ORGANIC CHEMISTRY

UNIT 2 NOTES

- ALKANES
- ALKENES
- CONJUGATED DIENES

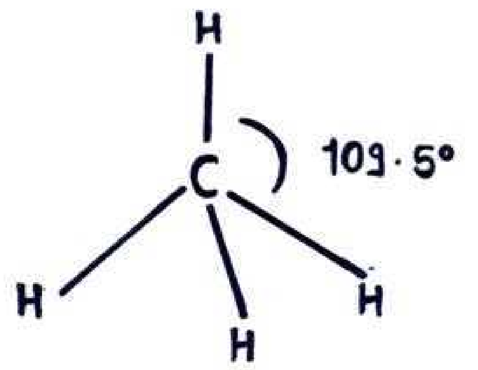
Rx Pharma Education

ALKANES

- Alkanes are the simplest hydrocarbons or organic compounds.
- Alkanes are acyclic saturated hydrocarbons that means all the carbon-carbon bonds in alkanes are single bond.
- The general formula of alkanes is C_nH_{2n+2}.
- Alkanes contain strong C-C & C-H covalent bonds.
- Since alkanes contain strong covalent bonds, hence they are relatively chemically inert.
- Methane is the simplest alkane.
- They are also known as Paraffins.
- Examples: CH_4, C_2H_6, C_3H_8 etc.

Structural Properties of Alkanes

- Each carbon atoms in alkanes are SP^3 hybridized.
- All the carbon-carbon and carbon-hydrogen bonds in alkanes are strong sigma bonds (σ).
- The bond length of alkanes between Carbon-Carbon atom = 1.54 Å
  Carbon-hydrogen atom = 1.12 Å
- Alkanes forms tetrahedral structure with bond angle 109.5°.



Methane

METHOD OF PREPARATION OF ALKANES

Alkanes can be prepared from following various methods

- Hydrogenation of Alkenes or Alkynes
- Reduction of Alkyl halides
- Decarboxylation of Carboxylic Acids
- Hydrolysis of Grignard Regent
- Wurtz Synthesis

① Hydrogenation of Alkenes or Alkynes

Hydrogenation of Alkenes or Alkynes in the presence of nickel or platinum at 200 - 300° C yeilds Alkanes

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow[200-300^\circ C]{Ni} \underset{\text{Ethane}}{CH_3-CH_3}$$

② Reduction of Alkyl Halides

Reduction of Alkyl halides with nascent hydrogen. in the presence of some reducing agents like Zn-Cu or C_2H_5OH yeilds Alkanes

$$\underset{\text{Methyl Iodide}}{CH_3-I} + 2[H] \xrightarrow[\text{or } C_2H_5OH]{Zn-Cu} \underset{\text{Methane}}{CH_4} + HI$$

③ Decarboxylation of Carboxylic Acids

Alkanes can be prepared by heating a mixture of sodium salt of carboxylic acid with soda lime ($NaOH + CaO$)

$$\underset{\text{Sodium Acetate}}{CH_3COONa} + NaOH \xrightarrow[CaO]{\Delta} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

④ Hydrolysis of Grignard Regent

Hydrolysis of grignard reagent yeilds Alkanes.

$$\underset{\text{Methyl Magnesium Iodide}}{CH_3MgI} + H_2O \longrightarrow \underset{\text{Methane}}{CH_4} + Mg\begin{matrix} \diagup I \\ \diagdown OH \end{matrix}$$

⑤ Wurtz Synthesis

Reaction between a solution of alkyl halide & metallic sodium in the presence of dry ether yeilds Alkanes

$$\underset{\text{Bromo Methane}}{CH_3Br} + 2Na + CH_3Br \xrightarrow{\text{ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

Chemical Reactions of Alkanes

Alkanes undergo following chemical reactions :

- Halogenation
- Nitration
- Sulphonation
- Oxidation
- Pyrolysis
- Aromatisation

HALOGENATION OF ALKANES

- As we know that Alkanes contains strong covalent sigma bonds hence they do not reacts easily.
- But under the presence of UV light or very high temperature they undergo substitution reaction (mostly).
- Halogenation of Alkanes can also be known as Free radical substitution reaction in alkane.
- When halogens (F, Cl, Br, I) reacts with an alkane to form haloalkanes or Alkyl halide in the presence of UV light or heat then it is called halogenation of alkanes.
- Example : Chlorination of methane

Chlorination of Methane

$$CH_4 + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} CH_3Cl + HCl$$

The reaction will not stop here it continues untill all the hydrogen of alkane (methane) is substituted with chlorine.

$$CH_3Cl + Cl_2 \xrightarrow{\Delta} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{\Delta} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{\Delta} CCl_4 + HCl$$

(Carbon tetrachloride)

Mechanism of Halogenation

- The halogenation of alkane is a three step process via Free Radical formation.
- Free radicals are those substances that contain single unpaired electron.
- These are the following three steps :

① Chain Initiation
② Chain Propagation
③ Chain Termination

CHAIN INITIATION STEP

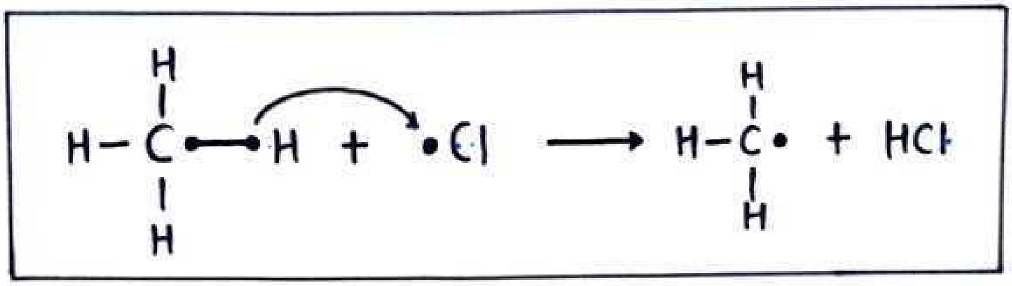
In chain initiation step chlorine molecule gets splitted by homolytic fission to form chlorine free radical.

$$Cl - Cl \xrightarrow[\Delta]{\text{UV light}} \dot{C}l + \dot{C}l$$

CHAIN PROPAGATION STEP

Chain propagation is further divided into two steps :

Step First : In first step chlorine free radical attacks on CH_4 to produce methyl free radical



Step Second : In second step methyl free radical again attacks on chlorine molecule to form chlorine free radical and chloromethane

$$CH_3\bullet + Cl{-}Cl \longrightarrow CH_3Cl + Cl\bullet$$

CHAIN TERMINATION STEP

In chain termination step all the free radicals combine or react with each other & no new free radical is forms which tends the reaction towards end.

$$CH_3\bullet + \bullet Cl \longrightarrow CH_3Cl$$

HYBRIDIZATION

Hybridization is defined as intermixing of atomic orbitals of same or nearly same energy to give new hybrid orbitals of exactly same energy, shape and size.

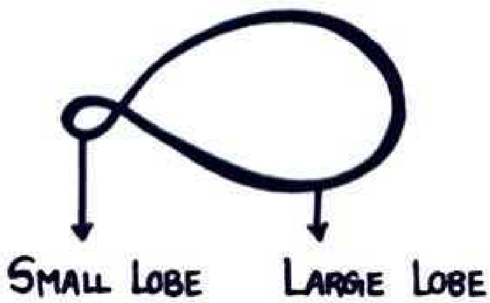
Example: [S] [P_x | P_y | P_z] ⟶ [SP_3 | SP_3 | SP_3 | SP_3]

Characteristics of Hybridization

- All the hybrid orbitals have exactly same properties i.e size, shape energy etc.
- The no. of hybrid orbitals = No. of intermixing orbitals.
- The name of hybrid orbital is done on the name of intermixing orbitals. i.e. →
  - $1s + 2p = sp^2$
  - $1s + 3p = sp^3$
  - $1s + 3p + d = sp^3d$ & so on ...

Shape of Hybrid Orbitals

- Hybrid orbitals contains one small lobe and one large lobe.
- Generally small lobe is not represented.



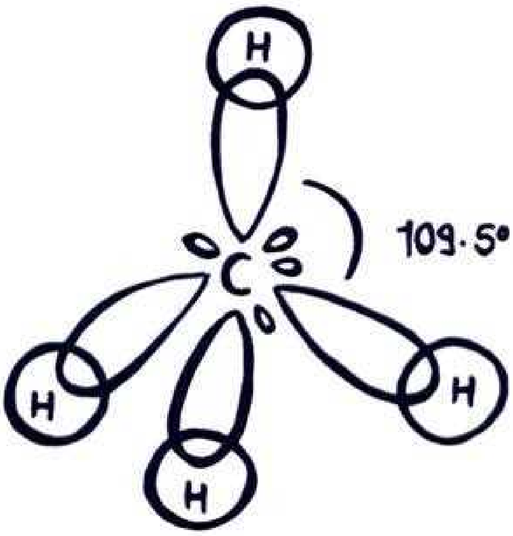
sp^3 HYBRIDIZATION IN ALKANES

- All the carbons of alkanes shows sp^3 Hybridization.
- In sp^3 hybridization one s orbital combines with three p orbitals to form four equivalent sp^3 hybrid orbitals
- Each sp^3 hybrid orbital shows 25% s orbital characteristics and 75% p orbital characteristics.

Example : sp^3 hybridization of carbon in alkanes.

Ground State :	↑↓	↑↓	↑	↑		
Excited State :	↑↓	↑	↑	↑	↑	
Hybridised State :	↑↓	↑	↑	↑	↑	
	s	sp^3	sp^3	sp^3	sp^3	

- The carbons of Alkanes shows tetrahedral arrangement.
- The angle between two orbitals is 109.5°.



PARAFFINS

- Paraffins are nothing but simply the Alkanes
- It is made up of two words - Parum = Little
  Affinis = Affinity
- They are relatively inert towards chemical reagent.

Uses of Paraffins

- Paraffins are widely used as fuel component for diesel and tractor engines.
- Liquid paraffin is a distilled and refined form of kerosine that can be burned in lamps and other devices.
- It is also used as fuel for jet engines and rockets.
- Liquid paraffin is a very highly refined mineral oil that also contains medical properties and commonly used to treat dry skin, constipation etc.
- Liquid paraffin is mainly used as a lubricant in various industries.
- It is also used as fuel for cooking.
- It is also used in penicillin production.
- It is widely used in cosmetic industries to make creams, petrolium jelly etc.
- It is also used as ingredients in many agricultural insecticides.

ALKENES

- Alkenes belongs to the class of hydrocarbons containing carbon-carbon double bond.
- Since they contain carbon-carbon double bonds, hence they are also known as Unsaturated Hydrocarbons.
- The general formula for alkenes = C_nH_{2n}
- The first member or the smallest alkenes is Ethene ($CH_2=CH_2$) also known as Ethylene.
- Alkenes are also known as Olefins.
- Example : Ethene, Propene, Butene etc.

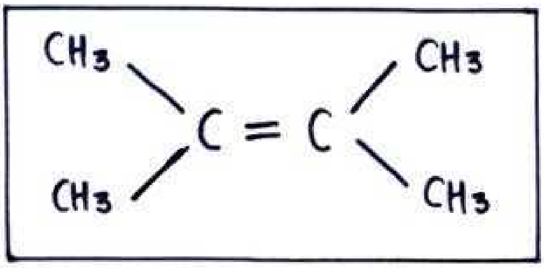
STABILITY OF ALKENES

- Alkenes are less stable and more reactive compare to Alkanes.
- Different Alkenes shows different stability.
- Relative stability of alkenes depends on following factors :

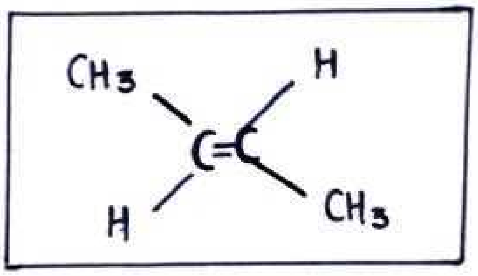
① Degree of substitution
② On the basis of orientation
③ On the basis of conjugations

① Degree Of Substitution

More the substituents (mainly alkyl group) attached to the double bonded carbon, more the stability of alkenes.

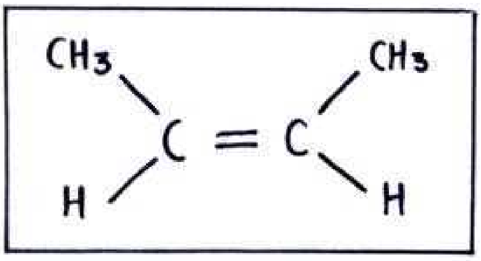


>



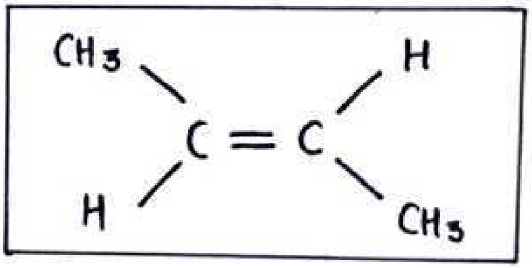
② Orientation

Trans form of alkenes are more stable than cis form because trans form have opposite orientation of Alkyl groups on double bonded carbon atom.



CIS FORM

<



TRANS FORM

③ Conjugation

Conjugated alkenes are more stable than isolated alkenes.

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

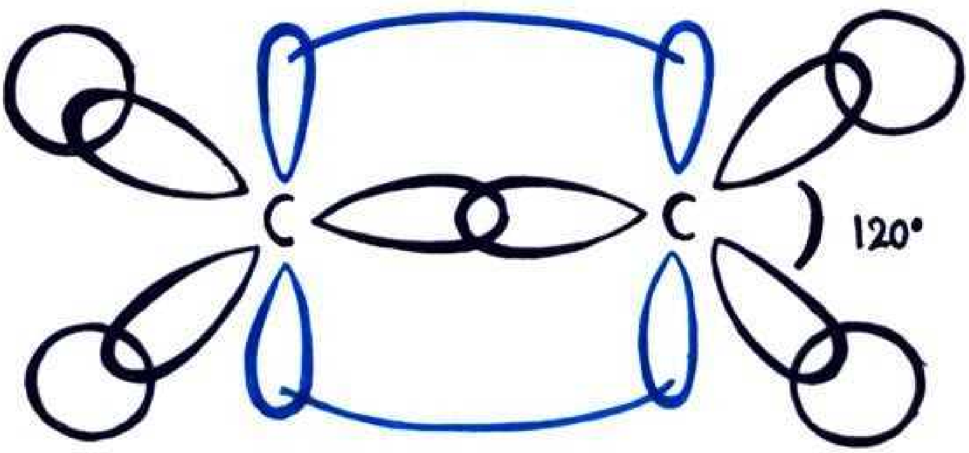
SP² HYBRIDIZATION IN ALKENES

- When 1 s orbital combines with two p orbitals to form new hybrid orbitals of same size, shape and energy then this type of hybridization is known as sp^2 hybridization.
- The carbons of simplest alkene i.e. ethene shows sp^2 hybridization.

In the case of Ethene

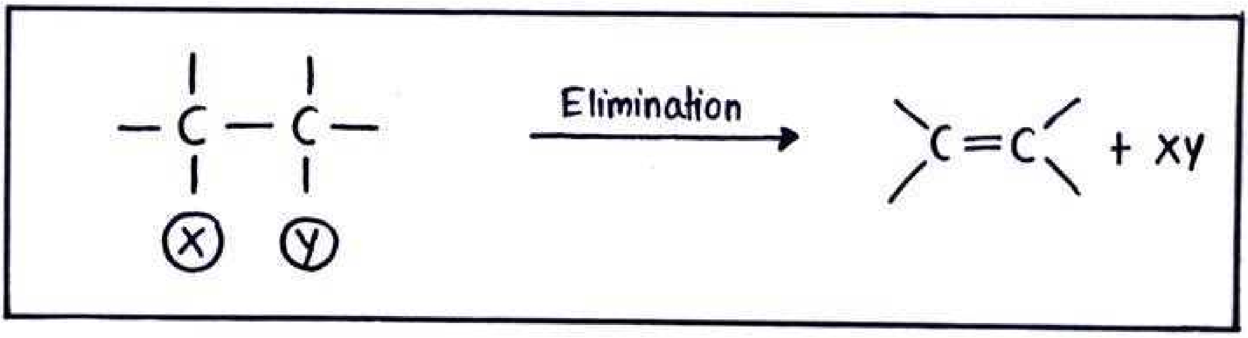
GROUND STATE :	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ ☐
EXCITED STATE :	$\uparrow\downarrow$	$\uparrow$	$\uparrow$ $\uparrow$ $\uparrow$
HYBRIDIZED STATE :	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\uparrow$ (HYBRIDIZED ORBITAL (sp^2))	$\uparrow$

STRUCTURE OF ETHENE



E1 & E2 Reaction

- E1 and E2 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 one step mechanism is known as E2 Reaction while the two step mechanism is known as E1 Reaction.
- Elimination reaction is nothing but a method of preparation of Alkenes.
- The Degree of Unsaturation increases with Elimination Reaction.



Types Of Elimination Reaction

Elimination reaction are of two types :

① E1 Reaction

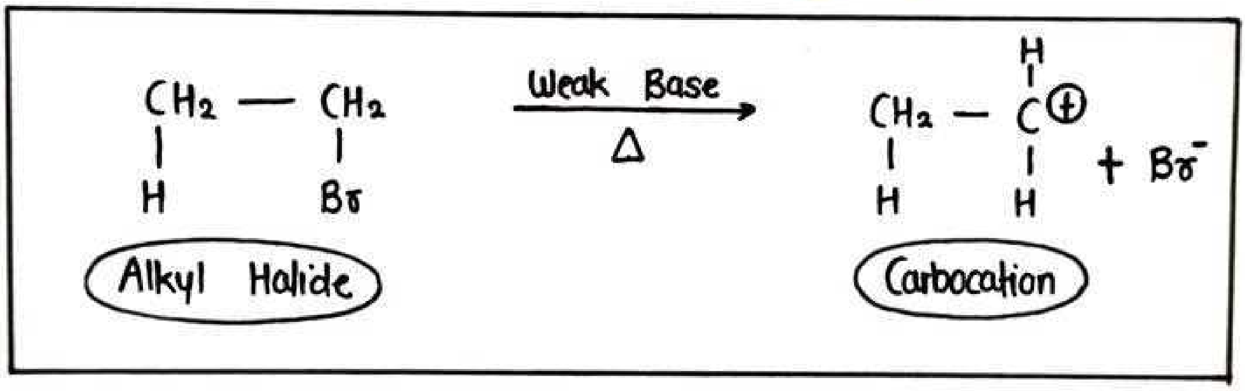
② E2 Reaction

E1 REACTION

- E1 reaction stands for Unimolecular Elimination Reaction.
- It is a two step process.
- This reaction follows first order kinetics.
- Weak base used in E1 Reactions.
- The reaction is proceed at high temperature.
- The reaction is Endothermic.

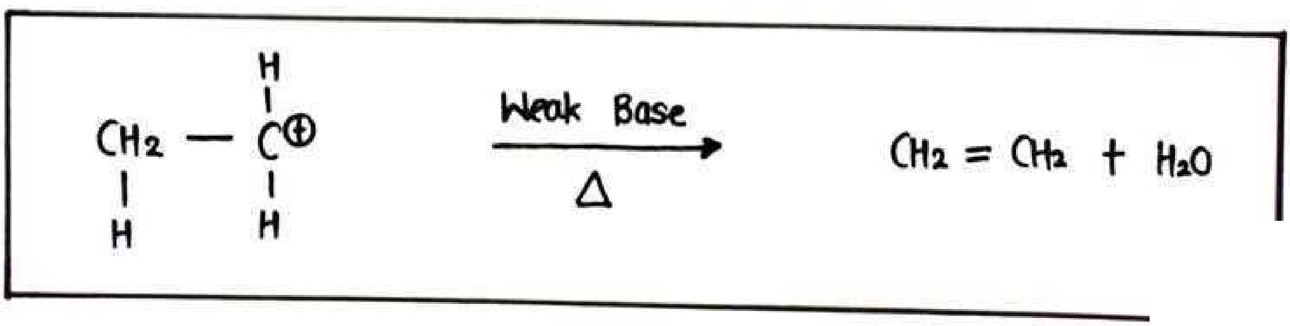
STEP - I

Formation of Carbocation (Rate determining Step)



STEP - II

Loss of proton from the carbon atom adjacent to carbon containing positive charge.



E₂ REACTION

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

E₂ REACTION MECHANISM

$$\underset{\underset{H}{|}}{CH_2} - \underset{\underset{Br}{|}}{CH_2} \xrightarrow[\Delta]{KOH} CH_2 = CH_2 + H_2O + KBr$$

E₁ VERSUS E₂ REACTION

E₁ REACTIONS	E₂ REACTION
• It is a unimolecular elimination	• It is a bimolecular elimination.
• It follows 1st order kinetics	• It follows 2nd order kinetics.
• It is a two step process	• It is a one step process.
• It requires weak base	• It requires strong base.
• Formation of carbocation takes place	• No carbocation formation takes place.

Factors Affecting E_1 & E_2 Reaction

Carbocation Formation : Formation of carbocation is a slow & rate determining step in E_1 reaction. Increasing the number of substituent (R-Group) on C-atom increases the stability of carbocation that ultimately increases rate of E_1 Reaction.

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

Leaving Group : More easily the leaving group (halogens) removed from carbon faster will be the Elimination Reactions.

$$R-I > R-Br > R-Cl > R-F$$

Nature of Base : In E_1 reaction the base used should be weak because if strong base is used then the reaction will be converted into E_2.

Solvent Used : Generally polar protic solvents are used in elimination reactions as they reduces the force of attraction between carbon & halogens.

Temperature : Generally these reactions are carried at high temperature.

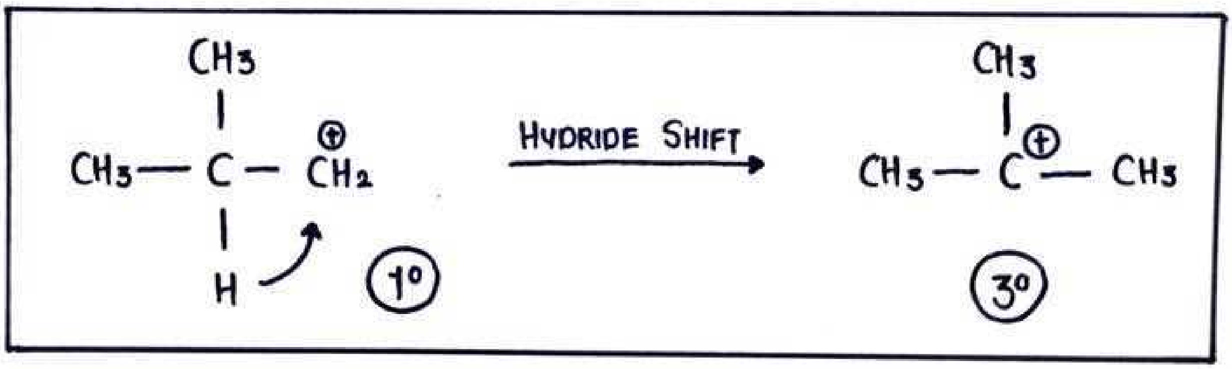
REARRANGEMENT OF CARBOCATIONS

- The shifting of bonding atom or groups in a carbocation for the formation of a more stable carbocation is known as Rearrangement of Carbocations.
- The shifting can be of two types :

① Hydride Shifting
② Methyl Shifting

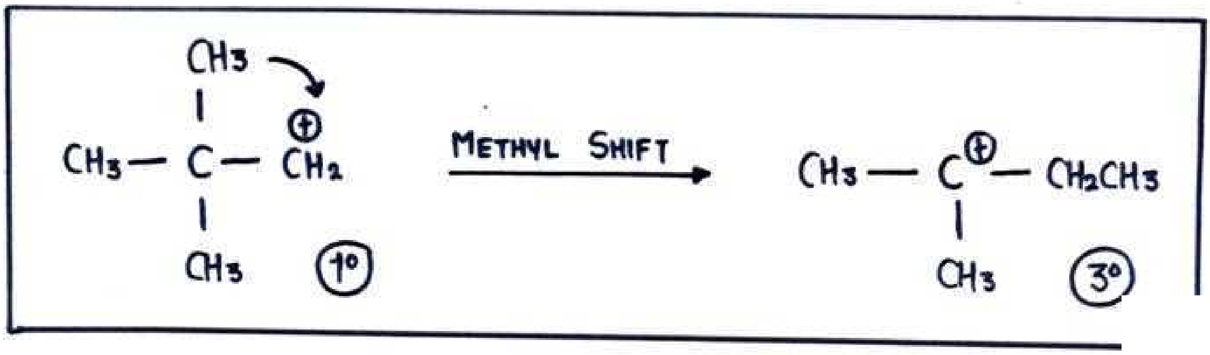
HYDRIDE SHIFTING

Shifting of hydrogen atom is known as Hydride Shifting.



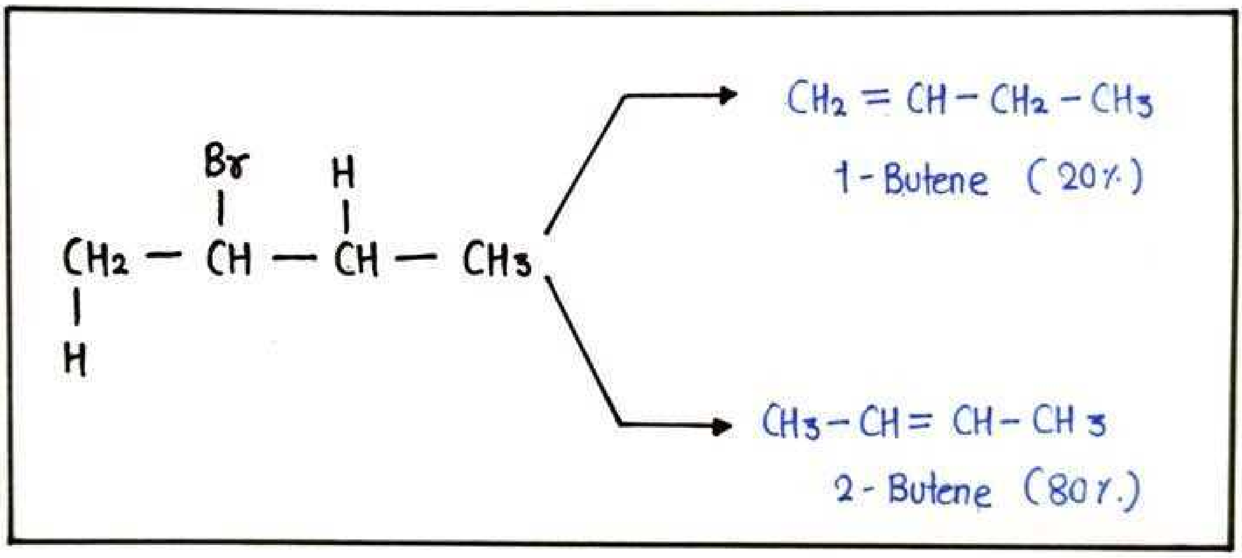
METHYL SHIFTING

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



SAYTZEFF'S RULE

- Saytzeff's rule is also known as Zaitsev's Rule.
- In the Elimination reactions when the Alkyl halide group have two or more β carbon then more 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.

ELECTROPHILIC ADDITION REACTIONS

- Alkenes are more reactive compare to Alkanes (due to 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 ~~Electrophilic~~ Addition Reaction.
- Now addition of an 'Electrophile' in an addition reaction is known as Electrophilic Addition Reaction.

Example

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

- 1 π bond breaks and 2 σ bond forms during addition reaction.

Mechanism Of Addition Reaction

STEP - I

The reagent (E-Nu) like HBr ionizes to give electrophile & nucleophile.

$$HBr \longrightarrow H^+ (E) + Br^- (Nu)$$

STEP - II

Electrophile (H^+) attacks on = bond to form σ bond & carbonium ion.

$$CH_2=CH_2 + H^+ \longrightarrow CH_3-\overset{\oplus}{C}H_2$$

STEP - III

Addition of Nucleophile on carbonium ion

$$CH_3-\overset{\oplus}{C}H_2 + Br^- \longrightarrow CH_3-CH_2Br$$

MARKOVNIKOV'S RULE

- The rule or principle was given by russian chemist Markovnikov.
- According to Markovnikov's rule during the addition reactions of alkenes the hydrogen atom (H^+) is added to that carbon atom which has maximum number of hydrogen atom.
- The rule is basically given of unsymmetrical Alkenes.

- 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 which has minimum number of hydrogen atom.

Example

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

Mechanism

STEP - I

Formation of Carbocation (two carbocation formation possible)

$$CH_3-CH=CH_2 + H-Cl \longrightarrow CH_3-\overset{\oplus}{CH}-CH_3 + Cl^- \;(2^\circ)$$

$$CH_3-CH=CH_2 + H-Cl \longrightarrow CH_3-CH_2-\overset{\oplus}{CH_2} + Cl^- \;(1^\circ)$$

STEP - II

Attack of Nucleophile to 2° carbocation.

$$CH_3-\overset{\oplus}{CH}-CH_3 + Cl^{\ominus} \longrightarrow CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$

ANTI MARKOVNIKOV'S RULE

- The rule was given by american scientist MS. Kharasch.
- This rule is also known as 'Kharasch Effect' or 'Peroxide Effect'.
- According to Anti-Markovnikov's rule if the addition reactions of unsymmetrical alkenes are performed in the presence of Organic Peroxides (R-O-O-R) then Hydrogen atom is added to the carbon atom having minimum number of Hydrogen.

Mechanism

STEP-I

Peroxides dissociates to give alkoxy free radicals.

$$R-O-O-R \xrightarrow{\Delta} 2R-\dot{O}$$

STEP-II

Alkoxy free radicals attacks on HBr to form bromine free radical

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

STEP-III

Bromine free radical attacks on alkene to give 1° & 2° free radicals.

$$\dot{Br} + CH_3-CH=CH_2 \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\dot{C}H_2 \quad (1°)$$

$$\dot{Br} + CH_3-CH=CH_2 \longrightarrow CH_3-\dot{C}H-CH_2Br \quad (2°)$$

STEP-IV

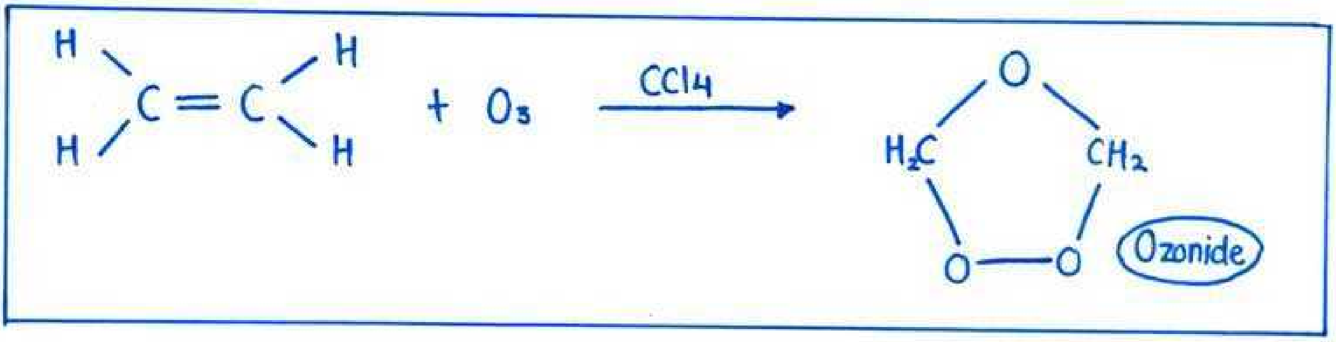
More stable free radical (2°) reacts with HBr to give final product

$$CH_3-\dot{C}H-CH_2Br + HBr \longrightarrow CH_3-CH_2-CH_2Br + \dot{Br}$$

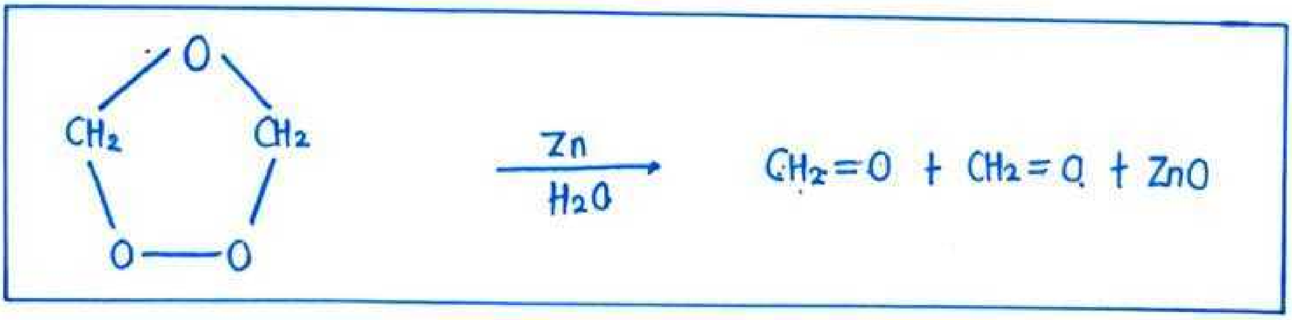
OZONOLYSIS

- Ozonolysis is a type of chemical reaction in which ozone is passed through an Alkene in an inert solvent like CCl_4 to form Ozonide.
- Ozonides are explosive compounds hence they are are further reacted in the presence of zinc and water to give carbonyl compounds (Aldehyde and ketones).
- Ozonolysis is basically a method of cleavage (breakage) of Alkene double bonds by reaction with ozone. (O_3)

STEP- I



STEP - II



CONJUGATED DIENES

- Organic compounds or Hydrocarbons that contain two carbon-carbon double bonds are called Dienes or Diolefin.
- Dienes occurs ocassionally in nature.

Types Of Dienes

Dienes are of three types :

① Conjugated Dienes
② Cumulated Dienes
③ Non- Conjugated Dienes

Conjugated Dienes

They contain alternate double bonds separated by one single bond.

$$CH_2 = CH - CH = CH_2$$

Cumulated Dienes

In cumulated dienes double bonds are adjacent to each other

$$CH_2 = CH = CH_2$$

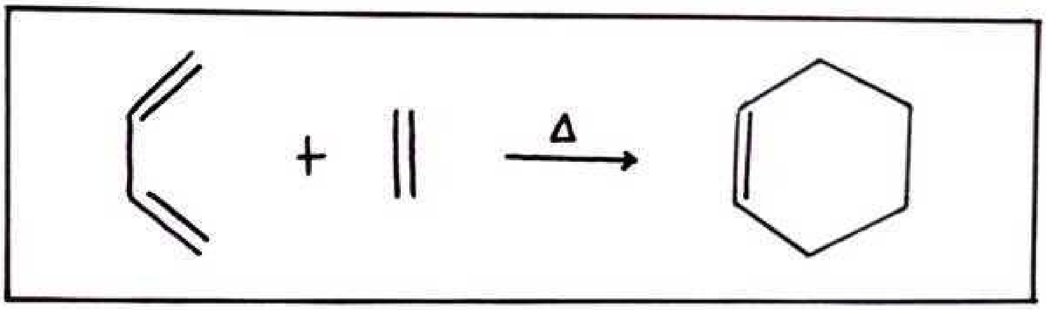
Non- Conjugated Dienes

Doube bonds are separated by 2 or more single bonds.

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

DIEL'S - ALDER REACTION

- The reaction was given by Otto Paul Hermann Diels and kurt Alder.
- They also awarded with Nobel Prize in 1950 for their discovery.
- The Diel's Alder reaction is an organic chemical reaction between a conjugated diene and an Alkene to form Cyclohexene.



Mechanism of Diel's Alder Reaction

- Diel's Alder reaction is a single step process.
- Electrons from the dienophile attacks on Carbon (C) 1 on the diene resulting in the formation of single bond between C_1 & C_6
- Double bond between C_1 & C_2 relocates to between C_2 & C_3
- Double bond between 3 & 4 broken & electrons form a single bond between 4 and 5 to form our final product.
- Finally Cyclohexene forms.