<u>Course -4: ORGANIC CHEMISTRY -I</u>

UNIT-I:

STRUCTURAL THEORY IN ORGANIC CHEMISTRY:

In Organic chemistry usually, we find covalent bonds. Covalent bond is formed by the sharing of electrons between two atoms. Chemical reactions may happen by breaking and making of bonds. In order to know the reaction outcome, it essential to learn the way of breaking of chemical bonds

Bond fission: Splitting of chemical bonds is known as the Bond Fission or Bond cleavage i.e. dissociation of molecule into fragments

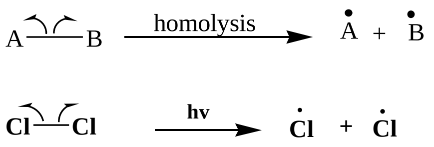
Types of bond fission:

Bond fission can be classified into two types

1. Homolytic fission or Homolysis
2. Heterolytic fission or Heterolysis

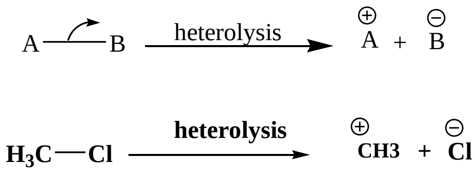
Homolytic fission or Homolysis:

Bond fission which occurs by equally sharing of bond electrons between two atoms is called homolytic fission or Homolysis. In this fission free radicals are obtained as products



- is called as half headed arrow to represent the movement of electrons (equal sharing) in a bond
- This type of fission occurs in the following cases
  a. When the substrate is irradiated with UV radiation
  b. When enough heat is given to the substrate
  c. When the compound is exposed to a high temperature condition.

Heterolytic fission or Heterolysis: Bond fission which occurs by unequal sharing of bond electrons between two atoms is called Heterolytic fission or Heterolysis. In this fission carbocation and carbanion are formed



Atom or group with more electronegativity gets negative charge and atom or group with more electro positivity gets positive charge

 is called as double headed arrow to represent the movement of electrons in heterolysis

Organic Reagents:

In general, organic reaction can be written as *substrate + reagent → product*

Any chemical compound which brings about the chemical change in substrate

There are three types of Organic Reagents

1) Electrophiles
2) Nucleophiles
3) Free radicals

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

a) Positive Electrophiles: they carry 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 attack at a position of positively charged center of the molecules. these are two types

a) Negative Nucleophiles: they carry Negative charge

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

b) Neutral Nucleophiles: these are Neutral species and acts as Lewis Bases

   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

Bond Polarisation: (Displacement of electron pair)

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

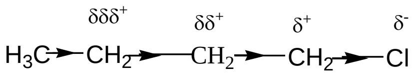
Inductive effect:

Polarization of σ bond due to the presence of electron withdrawing or electron donating atom/group is called as Inductive effect

Withdrawal of the electron density towards more electronegative element through sigma bond results in partial charge separation between atoms more electronegative atom gets partial negative charge (it represented with δ^-), other atom gets partial positive charge δ^+

Let us consider the example

Butyl chloride $CH_3 – CH_2 - CH_2 - CH_2 -Cl$



Here the chloride is more electronegative compared to carbon so electron density is transmitted from Carbon chain to Cl

Salient of features:

1. it is a permanent effect

2. In order to exhibit inductive effect two atoms must differ in electronegativity

3. Electron density is moved through **sigma bonds** only, not occur in pi bonds

4. This is effective up to 3 sigma bonds, weaker after that in the carbon chain

Negative inductive effect (-I):

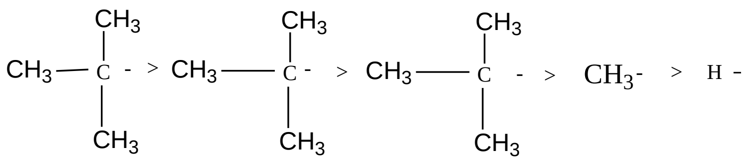
The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by -I.

examples of groups in the decreasing order of their -I effect:

$NH_3^+ > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > –CH=CH_2 > H$

2) Positive inductive effect (+I):

It refers to the electron releasing nature of the groups or atoms and is denoted by +I. examples of groups in the decreasing order of their +I effect.



Application of inductive effect

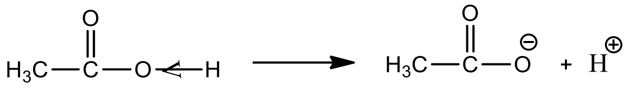
(a) Basicity of amines

(b) Acidity of carboxylic acids

(c) Stability of carbonium ions.

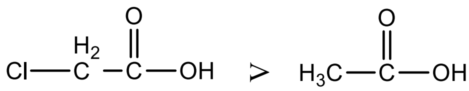
Applications of Inductive effect:

(a) 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

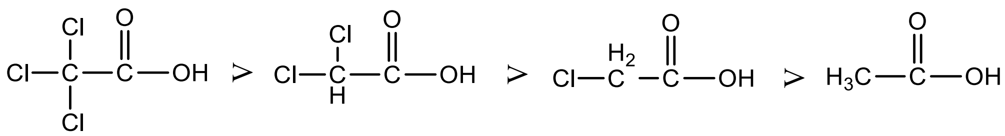
Negative inductive effect groups (– I.E) increases the acidic strength of carboxylic acids because they stabilize carboxylate ion by withdrawing electron density on it. Positive inductive effect groups (+ I.E) decreases the acidic strength of carboxylic acids.
Ex: Chloro acetic acid is stronger than acetic acid



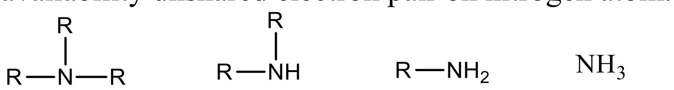
Chloro aceticacid   aceticacid

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

Ex:

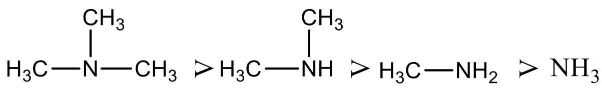


(B) Basic Strength of Amines: Basic character of amines is mainly due to presence of unshared electron pair on nitrogen atom. Basic strength of amines depends on the availability unshared electron pair on nitrogen atom.

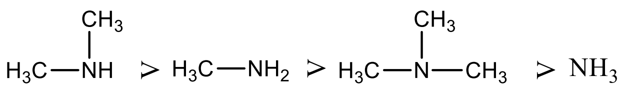


3^0 amine 2^0 amine 1^0 amine   ammonia

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

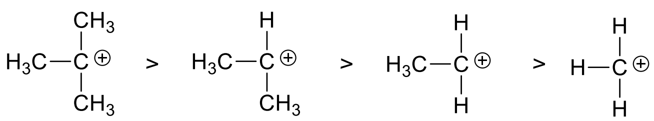


But actual basic strength is



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

(C) Stability of Carbocations: The relative stability of carbocations is



Tertiary(3^0)   Secondary(2^0)   Primary(1^0)   Methyl

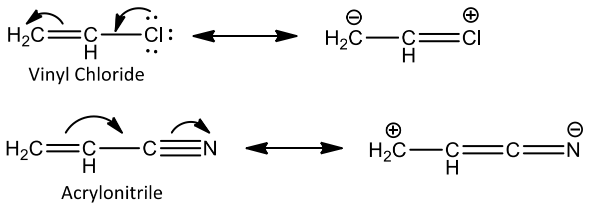
+I.E groups increases the stability of carbocations, because they reduces its positive charge by releasing electrons to positive carbon and thus it's stabilizes. - I.E groups decreases the stability of carbocations.

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 free radicals ($3^0 > 2^0 > 1^0 >$ 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:

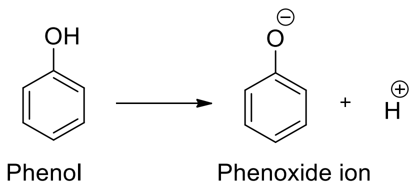


It is divided into two types

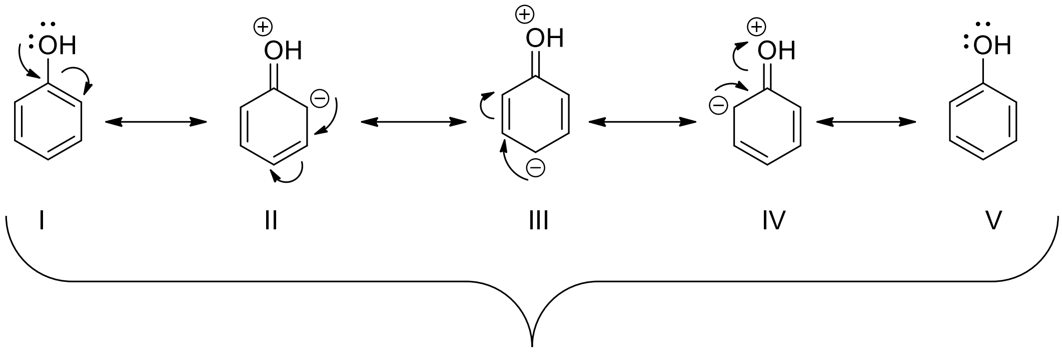
1) **Positive Mesomeric effect (+M):** the groups which donates electrons to the conjugated π-system through resonance is called as +M Effect groups.
   Ex: -OH, -OR, -SH, $-NH_2$, F, Br, I etc.
2) **Negative Mesomeric effect (- M):** the groups which withdraw electrons towards themselves through resonance 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 loses H+ ion and form phenoxide ion.

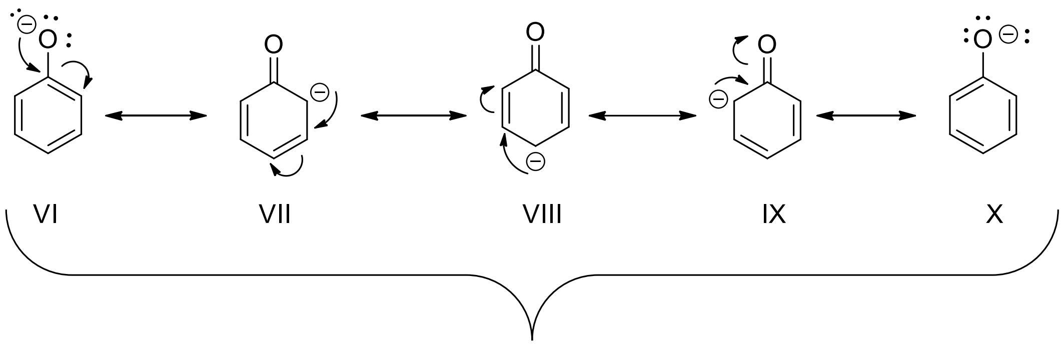


Phenol has the following resonance structures



Resonance structure of Phenol

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

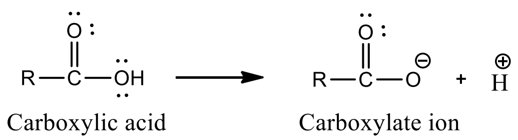


Resonance structure of Phenoxide ion

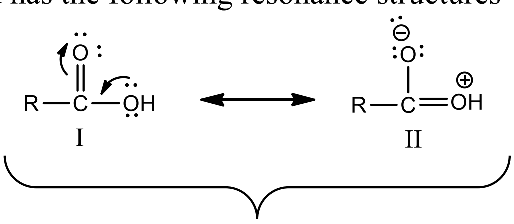
The resonance structures of phenoxide carry only one charge (-ve charge). According to resonance rules single charged resonance structures are more stable than charge separation resonance structures. Therefore, phenoxide ion is more stable than phenol, hence phenol loses proton and act an acid.

- **Acidity of Carboxylic acids:**

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

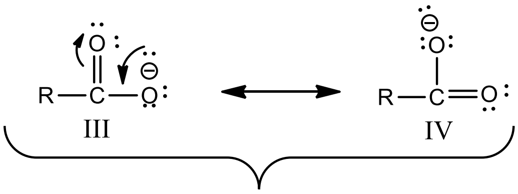


Carboxylic acid has the following resonance structures



Resonance structures of Carboxylic acid

Carboxylate ion has the following resonance structures

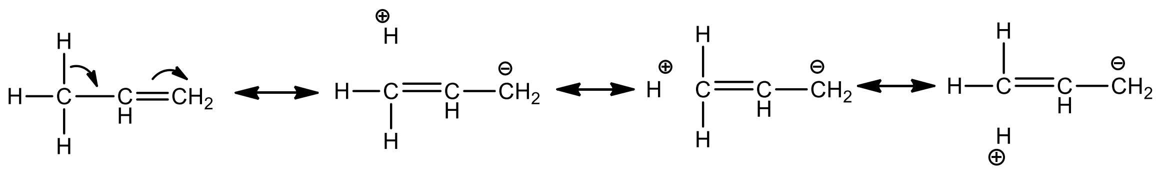


Resonance structures of Carboxylate ion

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 losing proton and acts an acid.

Hyperconjugation:

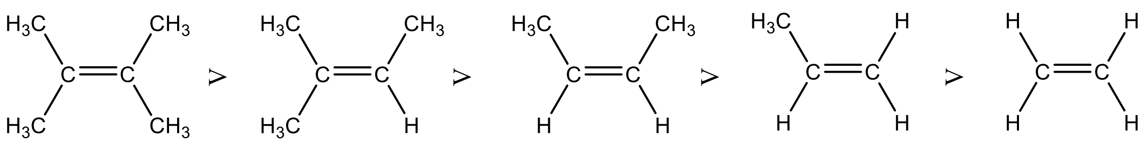
Delocalization of an α C-H sigma electrons into adjacent π-orbital or empty p-orbital (sp2 hybrid carbon) is called Hyperconjugation. It is also called as "No bond resonance" or "Baker-Nathan effect".
As the number of α C-H hydrogens increases its hyperconjugation structures increases, hence stability increases
Ex: Hyperconjugation in Propene



Hyperconjugation resonance structures of 1-Propene

Applications of Hyperconjugation: By using this we can explain the stability of Alkenes, Carbocations and Free radicals.

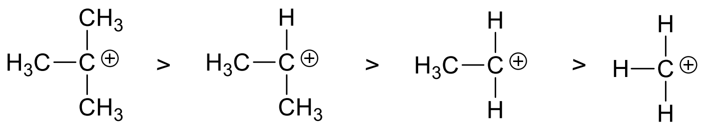
- **Stability of Alkenes:**
  The stability of alkenes increases with increase in the number of α-CH hydrogens on the double bond. This is due to increase in the number of contributing Hyperconjugation structures.
  The increasing order of stability of some of the alkenes as follows.



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 hyperconjugation resonance structures decreases hence its stability decreases.

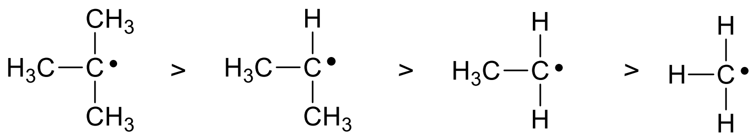
- **Relative stability of Carbocations:** the stability of carbocations can be explained on the basis of Hyperconjugation effect.
  The relative stability of carbocations is as follows



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 Free radicals:** the stability of Free radicals can be explained on the basis of Hyperconjugation effect.
  The relative stability of Free radicals 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 Free radicals from left to right number of α-CH hydrogens decreases as a result its hyper conjugation resonance structures decreases hence its stability decreases.

Types of Organic Reactions:

There are four types of organic reactions

1) Substitution reactions
2) Addition reactions
3) Elimination 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

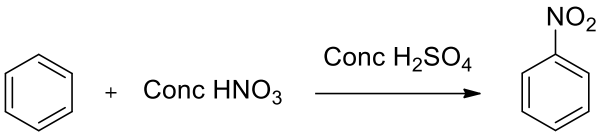
- **Free radical substitution reactions**: In substitution reaction if free radicals are involved as reaction intermediates those reactions are called as Free radical substitution reactions
  Ex: Chlorination of Methane

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

- **Nucleophilic substitution reactions**: The substitution reaction in which one nucleophile (strong) is substituted by another nucleophile (weak) is called as nucleophilic substitution reactions
  Ex: Base hydrolysis of Alkyl halide

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

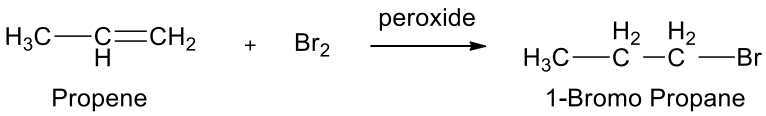
- **Electrophilic substitution reactions**: In these reactions an electrophile is displaces a functional group or hydrogen atom.
  Ex: Nitration of benzene



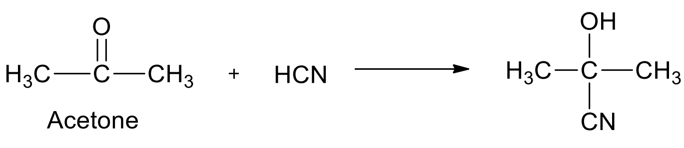
2). Addition reactions: generally unsaturated organic compounds (alkenes, alkynes) undergo addition reactions. In these reactions two reactants simply add together to form addition product.

These are further divided into three types

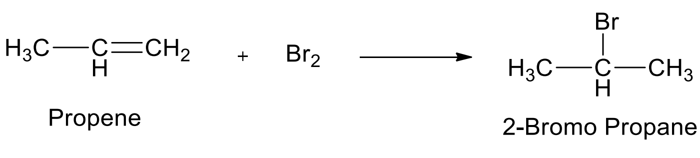
- **Free radical addition reactions**: In addition, reaction if free radicals are involved as reaction intermediates those reactions are called as Free radical addition reactions
  Ex: Addition of HBr to propene in presence of peroxide (Anti Markovnikov's addition of HBr to alkene)



- **Nucleophilic addition reactions**: These reactions involve an initial attack of Nucleophile
  Ex: Addition HCN to Acetone

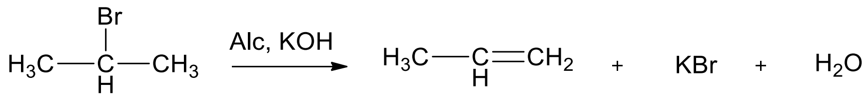


- **Electrophilic addition reactions**: In these reactions an initial attack of electrophile is takes place on multiple bonds.
  Ex: Addition of HBr to propene (Markovnikov's addition of HBr to alkene)

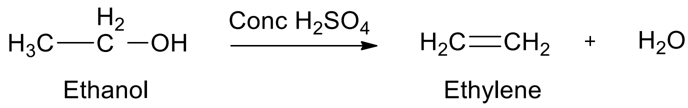


3). Elimination Reactions: These reactions involve the elimination of simple molecules like H_2O, NH_3, HCl, HBr etc. from reactants to form products.

Ex: a) Dehydrohalogenation of alkyl halides



b) Dehydration of alcohols



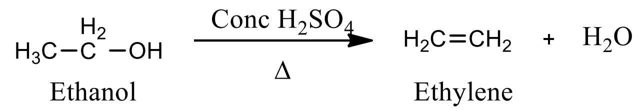
Alkenes

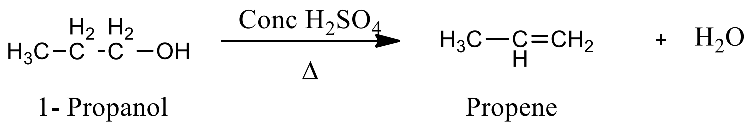
Alkenes are having general formula C_nH_{2n}.These are unsaturated hydrocarbons in which at least one carbon – carbon double bond is present. These are also called as olefins

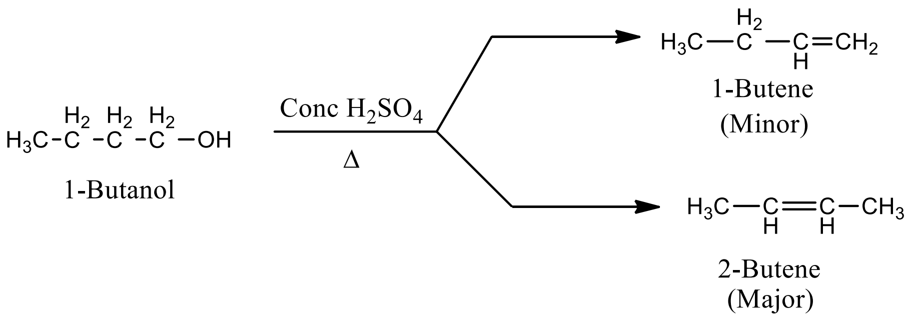
Ex: CH_2=CH_2 (Ethylene), CH_3-CH=CH_2 (Propene)

Methods of preparation of alkenes:

1) **By dehydration of alcohols:** Heating of alcohols in the presence of an acid catalyst (like Conc H_2SO_4, H_3PO_4, and P_2O_5 etc.) at 170^{0}C - 200^{0}C alkenes are formed.
Ex:







2) **By dehydrohalogenation of alkyl halides:** on heating an alkyl halides with alcoholic KOH alkenes are formed by the elimination of HX.
Ex: