

ELECTRON DISPLACEMENT EFFECTS

INDUCTIVE EFFECT

DR.JESY.E.J.

Chapter 3. Electronic Displacements

Permanent Effect	Temporary Effect
1. Inductive Effect (IE)	4. Inductomeric Effect
2. Mesomeric Effect (ME)	5. Electromeric Effect
3. Hyperconjugation (hc)	

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

Partial polarization of e⁻s forming 'σ' bond towards more electronegative atom.

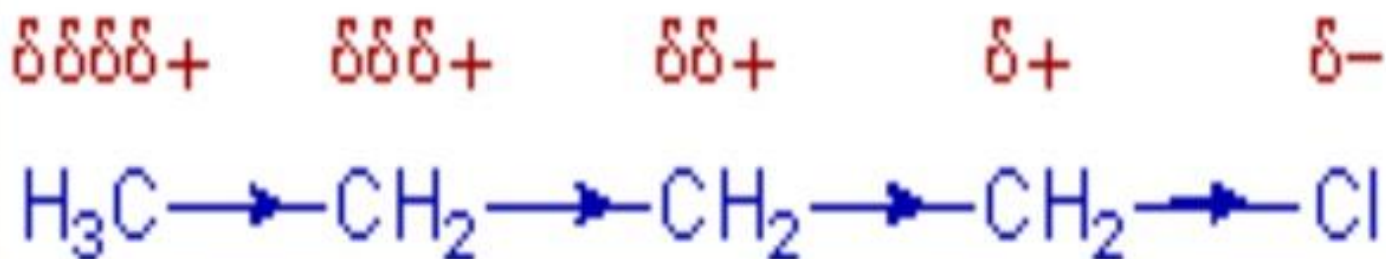


Characteristics of inductive effect:

- It is a permanent effect.
- It is operated only in sigma (σ) bonds.
- Only σ 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.

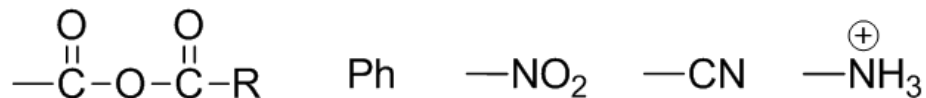
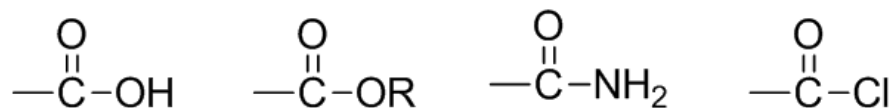
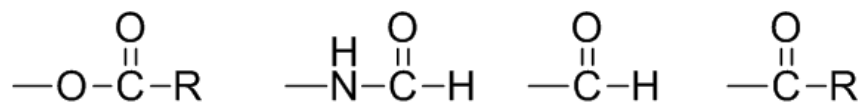
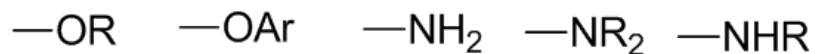
INDUCTIVE EFFECT

The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect.

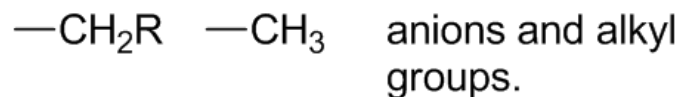
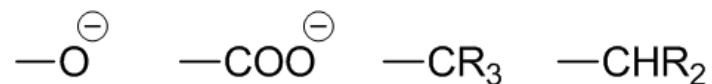


+I and -I Inductive effecting groups

-ve Inductive effect group (-IE)

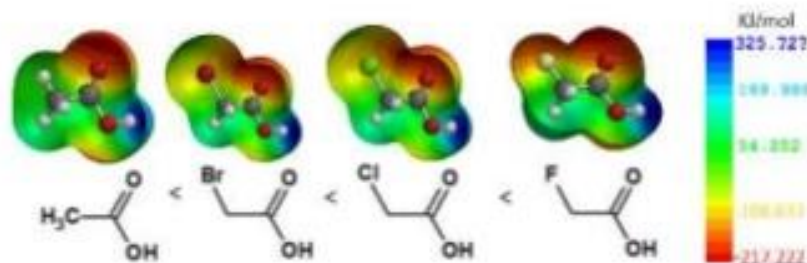


+ve Inductive effect group (+IE)



Inductive Effects on Acidity

The increased acidity of carboxylic acids can be attributed to electrostatic effects, such as induction. More electronegative groups will greatly change the distribution of electron density in the molecule by withdrawing electrons. This effect will make the proton more acidic.



Acidity increases as more electronegative substituents are added to the molecule and withdraw electron density from the acidic proton

The relative distance of the electronegative group also affects the acidity of carboxylic acids. The closer the electron withdrawing substituent is to the reactive proton, the more acidic the molecule becomes.

Compound	pKa
CH ₃ CO ₂ H	4.74
BrCH ₂ CO ₂ H	2.9
ClCH ₂ CO ₂ H	2.85
FCH ₂ CO ₂ H	2.65
CH ₃ CH ₂ ClCO ₂ H	2.89
CH ₃ ClCH ₂ CO ₂ H	4.05
ClCH ₂ CH ₂ CO ₂ H	4.53

Inductive Effects

pKa Values

$\text{H}-\text{COOH}$	3.75	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{COOH}$	4.8
CH_3-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

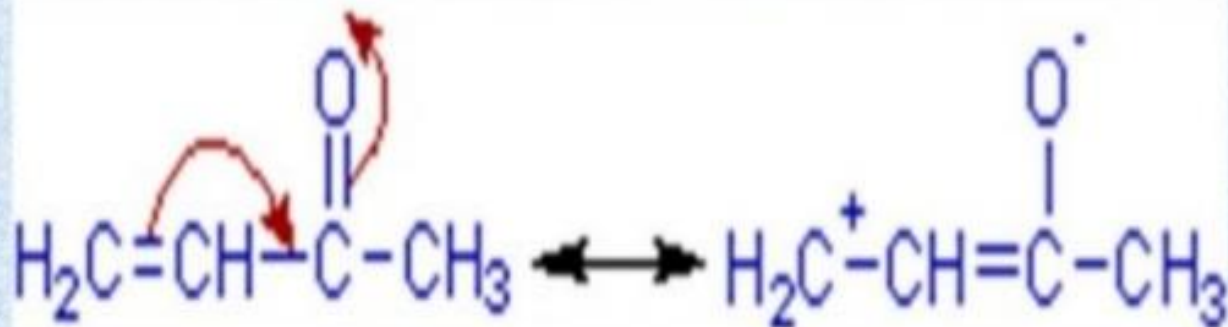
When the chlorine atom is moved further away from the carboxyl group, acidity decreases

distance

RESONANCE EFFECT

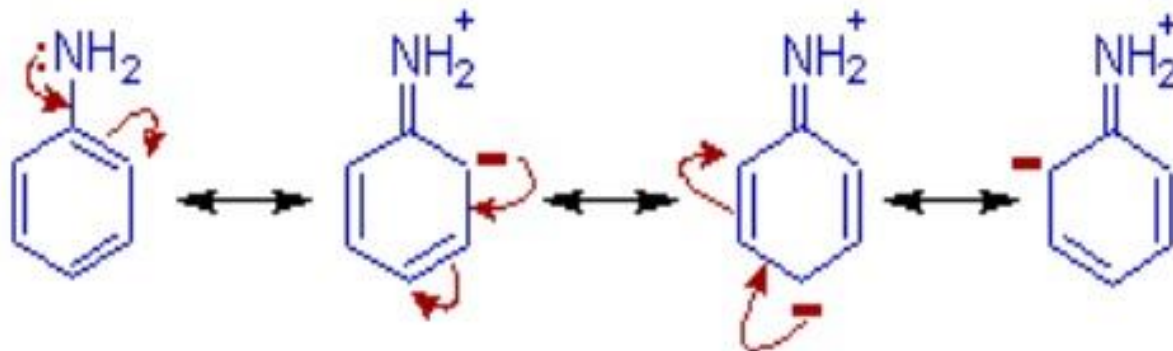
RESONANCE EFFECT OR MESOMERIC EFFECT :

The mesomeric effect is defined as the polarity produced in the molecule by the interaction of two π bonds or between a π bond and lone pair of electrons present on an adjacent atom. It is symbolized by M or R.

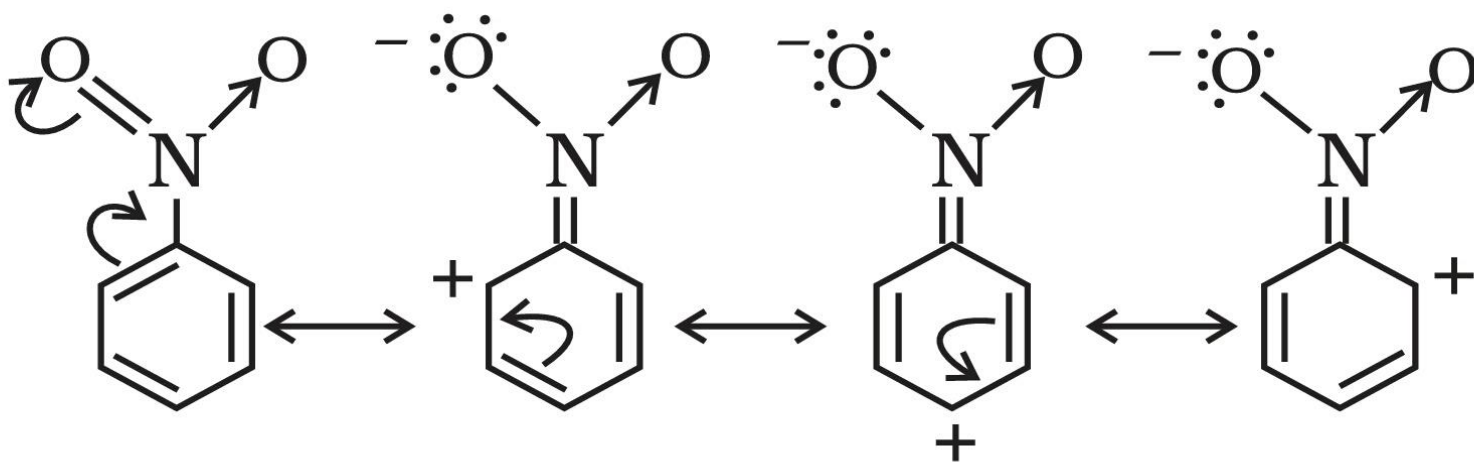


Positive resonance or mesomeric effect (+M or +R):

- The -NH_2 group in aniline also exhibits +R effect. It releases electrons towards benzene ring through delocalization.



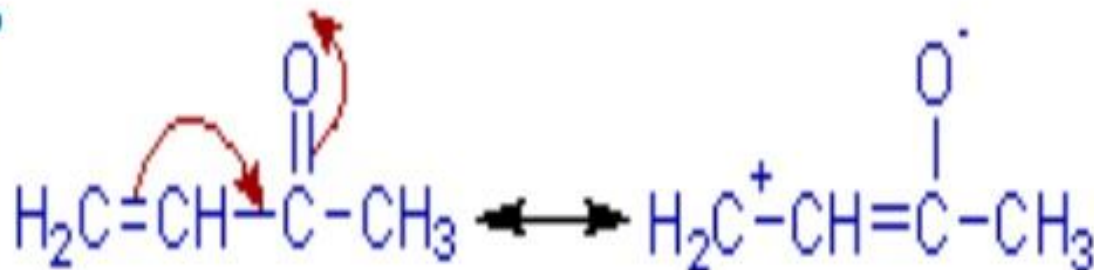
RESONANCE EFFECT OF NITROBENZENE



Negative mesomeric effect (-M or -R):

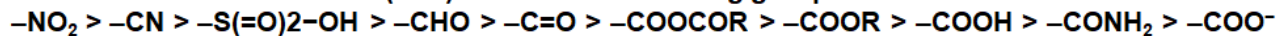
- Example:

- 1) The negative resonance effect (-R or -M) of carbonyl group is shown below. It withdraws electrons by delocalization of π electrons and reduces the electron density particularly on 3rd carbon.

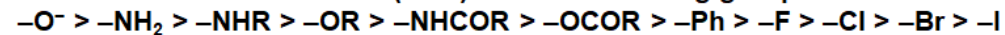


- Mesomeric Effect (-ME) π electrons are involved	+ Mesomeric Effect (+ME) non-bonding 'n' electrons are involved
<div style="text-align: center;"> $\text{H}_2\text{C}=\overset{\curvearrowright}{\text{C}}(\text{H})-\overset{\curvearrowright}{\text{C}}(\text{H})=\overset{\ominus}{\text{O}} \longleftrightarrow \text{H}_2\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{C}}(\text{H})=\overset{\oplus}{\text{C}}(\text{H})-\overset{\ominus}{\text{O}}$ </div> <div style="display: flex; justify-content: space-around; text-align: center;"> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \\ \text{aldehyde} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{R} \\ \text{ketone} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \\ \text{acid} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR} \\ \text{ester} \end{array}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{Cl} \\ \text{acylchloride} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \\ \text{amide} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}-\text{R} \\ \text{anhydride} \end{array}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $-\text{C}\equiv\text{N}$ nitriles </div> <div> $-\text{NO}_2$ nitro </div> <div> $-\text{SO}_3\text{H}$ sulfonic acid </div> </div>	<div style="text-align: center;"> $\text{H}_2\text{C}=\overset{\curvearrowright}{\text{C}}(\text{H})-\overset{\curvearrowright}{\text{Cl}}: \longleftrightarrow \text{H}_2\overset{\ominus}{\text{C}}-\overset{\oplus}{\text{C}}(\text{H})=\overset{\oplus}{\text{Cl}}:$ </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $-\overset{\cdot\cdot}{\text{Cl}}:$ </div> <div> $-\overset{\cdot\cdot}{\text{Br}}:$ </div> <div> $-\overset{\cdot\cdot}{\text{I}}:$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{H}$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{R}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $\begin{array}{c} \text{H} \quad \text{O} \\ \mid \quad \parallel \\ -\overset{\cdot\cdot}{\text{N}}-\text{C}-\text{R} \\ \text{acetamide} \end{array}$ </div> <div> $\begin{array}{c} \text{O} \\ \parallel \\ -\overset{\cdot\cdot}{\text{O}}-\text{C}-\text{R} \\ \text{acetate} \end{array}$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{Ar}$ </div> <div> $-\overset{\cdot\cdot}{\text{O}}\text{Ph}$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div> $-\overset{\cdot\cdot}{\text{S}}\text{H}$ </div> <div> $-\overset{\cdot\cdot}{\text{S}}\text{R}$ </div> <div> $-\overset{\cdot\cdot}{\text{N}}\text{H}_2$ </div> <div> $-\overset{\cdot\cdot}{\text{N}}\text{HR}$ </div> <div> $-\overset{\cdot\cdot}{\text{N}}\text{HR}_2$ </div> </div> <div style="display: flex; justify-content: space-around; text-align: center; margin-top: 10px;"> <div>thiols</div> <div>thioether</div> <div>amines</div> </div>

Order of - Mesomeric Effect (-ME) electron withdrawing groups:

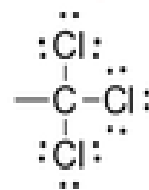
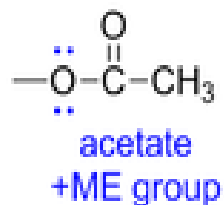
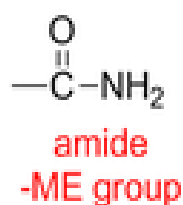


Order of + Mesomeric Effect (+ME) electron donating groups:

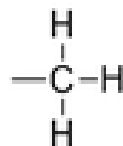


In **-ME** group there will be **no lone pair** electrons.

For example:



neither +ME nor -ve



neither +ME nor -ve

Applications of Mesomeric Effect

- i. Stability of allyl and benzyl carbocations
- ii. Stability of allyl and benzyl free radicals
- iii. Acidity of carboxylic acids
- iv. Basicity of amines

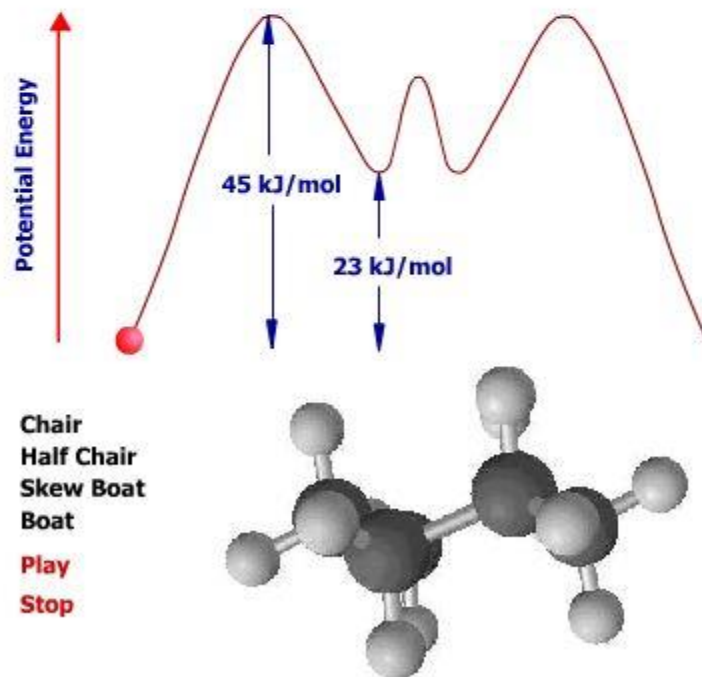
STERIC EFFECT

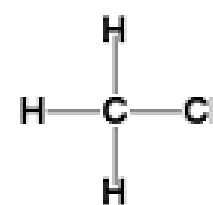
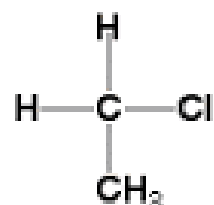
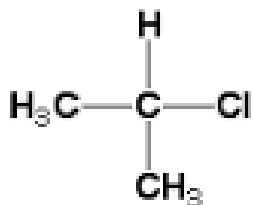
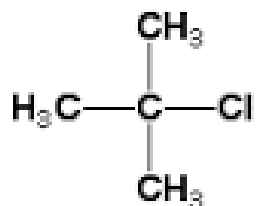


Steric Effects

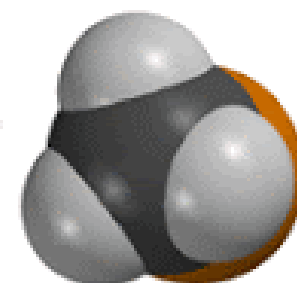
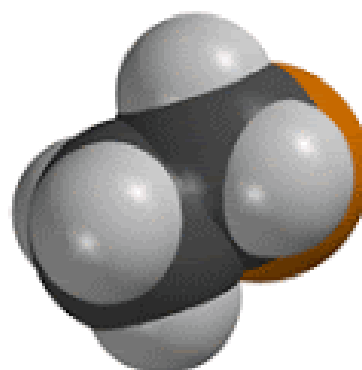
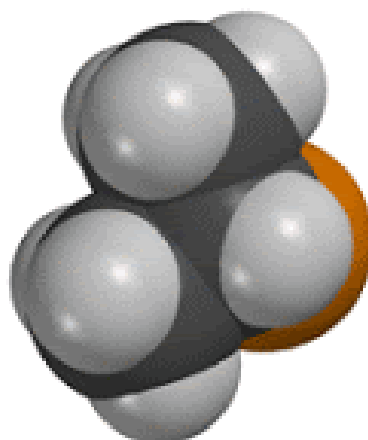
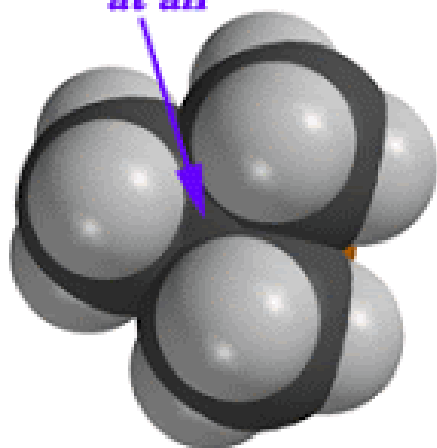
When atoms in a molecule get too close together as parts of the molecule vibrate or rotate, electric repulsions between electrons may hinder some conformations and favor others (**Steric effects**).

Steric effects lead to conformations in which repulsions are minimized; this lowers the potential energy of the molecule (more stable).





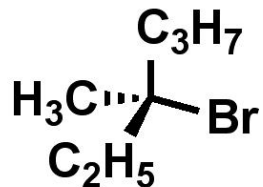
*Not accessible
at all*



Accessibility of electrophilic carbon atom to nucleophilic attack



Reaction rate in S_N2 reactions



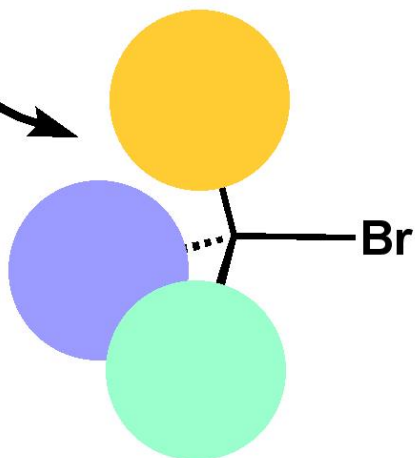
+

KOH



No Reaction

Difficult to attack



No Reaction

Electronic vs Steric Effects

More Information Online WWW.DIFFERENCEBETWEEN.COM

DEFINITION

Electronic Effects

Electronic effects are the effects of bonding electrons of a molecule on its structure and properties

Steric Effects

Steric effects are the effects of nonbonding electrons of a molecule on its structure and properties

NATURE

Bonding

Nonbonding

INFLUENCES

Influence the structure, reactivity, and properties of a molecule

Influence the conformation and reactivity

Organic reactions are the chemical reactions that are undergone by organic compounds (the chemical compounds containing carbon). A few important types of organic reactions are illustrated below.



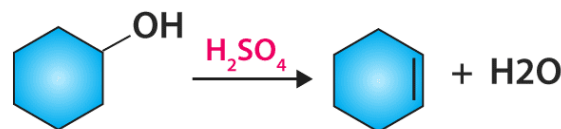
Substitution



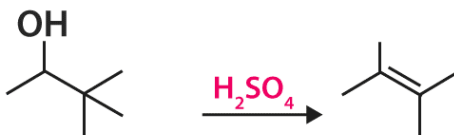
Addition



Elimination

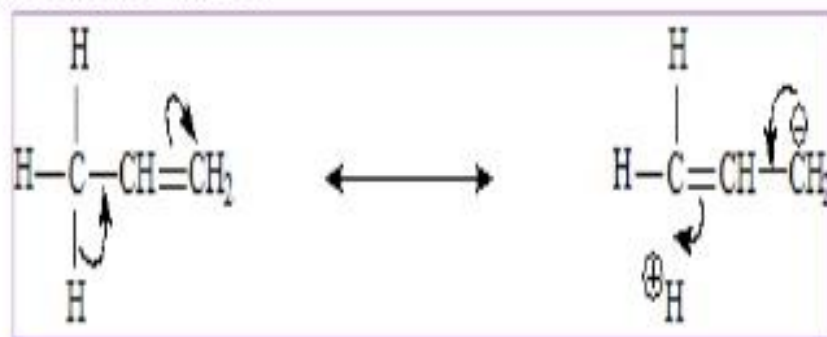


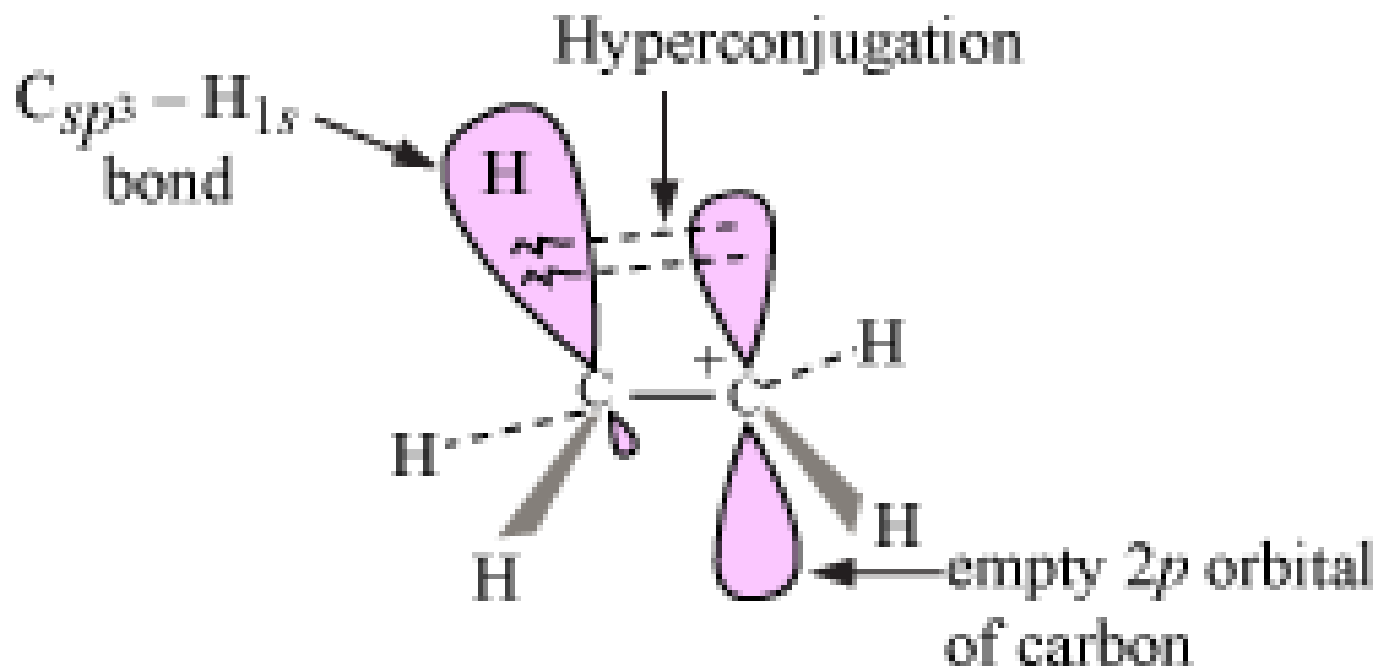
Rearrangement



Hyperconjugation: No bond resonance

- ▶ The electrons of the sigma bond between C and H are involved in delocalization.
- ▶ In structure to the right: No bond between C and H due to migration of the sigma bond. Hence Hyperconjugation is also called as 'NO BOND RESONANCE'.
- ▶ This does not indicate that hydrogen is completely detached from the structure, but some degree of ionic character in the C – H bond and some single bond character between carbon – carbon double bond.





HYPERCONJUGATION

VERSUS

RESONANCE

Hyperconjugation is the stabilization effect on a molecule due to the interaction between a sigma bond and a pi bond

Involves sigma bond orbitals and p orbitals or pi bond orbitals

Causes the sigma bond length to be shortened

Resonance is the stabilizing of a molecule through delocalization of bonding electrons in the pi orbital

Involves only pi bond orbitals

Has no effect on sigma bonds

Visit www.pediaa.com