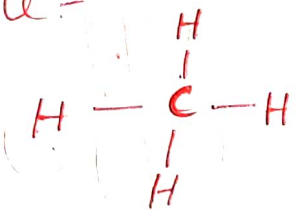
UNIT-II

ALKANES :-

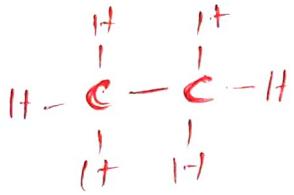
- An Alkanes Consists of hydrogen and Carbon atoms arranged in a tree structure in which all the Carbon-Carbon bonds are Sigle.
- Alkanes have the general Chemical formula

$$= C_n H_{2n+2}$$

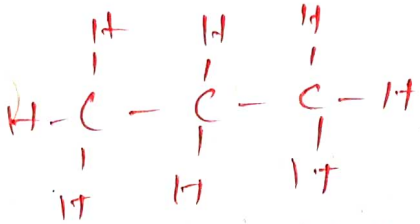
Example :-



Methane (CH_4)



Ethane (C_2H_6)



Propane (C_3H_8)

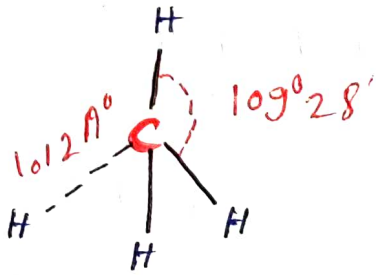
Alkanes have following Structural Characteristics :-

→ Every Carbon atom is Sp^3 hybridized, its four bonding orbitals are directed towards the four corners of a regular tetrahedron.

→ All the Carbon-Carbon and Carbon hydrogen bonds are strong Sigma bonds.

→ The bonds lengths between Carbon-Carbon is 1.54 A° and Carbon-hydrogen are 1.12 A°.

- The bond Angles in Alkanes are tetrahedral angles having a value of 109.5° (109°28')



✱ Sp^3 hybridization in Alkanes :-

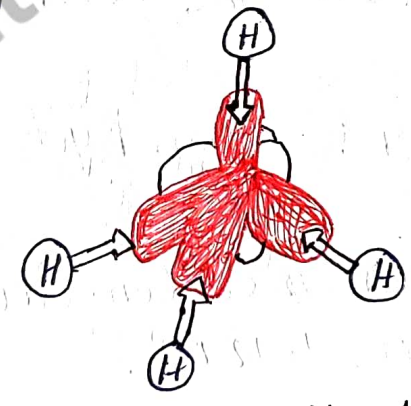
→ In Sp^3 hybridization one S-orbital combines with all the three P-orbital to form four equivalent sp^3 hybrid orbital.

- They have a tetrahedral arrangement and the angle between two orbitals is 109.5 degrees.
- Shape of the Molecules in which central atom is Sp^3 hybridized is tetrahedral.

A Schematic of an sp^3 hybrid orbital

For Methane :

- 4 equivalent C-H σ bond can be made by the interaction of C-sp^3 with a H 1s.



- Now in Methane, H_2C-CH_3 the hybridization can be explained as:
- Both Care Sp^3 hybridized.
- 6 C-H σ bonds are made by the interaction of Csp^3 with H1s orbitals (indicated by green arrows)

- 1 C-C σ bond is made by the interaction of Csp^3 with another Csp^3 orbital.

★ PARAFFIN :-

- The Saturated hydrocarbons are Called Paraffins, as they are relatively inert towards Chemical reagents in IUPAC nomenclature, Paraffin are termed alkanes.
- Paraffin is also known as liquid paraffin, paraffin oil or kerosene, is a Combustible hydrocarbon liquid that is burned as a fuel.
- It is a mixture of different types of Simple hydrocarbons, it is less volatile than gasoline and it boils at 302-527° Fahernheit.

Application or uses of Paraffins :-

1. Used for Industrial and textile Purposes :-
   - ~~one of~~ Liquid paraffin is mainly used as a Lubricant in various industrial Setting.
2. Used as Liquid Paraffin fuel :-
   - one of the primary used of liquid Paraffin is fuel. L.P is a highly distilled and refined from of kerosens that Can be burned in Lamps and other devices.
3. Used for Medicinal and Cosmetic Purposes :-
   Liquid Paraffin has many uses in the medical field.

- Because liquid paraffin passes through the body's intestinal tract without being absorbed it can be used as a laxative.

4. Other uses of paraffin :-

- Liquid paraffin is highly useful in many other fields, for example, it is an ingredients in many agriculture insecticides, it is often used in infrared spectroscopy.

☆ Stabilities of Alkenes :-

— The relative thermodynamic stabilities of various alkenes can be determined by heats of hydrogenation.

For Example :-

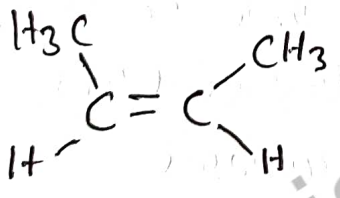
The Reation of 1-butene and both Cis- and trans-2-butene with dihydrogen afford the same product,

- Consequently differences in heats of hydrogenation accurately reflect the differences in thermodynamic stabilities of these three alkenes.

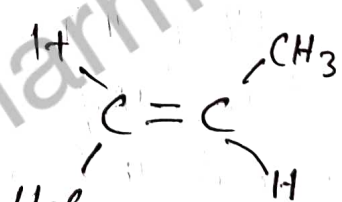
- These heats are: 1-butene - 30.3 kcal/mol;
  Cis-2-butene - 28.6 kcal/mol
  Trans-2-butene - 27.6 kcal/mol

- The order of stabilities -

  Trans-2 butene > 1-butene

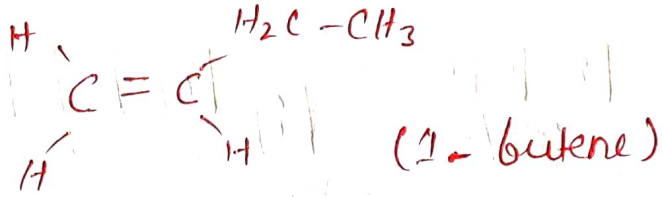


Cis-2-butene



Trans-2-butene

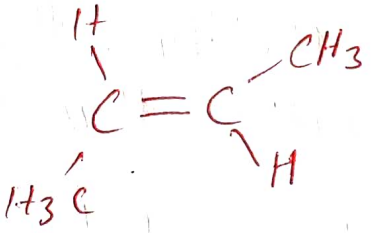
1: First :- The presence of alkyl groups directly attached to the double bond tends to stabilize the system.



(1- butene)

2: Second factor :- is relevant to the relative stability order of the two di-substituted double bonds i.e. cis and trans 2-butene.

- The trans isomer, which has no such steric effect, is therefore the more stable isomers.



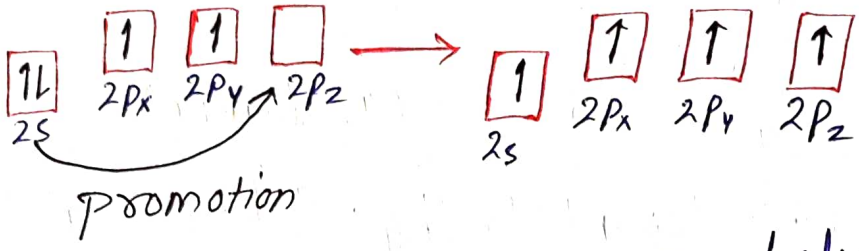
(trans-2-butene)

☆ Sp^2 Hybridization of Alkenes :-

- The Simplest alkene, ethene, has a planar structure, where the two Carbon atoms and four hydrogens atoms that are attached to theses Carbon atom lie in a plane.
- An orbital view of the bonding in ethene -
- Ethene is built from hydrogen atom ($1s^1$) and Carbon atoms ($1s^2 2s^2 2p_x^1 2p_y^1$).
- The Carbon atom does have enough unpaired electrons to form the required number of bonds, so it needs

to promote one of the $2s^2$ pair into the empty $2p_z$ orbital.

- This is exactly the same as happens whenever Carbon forms bonds.
- So in the first there is promotion of an electron.



- There is only a small energy gap between the 2s and 2p orbital, and an electron is promoted from the 2s to the empty 2p to give 4 unpaired electrons.
- When the Carbon atoms hybridize their outer orbitals before forming bonds, this time they only hybridize three of the orbitals rather than all four.
- They use the 2s electron and two of the 2p electrons but leave the other 2p electron unchanged.

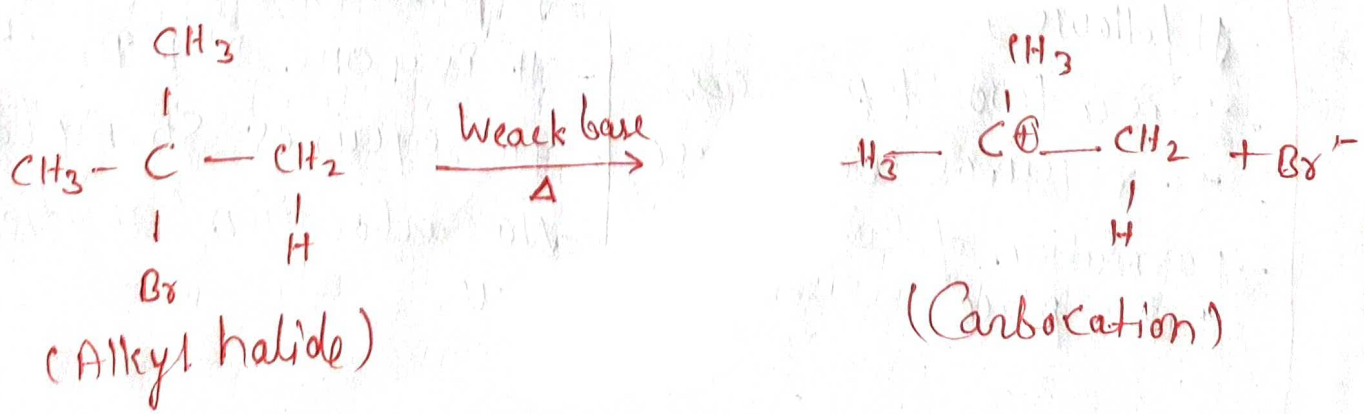
✱ E_1 and E_2 Reaction :-

- E_1 and E_2 reactions are nothing but the part of Elimination Reaction.
- An Elimination reaction is a type of organic reaction in which two Substituents are removed from a Molecule either in one or two steps.
- The Step Mechnism is known as E_2 Reaction while the two Step Mechnism is known as E_1 Reaction
- Elimination Reaction is nothing but a Method of preparation of Alkenes.
- The degree of unsaturation increases with Elimination Reaction

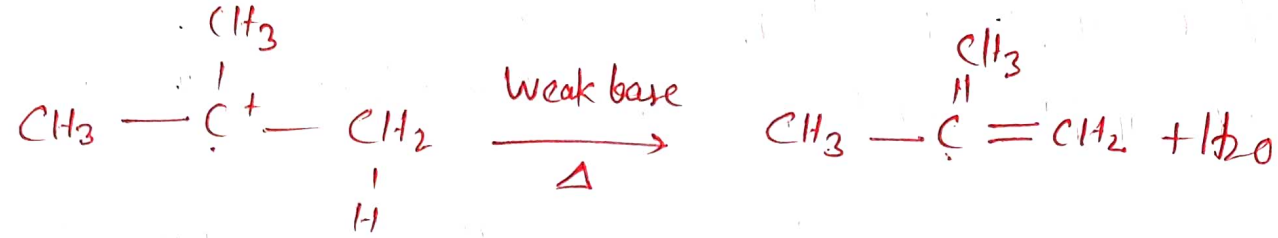
E_1 Reaction :-

- E_1 Reaction is unimolecular Elimination Reaction
- It is a two Step process.
- This Reaction is performed at high temperature.
- This reaction follows first order kinetics.

Step-I :- Formation of Carbocation



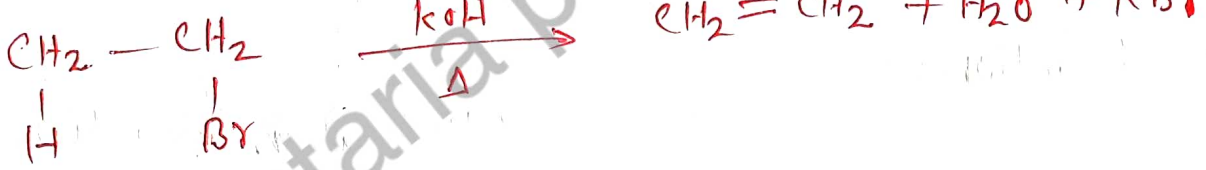
Step II - Loss of proton from the Carbon atom adjacent to the Carbon Containing positive Charge.



E_2-Reaction :-

- It is a one step process
- E_2 reaction stands for for Bimolecular Elimination Reaction
- The reaction follow Second order kinetics
- Strong base used in E_2 reaction
- The reaction is proceed at high temperature.

E_2 Reaction Mechnism :-



E_1 Versus E_2 Reaction :-

E_1 Reaction	E_2 Reaction
- It is a unimolecular eliminati - It follows 1st order kinetic - It is a two step process - It requires weak base - Formation of Carbo Cation takes place.	- It is a bimolecular elimination - It follows 2nd order kinetics - It is a one step process. - It requires Strong base. - No carbocation formation take plae.

Factor affecting E_1 or E_2 Reaction:-

(i) Effect of R :-

In an E_2 reaction, the reaction transforms $2\ sp^3$ C atom into Sp^2 C atom.

(ii) Leaving groups (-LG) :-

The C-LG bond is broken during the rate determining Step, so the rates does depend on the nature of the leaving group.

(iii) Base (B) :-

Since the base is involved in rate determining Step the nature of the base is very important is an E_2 reaction. More reactive base will favor an E_2 Reaction.

(iv) Stereochemistry :-

E_2 reaction occur most rapidly when the H-C bond and C-LG bonds involved are Coplanar Most often at 180° or antiperiplanar.

Order of reactivity of Alkyl Halide :-

- order of reactivity of alkyl halide for a given alkyl group is

RI > RBR > RCl

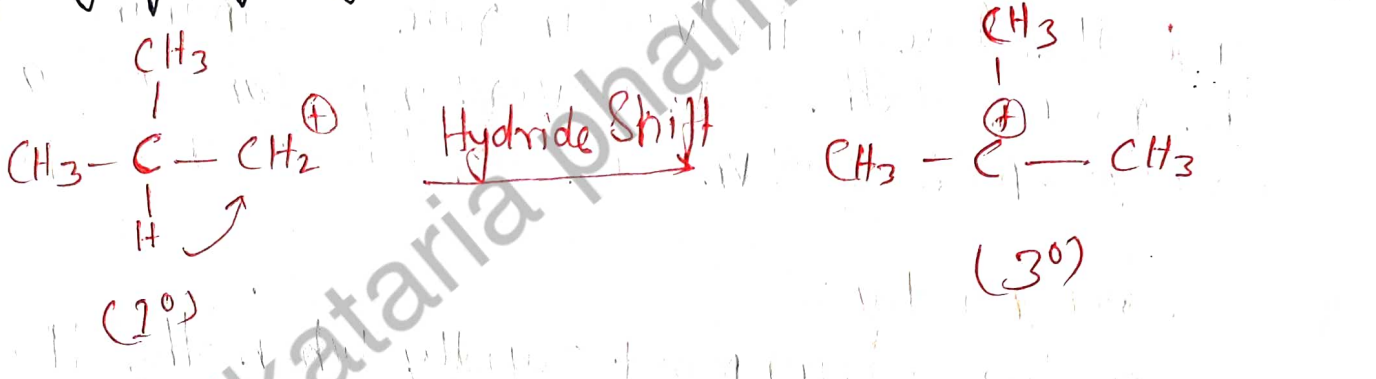
☆ Rearrangement of Carbocations :-

- Carbocation rearrangement are defined as the 'Movement' of an Carbocation from an unstable state to a more stable state through the use of various structural reoorgemizational shifts, within the Molecule.

- They are two types of rearrangements:
  1. Hydride Shift
  2. Alkyl Shifts.

① Hydride Shifting :-

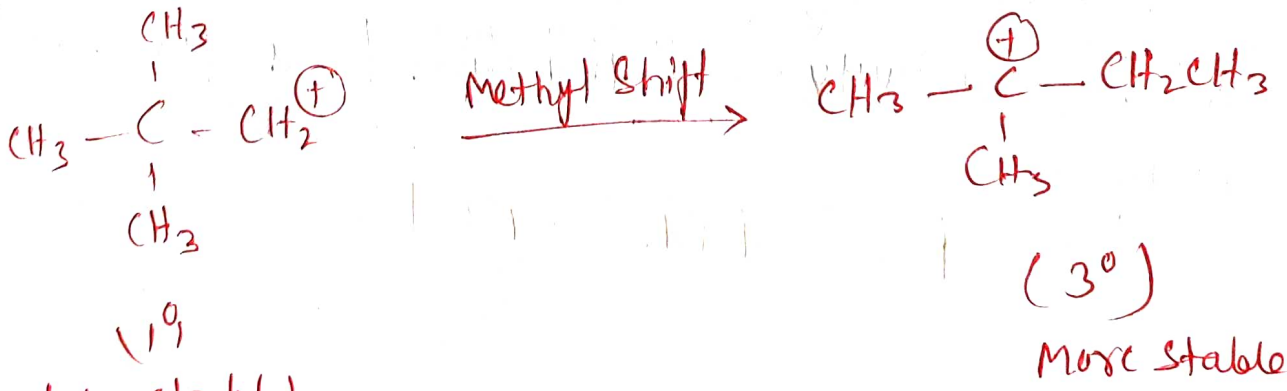
Shifting of hydrogen atom is known as hydride Shifting



(1°) (3°)

② Alkyl Shifting :-

Shifting of methyl group (CH_3) is known as methyl Shift.

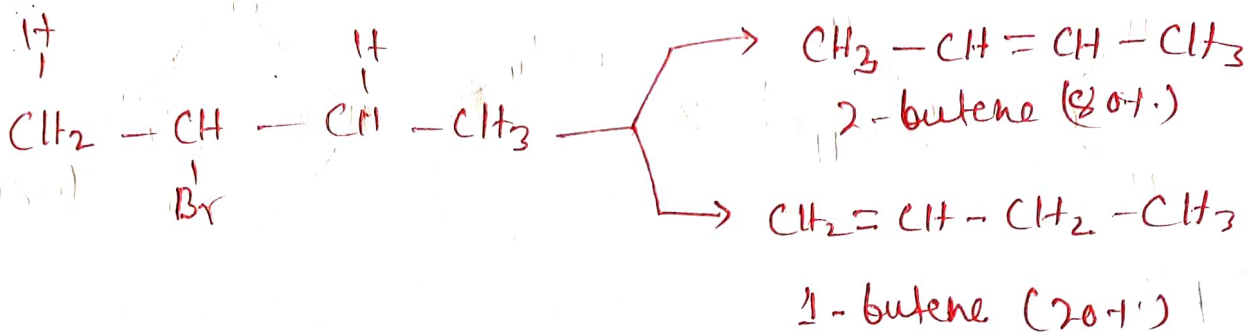


(1°) (unstable)

(3°) More Stable

★ SAYTZEFF'S RULE :-

- Saytzeff rule is also known as Zaitevs rule.
- In the elimination reactions when the Alkyl halide group have two or more β Carbon than 1 alkene product is formed.
- Now Saytzeff's rule states that if more than 1 Alkene product is formed as a result of elimination reaction then the Highly Substituted Alkene will be the major product of the reaction.

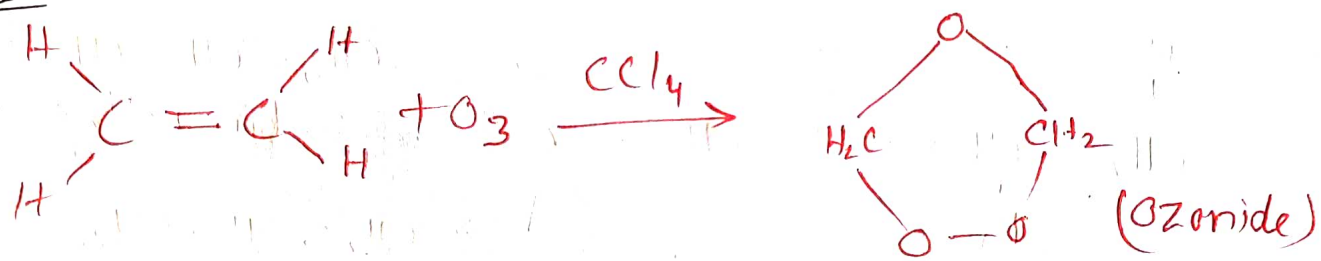


- In the above reaction the major product will be 2-butene (but-2-ene) while 1-butene will be the minor product.

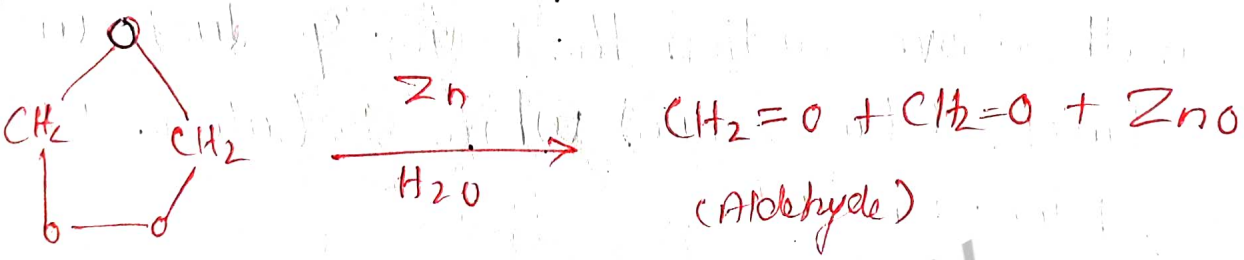
☆ OZONOLYSIS :

- Ozonolysis is an organic reaction where the Unsturated bonds of alkenes, alkynes, or azo Compounds are Claved with ozone.
- Alkenes and alkynes from organic Compounds in which the multiple Carbon - Carbon bond has been replaced by a Carbonyl group while azo compounds from nitrosamines.
- The outcomes of the reaction depends on the type of Multiple bond being oxidized and the work-up Conditions.

Step-I



Step-II



☆ Electrophilic Addition Reaction of Alkenes :-

- Alkenes are more reactive Compair to Alkanes (due to the π bond.
- When an atom or group of atom are Simply added to a double bond or triple bond without any Substitution or elimination then this type of reaction is known as Addition Reaction.
- Now addition of an 'Electrophile in an addition reaction known as electrophilic Aeldition Reaction.

- Example :-

$$CH_2=CH_2 + E-Nu \longrightarrow \underset{\displaystyle E}{\overset{\displaystyle |}{CH_2}}-\underset{\displaystyle Nu}{\overset{\displaystyle |}{CH_2}}$$

$$CH_2=CH_2 + HCl \longrightarrow \underset{\displaystyle H}{\overset{\displaystyle |}{CH_2}}-\underset{\displaystyle Cl}{\overset{\displaystyle |}{CH_2}}$$

- 1π bond breacks and 2σ bond forms during addition reaction

Mechnism of addition reaction :-

Step-I The reagent (E-Nu) like HBR ionizes to give electrophile & nucleophile.

$$HBR \longrightarrow H^+(E) + Br^-(N)$$

Step-II :- Electrophile (H^+) attacks on = bond to form σ bond & Carbonium ion.

$$CH_2 = CH_2 + H^+ \longrightarrow CH_3 - CH_2^{\oplus}$$

Step-III :- Addition of nucleophile on Carbonium ion.

$$CH_3 + CH_2^{\oplus} + Br^- \longrightarrow CH_3 - CH_2Br$$

Complete Reaction :-

$$CH_2 = CH_2 + HBr \longrightarrow \underset{\displaystyle H \quad Br}{\overset{\displaystyle CH_2 - CH_2}{\overset{\displaystyle | \quad\quad |}{}}}$$

☆ Markownikoff's orientation :-

According to Markovnikov's rule during the addition reactions of alkenes the hydrogen atom (H^+) is added to that Carbon atom which have maximum number of hydrogen atom.

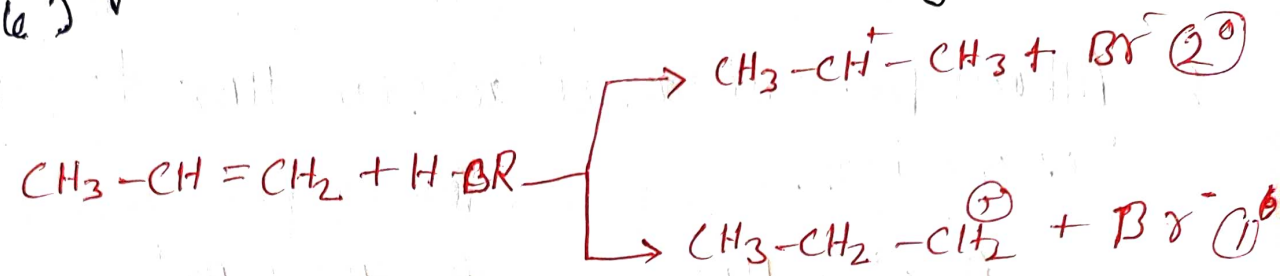
- Markovnikov's rule can also be explained in an another way that during the addition reaction of unsymmetrical alkenes the negative part of the adding reagent is added to that ⊙ Carbon atom ω

Example :-

$$CH_3 - CH = CH_2 \xrightarrow{HBr} \underset{\displaystyle Br \quad H}{\overset{\displaystyle CH_3 - CH - CH_2}{\overset{\displaystyle | \quad\quad |}{}}}$$

Mechnism:-

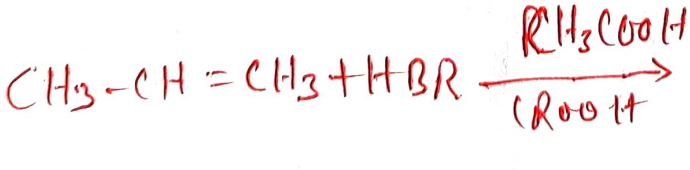
① Formation of Carbocation (two Carbocation formation possible)



② Attak of nucleophile to 2° Carbocation :-

★ Anti-Markovnikov's Rule :-

- This rule is also known as 'Kharasch Effect' or 'Peroxide effect'.
- According to Anti-markovnikov's rule if the presence of organic peroxides (R-O-O-R) than Hydrogen atom is added to the carbon atom having minimum number of hydrogen.



Mechnism:-

① Peroxides dissociates to give alkoxy free radicals.

$$R-O-O-R \xrightarrow{\Delta} 2R-O^{\bullet}$$

② Alkoxy free radicals attacks on HBr to form bromine free radical.

$$R-O^{\bullet} + HBR \longrightarrow R-OH + Br^{\bullet}$$

③ Bromine free radical attack on alkene to give $1^{\circ} > 2^{\circ}$ free radicals.

$$Br^{\bullet} + CH_3-CH=CH_2 \rightarrow \begin{cases} CH_3-\underset{Br}{CH}-\dot{C}H_2 & (1^{\circ}) \\ CH_3-\dot{C}H-CH_2Br & (2^{\circ}) \end{cases}$$

④ More stable free radical (2°) reacts with HBr to give final product.

$$CH_3-\dot{C}H-CH_2Br + HBR \longrightarrow CH_3-CH_2-CH_2Br + Br^{\bullet}$$

✱ Dienes :-

- HydroCarbons with two Carbon-Carbon double bonds are called as diene or alkadienes or diolefin.
- The general formula is C_nH_{2n-2} (similar to alkynes)

Types :- Dienes are of three types.

1. Conjugated dienes
2. Cumulative dienes
3. Non conjugated (isolated) Dienes.

1. Conjugated dienes: Double bonds are separated by one single bond.

Example :- $H_2C=CH-CH=CH_2$ (Buta-1,3 diene)

2. Cumulative dienes: — Double bonds are adjacent to each other.

Example :- $H_2C-CH=C=CH_2$ (Buta-1,2, diene

3. Non Conjugated Dienes: have two double bonds that are separated more than one single bond

Example :- Penta-1,4-diene

$$H_2C=CH-CH_2-CH=CH_2$$

Stability of Conjugated Dienes:-

- Conjugated diene are more stable than non-Conjugated dienes (both Isolated & Cumulated) due to factor such as delocalization of charge through resonance hybridization energy.
- This can also explane why allylic radicals are much more stable than secondary or even tertiary Carbocations.
- This is all due to the positioning of the the pi-orbital and ability for overlap to occur to strengthen the single bond between the two double bonds.

Diels-Alder Reaction :-

- The Diels-Alder reaction is an organic Chemical reaction between a Conjugated diene and a substituted alkene, commonly termed dienophile to form a substituted cyclohexen system.

→ The diels-Alder reaction is particularly useful in Synthetic organic Chemistry as a reliable method for forming 6-membered system with good

- Diels-Alder reaction Can be reversible under Certain Conditions. the revers reaction is known as the retro-Diels-Alder reaction.

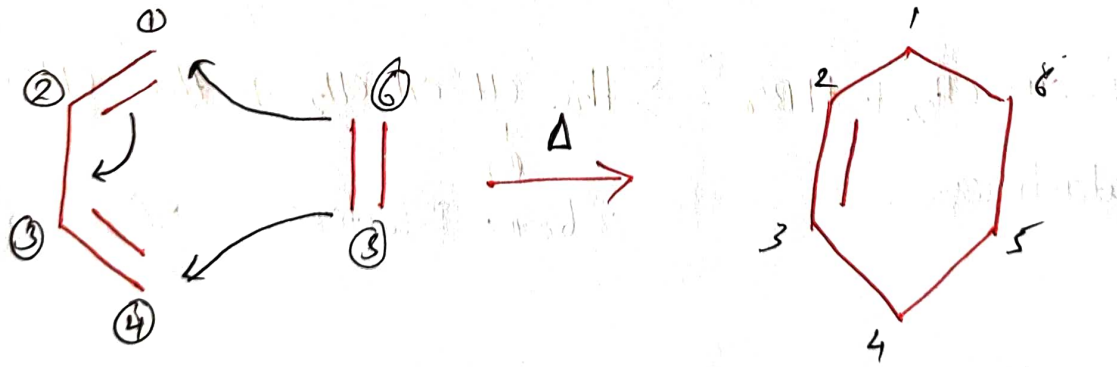
Mechnism of Diels-Alder reaction :-

→ Electrons form the dienophile attack Carbon (C) 1 on the diene resulting in a Single bond blw C_1 and C_6.

→ Electrons from the double bond blw C_1 and C_2 relocates to blw C_2 and C_3.

- Double bond blw C_3 and C_4 ~~and~~ are broken and the electrons form a Single bond blw C_4 and C_5 to form the product.

- All processes take place in a Single Step.



Diene (butadiene) | Dienophile (Ethylene) | Cyclic adduct (cyclohexene)

☆ Electrophilic Addition of Conjugated Dienes :-

- If a conjugated diene, such as 1,3-butadiene reacts with a limited amount of electrophilic reagent so that addition can occur at only on of the double bonds two addition products are formed.
- One is a 1,2 addition product, which is a result of addition at the 1- and 2- position and it is called 1,2 addition or direct addition.
- The other is a 1,4 addition product, that result of addition at the 1- and 4-position and it is called 1,4 addition or Conjugate addition.

Example :-

$H_2C=CH-CH=CH_2 + Cl_2 \longrightarrow H_2C-CH-CH=CH_2 + H_2C-CH=CH-CH_2$

(1,3-butadiene, 1 mol) + (1 mol) → (3,4-dichloro-1-butene, Cl, Cl) + (1,4 dichloro-2 butene, Cl, Cl)

$H_2C=CH-CH=CH_2 + HBr \longrightarrow H_2C-CH-CH=CH_2 + H_3C-CH=CH-CH_2$

1,3 butadiene → (3-bromo-1-butene, Br) + (1,bromo-2 butene, Br)

✱ Free Radical Addition Reaction of Conjugated Dienes :-

- Conjugated diens undergo free radical addition reaction via the formation of free radicals.
- Like other free radical reactions it also follows the three step mechenism such as chain inition step, chain Propagation step and chain termination step.
- Chain initiation and chain propagation step are Similar to that of other redical addition reaction of alkenes.
- but the chain propagation step involves two step.
- General Mechnism :-

1. Chain initiation Step: Formation of peroxide free radical upon exposure to UV light.

$$R_2O_2 \xrightarrow{\text{UV light}} 2RO^{\bullet}$$

2. Chain propagation step :-

(i) First propagation step :- Formation of resonance Stabilized Carbon free radical. It involves the initial attack of free radical at the site of Carbon atom which produces more Stable Carbon free radical

$$CH_3-CH=C-C=CH_2 + RO^{\bullet} \longrightarrow H_2C=C-CH-CH_2-OR$$

$$CH_2-CH=CH-CH_2-OR$$

(ii) Second propagation Step :-

The more stable Carbon free radical abstract a free radical from reagent and gives product.

$$H_2\dot{C}-CH=CH-CH_2-OR \longrightarrow RO-CH_2-CH_2=CH_2-CH_2-OR + \dot{O}R$$

1,4 Addition product.

(3) Chain termination Step :-

Two free radicals Combine to form a molecule and terminate the reaction.

$$RO^{\circ} + RO^{\circ} \longrightarrow R_2O_2$$

★ Allylic Rearrangement :-

- An Allylic rearrangement or allylic Shift is an organic reaction in which the double bond in an allyl chemical Compound shifts to the next Carbon atom.
- It is encountered in nucleophilic Substitution.
- In reaction Conditions that favour a S1 reaction mechnism the intermediate is a Carbo Cation for which several resonance structures are possible.
- This explains the product distribution after recombination with nucleophile.
- This type of process is called an S1 Substitution.