UNIT_-1

Structural theory in organic chemistry

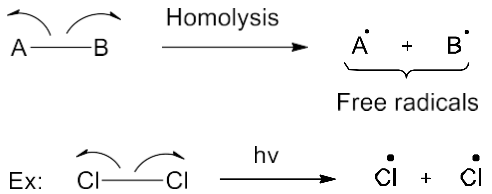
Organic chemistry: Organic chemistry is the branch of chemistry which deals with the study of carbon compounds. Ex: CH_4, C_2H_5Cl, CH_3CH_2OH etc.

Covalent Bond: it is formed by sharing of two electrons by two atoms.

I) Bond Fission: Generally organic compounds contain covalent bonds. The breaking of covalent is called Bond fission. The bond can be broken in two ways

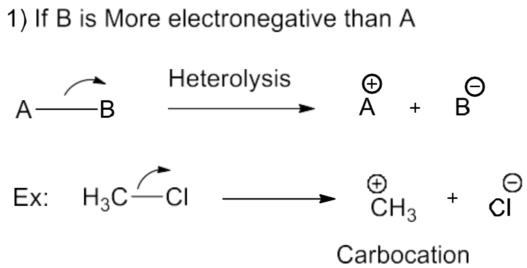
1) Homolytic Fission or Homolysis
2) Heterolytic Fission or Heterolysis

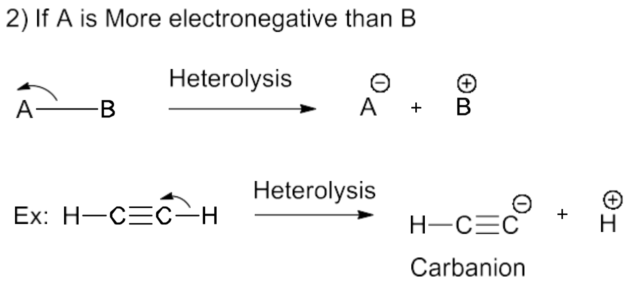
Homolytic Fission or Homolysis: In this type of fission shared electron pair is distributed equally between two bonded atoms.



a) It is shown by half headed arrow “  ”.
b) The two fragments formed in this cleavage are neutral species and each one has one unpaired electron. These species are called as free radicals.

Heterolytic Fission or Heterolysis: In this type of fission shared electron pair of the covalent bond is remains with one atom. Then the cleavage is called Heterolysis. In this type of fission **Carbocations** or **Carbanions** are formed.





II) Organic Reagents:

There are three types of Organic Reagents

1) Electrophiles
2) Nucleophiles
3) Free radicals

Electrophiles: These are electron deficient species and attacks at negatively charged centre of the molecules. These are act as Lewis Acids, these are two types

a) Positive Electrophiles: these are carrying positive charge

Ex: All carbocations, H^+, H_3O^+, Cl^+, NO_2^+ etc.

b) Neutral Electrophiles: these are Neutral species

Ex: $AlCl_3$, BF_3, SO_3 etc.

Nucleophiles: These are electron rich in species and attract a positively charged centre of the molecules. These are act as Lewis Bases, these are two types

a) Negative Nucleophiles: these are carrying Negative charge

Ex: All Carbanions, H^-, OH^-, Cl^-, $RCOO^-$ etc.

b) Neutral Nucleophiles: these are Neutral species

Ex: H_2O, NH_3.

Free Radicals: These are Neutral species and contains an unpaired or odd electrons

Ex: $Cl^{\cdot}$, $CH_3^{\cdot}$ etc.

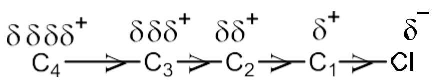
a) These are produced by homolysis of covalent bond
b) Free radicals are paramagnetic in nature due to presence of odd electron

<u>III) Bond Polarisation</u>: (Displacement of electron pair)

It is defined as displacement of electron pair in a covalent bond towards more electronegative atom.

<u>Inductive effect:</u> it is defined as permanent displacement of an electron pair in a sigma bond towards more electronegative atom or group in a carbon chain is called as Inductive effect.

a) It arises due to electro negativity difference between two atoms forming sigma bond
b) It is transmitted through sigma bonds and its effect decreases as the carbon chain length increases, significant up to 3 or 4 carbon atoms after that it is negligible.
c) It is denoted by $\longrightarrow$.



It is divided into two types

i) **Positive inductive effect (+ I.E)**: An atom or group which releases or donates electrons to the carbon chain is called Positive inductive effect.

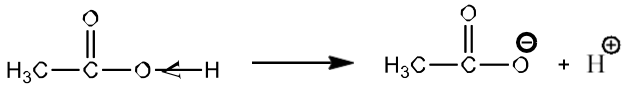
Ex: CH_3, C_2H_5 (All alkyl groups), O^-, COO^-, NH_2 etc.

ii) **Negative inductive effect (- I.E)**: An atom or group which withdraws electrons from the carbon chain is called Negative inductive effect.

Ex: NO_2, CN, CHO, COOH, F, Cl, Br, I etc.

Applications of Inductive effect:

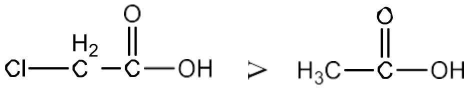
- **Acidic strength of Carboxylic acids:** Carboxylic acids are acidic in nature due to the presence of polar covalent bond in OH group. Acidity of carboxylic acids depends on extent of ionization to produce proton (H^+), i.e. depends on stability of carboxylate ion.



Carboxylate ion

Negative inductive effect groups (– I.E) increases the acidic strength of carboxylic acids becoz they stabilizes carboxylate ion by withdrawing electron density on it. Positive inductive effect groups (+ I.E) decreases the acidic strength of carboxylic acids.

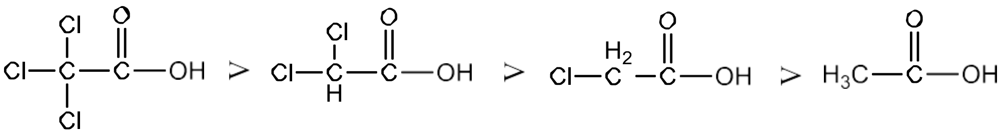
Ex: Chloro acetic acid is stronger than acetic acid



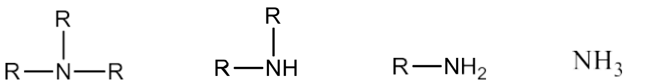
Chloro aceticacid aceticacid

The acidic strength increases as the number of –I.E. groups increases on the α-carbon.

Ex:



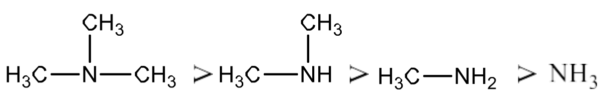
- **Basic Strength of Amines:** Basic character of amines is mainly due to presence of unshared electron pair on nitrogen atom. Basic strength of amines depends on the availability unshared electron pair on nitrogen atom.



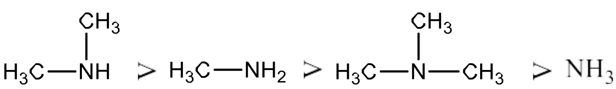
3^0 amine 2^0 amine 1^0 amine ammonia

Electron releasing groups (+I.E) increase the Basic Strength of amines becoz they increases the electron density on nitrogen as a result basic strength of amines increases. –I.E groups decreases the basic strength of amines increases.

Therefore the relative basic strength of methyl amines according to +I.E effect is

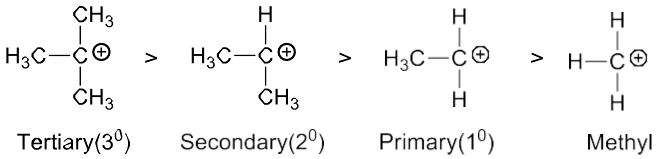


But actual basic strength is



3^0amine is less basic than 1^0 and 2^0 amines because of steric hindrance in 3^0amine.

- **Stability of Carbocations:** The relative stability of carbocations is



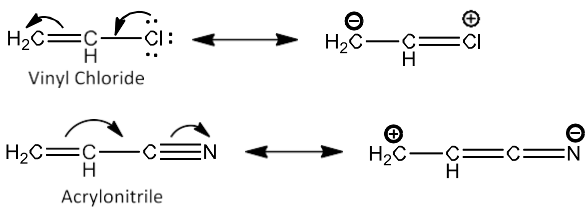
+I.E groups increases the stability of carbocations, because they reduces its positive charge by releasing electrons to positive carbon and thus it's stabilizes. - I.E groups decreases the stability of carbocations.

As the +I.E groups increases, stability of carbocations increases. Therefore tertiary carbocation having three electron donating +I. E groups (three methyl groups) is more stable than secondary having two +I. E groups (two methyl groups) which in turn more stable than primary (one methyl group). Methyl carbocation (no methyl groups) is least stable.

- In the same way we can explain the stability of freeradicals ($3^0 > 2^0 > 1^0 >$ Methyl) and carbanions (Methyl $> 1^0 > 2^0 > 3^0$) by using inductive effect.

Mesomeric Effect (M) or Resonance Effect: It is a permanent effect in which pi-electrons are transferred (delocalized) from a multiple bond to an atom (or) from a multiple bond to a single covalent bond (or) from an atom with lone pair of electrons to adjacent covalent bonds.

Ex:



It is divided into two types

1) **Positive Mesomeric effect (+M):** the groups which donates electrons to the conjugated π-system through resonance is called as +M Effect groups.

Ex: -OH, -OR, -SH, $-NH_2$, F, Br, I etc.

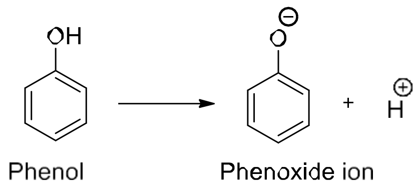
2) **Negative Mesomeric effect (- M):** the groups which withdraw electrons towards themselves through resonance are called as - M Effect groups.

Ex: NO_2, CN, CHO, COOH, SO_3H etc.

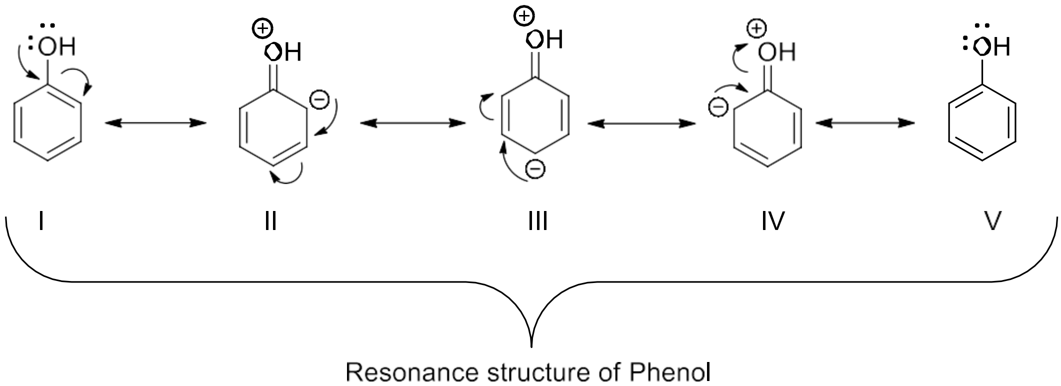
Applications of Mesomeric effect:

- **Acidity of Phenol:**

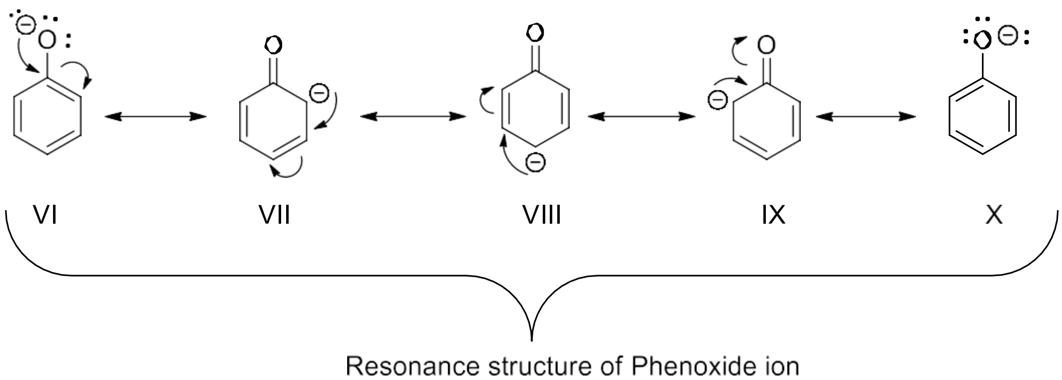
By using Mesomeric effect we can explain the acidity of phenol. Phenol is in acidic nature because it looses H+ ion and form phenoxide ion.



Phenol has the following resonance structures



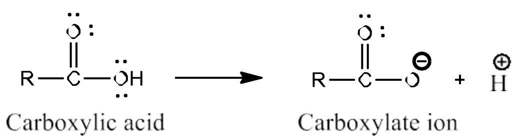
The structures II, III and IV of phenol involve charge separation and hence less stable. Phenoxide ion has the following resonance structures



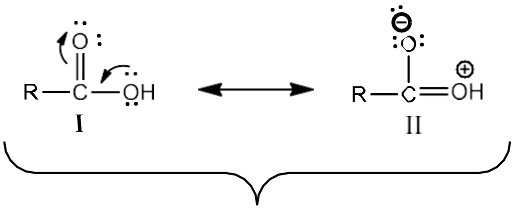
The resonance structures of phenoxide carry only one charge (-ve charge). According to resonance rules single charged resonance structures are more stable than charge separation resonance structures. Therefore phenoxide ion is more stable than phenol, hence phenol looses proton and act an acid.

- **Acidity of Carboxylic acids:**

By using Mesomeric effect we can explain the acidity of Carboxylic acids. Carboxylic acids are in acidic nature because they looses proton (H+ ion) and form Carboxylate ion.

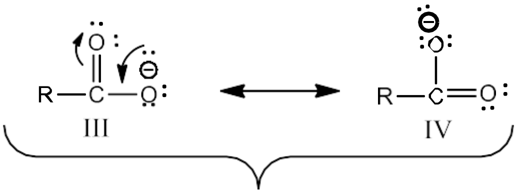


Carboxylic acid has the following resonance structures



Resonance structures of Carboxylic acid

Carboxylate ion has the following resonance structures



Resonance structures of Carboxylate ion

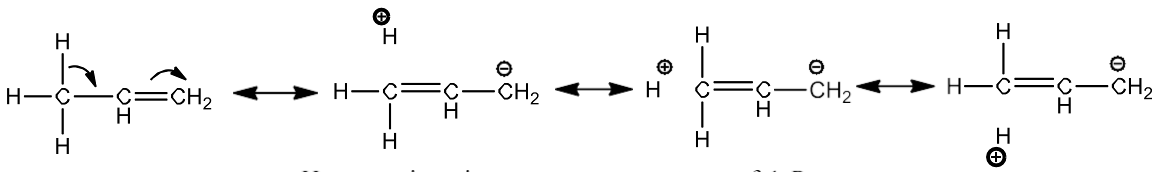
Carboxylate ion resonance structures (III & IV) are exactly equivalent structures and negative charge is dispersed on oxygen atoms but in case of carboxylic acid resonance structures is charge separation structures and positive charge is present on electronegative oxygen atom (II), hence according to resonance rules Carboxylate ion is more resonance stabilized than carboxylic acid. Therefore carboxylic acid ionizes by loosing proton and acts an acid.

Hyper conjugation:

Delocalization of an α C-H sigma electrons into adjacent π-orbital or empty p-orbital (sp2 hybrid carbon) is called Hyper conjugation. It is also called as "No bond resonance" or "Baker-Nathan effect".

As the number of α C-H hydrogens increases its hyper conjugation structures increases, hence stability increases

Ex: Hyper conjugation in Propene



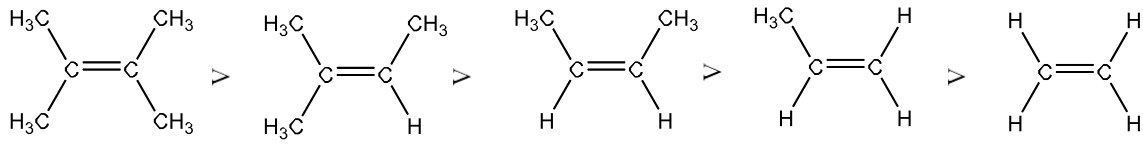
Hyperconjugation resonance structures of 1-Propene

Applications of Hyper conjugation: By using this we can explain the stability of Alkenes, Carboations and Freeradicals.

- **Stability of Alkenes:**

The stability of alkenes increases with increase in the number of α-CH hydrogens on the double bond. This is due to increase in the number of contributing Hyper conjugation structures.

The increasing order of stability of some of the alkenes as follows.

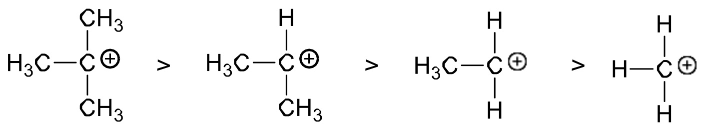


12 α–CH are present 12 Hyperconjugation structures possible	9 α–CH 9 HC str	6 α–CH 6 HC str	3 α–CH 3 HC str	zero α–CH Zero HC str

In above alkenes from left to right number of α-CH hydrogens decreases as a result its hyper conjugation resonance structures decreases hence its stability decreases.

- **Relative stability of Carbocations:** the stability of carbocations can be explained on the basis of Hyper conjugation effect.

The relative stability of carbocations is as follows

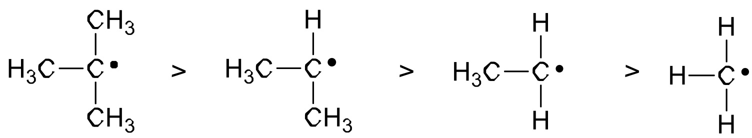


Tertiary(3^0)	Secondary(2^0)	Primary(1^0)	Methyl
9 α–CH are present 9 Hyperconjugation structures possible	6 α–CH 6 HC	3 α–CH 3 HC	Zero α–CH Zero HC

In above Carbocations from left to right number of α-CH hydrogens decreases as a result its hyper conjugation resonance structures decreases hence its stability decreases.

- **Relative stability of Freeradicals:** the stability of Freeradicals can be explained on the basis of Hyper conjugation effect.

The relative stability of Freeradicals is as follows



Tertiary(3^0)	Secondary(2^0)	Primary(1^0)	Methyl
9 α–CH are present 9 Hyperconjugation structures possible	6 α–CH 6 HC	3 α–CH 3 HC	Zero α–CH Zero HC

In above Freeradicals from left to right number of α-CH hydrogens decreases as a result its hyper conjugation resonance structures decreases hence its stability decreases.

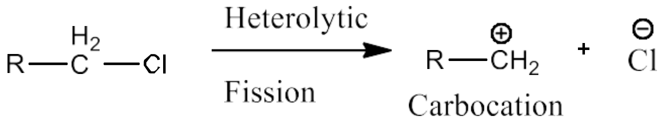
IV) Organic Reactive Intermediates:

A. Carbocation or Carbonium ion: A carbocation is a positively charged ion in which the positive charge is carried by a carbon atom with six electrons in its valence shell.

Ex: CH_3^+, $CH_3CH_2^+$ etc

- Carbocation is sp2 hybridized with trigonal planar structure and bond angle is 120^0.
- Relative stability order of carbocations is **Benzyl > Allyl > 3^0 > 2^0 > 1^0 > methyl**
- These are act as Lewis acids
- These are generated by heterolysis of covalent bond

Ex: Heterolysis of C-Cl bond

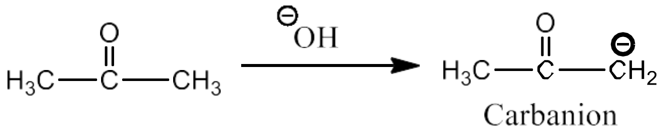


B. Carbanion: A Carbanion is a negatively charged ion in which the negative charge is carried by a carbon atom with eight electrons in its valence shell.

Ex: CH_3^{--}, $CH_3CH_2^{--}$ etc

- Carbanion is sp3 hybridized with pyramidal structure.
- Relative stability order of carbanions is **Benzyl** > **Allyl** > **methyl** > 1^0 > 2^0 > 3^0
- These are act as Lewis Bases
- These are generated by heterolysis of covalent bond

Ex: Heterolysis of C-H bond in ketones

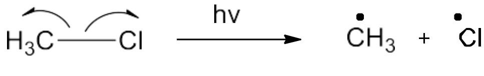


C. Freeradical: A Freeradical is neutral species in which an unpaired or odd electron is carried by a carbon atom with seven electrons in its valence shell.

Ex: Cl·, CH_3· etc.

- Carbanion is sp2 hybridized with trigonal planar structure
- Relative stability order of carbanions is **Benzyl > Allyl > 3^0 > 2^0 > 1^0 > methyl**
- Free radicals are paramagnetic in nature due to presence of odd electron
- These are generated by homolysis of covalent bond in presence of UV light, heat and peroxides.

Ex: Homolysis of C-Cl bond in alkyl halides



D. Carbene: It is neutral organic species containing a divalent carbon atom having six electrons

- It is an electron deficient species
- General formula of carbene is ":CR_2"

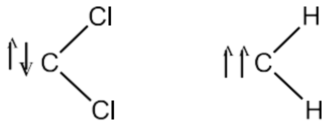
Ex:

Methyl Carbene Dichloro Carbene

- Carbenes are classified as either singlets or triplets depending upon their electronic structure

a) **Singlet Carbene:** In singlet carbene both the electron spins are in opposite direction i.e. spin paired and carbene carbon atom is sp2 hybridized with bent geometry

b) **Triplet Carbene:** In triplet carbene both the electron spins are in same direction and carbene carbon atom is sp hybridized with bent geometry



Singlet carbene Triplet carbene

- Triplet Carbenes are relatively more stable than singlet carbenes.

E. **Nitrenes: :** It is neutral organic species in which nitrogen atom contains six electrons

- It is an electron deficient species
- General formula of Nitrene is

- Nitrenes are classified as either singlets or triplets depending upon their electronic structure

a) **Singlet Carbene:** In singlet Nitrene, electron spins are spin paired and Nitrogen atom is sp2 hybridized

b) **Triplet Carbene:** In triplet Nitrene, electron spins are in same direction and Nitrene atom is sp hybridized.

V. Types of Organic Reactions:

There are four types of organic reactions

1) Substitution reactions
2) Addition reactions
3) Elimination reactions
4) Rearrangement reactions

1). Substitution reactions: The reactions in which substitution or replacement of an atom or group with another atom or group is called substitution reaction.

These are further divided into three types

- **Free radical substitution reactions**: In substitution reaction if free radicals are involved as reaction intermediates those reactions are called as Free radical substitution reactions

Ex: Chlorination of Methane

$$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$$

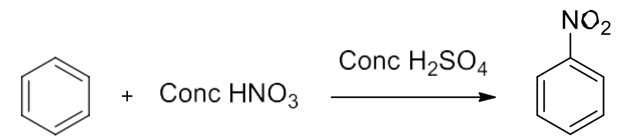
- **Nucleophilic substitution reactions**: The substitution reaction in which one nucleophile (strong) is substituted by another nucleophile (weak) is called as nucleophilc substitution reactions

Ex: Base hydrolysis of Alkyl halide

$$H_3C-Cl + NaOH \longrightarrow H_3C-OH + NaCl$$

- **Electrophilic substitution reactions**: In these reactions an electrophile is displaces a functional group or hydrogen atom.

Ex: Nitration of benzene

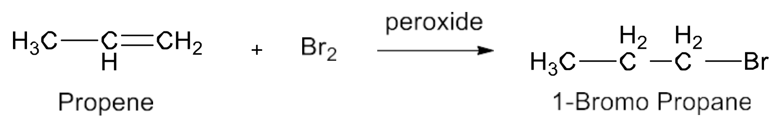


2). Addition reactions: generally unsaturated organic compounds (alkenes, alkynes) undergo addition reactions. In these reactions two reactants simply add together to form addition product.

These are further divided into three types

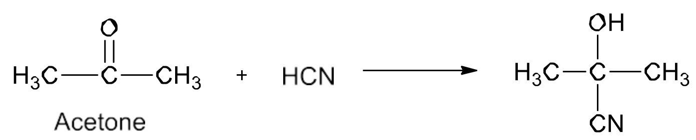
- **Free radical addition reactions**: In addition reaction if free radicals are involved as reaction intermediates those reactions are called as Free radical addition reactions

Ex: Addition of HBr to propene in presence of peroxide (Anti markovnikov's addition of HBr to alkene)



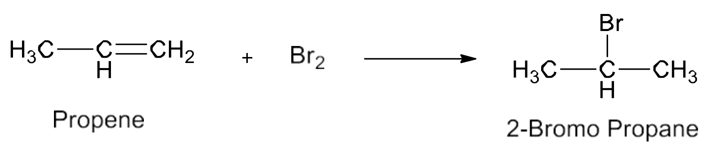
- **Nucleophilic addition reactions**: These reactions involve an initial attack of Nucleophile

Ex: Addition HCN to Acetone



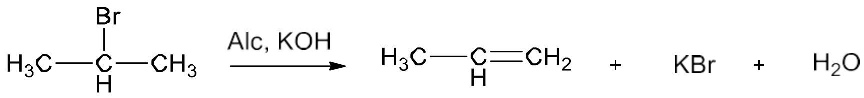
- **Electrophilic addition reactions**: In these reactions an initial attack of electrophile is takes place on multiple bonds.

Ex: Addition of HBr to propene (Markovnikov's addition of HBr to alkene)

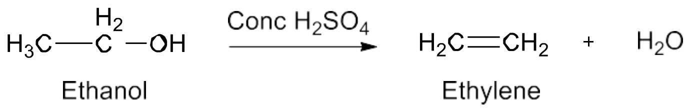


3). Elimination Reactions: These reactions involve the elimination of simple molecules like H_2O, NH_3, HCl, HBr etc. from reactants to form products.

Ex: a) Dehydrohalogenation of alkyl halides

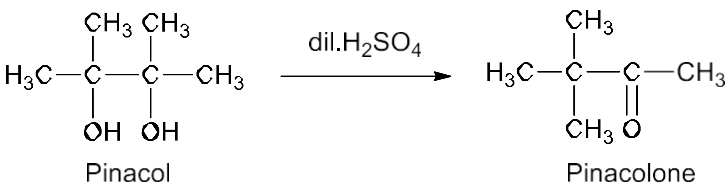


b) Dehydration of alcohols



4). Rearrangement Reactions: In these reactions migration of group or atom takes place at intermediate stage as a result rearranged carbon skeleton products are formed.

Ex: Pinacol – Pinacolone rearrangement



Unit-II (Alkanes)

1). **Methods of preparation of alkanes**

(1) From unsaturated hydrocarbons

The process of addition of hydrogen to an unsaturated compound in presence of a catalyst is called **hydrogenation or reduction.**

Alkenes and alkynes add one and two molecules of hydrogen in presence of a catalyst such as nickel , platinum, palladium to form alkanes. This hydrogenation of unsaturated hydrocarbons using ordinary nickel at a temperature of about 523-573 K is commonly known as **Sabatier and Sendern's reaction**.

$$H_2C{=}CH_2 \xrightarrow{H_2/Ni} H_3C{-}CH_3$$

$$HC{\equiv}CH \xrightarrow{H_2/Pd} H_3C{-}CH_3$$

2) From alkyl halides (Grignard reagent)

Alkyl halide especially bromide and iodide react with magnesium metal in presence of dry ethoxyethane to form alkyl magnesium halides. These are commonly known as **Grignard's reagent.**

$$R{-}X + Mg \longrightarrow R{-}Mg{-}X$$

$$H_3C{-}CH_2{-}Br + Mg \longrightarrow H_3C{-}CH_2{-}Mg{-}Br$$

Since carbon is more electronegative than magnesium, therefore, C-Mg bond is quite polar.

$$H_3C{-}CH_2{-}Mg{-}Br \xrightarrow{H_2O} H_3C{-}CH_3 + Mg(OH)Br$$

3). Wurtz reaction: Wurtz reaction is a convenient method for the preparation of symmetrical alkanes i.e. alkanes containing even number of carbon atoms.

When an alkyl halide is treated with metallic sodium in presence of dry di ether , a symmetrical alkane, containing double the number of carbon atoms present in the alkyl group is formed. This reaction is called **wurtz reaction.**

$$2\,R{-}X + 2Na \longrightarrow R{-}R + 2NaX$$

$$2\,CH_3{-}Br + 2Na \longrightarrow H_3C{-}CH_3 + 2NaBr$$

Mechanism

1). Through the intermediate formation of free radicle.

$$R{-}X + Na \longrightarrow \dot{R} + NaX$$

$$\dot{R} \quad \dot{R} \longrightarrow R{-}R$$

2). Through the intermediate formation of Organo metallic compound.

$$R{-}X + 2Na \longrightarrow R{-}Na + NaX$$

$$R{-}Na + R{-}X \longrightarrow R{-}R$$

If two different alkyl halides are used to prepare an alkane with odd number of carbon atoms, a mixture of three alkanes is actually produced.

$$R_1{-}X + 2Na + R_2{-}X \longrightarrow R_1{-}R_2 + 2NaX$$

Wurtz- Fittig Reaction

In which Aryl halide reacts with alkyl halides and sodium metal in the presence of dry ether to form substituted Aromatic compounds.