* Alkene (Olefin)

* General formula :→ C_nH_{2n}

Unsaturated Hydrocarbon

$>C=C<$ sp^2 bond length = 1·34 A or 134 Pm.

chain, position, ring chain, G.I.

→ Rxn of alkene with chlorine, given oily product so alkene also known as Olefin.

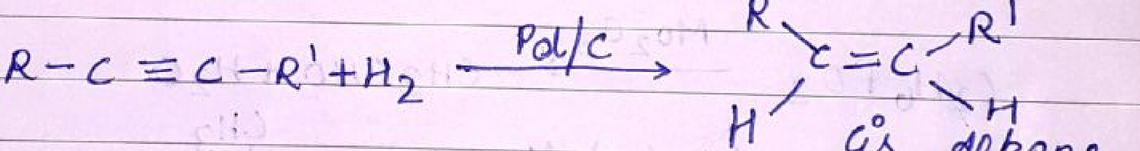
* Preparation of Alkene :→

① From alkyne (partial reduction) :-

$$CH \equiv CH + H_2 \xrightarrow{Pd/C} CH_2 = CH_2$$

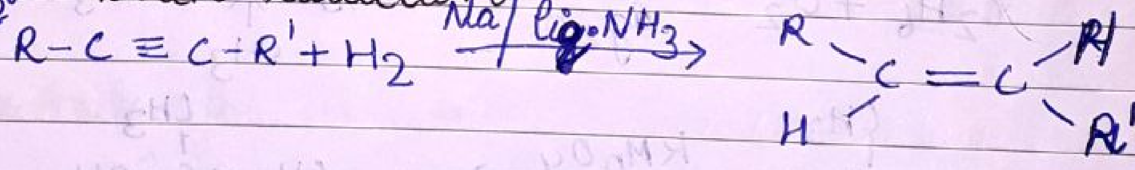
Pd/C — lindlar reagent.

$$R-C \equiv CH \xrightarrow{Pd/C} R-CH=CH_2$$

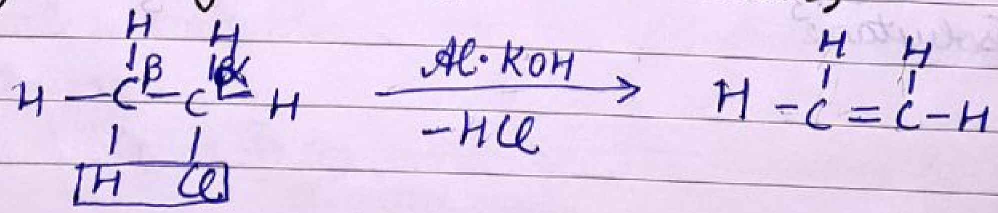


cis Alkene.

Imp. Birch Reduction



② Dehydrohalogenation (β-Elimination) :-



Note :→ if aq·KOH is used then substitution rxn carried out and product should be alcohol.

$$CH_3CH_2Cl \xrightarrow{aq\cdot KOH} CH_3CH_2OH$$

Elimination Reaction

$$\text{Elimination Reaction} \swarrow \searrow$$

α Elimination (1,1 elimination)

Ex. $CHCl_3$

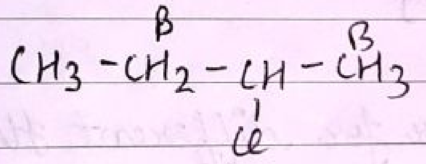
β elimination (1,2 elimination)

→ E_1 mechanism, E_2 mechanism

$$\overset{}{CH_3}\overset{\beta}{CH_2}\overset{\alpha}{CH_2}Cl \xrightarrow[-HCl]{\text{alcoholic KOH}} CH_3-CH=CH_2$$

$$CH_3CH_2-CH_2-CH_2-Cl \xrightarrow[-HCl]{Al\cdot KOH} CH_3CH_2-CH=CH_2$$

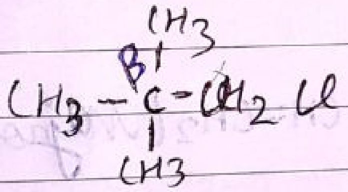
(Hoffmann Product)



$$CH_3-\overset{\beta}{CH_2}-\underset{Cl}{\underset{|}{CH}}-\overset{\beta}{CH_3}$$

→ $CH_3-CH_2-CH=CH_2$ (Minor)

→ $CH_3-CH=CH-CH_3$ (Major) Saytzeff product.



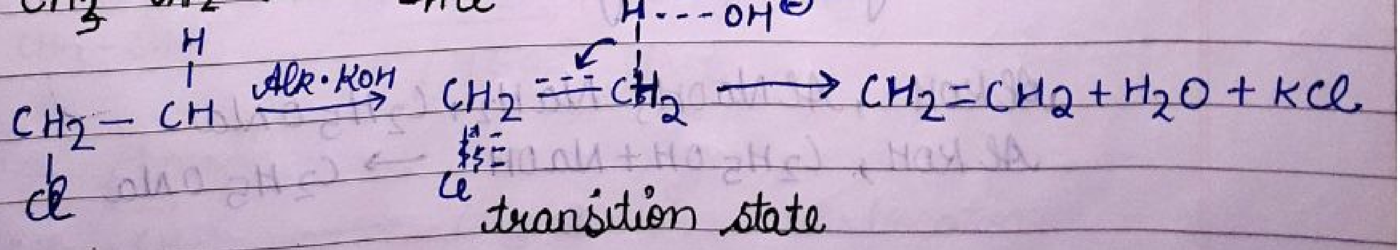
$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\beta|}{\underset{|}{C}}}}-CH_2Cl \xrightarrow{Al\cdot KOH} \times$$

β carbon have 0 Hydrogen

Saytzeff rule :→ during Dehydro Halogenation or Dehydration those alkene obtained as a Major Product which having higher alkyl substituent

Mechanism :- This is E_2 elimination (Bimolecular mechanism)

$$CH_3-CH_2-Cl \xrightarrow[-HCl]{Al\cdot KOH} CH_2=CH_2$$



$$\underset{Cl}{\underset{|}{CH_2}}-\overset{H}{\overset{|}{CH}} \xrightarrow{Alk\cdot KOH} CH_2 \cdots CH_2 \longrightarrow CH_2=CH_2+H_2O+KCl$$

transition state

characturstics of E_2 elimination :→

i) single step Mechanism

→ This is 2nd order Rxn (Bimolecular)

$$rate = K[R-X][Base]$$

→ Carbocation does not form so rearrangment should not be possible.

→ The Orientation of Proton and leaving group should be Anti peric palanar

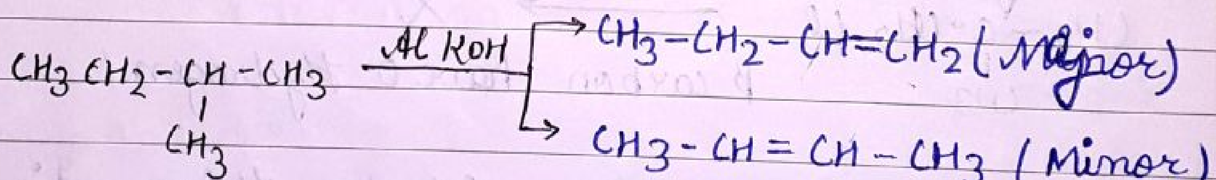
Reactivity order of different Alkene Halide for Dehydrohalogenation as

$$3^\circ > 2^\circ > 1^\circ$$

easily eli ← (at 3°) eliminate

leaving group capicty / order for different Halogen should be

$$I > Br > Cl > F$$



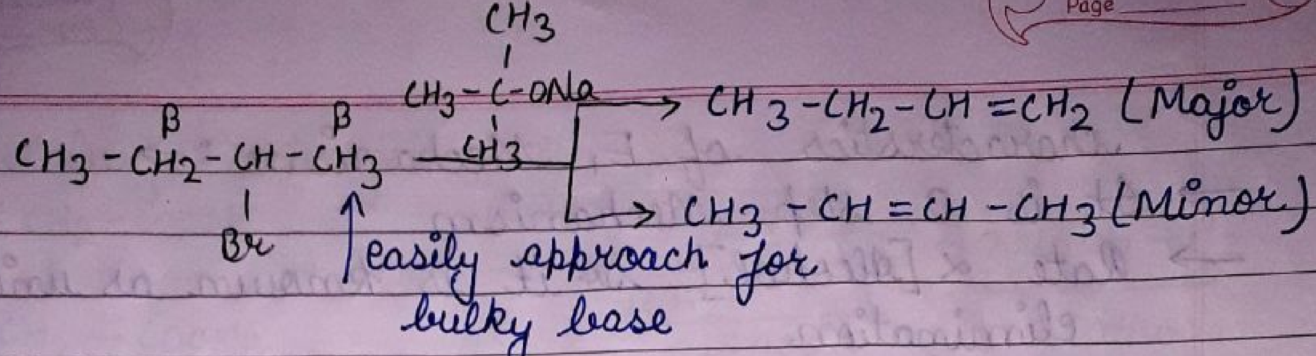
$$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow{Al\ KOH} \begin{cases} CH_3-CH_2-CH=CH_2\ (Major) \\ CH_3-CH=CH-CH_3\ (Minor) \end{cases}$$

→ In case of elimination of alkene Halide in presence of weekly base like $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-ONa$

It cannot be approach hidden β hydrogen, so, it remove those β hydrogen which are easily available for bulky base

Al KOH, Al NaOH; NaH_2, C_2H_5ONa

Al KOH, $C_2H_5OH + NaOH \longrightarrow C_2H_5ONa$

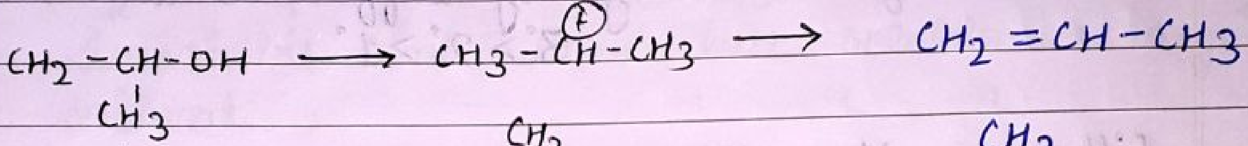


$$CH_3-\overset{\beta}{CH_2}-\underset{\underset{Br}{|}}{CH}-\overset{\beta}{CH_3} \xrightarrow[CH_3]{CH_3-\overset{\overset{CH_3}{|}}{C}-ONa} \begin{cases} CH_3-CH_2-CH=CH_2 \text{ (Major)} \\ CH_3-CH=CH-CH_3 \text{ (Minor)} \end{cases}$$

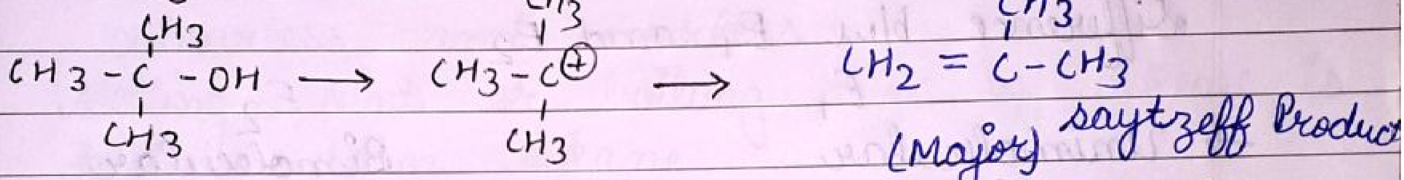
↑ easily approach for bulky base

Dehydration of Alkane →

$$CH_3CH_2OH \xrightarrow[\Delta]{conc\cdot H_2SO_4} CH_2=CH_2+H_2O$$

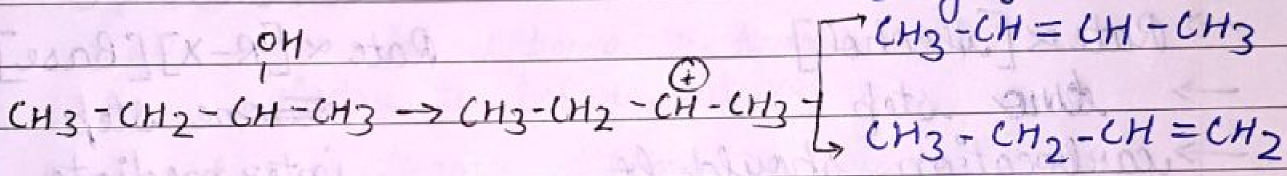


$$\underset{\underset{CH_3}{|}}{CH_2-CH-OH} \longrightarrow CH_3-\overset{\oplus}{CH}-CH_3 \longrightarrow CH_2=CH-CH_3$$

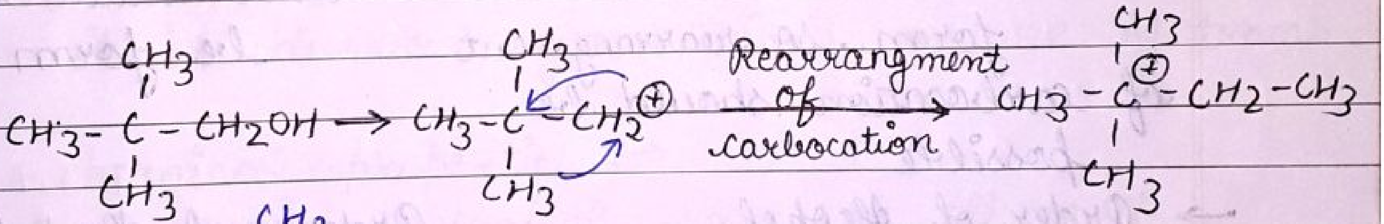


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}^{\oplus} \longrightarrow CH_2=\overset{\overset{CH_3}{|}}{C}-CH_3$$

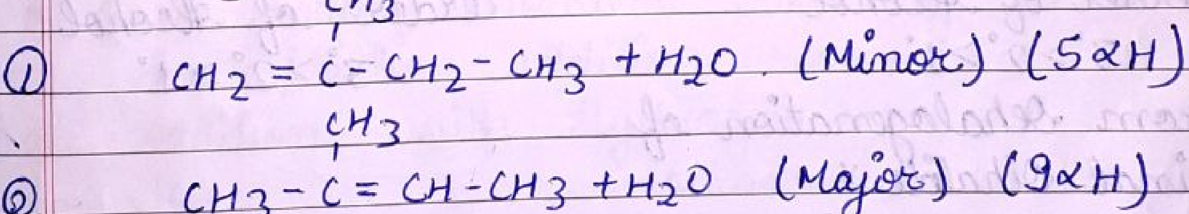
(Major) saytzeff Product



$$CH_3-CH_2-\overset{\overset{OH}{|}}{CH}-CH_3 \rightarrow CH_3-CH_2-\overset{\oplus}{CH}-CH_3 \begin{cases} CH_3-CH=CH-CH_3 \\ CH_3-CH_2-CH=CH_2 \end{cases}$$



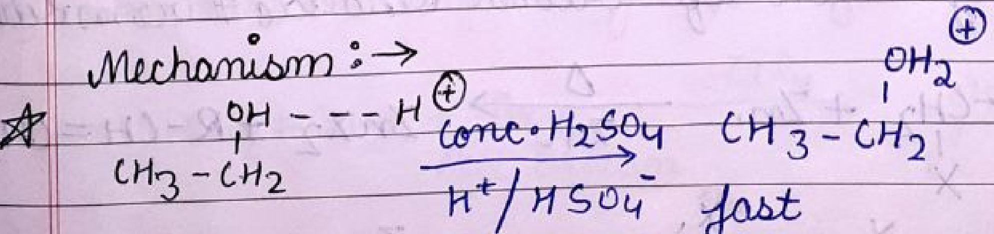
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH \rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2^{\oplus} \xrightarrow[\text{carbocation}]{\text{Rearrangment of}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}}-CH_2-CH_3$$



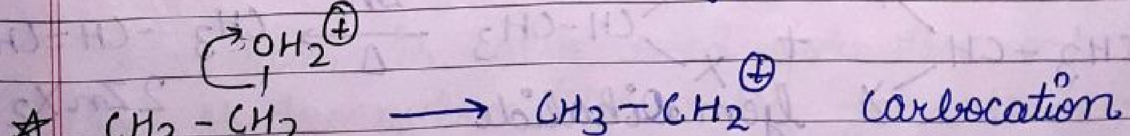
① $CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3+H_2O$ (Minor) (5αH)

② $CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3+H_2O$ (Major) (9αH)

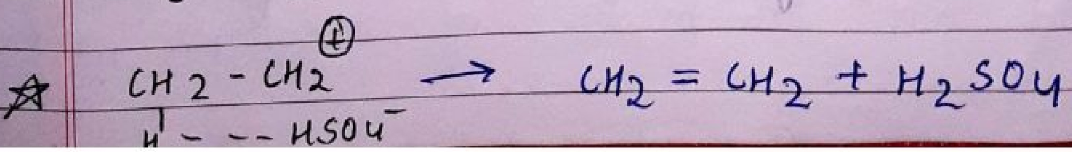
Mechanism :→



☆ $$\overset{\overset{OH---H^{\oplus}}{|}}{CH_3-CH_2} \xrightarrow[H^+/HSO_4^-]{conc\cdot H_2SO_4} \overset{\overset{OH_2^{\oplus}}{|}}{CH_3-CH_2}$$ fast



☆ $$\overset{\overset{OH_2^{\oplus}}{|}}{CH_3-CH_2} \longrightarrow CH_3-CH_2^{\oplus}$$ carbocation



☆ $$\underset{\underset{H---HSO_4^-}{|}}{CH_2-CH_2^{\oplus}} \longrightarrow CH_2=CH_2+H_2SO_4$$

characterstics of E_1 Mechanism :→

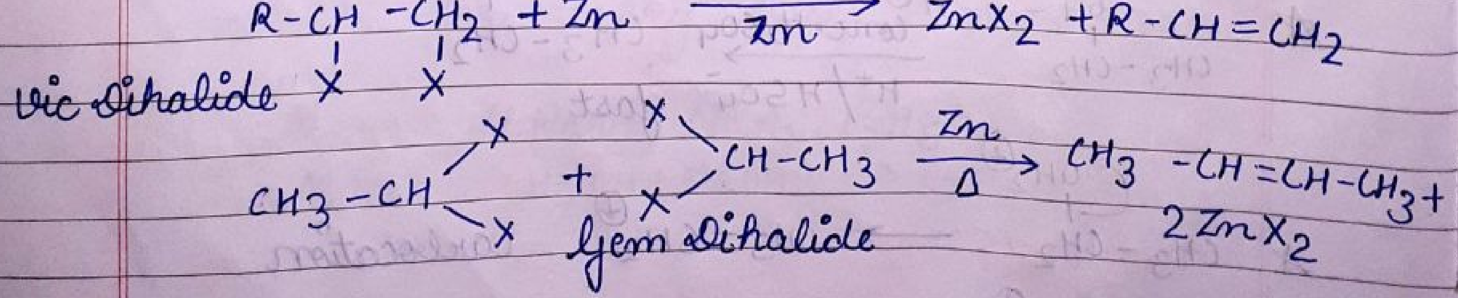
- → It is 2 step Mechanism
- → Rate ∝ [Alcohol] So it is known as unimolecular elimination
- → Here intermediate as carbocation
- → Carbocation Rearrangment should be possible for stability $1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$
- → Order of reactivity of different alcohol $3^\circ > 2^\circ > 1^\circ$

Difference b/w E_1 and E_2

E_1	E_2
→ Unimolecular	Bimolecular
→ Rate ∝ [Alcohol]	Rate ∝ [R-X][Base]
→ two step	~~two~~ one step
→ carbocation should be form. so, rearrangment of carbocation should be possible	intermediate should be form
→ Order of Alcohol $3^\circ > 2^\circ > 1^\circ$	Order of Alcohol $3^\circ > 2^\circ > 1^\circ$

→ ×From Dehalogenation of vicinal Dihalide ×

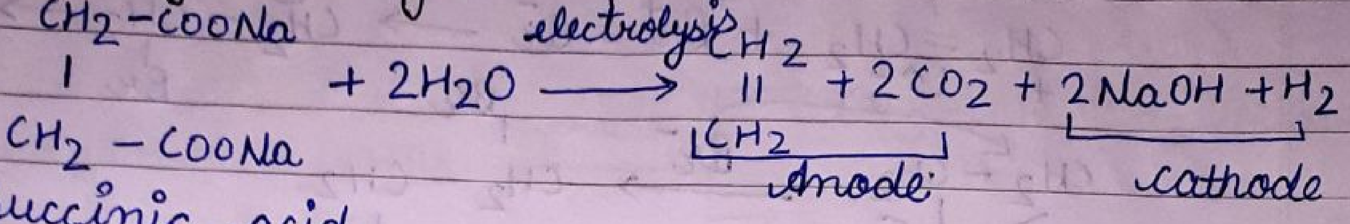
④ From Dehydration of Vicinal Dihalide + Gem Dihalide:-



$$R-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH_2}} + Zn \xrightarrow[Zn]{\Delta} ZnX_2 + R-CH=CH_2$$

$$CH_3-CH\langle^{X}_{X} + {}^{X}_{X}\rangle CH-CH_3 \xrightarrow[\Delta]{Zn} CH_3-CH=CH-CH_3 + 2ZnX_2$$

Kolbey Electrolysis :→



$$\begin{array}{l}CH_2-COONa\\ \quad |\\ CH_2-COONa\end{array} + 2H_2O \xrightarrow{electrolysis} \underbrace{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2CO_2}_{Anode} + \underbrace{2NaOH + H_2}_{cathode}$$

Succinic acid

Physical properties :→

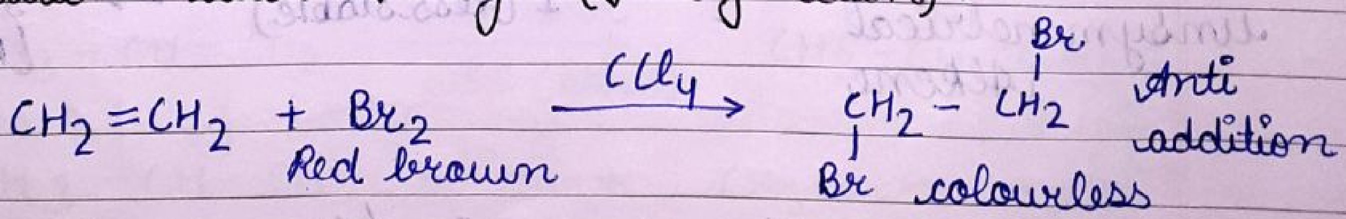
- C_2 to C_4 gases C_5 to C_{16} liquid C_{17} to above solid
- Insoluble in water but soluble in organic solvent.
- colourless and ordorless.
- Melting point or boiling point of alkene is higher than Alkane
- B.P → cis Alkene > trans alkene. (due to polar nature)
- M.P → trans Alkene > cis alkene. it is due to symmetrical nature of trans.

chemical properties :→

The main chemical rxn of Alkene is electrophillic addition rxn.

1) Addition with Hydrogen :→
Alkane should be form

2) Addition with Halogen (Halogenation) :→



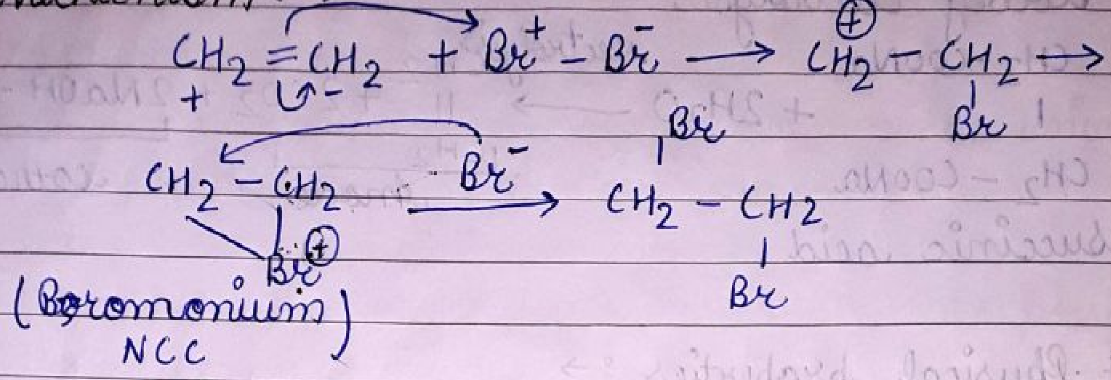
$$CH_2=CH_2 + \underset{\text{Red brown}}{Br_2} \xrightarrow{CCl_4} \underset{\text{colourless}}{\underset{Br}{\underset{|}{CH_2}}-\overset{Br}{\overset{|}{CH_2}}}$$

Anti addition

This rxn is also used for test of unsaturation in Hydrocarbon (Generally for alkene + alkyne)

NCC → Non classical carbonium

Mechanism :→



Addition with hydrogen Halide (HX) :→

$$CH_2=CH_2 + H^+X^- \longrightarrow CH_3CH_2-X$$

$HX = HCl, HBr, HI$

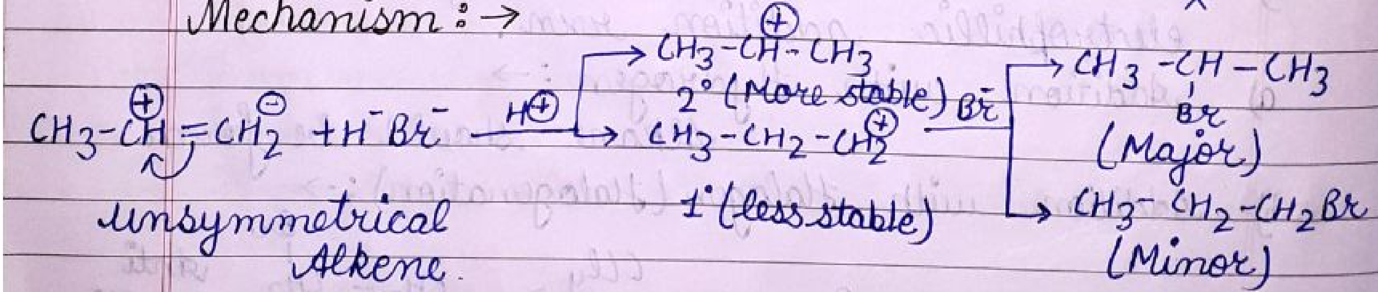
$HI > HBr > HCl$

Markonikov's addition -

according to this addition of Hydrogen Halide with unsymmetrical alkene. Halogen attach with those carbon which having lower no. of Hydrogen.

$$CH_3-CH=CH_2 + H^+X^- \longrightarrow CH_3-\underset{X}{CH}-CH_3$$

Mechanism :→



Anti Markonikov's addion/Kharash effect/Peroxide effect/Anti Markoni rule

→ It is applicable only for HBr (~~HCl~~ ~~HI~~)
→ carried out in presence of Benzoyle peroxide

→ It is free radical Addition Mechanism

$$CH_3CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} \begin{cases} CH_3-\underset{Br}{CH}-CH_3 \ \text{[Minor]} \\ CH_3-CH_2-CH_2-CH-Br \ \text{[Major]} \end{cases}$$

$$C_6H_5-C-O-O-\underset{\overset{\|}{O}}{C}-C_6H_5 \longrightarrow C_6H_5COO^{\circ} + C_6H_5COO^{\circ}$$

$$C_6H_5-COO^{\cdot} \longrightarrow \dot{C}_6H_5 + CO_2$$

$$\dot{C}_6H_5 + H-Br \rightarrow C_6H_6 + \dot{Br}$$

d) Addition of water :→

Acid catalytic hydration

Hydroboration oxidation rxn

Mercurous demercurous rxn

i) Acid catalytic Hydration :→

Addition of water according to Marconikov rule

$$CH_3-CH=CH_2 + H_2O \xrightarrow[\substack{H^+/H_2O \text{ or} \\ H^+/SO_4^-}]{\text{dil } H_2SO_4 \text{ or}} CH_3-\underset{OH}{CH}-CH_3$$

H form acid

OH from water

Mechanism :-

$$CH_3-CH=CH_2 \xrightarrow[\text{RDS (slow)}]{H^{\oplus} \text{ acid}} CH_3-\overset{\oplus}{CH}-CH_3$$

$$CH_3-\overset{\oplus}{CH}-CH_3 \xrightarrow{H_2\ddot{O}:} CH_3-\underset{\oplus OH-H}{CH}-\dot{C}H_3 \xrightarrow[+HSO_4^-]{-H^+}$$

$$CH_3-\underset{OH}{CH}-CH_3 + H_2SO_4$$

- → Two step Mechanism
- → Intermediate is carbocation so, carbocation rearrangment should be possible
- → Here, water act as nucleophile

ii) Hydroboration Oxidation :→

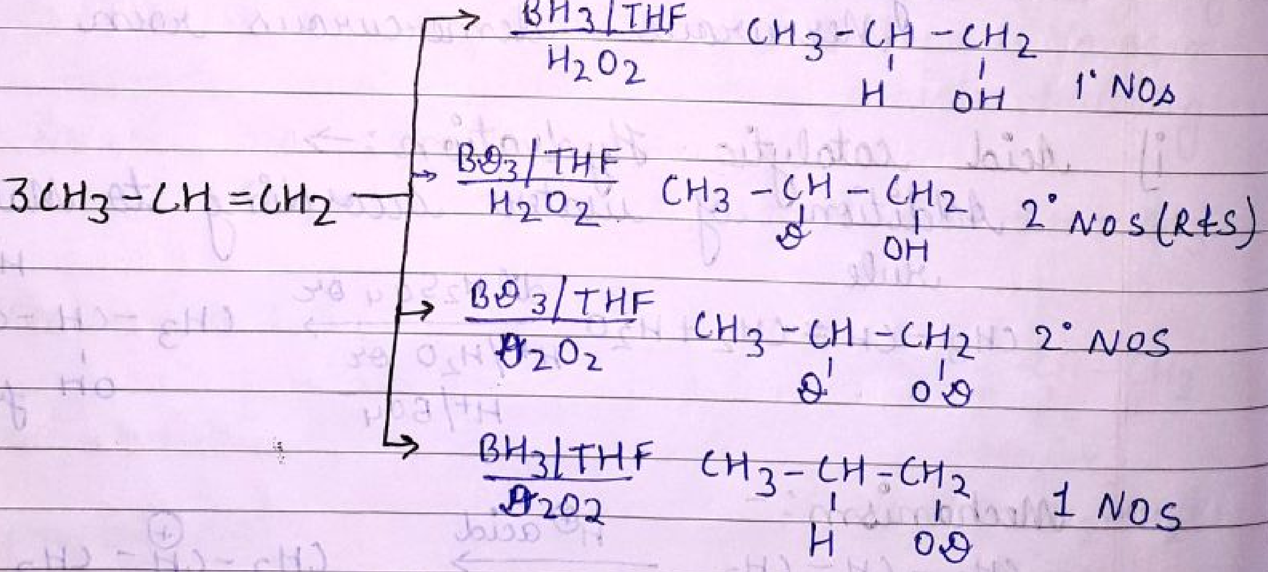
Addition according to Antimarconicov rule.

$CH_3-CH_2=CH_2+H_2O \xrightarrow{BH_3|TH_3}$  $(CH_3CH_2CH_3)_3B \xrightarrow{H_2O_2}$

$3CH_3CH_2\underline{CH_2}-OH+H_3BO_3$

↳ Here H from diborane

↳ from H_2O_2



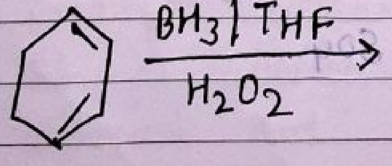
$3CH_3-CH=CH_2 \xrightarrow[H_2O_2]{BH_3/THF} CH_3-\underset{H}{CH}-\underset{OH}{CH_2}$ 1° NOs

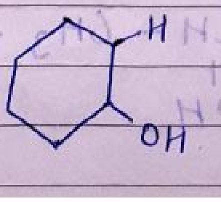
$\xrightarrow[H_2O_2]{B\Theta_3/THF} CH_3-\underset{\Theta}{CH}-\underset{OH}{CH_2}$ 2° NOS(Rts)

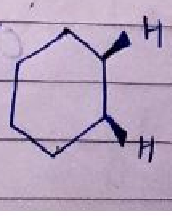
$\xrightarrow[\Theta_2O_2]{B\Theta_3/THF} CH_3-\underset{\Theta}{CH}-\underset{O\Theta}{CH_2}$ 2° NOS

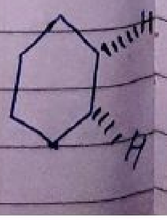
$\xrightarrow[\Theta_2O_2]{BH_3/THF} CH_3-\underset{H}{CH}-\underset{O\Theta}{CH_2}$ 1 NOS

- → In Hydroboration rxn H^+ come from diborane & OH^- comes from Hydrogen peroxide
- → It is syn addition

Q 

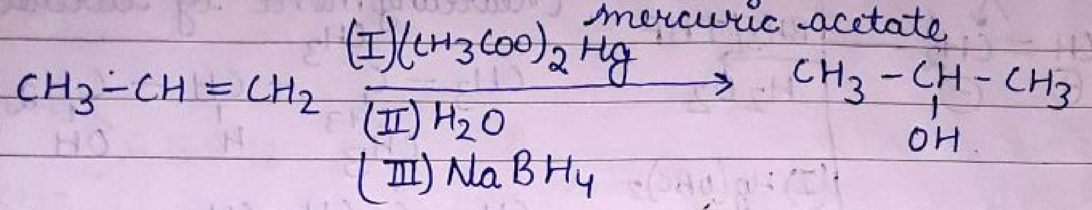
a) 

b) 

c) 

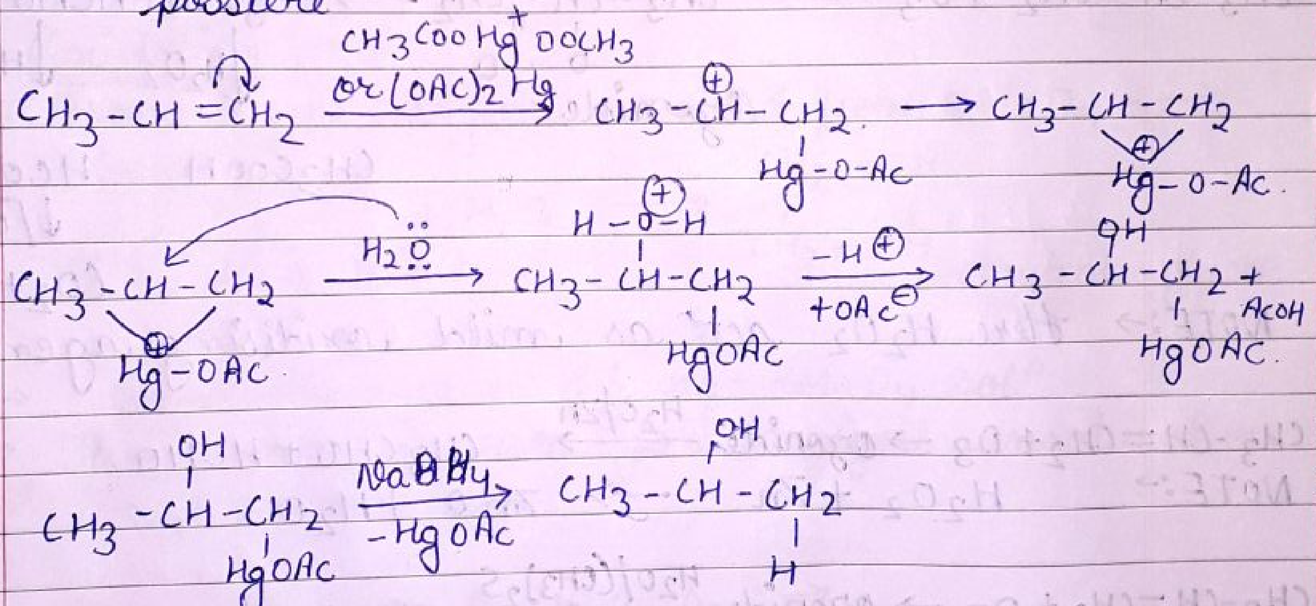
$\underset{0.S.-1}{NaBH_4}$ → strong reducing agent

iii) Oximercuration, demercuration :→

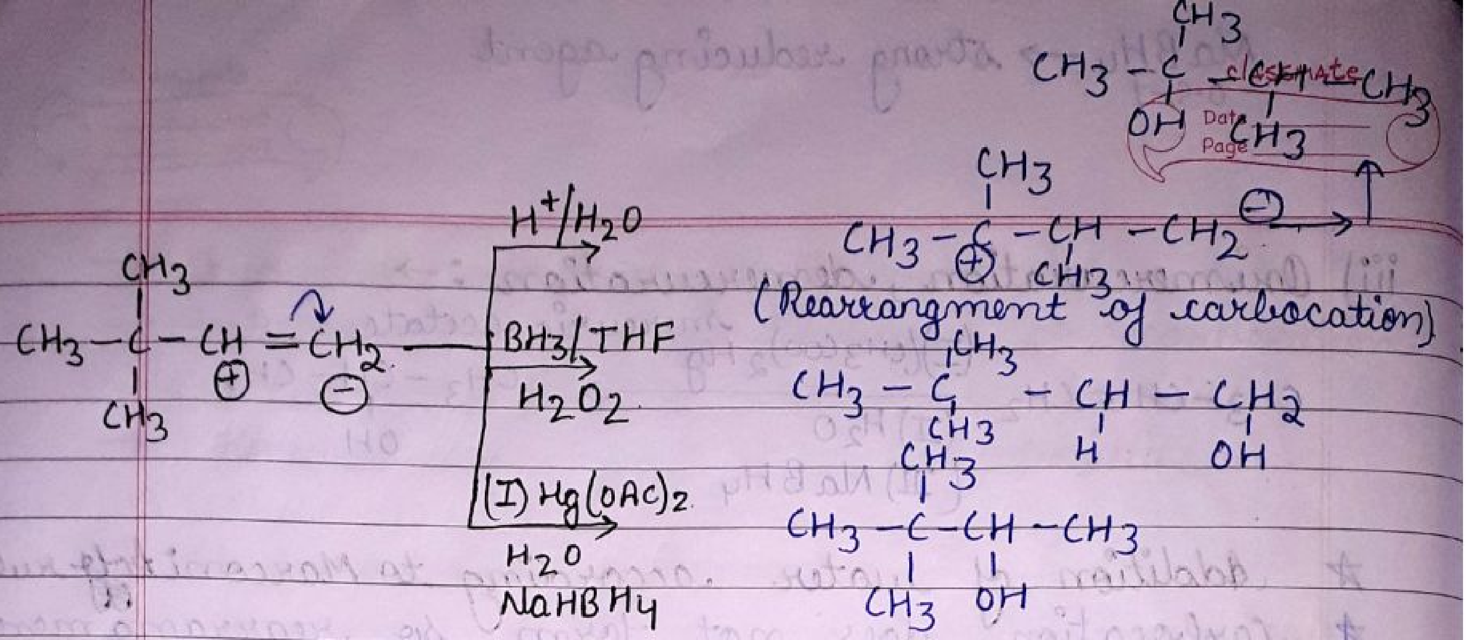


$$CH_3-CH=CH_2 \xrightarrow[\text{(II) } H_2O \text{ (III) } NaBH_4]{\text{(I) } (CH_3COO)_2Hg \text{ mercuric acetate}} CH_3-\underset{OH}{CH}-CH_3$$

☆ Addition of water according to Marconikoff rule
☆ carbocation does not form. so, rearrangment of carbocation does not occur.
☆ syn or Anti both type addition should be possible

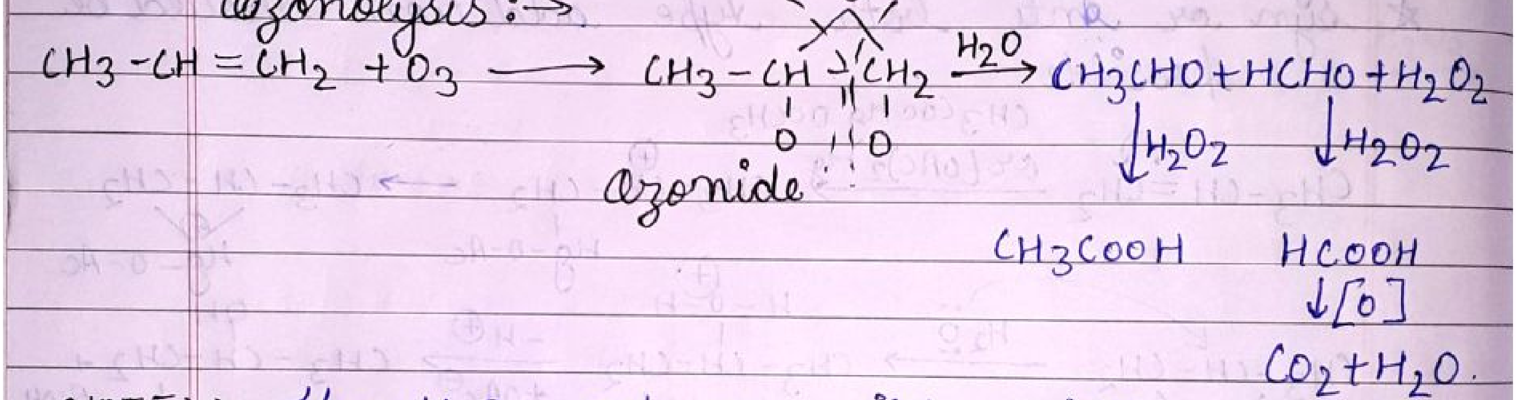


Acid catalytic Hydration	Hydroboration	Mercurous-mercurous
→ Formation of carbocation	—	—
→ Rearrangment of carbocation	—	—
→ Marconi Cov Add.	Anti M.A.	Marconi Cov A.
→ syn/Anti Add.	Syn addition	Syn-Anti addition



(Rearrangment of carbocation)

Ozonolysis :→



NOTE :→ Here H_2O_2 act as mild oxidising agent

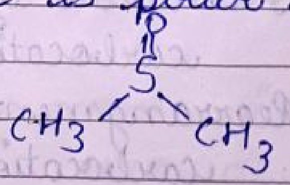
$CH_3-CH=CH_2+O_3 \rightarrow$ ozonide $\xrightarrow{H_2O/Zn}$ $CH_3CHO+HCHO$.

NOTE :→ $H_2O_2+Zn \longrightarrow ZnO+H_2O$.

$CH_3-CH=CH_2+O_3 \rightarrow$ ozonide $\xrightarrow{H_2O/(CH_3)_2S}$ $CH_3CHO+HCHO$

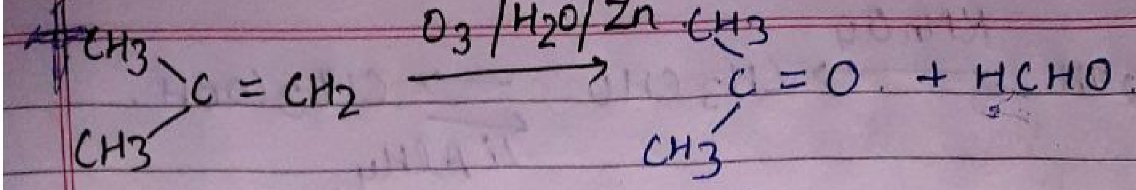
$H_2O_2+(CH_3)_2S \longrightarrow (CH_3)_2SO+H_2O$
DMSO

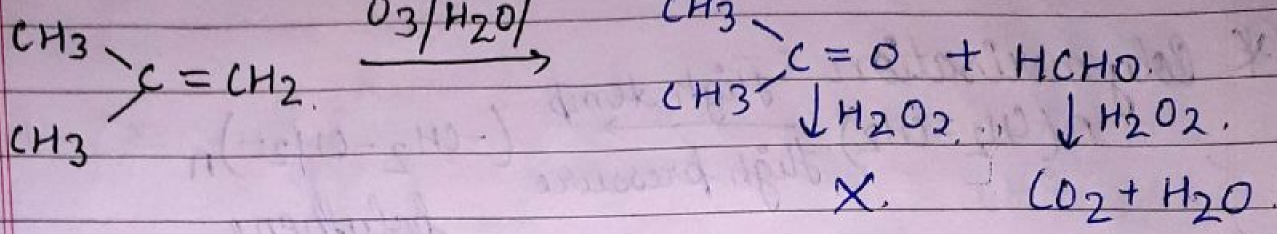
DMSO → Di methyl sulpho oxide, it is polar aprotic solvent.

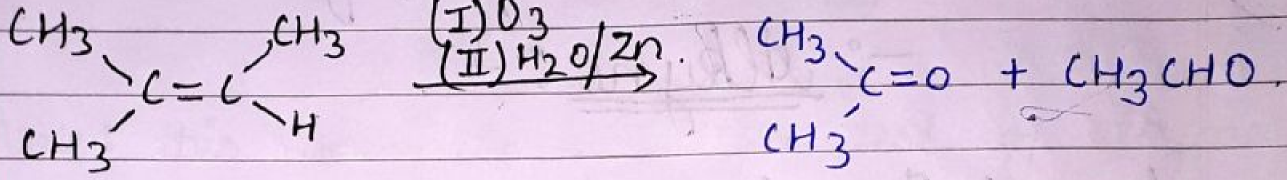


$CH_2=CH_2 \xrightarrow{(I)O_3} 2HCHO \xrightarrow{H_2O_2} CO_2+H_2O$

$CH_2=CH_2 \xrightarrow[Zn]{(I)O_3} 2HCHO$.

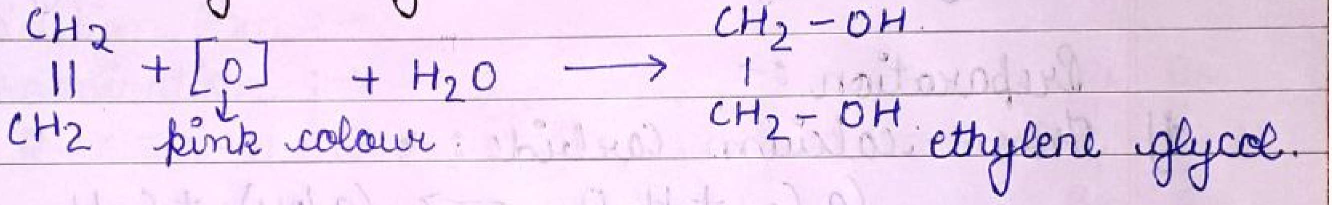






* Oxidation :→

ⓐ From Bayer reagent or Dilute/cold $KMnO_4$ →



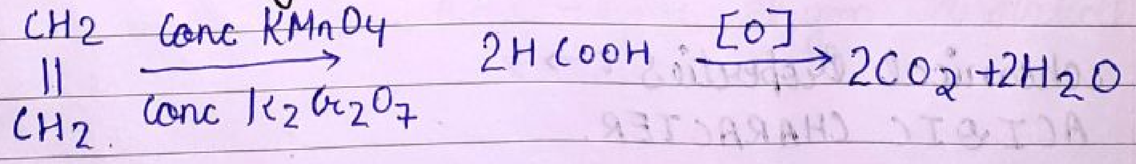
$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + [O] + H_2O \longrightarrow \begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix}$$

pink colour ethylene glycol.

→ Bayer Reagent = 1% aq. $KMnO_4$ solⁿ

→ This rxn is used for anglysis unsaturation in Hydrocarbon.

ⓑ Hot, strong $KMnO_4/K_2Cr_2O_7$:→



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow[\text{conc } K_2Cr_2O_7]{\text{conc } KMnO_4} 2HCOOH \xrightarrow{[O]} 2CO_2 + 2H_2O$$

$$CH_3-CH=CH_2 \longrightarrow CH_3COOH ~~+ CO_2 + H_2O~~ . HCOOH$$
$$\downarrow$$
$$H_2O + CO_2.$$