UNIT: 2. Alkenes

→ These are hydrocarbon having carbon-carbon double bond.

→ formula → C_nH_{2n} (n= number of atom)

→ These are unsaturated compound.

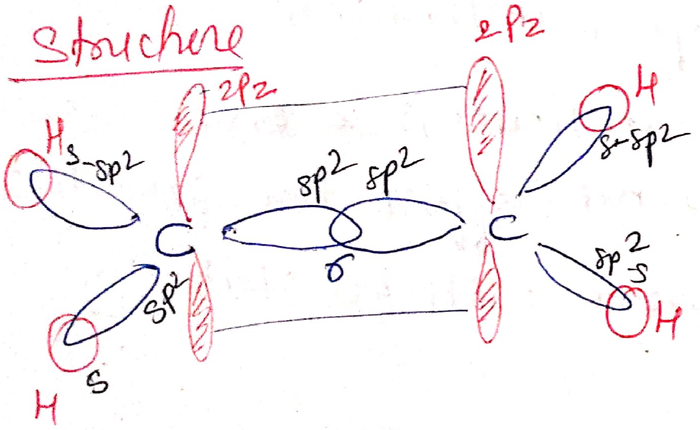
→ They are also called Olefines. (oleum = oil, ficare = to make).

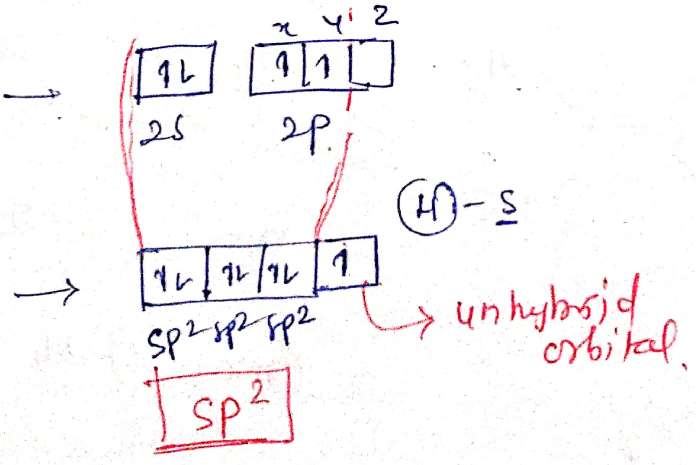
→ Lower member forms oily product on reaction c̄ Cl_2 & br_2.

e.g. $CH_2=CH_2$ Ethylene.

$CH_3-CH_2=CH_2$ Propylene etc.

Structure



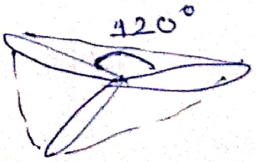


→ C is sp² hybridized

→ It have σ & π bond

→ more reactive than Alkane.

→ structure is triangular planner.



* 2Pz forms π bond.

Nomenclature

simple	IUPAC
$CH_2=CH_2$ (Ethylene)	Ethene

Stability of Alkene

1) Due to presence of π bonds alkenes are less stable than alkane

2) Different form of alkenes have different stability.

Stability depends on following factors.

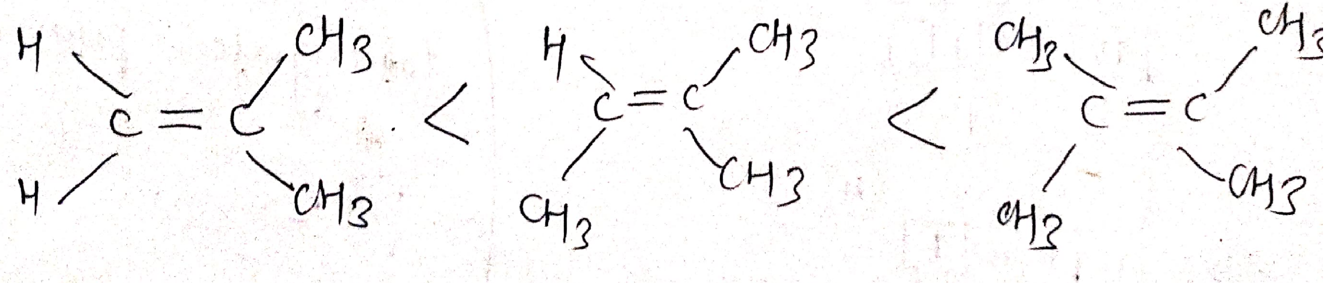
1) No. of substituents
2) gr's orientation
3) Conjugation in alken.

① No. of Substituents

stability ∝ alkyl group substitution

→ Mainly alkyle group substituents & other also attached to double bond affect the stability.

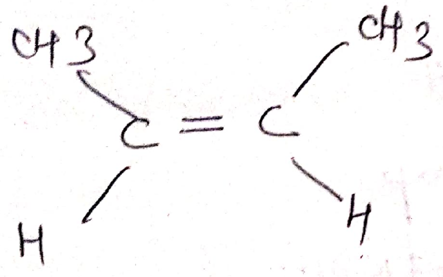
→ more substituent, more will be stability.



(least stable) (more stable)

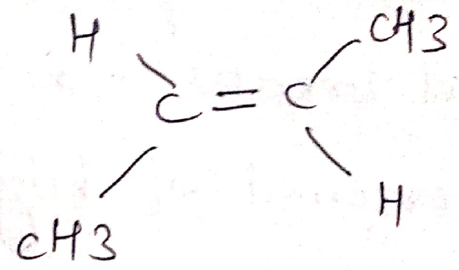
② Orientation

- In alkenes cis form is less stable than trans form.
- As cis form have simillar orientation while trans have opposite orientation of alkyl group on double bond.



cis

<



(Trans)

③ Conjugation

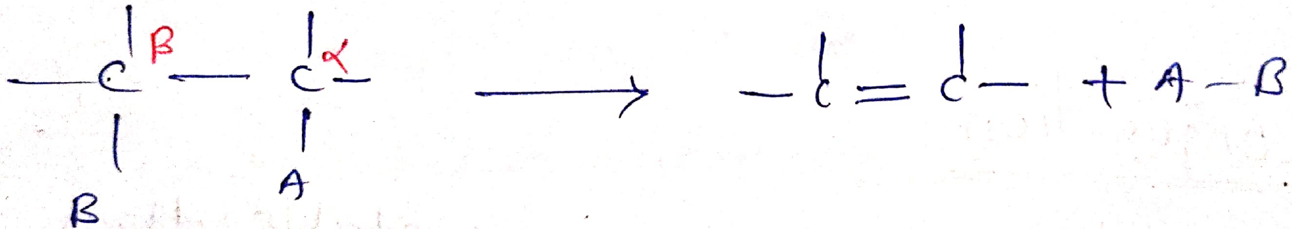
→ conjugated alkenes are more stable than isolated alkenes.

$$CH_3-CH=CH-CH=CH_2 > CH_2=CH-CH_2-CH=CH_2$$

(conjugation)

Elimination Reaction

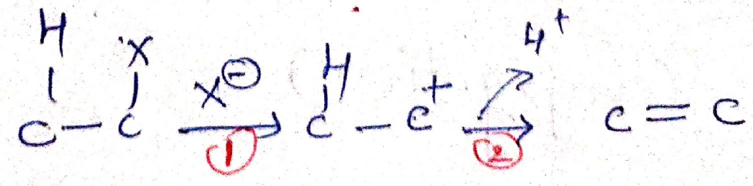
- → It is a type of organic reaction in ē pair of atom / group or lower group are removed from a organic molecule.
- → In this reaction saturated c compound converted to unsaturated.
- → It's a reversed process of addition reaction
- → 2σ bond breaks → 1σ + 1π
- → It's performed at high temp.
- → It's a endothermic reaction.



$$-\overset{|}{\underset{\underset{B}{|}}{C}}{}^{\beta}-\overset{|}{\underset{\underset{A}{|}}{C}}{}^{\alpha}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- + A-B$$

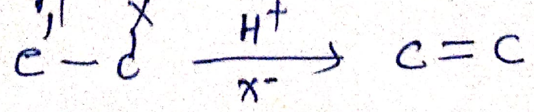
Types of Elimination Reaction

① E₁ Reaction →



$$\overset{H}{\overset{|}{C}}-\overset{X}{\overset{|}{C}} \xrightarrow[①]{X^{\ominus}} \overset{H}{\overset{|}{C}}-\overset{+}{C} \xrightarrow[②]{4^+} C=C$$

(ii) E2 Reaction ⟶



$$\overset{H}{\overset{|}{C}}-\overset{X}{\overset{|}{C}} \xrightarrow[X^-]{H^+} C=C$$

E1 Elimination Reaction

→ It's a unimolecular reaction as it depends on only one molecule

→ It's first order kinetic reaction

→ It's a two step process
  ↳ Carbocation
  ↳ Deprotonation

→ endothermic

→ At high temperature.

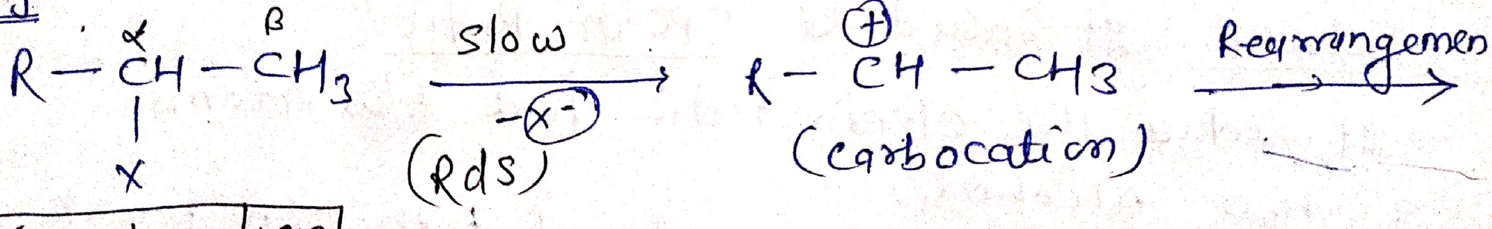
⇒ order of E① = 3° > 2° > 1°

Steps

Rds = rate determining step.

① Carbocation formation

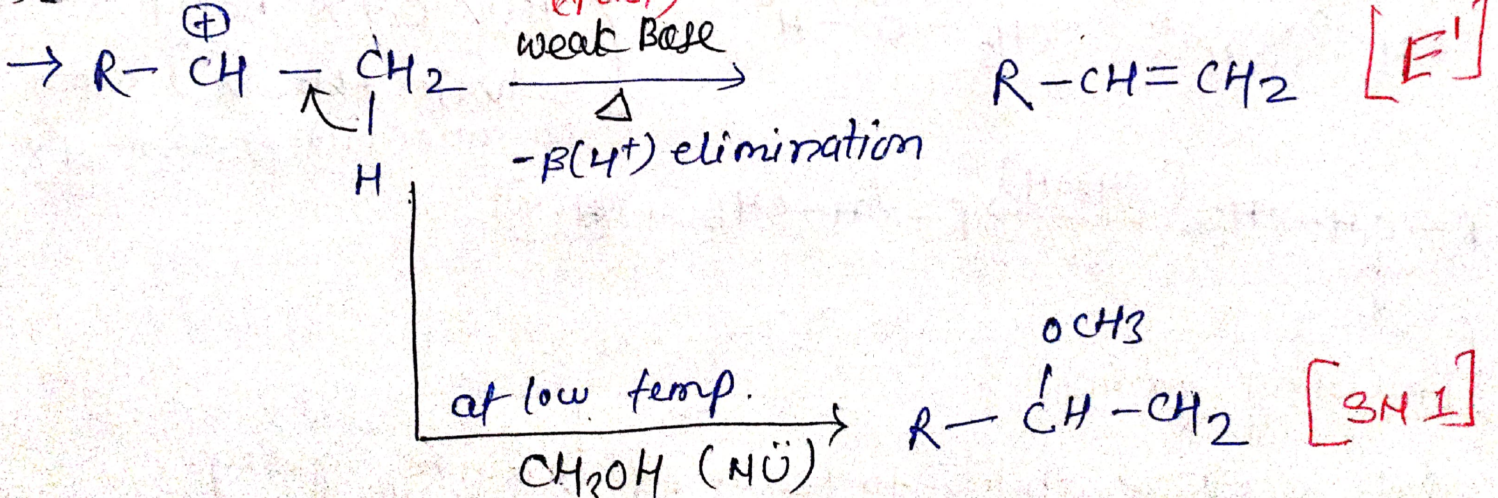
e.g.



$$R-\overset{\alpha}{\underset{X}{\underset{|}{CH}}}-\overset{\beta}{CH_3} \xrightarrow[\substack{-X^- \\ (Rds)}]{slow} R-\overset{\oplus}{CH}-CH_3 \xrightarrow{Rearrangement}$$

(carbocation)

(II) Deprotonation



$$\rightarrow R-\overset{\oplus}{CH}-\underset{H}{\underset{|}{CH_2}} \xrightarrow[\substack{\Delta \\ -\beta(H^+)\ elimination}]{\substack{(fast) \\ weak\ Base}} R-CH=CH_2 \quad [E^1]$$

$$\xrightarrow[CH_3OH\ (N\ddot{u})]{at\ low\ temp.} R-\overset{OCH_3}{\overset{|}{CH}}-CH_2 \quad [SN1]$$

Some IMPORTANT POINT / factor affecting E1.

① Why it is unimolecular (E-1)

→ B/c Rate of reaction depends only on one molecule (substrate, not on reagent)

② It follow 1st order kinetics.

→ B/c Rate of reaction depends only on substrate

e.g. $$\boxed{Rate = K\left[R-\underset{\underset{X}{|}}{CH}-CH_3\right]}$$

→ Rate of reaction is unaffected by conc^n of base. It depends on hallides conc^n.

③ Why weak base

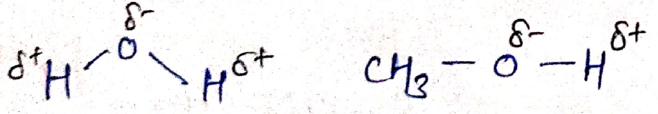
e.g. H_2O, EtOH, MeOH

→ If strong base taken then it directly attack on (X^-). & NO carbocation will form.

④ Solvent : It should be "polar-Protic"

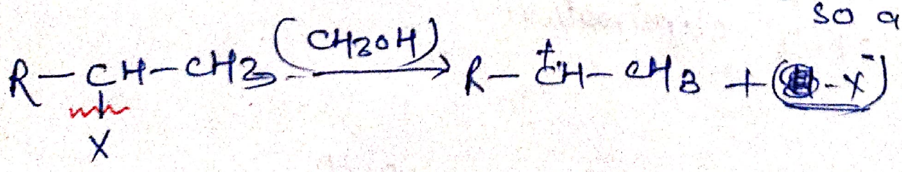
→ It reduce the electrostatic force b/w atoms.

e.g. H_2O, Alcohol.



} both can break the C–X bond & solvate the (X^-) atom

so વાપમાં જાગે ને રોકેગા H^+X^-



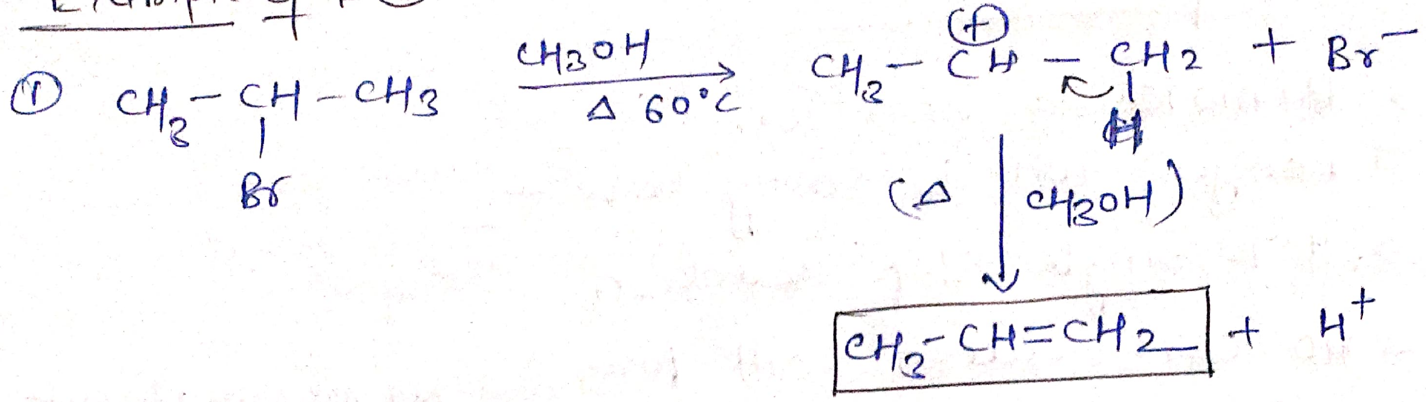
$$R-\underset{\underset{X}{|}}{CH}-CH_3 \xrightarrow{(CH_3OH)} R-\overset{+}{C}H-CH_3 + (H-X^-)$$

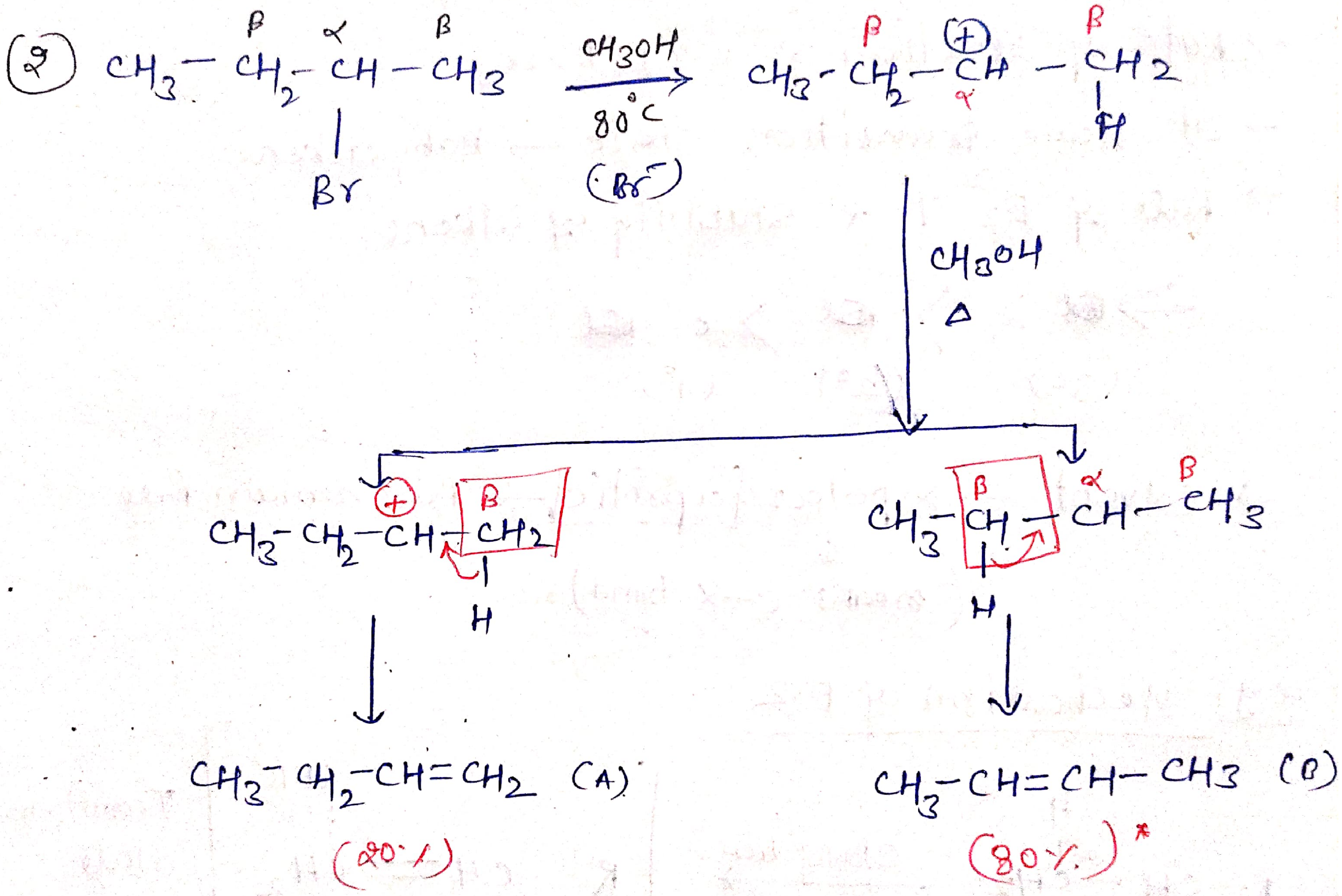
⑤ Leaving group

Rate of E① ∝ ability to leave of leaving group.

order I > Br > Cl > F

Example of E①

①

$$CH_3-\underset{Br}{CH}-CH_3 \xrightarrow[\Delta\ 60^{\circ}C]{CH_3OH} CH_3-\overset{\oplus}{CH}-\underset{H}{CH_2} + Br^- \xrightarrow[(\Delta]{CH_3OH)} \boxed{CH_3-CH=CH_2} + H^+$$

②

$$CH_3-\overset{\beta}{CH_2}-\underset{Br}{\overset{\alpha}{CH}}-\overset{\beta}{CH_3} \xrightarrow[80^{\circ}C\ (Br^-)]{CH_3OH} CH_3-\overset{\beta}{CH_2}-\underset{\alpha}{\overset{\oplus}{CH}}-\underset{H}{\overset{\beta}{CH_2}} \xrightarrow[\Delta]{CH_3OH}$$

$$CH_3-CH_2-\overset{\oplus}{CH}-\underset{H}{\boxed{\overset{\beta}{CH_2}}} \longrightarrow CH_3-CH_2-CH=CH_2\ (A)$$

(20%)

$$CH_3-\underset{H}{\boxed{\overset{\beta}{CH}}}-\overset{\alpha}{CH}-\overset{\beta}{CH_3} \longrightarrow CH_3-CH=CH-CH_3\ (B)$$

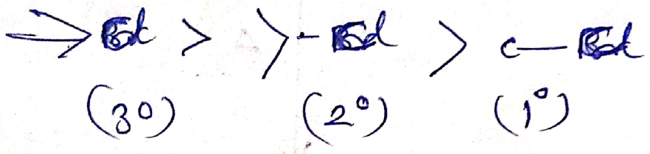
(80%) *

* Saytzeff Rule

→ when small base attacks then more stable alkene will be major product. so product B is more stable as it follow conjugation & orientation.

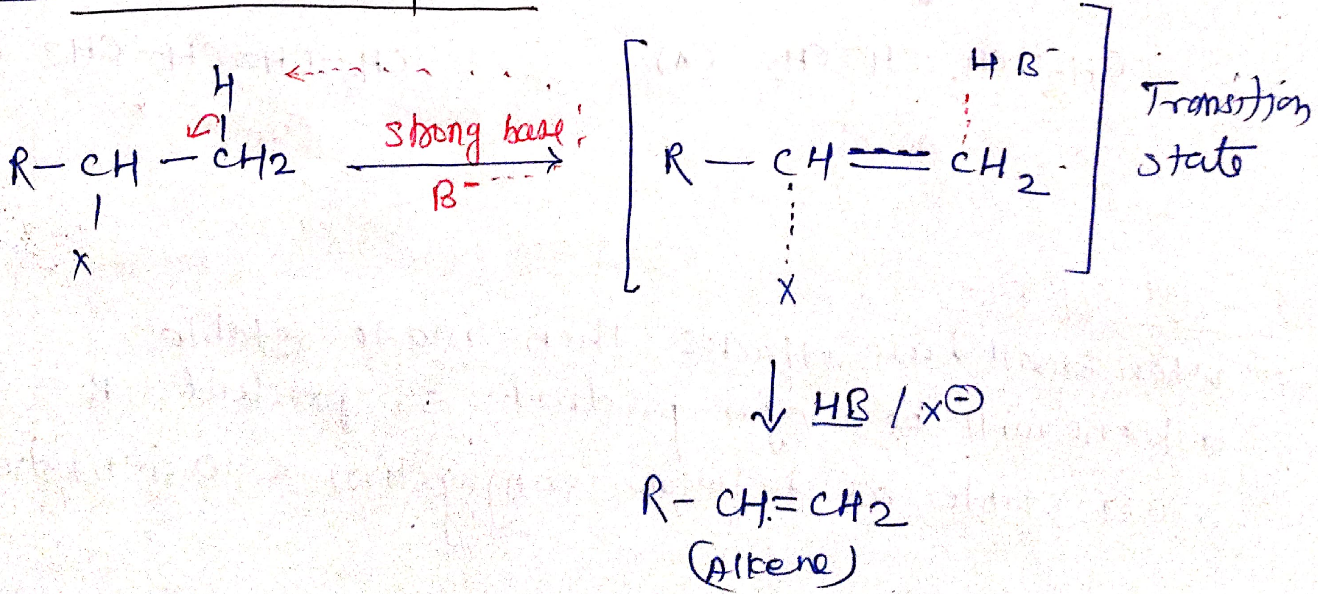
E-2 - Elimination

- → Bimolecular reaction.
- → Reagent will be strong base. → alc. KOH, alc. NaOH, R-O⁻
- → It is single step reaction.
- → No carbocation will form, so No rearrangement
- → It is also called α-β elimination.
- → Rate of reaction ∝ [R-X] [Base]
- → It have transition state → Baby alkene
- → Rate of E2 ↑ ∝ stability of alkene.



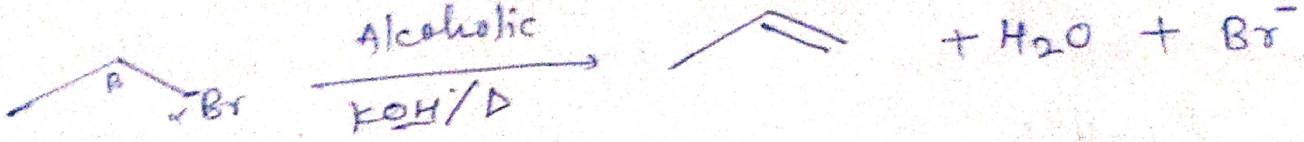
- → Solvent → polar $\boxed{\text{aprotic}}$ → Base remain free
  ↓
  (breaks C—X bond)

eg. Mechanism of E-2

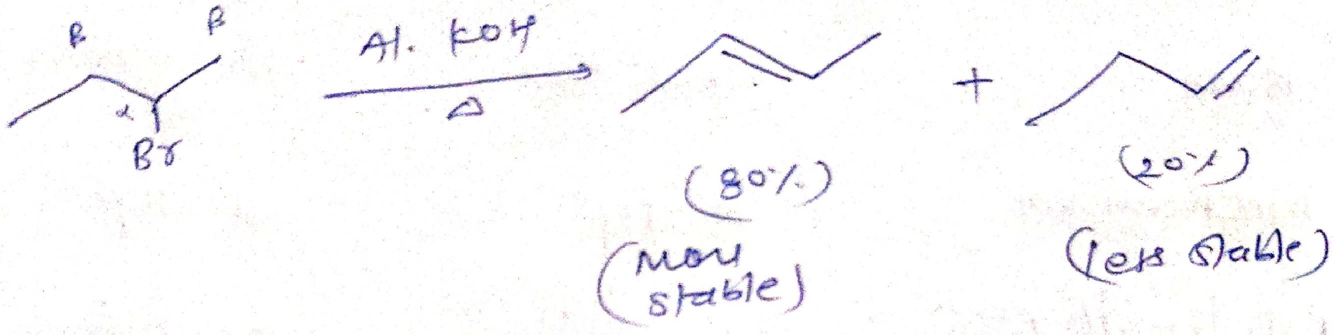


e.g.

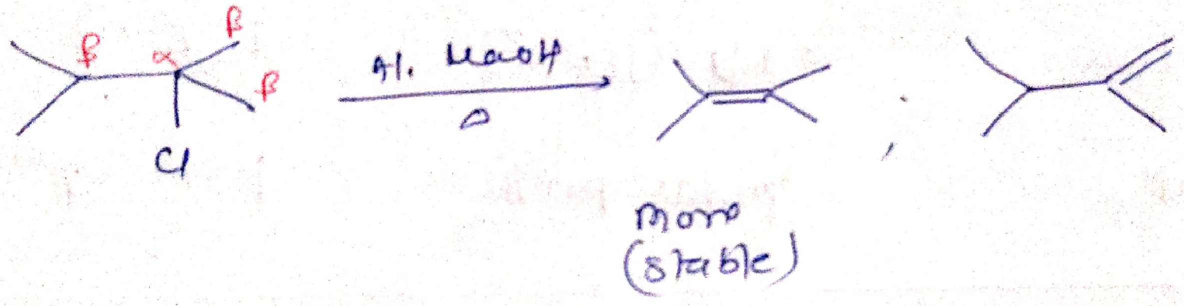
①


β
α Br
Alcoholic
KOH/Δ
+ H2O + Br⁻

②


β
β
α
Br
Al. KOH
Δ
+
(80%)
(More stable)
(20%)
(less stable)

③


β
α
β
β
Cl
Al. NaOH
Δ
More (stable)

E_1 Vs E_2

Reaction Parameter	E_1	E_2
1) Alkyl hallide structure	3°>2°>>>>1°	3°>2°>1°
2) Base	weak base	strong base
3) Mechanism	2 step	1 step.
4) Rate limitting step	C^+ formation	transition state.
5) Rate law	$=K[R-X][base]$	$=K[R-X]$
6) Solvent	polar protic	polar aprotic

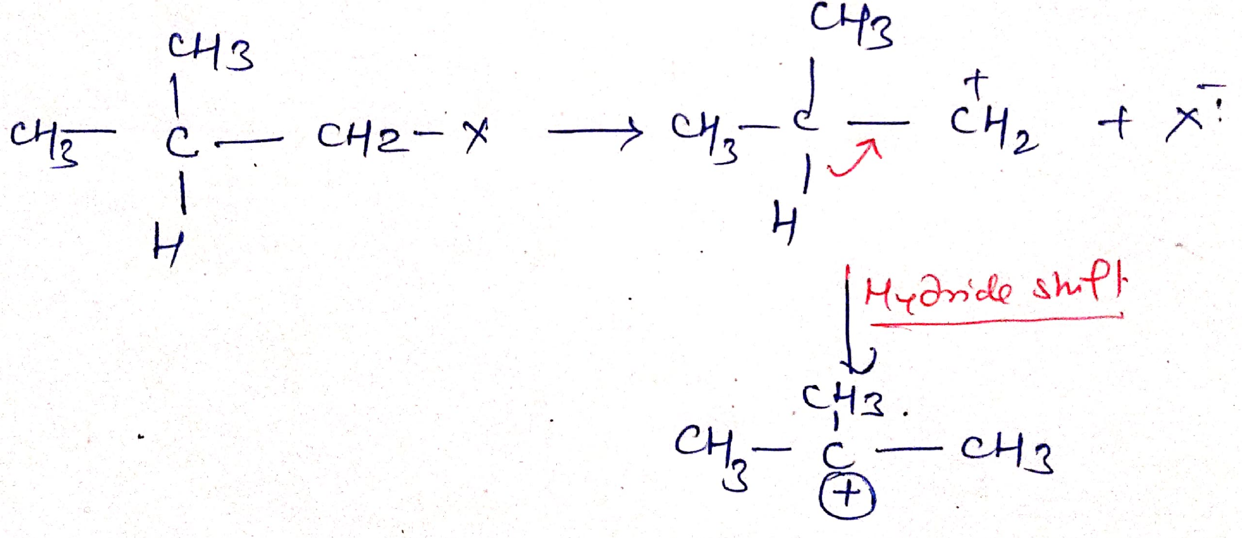
Rearrangement of Carbocations

→ Shifting of bonding atom or group in a carbocation for the formation of more stable carbocation is k/n as Rearrangement of carbocations.

⇒ Two types of shifting
① Hydride ② Methyle

① Hydride shifting

Shifting of H2

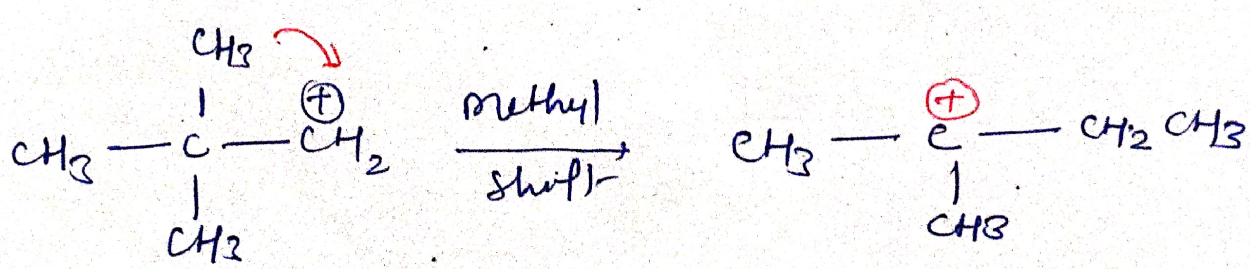


$$CH_3-\overset{CH_3}{\underset{H}{C}}-CH_2-X \longrightarrow CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{+}{C}H_2 + X^{-}$$

$$\Big\downarrow \text{Hydride shift}$$

$$CH_3-\overset{CH_3}{\underset{\oplus}{C}}-CH_3$$

② methyl shift



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{C}H_2 \xrightarrow[\text{shift}]{\text{methyl}} CH_3-\overset{\oplus}{\underset{CH_3}{C}}-CH_2CH_3$$

ELECTROPHILIC ADDITION REACTION

→ Alkenes have π bond so they are reactive.

→ In addition reaction π bond breaks & 2 new σ bonds forms.

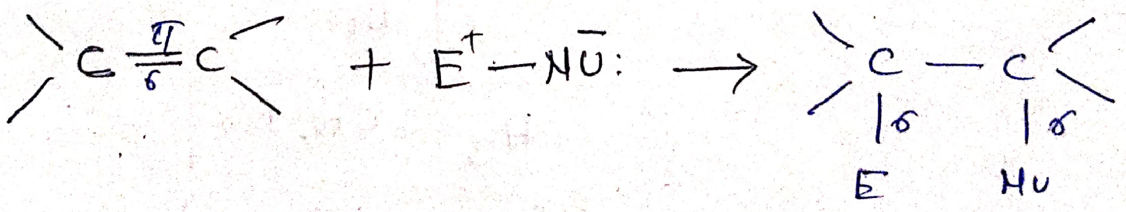
→ This reaction is mainly procedes by Electrophil. hence it's Electrophillic addition reaction.

Electrophile 1) It is a electron deficient species
2) having +ve charge
3) It attracted to region of high electron density.

e.g. +ve charged atoms. (H^+, Br^+, Cl^+)

Nucleophile : 1) Electron rich.
2) Can donate electron
3) Attracted towards less e^- density region.

e.g. Br^-, Cl^-, HO^-, $OS\bar{O}_3H$

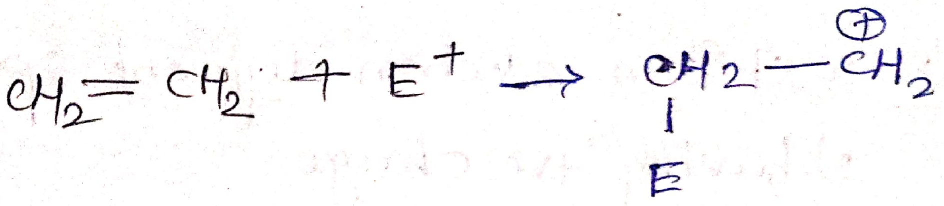


Steps

1) Reagent ionize to give electrophil & nucleophile

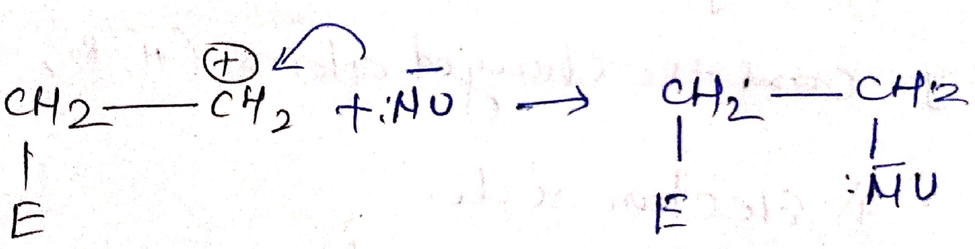
$E-Nu \longrightarrow E^+ + :\bar{Nu}$

2) Electrophile attack the $C=C$ to form co-valent bond.



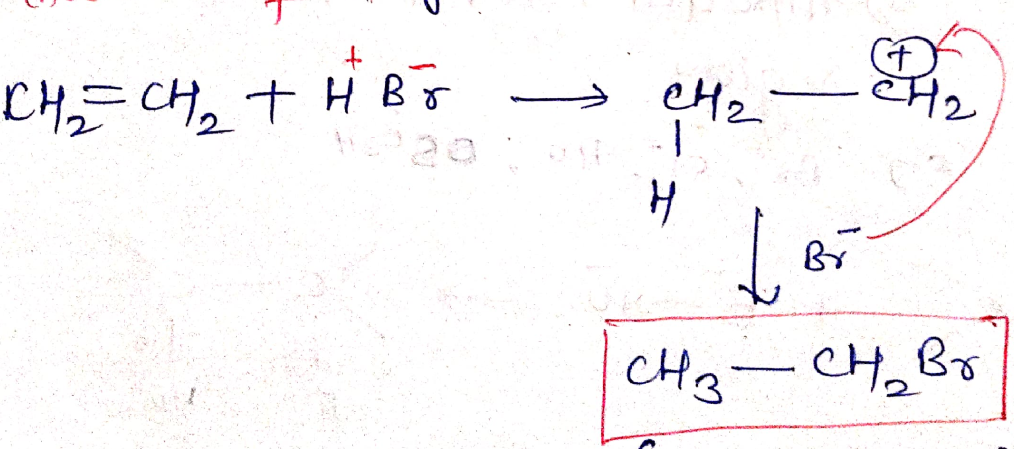
$CH_2=CH_2 + E^+ \rightarrow \underset{E}{\underset{|}{CH_2}}-\overset{\oplus}{C}H_2$

3) Nucleophile attack on Carbocation.



$\underset{E}{\underset{|}{CH_2}}-\overset{\oplus}{C}H_2 + :\bar{Nu} \rightarrow \underset{E}{\underset{|}{CH_2}}-\underset{:\bar{Nu}}{\underset{|}{CH_2}}$

e.g. ① (Addition of Halogen acid)



$CH_2=CH_2 + \overset{+}{H}\overset{-}{Br} \longrightarrow \underset{H}{\underset{|}{CH_2}}-\overset{\oplus}{C}H_2 \xrightarrow{Br^-} \boxed{CH_3-CH_2Br}$

(bromoethane)

② Addition of hallogen

$CH_2=CH_2 + Br \xrightarrow[\text{solvent}]{\text{inert}} Br-CH_2-CH_2-Br.$

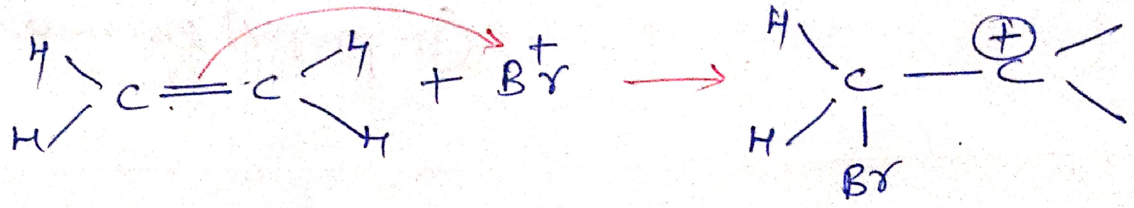
(CCl4)

⇒ $Br_2 \longrightarrow Br^+ + :Br^-$ → bromide ion

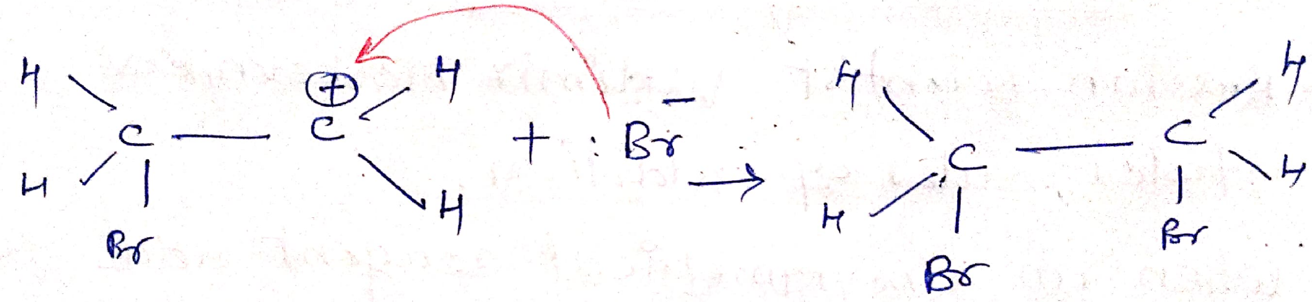
↓

bromonium ion

⇒



⇒



(1, 2 dibromo ethane)

③ Addition of H_2 (catalytic hydrogenation)

$$CH_2=CH_2 + H_2 \xrightarrow[\Delta]{Ni/Pd} CH_3-CH_3$$

$$CH_3-CH_2=CH_2 + H_2 \xrightarrow[\Delta]{Ni} CH_3-CH_2-CH_3$$

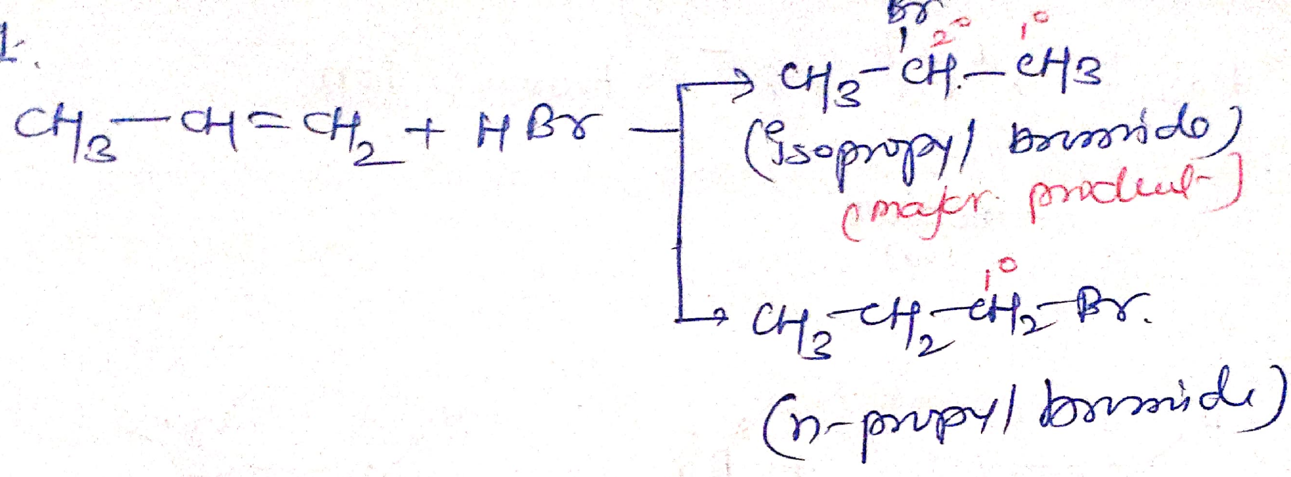
(Propane)

(unsaturated ⟶ Saturated)

* This is simple addition reaction, Not a ET NO reaction.

→ Performed at pressure.

e.g.



$$CH_3-CH=CH_2 + HBr \rightarrow \begin{cases} CH_3-\overset{Br}{\overset{|}{CH}}-CH_3 \text{ (Isopropyl bromide) (major product)} \\ CH_3-CH_2-CH_2-Br \text{ (n-propyl bromide)} \end{cases}$$

Markovnikov Rule

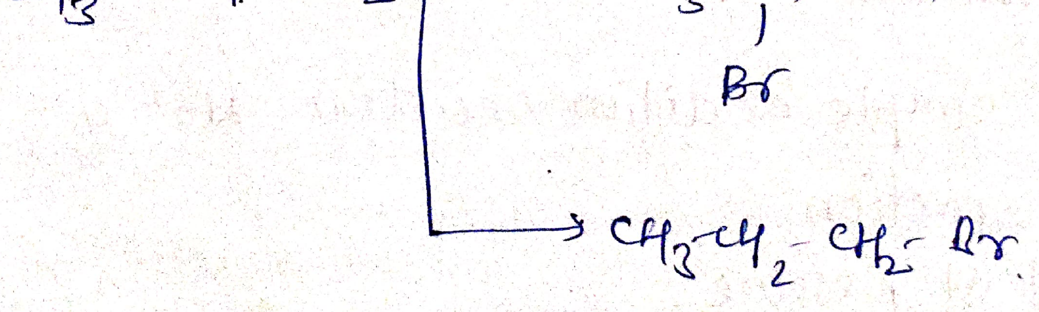
→ Russian scientist Vladimir Markovnikov states rules of addition.

i.e when an unsymmetrical reagent adds to an unsymitrical alkene then positive part attached to the double bond 'c' c̄ bears greatest number of H_2 atom.

⇒ It can also be stated that -ve part of reagent attached to the double bond 'c' which have least number of H-atom.

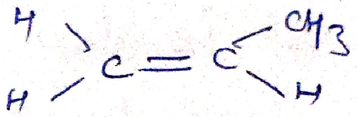
* Performed by electrophil reaction.

e.g.

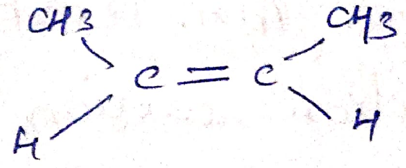


$$CH_3-CH=CH_2 \xrightarrow{HBr} \begin{cases} CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \\ CH_3-CH_2-CH_2-Br \end{cases}$$

Asymmitrical → carbon - carbon at double bond have different substitution.



Symmitrical → carbon (both) have same substituents.



* In asymmitrical alkene/alkyne two product are possible.

*

$$CH_3-CH=CH_2 + H-Br \xrightarrow{ccl_4} \begin{cases} (A)\ CH_3-CH_2-CH_2-Br & (1^\circ) \\ (B)\ CH_3-\overset{Br}{CH}-CH_3 & (2^\circ) \end{cases}$$

here product B is more stable so it is a major product.

Mechanism of Markonivkov Reaction

step 1 : ionization & formation of E^+ & $N\bar{u}$:

$$H-Br \longrightarrow H^+ + \bar{Br}:$$

Step-2

$$CH_3-CH=CH_2 + H^+ \longrightarrow \begin{cases} CH_3-\overset{H}{CH}-\overset{\oplus}{CH_2} & 1^\circ \\ CH_3-\underset{+}{CH}-CH_3 & 2^\circ \end{cases}$$

Step 3 : Nucleophil attack on more stable carbonium ion

$$CH_3-\overset{\oplus}{CH}-CH_3 + \bar{Br} \longrightarrow CH_3-CH-CH_3$$

Antimarkovnikov's Rule

→ It is also called Kharasch Effect as given by Mr. Kharasch scientist.

→ As per Anti markonivkov's Rule, In the addition reaction of unsymmitrical alkene, the Hydrogen will attached to that carbon of double bond where less number of H is present.

→ This reaction is performed in presence of R–O–O–R (Peroxide).

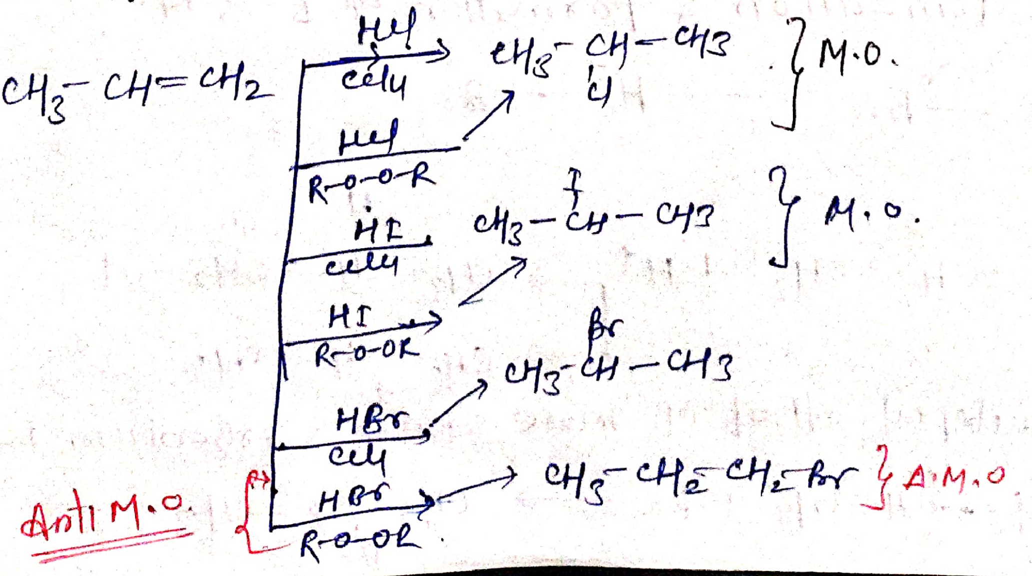
→ It's M.O.A. based on free radical Mechanism.

$$CH_3-CH=CH_2 \xrightarrow[R-O-O-R]{HBr} CH_3-CH_2-CH_2-Br$$

→ only $\boxed{HBr}$ shows Antimarkoniv-kove rule.

This effect is not possible in HCl / HI.

eg-



Mechanism

Step 1: Peroxide dissociate to give two free radicals.

$$R-O \wr O-R \xrightarrow{heat} R-\dot{O} + \dot{O}-R$$

Step-II

free radical attacks on reagent (HBr) and form $\dot{Br}$

$$R-\dot{O} + H-Br \longrightarrow R-OH + \dot{Br}$$

Step-III

Bromine free radical attack on alken to give 1°, 2° free radical

$$CH_3-CH=CH_2 + \dot{Br} \longrightarrow CH_3-\dot{CH}-CH_2Br$$

$$\longrightarrow CH_3-\overset{Br}{CH}-\dot{CH}_2$$

Step-IV

More stable free radical react c̄ HBr.

~~$CH_3=\overset{Br}{CH}$~~

$$CH_3-\dot{CH}-CH_2Br \xrightarrow{HBr} \boxed{CH_3-CH_2-CH_2Br} + \dot{Br}$$

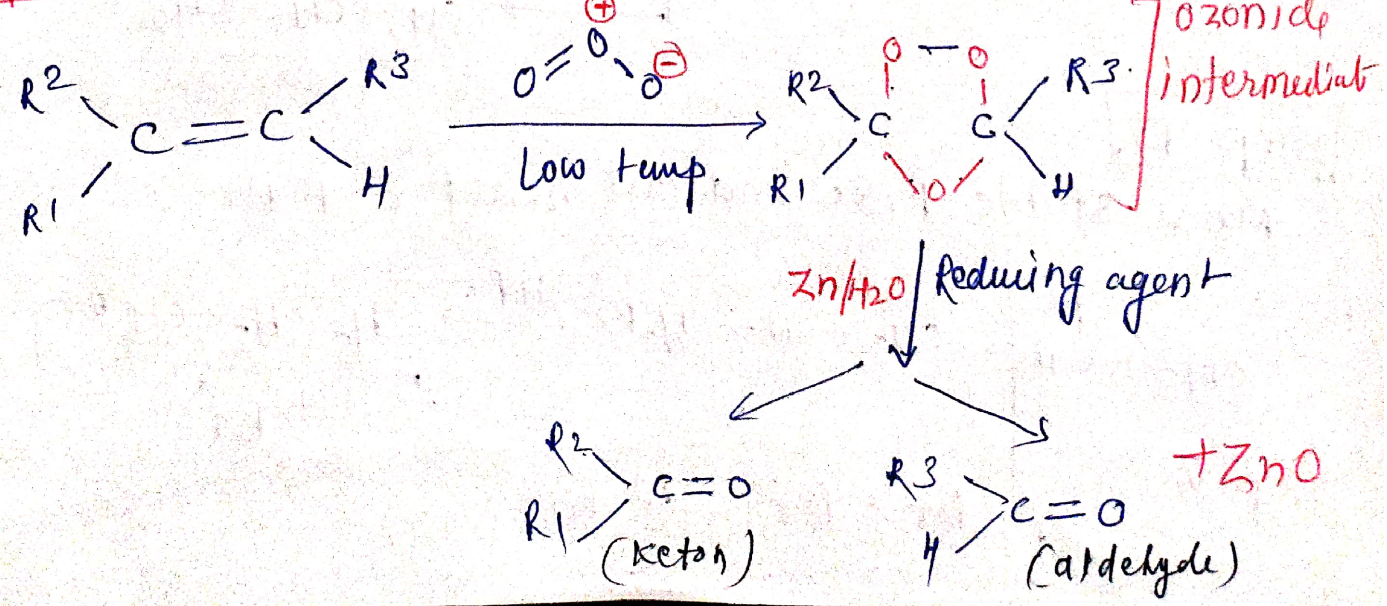
(Step-V) → $\dot{Br} + \dot{Br} \longrightarrow Br_2$

OZONOLYSIS

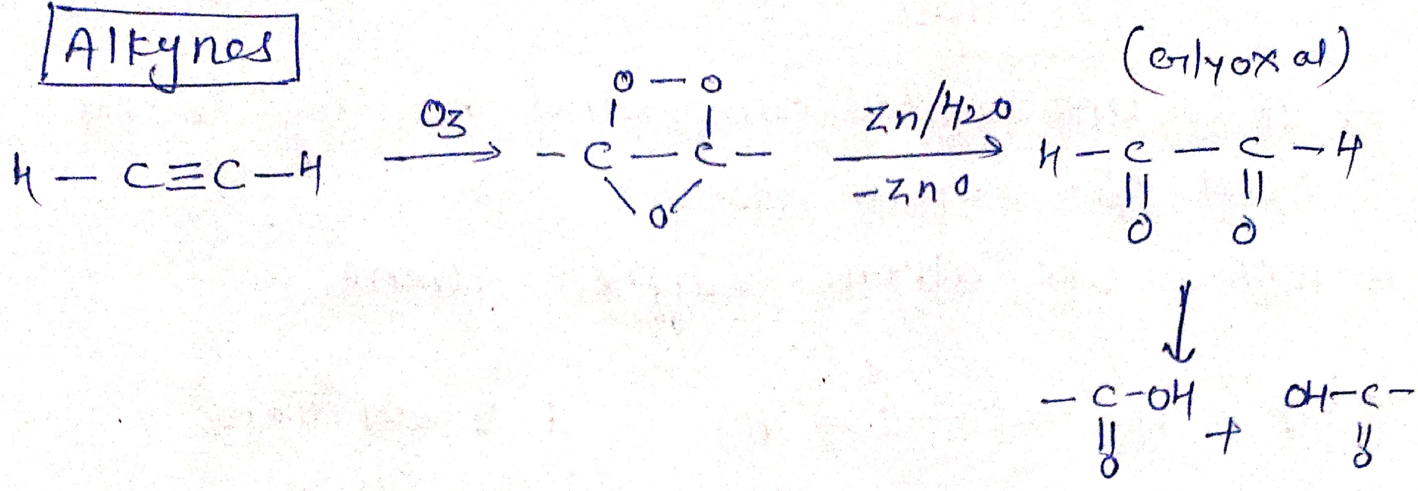
- → It is an organic reaction that uses O_3 (ozone) to cleave unsaturated bond of alkenes.
- → The reaction replace C=C bond c̄ carbonyl compound, (i.e. aldehyde & ketone) & carboxyllic compounds.
- → The reaction generate an ozonoide intermediate c̲ then treated c̄ a reducing agent ($(CH_3)_2S$, Zn) c̲ give then CHO, C=O.
- → Ozonoides can be treated c̄ H_2O_2 (oxidizing agent) c̲ convert aldehyde to acid.
- → More e^- rich alkene tend to react faster.
- → alkyne can also undergo ozonolysis.

Mechanism

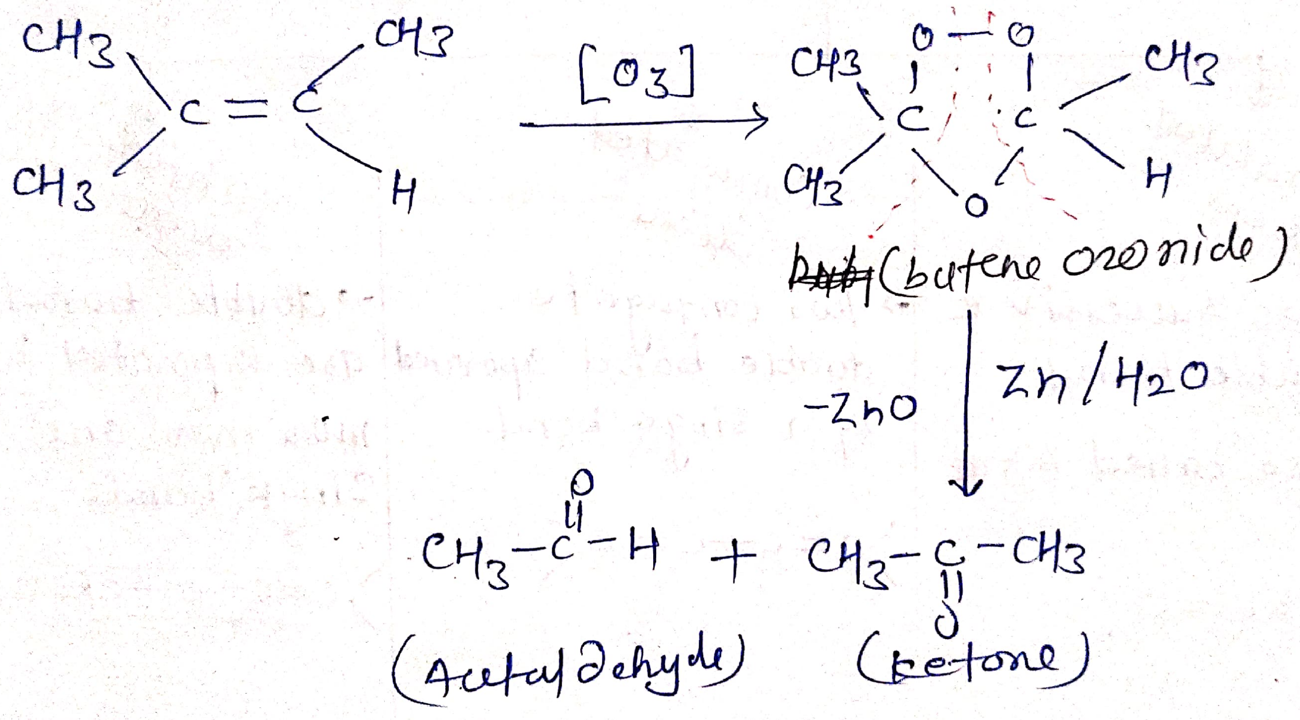
Step 1 → Ozonolysis



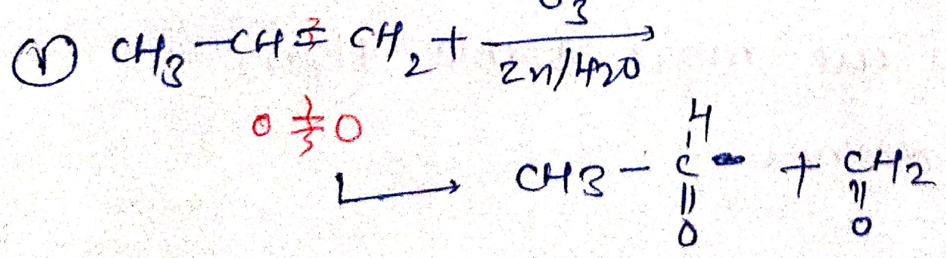
Alkynes



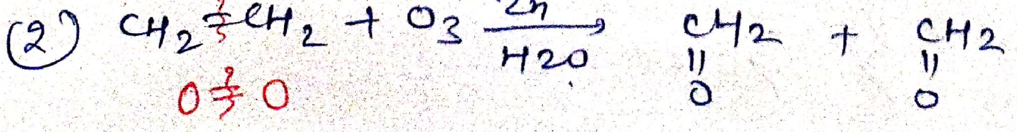
e.g.



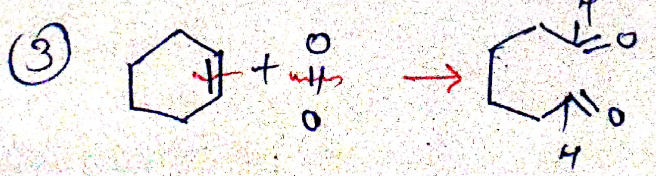
In short:



$$CH_3-CH=CH_2 + \xrightarrow[Zn/H_2O]{O_3} CH_3-\underset{\overset{\|}{O}}{\overset{H}{C}} + \underset{\overset{\|}{O}}{CH_2}$$



$$CH_2=CH_2 + O_3 \xrightarrow[H_2O]{Zn} \underset{\overset{\|}{O}}{CH_2} + \underset{\overset{\|}{O}}{CH_2}$$

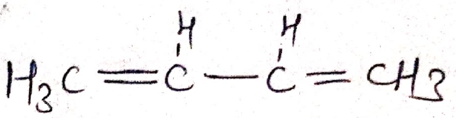


Dienes

→ It is unsaturated compound having 2 double bond b/w Carbon atoms.

→ IUPAC : Like alkene , suffix = -diene.

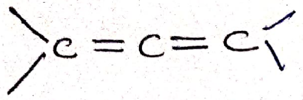
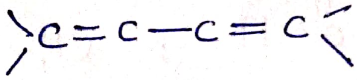
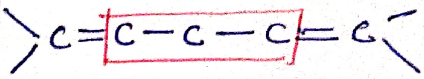
→ e.g.



$H_3C=\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=CH_3$

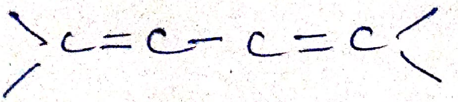
1, 3 but diene

Types of dienes

Comulated diene	Conjugated diene	Isolated diene.
→ two successive double bond → also called **Allene** 	→ two conjugate double bond. seperated by a single bond. 	→ double bond are seperated by more than one single bond. 

Stability of dienes

⇒ Conjugated dienes are more stable than non-conjugated dienes.



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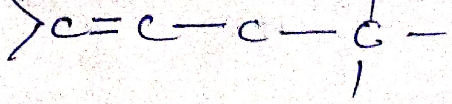


Diels-Alder Reaction

1) This reaction was discovered by the German chemist otto Diels & Kurt Alder in 1928.

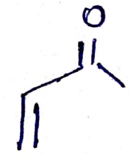
2) This reaction can be used to form six membered ring.

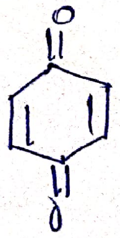
3) This is an intereaction b/w 4π electron & $2\pi\ e^-$.

4) It is a cycloaddition reaction.

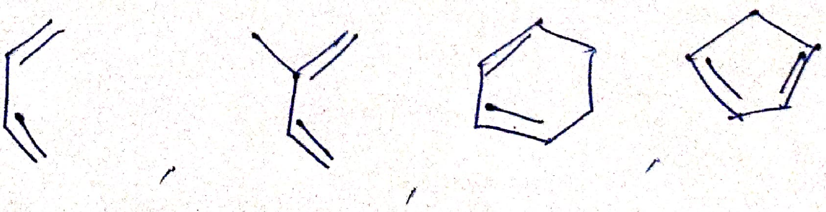
5) It is a chemical reaction b/w substituted alkene & a conjugated dienes. substituted diene is commonly reffered as dienophile.

e.g. dienophile →



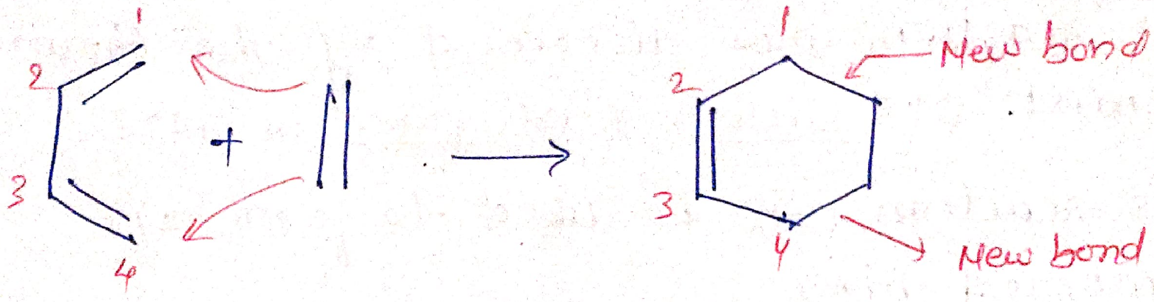


dienes →



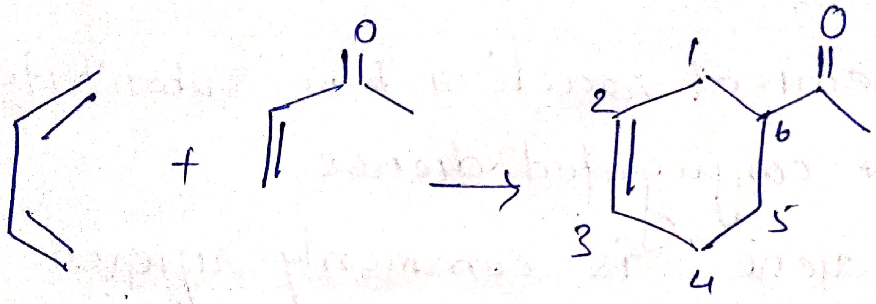
Reaction

①



cyclohexine.

②



Allylic Rearrangement

Some Carbon positions

(I) Allylic (II) Benyle.

(III) vinyl (IV) ~~Aryle~~ /phenyl.

(I) Allylic

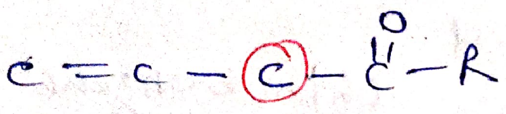
$C=C-\textcircled{C}$ ← Allylic Carbon

$\boxed{C=C-\textcircled{C}-OH}$

allylic alcohol

$C=C-\textcircled{C}-Br$

(Allyl bromide)



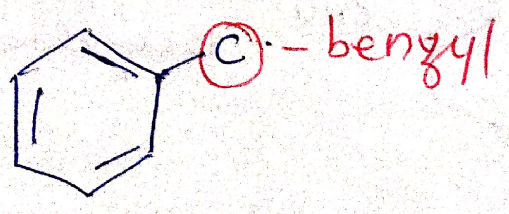
$C=C-\textcircled{C}-\overset{O}{\overset{\|}{C}}-R$

Allyl ketone

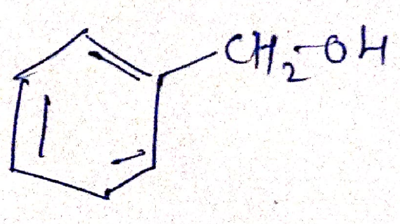
$C=C-\overset{\oplus}{\textcircled{C}}$

allyl carbocation

② ~~Benzyl~~ Benzyl

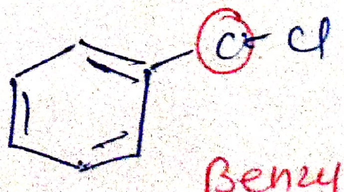


1)

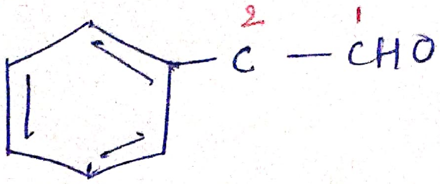


Benzyl alcohol

2)



Benzyl chloride



= 2 benzyl ethanal

(III) Vinyl

$C = C$ ← vinyl C

e.g.,

$C = C - OH$

vinyl alcohol

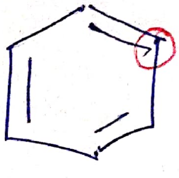
$C = C - Cl$

(vinyl chloride)

$C = C - NH_2$

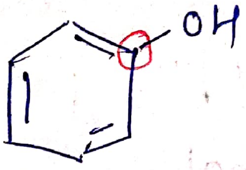
vinyl amino

(IV) Phenyl



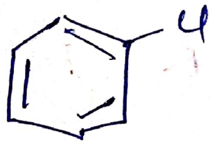
vinyl carbon

e.g.,

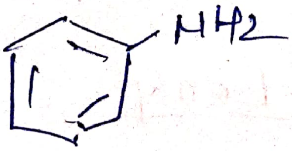


– phenol

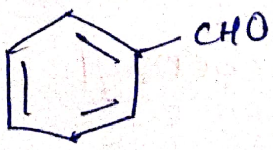
(Not phenyl alcohol)



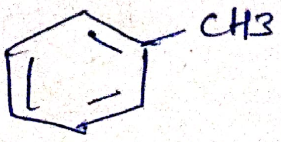
chlorobenzene



Anilin



Benzaldehyde

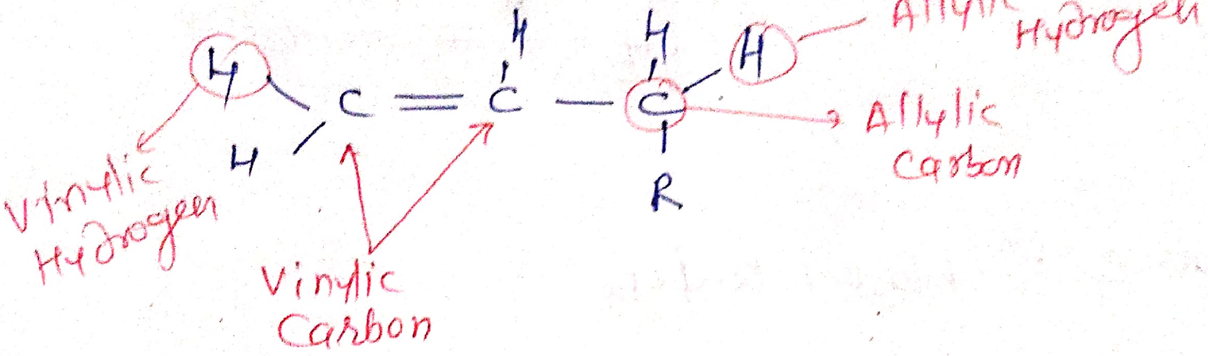


Toulene.

Allylic Rearrangement

⇒ An Allyl group is a substituent & structural formula " $H_2C=CH-CH_2-R$

here

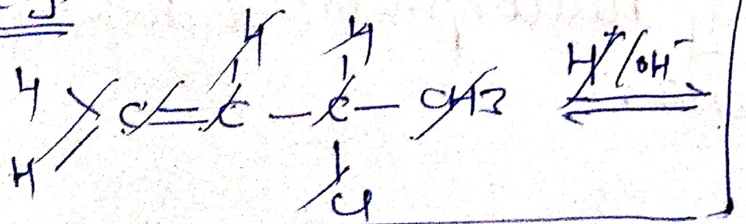


⇒ Allylic carbon = get rearranged.

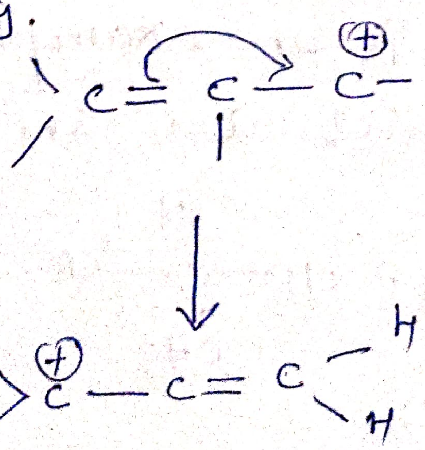
⇒ It is an organic reaction in which the double bond in an allyl chemical compound shift to the next carbon atom.

⇒ Intermediate is carbocation so several resonating structure can be formed.

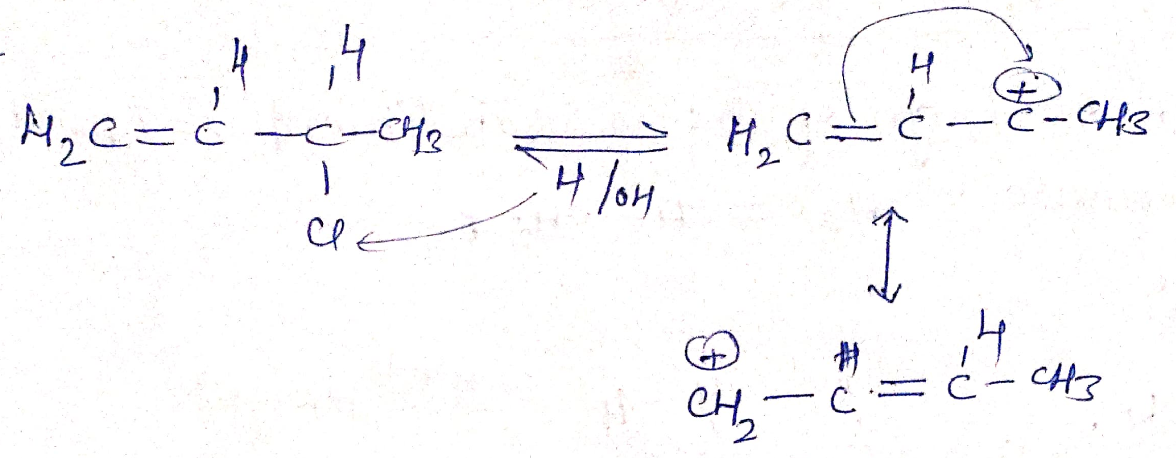
e.g.



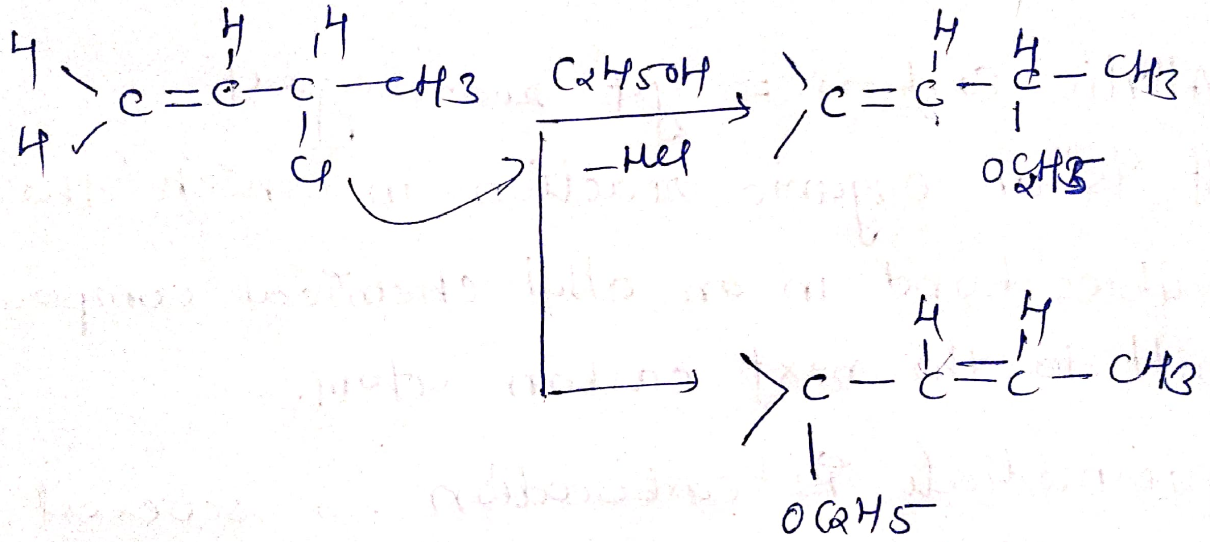
e.g.



e.g.

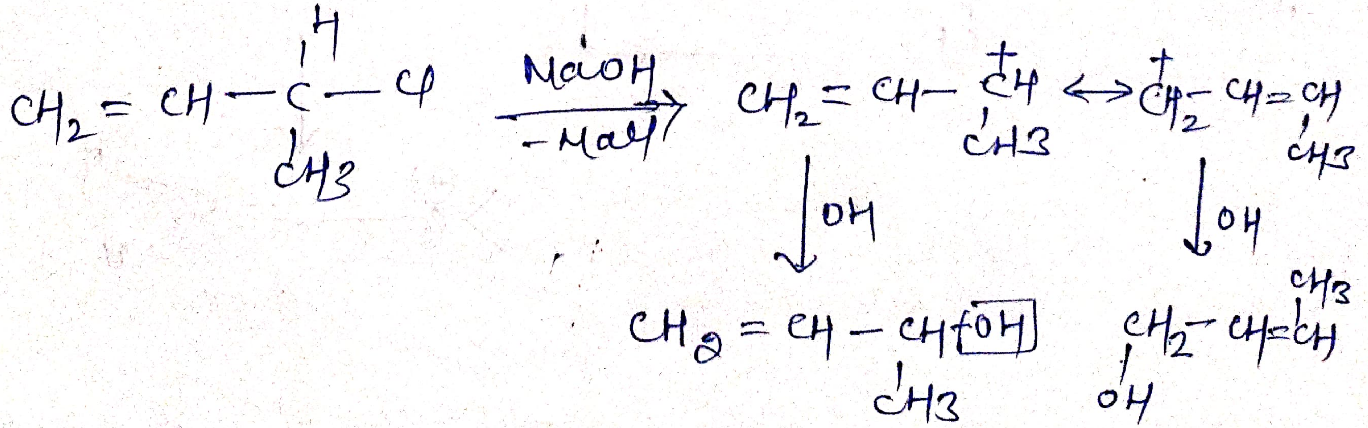


e.g. Reaction of 3-chloro-1 butene



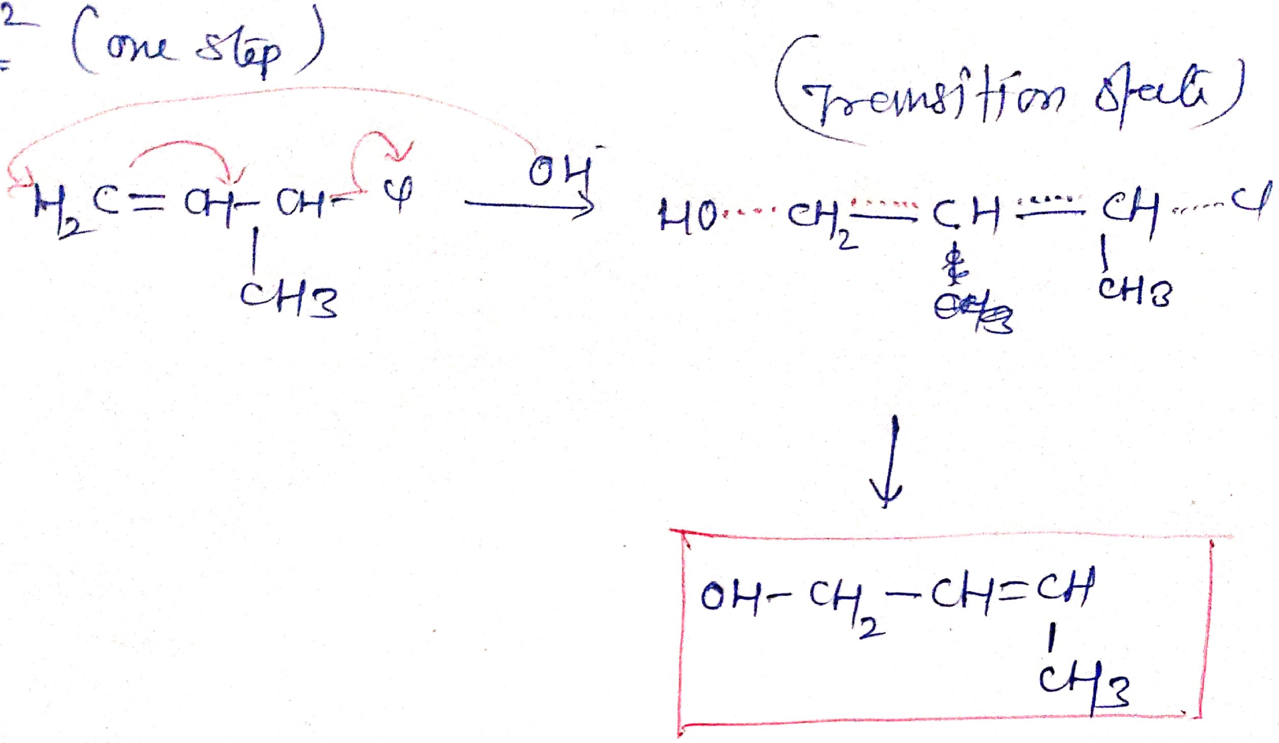
⇒ Mechanism (SN')

→ It is an example of nucleophillic substitution which are SN' & SN2.



(3-butene 2-ol)

S_N2 (one step)


(Transition state)
$H_2C=CH-CH(CH_3)-Cl$
OH^-
$HO\cdots CH_2\cdots CH\cdots CH(CH_3)\cdots Cl$
CH_3
$OH-CH_2-CH=CH(CH_3)$