$>C=C<$ $+Br_2$ $\xrightarrow[\text{solvent}]{\text{Non polar}}$ dibromide.

Addition reaction

- electrophilic addition — 2 step
- Nucleophilic addition — 2 step
- free radical — 2 step

→ **E⁺ addition**

$$>C=C< + E^+ \longrightarrow >\overset{+}{C}-\underset{E}{\overset{|}{C}}< \xrightarrow{Y^-} >\underset{Y}{\overset{|}{C}}-\underset{E}{\overset{|}{C}}<$$

$$>C=C< + E-Nu \longrightarrow >\underset{E}{\overset{|}{C}}-\overset{|}{\underset{|}{C}}-Nu$$

Reagent — Product

Ad E^2 Mechanism, Bimolecular E⁺ addition → Mostly यही Mech होता है

↳ Through cyclic halonium ion or a carbo-cation intermediate

↳ Some case में AdE3 Mech भी होता है

$$>C=C< + Br_2 \rightleftarrows >\underset{\pi\text{-complex}}{\overset{Br_2}{\overset{|}{C}=C<}}$$

$$>\overset{Br_2}{\overset{|}{C}}=C< + Br^- \longrightarrow >\underset{Br}{\overset{|}{C}}-\overset{Br}{\overset{|}{C}}< + Br_2$$

यदि π complex बना रहे तो AdE3 होगा

⟹ Increase the polarity & ion solvating ability of the solvent, also stabilizes a carbocation more than the halonium ion intermediate & enantioselectivity को decrease करता है

↳ तो anti addition कम हो जाएगा {syn + anti}

→ Mainly anti addition, cyclic halonium आयन बनाते हैं इस पर both side से attack होता है, so दो product बनाते हैं

as

cis-2-butene + Br_2 → cyclic halonium ion (achiral)

→ a + b

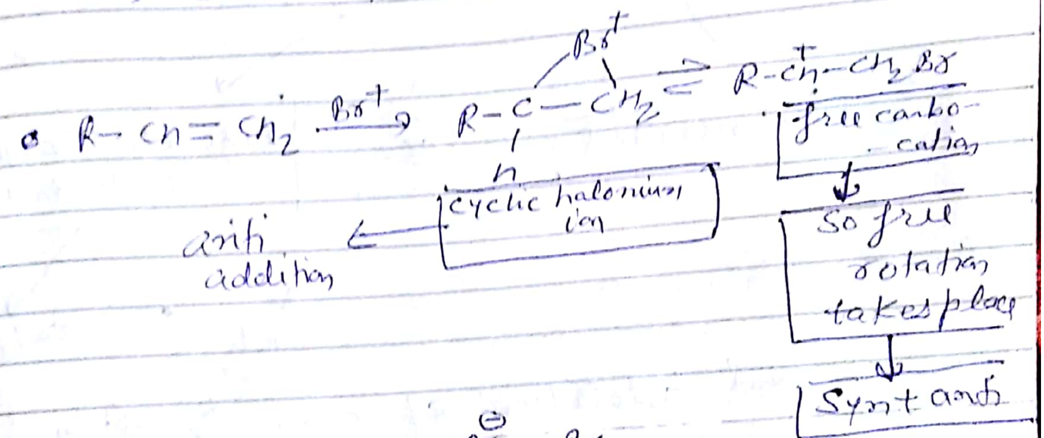
Two product

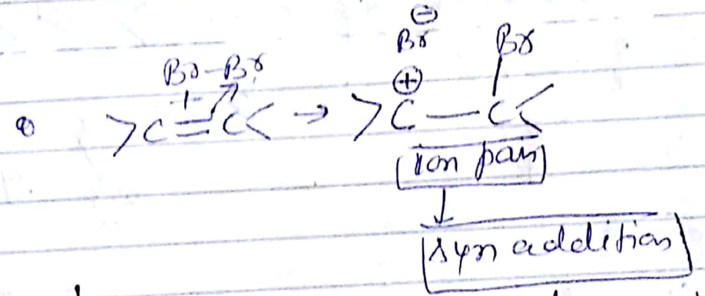
racemic mixture

(X) (as) Addition of X_2 → E+ addition

→ 2 step

→ Carbocation or cyclic





→ If the intermediate involved is the ion-pair. It could collapse faster than rotation about the C–C. So syn addition takes place.

→ But यदि carbocation free है then C–C bond के around free rotation

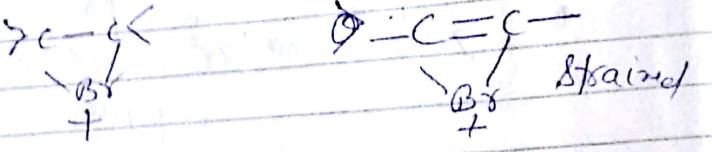
Syn addition → एक alkene aryl gp के साथ conjugated हो तो syn-addition dominant हो जाता है since ion pair का formation होता है

- **Bromination** → cyclic, anti 2 steps carbocation को stabilize करने वाला factor ↑ होता है
- **Chlorination** → same, but it is not as stereospecific as bromination.

$C=C + X_2$

- concerted (or)
- discrete charged intermediate
  - cyclic
  - or carbocation

→ E^+ addition of alkene > alkyne



cis-alkene + Br_2 → ± Mixture (cis trans ±)

trans-alkene + Br_2 → meso

trans + trans → meso

(8) Aliphatic system → Normally cyclic or bridged ion involve होता है

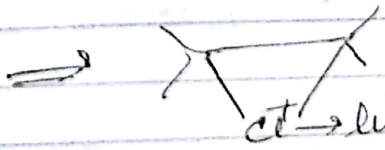
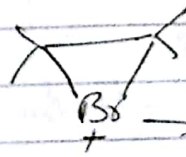
(X) Aromatic system → as Styrene
Borderline case होता है

If Phenyl ring has electron releasing gr
→ Sufficient stabilization
→ allow carbocation intermediate

If Ph-gr has e⁻ withdrawing gr
→ Bridged intermediate
→ Syn + anti
→ more

⇒ cyclic alkene →  + Br_2 → ?
Trans, anti parallel intermediate, cyclic halonium ion

→ >C—C< → यदि यह symm. है, तो Nu किसी भी side पर attack कर सकता है
(+) → But यदि यह ~~unsubstituted~~ & unsymm है, तब Nu mainly highly substituted C पर attack करेगा।

⇒  & 
Cl → less stable
↓
more E·N, weaker bridging gr, so lesser selectivity

Br → more stable
Since gr is less E·N than Cl, so यह +ve charge को better करके to accommodate कर सकते है So has more selectivity, Since gr is ~~no~~ has stronger

(8) **Selectivity** → Measure of a compound's ability to ~~determine~~ discriminate b/w different reaction position, indicated by ratio of rate constant (K_1/K_2)

↳ More the reactive, more the selective

⇒ **Markownikoff's rule** → Based on the stability of carbocation

⇒ **Addition of HX** → like to X_2

↳ Regio selectivity acc. to M. Rule

↳ Reactivity of alkyne to E+ addition increased by e^- releasing substituent & increased by e^- withdrawing substituent.

⇒ **Peroxide effect or Anti M. Rule** → Free radical Mech.

$CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br$ (obtained)

↳ $CH_3-\underset{Br}{CH}-CH_3$ (not obtained)

Mech

① $RO-OR \xrightarrow[\text{homolysis}]{h\nu} 2R\dot{O}$ alkoxy radical

② $R\dot{O} + HBr \rightarrow ROH + \dot{B}r$

③ $CH_3-CH=CH_2 \xrightarrow{\dot{B}r} CH_3\dot{C}HCH_2Br$ (2°) (More stable)

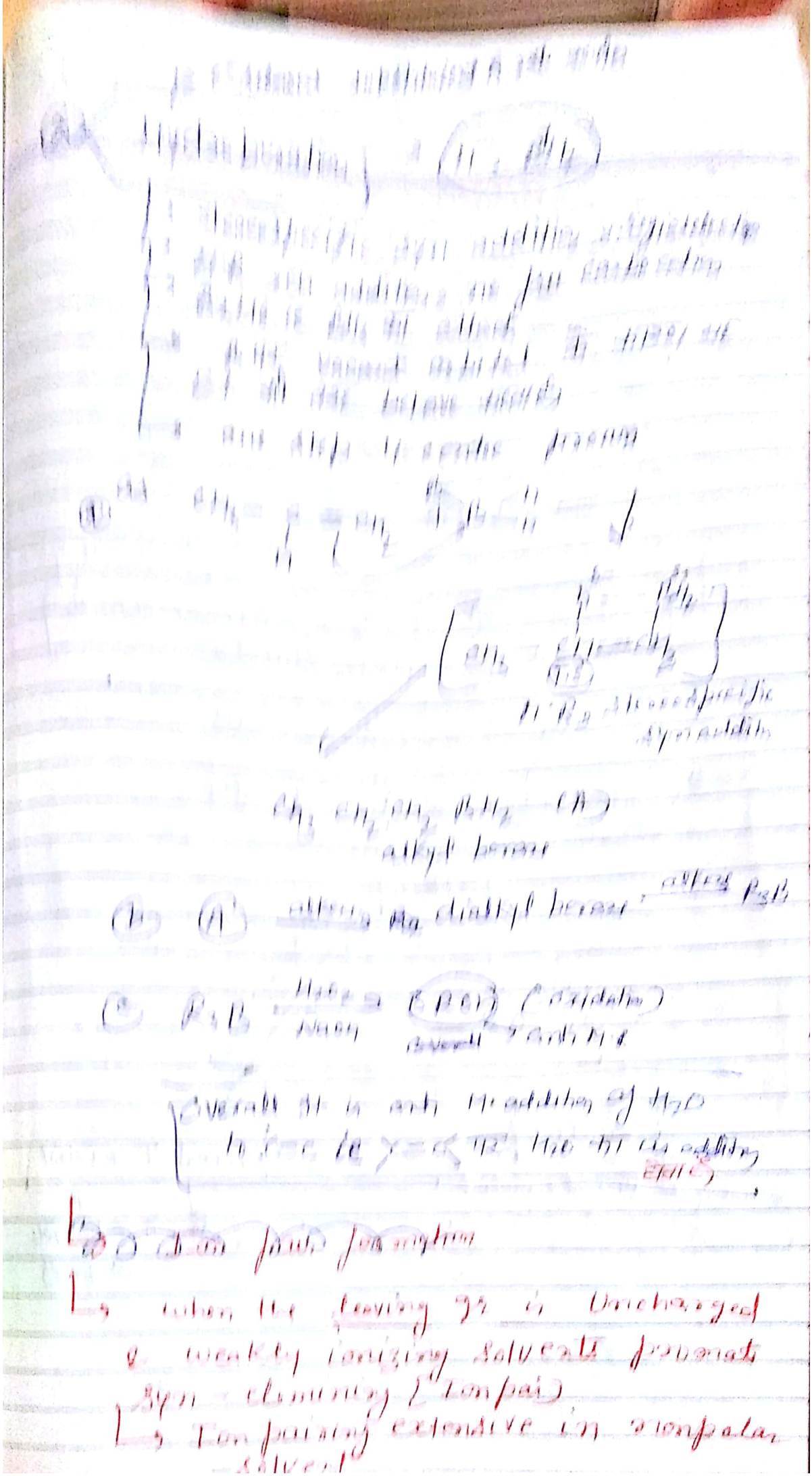
↓ HBr

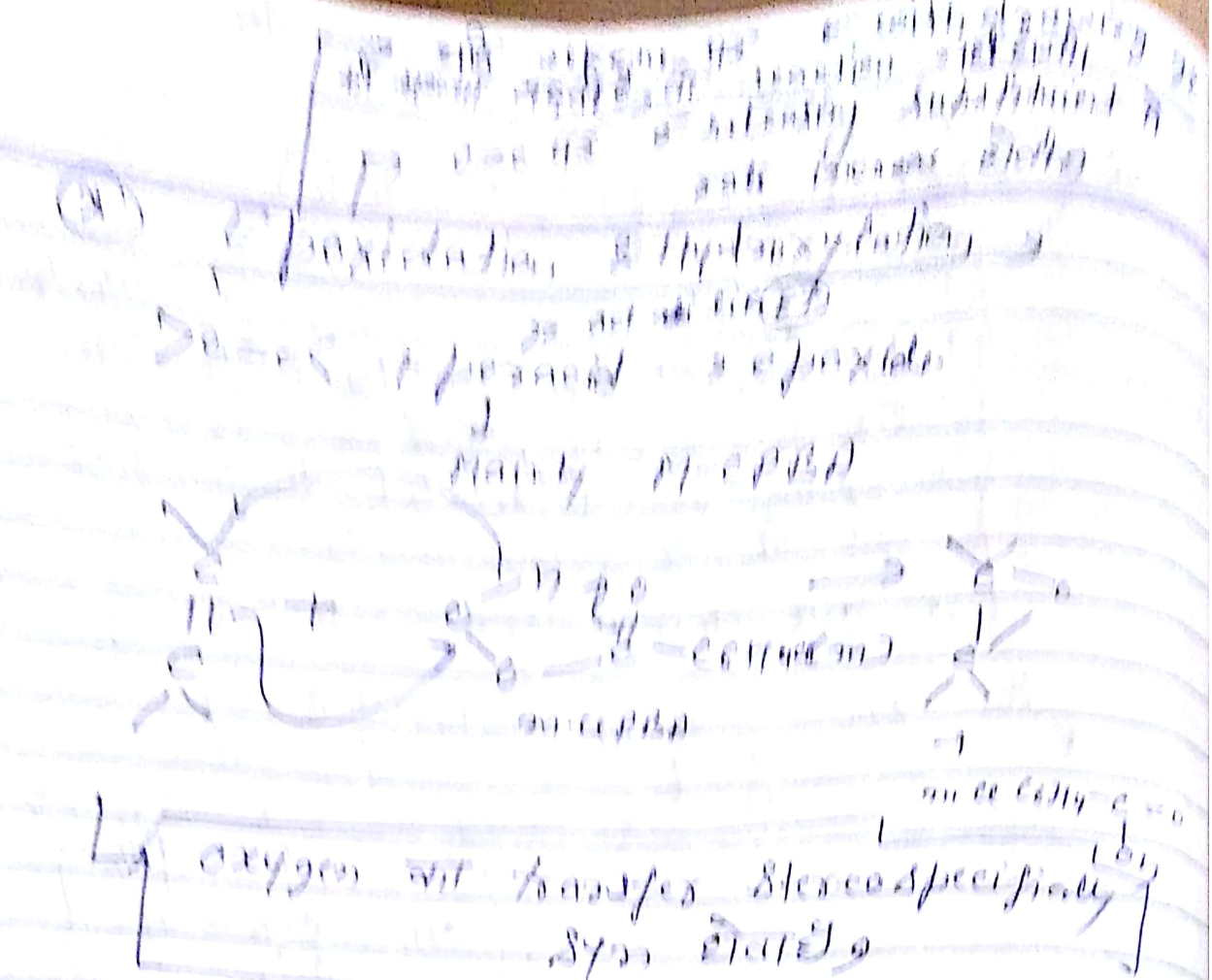
$CH_3CH_2CH_2Br + \dot{B}r$ (obtained)

$CH_3-CH=CH_2$ ↓ $\dot{B}r$ → $CH_3-\underset{Br}{CH}-\dot{C}H_2$ 1° (Less stable)

✗

$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}$

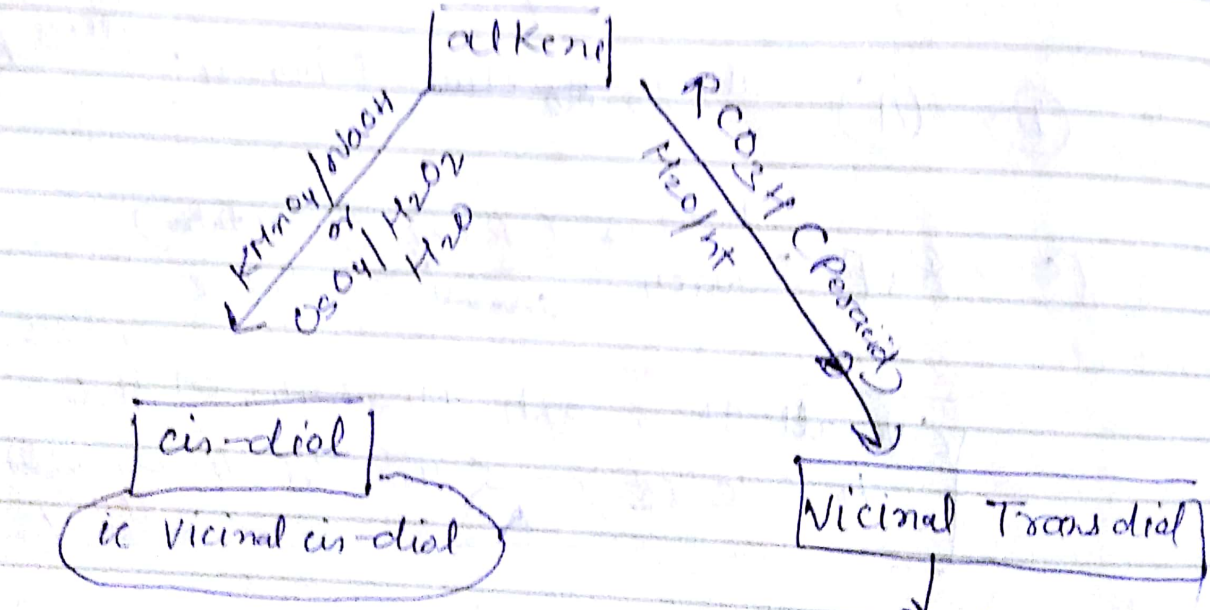




oxygen will transfer stereospecifically
syn addition

cis → cis , trans → trans

Hydroxylation of alkene



I.° Inversion of config. takes place as the acid as nucleophile

b) alkene + peracid → epoxide

[illegible]

epoxide ↓ H_2O/H^+ (acid catalysis) → (vicinal trans diol)

I.° cyclo alkene + peracid → cyclo alkene epoxide ↓ diaxial (trans) product

Addition of $KMnO_4$ →

(Ex) Alkene $\xrightarrow[KMnO_4]{alkaline}$ cis-diol

as $R-CH=CHR \xrightarrow[KMnO_4]{alkaline}$ ~~cis-diol~~ $R-CH(OH)-CH(OH)R$ cis-diol

(M) $KMnO_4 \rightarrow K^+ + MnO_4^-$

$RCH=CHR + MnO_4^- \rightarrow$ R-CH—CH-R with the two O atoms bonded to Mn(=O)(O) in a ring (not isolated) — cyclic manganese ester

↓

$R-CH(OH)-CH(OH)R$ (cis) $\xleftarrow{OH^-}$ $R-CH(OH)-CH(OMnO_2^-)R$

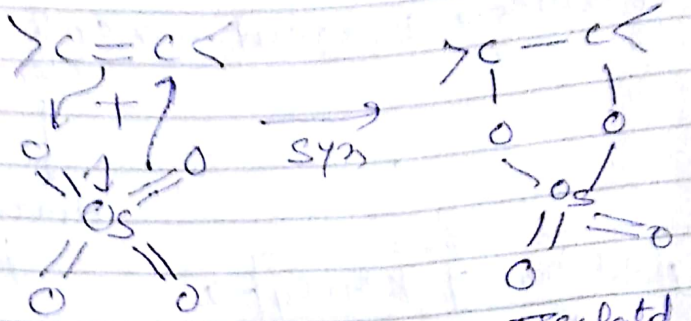
Reaction with OsO_4 (cis)

$$>C=C< \xrightarrow[\text{(ii) } H_2O_2/H_2O]{\text{(i) } OsO_4} >C(OH)-C(OH)<$$

cis diol

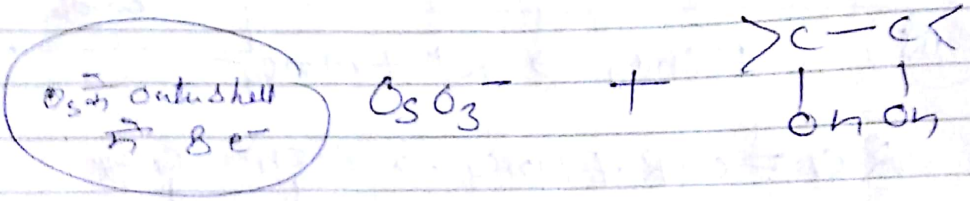
↳ Hydroxylation on the less hindered side of alkene takes place.

Mech →



Isolated

$\xrightarrow{H_2O_2}$



(A) Hydration of alkene → H_2O ka addition

(a) Acid catalyzed addition of H_2O

(b) Oxymercuration, Reduction

(a) Acid – catalyzed addition of water

$>C=C< + H_2O \xrightarrow{H^+} >C(H)-C(OH)<$ (alcohol)

- acc. to M. Rule
- Formation of Most Stable carbocation

(i) $>C=C< + H^+ \underset{\text{slow}}{\rightleftharpoons} >C(H)-C^{\oplus}<$

(ii) $>C(H)-C^{+}< + H_2O \xrightarrow[-H^+]{\text{fast}} >C(H)-C(OH)<$ (Product)

More Stable carbocation

[reaction of alkene with mercuric acetate in aq THF]

(b) Oxymercuration Reduction

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

[M. Rule]

[overall reaction is Addition of HgOAc]

[Mech]

(i) $Hg(OAc)_2 \rightarrow \overset{\oplus}{Hg}OAc + AcO^{\ominus}$

(ii) $R-CH=CH_2 + \overset{\oplus}{Hg}OAc \rightarrow R-CH\!-\!CH_2$ (bridged $\overset{\oplus}{Hg}OAc$)

(iii) $R-CH-CH_2$ (bridged $\overset{\oplus}{Hg}OAc$) $+ H_2\ddot{O} \rightarrow R-\underset{\overset{\oplus}{O}H_2}{CH}-CH_2HgOAc$

[SN² type]

(iv) $R-\underset{\overset{\oplus}{O}(H)H}{CH}-CH_2-HgOAc \xrightarrow{AcO^{\ominus}} R-\underset{OH}{CH}-CH_2HgOAc + AcOH$

(v) $R-\underset{OH}{CH}-CH_2HgOAc \xrightarrow{NaBH_4} CH_3-\underset{OH}{CH}-CH_3 + Hg + AcO^{\ominus}$

[NaBH₄ convert C–Hg to C–H bond]

(3) H_2O का addition more substituted carbon पर होता है

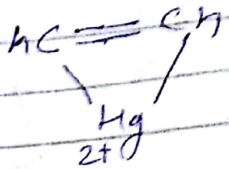
(4) Acid catalysed Hydration of alkyne

- acc. to M. Rudy
- require mercuric ion

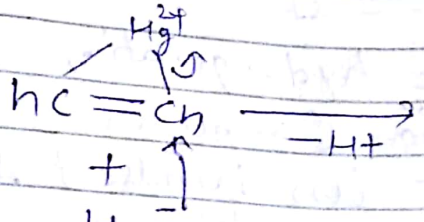
$HC\equiv CH \xrightarrow[H_2O]{Hg^{2+}, H_2SO_4} CH_3CH$

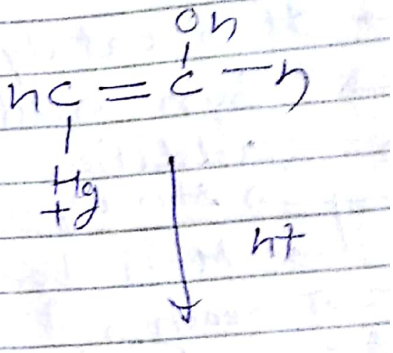
Mech

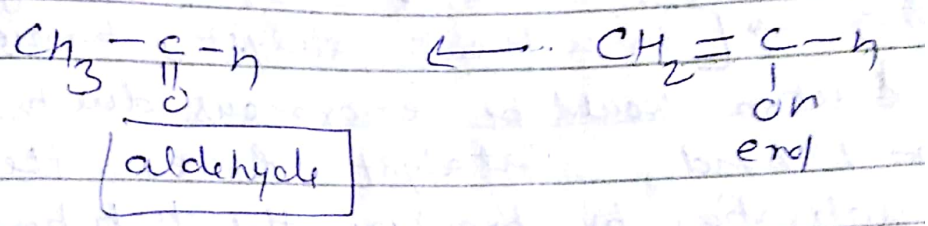
(1) $CH\equiv CH + Hg^{2+} \rightleftharpoons HC\equiv CH$ (Hg^{2+})



(II)







aldehyde

end

overall reaction

$R-C\equiv CH \xrightarrow[H_2SO_4]{Hg^{2+}, H_2O} CH_3COCH_3$