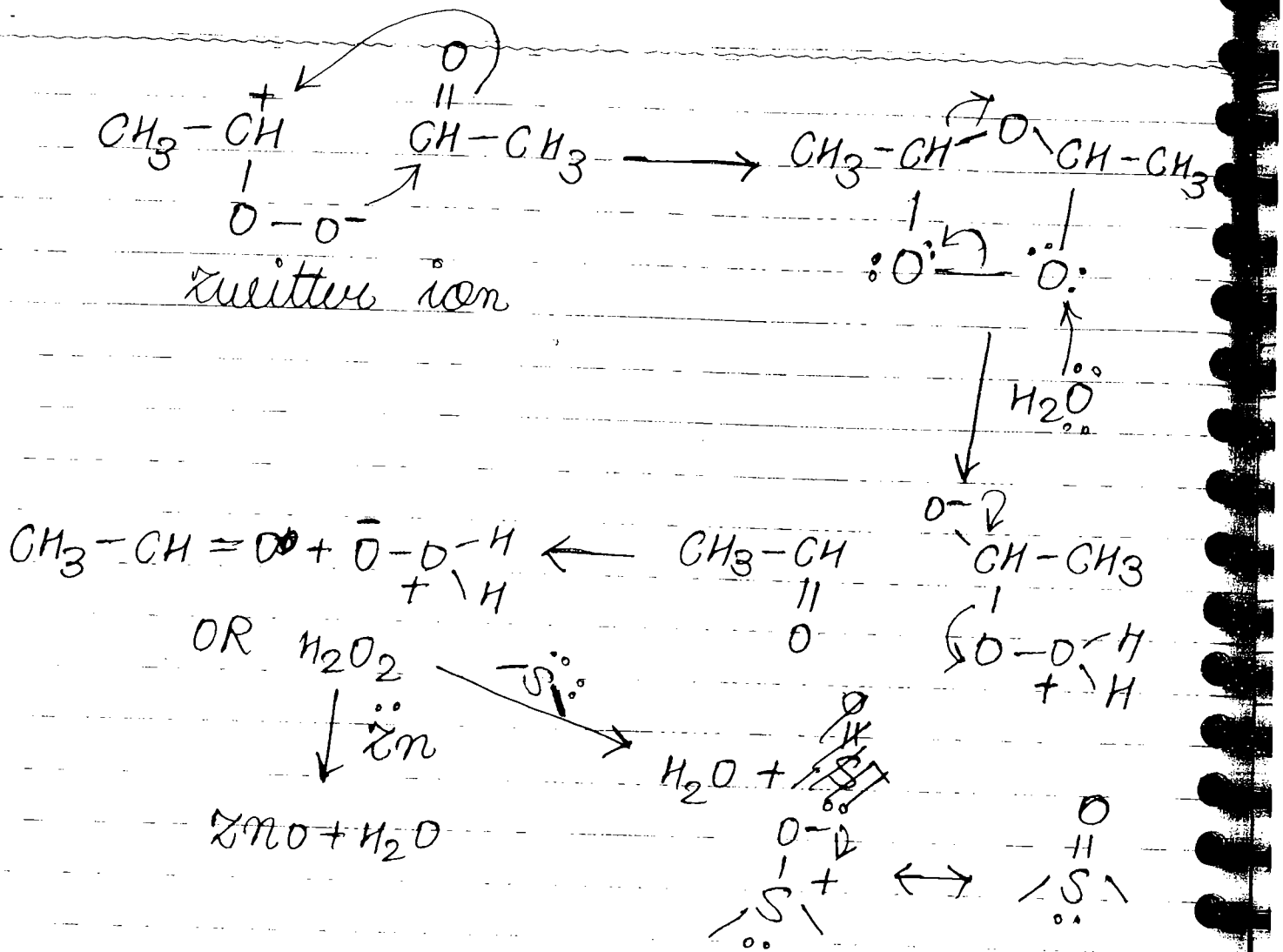
Mechn. →

$CH_3-CH=CH-CH_3 \longrightarrow CH_3-CH\cdots CH-CH_3 \longrightarrow$





Molozonide

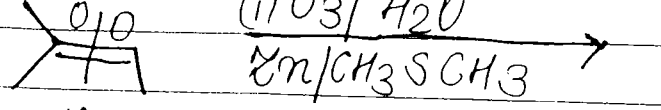


Some facts →

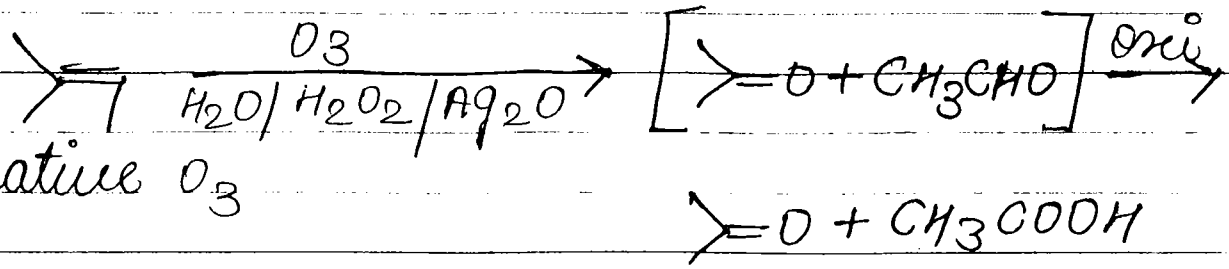
(1) In ozonolysis double bond is replaced is 2 oxygen atom.

(2) role of Zn → to consume H_2O_2 so that further oxydation of product not possible.

Types of ozonolysis →

(A) 

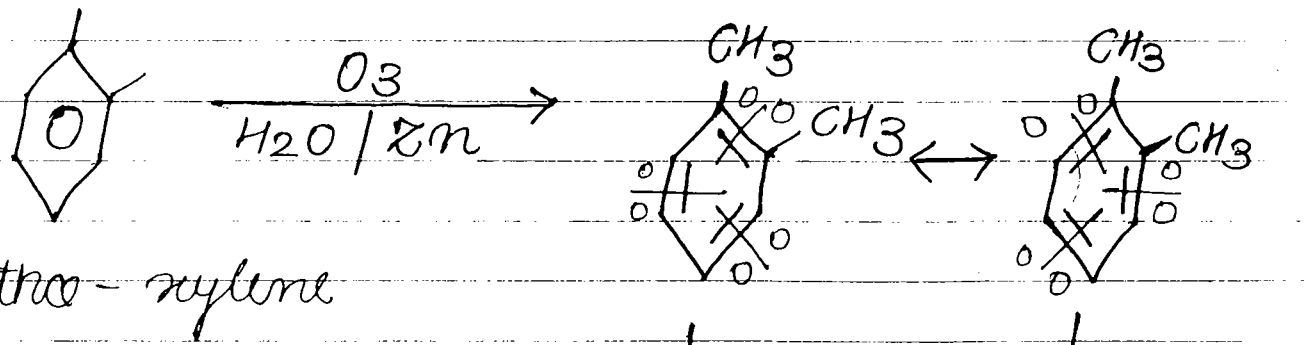
Reductive - O_2

(B) 

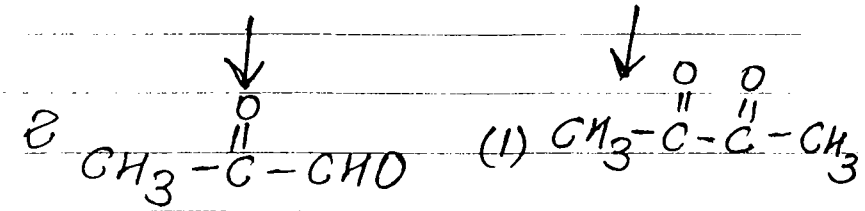
Oxidative O_3

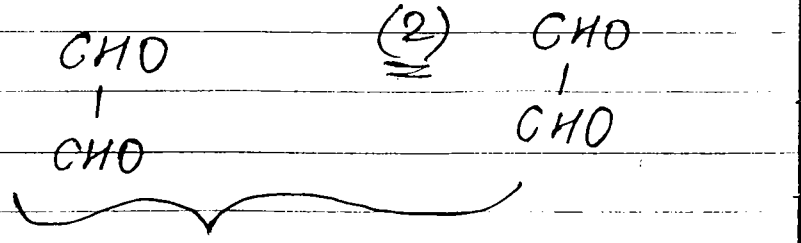
(3) In ozonolysis of benzene consider both Kekule structure.

Kekule structure



ortho - xylene





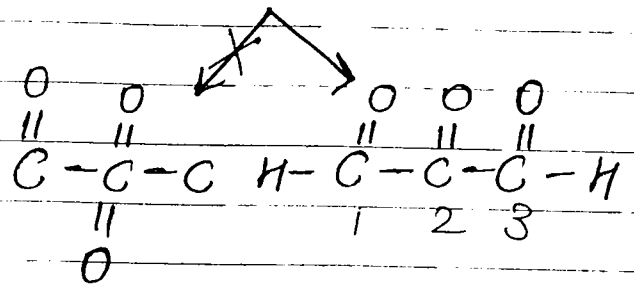
1 : 2 : 3

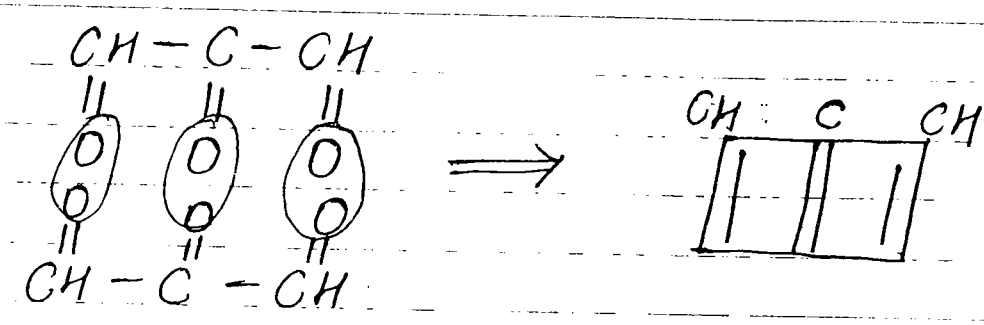
Benzene Reso.

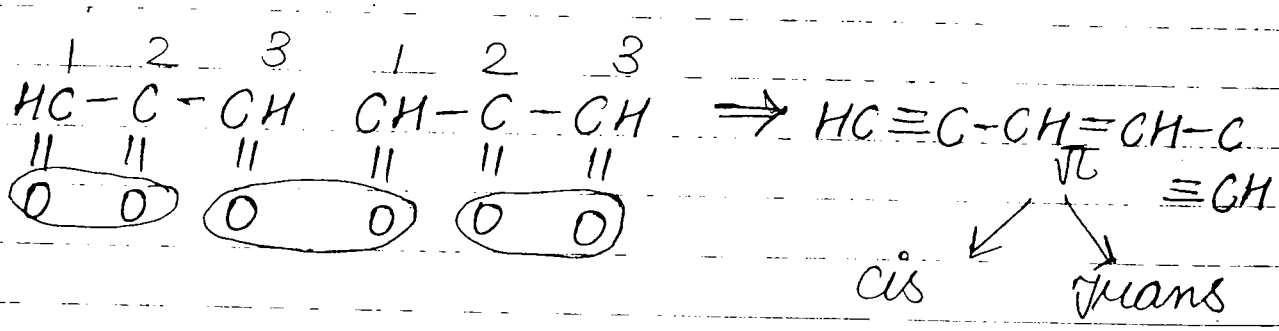
(4) Retro - ozonolysis → If product is given then identify reactant.

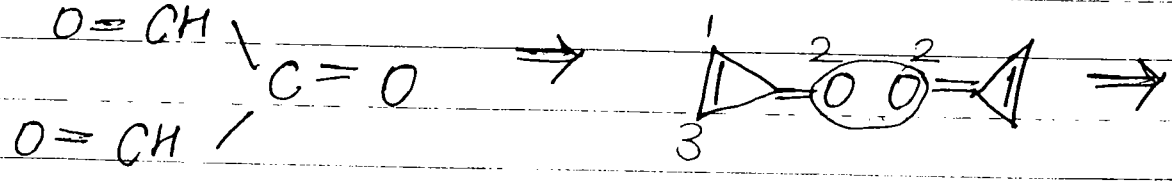
→ B C_6H_4 $\xrightarrow[H_2O/Zn]{O_3}$ $CH_2\ C_3H_2O_3$

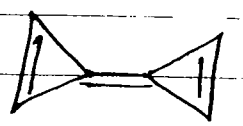
Identify

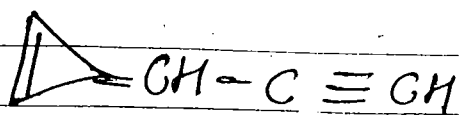


(A) 

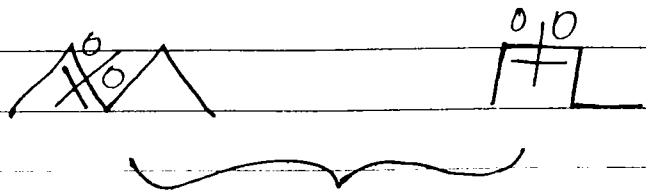
(B) 

(C) 



(d) 

cis and trans give identical product by ozonolysis.

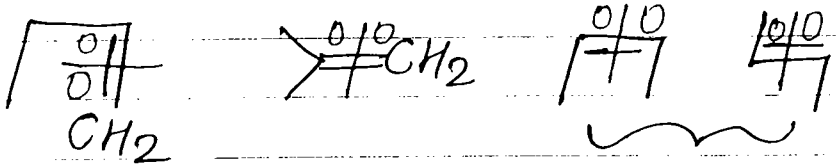


CH_3CHO

CH_3-CH_2-CHO

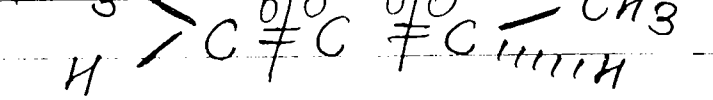
Hint →

(1) $CH_2=O$ → Terminal π bond



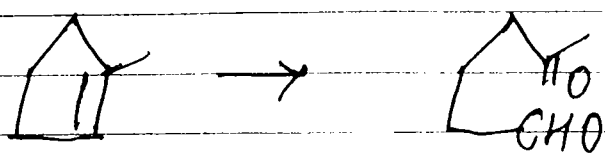
(2) CH_3CHO

(2) CO_2 → allene

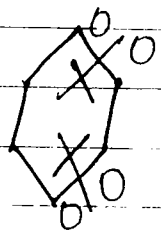


(3) One type of product → Symm.

(4) One product → cyclic

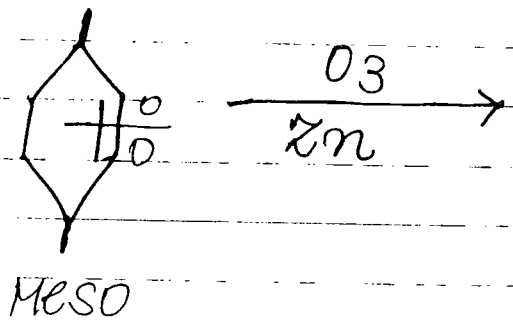


(5) $\begin{matrix} CHO \\ | \\ CHO \end{matrix} \rightarrow$ meso, alkyne

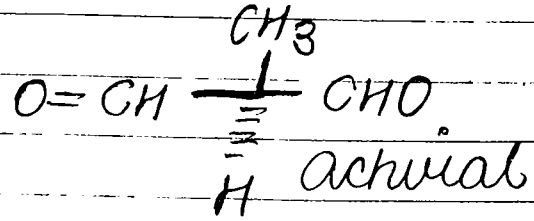


$HC \equiv CH$

(6) Stereochemistry

(A) 

meso

(B) $CH_3-CH=CH-C-CH=CH_2 \rightarrow CH_3CHO$ + 

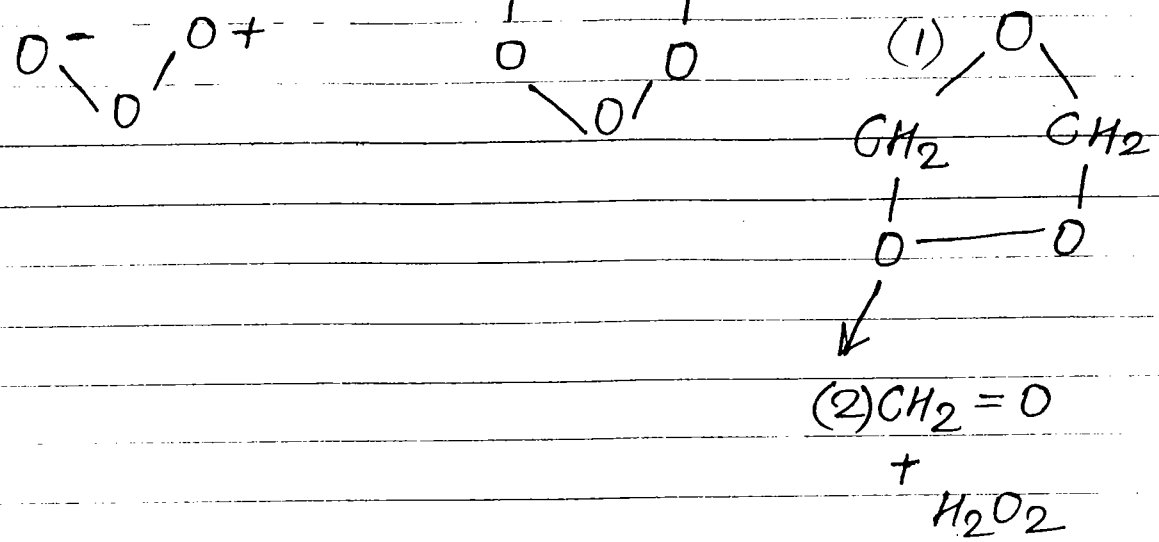
achiral

$CH_2=O$

(C) x = no. of molozonide

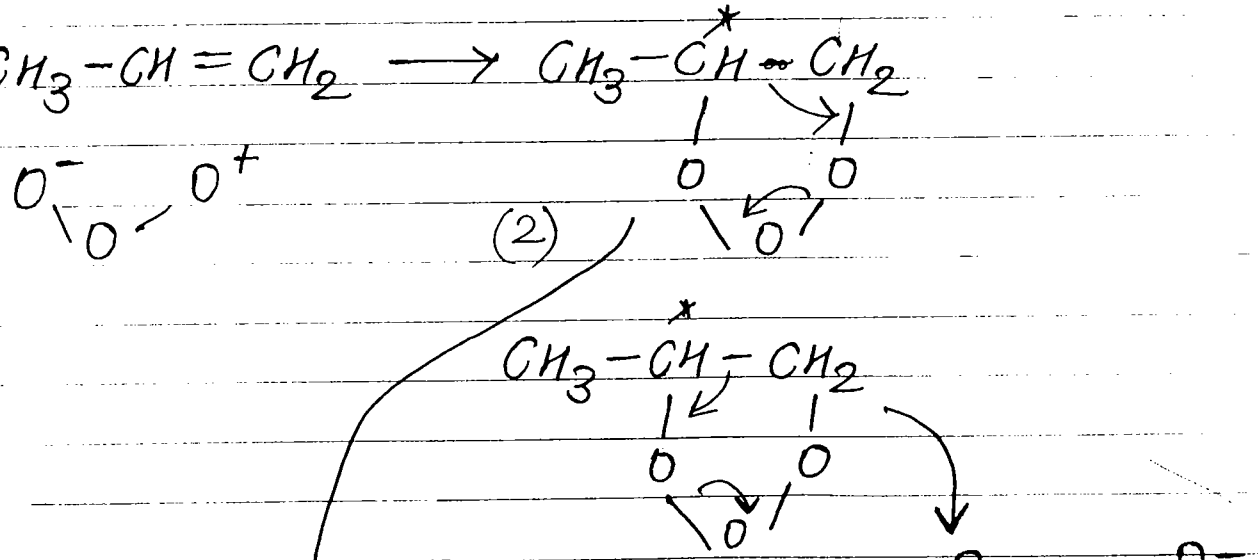
y = " " ozonide

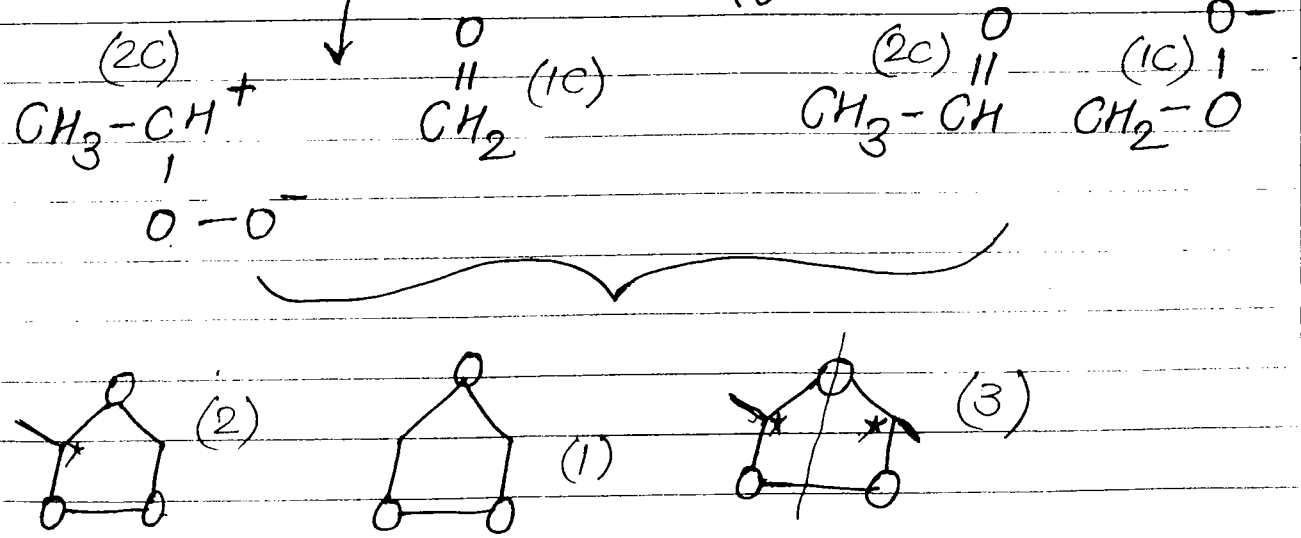
(1) $CH_2 = CH_2 \longrightarrow$ (1) $CH_2 - CH_2 \longrightarrow$



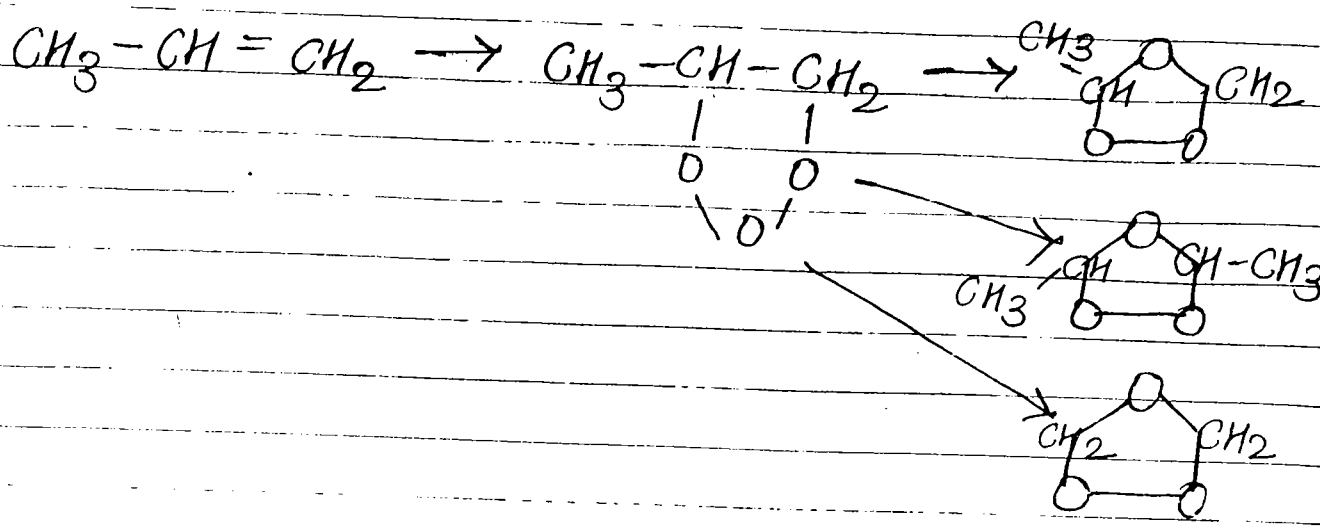
(2) $CH_2 = O$ + H_2O_2

(2) $CH_3 - CH = CH_2 \longrightarrow CH_3 - \overset{*}{C}H - CH_2$





3 + 2 + 1 = (6)


CH3 – CH = CH2
CH3 – CH – CH2
O O
O
CH3
CH
CH2
CH
CH – CH3
CH3
CH2
CH2