

# **SEM III**

# **CHE3C03 ORGANIC CHEMISTRY**

## **Module 1**

## **Organic Chemistry- Some Basic Concepts**

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# **BOND FISSION**

**1. HOMOLYSIS**

**2. HETEROLYSIS**



**Reaction Arrow**



**Retrosynthetic Arrow**



**Resonance Arrow**



**Equilibrium Arrow**



**Curly Arrow (2 Electrons)**



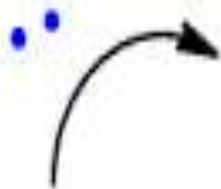
**Curly Arrow (1 Electron i.e. radical)**



**Dipole Arrow (points towards negative end)**

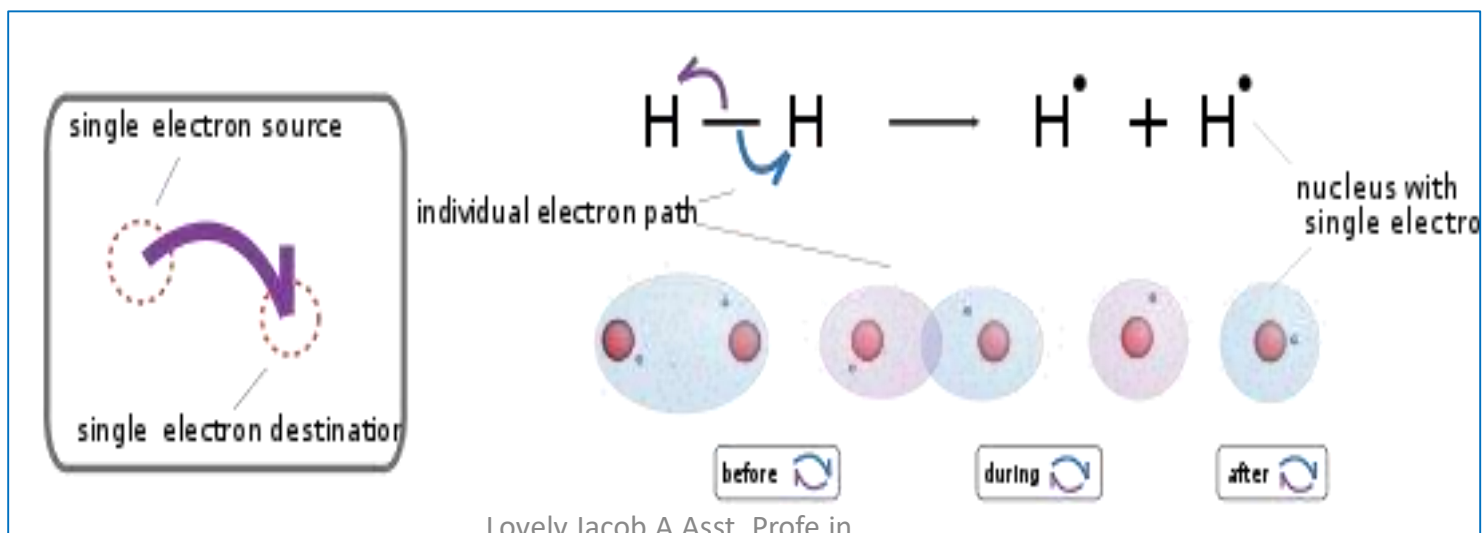
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two electrons flowing



A curved arrow

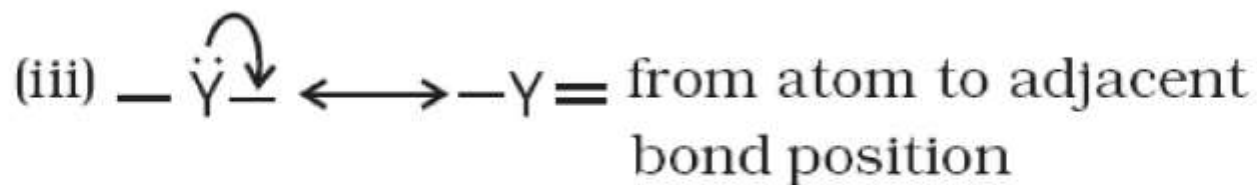
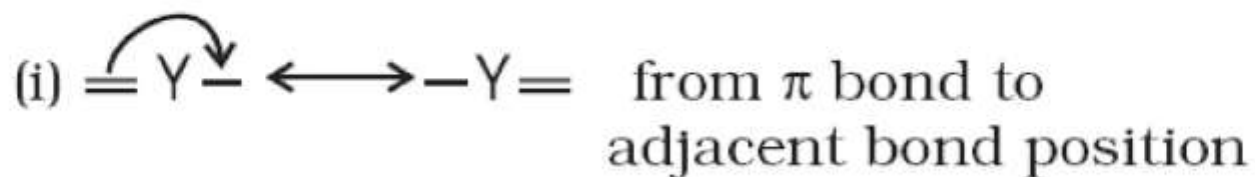
The tail indicates where the electrons come from while the head indicates where they are going to



# Electron Movement in Organic Reactions

The movement of electrons in organic reactions can be shown by curved-arrow notation.

Presentation of shifting of electron pair is given below :



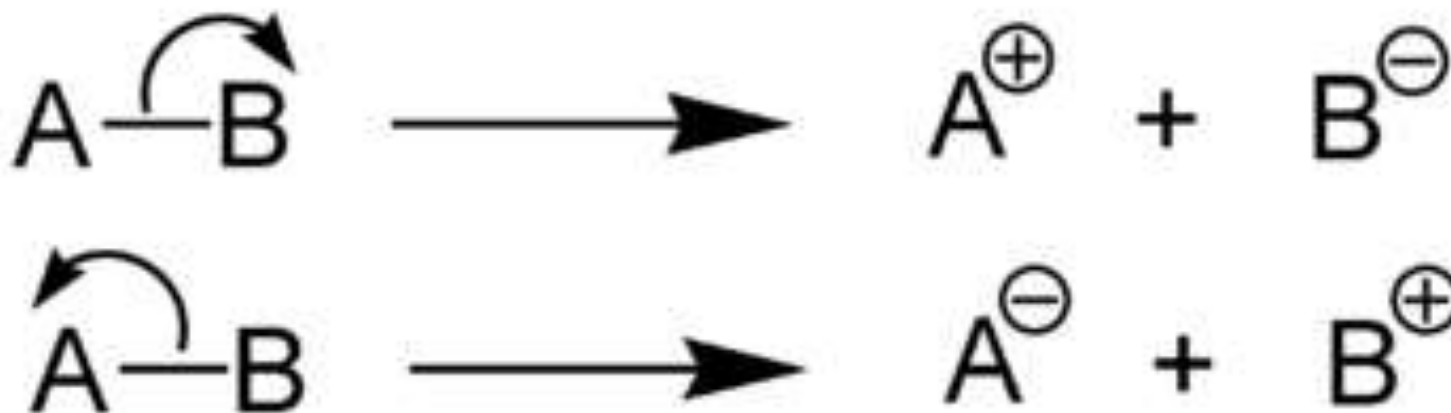
# HOMOLYSIS

**Homolytic fission** is a type of bond fission that involves the dissociation of a given molecule wherein one electron is retained by each of the original fragments of the molecule. Therefore, when a neutrally charged molecule is subjected to homolytic fission, two free radicals are obtained as the product



# HETEROLYSIS

**Heterolytic fission** is a type of bond fission in which a covalent bond between two chemical species is broken in an unequal manner, resulting in the bond pair of electrons being retained by one of the chemical species



# Bond Cleavages



Homolytic

Heterolytic



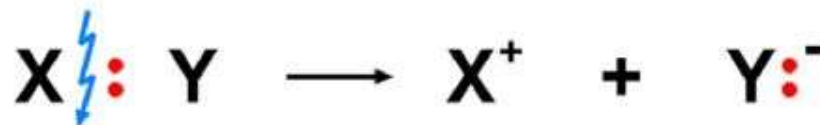
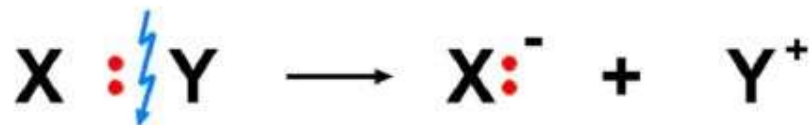


# Homolytic and heterolytic fission

There are **3 ways to split** the shared electron pair in an **unsymmetrical** covalent bond.

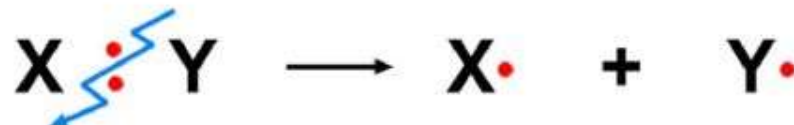
## UNEQUAL SPLITTING

produces **IONS**  
known as **HETEROLYSIS** or  
**HETEROLYTIC FISSION**

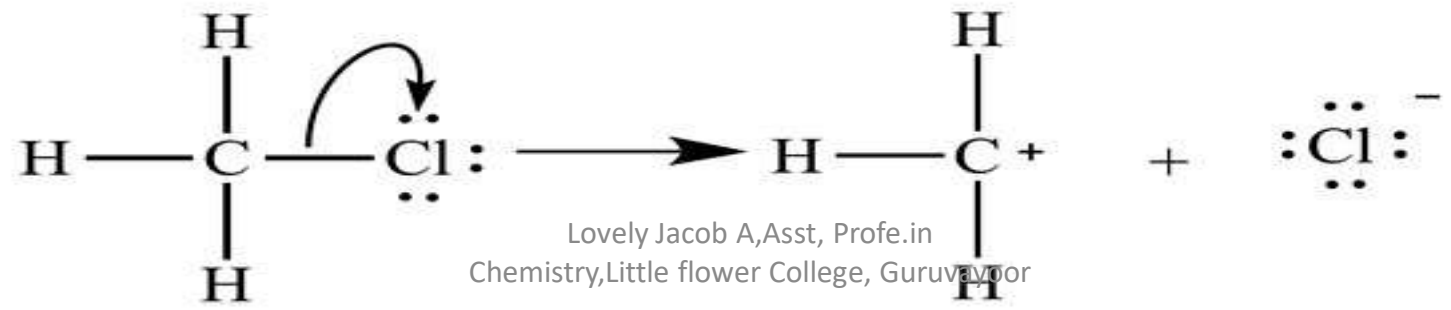
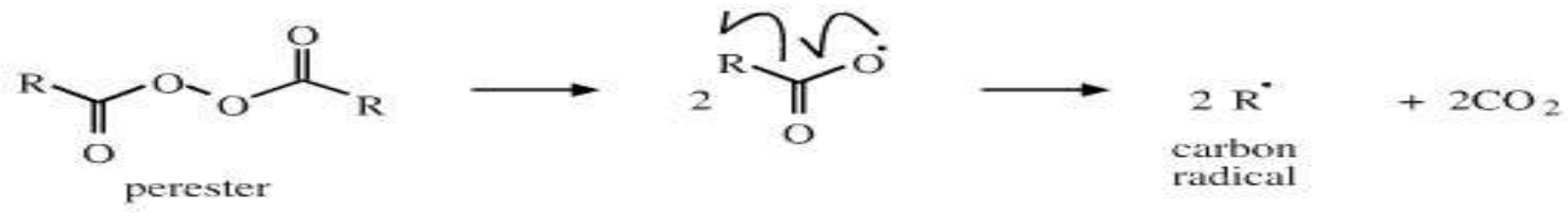


## EQUAL SPLITTING

produces **RADICALS**  
known as **HOMOLYSIS** or  
**HOMOLYTIC FISSION**



- If several bonds are present the **weakest bond is usually broken first**
- Energy to break bonds can come from a variety of energy sources - heat / light
- In the reaction between methane and chlorine either can be used, however...
- In the laboratory a source of UV light (or sunlight) is favoured.



**Large amount of energy is required to spark the homolytic fission** of a molecule.

- When the molecule is subjected to ultraviolet radiation
- When the molecule is subjected to the required amount of heat in order to overcome the required bond dissociation energy for the homolytic fission
- When carbon compounds are subjected to extremely high temperatures in the absence of oxygen in order to facilitate the pyrolysis of the molecule

**Heterolytic fission usually requires a lower bond dissociation energy than homolytic fission.**

# Homolytic and Heterolytic

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- ▶ **Breaking of Covalent Bonds!**
- ▶ **Homolytic**
  - ▶ Bond broken and 1 electron goes to each fragment
  - ▶ Forms radicals
    - ▶ Contain one unpaired electron
    - ▶ Reactive and unstable
  - ▶ Single headed arrow
- ▶ **Heterolytic**
  - ▶ Both electrons go to more electronegative fragment
  - ▶ Form ions
    - ▶ Cation- positive charge from losing an electron
    - ▶ Anion- negative charge from gaining a lone pair of electrons
  - ▶ Double headed arrow

Homolytic fission usually occurs only in homonuclear diatomic molecules but heterolytic fission can take place in any singly bonded covalent molecule.

# Electrophile and Nucleophile

A **nucleophile** is a chemical species which, in relation to a response, gives an electron pair to form a chemical bond. A nucleophile is usually charged negatively or neutral with a lone couple of donable electrons.  $\text{H}_2\text{O}$ ,  $-\text{OMe}$  or  $-\text{OtBu}$  are some of the examples. Overall, the ***electron-rich is a nucleophile.***

Any molecule, ion or atom that is in some manner deficient in electron can act as an **electrophile**.

Electrophiles are generally charged positively or are neutral species with empty orbitals attracted to a centre wealthy in electrons.

## What is Electrophile?

Positively loaded or neutral species are called electrophiles that are deficient in electrons and can accept a couple of electrons. These are also called species that love electron (philic).

- The term electrophile can be split into “electro” derived from electron and “phile” which means loving.
- They are electron deficient and hence electrons loving.
- They are positively charged or neutrally charged.
- They attract electrons. Movement of electrons depends on the density.
- They move from high-density area to low density area.
- They undergo electrophilic addition and [electrophilic substitution](#) reactions.
- An electrophile is also called as Lewis acid. (Acid is a proton donor or electron acceptor)

- **What is Nucleophile?**
- A nucleophile is a reagent comprising an unparallelled or lone electron pair atom. As a nucleophile is wealthy in electron, it looks for deficient electron locations, i.e. nucleus means loving nucleus. Nucleophiles act as Lewis bases, according to Lewis ' notion of acids and bases.
- The term nucleophile can be split into “nucleo” derived from the nucleus and “phile” which means loving.
- They are electron rich and hence nucleus loving. They are negatively charged or neutrally charged.
- They donate electrons.
- Movement of electrons depends on the density.
- They move from low-density area to high-density area.
- They undergo nucleophilic addition and nucleophilic substitution reactions.
- A nucleophile is also called as Lewis base. **(Base is is a proton acceptor or electron donor)**

# ELECTROPHILE VERSUS NUCLEOPHILE

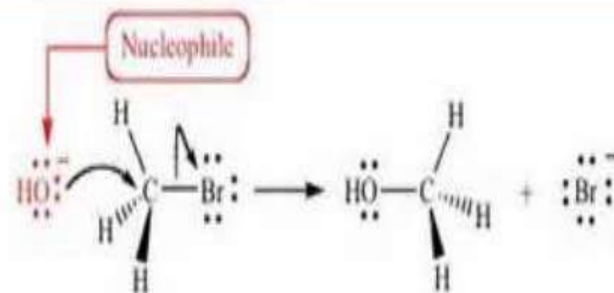
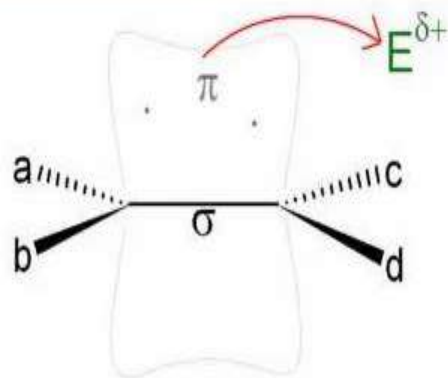
Nucleophile	Electrophile
Accepts protons and donates electrons	Donates protons and accepts electrons
Electron-rich atom, molecule, ion	Electron-deficient ion, atom or molecule
Negatively or neutrally charged	Positively or neutrally charged
Undergoes nucleophilic substitution and addition	Undergoes electrophilic addition and substitution
Interchangeably called Lewis Base	Interchangeably called Lewis Acid

## Nucleophiles and electrophiles- often needed in organic reactions

- Nucleophile- nucleus lover
- Has free electronpair and whole or part negative charge
- The larger the negative charge - the better the nucleophile
- Eg:  $C=C$ ,  $H_2O$ ,  $OH^-$ ,  $CN^-$ ,  $NH_3$
- Electrophile-electron lover
- Has whole or part positive charge
- The larger the positive charge - the better the Electrophile
- Eg:  $C=O$ ,  $H^+$ ,  $C-Cl$



	<b>Electrophile</b>	<b>Nucleophile</b>
<b>Definition</b>	Positively charged or neutral but electron deficient atom or group of atoms is called electrophile.	Negatively charged or neutral but electron rich atom or group of atoms is called nucleophile.
<b>Example</b>	<b>Neutral but electron deficient species:</b> BF <sub>3</sub> , AlCl <sub>3</sub> , SO <sub>3</sub> , FeCl <sub>3</sub> etc.	<b>Neutral but electron rich species:</b> H <sub>2</sub> O, R-O-H, R-O-R, :NH <sub>3</sub> , :NH <sub>2</sub> R, :NHR <sub>2</sub> , :NR <sub>3</sub> , R-S-H etc.
	<b>Positively charged species:</b> H <sup>+</sup> (proton), H <sub>3</sub> O <sup>+</sup> (hydronium ion), <sup>+</sup> CH <sub>3</sub> (carbonium ion), <sup>+</sup> NO <sub>2</sub> (nitronium ion), Cl <sup>+</sup> (chloronium ion), Br <sup>+</sup> (bromonium ion), I <sup>+</sup> (iodonium ion), NH <sub>4</sub> <sup>+</sup> (ammonium ion) etc.	<b>Negatively charged species:</b> Cl <sup>-</sup> (chloride ion), Br <sup>-</sup> (bromide ion), I <sup>-</sup> (iodide ion), HO <sup>-</sup> (hydroxide ion), CN <sup>-</sup> (cyanide ion), NO <sub>2</sub> <sup>-</sup> (nitrite ion) etc.



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PGT Chemistry

KVS, ZIET , Bhubaneswar

# What are reagents in chemistry?

- A reagent is a compound or mixture added to a system to cause a chemical reaction or test if a reaction occurs. A reagent may be used to tell whether or not a specific chemical substance is present by causing a reaction to occur with it.
- It may be atomic, molecular, cationic, anionic or free radical species.

## Types of Organic Reagents

Organic reagents are categorized into **three** sections **according to their charge** as **electrophile**, **nucleophile** and **free radicals**.

- **Electrophiles** have less electrons density
- **Nucleophiles** have high electrons density
- **Free radicals** don't have special charge. But **free radicals** are very reactive and react very fast.

# 1. Electrophilic Reagents

- They are also called as electrophile.
- Electrophile has electron deficient atom or vacant orbital or incomplete octate at the valence shell.
- These species carry either positive charge or electron deficient molecules. So a reagent which can accept an electron pair in a reaction is called an electrophile. Generally these contain two electrons less than the octet. These attack regions of high electron density in the substrate molecule to complete the octet. These are represented by E+.
- Electrophiles are lewis acid (A **Lewis acid** is therefore any substance, such as the H<sup>+</sup> ion, that can accept a pair of nonbonding electrons. In other words, a **Lewis acid** is an electron-pair acceptor.)
- An electrophile is a species that accepts a pair of electrons to form a new covalent bond
- There are 2 types of electrophiles.
- **(a) Neutral electrophile:** These species carry neither positive charge nor negative charge
- **Example:** AlCl<sub>3</sub>, BF<sub>3</sub>, Carbene, Nitrene, free radicals SO<sub>3</sub>, , Acid chlorides etc.
- **(b) Positive electrophile:** they are also called **Positively charged Electrophile**
- **Examples:** H<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, Cl<sup>+</sup>, Br<sup>+</sup>, NO<sub>2</sub><sup>+</sup>, NO<sup>+</sup>, Carbonium ion, nitrosonium ion, diazonium ion
- **Note:** cation of IA group and IIA group like Na<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup> and also NH<sub>4</sub><sup>+</sup> are not Positive electrophile

## 2. Nucleophilic reagents

- They are also called as **nucleophile**
- A **nucleophile** is a chemical species that donates an electron pair to an electrophile to form a chemical bond in relation to a reaction.
- All molecules or ions with a free pair of electrons or at least one *pi* bond can act as **nucleophiles**. Because **nucleophiles** donate electrons, they are by definition **Lewis bases**.
- They have electron rich atoms and lone pairs of electron so they are negatively charged species
- Nucleophiles are from “nucleus loving”, or “positive-charge loving
- A nucleophile is a reactant that provides a pair of electrons to form a new covalent bond.
- There are 2 types nucleophiles.
- **(a) Neutral nucleophile:**
- $\text{NH}_3$ ,  $\text{RNH}_2$ ,  $\text{H-O-H}$ ,  $\text{R-OH}$ ,  $\text{R-O-R}$ ,  $\text{R-S-R}$ .
- **Important Note:**
- $\text{LiAlH}_4$ : it can donate H ion with a lone pair of electron
- $\text{LiBH}_4$ : it can donate H ion with a lone pair of electron
- $\text{RMgX}$ : Grignard Reagent: here R acts as a nucleophile but  $\text{Mg}^{++}$  is not an electrophile
- **(b) Negative nucleophile:**
- **Examples:**  $\text{Cl}^-$  (chloride ion),  $\text{Br}^-$  (Bromide ion),  $\text{I}^-$  (Iodide ion),  $\text{OH}^-$ ,  $\text{CN}^-$  Carbanions like  $\text{CH}_3^-$ ,  $\text{CH}_3\text{CH}_2^-$  etc.

# Amphiphile & 3.Free radical

- **1. Amphiphile:** they behave as electrophile as well as nucleophile.

**Examples:** H<sub>2</sub>O, HCHO, R-CN

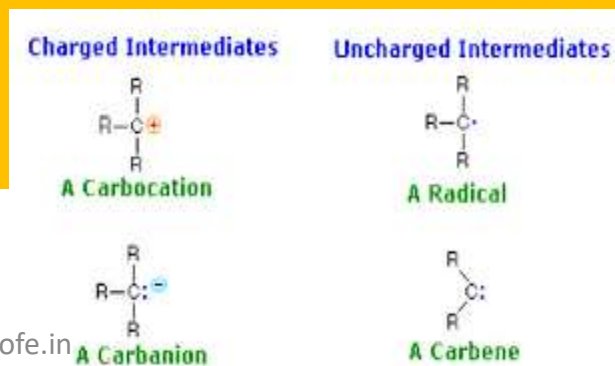
## 3. Free radical

A **radical** is an atom, molecule, or ion that has an unpaired valence electron. With some exceptions, these unpaired electrons make radicals highly chemically reactive.

A notable example of a radical is the hydroxyl radical (HO•), a molecule that has one unpaired electron on the oxygen atom. Two other examples are triplet oxygen and triplet carbene (:CH<sub>2</sub>) which have two unpaired electrons.

# Reaction intermediates

- A **reaction intermediate** or an **intermediate** is a molecular entity that is formed from the reactants (or preceding **intermediates**) and reacts further to give the directly observed products of a chemical **reaction**. Most chemical **reactions** are stepwise, that is they take more than one elementary step to complete.
- An **intermediate** is a short-lived, high-energy, highly reactive molecule. When generated in a chemical reaction, it will quickly convert into a more stable molecule.
- When their existence is indicated, reactive intermediates can help to explain how a chemical reaction takes place.

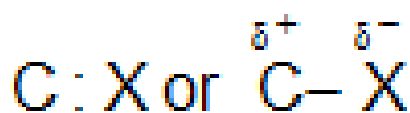


# Electron displacement Effects

- An **electron displacement** occurs when **electrons** move toward one side or part of a molecule. **Electronic displacements** are often responsible for the **chemical** reactivity of some molecules and the relative inertness of others. There are four different types of **electron displacements** operates in **covalent bonds**.
- **Inductive effect**
- **Mesomeric and Resonance effect**
- **Electromeric effects**
- **Hyperconjugation**

# Inductive Effect

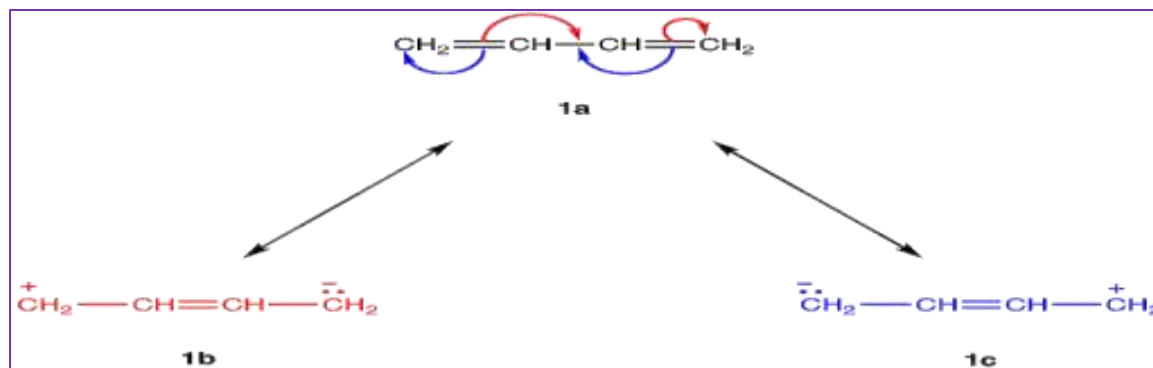
- In a covalent bond between the two dissimilar atoms, the electron pair forming the bond is never shared absolutely equally between the two atoms but is attracted a little more towards the more electronegative atom of the two.
- eg. The electron pair forming the C–X bond is somewhat more attracted towards the atom X with the result – it attains a partial negative charge (–) while the carbon atoms attain a partial positive charge (+)





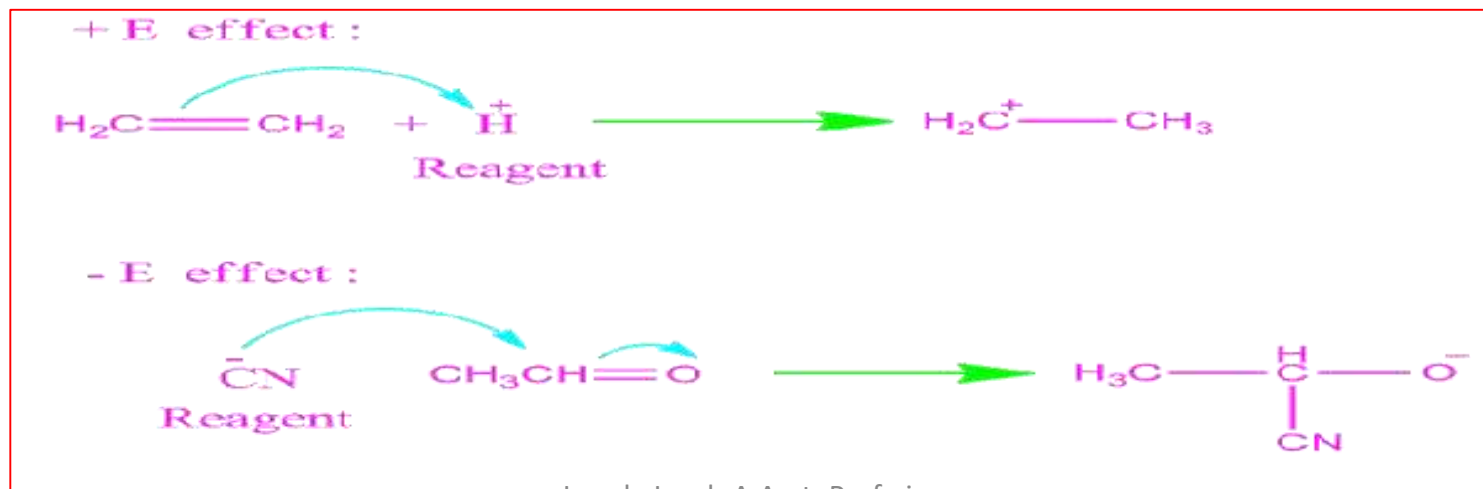
# Resonance & Mesomeric Effect

There are many organic molecules which can not be represented by a single lewis structure. In turn, they are assigned more than one structure called canonical forms or contributing of resonating structures. The phenomenon exhibited by such compounds is called resonance. For example, 1, 3 – butadiene has following resonance structure.



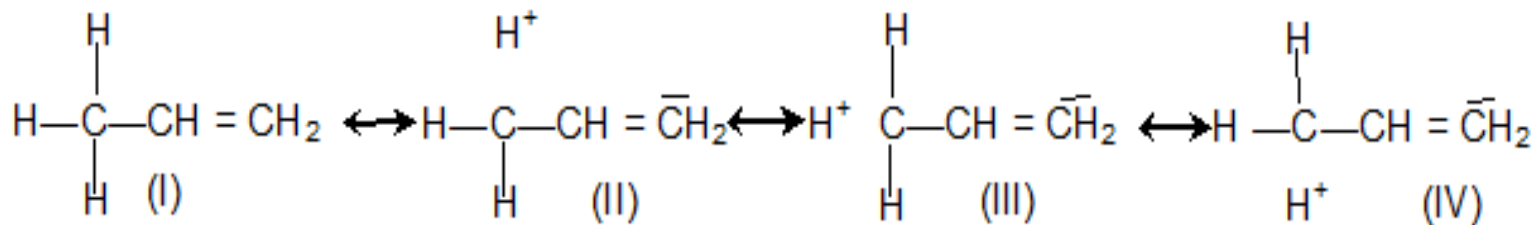
# Electromeric Effect

- It is a temporary effect in which a shared pair of electron (p - electron pair) is completely transferred from a double bond or triple bond to one of the atoms joined by the bond at the requirement of attacking reagent.
- When multiple bond is present between two similar atom (symmetric alkenes or alkynes) electronic shift can take place in any direction



# Hyperconjugation

- It is the delocalisation of sigma electron. Also known as sigma-pi conjugation or no bond resonance
- **Occurrence:** Alkene, alkynes, Free radicals (saturated type) , carbonium ions (saturated type)
- **Condition:** Presence of alpha –H with respect to double bond, triple bond carbon containing positive charge (in carbonium ion)



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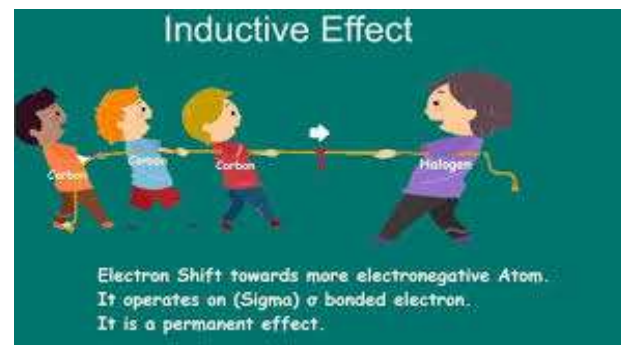
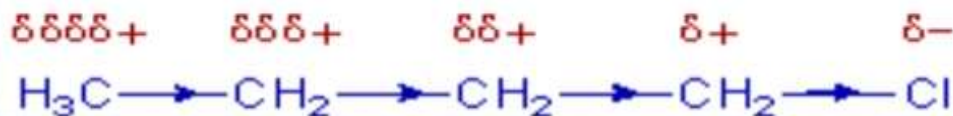
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# 1.INDUCTIVE EFFECT-a detailed study

When an electron-releasing or an electron-withdrawing species is introduced to a chain of atoms (generally a carbon chain), the corresponding negative or positive charge is relayed through the carbon chain through the C-C  $\sigma$  - bond by the atoms belonging to it. This causes a permanent dipole to arise in the molecule and is referred to as the inductive effect.

## **INDUCTIVE EFFECT**

*The polarization of a  $\sigma$  bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect.*



# Types of Inductive Effect

1. **Negative inductive effect or -I effect**
2. **Positive inductive effect +I effect**

## -I Effect (Negative Inductive Effect)

- When an electronegative atom, such as a halogen, is introduced to a chain of atoms (generally carbon atoms), the resulting unequal sharing of electrons generates a positive charge which is transmitted through the chain.
- This causes a permanent dipole to arise in the molecule wherein the electronegative atom holds a negative charge and the corresponding effect is called the electron withdrawing inductive effect, or the -I effect.

## +I Effect (Positive Inductive Effect)

- When a chemical species with the tendency to release or donate electrons, such as an alkyl group, is introduced to a carbon chain, the charge is relayed through the chain and this effect is called the Positive Inductive Effect or the +I Effect

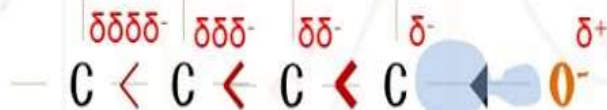
# Inductive Effect

Electronic Effect  
Reaction Mechanism



**-I Effect** (minus I effect)

Pulling Electrons



**+I Effect** (plus I effect)

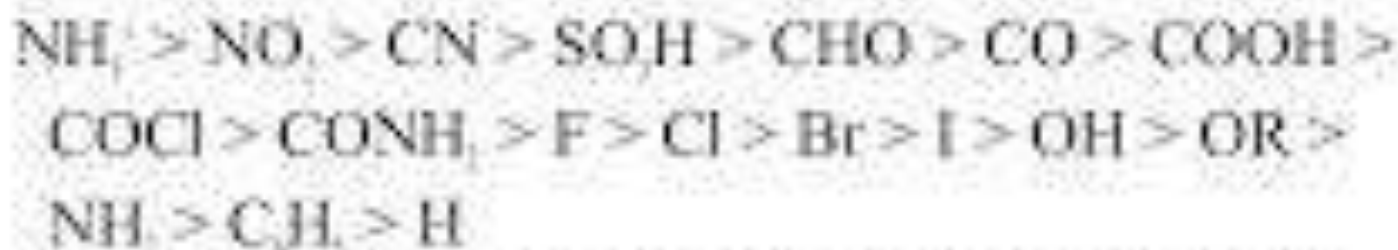
Pushing Electrons

- Polarization transmission along **Sigma Bond**
- Polarization gets weaker as it reaches atoms farther away
- Inductive force is weaker compared to Mesomeric as it is transferred through Sigma bond in a linear manner

H					
2.1					
Li	Be				
1.0	1.5				
Na	Mg	B	C	N	O
0.9	1.2	2.0	2.5	3.0	3.5
		Al	Si	P	S
		1.5	1.8	2.1	2.5
					Cl
					3.0

## Types of inductive effect

**1) Negative inductive effect (-I):** The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:

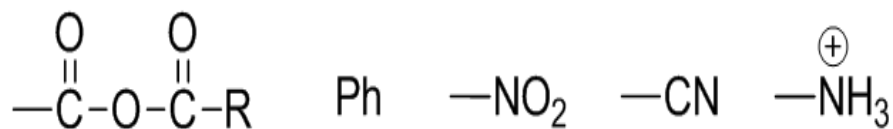
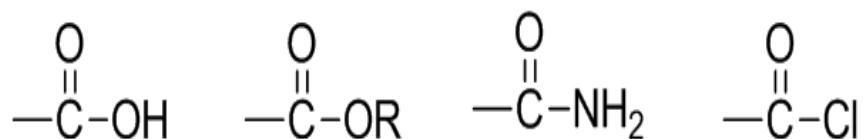
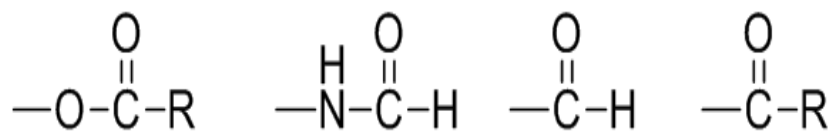
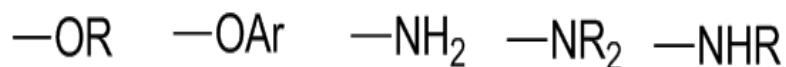
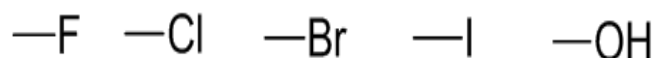


**2) Positive inductive effect (+I):** It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.

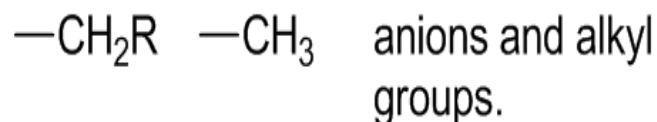
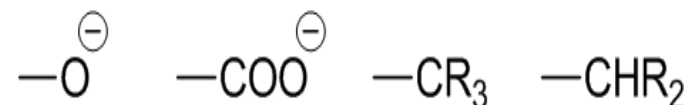


## +I and -I Inductive effecting groups

### -ve Inductive effect group (-IE)



### +ve Inductive effect group (+IE)



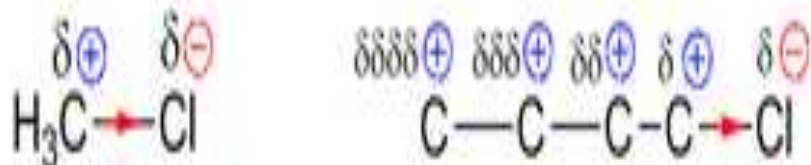


- **Why alkyl groups are showing positive inductive effect?**
- Though the C-H bond is practically considered as non-polar, there is partial positive charge on hydrogen atom and partial negative charge on carbon atom. Therefore each hydrogen atom acts as electron donating group. This cumulative donation turns the alkyl moiety into an electron donating group.



### 3. 1. Inductive effect (IE) or polarization effect

Partial polarization of e's forming ' $\sigma$ ' bond towards more electronegative atom.



Characteristics of inductive effect:

- It is a permanent effect.
- It is operated only in sigma ( $\sigma$ ) bonds.
- Only  $\sigma$  electrons are involved.
- In inductive effect electrons are partially displaced.
- IE is transmitted along the chain.
- As length of the chain increases the IE decreases.

# Applications of Inductive effect

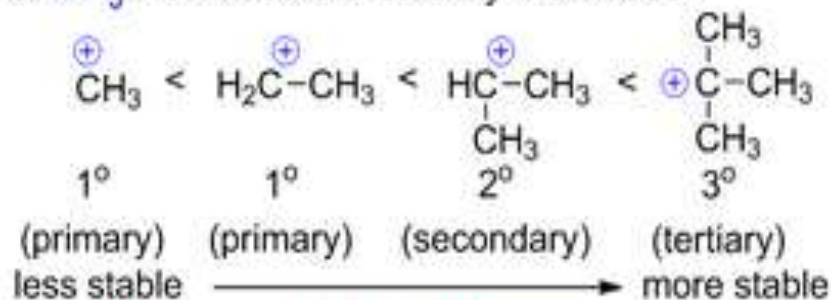
## Applications of Inductive Effect

- (i) Stability of alkyl carbocations
- (ii) Acidity of carboxylic acids
- (iii) Basicity of amines

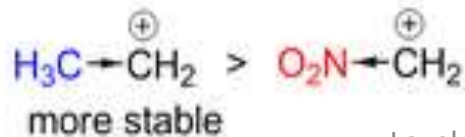
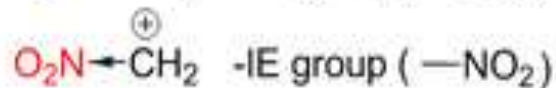
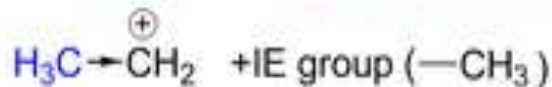
### (i) Stability of alkyl carbocations

(a) + Inductive effect (+IE) group (CH<sub>3</sub>) increases the stability of carbocations.

As the number of CH<sub>3</sub> increases the stability increases.

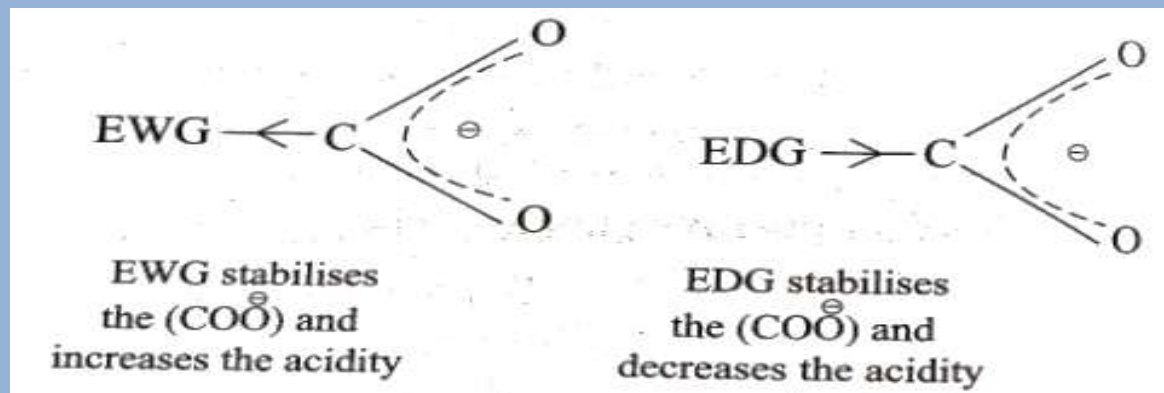


(b) - Inductive effect (-IE) group (NO<sub>2</sub>) decreases the stability of carbocations.



# Inductive Effect on Acidity and Basicity

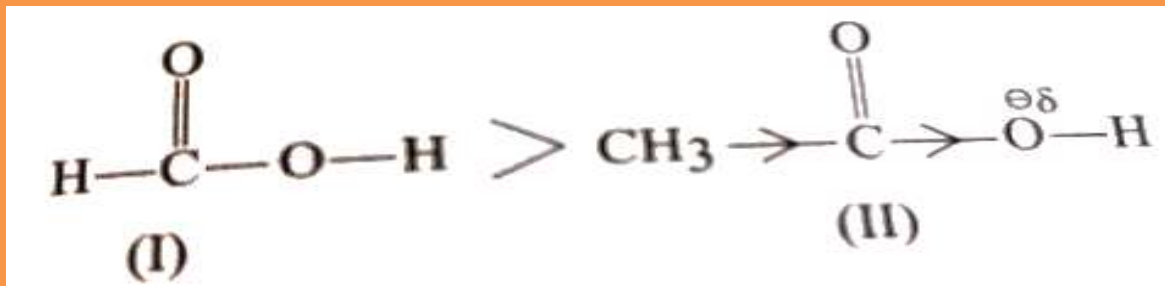
- Using the inductive effect, we can predict the **acidity and basicity** of compounds.
- **Electron withdrawing groups increase the acidity** of a compound.
- **Electron donating groups decrease the acidity** of a compound.
- **Dispersal of the charge –Stabilize the ion**
- **Intensification of the charge –Destabilize the ion**



Thus it can be said that,

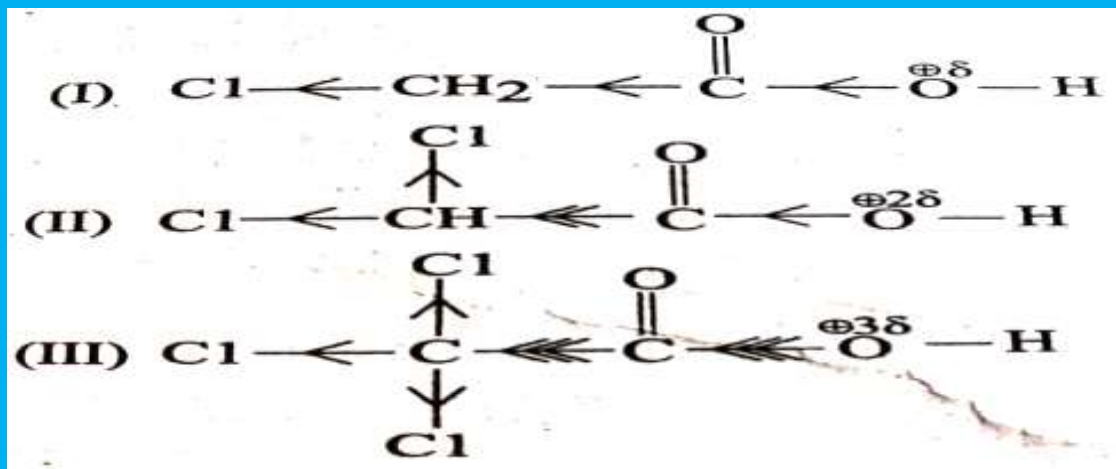
- +I groups decrease acidity (or increase basicity)**
- I groups increase acidity (or decrease basicity) of compounds.**

- **For Example**, formic acid (HCOOH) is more acidic than Acetic acid (CH<sub>3</sub>COOH). Why?



- Due to the **+I inductive effect of the methyl group** attached to the carboxylic acid group.
- **Note: If Ka of acid is high, it is a Strong acid, but if PKa of acid is high, it is said to be a weak acid**
- **[pka = -log(ka)] Same logic applies to bases.**

- Consider, the acidity of mono-, di- and trichloroacetic acid. Which is more Acidic? Why?



It can be said that the presence of three Cl atoms make oxygen highly electron deficient and thereby, polarising the O-H bond the most. Therefore the acidity order for the above compounds would be, III > II > I.

# Inductive Effects

## pKa Values

$\text{H}-\text{COOH}$	3.75	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{COOH}$	4.8	↑ distance
$\text{CH}_3-\text{COOH}$	4.75	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2-\text{COOH} \\   \\ \text{Cl} \end{array}$	4.5	
$\text{CH}_3\text{CH}_2-\text{COOH}$	4.87	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{COOH} \\   \\ \text{Cl} \end{array}$	4.0	
$\text{CH}_3\text{CH}_2\text{CH}_2-\text{COOH}$	4.81	$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{CH}-\text{COOH} \\   \\ \text{Cl} \end{array}$	2.9	
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{COOH} \\   \\ \text{CH}_3 \end{array}$	5.02			

Alkyl groups release electrons. This decreases acidity

When the chlorine atom is moved further away from the carboxyl group, acidity decreases

# Basicity-Aromatic Amines



Amine	Structure	pK <sub>a</sub> of Conjugate Acid
<b>Aromatic Amines</b>		
Aniline		4.63
4-Methylaniline		5.08
4-Chloroaniline		4.15
4-Nitroaniline		1.01
<b>Heterocyclic Aromatic Amines</b>		
Pyridine		5.25
		6.95

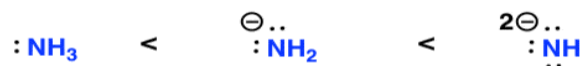
**Weaker bases**

**Intermediate**



## 1. The Effect of Charge

Basicity increases with increased negative charge

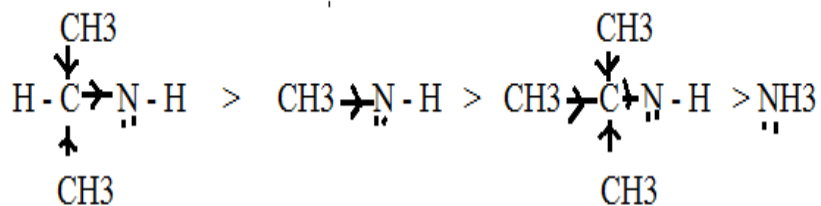


Least basic

Most basic

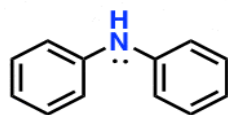
pK<sub>a</sub>H = 9.2

pK<sub>a</sub>H = 38



## 2. Resonance-Stabilized Amines Are Less Basic

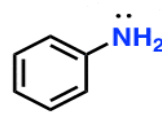
Amine lone pairs that are conjugated with pi bonds (i.e. that can participate in resonance) are stabilized relative to non-conjugated amines  
Resonance stabilization decreases basicity



Least basic

pK<sub>a</sub>H = 0.78

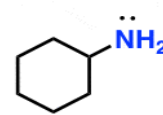
<



Aniline

pK<sub>a</sub>H = 4.6

<



Cyclohexylamine

Most basic

pK<sub>a</sub>H 11.2



# Which is more acidic? Why?

Try to find out

- Formic acid, acetic acid, propionic acid
- Fluoroacetic acid, Chloroacetic acid, Bromoacetic acid, Iodoacetic acid
- 2-chloropropanoic acid, 3-chloropropanoic acid

# Resonance or Mesomeric Effect-a detailed study

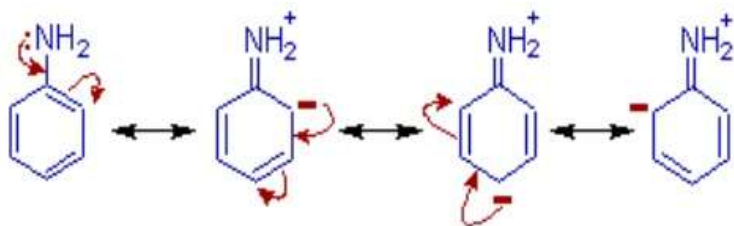
The **Mesomeric effect** is a property of substituents or functional groups in a chemical compound. It is defined as the polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electrons present on an adjacent atom.

## Mesomeric Effect ( M-Effect)

- It refers to the polarity produced in a molecule as a result of interaction between two pi bonds or a pi bond and lone pair of electrons.
- The electron withdrawing or releasing effect attributed to a substituent through delocalization of  $\pi$  electrons, which can be visualized by drawing various canonical forms, is known as **mesomeric effect or resonance effect**. It is symbolized by M or R.

## Positive resonance or mesomeric effect (+M or +R):

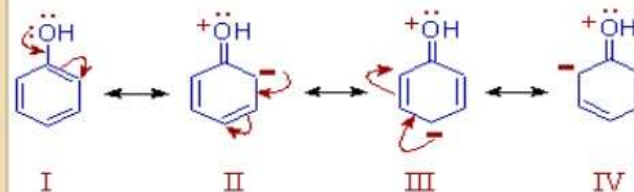
- The  $\text{-NH}_2$  group in aniline also exhibits +R effect. It releases electrons towards benzene ring through delocalization.



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## Positive mesomeric effect (+M or +R):

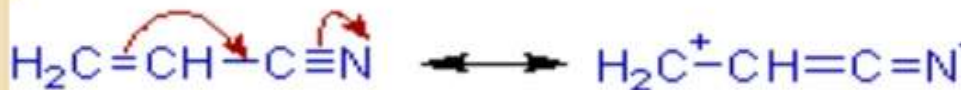
- 1). In phenol, the  $\text{-OH}$  group shows +M effect due to delocalization of lone pair on oxygen atom towards the ring. Thus the electron density on benzene ring is increased particularly on ortho and para positions.



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## Negative mesomeric effect (-M or -R):

- 2) The negative mesomeric effect (-R or -M) shown by cyanide group in acrylonitrile is illustrated below. The electron density on third carbon decreases due to delocalization of  $\pi$  electrons towards cyanide group.



Lovely Jacob A, Asst, Profe.in  
Chemistry, Little flower College, Guruvayoor

## Positive resonance or mesomeric effect (+M or +R):

- The groups show positive mesomeric effect when they release electrons to the rest of the molecule by delocalization. These groups are denoted by +M or +R. Due to this effect, the electron density on rest of the molecular entity is increased.
- E.g. -OH, -OR, -SH, -SR, -NH<sub>2</sub>, -NR<sub>2</sub> etc

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## TYPES

### • Negative mesomeric effect (-M or -R):

- It is shown by substituents or groups that withdraw electrons by delocalization mechanism from rest of the molecule and are denoted by -M or -R. The electron density on rest of the molecular entity is decreased due to this effect.
- E.g. -NO<sub>2</sub>, Carbonyl group (C=O), -C≡N, -COOH, -SO<sub>3</sub>H etc.

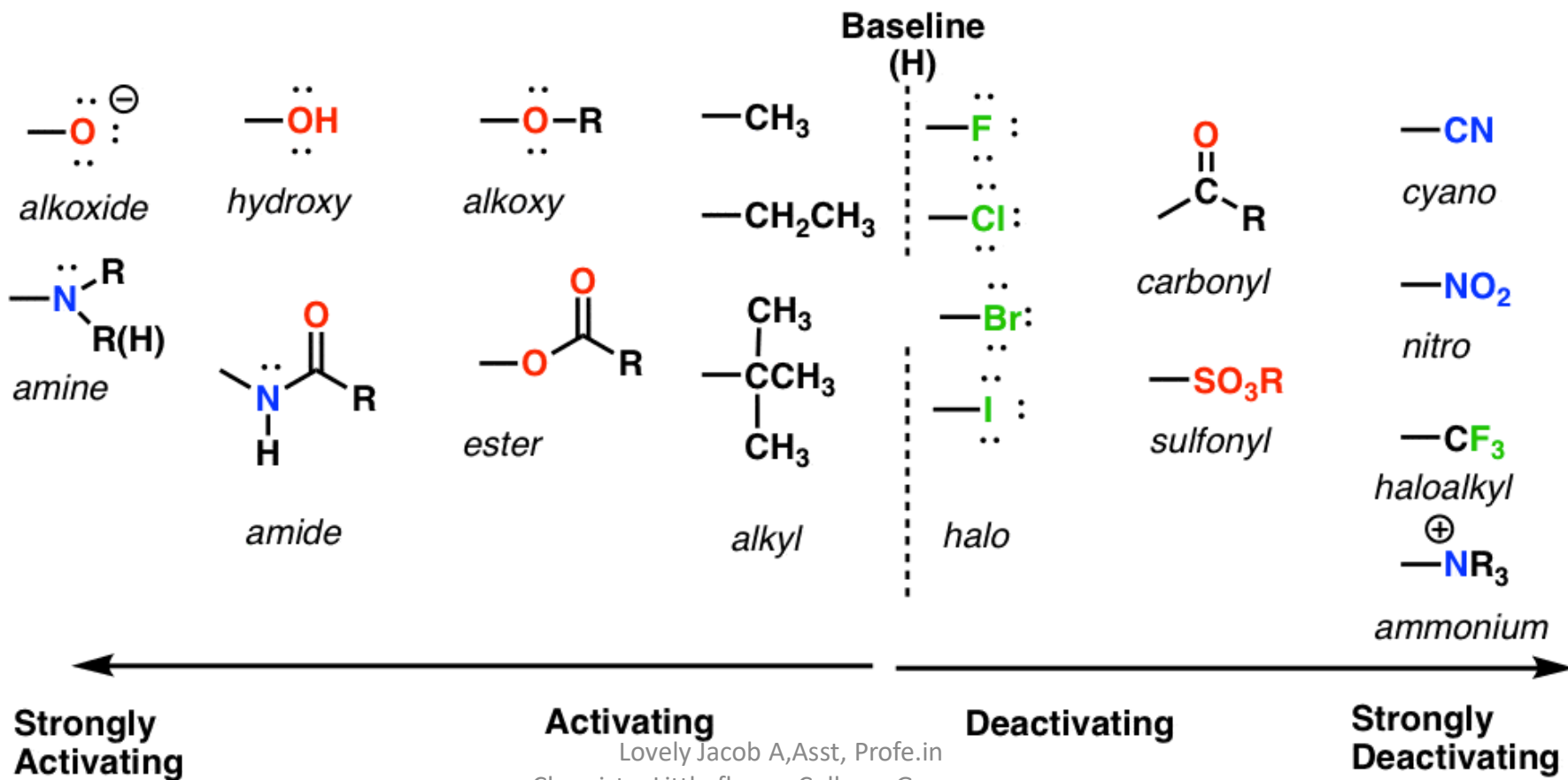
## Summary: The effect of substituents on the rate of electrophilic aromatic substitution

- **Activating groups** increase the rate of reaction, relative to H
- **Deactivating groups** decrease the rate of reaction, relative to H

Activating groups tend to **donate** electron density to the ring

Deactivating groups tend to **withdraw** electron density to the ring

Donation/withdrawal can occur through both inductive effects ("sigma" donation/accepting) and via donation/withdrawal of a lone pair ("pi" donation/accepting)



## Inductive effect vs Resonance effect

Inductive effect	Resonance effect
Based on electronegativity.	Based on Conjugation.
Electron moves via sigma bonds.	Electron moves via pi bonds or lone pairs.
It involves displacement of only $\sigma$ electrons and hence occurs only in saturated compounds.	It involves delocalization of $\pi$ (pi) or n lone pairs of electrons and hence occurs in unsaturated and conjugated systems.
During inductive effect the electron pair is only slightly displaced towards the more electronegative atom and hence only partial positive and negative charges appear.	During resonance effect, the electron pair is completely transferred and hence full positive and negative charges appear.
Inductive effect are transmitted over short distance over short distances in saturated carbon chains and the magnitude of the effect decreases rapidly as distance from the heteroatom increases. The effect almost become negligible beyond three carbon atoms from the heteroatom.	<p>The resonance effect are transmitted all along the length of the conjugated system without suffering much change in magnitude.</p> <div style="text-align: center;"> <p> <math>\text{CH}_3\text{-CH}=\text{CH}-\text{CH}=\text{O} \leftrightarrow</math>  <i>Crotonaldehyde</i>  <math>\text{CH}_3\text{-CH}=\overset{+}{\text{C}}\text{H}-\overset{-}{\text{O}}\text{H}</math>  <math>\leftrightarrow \text{CH}_3\text{-}\overset{+}{\text{C}}\text{H}=\overset{-}{\text{C}}\text{H}-\text{CH}=\text{O}</math> </p> <p style="font-size: small;">             4 3 2 1                      4 3 2 1              4 3 2 1                      4 3 2 1           </p> </div> <p><b>C3 in crotonaldehyde is almost as positive as C1.</b></p>

# Electromeric Effect – a detailed study

- The **instantaneous formation of a dipole in the molecule** of an organic compound due to the **complete transfer of shared pi electron pairs** to one of the atoms under the **influence of an attacking reagent** is referred to as the Electrometric effect.
- This effect can be observed in organic compounds that **contain at least one multiple bond**.
- When the atoms participating in this multiple bond come under the influence of an attacking reagent, one pi bonding pair of electrons is completely transferred to one of the two atoms.
- The electrometric effect is a **temporary effect** that remains as long as the attacking reagent is present and exposed to the organic compound. Once this attacking reagent is removed from the system, the molecule that was polarized goes back to its original state.

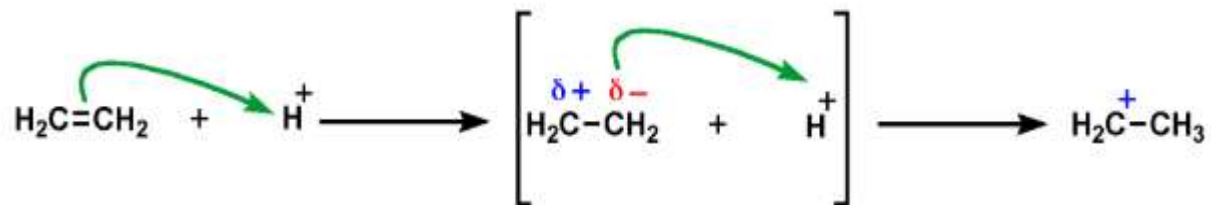
# Types of Electromeric Effects : +E effect and the -E effect.

This classification is done based on **the direction in which the electron pair is transferred**.

## +E Effect

This effect occurs when the **electron pair of the pi bond is moved towards the attacking reagent**. The +E effect can be observed in the addition of acid to alkenes. The attacking reagent attaches itself to the atom which obtained an electron pair in the transfer.

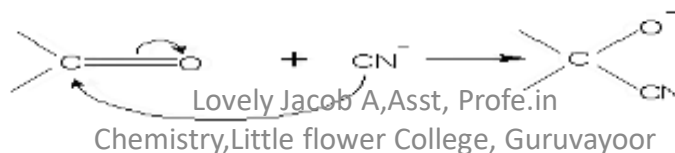
The +E effect is generally observed when the **attacking reagent is an electrophile** and the pi electrons are transferred towards the positively charged atom.



## -E Effect

This effect occurs when the **electron pair of the pi bond is moved away from the attacking reagent**. The attacking reagent attaches itself to the positively charged atom in the molecule, i.e. the atom which lost the electron pair in the transfer.

The -E effect is generally observed when the **attacking reagent is a nucleophile** and the pi electrons are transferred to the atom which the attacking reagent will not bond with.





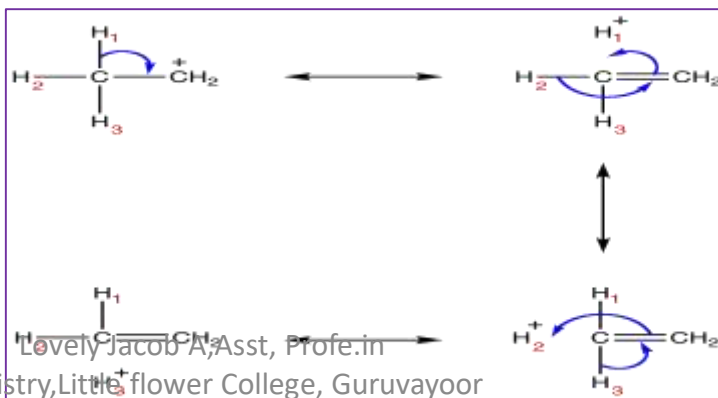
## ❑ Differences between inductive effect and electromeric effect

<u>Inductive effect</u>	<u>Electromeric effect</u>
1) It is a permanent effect	1) It is a temporary effect
2) The presence of multiple bond is not essential	2) The presence of a multiple bond is essential.
3) The polarity of bond is essential	3) The polarity of bond is not essential.
4) Partial charge separation takes place	4) Complete charge separation takes place
5) No ions are formed	5) Ions are formed.
6) Attacking reagent is not Required	6) Attacking reagent is required
7) The displaced electrons do not leave their molecular orbitals . however, distortion of electron position cloud take place	7) The displaced electrons leave their orbitals and attain a new position
8) It involves mere displacement of electrons	8) It involves complete transference of $\pi$ –electrons.

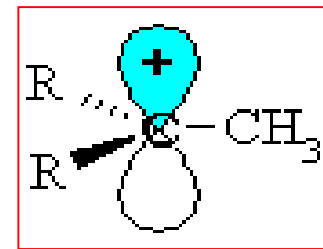
# Hyper Conjugation-a detailed study

- **Hyperconjugation** is the stabilising interaction that results from the interaction of the electrons in a  $\sigma$ -bond (usually **C-H** or **C-C**) with an adjacent empty or partially filled p-orbital or a  $\pi$ -orbital to give an extended molecular orbital that increases the stability of the system.
- Based on the valence bond model of bonding, hyperconjugation can be described as "double bond - no bond resonance" but it is not what we would "normally" call resonance.
- What is the key difference between hyperconjugation and resonance ?  
Hyperconjugation involves a sigma orbital component, usually a **C-C or C-H bond**. Resonance involves pi orbitals
- Hyperconjugation is a factor in explaining why increasing the number of alkyl substituents on a carbocation or radical centre leads to an increase in stability.

## Baker - Nathan Effect

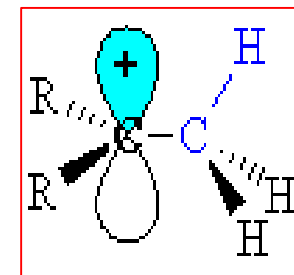


# Let's consider how a methyl group is involved in hyperconjugation with a carbocation centre.



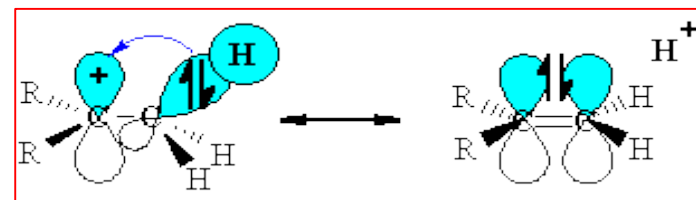
➤ First we need to draw it to show the C-H  $\sigma$ -bonds.

Note that, the **empty p orbital** associated with the **positive charge at the carbocation centre** is in the same plane (*i.e.* coplanar) with one of the C-H  $\sigma$ -bonds (shown in blue.)

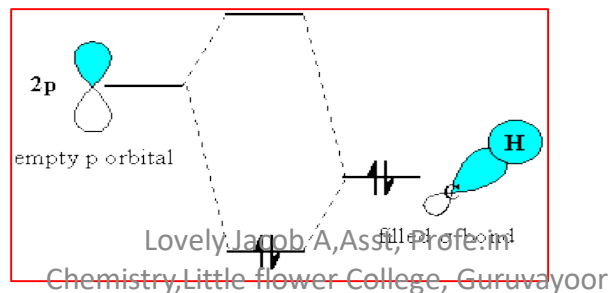


➤ This geometry means the electrons in the  $\sigma$ -bond can be stabilised by an interaction with the empty p-orbital of the carbocation centre.

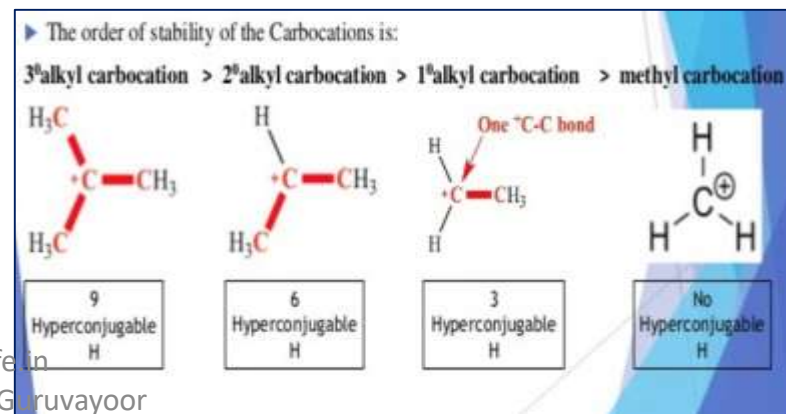
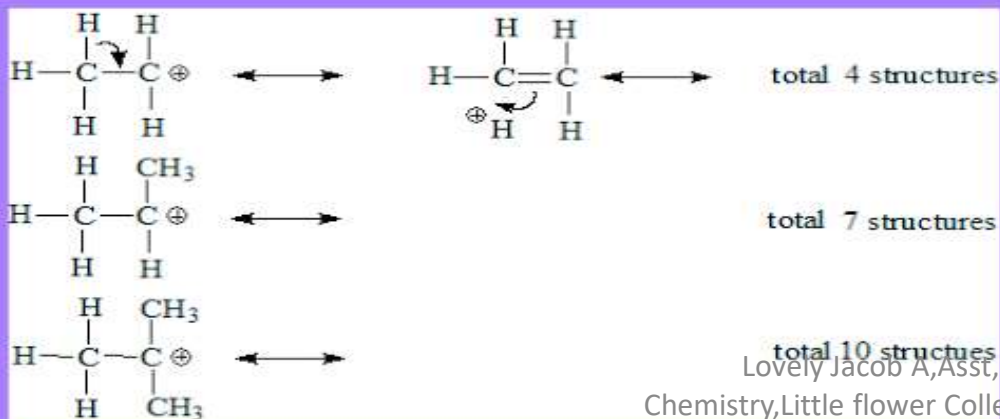
➤ (this diagram shows the **similarity with resonance** and the structure on the right has the "**double bond - no bond**" character)

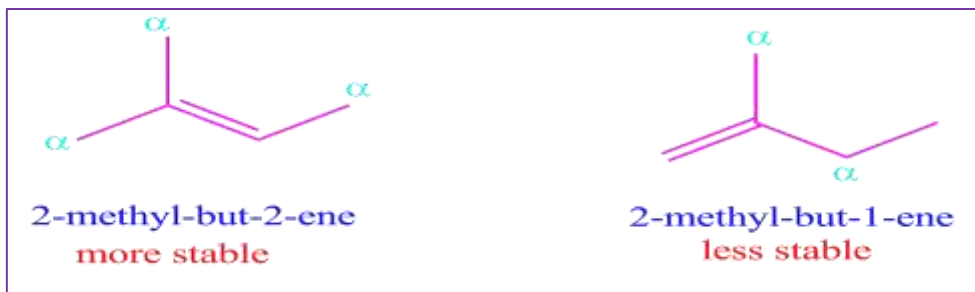
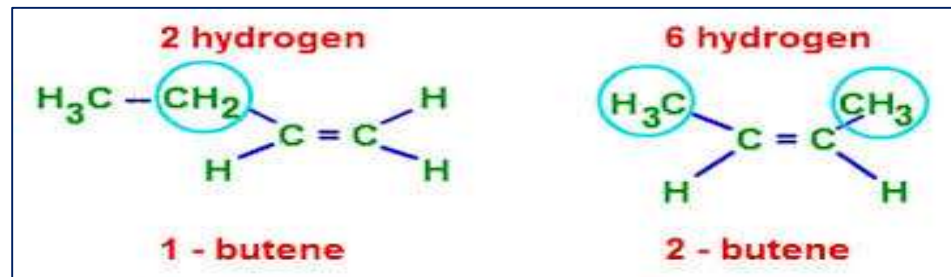
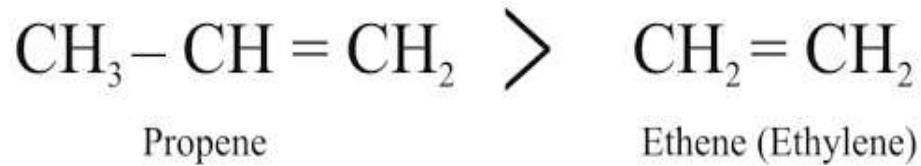


➤ The stabilisation arises because the orbital interaction leads to the electrons being in a **lower energy orbital**.



- The **C-C**  $\sigma$ -bond is free to rotate, and as it does so, each of the **C-H**  $\sigma$ -bonds in turn undergoes the stabilising interaction.
- The ethyl cation has 3 **C-H**  $\sigma$ -bonds that can be involved in hyperconjugation.
- The more hyperconjugation there is, the greater the stabilisation of the system.
- For example, the t-butyl cation has 9 **C-H**  $\sigma$ -bonds that can be involved in hyperconjugation.
- Hence  $(CH_3)_3C^+$  is more stable than  $CH_3CH_2^+$
- The effect is not limited to **C-H**  $\sigma$ -bonds, appropriate **C-C**  $\sigma$ -bonds can also be involved in hyperconjugation.





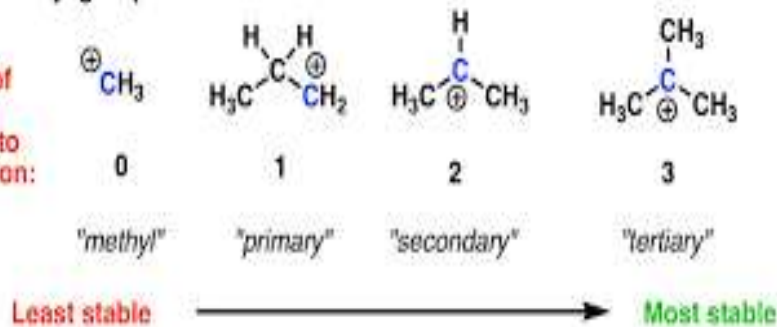
▶ Stability of alkenes will increase with increase in number of Hydrogen  $\alpha$  to unsaturated system.

▶ Increasing order of stability of alkenes because of Hyperconjugation:

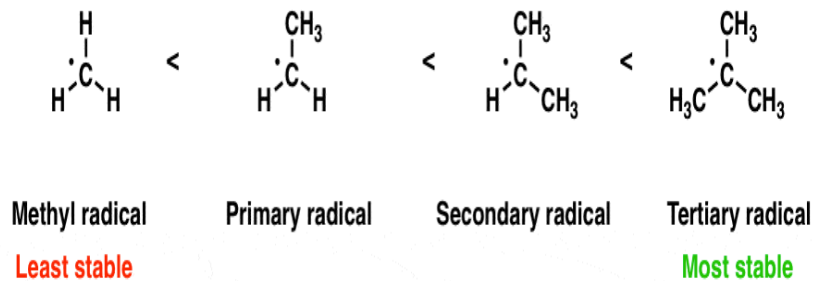
Alkene	Number of Hyperconjugable Hydrogen ( $\alpha$ to unsaturated function)
$\text{CH}_2=\text{CH}_2$	0
$(\text{CH}_3)\text{CH}=\text{CH}_2$	3
$(\text{CH}_3)_2\text{C}=\text{CH}_2 \approx (\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)$	6
$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_3)$	9
$(\text{CH}_3)_3\text{C}=\text{C}(\text{CH}_3)_2$	12

### 1. Adjacent alkyl groups stabilize carbocations

Number of carbons attached to carbocation:



### Radical stability increases in the order methyl < primary < secondary < tertiary

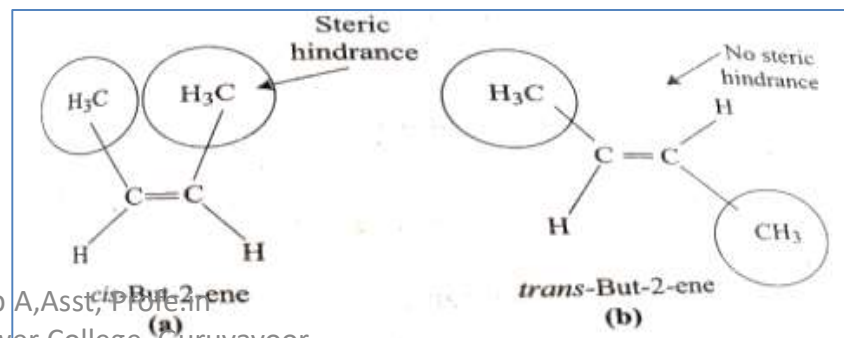
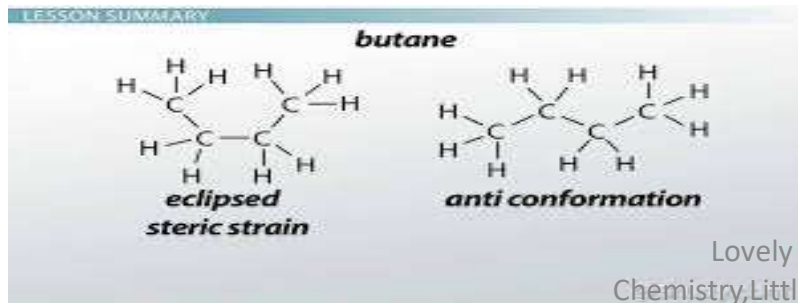


# Steric Effect

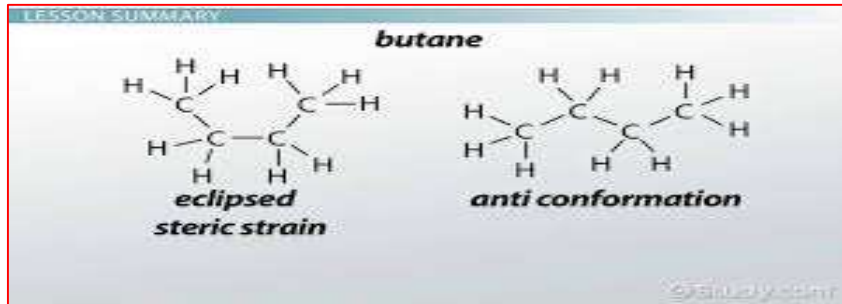
**Steric effects** are nonbonding interactions that influence the shape and reactivity of ions and molecules. Steric effects result from repulsive forces between overlapping electron clouds.

**Steric hindrance** is a **consequence of steric effects**. Steric hindrance is the slowing of chemical reactions due to steric bulk. Steric hindrance is often exploited to control selectivity, such as slowing unwanted side-reactions. It arises because of **inter-electronic repulsions** due to spatial crowding amongst bulky groups.

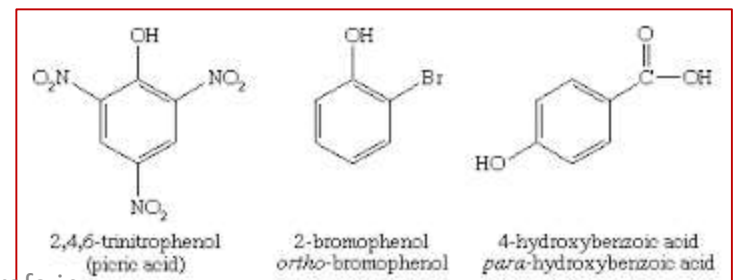
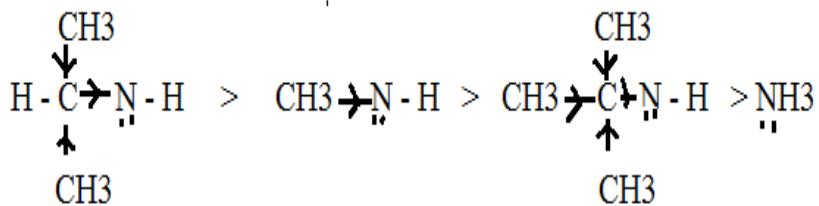
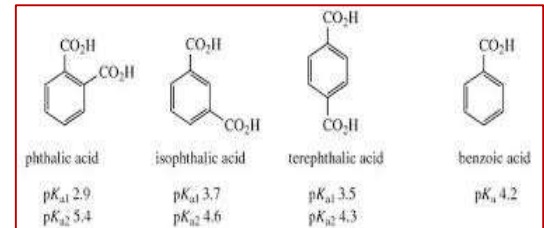
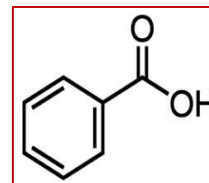
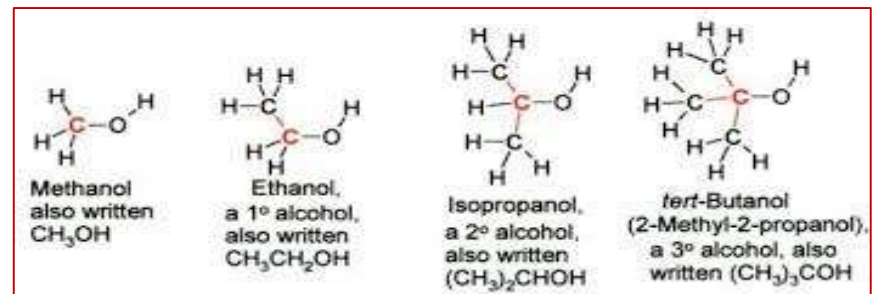
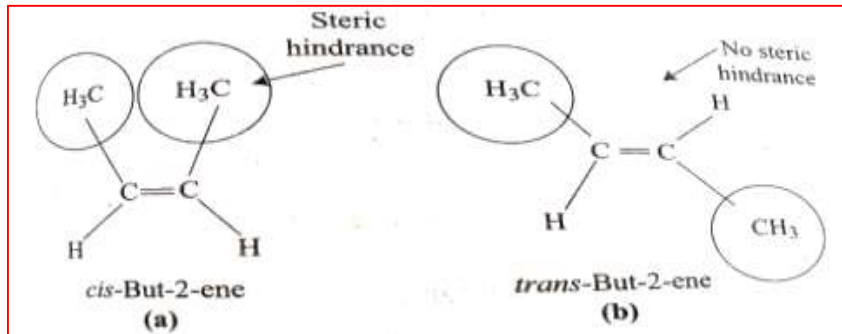
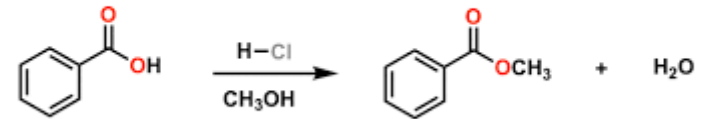
Using steric factors, we can conclude that trans-2-butene is more stable than cis-2-butene.

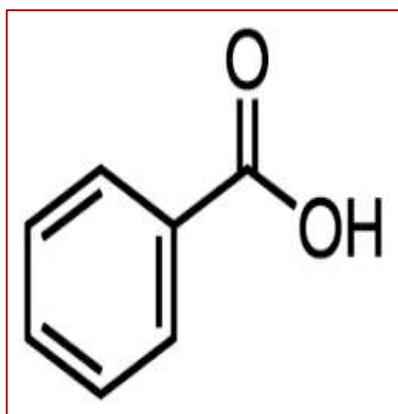
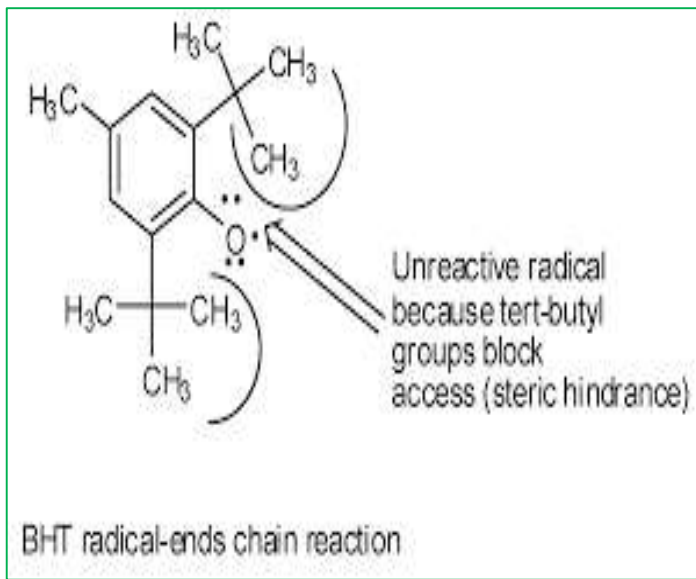


# Applications

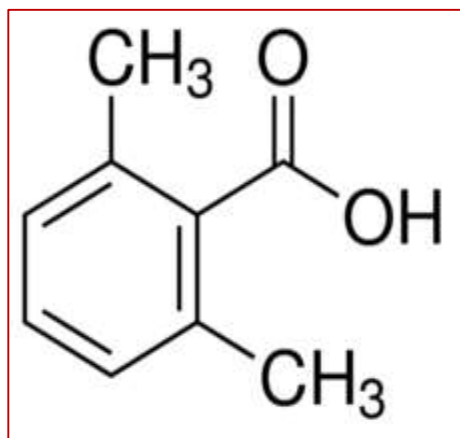


Fischer esterification example

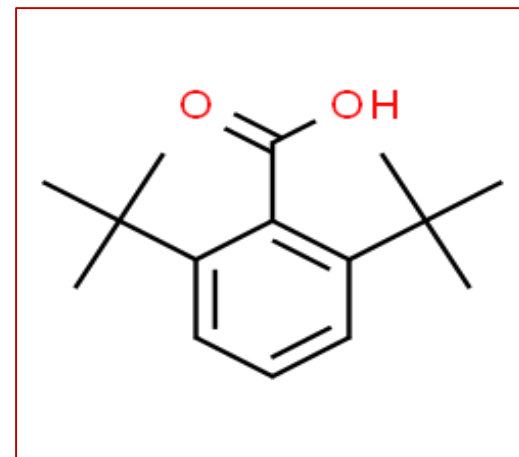




**Acidity of benzoic acid**



**O-dimethyl benzoic acid**



**O-t-But benzoic acid**



# REACTION INTERMEDIATES

molecule to the reaction site on the acid.

## REACTION INTERMEDIATES

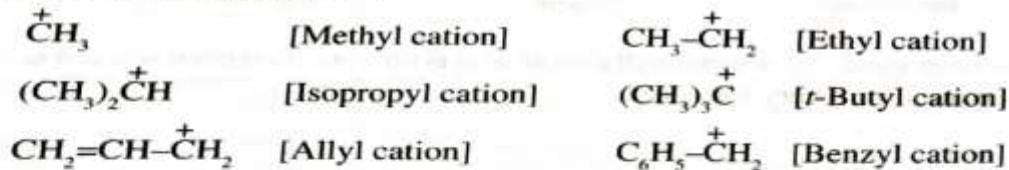
Most organic reactions occur through a series of steps. These steps involve the formation and reaction of several intermediate structures which exist only for a very short period of time as they are very reactive species. The intermediate species formed and utilized during the stepwise progress of a reaction to reach its preferred products are called *reaction intermediates* or *reactive intermediates*. These may be cations, anions or neutral species with one or more unpaired electrons. As they do not live very long, it is not possible to isolate one and store it unless very special methods are adopted. However, their formation and existence for very short periods have been established and identification has been possible in many cases by sophisticated techniques like spectroscopy. Typical examples for reaction intermediates are *carbocations*, *carbanions*, *free radicals*, etc.

### (A) CARBOCATIONS

A *carbocation* (formerly called *carbonium ion*) is a cationic reaction intermediate species that has a carbon that bears a positive charge and is two electrons short for completing its octet.

Since the positively charged carbon centre in a carbocation has only six valence electrons around it and is thus electron-deficient, it has a strong tendency to accept a pair of electrons to complete its octet. Hence, a carbocation is a very short-lived, highly reactive species.

Examples for carbocations are:

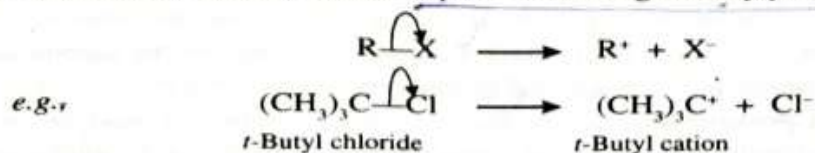


[Some authors prefer to use *carbocation* in place of *cation* in naming carbocations, *i.e.*, methyl carbocation, ethyl carbocation, etc.]

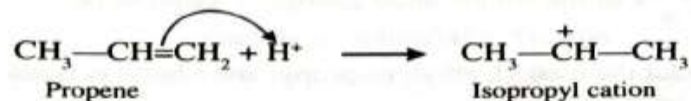
### Formation

Carbocations are formed by the heterolytic cleavage of covalent bonds in which carbon is connected to an atom or group more electronegative than itself. During heterolysis, the more electronegative atom or group departs carrying both the bonding electrons, leaving behind a species which has a carbon carrying a positive charge. Two examples are given below.

- (i) Ionization of an alkyl halide in polar solvents generally yields the alkyl cation.



- (ii) Protonation of alkenes, carbonyl compounds, nitriles, etc. during their polar addition reactions yield carbocations. *e.g.*, The first step in the Markownikoff addition of a polar reagent like HBr to propene is shown below.



### Hybridization and structure

The positively charged carbon in a carbocation is  $sp^2$  hybridized. The three  $sp^2$  hybrid orbitals contain an unpaired electron each and are arranged in a planar triangular fashion. One vacant  $p$  orbital of the carbon remains unhybridized and stands perpendicular to the above plane. The  $sp^2$  orbitals are used to form  $\sigma$ -bonds with three atoms or groups creating bond angles of  $120^\circ$  so that the carbocation has a planar triangular (*i.e.*, trigonal planar) structure with regard to the positively charged carbon.

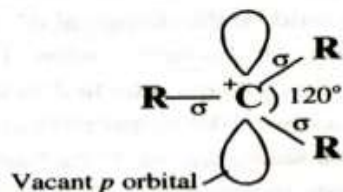


Fig. 1.10: Planar triangular structure of a carbocation

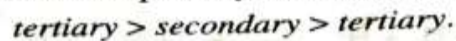
**Stability**

The stability of a carbocation depends considerably on its structure. One important aspect in this regard is connected to the extent of dispersal of the positive charge on the carbon of the carbocation. Any structural factor that tends to disperse the positive charge on the carbon and distribute it over the rest of the molecule tends to stabilize the carbocation whereas any factor that tends to intensify the positive charge on the carbon tends to destabilize the carbocation.

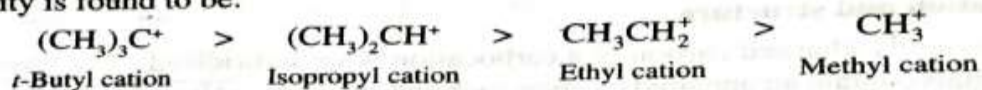
For example, the presence of electron-donating group(s) attached to the positively charged carbon tends to decrease the positive charge on the carbon and disperse it, and thereby tends to stabilize the carbocation. On the other hand, the presence of electron-attracting group(s) tends to intensify the positive charge on the carbon and thereby tends to destabilize the carbocation. Further, dispersal of the positive charge on the carbon may be possible through resonance or delocalization of electrons in a carbocation; this obviously will tend to stabilize carbocation. A few examples are considered below.

**(a) Stability of alkyl cations**

The order of stability of the simple alkyl cations is found to be:

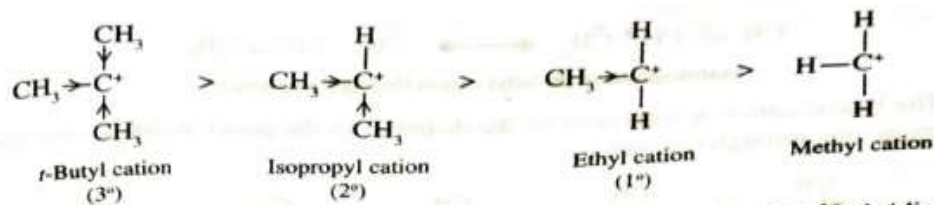


e.g., When we consider the methyl, ethyl, isopropyl and *t*-butyl cations, the order of stability is found to be:

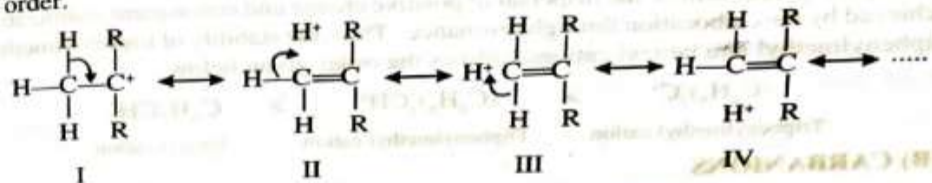


This can be explained on the basis of *inductive effect* and *hyperconjugation effect*.

- (i) **Inductive effect**: The alkyl groups show electron-releasing inductive effect (+I effect) in the direction of the positive charge in a carbocation. Through +I effect, an alkyl group thus disperses the positive charge, thereby stabilizing the carbocation. Obviously, the greater the number of alkyl groups attached to the positive carbon, the greater would be the dispersal of charge and, consequently, the greater would be the stability of the carbocation. Thus, a 3° carbocation like the *t*-butyl cation with three alkyl groups attached to the positive carbon would be more stable than a 2° carbocation like isopropyl cation with two alkyl groups which would however be more stable than a 1° carbocation like the ethyl cation with only one alkyl group while the methyl cation with no alkyl group attached to the positive carbon would be the least stable among the group.



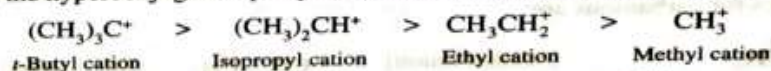
ii) **Hyperconjugation effect**: The positive carbon in a carbocation is  $sp^2$  hybridized and has a vacant unhybridized  $p$ -orbital; this makes  $\sigma$ - $p$  hyperconjugation possible. We know that the greater the number of  $\alpha$ -hydrogens attached to the positive carbon, the greater will be the number of hyperconjugative contributing structures and the greater will be the stabilization of the carbocation. For carbocations, the number of  $\alpha$ -hydrogens and, hence the number of hyperconjugative structures, decreases in the order:  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$ . So, the order of stabilization through hyperconjugation would also decrease in the same order.



When both Rs are  $\text{CH}_3$ : *t*-butyl cation – 9  $\alpha$ -H's – 10 contributing structures.  
 When one R is  $\text{CH}_3$  & the other R is H: isopropyl cation – 6  $\alpha$ -H's – 7 contributing structures.

When both Rs are H: ethyl cation – 3  $\alpha$ -H's – 4 contributing structures.  
 $\text{CH}_3^+$ : methyl cation – No  $\alpha$ -H's – No contributing structures.

Thus, as found when considering the stability in terms of inductive effect, from the hyperconjugative perspective also, the stability follows the order:



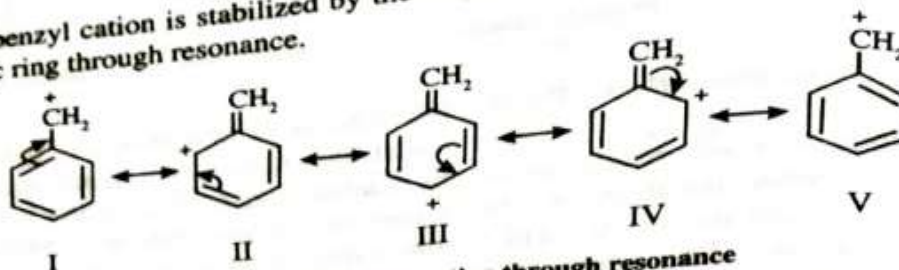
(b) **Stability of unsaturated carbocations, and carbocations containing one or more phenyl rings**

The allyl cation achieves dispersal of the positive charge and consequent stabilization through resonance.



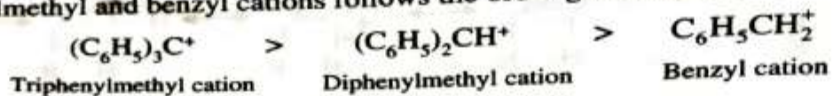
Stabilization of the allyl cation through resonance

The benzyl cation is stabilized by the dispersal of the positive charge over the aromatic ring through resonance.



Stabilization of the benzyl cation through resonance

Obviously, the greater the number of phenyl groups attached to the positively charged carbon, the greater will be the number of resonance structures possible and thereby the greater will be the dispersal of positive charge and consequent stabilization achieved by the carbocation through resonance. Thus, the stability of triphenylmethyl, diphenylmethyl and benzyl cations follows the order given below:

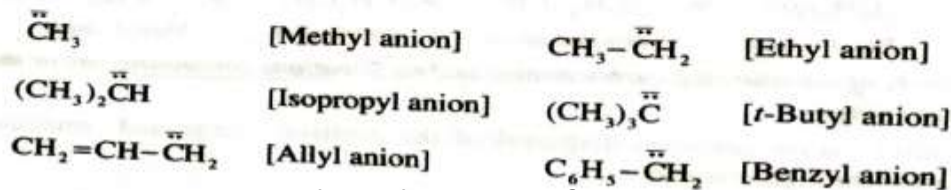


### (B) CARBANIONS

A carbanion is an anionic reaction intermediate species that has a carbon which bears a negative charge. Examples for such species are methyl anion ( $\text{CH}_3^-$ ), ethyl anion ( $\text{CH}_3-\text{CH}_2^-$ ), etc.

The negatively charged carbon centre in a carbanion has an octet of valence electrons around it. In spite of this fact, due to the formal charge present on the carbon, carbanions are very short-lived, highly reactive species. Being electron-rich with an unshared pair at the negative carbon centre, they are essentially nucleophiles and Lewis bases. They are easily attacked by electron-seeking reagents (electrophiles).

Examples for carbanions are:



[Some authors prefer to use the term *carbanion* in place of *anion* in naming carbanions, *i.e.*, methyl carbanion, ethyl carbanion, etc.]

### Formation

Some important methods by which carbanions are formed are the following:

- (i) By heterolytic fission of a bond in such a way that the bonding electrons are retained by the carbon atom: *e.g.*, Abstraction of the terminal hydrogen of acetylene with a strong base yields the acetylide ion (a carbanion).



- (ii) By the decomposition of certain anions like the carboxylate ion. *e.g.*, The loss of  $\text{CO}_2$  from the acetate ion yields the methyl anion.



- (iii) By the decomposition of organometallic compounds. *e.g.*, Decomposition of an alkyl magnesium halide (Grignard reagent) yields the corresponding alkyl anion.



### Hybridization and structure

In simple alkyl carbanions, the carbon carrying the negative charge is  $sp^3$  hybridized and the  $sp^3$  hybrid orbitals are arranged in a tetrahedral fashion. Three  $sp^3$  orbitals are used to form  $\sigma$ -bonds with three atoms or groups and the remaining  $sp^3$  orbital contains the unshared electron pair. Thus, a simple alkyl anion has a *pyramidal* shape similar to that of ammonia. Due to lone pair-bond pair repulsions, the bond angles in alkyl carbanions are less than the normal tetrahedral angle of  $109^\circ 28'$ , normally between  $97$  and  $100^\circ$ .

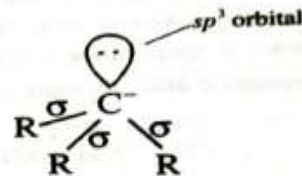


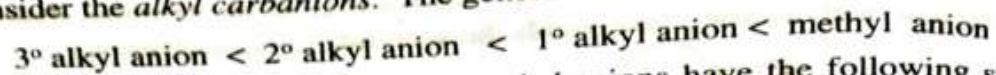
Fig. 1.11: Pyramidal structure of an alkyl anion

### Stability

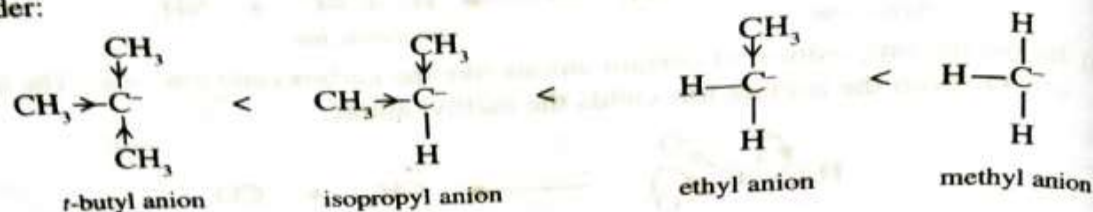
Let us first consider the stability of simple alkyl anions. We know that the stability of a charged system is increased by the dispersal of its charge and decreased by its

intensification. It is therefore obvious that any factor assisting dispersal of the negative charge on the carbon would stabilize a carbanion and any factor that tends to intensify the negative charge on the carbon would destabilize it. Thus, carbanions are stabilized by electron-withdrawing groups attached to the negative carbon and destabilized by electron-donating substituents.

Consider the *alkyl carbanions*. The general stability order is found to be:

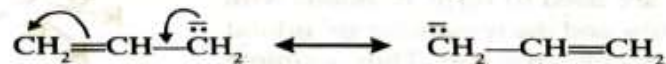


e.g., The *t*-butyl, *isopropyl*, *ethyl* and *methyl* anions have the following stability order:



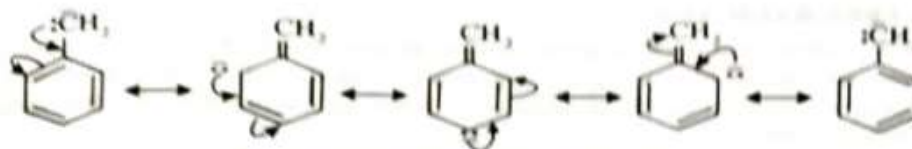
This is because the electron-releasing inductive effect (+I effect) of each alkyl group (here, methyl group) intensifies the negative charge on the carbon. The greater the number of alkyl groups attached to the negative carbon, the greater the intensification of the negative charge on it and the lower the stability of the ion. Obviously, such destabilization is the most for a  $3^\circ$  carbanion and the least for  $\text{CH}_3^-$ .

Now let us consider the stability of carbanions in which the unshared electron pair on the negative carbon can enter into conjugation with a multiple bond or an aromatic system; a typical example is the *allyl anion* ( $\text{CH}_2=\text{CH}-\text{CH}_2^-$ ). The possibility for such conjugation causes the dispersal of the negative charge on carbon through resonance and consequent stabilization of the allyl anion.



#### Resonance stabilization of the allyl anion

Similarly, in the *benzyl anion* ( $\text{C}_6\text{H}_5-\text{CH}_2^-$ ), the unshared pair on the negative carbon can enter into conjugation with the phenyl ring; delocalization of the electron pair causes the dispersal of the negative charge over the aromatic ring and the anion gets stabilized through resonance.

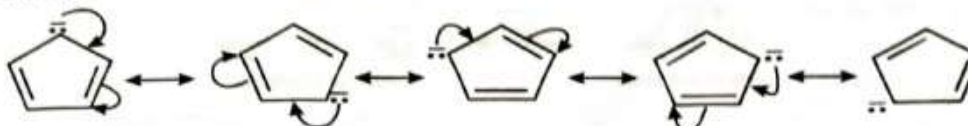


Resonance stabilization of the benzyl anion

These resonance-stabilized carbanions would therefore be more stable than the simple alkyl carbanions. The larger the number of phenyl groups attached to the negative carbon, the greater will be the dispersal of the negative charge through delocalization and the more stable will be the carbanion. Thus, stability increases in the order:

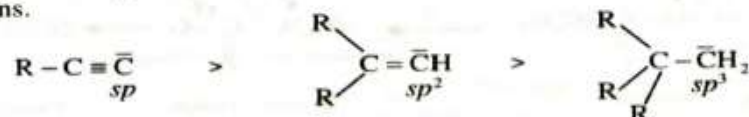


A carbanion with unusual stability is the *cyclopentadienyl anion* ( $\text{C}_5\text{H}_5^-$ ) having a six  $\pi$ -electron system (4 from the two  $\pi$ -bonds + 2 from the unshared pair). It forms an example for a conjugated system with  $(4n + 2)$   $\pi$ -electrons which is accorded aromaticity and high stability by the *Hückel's*  $(4n + 2)$  rule of aromaticity. The six  $\pi$ -electrons including the unshared pair on the negative carbon are completely delocalized over the pentagonal ring of the five  $sp^2$  hybridized carbon atoms bringing stability to the anion through resonance.



Resonance stabilization of the cyclopentadienyl anion

There is also a connection between the state of hybridization of the negatively charged carbon and the stability of a carbanion. As the  $s$ -character of the hybrid orbitals of that carbon increases, the electrons are more attracted to the nucleus and a lowering of energy occurs, thereby resulting in the following stability order for the carbanions.



Order of stability with respect to change in the state of hybridization of carbon



**(C) FREE RADICALS**

*Free radicals* are atoms or groups having an *unpaired electron*; such odd-electron species are neutral, highly reactive reaction intermediates formed by the homolytic cleavage of covalent bonds in molecules. Some typical examples for free radicals are given below.

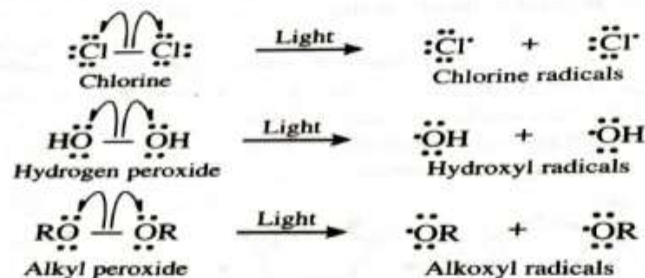
$\text{Cl}^\bullet$  (Chlorine radical),  $\text{CH}_3^\bullet$  (methyl radical),  $(\text{CH}_3)_3\text{C}^\bullet$  (*t*-butyl radical),  $\text{C}_6\text{H}_5^\bullet$  (phenyl radical),  $\text{C}_6\text{H}_5-\text{CH}_2^\bullet$  (benzyl radical).

Free radicals are highly reactive and short-lived because of the tendency of the odd electron present in them to become paired. They are paramagnetic on account of the presence of the unpaired electron.

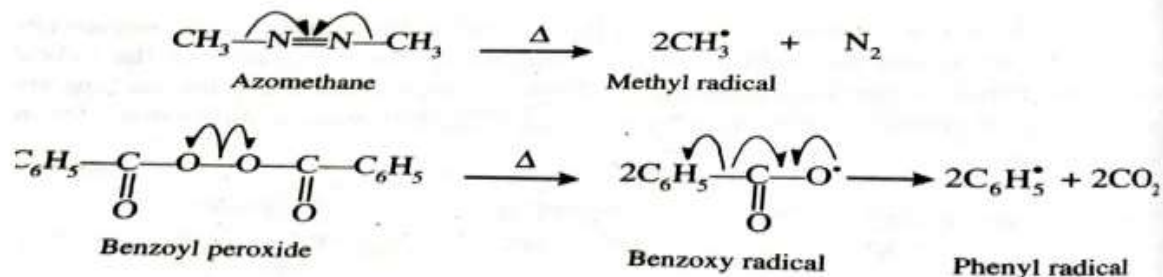
**Formation**

Some important methods by which free radicals are formed are the following:

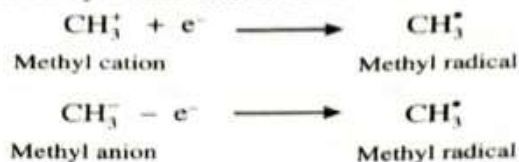
(i) Photochemical homolysis: *e.g.*,



(ii) Thermal homolysis: *e.g.*,



(iii) Gain of electron by a carbocation or loss of electron by a carbanion.



### Hybridization and structure

The carbon bearing the unpaired electron in a simple *alkyl* free radical is  $sp^2$  hybridized. The three  $sp^2$  hybrid orbitals contain an unpaired electron each and are arranged in a planar triangular (i.e., trigonal planar) fashion. One  $p$  orbital of the carbon, having an unpaired electron remains unhybridized and stands perpendicular to the above plane. The  $sp^2$  orbitals are used to form  $\sigma$ -bonds with three atoms or groups creating bond angles of  $120^\circ$  so that the alkyl radical has a planar triangular structure.

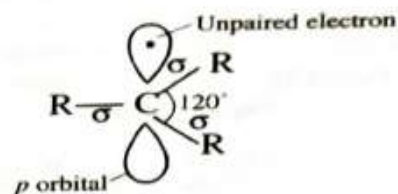
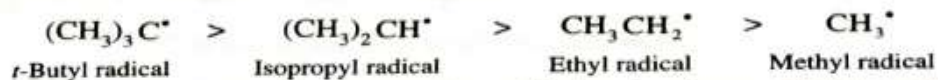


Fig. 1.12: Planar structure of a simple alkyl free radical

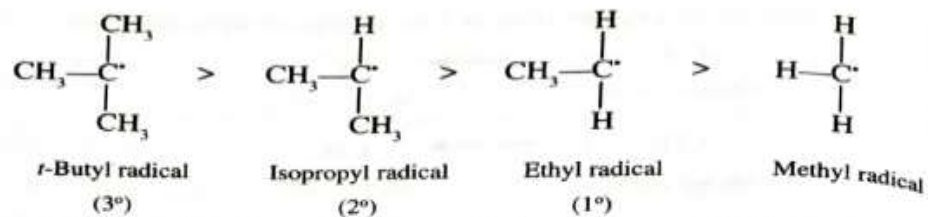
### Stability

The general order of stability for free radicals is:  $3^\circ > 2^\circ > 1^\circ$   
 e.g., The stability order for the following alkyl radicals is:



Hyperconjugation effect is important in explaining the above stability order for simple alkyl free radicals. In general, the greater the number of  $\alpha$ -hydrogens, the greater will be the number of hyperconjugative structures that can be written for the alkyl radical and the greater will be its stability. In the case of the *t-butyl radical*, there are 9 C–H  $\sigma$ -bond orbitals that can potentially overlap with the  $p$ -orbital of the carbon containing the odd electron. The *isopropyl radical* has 6 such C–H  $\sigma$ -bond orbitals, *ethyl radical* has 3 and *methyl radical* has none. Thus, stabilization through hyperconjugation is also in the order:

$t$ -butyl radical > isopropyl radical > ethyl radical > methyl radical  
 which is also the stability order of the free radicals, as shown below.

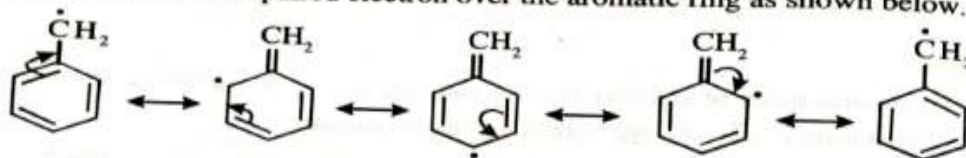


If the structures of the free radicals are such that resonance stabilization is possible then such free radicals would be more stable than the simple alkyl free radical. Resonance stabilization becomes possible when delocalization of the unpaired electron is possible over a multiple bond or an aromatic system. *e.g.*, The allyl radical ( $\text{CH}_2 = \text{CH} - \text{CH}_2^\bullet$ ) is resonance-stabilized through the delocalization of the unpaired electron as shown below.



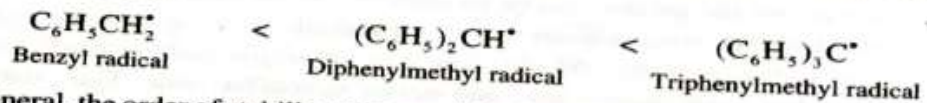
Resonance stabilization of the allyl radical

The benzyl radical ( $\text{C}_6\text{H}_5 - \text{CH}_2^\bullet$ ) is resonance-stabilized through the delocalization of the unpaired electron over the aromatic ring as shown below.

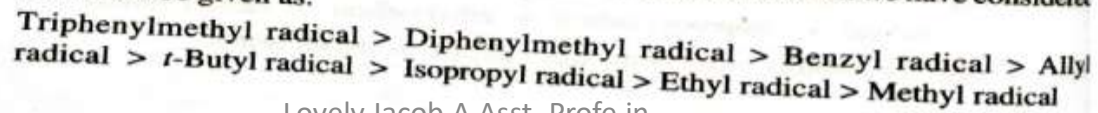


Resonance stabilization of the benzyl radical

The larger the number of phenyl groups attached to the carbon bearing the unpaired electron, the greater will be the extent of delocalization, the greater will be the number of resonance structures and the more stable will be the free radical. Thus, stability increases in the order:



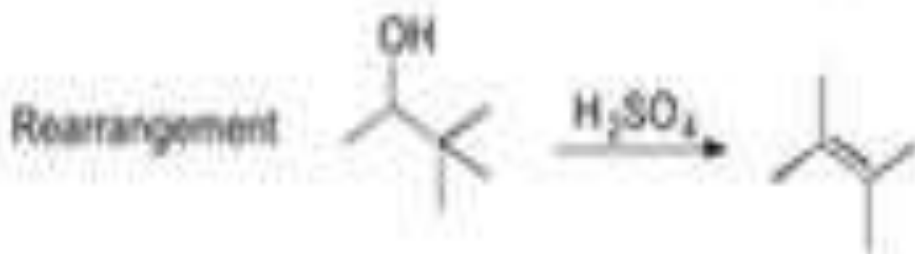
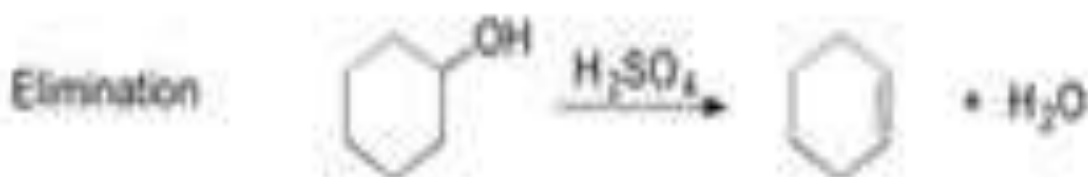
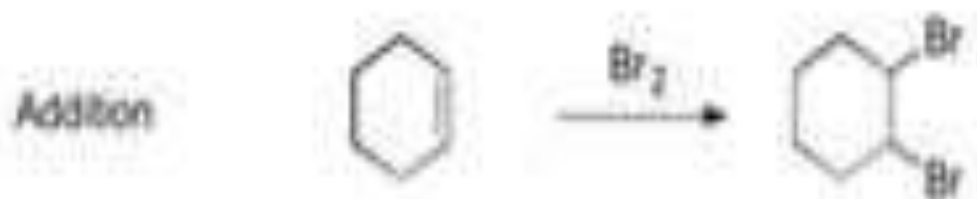
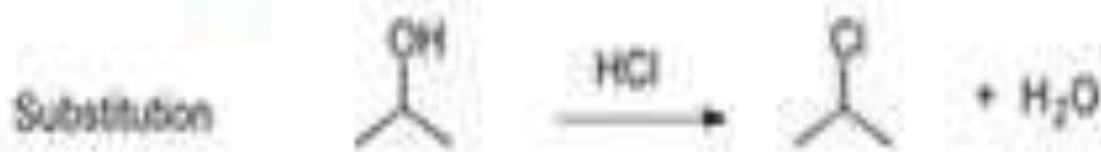
In general, the order of stability of some of the free radicals that we have considered so far can be given as:



## Types of reactions

- Addition reactions
- Substitution reactions
- Elimination Reactions
- Rearrangement reactions
- Organic Redox reactions

# Various Types Of Organic Reactions

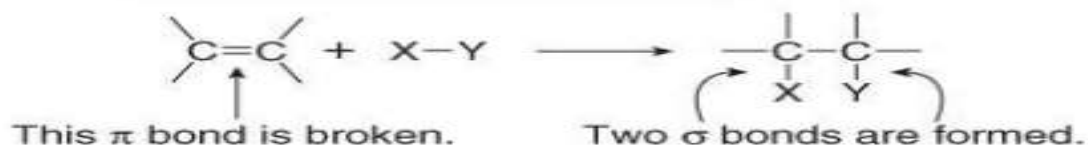


# 1.ADDITION REACTION

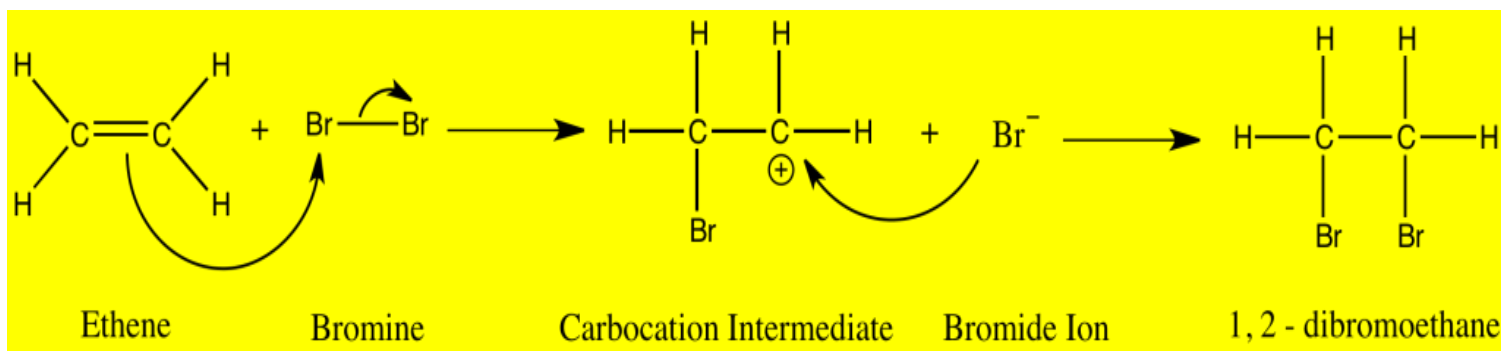
## Addition Reaction

- Addition reactions** occur when two reactants combine to form a single new product with no atoms left over.

### A general addition reaction



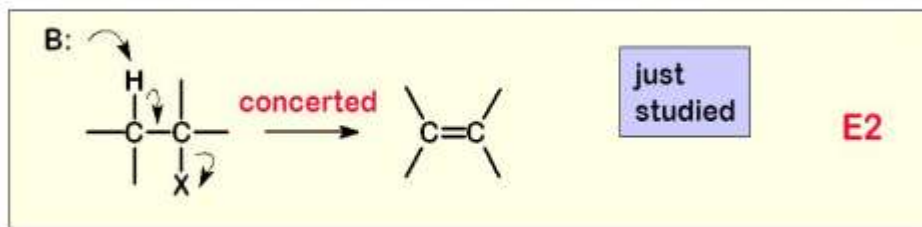
- In an addition reaction, new groups X and Y are added to the starting material. A  $\pi$  bond is broken and two  $\sigma$  bonds are formed.



# 2.ELIMINATION REACTION

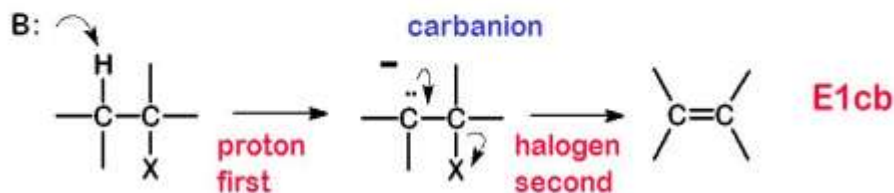
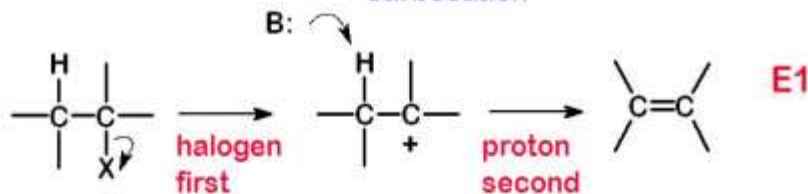
An elimination reaction is a type of organic reaction in which **two substituents are removed from a molecule** in either one or two-step mechanism. The **one-step mechanism** is known as the **E2** reaction, and the **two-step mechanism** is known as the **E1** reaction.

Three types of elimination reactions are conceivable



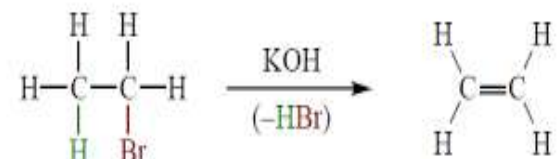
just studied

carbocation



carbanion

Elimination Reactions:



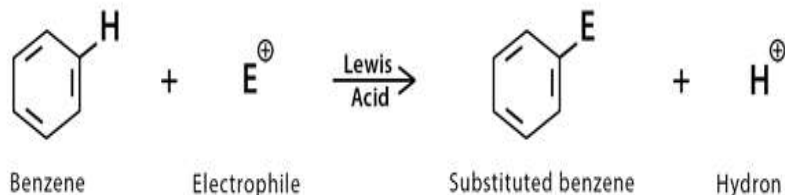
An elimination reaction (**Dehydrohalogenation**)

# 3.SUBSTITUTION REACTION REACTION

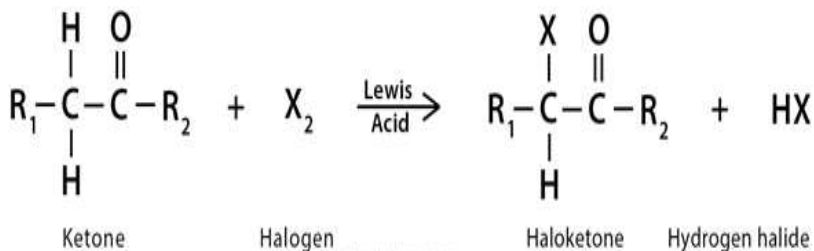
A **substitution reaction** is a chemical reaction during which **one functional group** in a chemical compound is **replaced by another functional group**. There are **two types of substitution reactions: nucleophilic and electrophilic**.

## Electrophilic Substitution

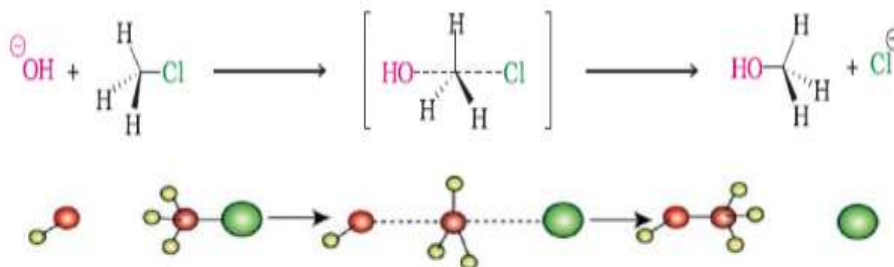
### Electrophilic Aromatic Substitution



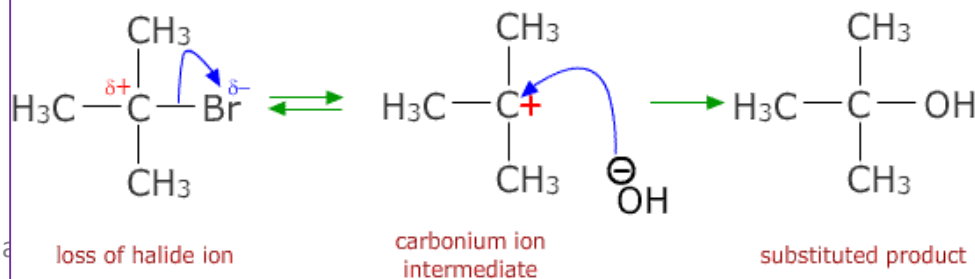
### Electrophilic Aliphatic Substitution



### (a) Substitution nucleophilic bimolecular ( $SN^2$ )

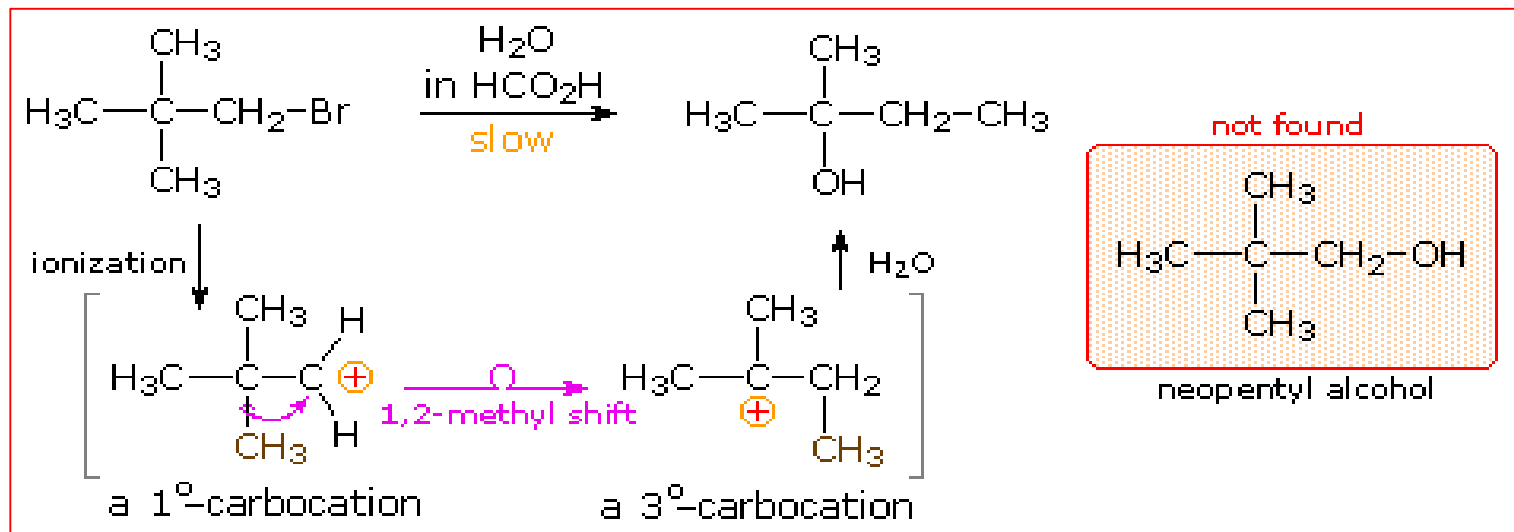
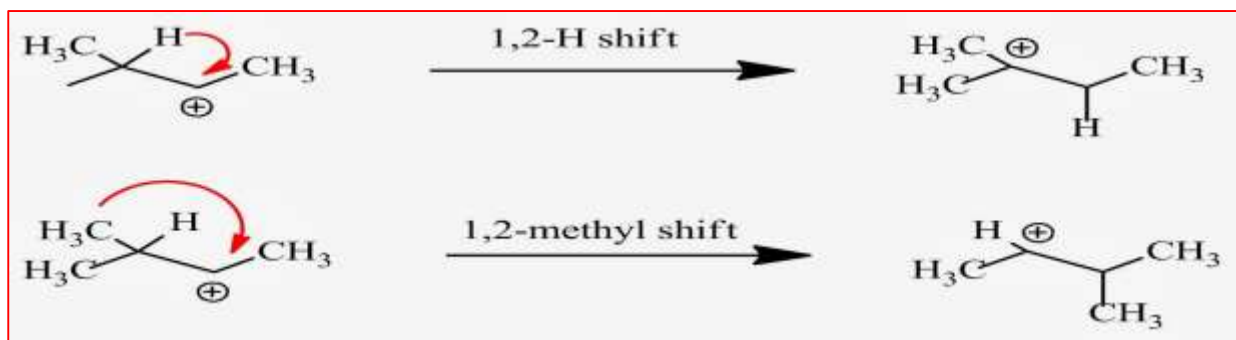


### Unimolecular nucleophilic substitution - $SN1$



# 4. REARRANGEMENT REACTION

A **rearrangement reaction** is a broad class of organic reactions where the **carbon skeleton of a molecule is rearranged** to give a **structural isomer of the original molecule**. Often a substituent moves from one atom to another atom in the same molecule.

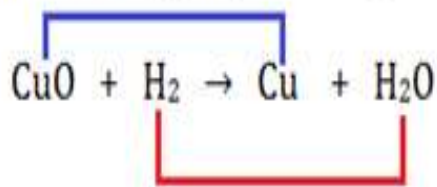




# 5. REDOX REACTION

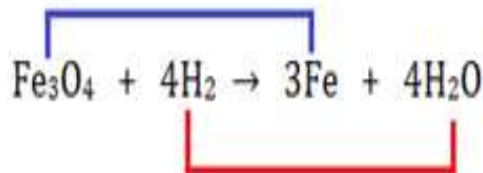
An **oxidation-reduction (redox) reaction** is a type of chemical reaction that involves a **transfer of electrons between two species**. An **oxidation-reduction reaction** is any chemical reaction in which the **oxidation number of a molecule, atom, or ion changes by gaining or losing an electron**

Removal of oxygen [Reduction]

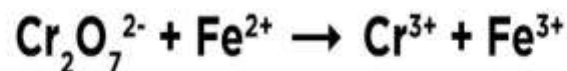


Addition of oxygen [Oxidation]

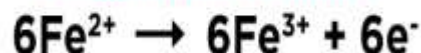
Removal of oxygen [Reduction]



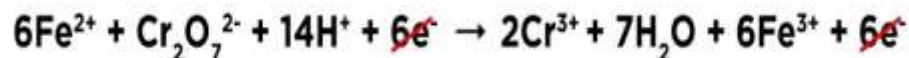
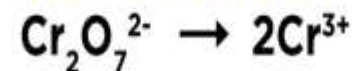
Addition of oxygen [Oxidation]



oxidation half-reaction



reduction half-reaction



**Step 7: Combine the Half-Reactions**

**THANK YOU**