

# Alkanes, Alkenes And Conjugated dienes

## Alkanes :-

$\text{Sb}^3$  hybridization in Alkanes :-

Hybridization:- Mixing of two ~~other~~ atomic orbital have different shape, bond angle and geometry and to form newly equivalent atomic orbital has same energy.

Three types of hybridization :-

- 1)  $sp^3$  or Tetrahedral hybridization
  - 2)  $sp^2$  or Trigonal hybridization.
  - 3)  $sp$  or Diagonal hybridization

E.g.:  $C_6^{12}$  → At ground state

$\downarrow$  Tetra Valency  $1s^2, 2s^2, 2p_2^1, 2p_y^1, 2p_z^1$  diaValent

An excited state

$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

At hybrid state electronic configuration of carbon atom

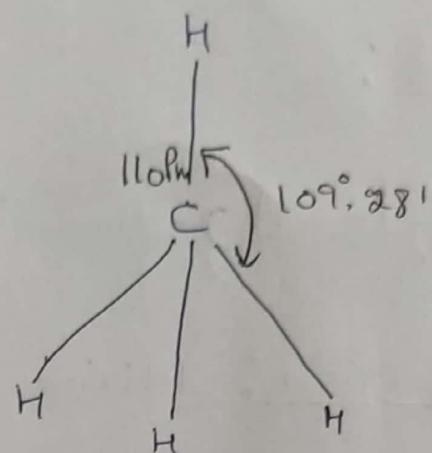
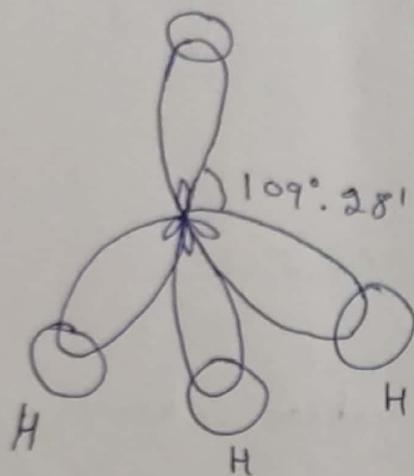
$2s^1, 2p^3, 3p^3, \underline{3p^3}$

1	1	1	1
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## 5 - Spherical Shape

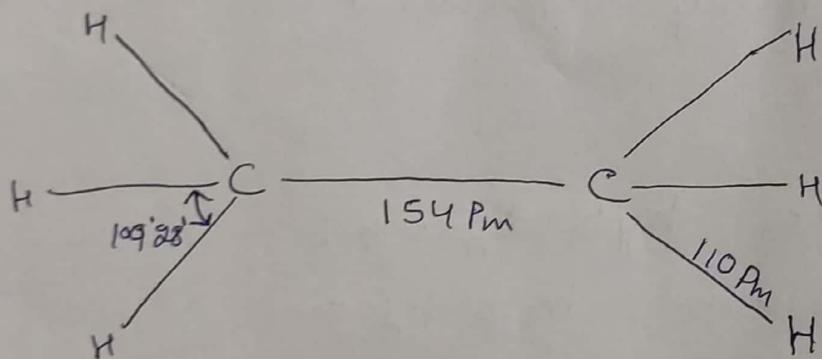
b - Dumb bell shape

In Methane :-



Tetrahedral Shape

In Ethane :-



$\text{sp}^3$  hybridization in Alkanes :-

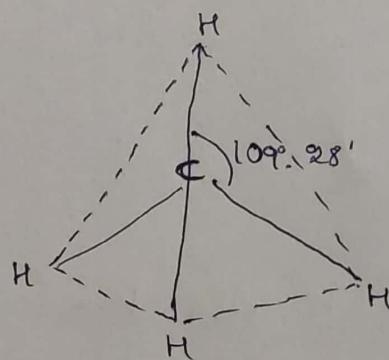
In this 1st and 3P orbital combine to form four equivalent hybrid orbitals. As these four equivalent hybrid orbital are directed towards the corner of regular tetrahedral is known as Tetrahedral hybridization.

All saturated compounds carbon such as alkanes involve  $\text{sp}^3$  hybridization.

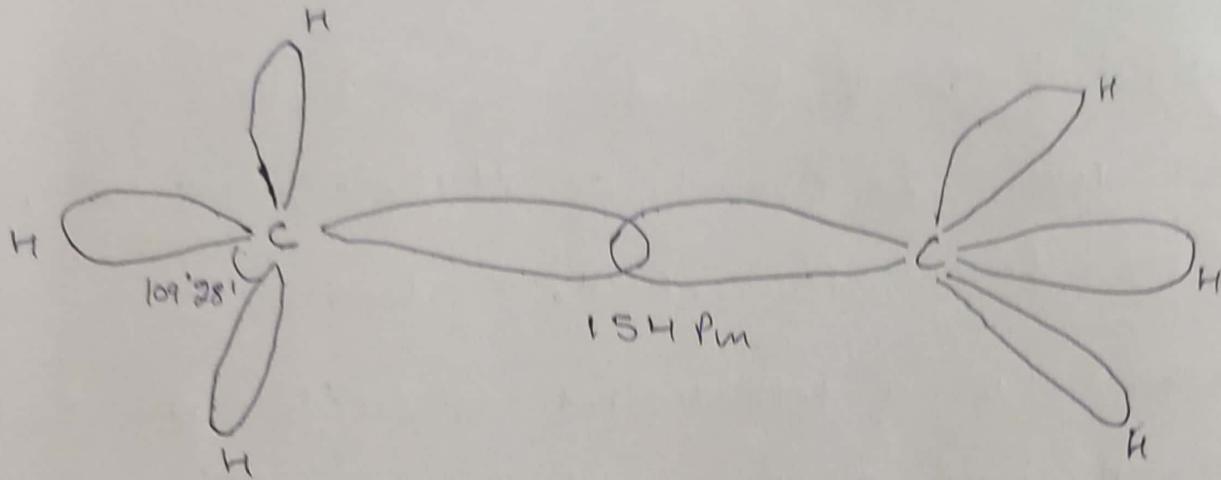
For example :- Methane ( $\text{CH}_4$ ) molecule, carbon is  $\text{sp}^3$  hybridized. Each of the four  $\text{sp}^3$  hybrid orbital overlap with  $1s$  orbital of 4 Hydrogen atom to form four  $\text{sp}^3-\text{s}$ ,  $\text{C}-\text{H}$ ,  $\sigma$ -bonds.

So, Methane is a tetrahedral molecule with each  $\text{H}-\text{C}-\text{H}$  bond angle equal to  $109^\circ 28'$ .

All the four  $\text{C}-\text{H}$  bonds are equivalent and are 110 pm long. Each  $\text{C}-\text{H}$  bond has a bond dissociation energy of 415 kg/mol.



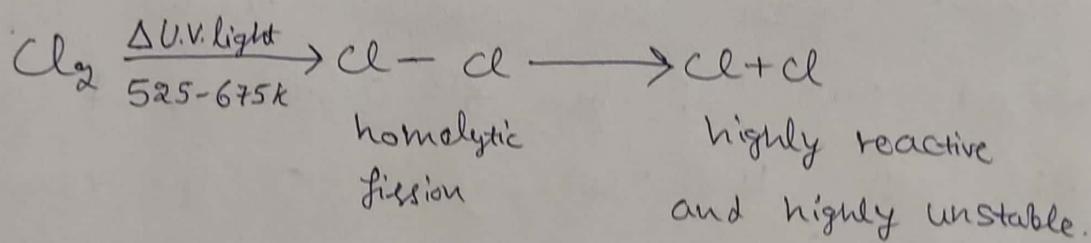
In Ethane both the carbon atoms are  $\text{sp}^3$  hybridized. One of the  $\text{sp}^3$  orbital of 1 carbon overlap with the  $\text{sp}^3$ -orbitals of the other carbon along their internuclear axis forming  $\text{sp}^3-\text{sp}^3$ ,  $\text{C}-\text{C}$   $\sigma$ -bond. The remaining three  $\text{sp}^3$ -orbitals on each carbon overlap with  $1s$ -orbitals of 3 H-atoms along their internuclear axis forming in all six  $\text{sp}^3-\text{s}$ ,  $\text{C}-\text{H}$  sigma bonds.



## Mechanism of halogenation of Alkanes :

1. > Chain initiation
  2. > Chain propagation
  3. > chain termination

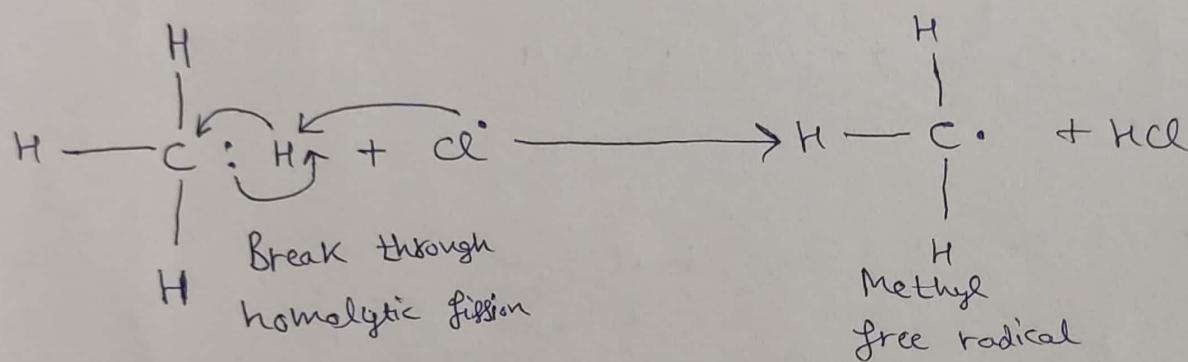
i) Chain initiation :- It is also known as free radical formation.



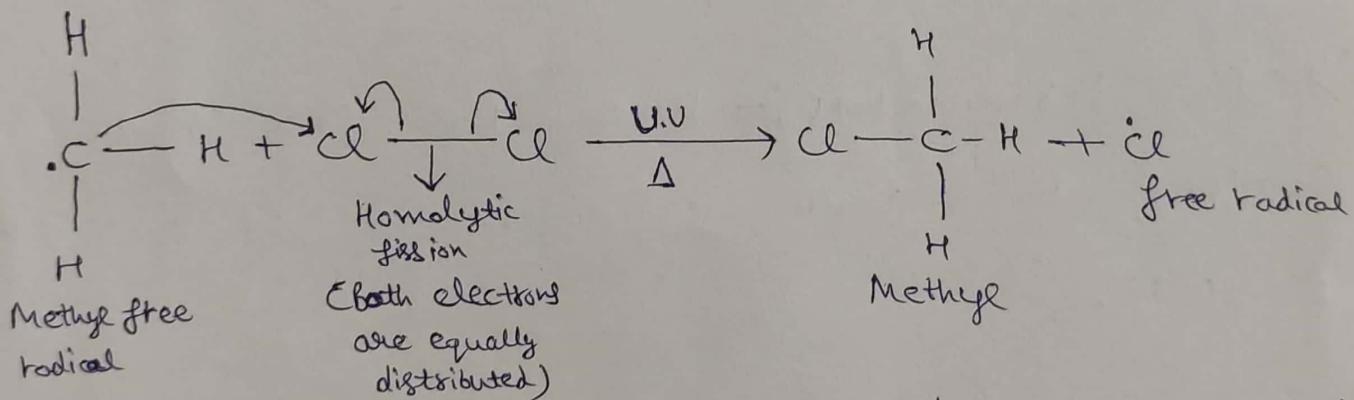
ii) Chain propagation:- There is free radical is consumed and there is formation of another free radical.

The chlorine free radical produced above collides with methane molecule and forms methyl free radical + HCl molecule (Step 1). The methyl free radical thus produced reacts with a molecule of chlorine forming methyl chloride and another chlorine free radical (Step 2).

### Step - 1

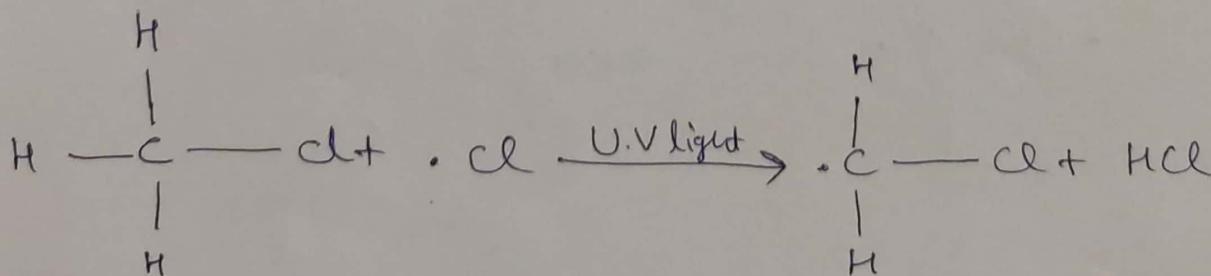


### Step - 2

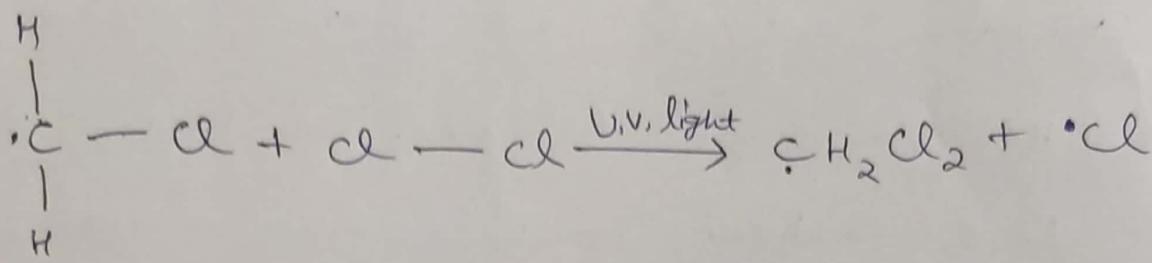


the above steps are repeat again and again and chain get propagated.

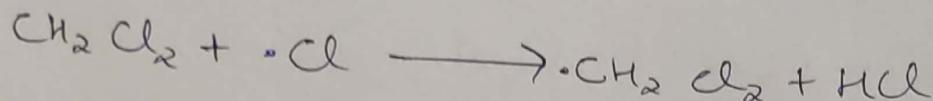
### Step - 3



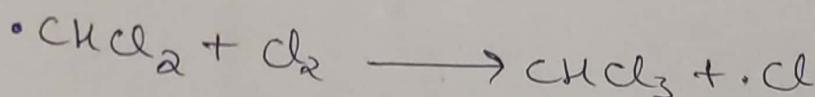
Step - 4



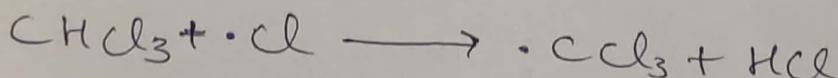
Step - 5



Step - 6



Step - 7



Step - 8



iii) > Chain termination :- When two free radical will combine then there is a formation of neutral molecule.



Paraffin :- Paraffin is a Alkane hydrocarbon that has a variety of isomers. It is also known as liquid paraffin.

### Paraffin Uses :-

- ① Paraffin is used in industries such as medicine, agriculture and cosmetics.
- ② Paraffin is widely used as fuel for jet engines and rockets and as fuel or a fuel component for diesel and tractor engines.

### Stabilities of alkenes :-

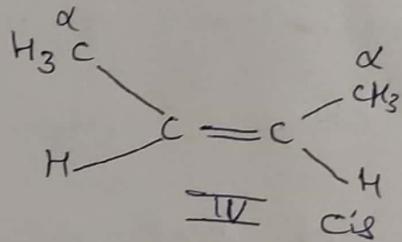
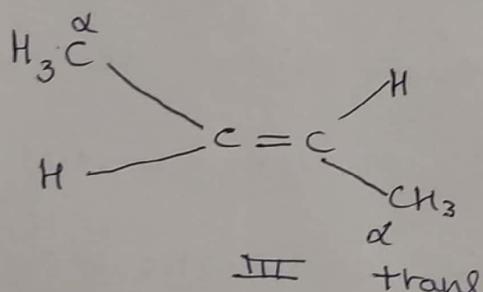
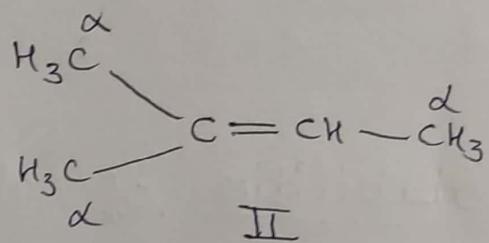
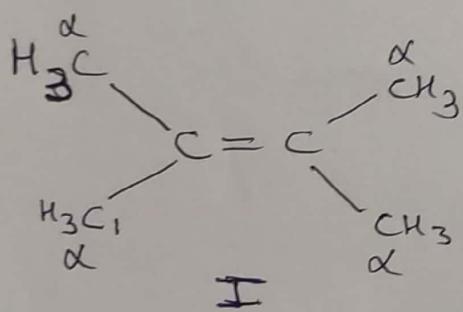
An alkene which has lower ~~heat~~ heat of hydrogenation is more stable than its isomers which have higher heat of hydrogenation.

Heat of hydrogenation is an exothermic reaction and it may be defined as the amount of heat evolved when 1 mole of alkene is hydrogenated. Thus the lower heat the hydrogenation more stable will be the alkene.

The heat of hydrogenation of some alkenes are:-

- 1) An unsaturated alkene such as ethene has the highest heat of hydrogenation.
- 2) Trans-isomers are more stable than cis-isomer.
- 3) Greater the number of Alkyl groups attached to the doubly bonded carbon atoms, more stable is the alkene.

Structures :-



$$\text{I} > \text{II} > \text{III} > \text{IV}$$

The relative stabilities of the above alkenes can be explained as:-

- 1) Alkenes I, II, III and IV have 12, 9, 6  $\alpha$ -hydrogens respectively.  
So, greater the number of hyper conjugation (greater number of  $\alpha$ -hydrogen) structure, more stable is the alkene.

The relative stability of these Alkene

$$\text{I} > \text{II} > \text{III} > \text{IV}$$

2> In cis structure (IV) the 2 methyl group lie on the same side of double bond and form steric hindrance. Therefore heat of hydrogenation is more in IV than III. So trans structure (III) is more stable than cis (IV).

### $Sp^2$ hybridization in Alkene :-

e.g:-  $C_2H_4$  ( $CH_2=CH_2$ )

Ethene

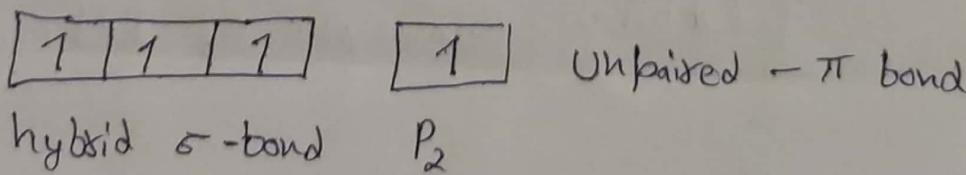
In this type of hybridization 1s and 2p orbitals combine to form three equivalent  $Sp^2$  hybrid orbitals while the 3rd 2p orbital remains unhybridized. These three  $Sp^2$  orbitals i.e. in a plane and are directed towards the three corners of an equilateral triangle so this hybridization is also called Trigonal hybridization.

At Excited State  $\ominus$  Configuration

$1s^2, 2s^1, 2p$

1	1	1	1
$p_x$	$p_y$	$p_z$	

At hybridized state  $1s^2, 2s^1, 2p$



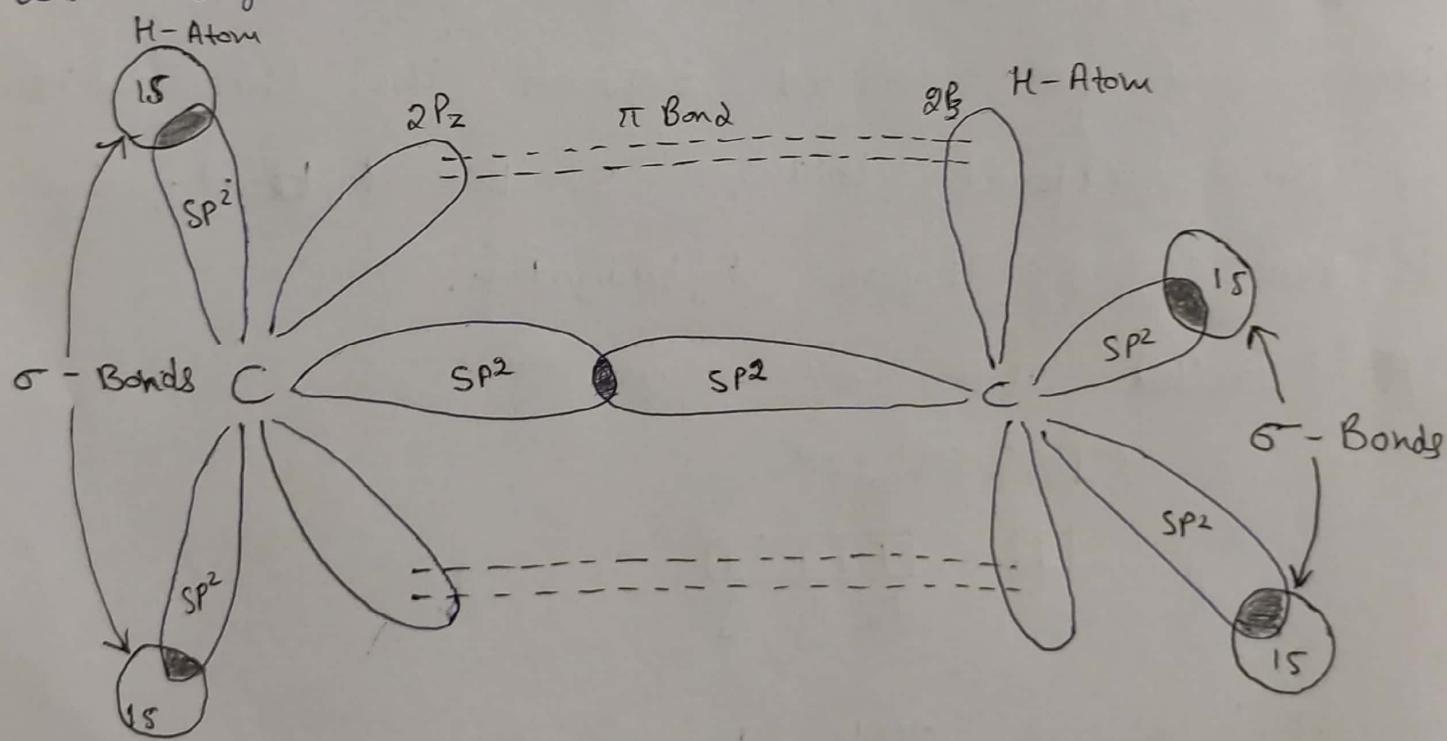
At excited state one orbital of  $1s$  S and two orbital of P, undergo mixing to form  $3sp^2$  orbital having same shape and energy.

At hybrid state each carbon has  $sp^2$  orbital which will form  $\sigma$ -bond and one unhybrid orbital to form  $\pi$ -bond.

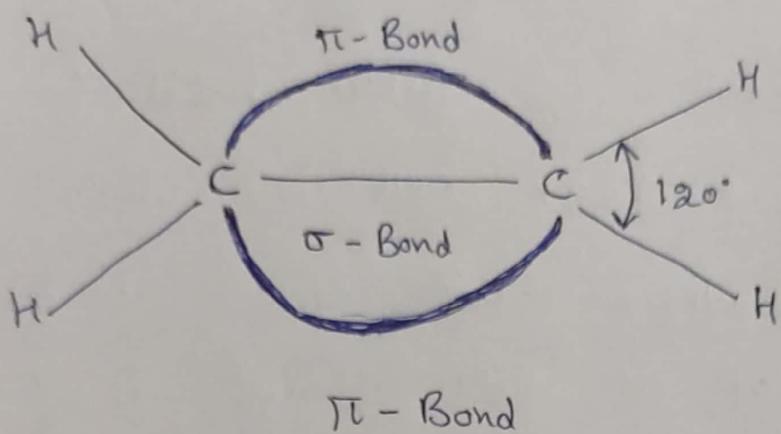
Out of three orbital in p-orbital any two orbital can participate in hybridization along with S-orbital.

If  $P_x$  and  $P_y$  is participate in hybridization than  $P_z$  remain unhybridized.

Geometry of  $sp^2$  orbital is trigonal planar and bond angle is  $120^\circ$ .



Orbital Structure of Ethene



$\pi$ -electron could consist of two equal halves one lying above and other below the plane of C and H atoms.

In ethene each carbon is  $sp^2$  hybridized one of the  $sp^2$  orbital each carbon overlap mutually along the inter nuclear axis  $sp^2-sp^2$ , C-C  $\sigma$ -bond.

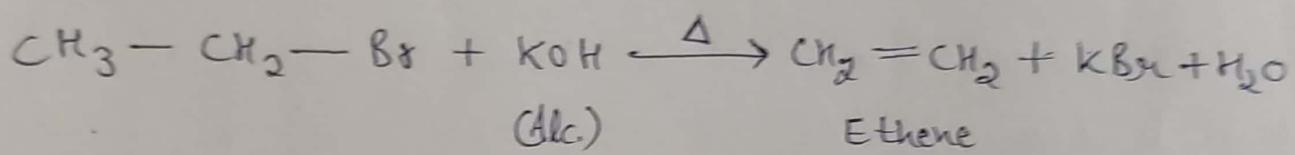
The remaining two  $sp^2$  orbital of each carbon overlap with 1s orbital of two H atom to form four  $1s^2-s$ , CH  $\sigma$ -Bond. Unhybridized i.e.  $p_z$  orbital that perpendicular (⊥) to the molecular plan.

The  $p_z$  unhybridized orbital of 1c sideways overlapping with unhybridized of adjacent carbon atom to form  $\pi$  bond.

## Preparation of alkenes :-

## Dehydrohalogenation of Alkyl halides :-

Alkyl halides was react with base then there is a removal of hydrogen halide from the adjacent carbon atom of an Alkyl halide is called Dehydrohalogenation.



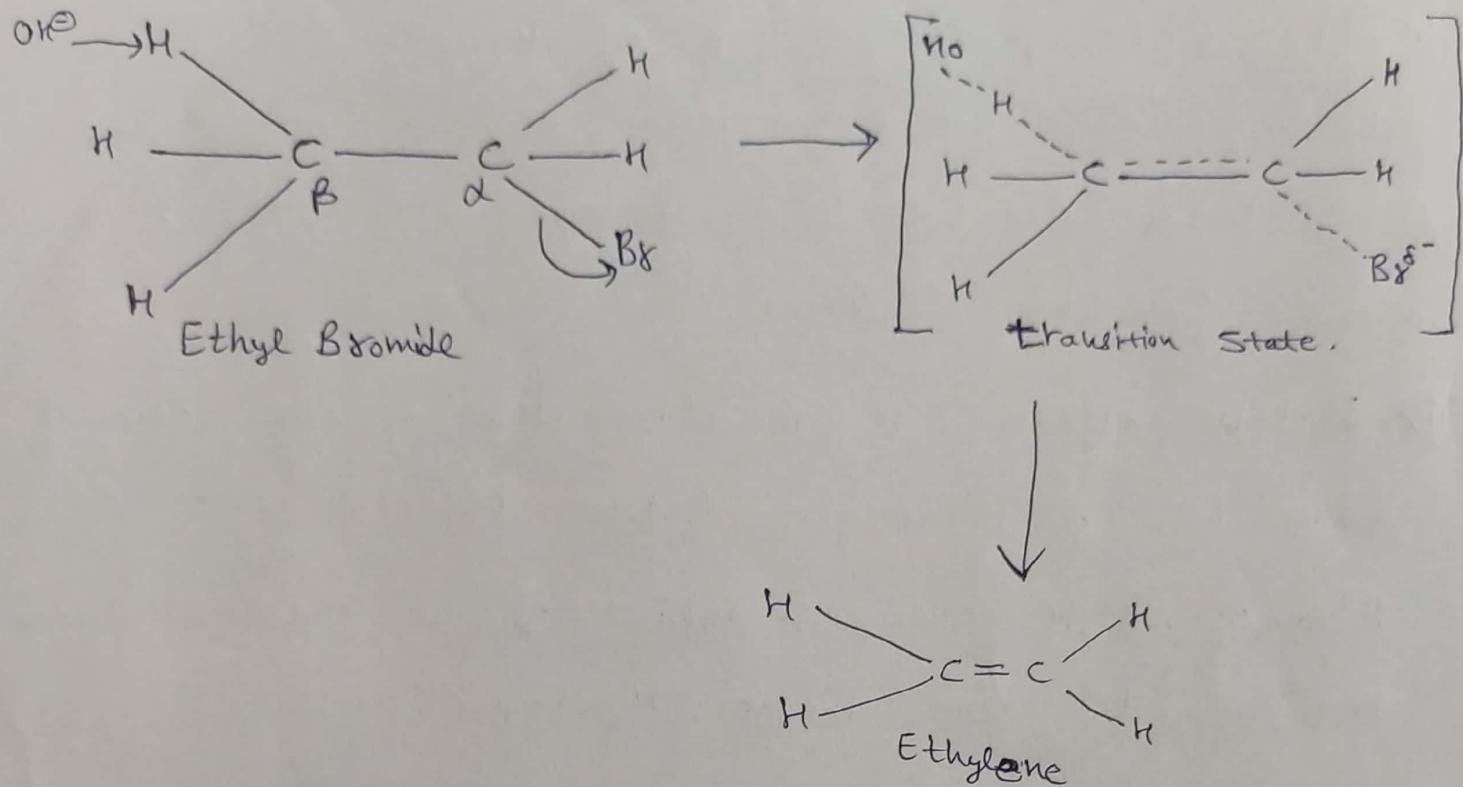
Elimination is two types :-  $E_1$  &  $E_2$

## E<sub>2</sub>    Elimination    Reaction :-

This reaction is based on E<sub>2</sub> elimination reaction  
E<sub>2</sub> elimination is also known as molecular reaction.

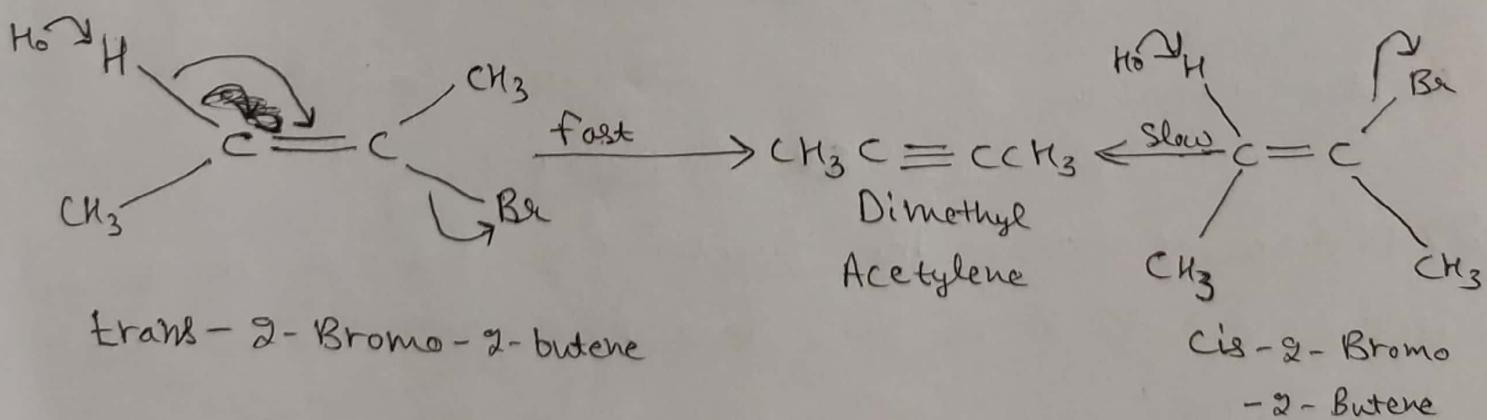
It is one step process and involves an intermediate transition state. Base (KOH) abstracts a proton away from the carbon and simultaneously a halide ion departs and formation of double bond.

### Mechanism :-



### Steroechemistry of $E_2$ Elimination Reaction :-

$E_2$  Elimination reaction are much faster when the two leaving group (Hydrogen and halogen) are trans to each other rather than cis. Trans - 2-Bromo - 2-Butene to form dimethyl acetylene more readily than the cis isomer.



## Evidence for E<sub>2</sub> Mechanism :-

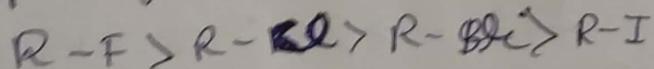
- i) It follows 2nd order of kinetic as the rate determining step involves reaction b/w a molecule of Alkyl halide and molecule of base and there is no scope for rearrangement.
- ii) Isotope effect :- i) This elimination reaction shows large no. of Hydrogen isotope effect.  
Absence of H exchange :- Typical second order elimination reaction does not involve Hydrogen exchange.

## Factors Affecting E<sub>2</sub> Elimination Reaction :-

- 1) Nature of Alkyl halide :- Nature of Alkyl halide are important ~~substrate~~ substrate in elimination reaction. Alkyl halide must have a good leaving group (halide ion). Better the leaving group more will be rate reaction. The reactivity of Alkyl halide follows the sequence for elimination as



As the strength of carbon halogen bond follows the sequence



- 2) Nature of Base :- The function of base is to abstract Hydrogen as a proton. The rate of reaction depend upon the nature of the base, a stronger base

Pulls a proton away from the substrate faster.  
So stronger the base more will be the rate of reaction. Strong base like KOH is used.

3) Nature of Solvent :- Less polar solvents favours E<sub>2</sub> Elimination.

4) Nature of Alkyl groups :- The order of reactivity of Alkyl groups ie  $3^\circ > 2^\circ > 1^\circ$ , As there is greater stability of highly branched alkene, which is being formed from highly branched Alkyl group.

### Characteristics of E<sub>2</sub> Reaction :-

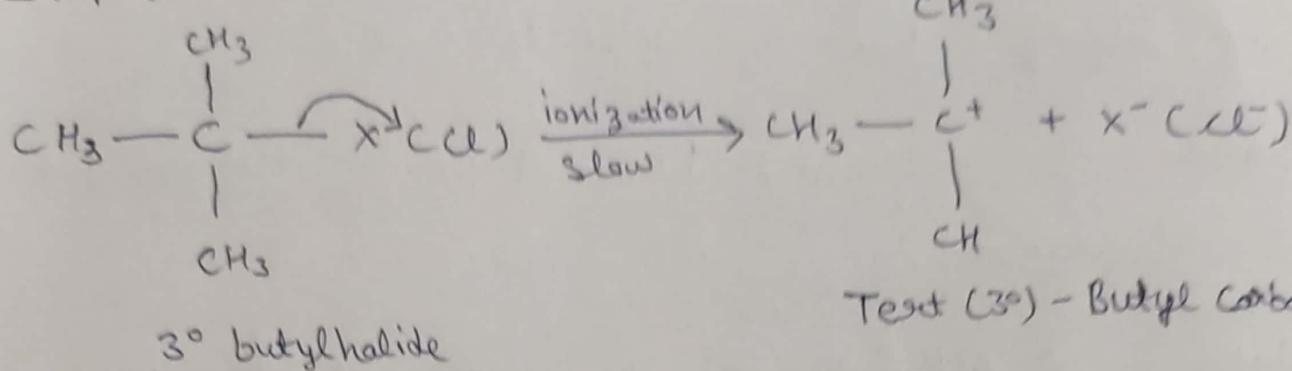
- ① It follows 2nd order kinetics.
- ② It doesn't involve rearrangements.
- ③ It shows a large hydrogen isotope effect.
- ④ It is not accompanied by hydrogen exchange.
- ⑤ It is Bimolecular reaction.
- ⑥ It is one step reaction.

E<sub>1</sub> Elimination Reaction :- It is also known as Unimolecular elimination reaction.

- It follows 1st order kinetics.
- It involves two step reaction.
- Many  $2^\circ$  and  $3^\circ$  Alkyl halides undergo elimination rxn by this method. This step is slow and hence rate determining step of the reaction.

## Mechanism :-

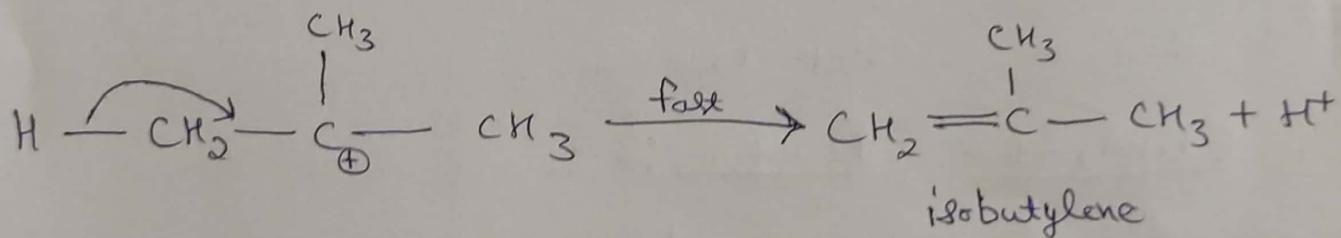
### Step I



E<sub>1</sub> elimination reaction is equal molecular reaction. 2° and 3° alkyl halide undergoes elimination by this method. It is two step process which involve intermediate formation of carbocation.

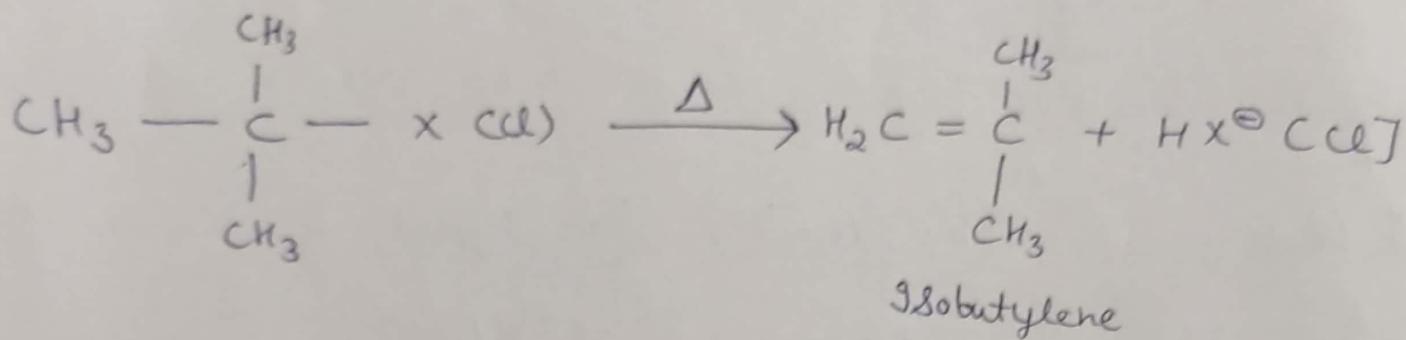
The first step involve ionisation of alkyl halide to form carbocation. This step is slow.

### Step II :-



$$\text{Rate} = k [\text{Alkylhalide}]$$

## Overall reaction :-



## Evidence for E<sub>1</sub> Mechanism :-

i) It follows 1<sup>st</sup> Order Kinetics

$$R = K [\text{Alkyl halide}]$$

ii) Not accompanied by a primary hydrogen isotope effect.

iii) It involve the formation of carbocations so always accompanied by rearrangement.

## Factor Affecting E<sub>1</sub> Elimination Reaction :-

i) Nature of Alkyl ~~halide~~ group :- The order of reactivity of Alkyl group is  $3^\circ > 2^\circ > 1^\circ$ . The reactivity of E<sub>1</sub> increases because of greater stability of carbocation begin formed in the rate determining step.  $3^\circ$  carbocation are more stable and produced.

2. Nature of Base :- The nature and concentration of base does not effect  $E_1$  elimination reaction as it doesn't take part in rate determining step.

3. Nature of Alkyl halide :- The effect is same in  $E_2$  Elimination reaction  $3^\circ > 2^\circ > 1^\circ$ .

As the overall rate of reaction depend upon stability of carbocation.

4. Nature of solvent :- Highly polar Solvents favoured  $E_1$  elimination reaction, as it helps to stabilize the carbocation formed in the rate determining step.

$E_1$  reaction versus  $E_2$  reaction.  
OR

Difference between  $E_1$  and  $E_2$  reaction :-

$E_1$	$E_2$
1. Unimolecular reaction.	1. Bimolecular reaction.
2. Two Step reaction.	2. One Step reaction.
3. Follow 1st order Kinetics.	3. Follow 2nd order Kinetics.

4. There is formation of carbocation.	4. There is non formation of carbocation.
5. Rearrangement of chemical reaction.	5. No rearrangement of chemical reaction.
6. No strong Base is required.	6. Strong Base is required
7. No stereochemistry is required.	7. Stereochemistry is required.
8. Rate of reaction depend upon conc. of Alkyl halide.	8. Rate of reaction depends upon concentration of Alkyl halide and Base.
9. Highly polar solvent is required.	9. Less polar Solvents is required.

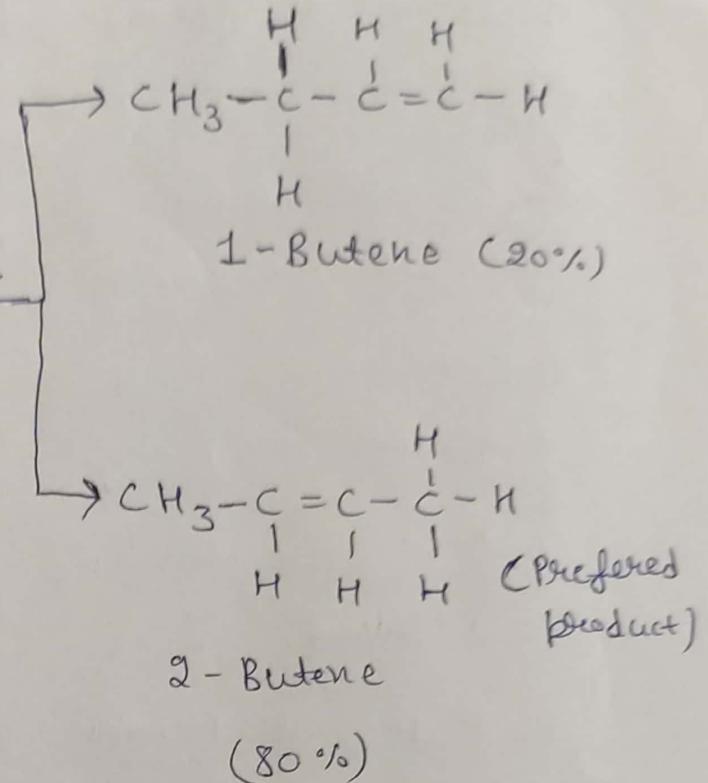
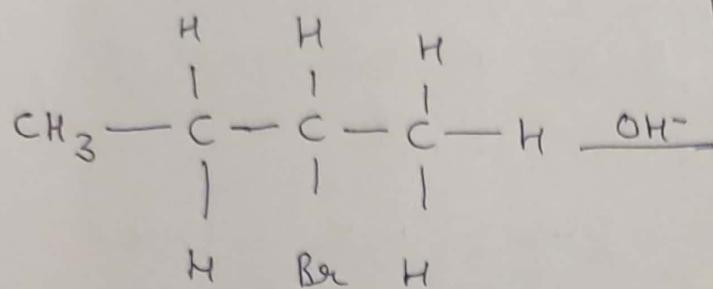
Orientation of Elimination Reaction (SAYTZEFF RULE):-

Dehydrogenation of Alkyl Halides gives a mixture of isomeric Alkenes which isomers will predominate depends upon the orientation of elimination.

For example :- 2-Bromobutane on dehydrogenation gives 1-Butene C attack by Base at  $\beta$ -hydrogen of  $C_1$ ) and 2-Butene C attack by base on  $\beta$ -hydrogen on  $(C_3)$ .

2-Butene is the preferred product i.e. alkene which is more stable will be formed in greater amount.

Reaction :-

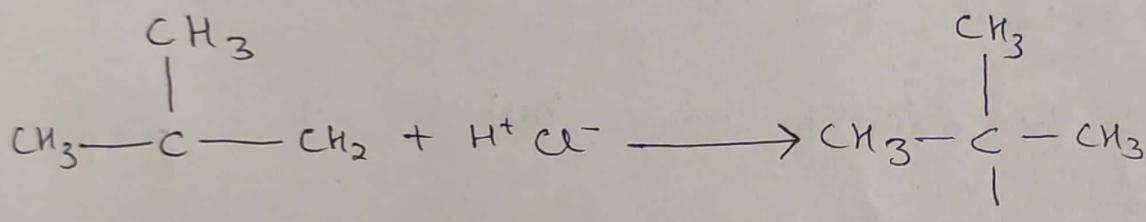


Acc. to Styzeff rule state that base i.e. KOH(OH)  
will attack on lesser no. of H atom and to  
give a more stable product.

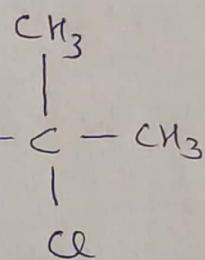
2-Butene is a disubstituted alkene having 2 Alkyl groups attach to the double bond whereas having only one Alkyl group. A disubstituted alkene is keener over a monosubstituted alkene. Acc. to Styzeff rule which state that in which dehydrogenation the prefer product is the alkene which is highly substituted.

Markownikoff's Rule :- It states that the addition of unsymmetrical reagent such as  $\text{Hx}$ ,  $\text{H}_2\text{O}$ ,  $\text{HOX}$  etc. to unsymmetrical alkene occurs in such a way that the -ve part of the adding molecule (addendum) goes to that carbon atom of the double bond which carries lesser number of hydrogen atom.

For example :-

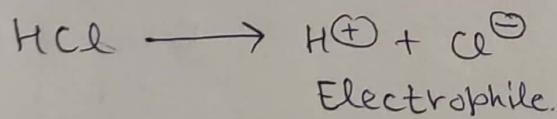


2-Methyl Propene

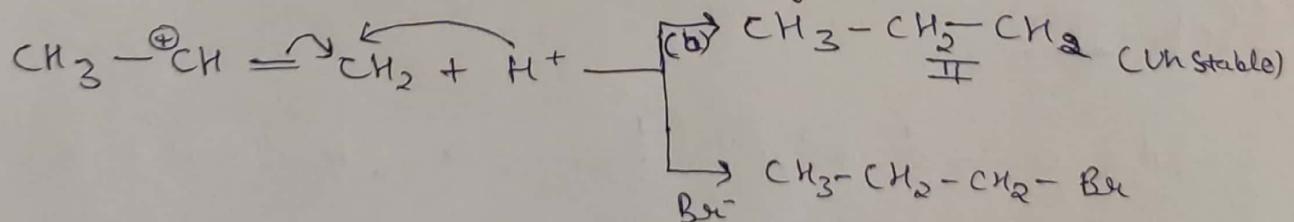


2-Chloro-2-Methyl  
Propane.

Mechanism :- Step-I :- Generation of electrophil ( $\text{E}^+$ ) by cleavage of Halo acid. ( $\text{HCl}$ )



Step-II :-  $\text{E}^+$  combination  $\in$  unsymmetrical alkene

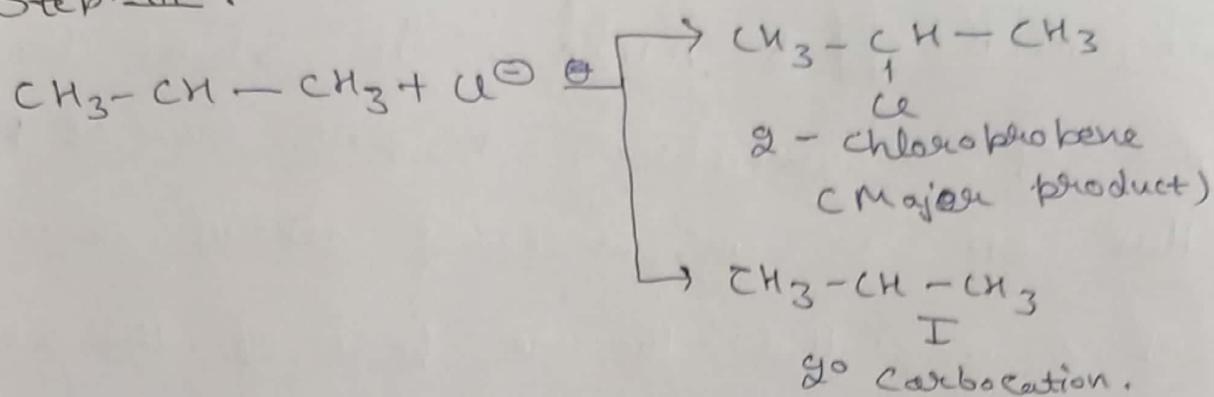


1-Bromo-2-butene

(Minor product  
stable)

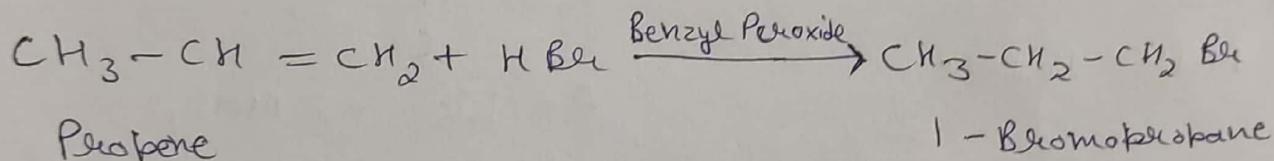
$2^\circ$  Carbocation is more stable than  $1^\circ$  carbocation because it contain  $2$ -Methyl group.

Step-III :-

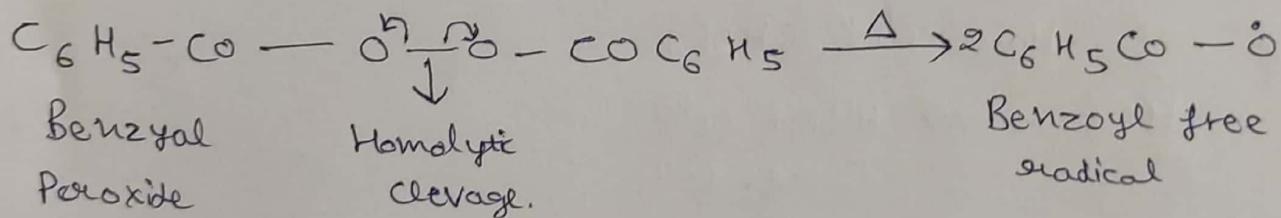


Anti-Markownikoff's Rule (Peroxide effect); -

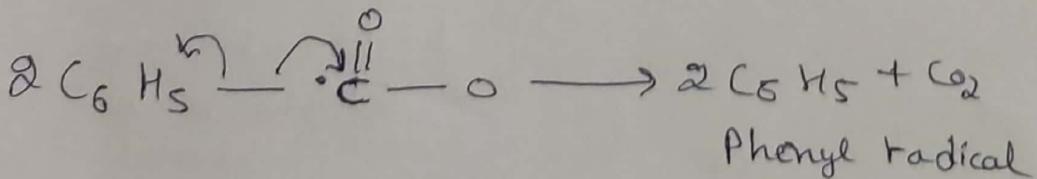
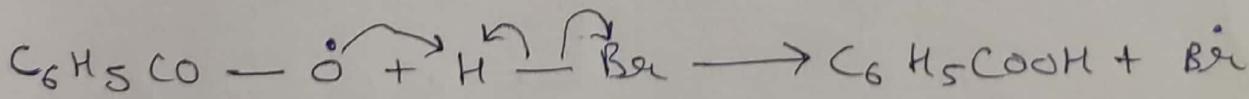
It is opposite of Markownikoff's rule it states that the addition of unsymmetrical reagent to unsymmetrical alkene occurs in such a way -ve part of adding molecule goes to the carbon atom of double bond that carry more number of H atom.



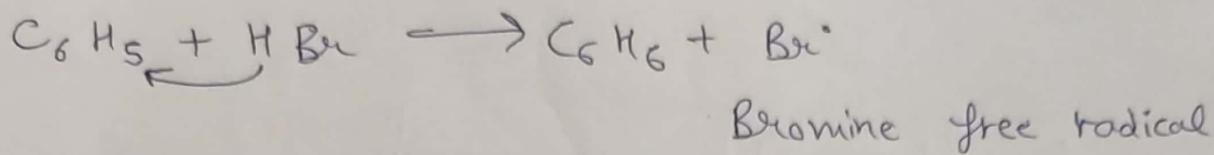
## Mechanism:-



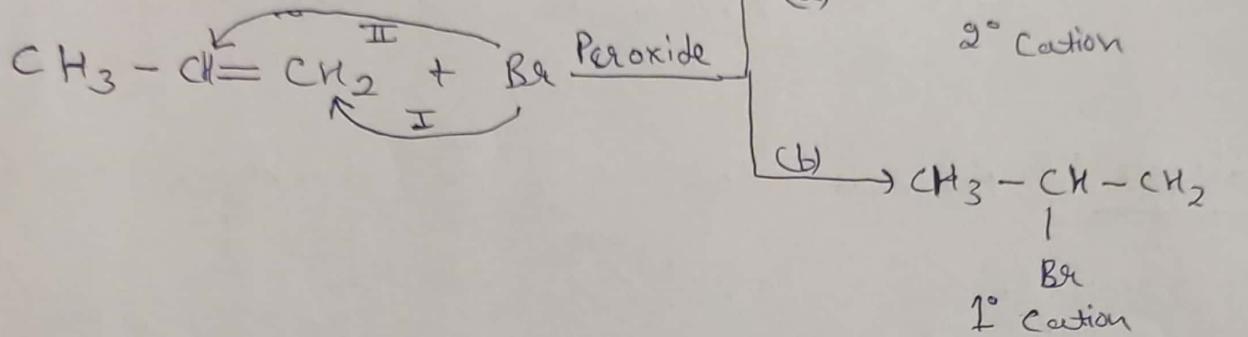
## Step-II:-



Step - II :-

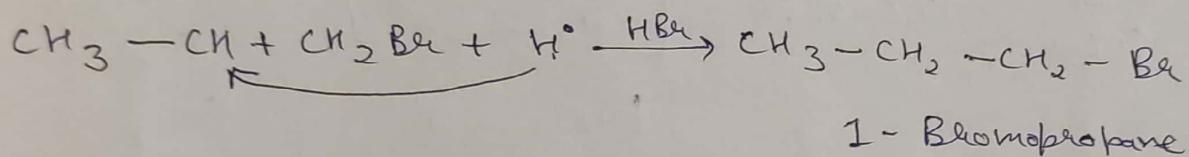


Step - III :-



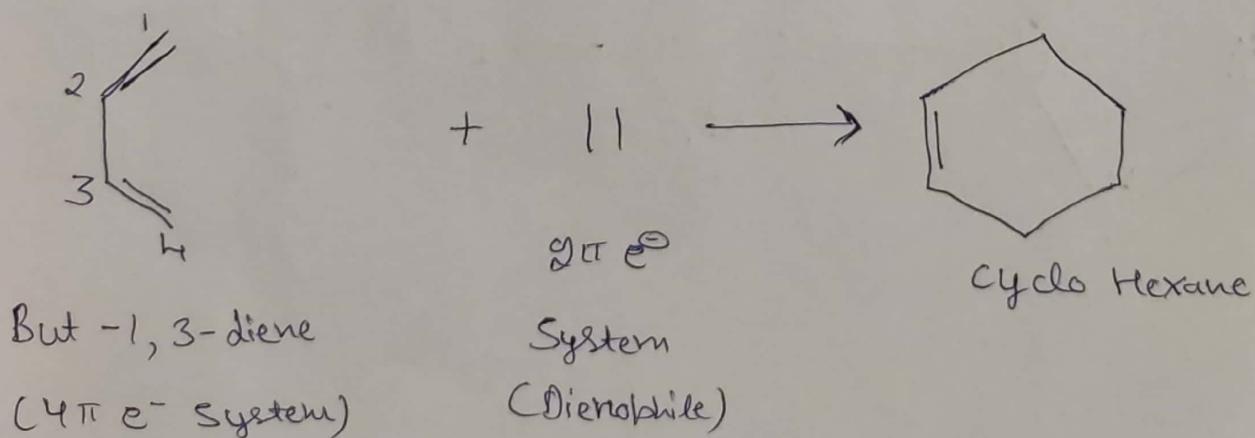
Step - IV :-

This  $2^{\circ}$  Carbocation

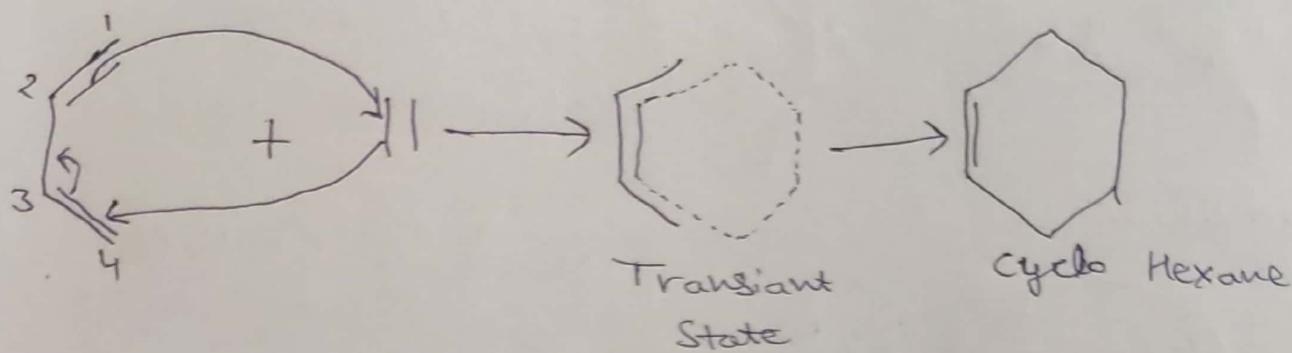


Conjugated Dienes :- That have two or more Double Bond double bond they may not adjacent carbon each other ( $=$  bond,  $-\sigma$  bond) ( $=$  bond).

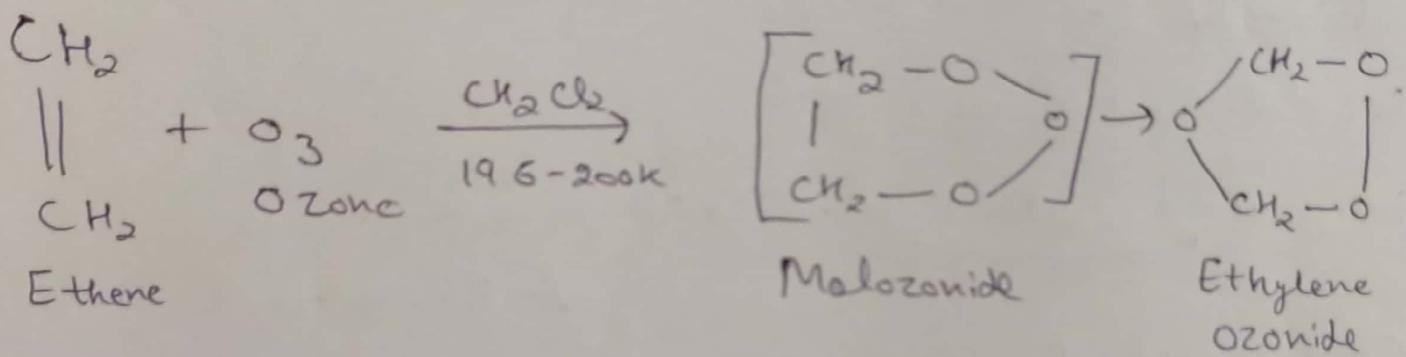
Diels - Alder Reaction (Cyclo addition Reaction) :-



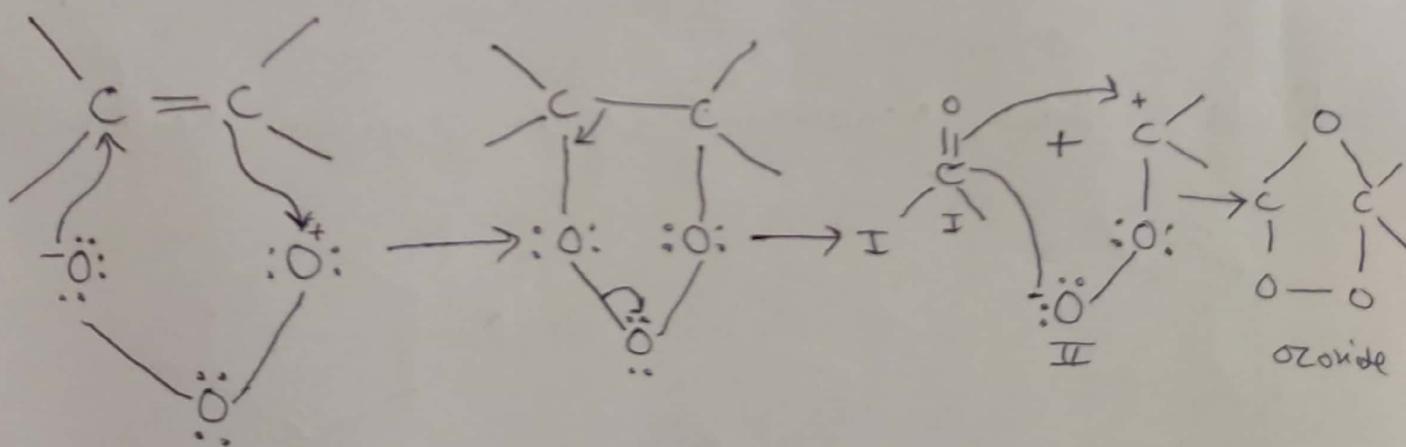
### Mechanism :-



Ozonolysis :- Addition of  $O_3$  to alkene is known as Ozonolysis.

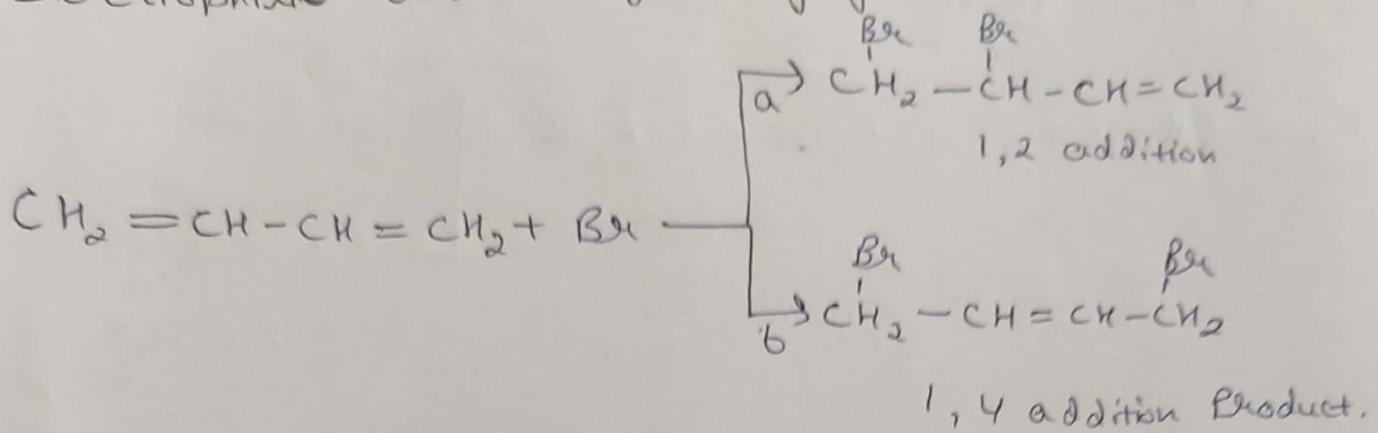


### Mechanism :-



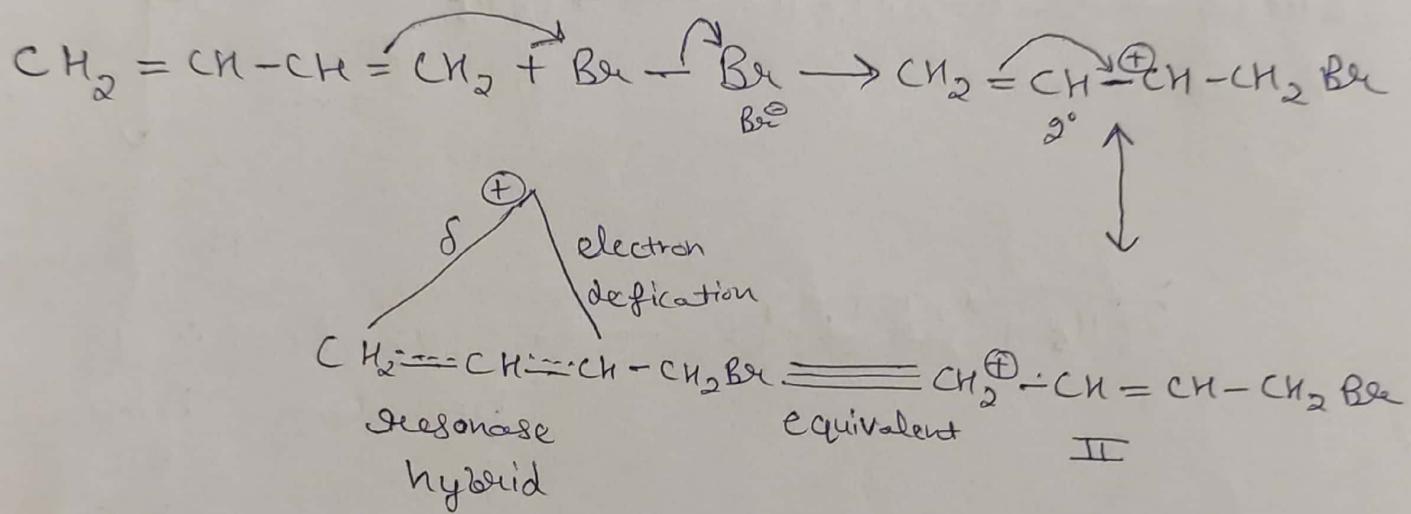
(13)

# Electrophilic addition of Conjugated diene reaction :-

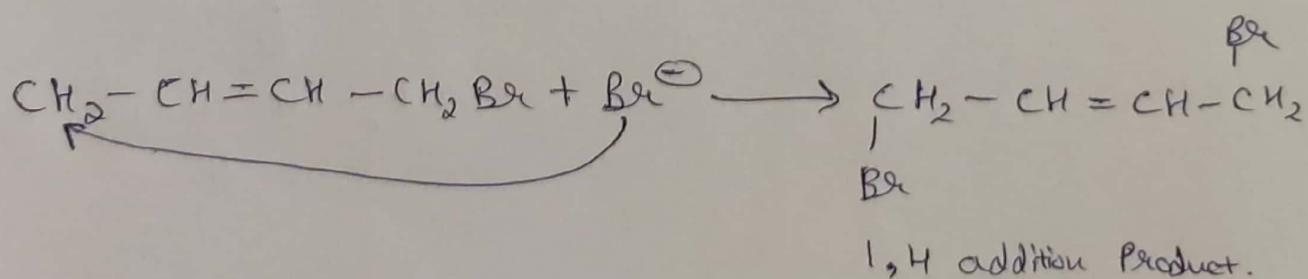
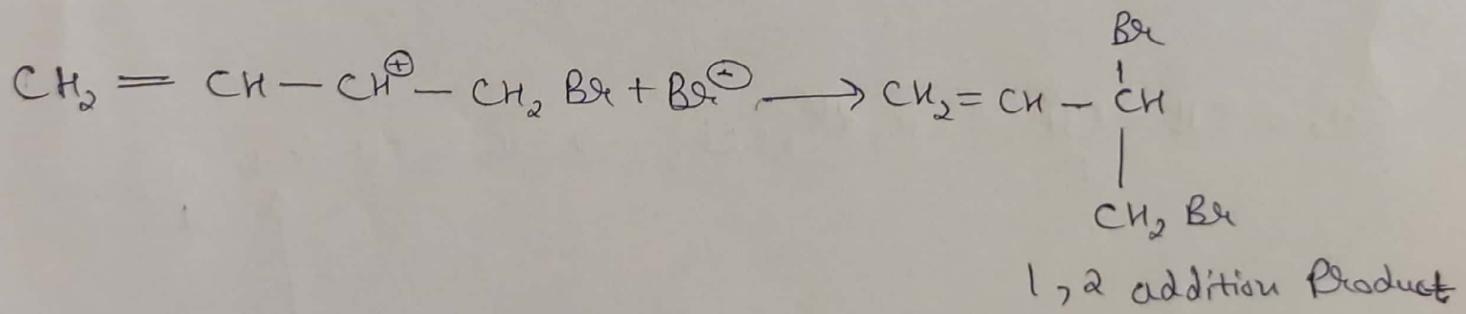


## Mechanism :-

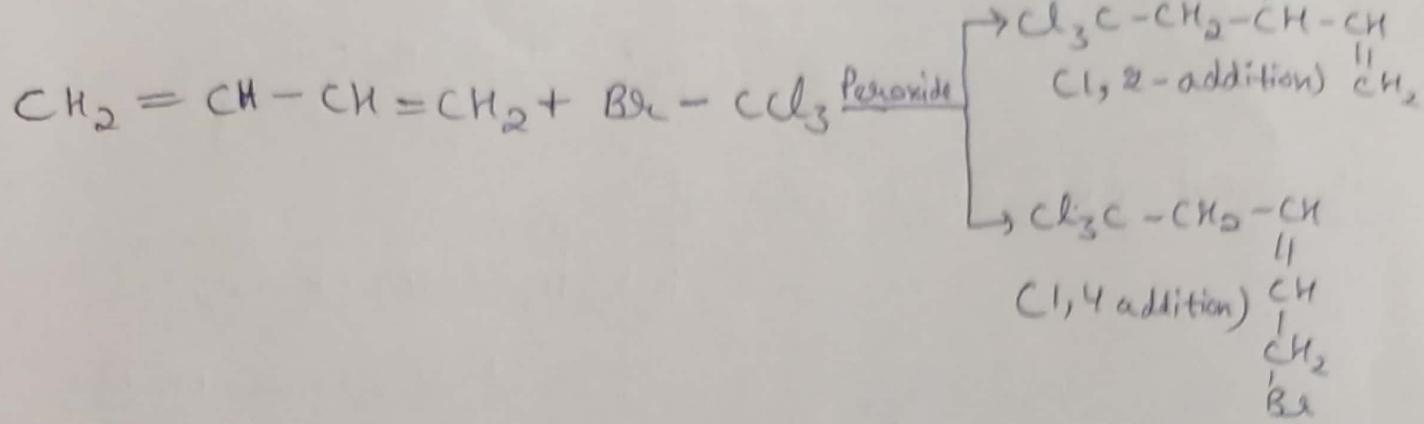
### Step-I



### Step-II

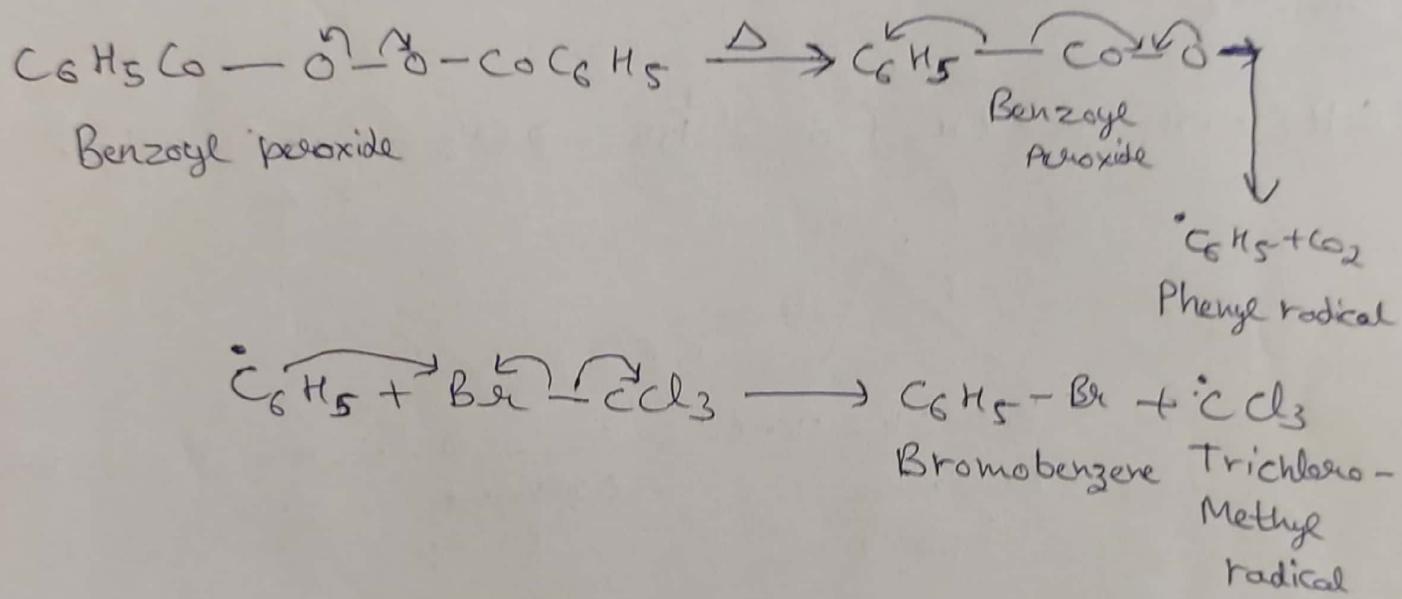


Free radical Addition Reaction (Conjugated diene Rxn) :-

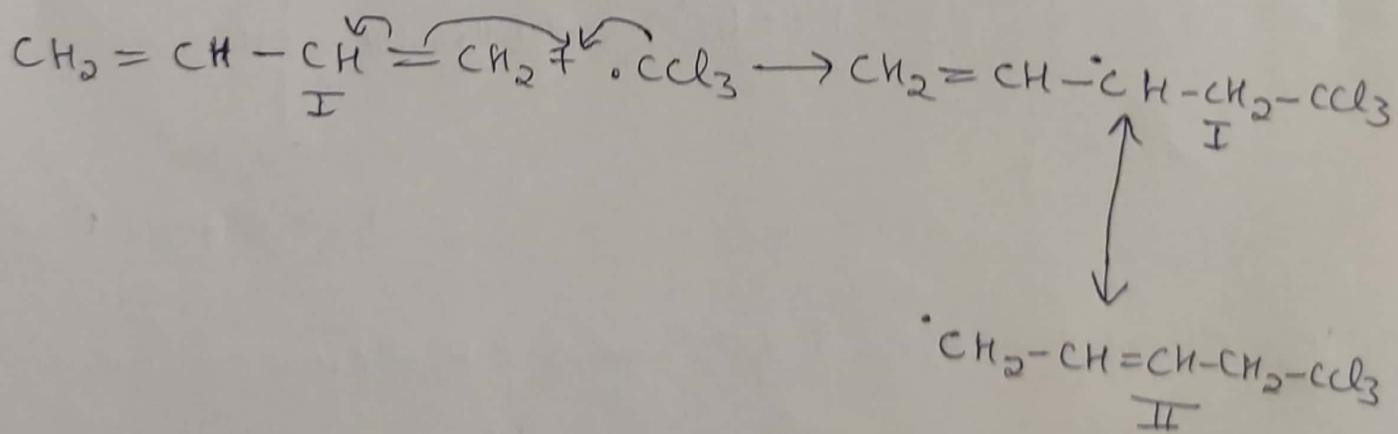


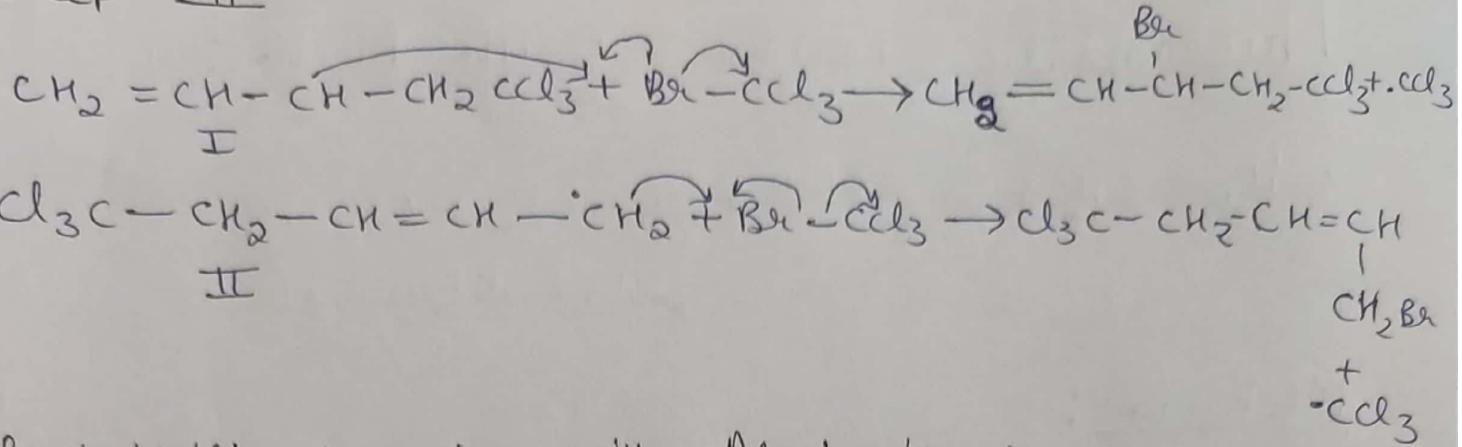
Mechanism:-

Step-I :-



Step-II

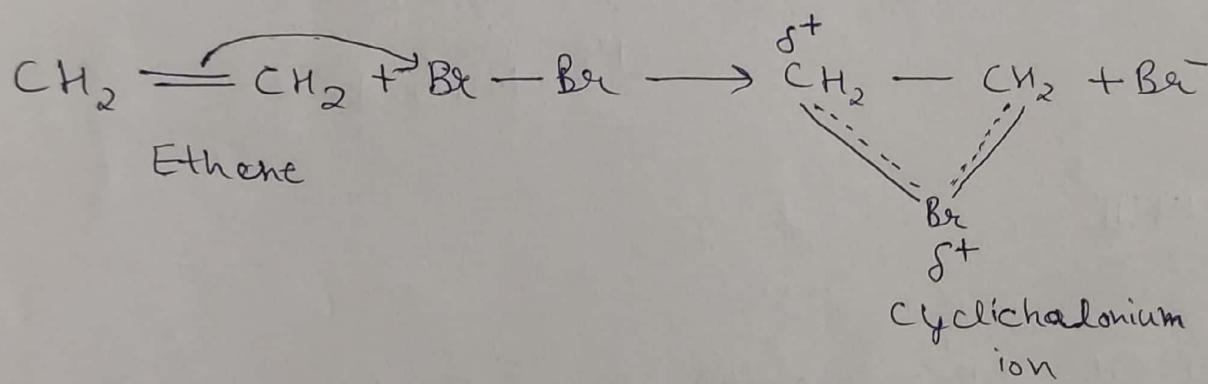
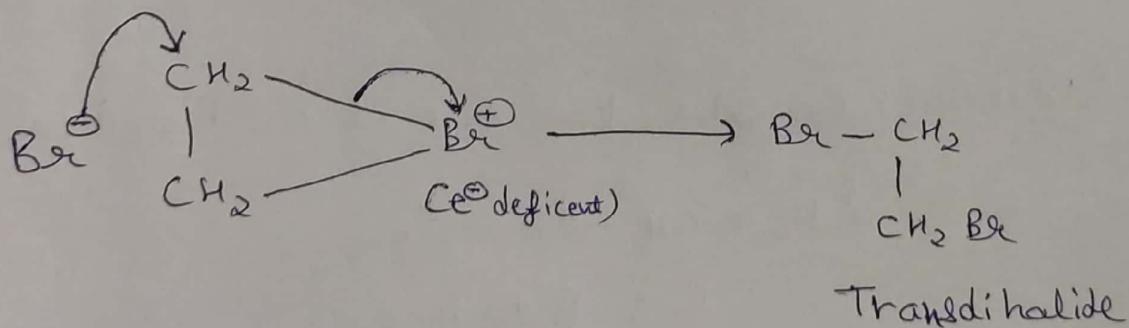


Step - III

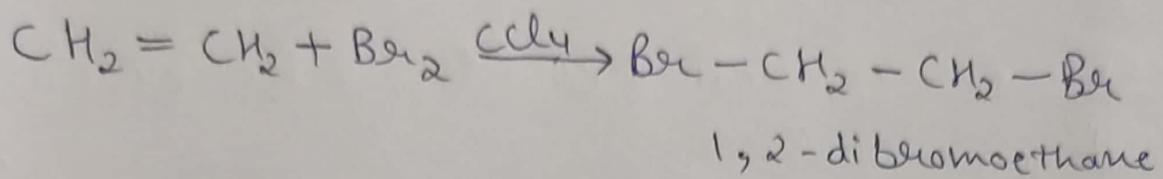
Electrophilic reaction with Mechanism :-

They form cyclohalonium electrophilic reaction

Mechanism :-

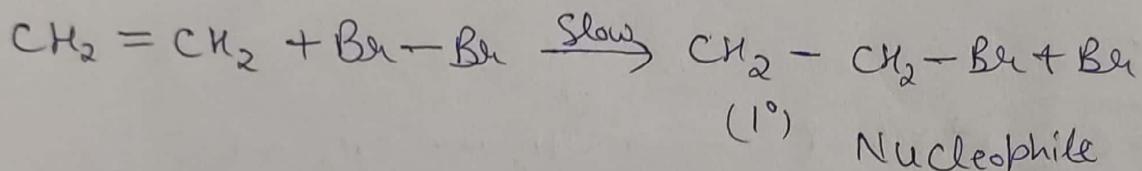
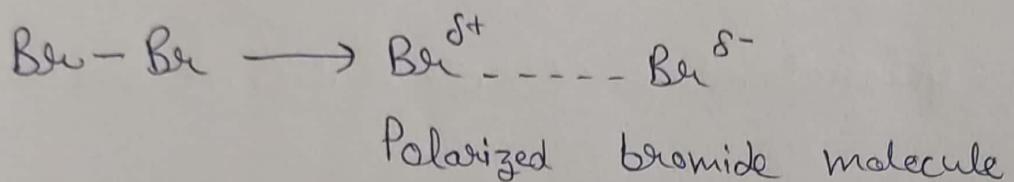
Step - IStep - II

# Nucleophilic reaction with Mechanism :-

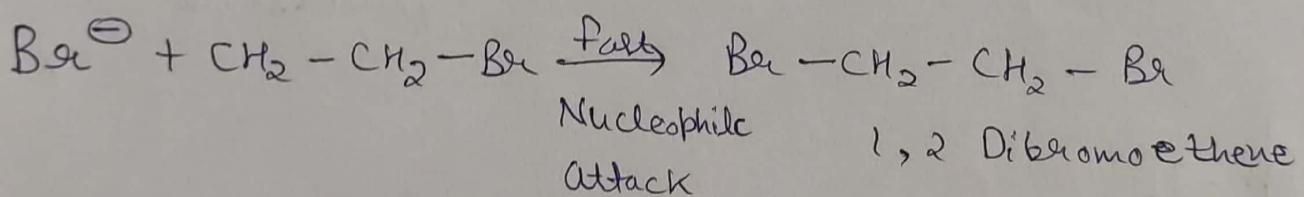


## Mechanism :-

Step - I

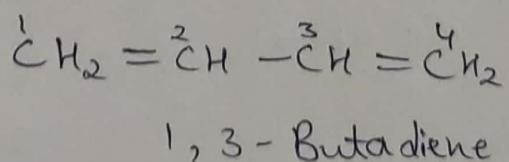


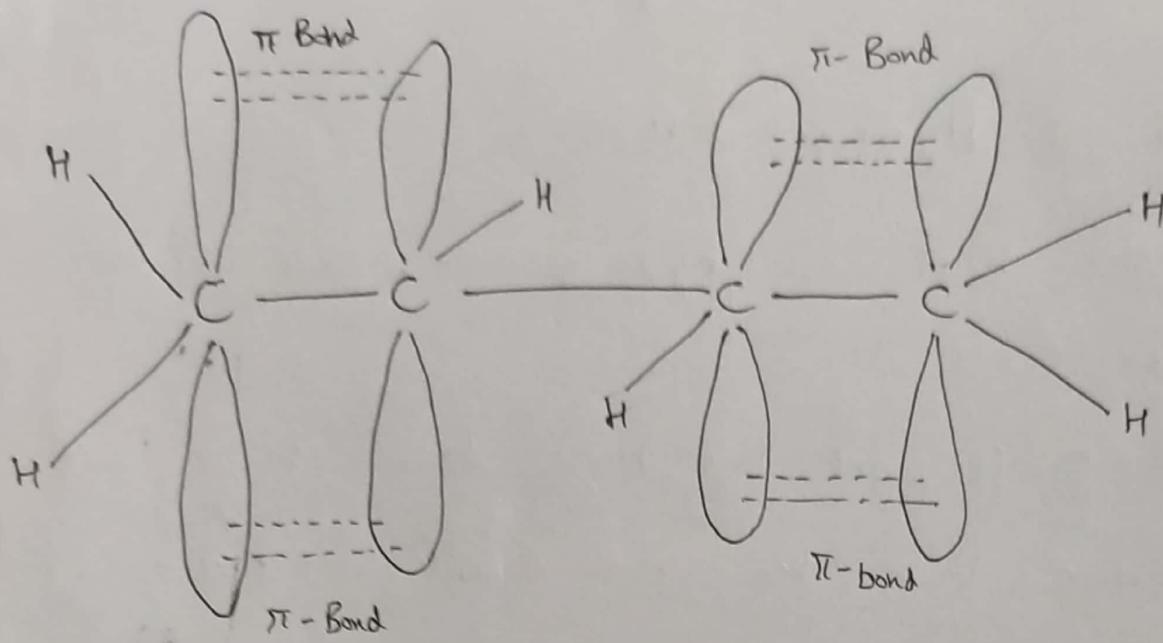
Step - II



## Stabilities of Conjugated Dienes :-

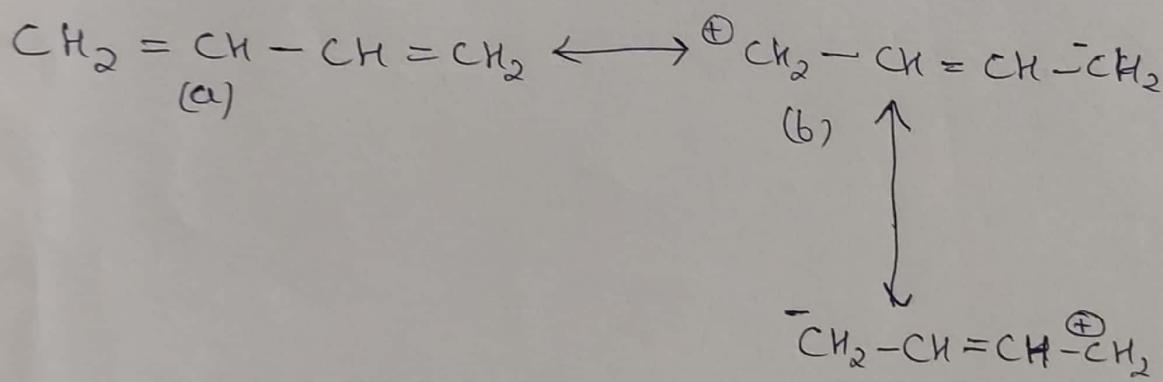
(i) Orbital Structure: Consider the case of 1, 3-Butadiene





The  $\pi$   $\text{e}^-$  of 1,3-Butadiene are delocalized which impart extra stability to the 1,3-Butadiene and other conjugated ions.

(ii) Redundance Theory :-



The resonance structure shows that (c) delocalized by the across the four carbon in this conjugated diene.

This delocalization of charge stabilized the conjugated diene.

### (iii) Heats of Hydrogenation :-

Higher the heat of hydrogenation, less stable of compound.

Therefore conjugated ions have lower heat of hydrogenation than the non conjugated dienes.

Therefore conjugated ions are more stable than the non-conjugated diene.

Lower heat of hydrogenation stability of compound.