Alkenes

Organic Chemistry

Chemical Reactions

Hydrogenation Reaction

Syn and Anti Addition

Halogenation Reaction

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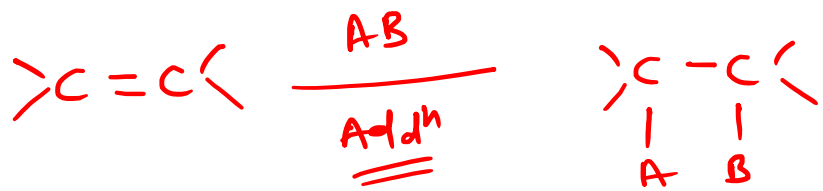
Alkene Chemical Properties

- **Alkenes** are more reactive than alkanes due to the presence of the double bond (σ+π)
- Types of Reactions:



(I) Addition Reaction

1. **Addition of Hydrogen (Hydrogenation)**
2. **Addition of Halogen (Halogenation)**
3. **Addition HX (Hydrohalogenation)**
4. **Addition of Water**
5. **Addition of Oxygen**
6. **Addition of O3 (Ozonolysis)**
7. **Addition of H2SO4**
8. **Addition of Alkene**

Alkene Chemical Properties

- **Alkenes** are more reactive than alkanes due to the presence of the double bond (σ+π)
- Types of Reactions:

(II) Substitution Reaction

(III) Oxidation Reaction

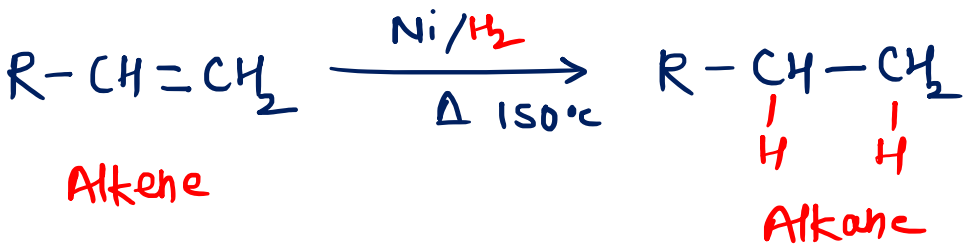
- ✓ **By Cold & dil. alkaline KMnO4**
- ✓ **Acidic KMnO4 and K2Cr2O7**
- ✓ **Hydroxylation**

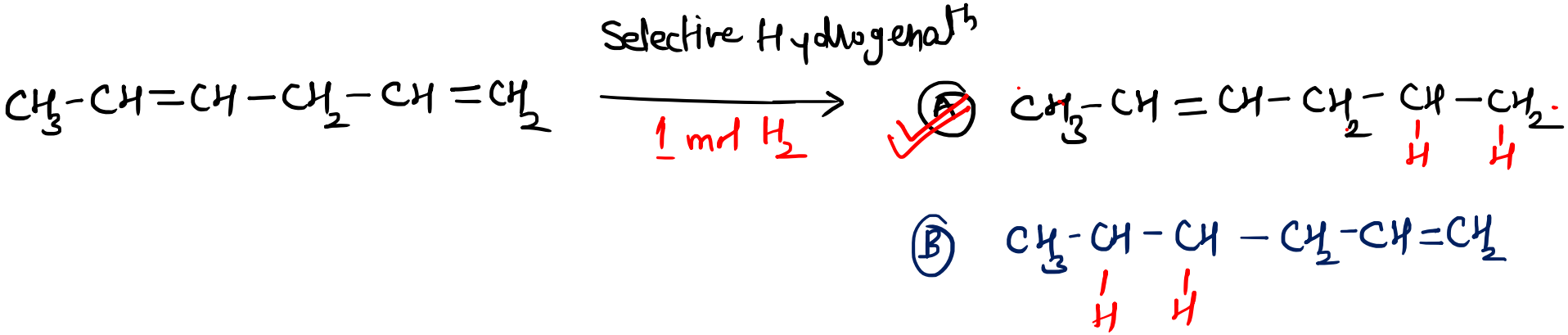
Alkene Chemical Properties

1. Hydrogenation of Alkene

- ✓ Sanderson & Sabatier Reaction
- ✓ Reducing Agent- Ni/H2 at 150-200°C

  Pt or Pd/ H2 at RT
- ✓ Syn Addition Reaction



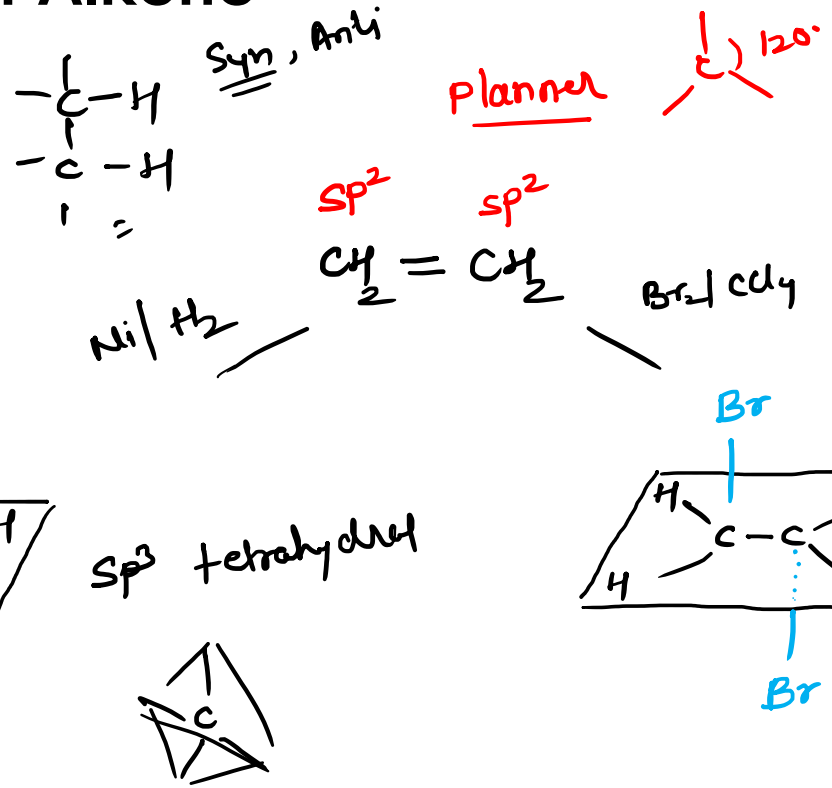


Alkene Chemical Properties

1. Hydrogenation of Alkene

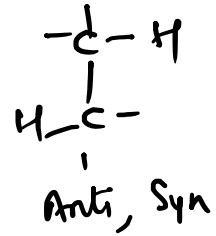
Syn Addition

Addition in **Same** Plane



Anti Addition

Addition in **Opposite** Plane



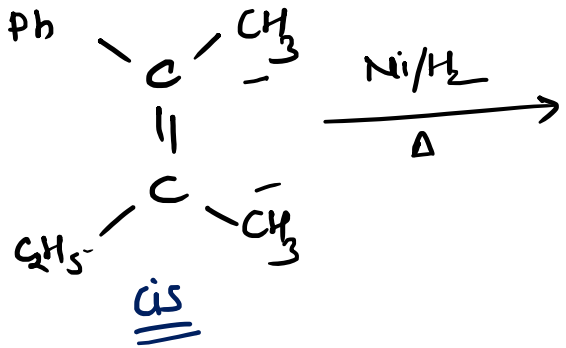
जहाँ जगह खली है वहां add कर दो

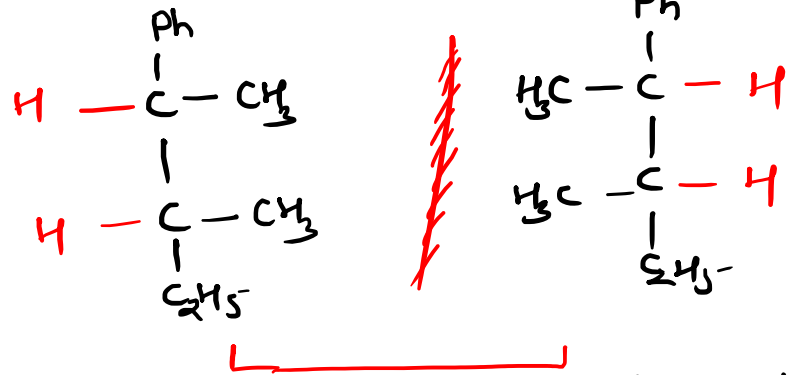
जहाँ जगह खली है वहां add कर दो,
फिर एक bond को rotate कर दो

Alkene Chemical Properties

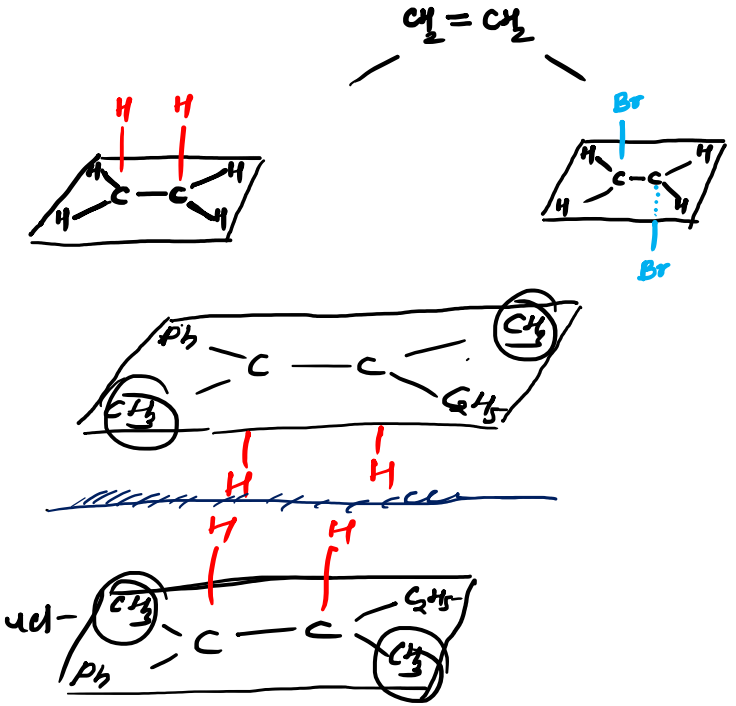
1. Hydrogenation of Alkene

Cis unsymmetrical alkene-Syn Addition- Racemic Mixture

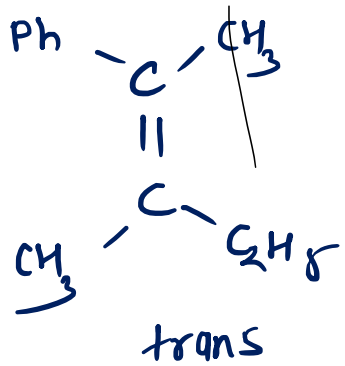


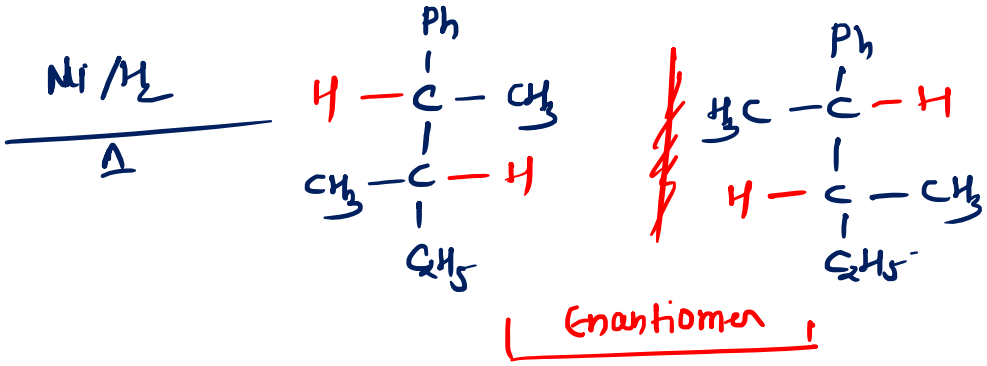


Enantiomer, optical Active, 2 product



Trans unsymmetrical alkene-Syn Addition- Racemic Mixture

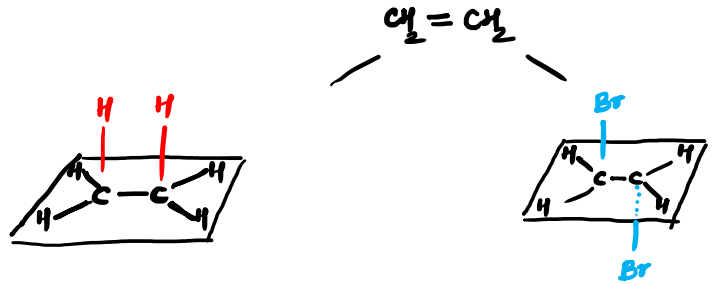




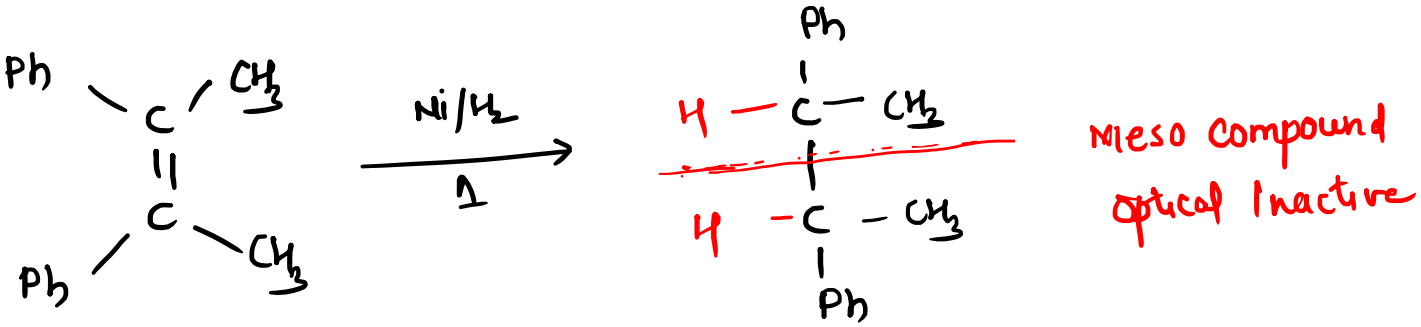
Enantiomer

Alkene Chemical Properties

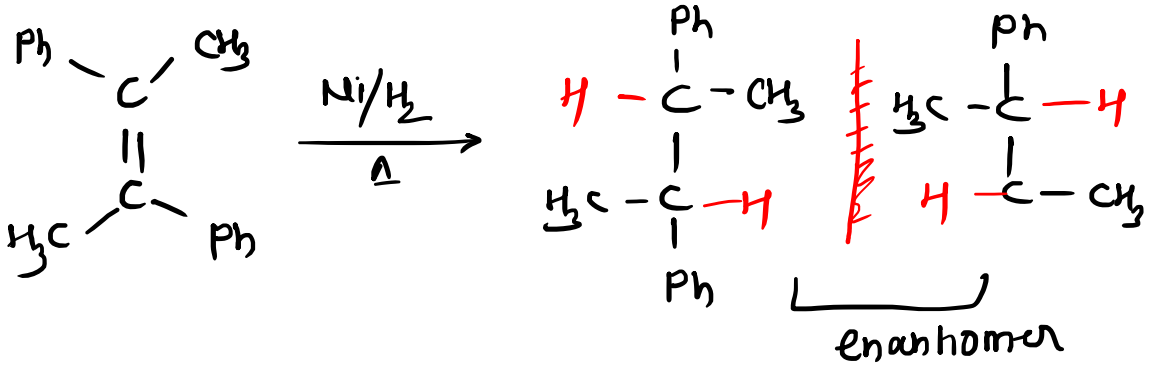
1. Hydrogenation of Alkene



Cis symmetrical alkene-Syn Addition- Meso Compound

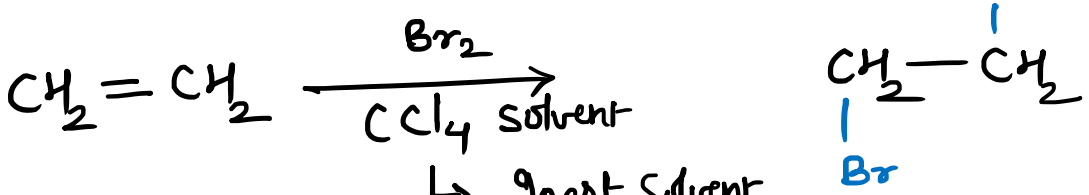


Trans symmetrical alkene-Syn Addition- Racemic Mixture



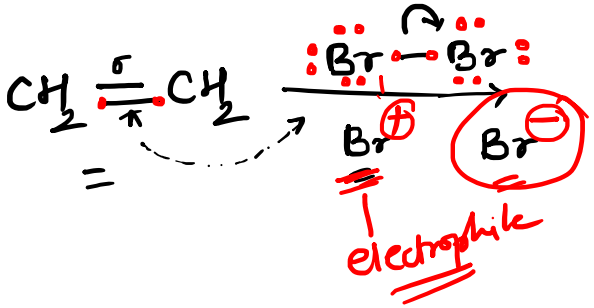
Alkene Chemical Properties

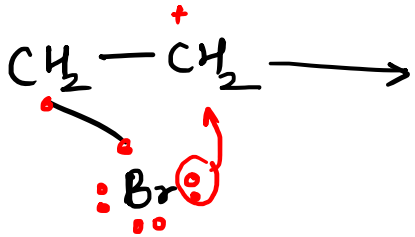
2. Halogenation of Alkene



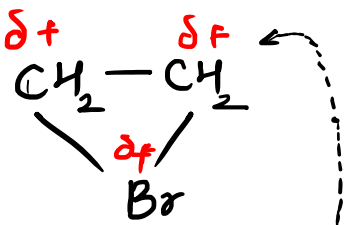
- ✓ Addition of halogen X_2 – Cl_2, Br_2
- ✓ Electrophilic (E+) Addition Reaction
- ✓ Anti Addition

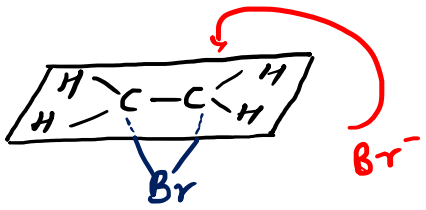
Mechanism



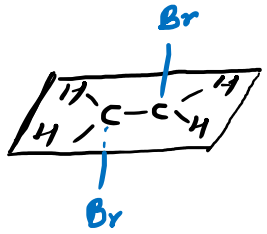


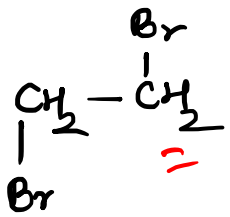
Non classical carbocation
- # More stable than carbocation
- # No Rearrangement
- # Complete octate





Anti Add^n

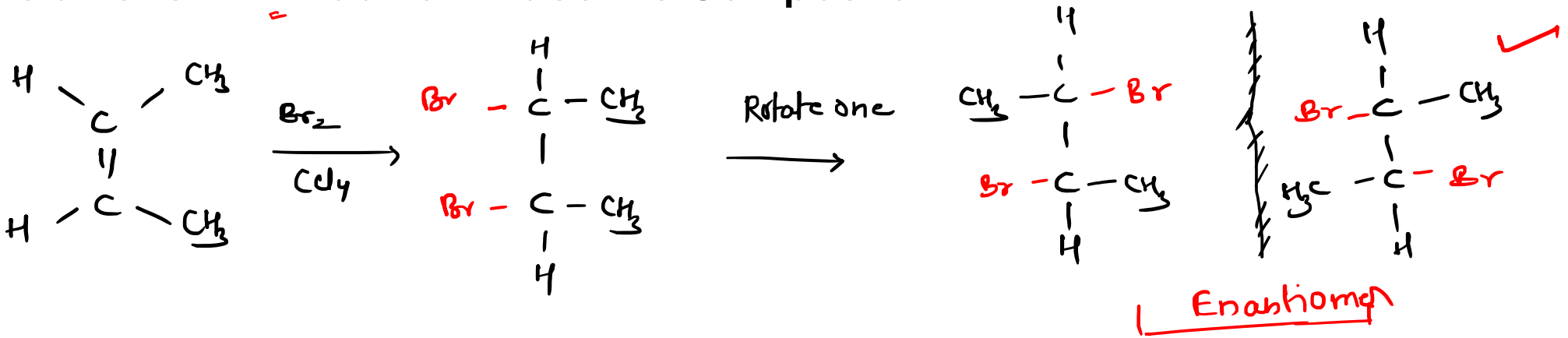




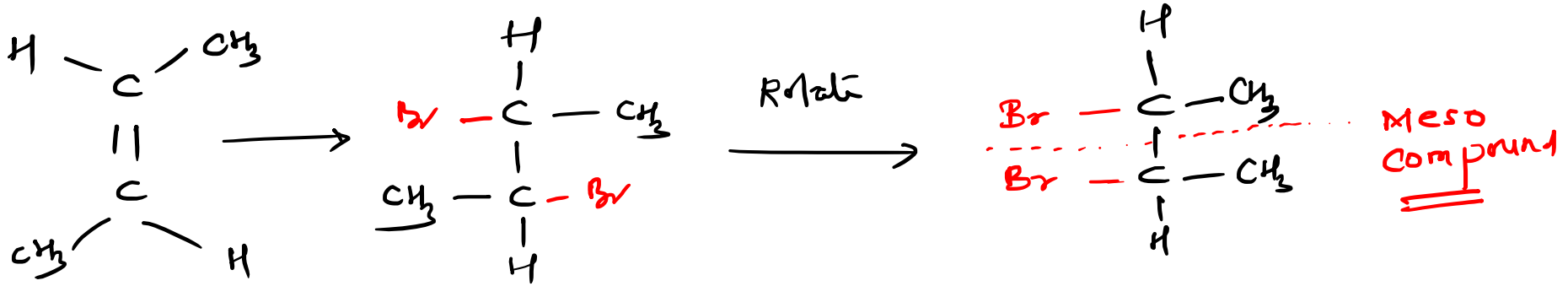
Alkene Chemical Properties

2. Halogenation of Alkene

Cis alkene-Anti Addition- Racemic Compound

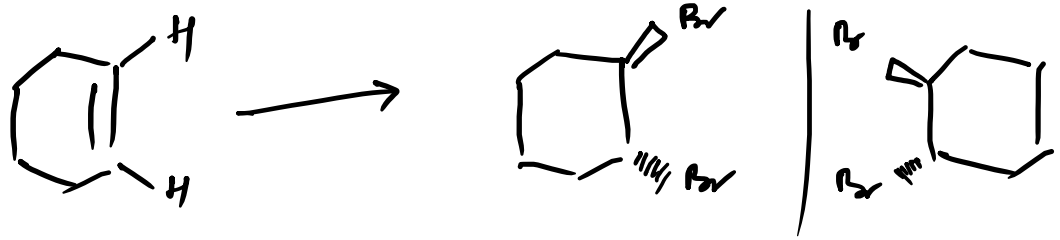


Trans alkene-Anti Addition- Meso Compound



Alkene Chemical Properties

2. Halogenation of Alkene



Alkenes

Organic Chemistry

Chemical Reactions

Hydrohalogenation

Morkovnikov's Rule

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Alkene Chemical Properties

3. Hydro-Halogenation of Alkene

HX - HCl, HBr

↳ Addition of HX -
↳ Electrophilic addition (E^+)
↳ Carbocation (Intermediate comp.)
↳ Carbocation Rearrangement
↳ Markovnikov's Rule can apply in Asymmetrical alkene
↳ Carbocation Rule > MO Rule

$CH_2=CH_2 \xrightarrow[CCl_4]{H^+Br} CH_3-\overset{+}{C}H_2 \longrightarrow CH_3-CH_2Br$

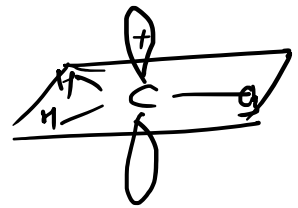
($CH_3-\overset{+}{C}H_2$: Carbocation)

Mechanism –

$CH_2=CH_2 \xrightarrow[CCl_4]{\delta^+ H \; Br \; \delta^-} CH_2^- - \overset{+}{C}H_2 \xrightarrow{I} CH_3-\overset{+}{C}H_2$ carbocation

Electrophilic Addⁿ

$CH_3-\overset{+}{C}H_2 \xrightarrow{Br^-\ (II)} CH_3-CH_2-Br$



Ex-

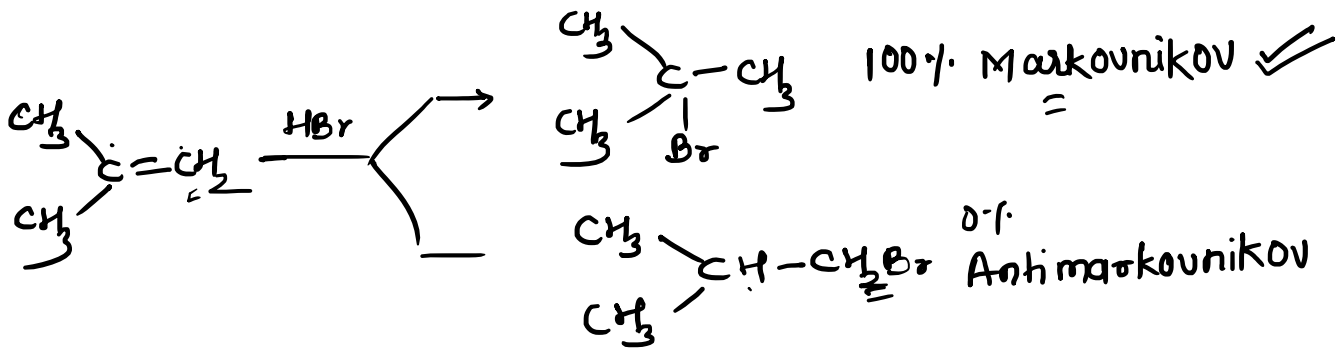
$CH_3-CH=CH_2 \xrightarrow[CCl_4]{HBr} CH_3-\overset{+}{C}H-CH_3 \longrightarrow CH_3-\underset{Br}{CH}-CH_3$

Alkene Chemical Properties

Markovnikov's Rule

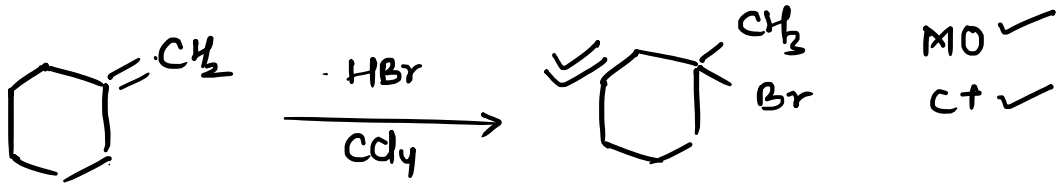
- In organic chemistry, **Markovnikov's rule** or **Markownikoff's rule** describes the outcome of some addition reactions. The rule was formulated by Russian chemist Vladimir Markovnikov in 1870
- The rule states that with the addition of a protic acid HX or other polar reagent to an asymmetric alkene, the **acid hydrogen (H)** or **electropositive part gets attached to the carbon with more hydrogen substituents**, and the **halide (X) group or electronegative part gets attached to the carbon with more alkyl substituents**

Electrofile H^+ को वहां जोड़ो C=C के जिस कार्बन पे हाइड्रोजन ज्यादा है और Cl^-/electronegative को जिसमे हाइड्रोजन कम है

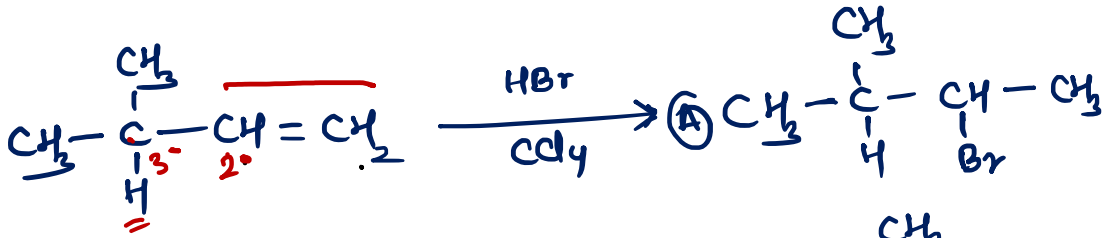


3. Hydro-Halogenation of Alkene

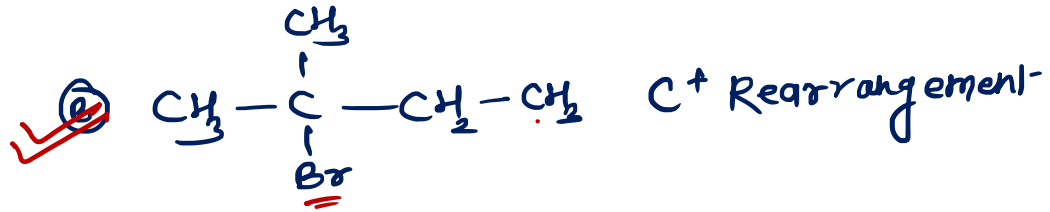
C^+ : $3^\circ > 2^\circ > 1^\circ$

↳ 

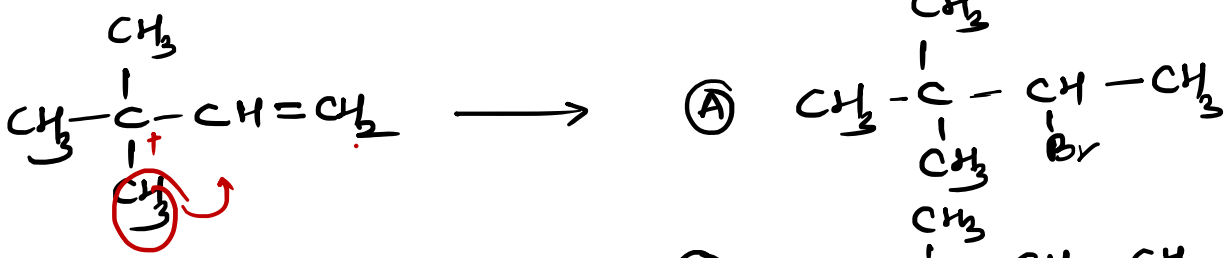
MO ✓
C^+ ✓

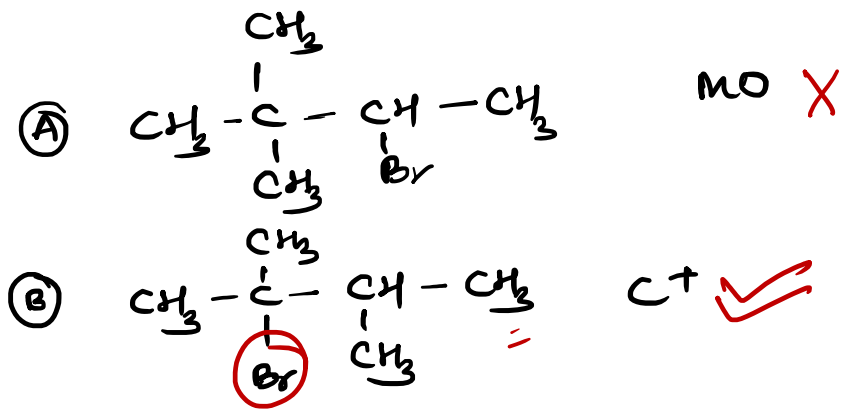
↳ 

MO ✗ XX



C^+ Rearrangement

↳ 

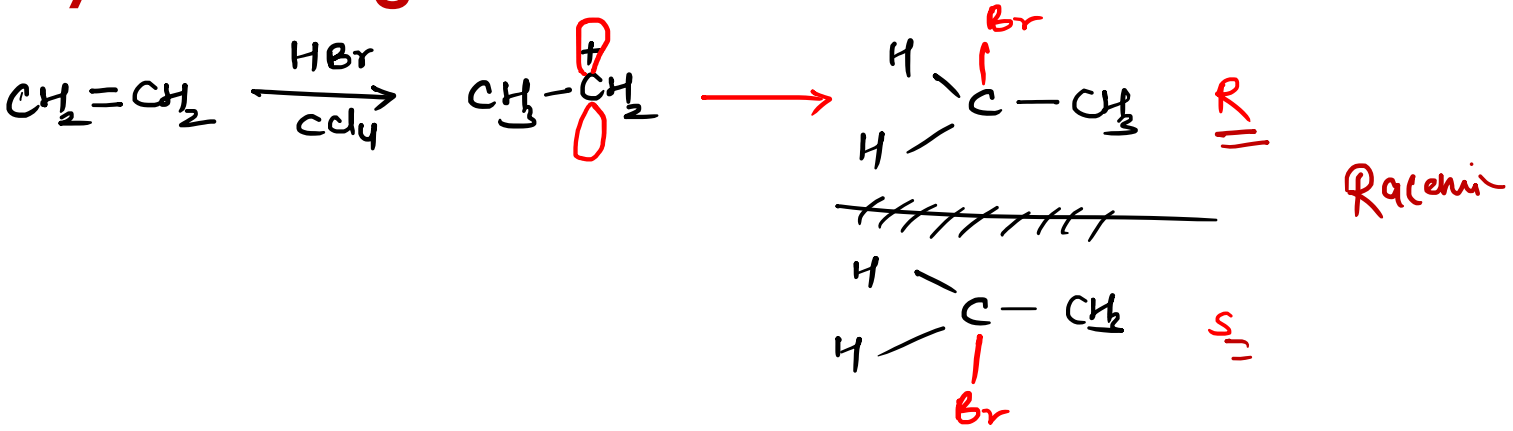


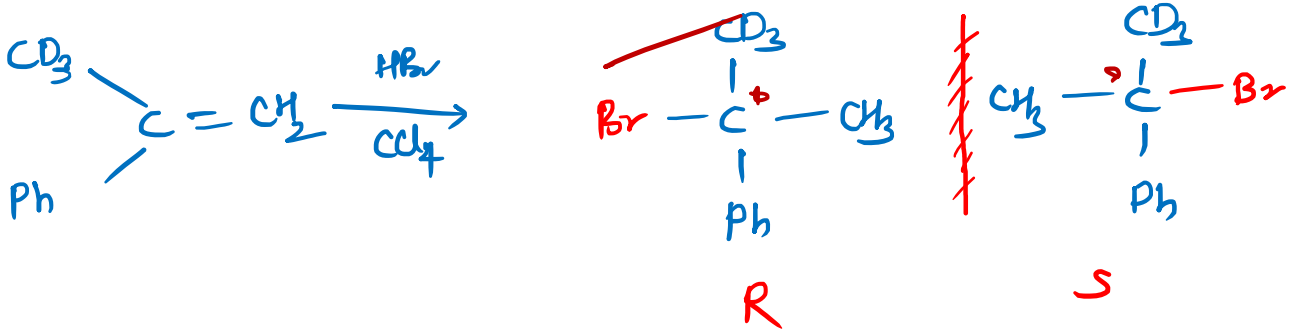
MO XXX

C^+ ✓

Alkene Chemical Properties

3. Hydro-Halogenation of Alkene

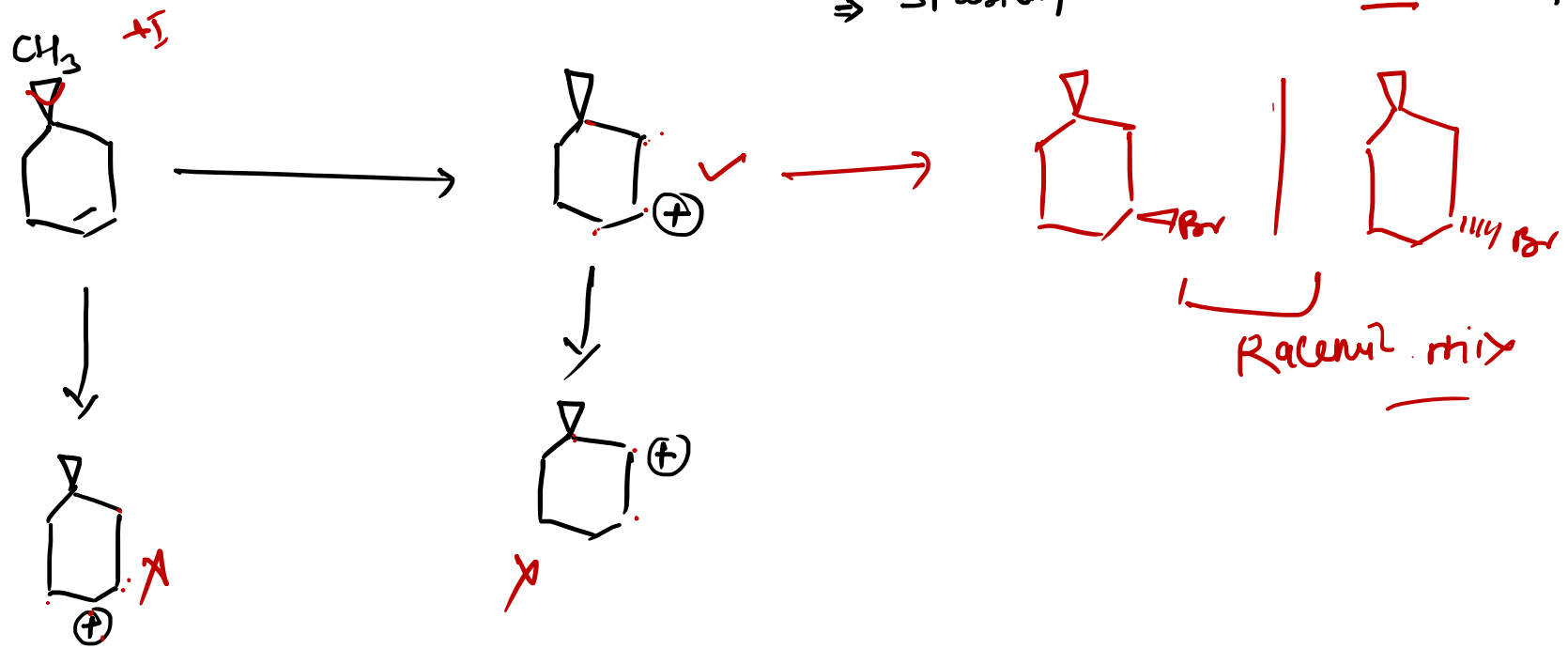




Alkene Chemical Properties

3. Hydro-Halogenation of Alkene

⇒ Stability Mech. - Resonance > Hyper conjugation > I effect



Alkenes

Organic Chemistry

Chemical Reactions

Hydration of Alkene

- ✓ 1. Acid Catalysed
- ✓ 2. Hydroboration/Oxidation
- ✓ 3. Oxymercuration/Demercuration

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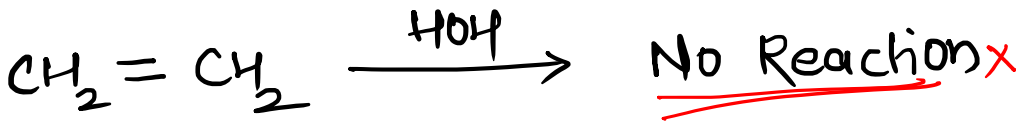
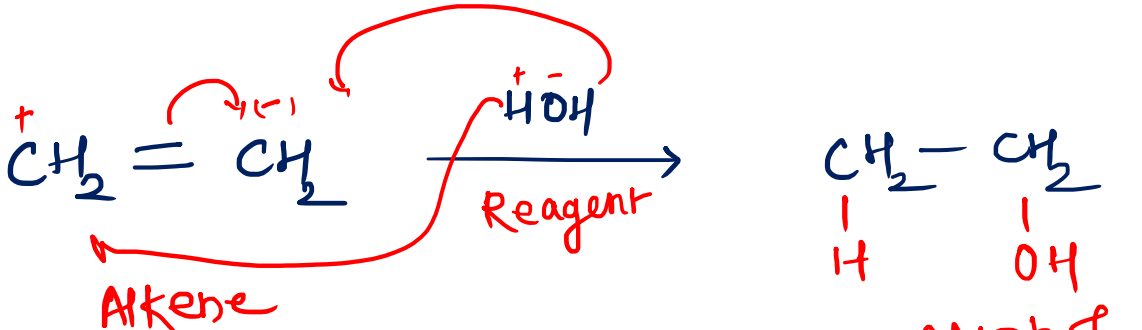
3. Hydration of Alkene

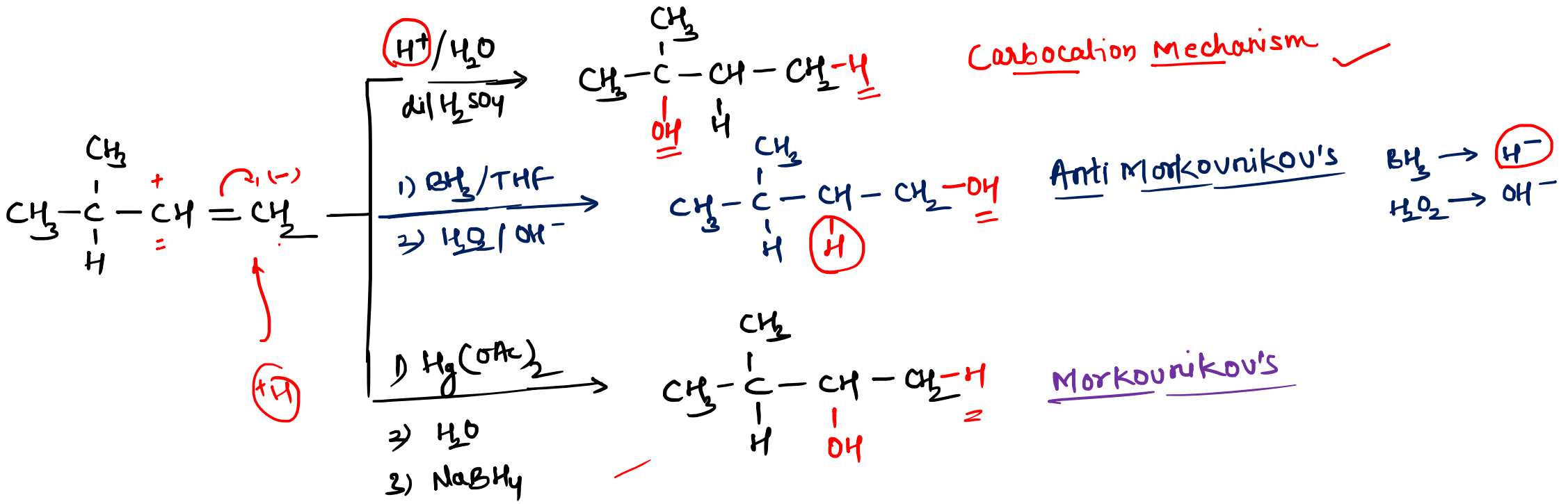


- ✓ 1. Acid Catalysed (dil H_2SO_4)
- ✓ 2. Hydroboration/Oxidation 1) B_2H_6/THF, 2) H_2O_2/OH^-
- ✓ 3. Oxymercuration/Demercuration 1)$Hg(AcO)_2$ 2) H_2O 3)$NaBH_4$/ OH^-



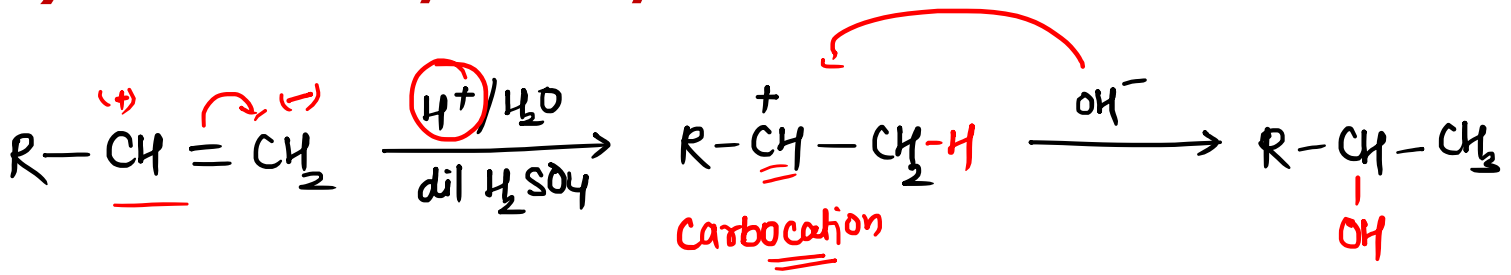
Alkene Chemical Properties

3. Hydration of Alkene



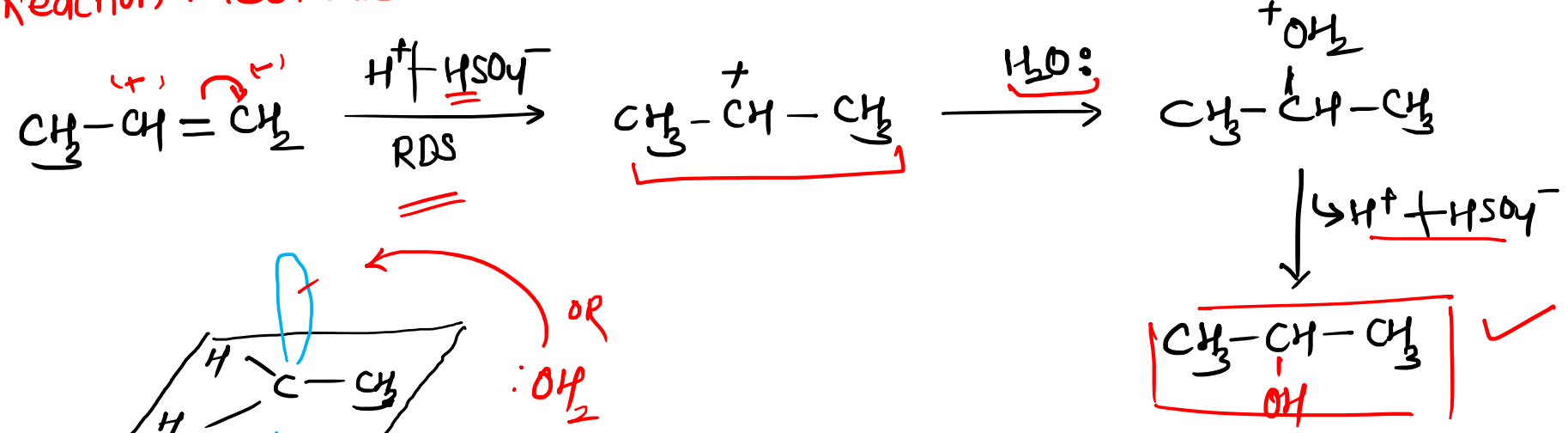
Alkene Chemical Properties

A) Acid Catalyzed Hydration



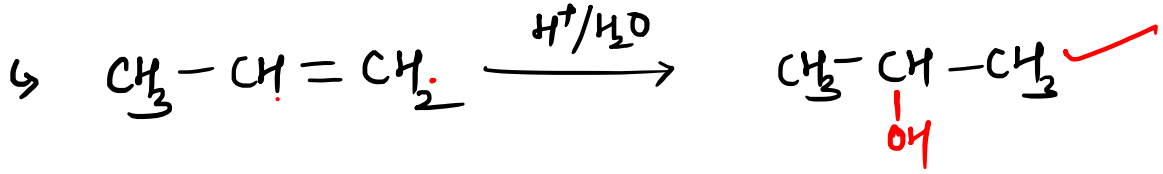
- ✓✓ E+ Addition Reaction
- ✓ Carbocation Intermediate
- ✓ Carbocation Rearrangement
- ✓ Rate - Stability of C+ before rearrangement

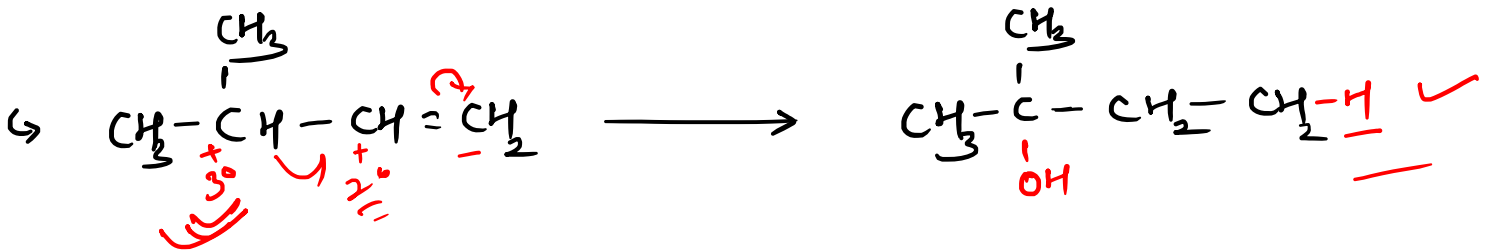
Reaction Mechanism -

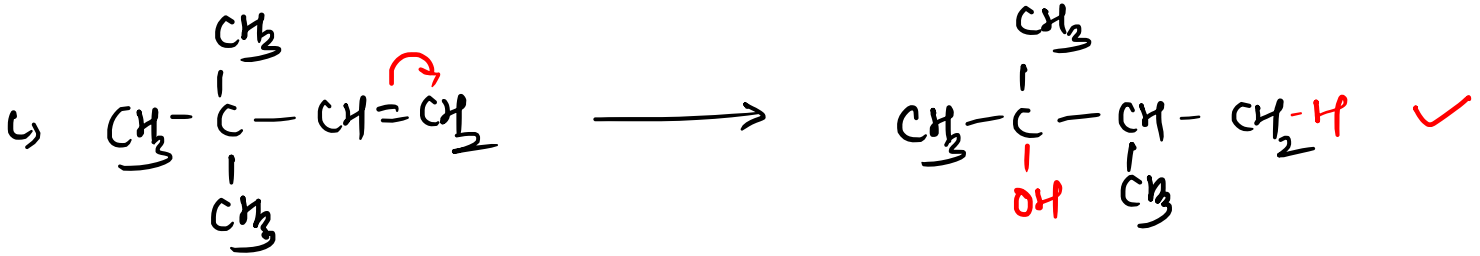


Alkene Chemical Properties

A) Acid Catalyzed Hydration



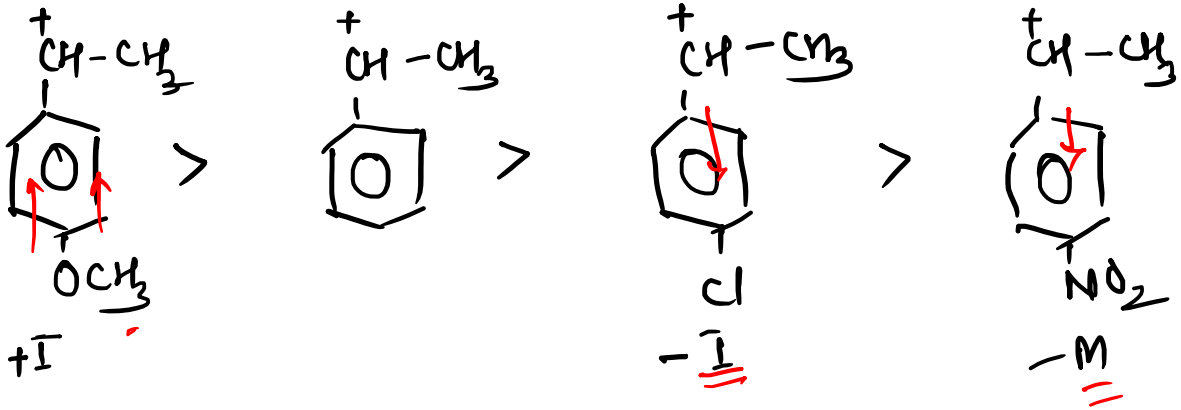


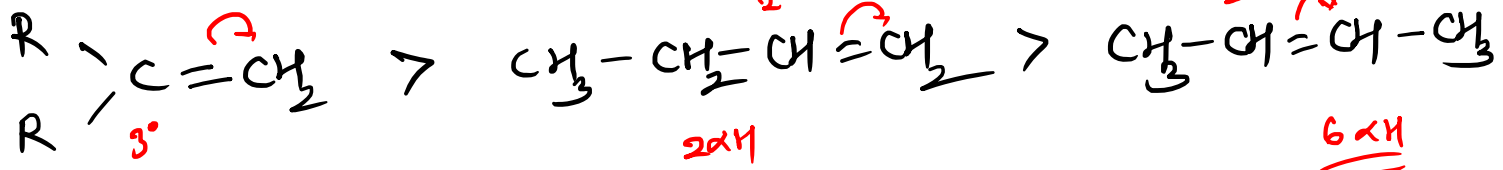


A) Acid Catalyzed Hydration

Rate of Hydrat^n (Acid catalysed)

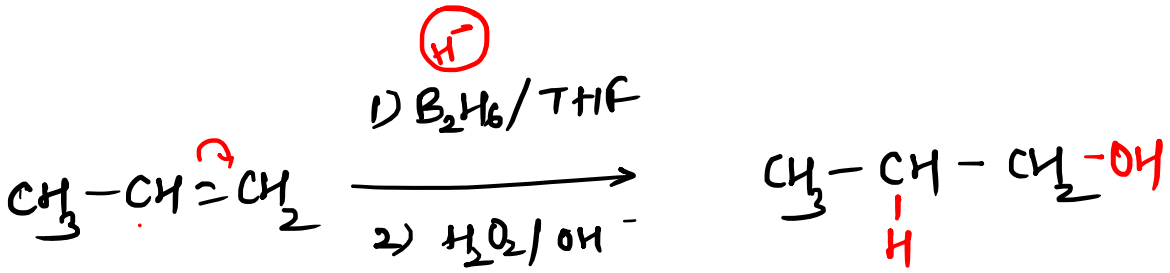
↳ C^+ $3^0 > 2^0 > 1^0$

↳ 

↳ 

Alkene Chemical Properties

B) Hydroboration/Oxidation



↳ (1) Anti Markovnikov's ✓

↳ (2) H^- ← BH_3 & OH^- ← H_2O_2

↳ (3) Rate $\propto \frac{1}{\text{steric hinderance}}$

↳ ✓ Syn Addition

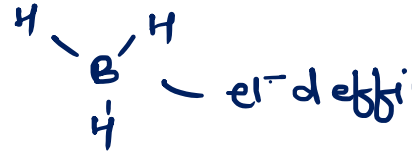
✓ Anti Markovnikov's

Hydrogen atom- add on less H-containing alkene C-atom

B) Hydroboration/Oxidation- Reaction Mechanism

I, Hydroboration :-

$B_2H_6 \longrightarrow 2BH_3$

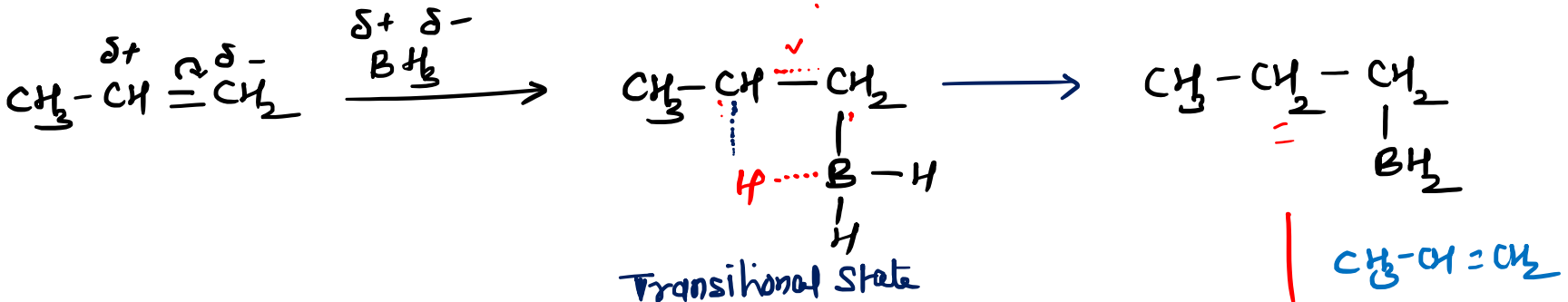


e⁻ deficient, unstable

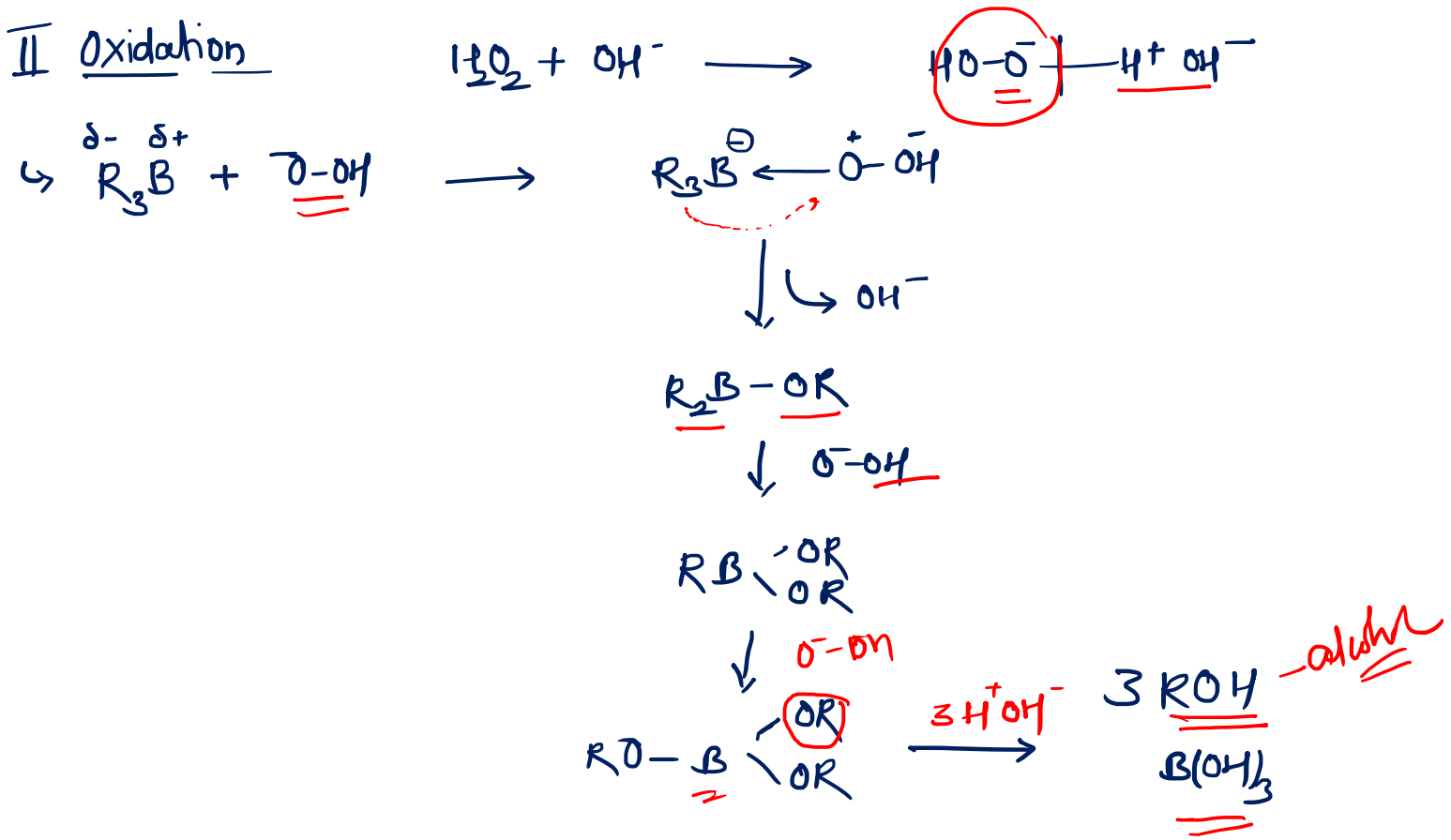
$\delta+ \quad \delta-$
BH_3

THF →  = prevent BH_3 to form B_2H_6

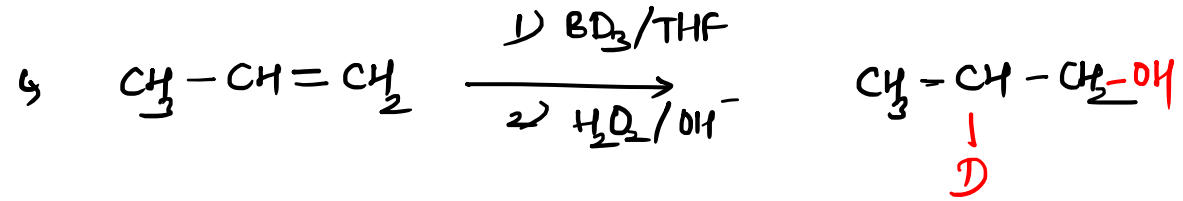
$\delta+ \quad \delta-$
BH_3

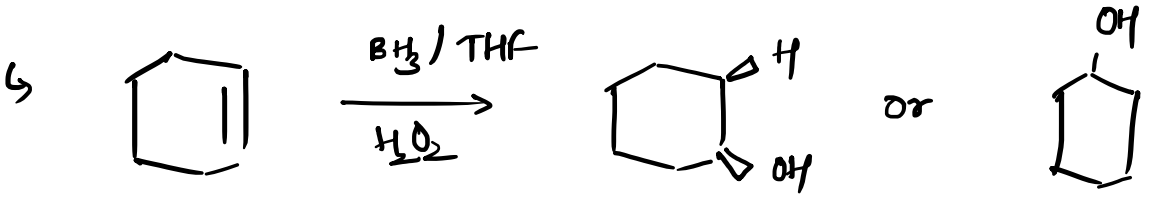


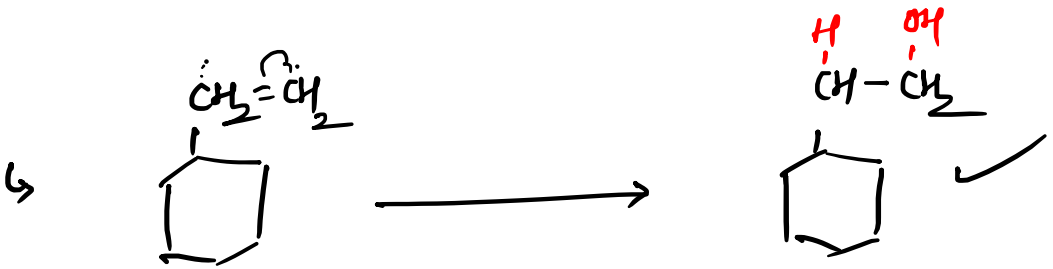
B) Hydroboration/Oxidation- Reaction Mechanism



B) Hydroboration/Oxidation- Reaction Mechanism

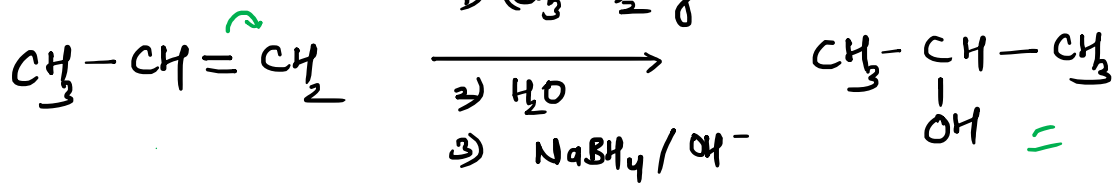




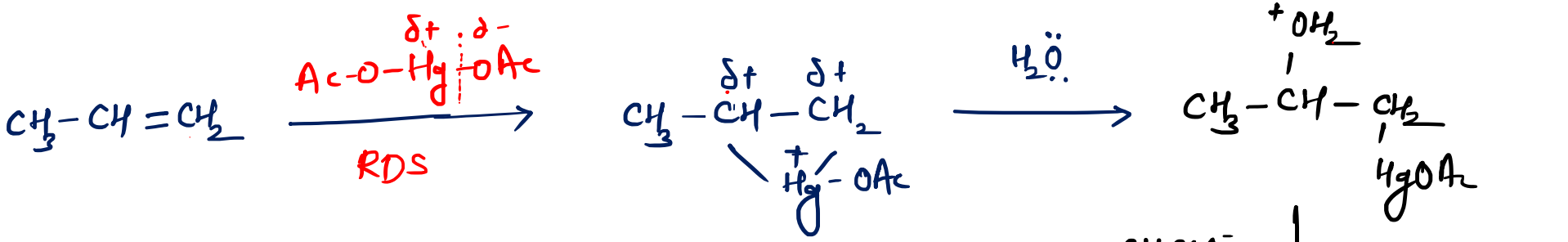


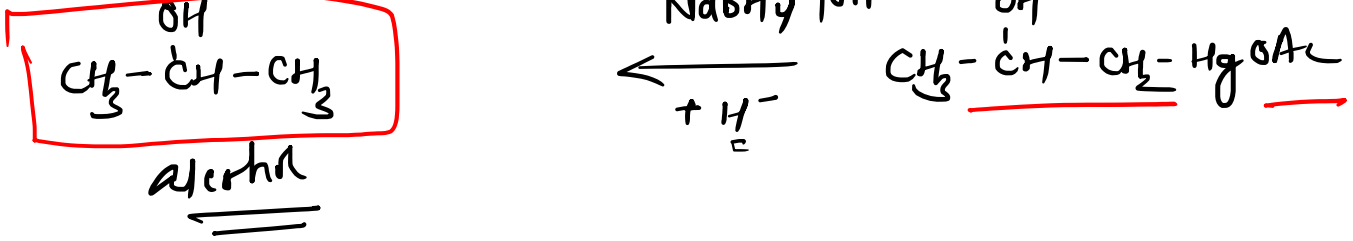
Alkene Chemical Properties

B) Oxymercuration & Demercuration



↳ MID Rule
↳ No- C^+ & rearrangement
↳ Syn or Anti addn





alcohol

Alkenes

Organic Chemistry

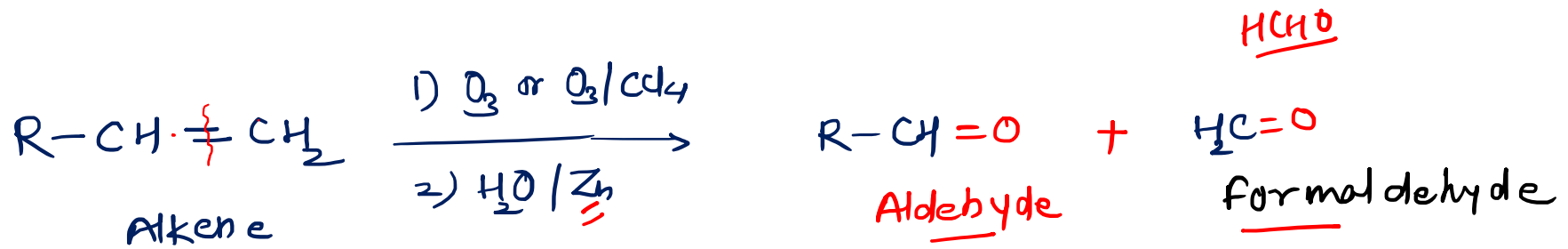
Chemical Reactions

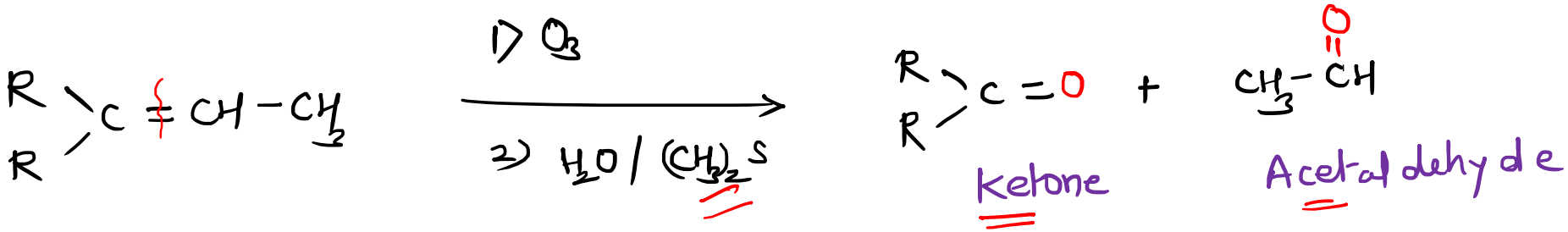
Ozonolysis of Alkene

B.Pharm. | POC-I | U 2 | L16

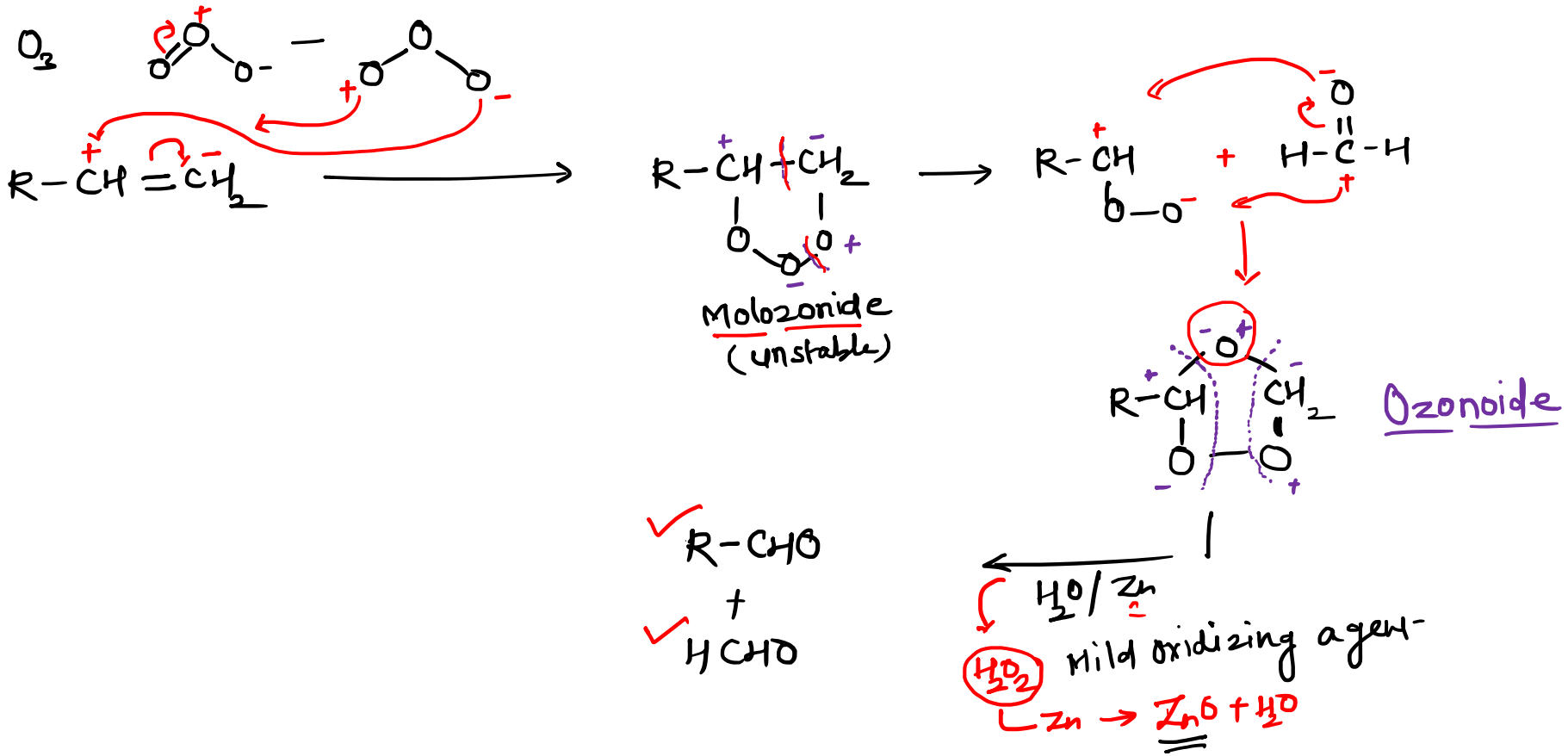
Alkene Chemical Properties

5. Ozonolysis of alkene or Addition of O3





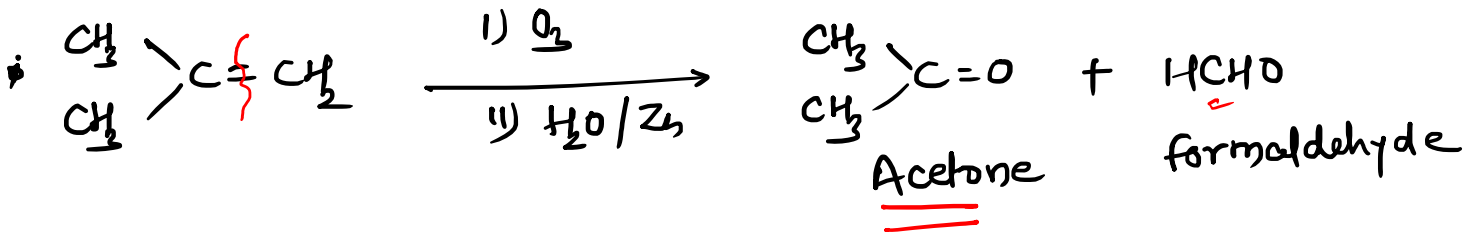
5. Ozonolysis or Addition of O3 : Mechanism

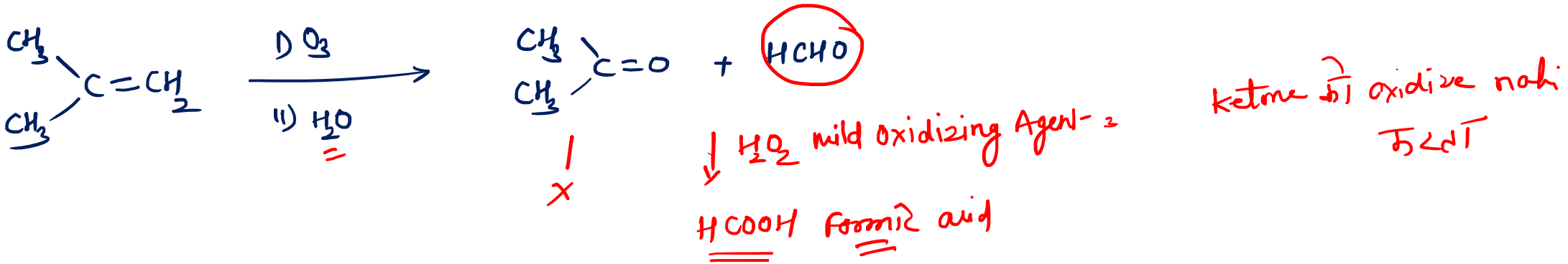


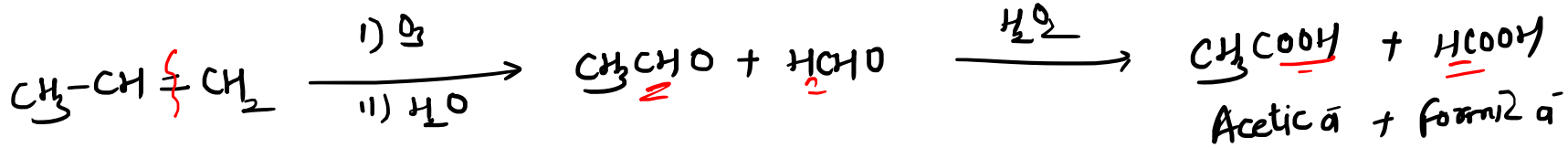
✓ R-CHO
+
✓ HCHO

Alkene Chemical Properties

5. Ozonolysis or Addition of O3







Alkene Chemical Properties

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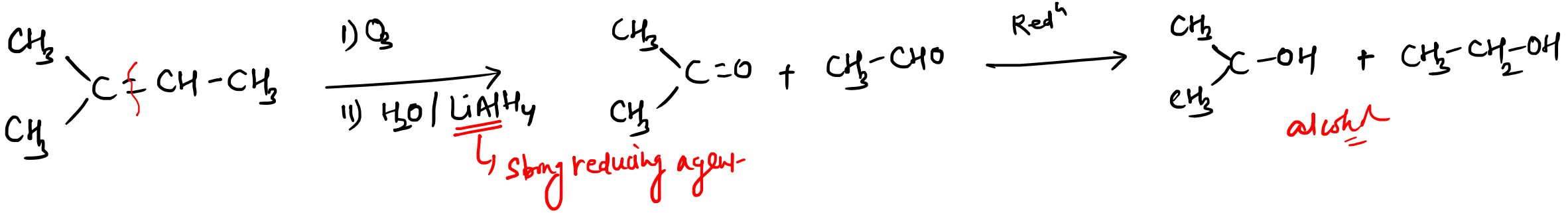
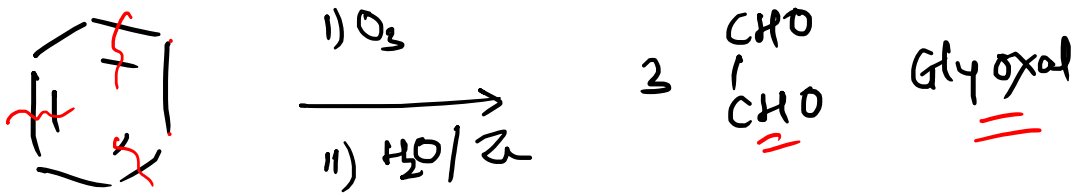
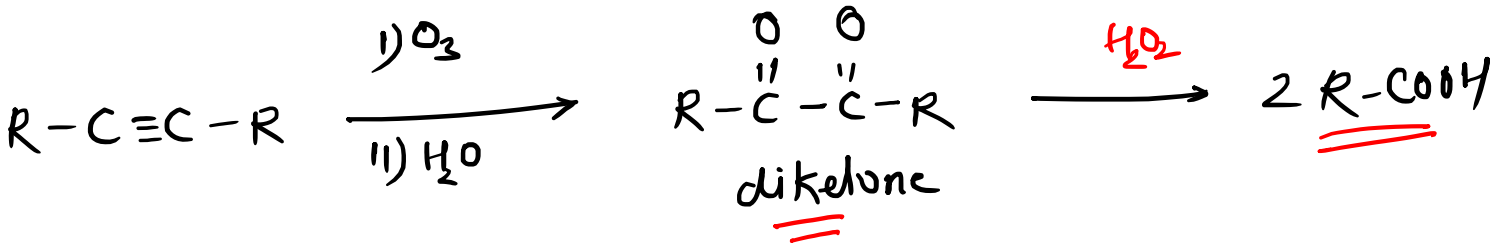






Alkenes

Organic Chemistry

Chemical Reactions

Substitution Reaction

Oxidation Reactions

B.Pharm. | POC-I | U 2 | L16

Alkene Chemical Properties

7. Substitution of Alkene by Halogen (Allylic substitution)

$CH_3-CH=CH_2 \xrightarrow{Cl_2/CCl_4} CH_3-\underset{Cl}{\underset{|}{CH}}-\overset{Cl}{\overset{|}{CH_2}}$

→ Halogenation Reaction
→ E+ Addition
→ Anti Addn

↳ $CH_3-CH=CH_2 + Cl_2 \xrightarrow{500^\circ C} \underset{Cl}{\underset{|}{CH_2}}-CH=CH_2$

→ Allylic H-atm is replaced by Cl-atom
→ At High temp - 500°C
→ Allylic substitution Reactn

7. Substitution of Alkene by Halogen (Allylic substitution)

Step 1. - chain initiation $Cl_2 \xrightarrow{\Delta} Cl^{\cdot} + Cl^{\cdot}$ homolytic fission

Step 2- Chain propogation -

$CH_2=CH-CH_2:H + Cl^{\cdot} \rightarrow HCl + CH_2=CH-CH_2^{\cdot}$ Allyl Radical

$CH_2=CH-\dot{C}H_2 + Cl:Cl \rightarrow CH_2=CH-CH_2Cl + Cl^{\cdot}$

Step 3 → Chain termination

$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$

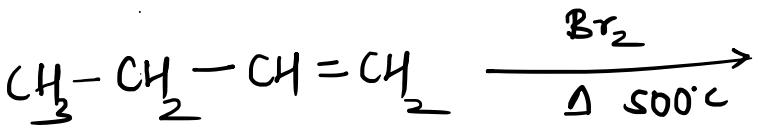
$CH_2=CH-\dot{C}H_2 + \dot{C}H_2-CH=CH_2 \rightarrow CH_2=CH-CH_2-CH_2-CH=CH_2$

$CH_2=CH-\dot{C}H_2 + Cl^{\cdot} \rightarrow CH_2=CH-CH_2Cl$

3-Chloro prop-1-ene

Alkene Chemical Properties

7. Substitution of Alkene by Halogen (Allylic substitution)



Alkene Chemical Properties

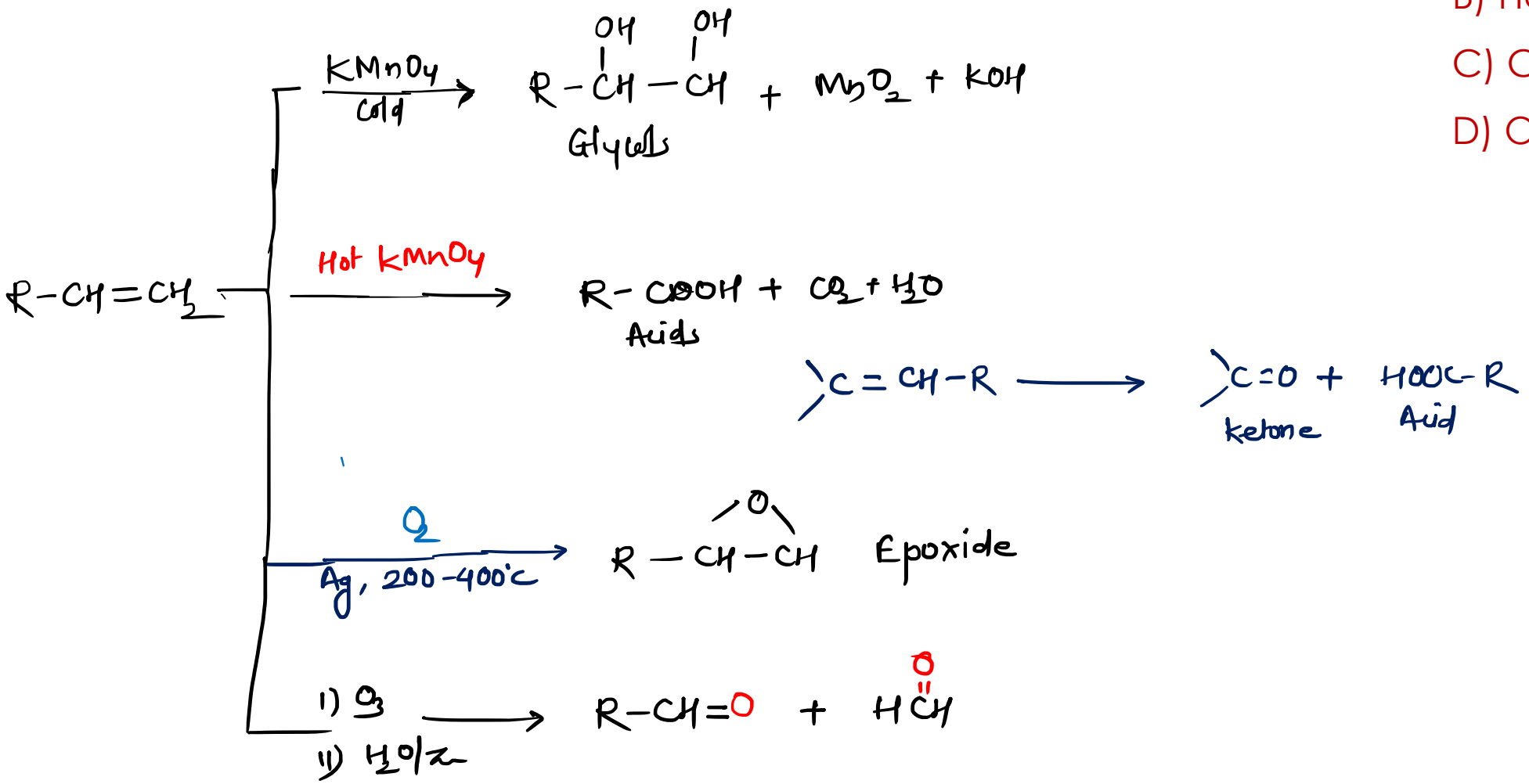
8. Oxidation of Alkene

A) Cold KMnO4

B) Hot KMnO4

C) Catalytic Oxidation

D) Ozonolysis



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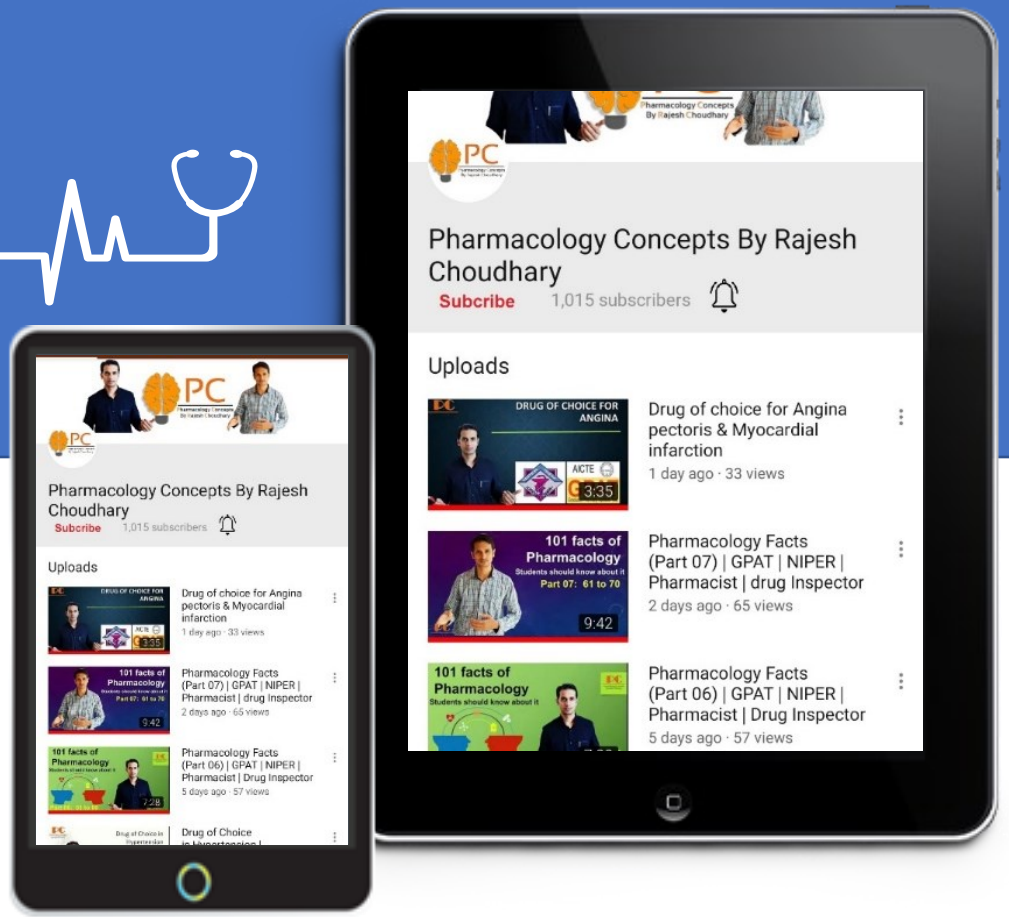
PC
Pharmacology Concepts
By Rajesh Choudhary

Thanks for Watching



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