# Organic Chemistry

## General Organic Chemistry

⇒ The word Organic means "Pertaining of life"

⇒ Early scientist consider that "The compounds like sugars fats, oils, dyes, proteins vatamins etc, which are obtained from living organsims like plants and animal were called organic compounds"

while

The compounds like salts, alum, nitre etc which are obtained from non-living thing are called Inorganic compounds.

**Vital force theory:-** (Given by Berzelius in 1780) (Swedish Chemist)

According to this theory organic compound cannot be senthysized in laboratory because (supernatural force is present) so it can only be obtained from living things or organism.

**Rejection of Vital force theory:-**

* Micheal Keneral

Animal Fat + NaOH ⟶ Soap + Glycerene
(Organic in nature)

$NH_4Cl + KCNO \rightarrow NH_4CNO + KCl$

* Friedrich Wohler (1828)

$$\underset{\text{(Ammonium Cyanate)}}{NH_4CNO} \underset{\text{(Rearrangement)}}{\overset{\text{heat}}{\rightleftharpoons}} \underset{\boxed{\text{Urea}}}{NH_2-\overset{\overset{O}{\|}}{C}-NH_2} \qquad \underset{\text{Thiourea}}{NH_2-\overset{\overset{S}{\|}}{C}-NH_2}$$

(Human Urine)

Inorganic

organic

* Kolb (1845) $CS_2$ (Carbon disulphide)

↓

Acetic Acid preparation

* Berthlot (1856) Methane ($CH_4$) preparation

| | Organic Compound | Inorganic Compounds |
|---|---|---|
| 1- | Contain C, H, O | All except C-H |
| 2- | Covalent in nature | Electrovalent, ionic, or covalent |
| 3- | Low Melting and Boiling Point | High Melting and Boiling Points |
| 4- | Mostly insoluble in water | Mostly soluble in water |
| 5- | Baad Conductors of electricity | Good Conductors |
| 6- | Volatile | Non-Valatile. |
| 7- | Cetenation occurs | absent |
| 8- | Available in Solid, Liquid, Gases | Generally in Solid |
| 9- | Mostly Colorless | Colored Compounds |
| 10- | Slow rate of reaction | Fast rate of reaction |
| 11- | Living things | Non-living things |
| 12- | Usually Biodegradable | Non-biodegradable |
| 13 | Enzymes, Protein, DNA RNA fuels, etc | Metals, non-metals & Salts etc. |

**Modren Defination:-**

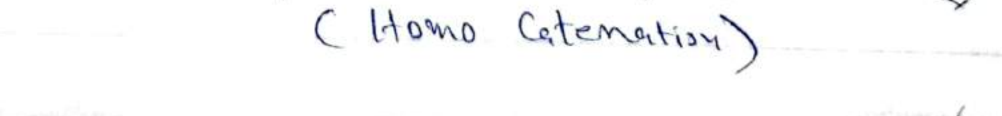
Study of compounds of C, H and their derivatives like $CH_4$, $CH_3OH$, $CH_3CN$ etc.

* Organic Compound → Covalent in nature

* Dipole - Dipole Force
* ~~Waal~~ Wander Waals forces
* Hydrogen Bonding

⇒ Why Large Numbers of Organic Compounds

* **Catenation:** Self linking Properties of Carbon is called Catenation



( Homo Catenation)

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$$

(Hetero Catenation)

Why Carbon exhibit Catenation

(⇒ due to smaller size)

⇒ Non Ionic / Covalent

Non-Crystalline, Semi Solid ($C \geq 18$)

Have polarity $\boxed{\overset{\delta+}{R} - \overset{\delta-}{X}}$

⇒ Electronegativity of Carbon is (2.5) is due to N (3.0) (2.1) Cl (3.0) O (3.5) so it can form strong covalent bond.

**Note:** No compound 100% Ionic in nature For Ionic E.N difference must be greater then 1.7 for Ionic Compounds

$(2.5)C - F\ (4.0) \quad 4-2.5 = \boxed{1.5 < 1.7}$

⇒ Organic Compound have slow rate of reaction because Bond Breaking and forming involved.

⇒ Soluble in Non-polar Solvent some are soluble in water due to hydrogen Bonding.

⇒ Show phenomenon of Isomerism (Same Molecular formula, different structural formula)

# Sources of organic compounds

**Coal:** (Destructive Distillation or Carbonization) 500 − 1000C° absence of air
→ Coal Gas
→ Coal Tar
→ Coke

⇒ Total Coal reserves in Pakistan = 184 Billion Tons

Peat → 40 − 60 % C Inferior quality coal, used in furnace
Lignite → 60-70 % C Soft Coal, used in thermal Station
Bituminous → 70 − 85 % C Common Coal, used in Homes
Anthracite → 90 − 95 % C Superior quality, used in industries

* Contain more then 200 Organic Compounds
* Graphite is difficult to ignite → not used as fuel.
* Cannel Coal or Candle Coal = Liptinite
* % age of S in Coal is $\boxed{1.8\%}$ can be removed by CuO

**Natural Gas:** It is mixture of low boiling ~~[illegible]~~ Hydrocarbons.

* Major portion is Methane Gas ($CH_4$) almost 80 − 90 %
* Used for power generation, in cement and fertilizer industries and for fuel for domestic purposes

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

**Petroleum:** (Black Gold)

$\boxed{\text{Rocks}}$
⇓
Blackish $\boxed{\text{Liquid}}$
⇓
Crude Oil

Fractional Distillation
→ T < 20°C ($C_1 - C_4$) Petroleum Gas (LPG) ⇒ For fuel
→ 20 - 60°C ($C_5 - C_6$) Petroleum Ether ⇒ as Solvent
→ 60 − 100°C ($C_6 - C_7$) Ligroin/Naphtha Solvent or Raw Material
→ 40° − 220°C ($C_6 - C_8$) Gasoline (Motor Oil) only 20%
→ 175 − 325 ($C_8 - C_{14}$) Kerosene Oil Heating fuel
→ T > 275°C ($C_{12} - C_{18}$) Diesal waxes product
50 − 60°C ($C > C_{18}$) Paraffin waxes Lubricant

**Cracking:** By fractional distillation of petrolium yield only 20% Gasoline. But demand is very High so Cracking of petrolium is done.

**Def:** - Conversion of Higher Hydrocarbon into lower Hydrocarbon is called Cracking

Kerosene Oil / Gas Oil $\xrightarrow[\text{Break Down}]{}$ Gasoline

$$\underset{\text{(Gas oil)}}{C_{16}H_{34}} \xrightarrow[700C^\circ]{Heat} \underset{\text{(Gasoline)}}{C_7H_{16}} + 3CH_2=CH_2 + CH_3-CH=CH_2$$

⇒ Thermal Cracking:- (Pyrolysis)
- * High T and P
  (150 - 900C°)
- * Bulton Process (370 - 400C°)

Cracking Induces
- ⇒ Dehydrogenation
- ⇒ Cycilzation
- ⇒ Isomerization

⇒ Catalytic Cracking:-

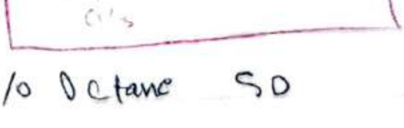
T = 500 C° P = 2 atm Catalyst = $\left( \text{Silica } (SiO_2) + \text{Alumina } (Al_2O_3) \right)$ Mixture

- * Better quality of gasoline with ↑ Octane Number.

⇒ Steam Cracking:-

T = 900 C° with Steam and Cooled Rapidly.
- * Produce lower unsaturated Hydrocarbon
- * used for manufacturing of Drugs, Plastic and Fertilizers etc.

**Octane Number:** (Percentage of iso-octane in the Iso-octane - Heptane mixture that matches the fuel being tested in a standard test engine.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{C}-CH_3$$

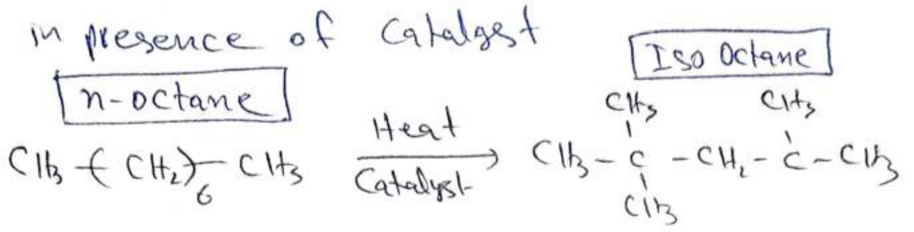
e.g.

Fuel having 80% Iso-octane and 20% Octane so its Octane Number is 80.

## Reforming

Fuel ⇒ Pre-ignition ⇒ Sharp metalic Sound ⇒ knocking ↓ Reduces efficieny of engine

1- Heating in absence of air and in presence of Catalyst



$$CH_3-(CH_2)_6-CH_3 \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{C}-CH_3$$

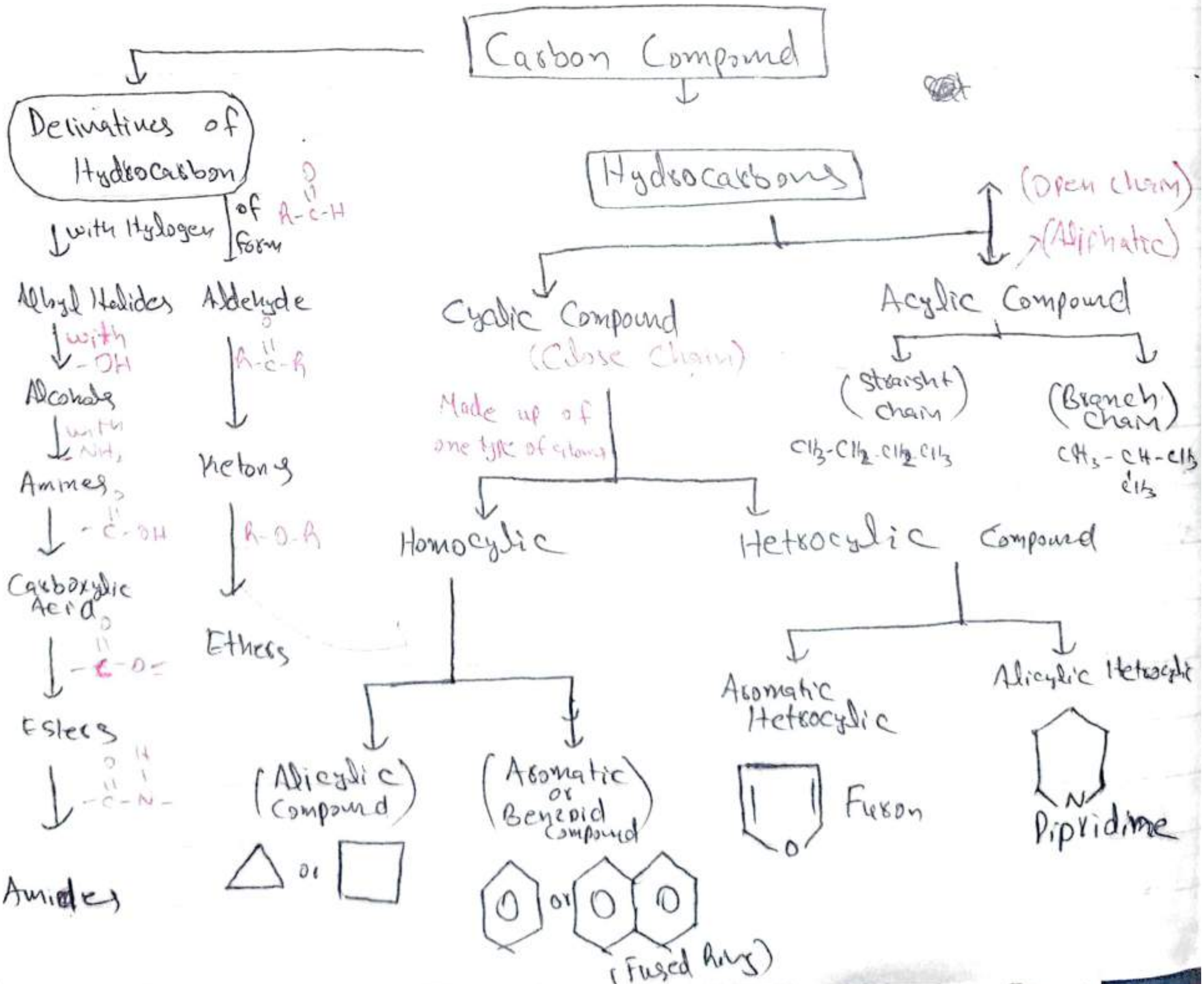
Increasing Octane Number

2- Adding anti knocking agent to fuel e.g TEL

TEL = Tetraethyl Lead $(CH_3CH_2)_4Pb$

**Aduese effect:** Reduce of Metalic Pb causes air Pollution

## Classification of Organic Compounds



## Acylic Hydrocarbon:

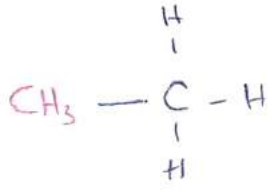
Saturated
(Have Single Bond)

For example
Alkanes $CH_3-CH_2-CH_2-CH_3$

Unsaturated
have Double or Triple
Bond (=) or (≡)

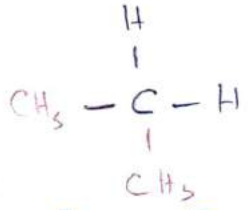
$CH_3=CH-CH_3$ Alkene
$CH_3-CH_2-C\equiv CH$ Alkyne

## Classes of Carbon Atom



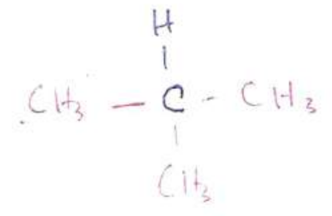
$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

1° or Primary



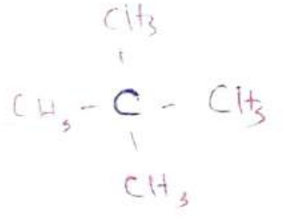
$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-H$$

2° or Secondary



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-CH_3$$

3° or Tertiary



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

4° or Quaternary

## Functional Group

Atom or group of atom present in a molecule which determine its chemical properties. It is site of chemical activity.

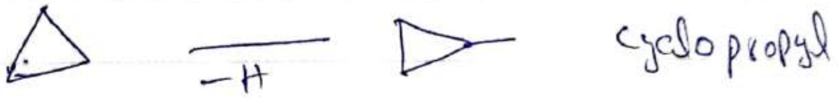
| | (Prefix) | (Suffix name) |
|---|---|---|
| $-SO_3H$ | Sulpho | Sulphonic acid |
| $-COOH$ | Carboxylic | oic acid |
| $-COO-R$ | Carboxy- | Alkanoic acid - Anhydride |
| $-COOR$ | Carbalkoxy ~~COOR~~ Alkoxy Carbony | oate |
| $-COCl$ | Chloroformyl | Oyl Chloride |
| $-CONH_2$ | Carbamoyl | Amide |

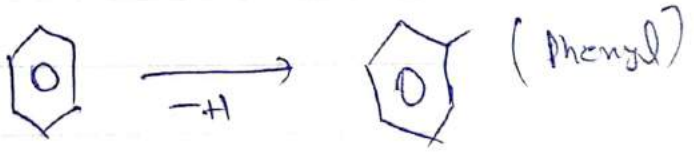
| | | |
|---|---|---|
| $-CN$ | Cyno | nitrile |
| ~~Iso~~ $-NC$ | Isocyno | Isonitrile or Carbylamine |
| $-CHO$ | Aldo or Formyl | -al |
| $-\overset{O}{\overset{\parallel}{C}}-$ | Keto or OXO | one |
| $-OH$ | Hydroxy | ol |
| $-SH$ | Mercapto | thiol |
| $-NH_2$ | Amino | amine |

## Hydro-Carbon Radical

$$\text{Alkane} \xrightarrow[-H]{} \text{Alkyl}$$

$$CH_4 \xrightarrow[-H]{} -CH_3 \text{ (Methyl group)}$$





Benzene

**IUPAC System** "International Union of Pure and Applied Chemists".

**Common Name**

- According to Method of preparation
- Name of a person or place

**For example**

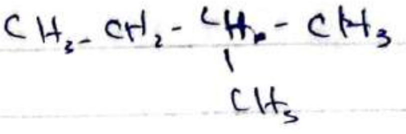
- Methane → Marsh Gas → Marshy Areas
- Acetic Acid → Derived from Latin word acetum means vinegar

Barbituric Acid → Barbara (Person Name)

⇒ n, iso and neo for Isomers.

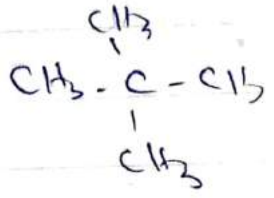
$CH_3-CH_2-CH_2-CH_2-CH_3$

n-Pentane



$CH_3-CH_2-\underset{CH_3}{CH}-CH_3$

Isopentane



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

Neopentane

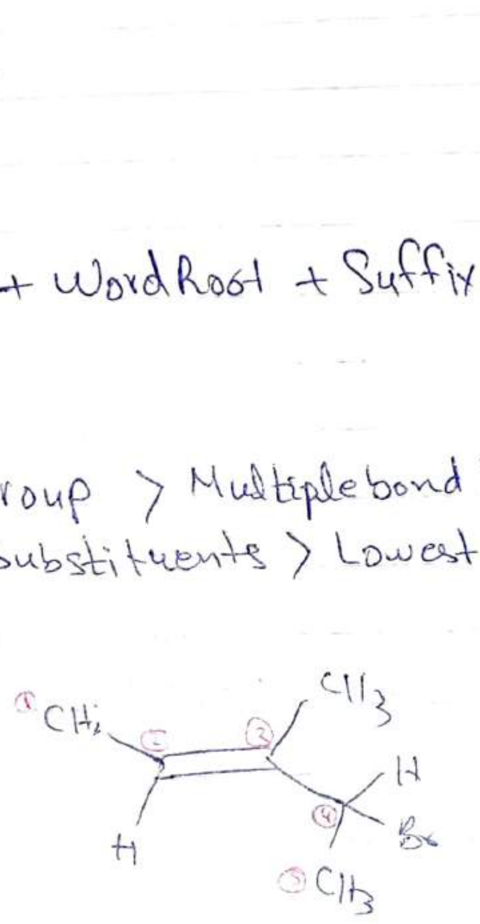
## IUPAC Name

Prefix + WordRoot + Suffix-1 + Suffix-2

Priority order:
Functional Group > Multiple bond > Number of Carbon atom > Number of Substituents > Lowest Locant > Alphabetical order

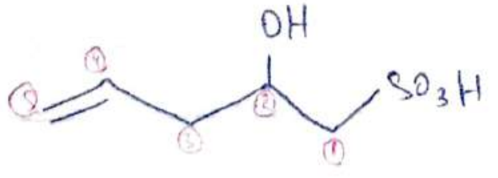
Example:

→



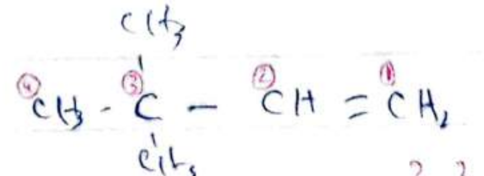
4-Bromo-3-methyl pent-2-ene

→



2-Hydroxy Pent-4-ene-1-Suphonic acid

→



$\overset{④}{C}H_3-\overset{CH_3}{\underset{CH_3}{\overset{③}{C}}}-\overset{②}{C}H=\overset{①}{C}H_2$

3,3-dimethyl-1-butene

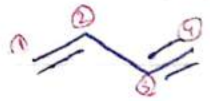
Suffixes - 2 (Priority)

Carboxylic Acid (-COOH) > Sulphonic acid ($-SO_3H$) > Anhydride ($-\underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-$) > Ester (RCOOR) > Acid Chloride (R-COCl)

> Acid Amide ($R-CONH_2$) > Cynide (-CN) > ($R-\overset{\overset{O}{\|}}{C}-H$) Aldehyde

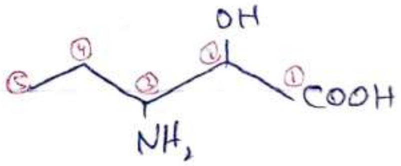
> $R-\overset{\overset{O}{\|}}{C}-R$ (Ketone) > Alcohol (-OH) > Thiol (R-SH) / > Amine ($-NH_2$)

> C=C > C≡C

→ 

But-1-en-3yne

Hex-4-ene-1-yne

→ 

3-Amino-2hydroxyl Pentanoic acid

Pent-1-ene-1-yne

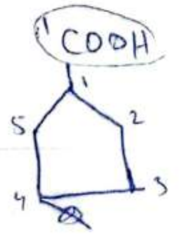
## ⇒ IUPAC Name For Cyclic Compounds

Prefix - Multiple Bond > Number of C-atom > Ring

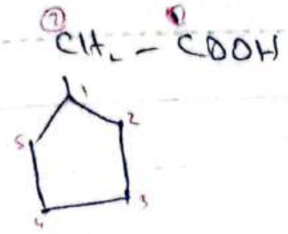
Principal Functional Group > Number of C-atom > Ring

**Note** If Carbon atom contain F.G is directly attached with ring then they are taken part of the Ring.

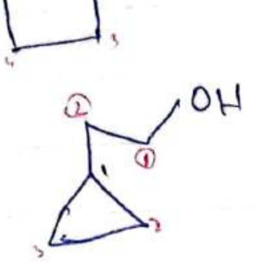
⇒ If no of Carbon atom are same than Priority Ring > Chain

→ 

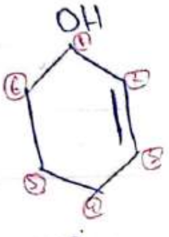
Cyclo Pentane-1-Carboxylic acid

→ 

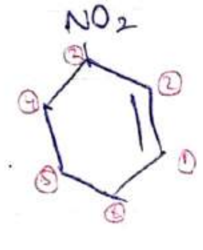
2-Cyclopentyl-ethan-1-oic acid

→ 

2Cyclopropyl-ethan-1-ol

→ 

Cyclohex-2-en-1-ol

→ 

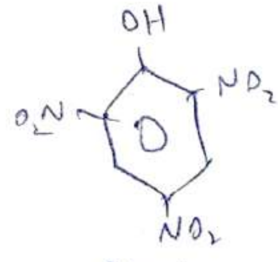
3-Nitrocyclohexene

## ⇒ IUPAC Name for Benzene Derivatives

→ If their is only one Functional group then you can use common name

Phenol

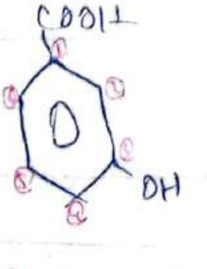
Toluene



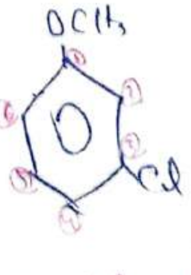
Picric acid

Benzoic acid

→ If more then one Functional group are present then number then according to IUPAC



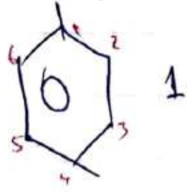
3-hydroxy Benzoic acid.



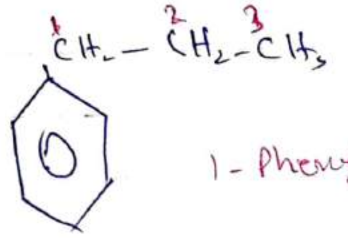
3-Chloro Anisole

→ If Hydro~~gen~~carbon is combination of both open and ring part then exept Methyl and ethyl open part is taken as main part.

⇒ 1-Methyl benzene

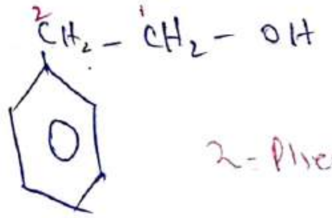


1-Ethyl Benzene

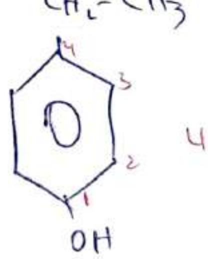


1-Phenyl Propane

→ If organic compound having F.G then part having F.G is taken as main part.

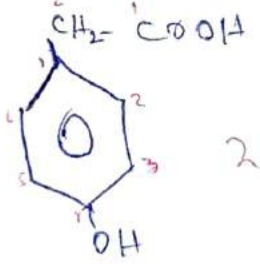


2-Phenyl Ethanol



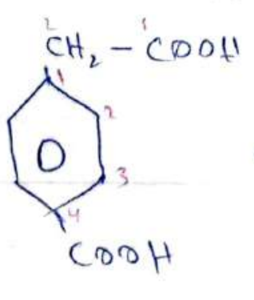
4-Ethyl Phenol

→ If Both part having F.G then part having P.F.G is taken as main part



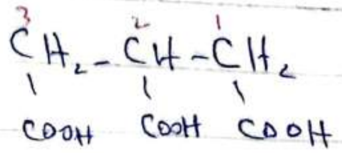
2 (4-Hydroxy Phenyl) ethanoic acid

→ If there is choice then priority is given to open part



2-(4-Carboxy Phenyl) ethanoic acid

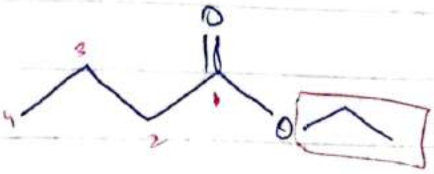
## Special Case.



$\underset{COOH}{\overset{3}{C}H_2}-\underset{COOH}{\overset{2}{C}H}-\underset{COOH}{\overset{1}{C}H_2}$

Propane-1,2,3-tricarboxylic Acid

Ester



Ethyl butan1- oate

Aldo formyl

$OH\overset{4}{C}-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}OOH$

4-Aldo-butan-1-oic acid

$OHC-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}OOH$

3-Formyl Propanoic acid

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## Hybridization:

* Pauling and Slater introduce it to explain the shape of molecule according to VBT.

* Atomic orbitals taking part in Hybridization = Hybrids orbital formed.

* Electrons do not undergo Hybrization
* A hybrid bond is always a sigma bond.
* Occurs at the time of Bond formation

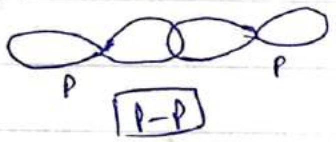
## Types

| SP | SP2 | SP3 |
|---|---|---|
| * One S and one P | One S and two P | One S and three P |
| * 50% S | 33.3 % S | 25 % S |
| * Shape linear | trigonal or Co-planer | Tetrahedral |
| * Bond angle 180° | 120° | 109° 28' |
| * $H-C\equiv C-H$<br>$\boxed{SP}$ | $H-\underset{H}{C}=\underset{H}{C}-H$ | $CH_3-CH_3$ |
| $CO_2, CS_2, BeCl_2, ZnCl_2$ |  | $CX_4$ $SiX_4$ |

| Sigma Bond (σ) | Pi Bond (π) |
|---|---|
| * Axial, head to head or linear Overlaping | Lateral or Sidewise Overlaping |
| * Stronger Bond then Pi | Weaker the σ |
| * Less Reactive | More reactive |
| * Stability ∝ Sigma Bond | Stability ∝ $\frac{1}{\pi}$ |
| * Reactivity ∝ $\frac{1}{\sigma}$ | Reactive ∝ π |

*


Note: Minimum 0 and Maximum 2 π bond present in Bonded atom



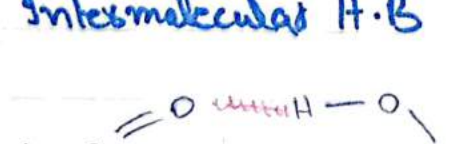
## Hydrogen Bonding:- Introduced by Latimer and Rodebush

- Weak Interaction between Hydrogen and Highly electronegative atom
- Electronegative atom should be small in size.
- F, O and N
- Dipole Ion or Dipole induce dipole interaction
- $HF > H_2O > NH_3$

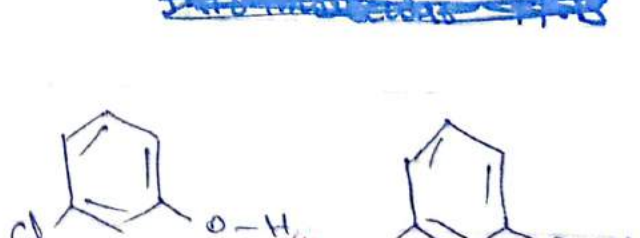
### Types

Intermolecular H.B

~~Intramolecular H.B~~



Formic acid



In m-chlorophenol

effect: Boiling Points, Melting Points, Solubility, thermal Stability, viscosity and surface tension increases.

* Alcohols are highly soluble in water but ethers are very less soluble in water
* Glycerol is highly viscus and have High boiling points due to more extent of H-bonding.

Glycerol > Glycol > Ethanol

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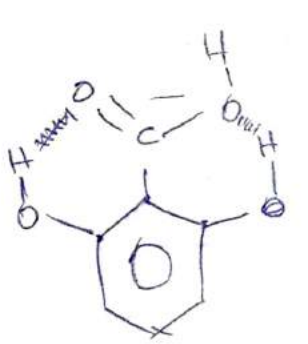
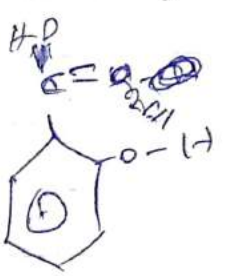
* Acid have High boiling points also dimerized due to H.B
* DNA and RNA Base are Held together by intermolecular H-Bonding

## Intramolecular H.B (chelation)





* Boiling Point, acidic nature, solubility etc decrease but volatile nature increased

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## Reaction Mechanism:

**Path 1** : Substrate + Reagent → Active Complex → Products

**Path II** : Substrate + Reagent → Active Complex →

Products ← (Reaction Intermediate)

## Reaction Intermediate:-

| Carbocation | Carbanion | Free Radical |
|---|---|---|
| $C^{\oplus}$ | $\overset{\ominus}{C}$ | $C^{\circ}$ |

Carbene, Nitrene, Arynes,

## Bond Cleavage:-

| Homalytic | Heteralytic | |
|---|---|---|
| $CH_3 - X$ | $CH_3 - Br$ | $CH_3 - Li$ |
| $\dot{C}H_3 + \dot{X}$ | $\downarrow$ | |
| Free radical | $\overset{\oplus}{C}$ | $^{\ominus}C$ |
| Generation | Ionic | Polar Solvent |
| UV, Non Ionic | | |
| Salvent, Heat | | |
| (non-polar) | | |

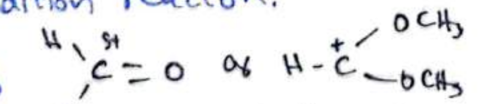
Organic Malecules (Substrate) $\xrightarrow[\text{Reagent}]{\text{Attacting}}$ Intermediat $\longrightarrow$ Product

$\downarrow$

By Product.

## Regent Types:

| Electrophile (~~Nucleous~~ electron Loving species) | Nucleophile (~~electron~~ Nucleous Loving species) |
|---|---|
| * An electrophile is an atom or malecule that can accept an $\bar{e}$ pair | A nucleophile is an atom or malecule that can donate $\bar{e}$ pairs. |
| * Either positively charge or neutral species | Either negatively charged or neutral species. |
| * It must contain one vacant orbital | It contain lone pair of $\bar{e}$. |
| * Electron deficient species | Electron rich species |
| * They are Lewis acids | Lewis bases. |
| * Participate in electrophillic subsitution and addition reacton. | Participate in nucleophillic addition and substitution reactions. |

e.g 

BF$_3$ AlCl$_3$ etc.

$CH_3\overset{\ominus}{O}$ $CH_3\ddot{N}H_2$

$I^-$ $Cl^-$ $\bar{C}N$

## Bond Cleavage:-

| Homolytic | Heterolytic | |
|---|---|---|
| $CH_3 - X$ | $CH_3 - Br$ | $CH_3 - Li$ |
| $\dot{C}H_3 + \dot{X}$ | ↓ | |
| Free radical | $\overset{\oplus}{C}$ | $\overset{\ominus}{C}$ |
| Generation | Ionic | Polar Solvent |
| UV, Non Ionic | | |
| Solvent, Heat | | |
| (non-polar) | | |

Organic Molecules (Substrate) $\xrightarrow[\text{Reagent}]{\text{Attacting}}$ Intermediat $\longrightarrow$ Product
↓
By Product.

## Regent Types:

| Electrophile (~~Nucleus~~ electron Loving species) | Nucleophile (~~electron~~ Nucleous Loving species) |
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| * An electrophile is an atom or malecule that can accept an $\bar{e}$ Pair | A nucleophile is an atom or malecule that can donate $\bar{e}$ pairs. |
| * Either positively charge or neutrall species | Eeither negatively charged or neutral species. |
| * It must contain one vacant orbital | It contain lone pair of $\bar{e}$. |
| * Electron deficient species | Electron rich species |
| * They are Lewis acids | Lewis bases |
| * Participale in electrophillic subsitution and addition reacton. | Participale in nucleophillic addition and substitution reactions. |
| e.g $H(H)C{=}O$ or $H-\overset{+}{C}(OCH_3)_2$ <br> $BF_3$ $AlCl_3$ etc. | $CH_3\overset{\ominus}{O}$ $CH_3\ddot{N}H_2$ <br> $I^-$ $Cl^-$ $\bar{C}N$ |

## Reaction Intermediate:

Those species which are formed during reaction but cannot be isolated as they destroy at once during completion of the reaction.

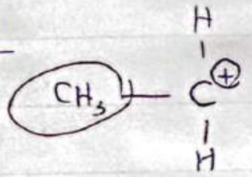
These are Highly reaction and very unstable and short lived.

Types of Reactive Intermediate

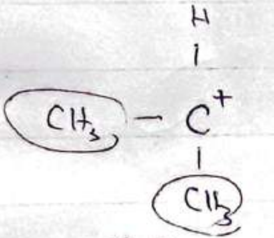
### 1.) Carbocations:-

Has at least on carbon atom with positive charge and 6 ē.
It is $Sp^2$ Hybridized with trigonal coplanar shape. It is diamagnetic in nature. Acts as electrophile and give rise to formation of racemic Mixture.

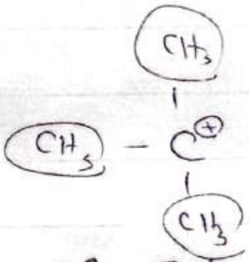
**Types:**



Primary (1°)

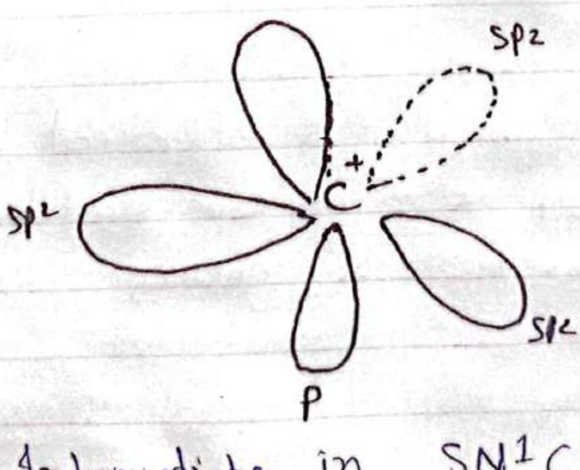


(2°) Secondary



3° Tertiary

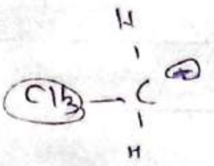
⇒ Some time also called Carbonium Ion. Carbo stand for 'Carbon' and Onium stands for 'Positive charge'.



⇒ Reaction Intermediate in SN1 (Nucleophillic substitution unimolecular), E1 reaction (unimolecular elimination), Electrophillic addition and Molecular rearrangement like pinacole - Pinacolone etc.

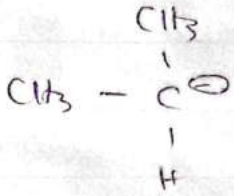
## 2- Carbanion:

Carbanion are anions of carbon having formal charge -1. It is $SP^3$ Hybridized with pyramidal shape. It is magnetic in nature.



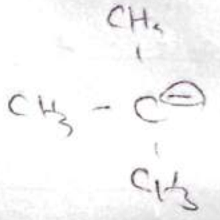
$CH_3-\overset{H}{\underset{H}{C}}^{\ominus}$

1°



$CH_3-\overset{CH_3}{\underset{H}{C}}^{\ominus}$

2°

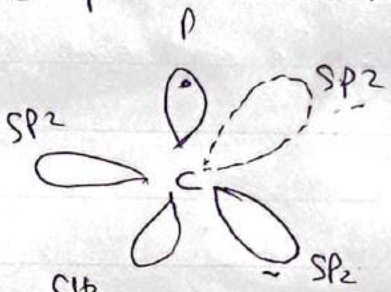


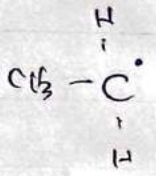
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}^{\ominus}$

3°

## 3- Free radicals

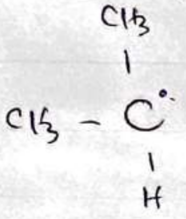
These are atoms or group with a free or odd elections.





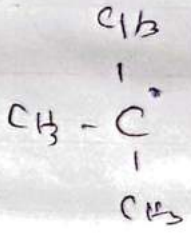
$CH_3-\overset{H}{\underset{H}{C^{\bullet}}}$

1°



$CH_3-\overset{CH_3}{\underset{H}{C^{\bullet}}}$

2°



$CH_3-\overset{CH_3}{\underset{CH_3}{C^{\bullet}}}$

3°

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## Electronic Effects

The behavior of an organic compound is influenced by the electron displacement taking place in its covalent Bonds. These displacement may be permanent or temporay

Electronic Effects

- Permanent
  - (i) Inductive
  - (ii) Hyperconjugation
  - (iii) Resonance
- Temparary
  - Electromeric effect.

## 1- Inductive Effect: (Operate through Sigma (σ) bond)

- * Permanent Dipole
- * Partial charge development not actual transfer of electron
- * Distance dependent effect can be neglected after 3rd Carbon atom
- * Reactivity ∝ Stability of Carbocations

May be

( -I effect )

(Electron withdrawing groups)

They withdraw the electron towards themselves and make others part electron deficient.

e.g $\xrightarrow{}$ $:\overset{+}{N}R_3 > \overset{+}{N}H_3 > NO_2 > CN > COOH > -F > -Cl > -Br > -I > OAr > COOR > OR > COR > SH > RS > OH > C \equiv CR > Ar > HC = CR_2$

(Decreasing order)

( +I effect )

(Electron donating groups)

They push the electron towards the rest of molecule and make it electron rich.

e.g $O^- > CO\bar{O}$ > tertiary alkyl Group ($(CH_3)_3C$) > Secondary alkyl Group ($(CH_3)_2CH$ > Primary alkyl group > Hydrogen

(Decreasing order)

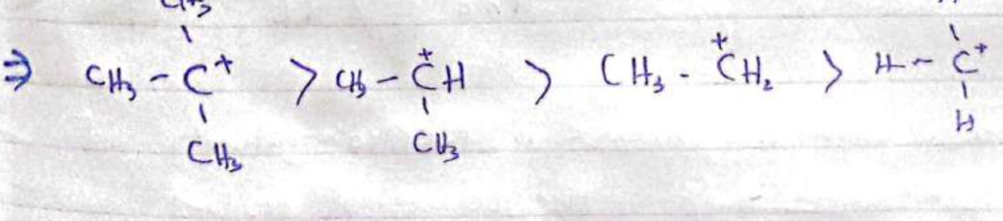
⇒ Application of Inductive effect:-

1- Stability of Carbocation:-

Stability ∝ +I effect

Stability ∝ $\frac{1}{-I \text{ effect}}$

Order of stability t > s > p Carbocations



$$\Rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} > CH_3-\underset{CH_3}{\overset{+}{C}H} > CH_3-\overset{+}{C}H_2 > H-\overset{H}{\underset{H}{C^+}}$$

$$\Rightarrow CH_3-\overset{+}{C}H_2 > \overset{+}{C}H_2-CH_2-C_6H_5 > CH_2Cl-\overset{+}{C}H_2 > CH_2NO_2\overset{+}{C}H_2$$

$$\Rightarrow CH_3\overset{+}{C}HOCH_3 > CH_3\overset{+}{C}HCH_3 > CH_3\overset{+}{C}HCOCH_3$$

$$I-CH_2COOH > CH_3COOH$$

(ii) Reactivity of compounds:-

$CH_3-CH_2 \rightarrow \ddot{C}l:$ or $CH_3-\overset{\delta+}{CH_2}-\overset{\delta-}{Cl}$

(↑ Site for attack of ē rich reagent)

due to (-I effect) alkyl Halide creates a centre of low electron density on adjacent carbon so this carbon is readily attacked by the negatively charged reagents

## (iii) Dipole Moments

-I effect ∝ Dipole Moment

Dipole moment is the product of distance and charge. Greater the power of the group to attract the shared pair of electrons, greater the dipole moment.

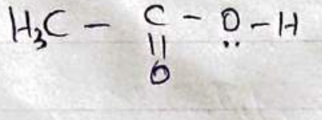
$CH_3 \rightarrow \ddot{I}:$ $CH_3 \rightarrow \ddot{B}r:$ $CH_3 \rightarrow \ddot{C}l:$

1.64 D 1.79D 1.83 D

Inductive effect increases →

## (iv) Acidity of Carboxylic Acids:-

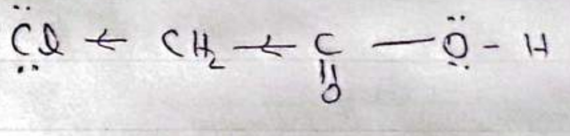
$\boxed{-I \text{ eff} \propto \text{Acidity}}$



$H_3C-\underset{\underset{O}{\|}}{C}-\ddot{O}-H$

Acetic Acid

Pka = 4.76



$:\ddot{C}l \leftarrow CH_2 \leftarrow \underset{\underset{O}{\|}}{C}-\ddot{O}-H$

Chloroacetic Acid

Pka = 2.86

* Acidity also increase with the increase in electronegativity of the Halogen present which help in the release of proton

$FCH_2COOH > Cl-CH_2-COOH > BrCH_2COOH > ICH_2COOH$

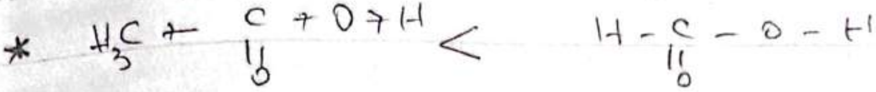
Distance dependent.

*

$CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2COOH > CH_2ClCH_2CH_2COOH > CH_3CH_2CH_2COOH$

α Chlorobutyric acid β chlorobutyric acid γ- chlorobutyric acid n-Butyric acid.

Acitic Acid formic acid



$$* \; H_3C - \underset{\underset{O}{\|}}{C} - O - H \; < \; H - \underset{\underset{O}{\|}}{C} - O - H$$

Pka=4.79 Pka = 3.77

So acitic acid is weaker than formic acid

(Note)
At High temperature
$CH_3COOH > CCl_3COOH$
It is due to thermodynamic
$\Delta G$ is 1.5KJ for $CH_3COOH$
$\Delta G$ is 27KJ for $CCl_3COOH$

(x) Basic Strength of Amines

Greater the tendency to donate electron pair for coordination with proton, more is the basic nature, or more the negative charge on nitrogen atom (due to +I effect of alkyl group) higher is the Basic strength

Strength depend upon +I effect and solvent and also steric Hinderence.

~~For gas phase~~

In gas phase ~~their is no solvent effect so order is~~

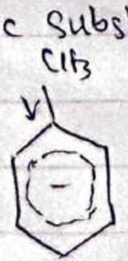
$$(R)_2\ddot{N}H > R\ddot{N}H_2 > (R)_3\ddot{N} > \ddot{N}H_3$$

( Basic strength decreasing order.)

As $(R)_3\ddot{N}$ (t. Amines) is less basic then S.Amines it is because t. Amines is stericilly Hindered and also it has no solvent effect ( Hydrogen bonding) so it is less basic

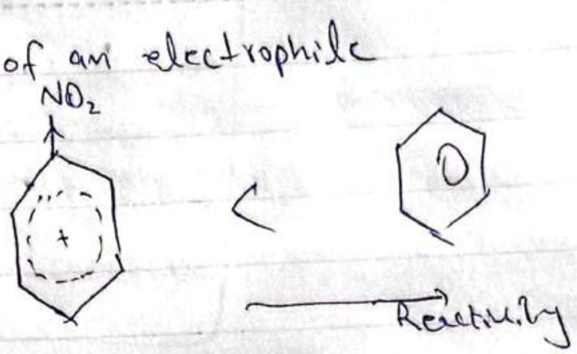
(xi) Relative reactivity of Toluene and Benzene in Aromatic Substitution reaction.

due to Inductive effect (+I) Toluene is more reactive in electrophilic substitution reaction



High electron density more electrophilic substitution

due to (-I) effect decrease the electron availability on ring and decrese the reactivity for benzene ring for the attack of an electrophile



(Less electron Density)


→ $\leftarrow \ddot{O}H > H - \ddot{O}H > CH_3 \rightarrow OH$

(−I effect) (+I effect)

→ Acidic strength ∝ S character

→ Basic Strength ∝ $\frac{1}{\text{S character}}$

$HC \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$

Decreasing acidic strength

$CH_3 - \overset{\ominus}{C}H_2 > CH_2 = \overset{\ominus}{C}H > CH \equiv \overset{\ominus}{C}$

Decreasing order of Basic strength

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~~Note~~

→ Stability of free radical:

Stability ∝ +I ∝ $\frac{1}{-I}$

Same as in case of $C^+$

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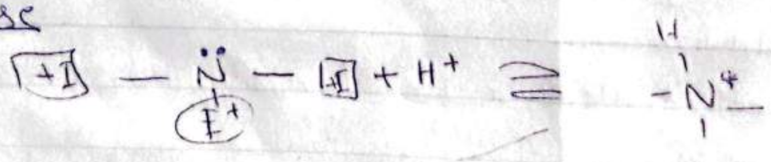
→ Amine Basic strenth

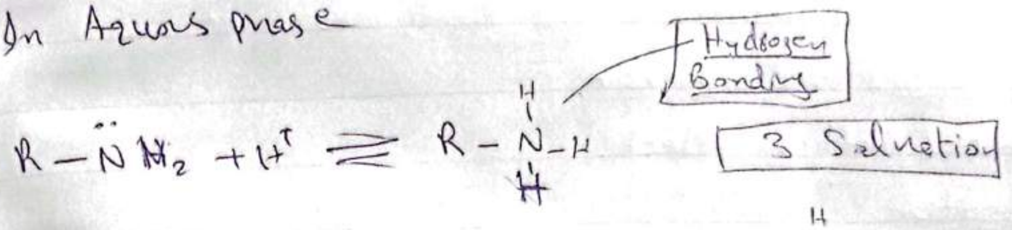
Gas phase


$\boxed{+I} - \underset{\boxed{I^+}}{\ddot{N}} - \boxed{+I} + H^+ \rightleftharpoons -\overset{H}{\underset{|}{N^+}}-$

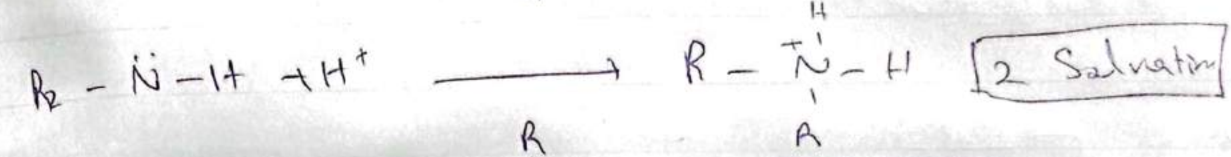
$3^\circ > 2^\circ > 1^\circ$

Note: $\boxed{pKa \downarrow \; Ka \uparrow \; A.S \uparrow}$

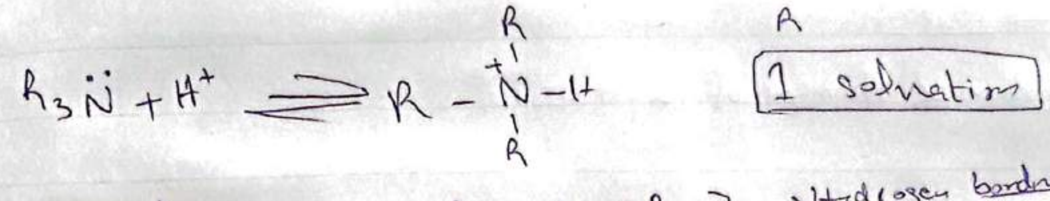
In Aquous phase



$R-\ddot{N}H_2 + H^+ \rightleftharpoons R-\overset{H}{\underset{H}{N}}-H$ $\boxed{3 \text{ Salvation}}$



$R_2-\dot{N}-H + H^+ \longrightarrow R-\overset{H}{\underset{R}{\overset{+}{N}}}-H$ $\boxed{2 \text{ Salvation}}$



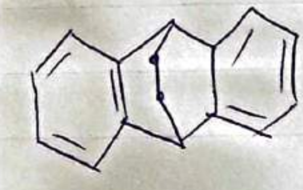
$R_3\ddot{N} + H^+ \rightleftharpoons R-\overset{R}{\underset{R}{\overset{+}{N}}}-H$ $\boxed{1 \text{ solvation}}$

when R = me $2^\circ > 1^\circ > 3^\circ$ } → Hydrogen bonding
when R = Et $2^\circ > 3^\circ > 1$ } → Sterically hindrance.

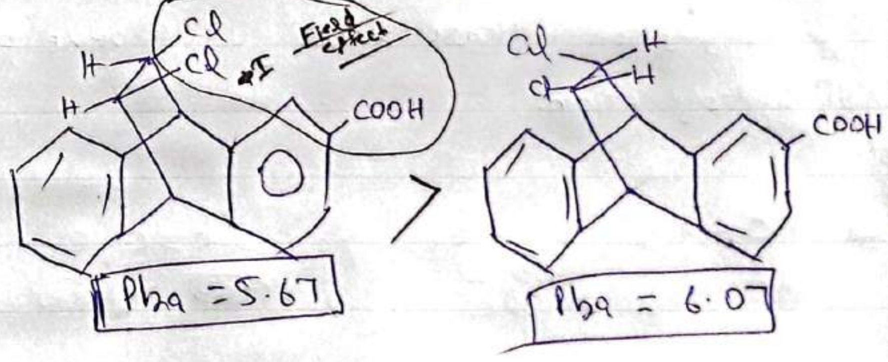
⟷

## Field Effect:

The electrostatic interaction between two charges centre in the same molecule through space or solvent molecules.



Derivation of Anthracene



COOH $\boxed{\begin{matrix}pKa\\2.85\end{matrix}}$ 1st
|
$CH_2$
|
COOH $\boxed{5.70}$ 2nd

} Malonic Acid

$HO_2C-CH_2-COOH + H_2O \rightleftharpoons HO_2C-CH_2COO^- + H_3O^+$

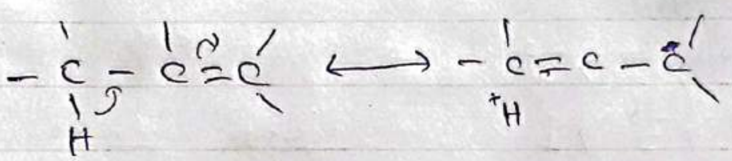
${}^-O_2C-CH_2COOH + H_2O \rightleftharpoons {}^-O_2C-CH_2COO^- + H_3O^+$

## Hyperconjugation:. (also called No Bond resonance)

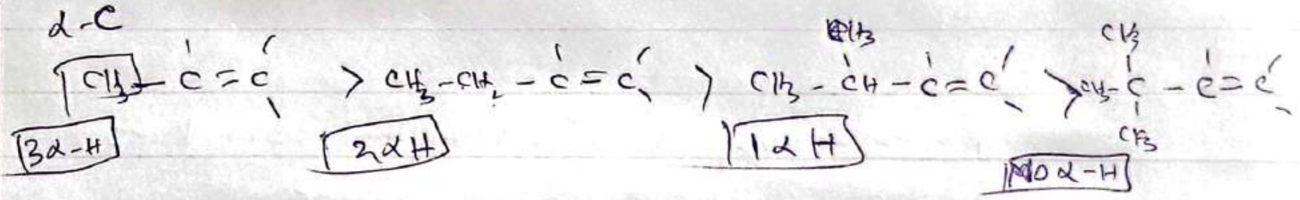
- * Developed by Baber and Nathan
- * also called Baber-Nathan effect.
- * $\sigma - \pi$ Conjugation
- * Conditions:

→ $\alpha$-C → $\boxed{sp^3}$

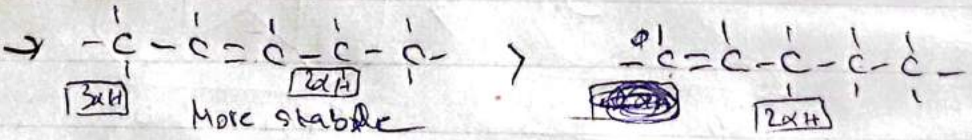
→ Hyperconjugation ∝ Number of $\alpha$-H atoms.

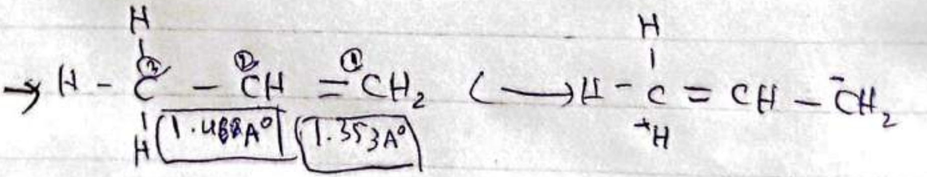


Example :/

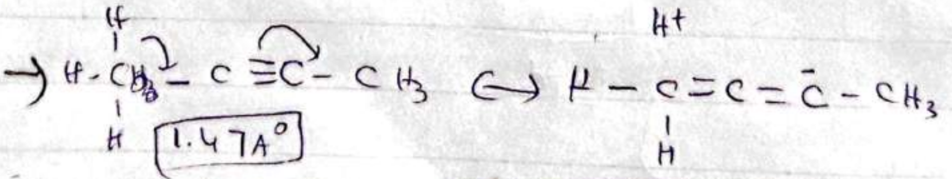


Hyperconjugation increase stability in alkene by decreasing heat of hydrogenation.





$C_2 - C_3 = 146$ pm
Nand = 154 pm
$C_1 = C_2$ = is shorter than ethene



Actual is $\boxed{C-C = 1.54 A°}$

→ Stability of $C^+$ and $\dot{C}$ ∝ Hyperconjugation ∝ N of $\boxed{\alpha\text{-H}}$

## Electromeric (E) Effect:

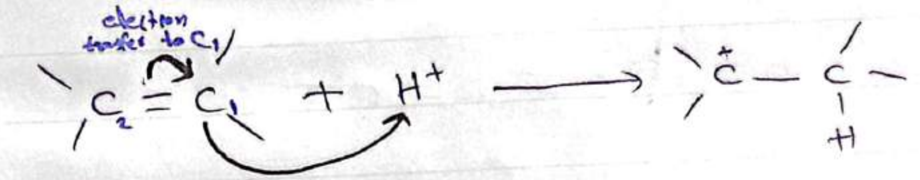
It involve the transfer of π ē by the demand of attacking reagent towards more electronegative species

It may be +E or -E

+E effect:

when transfer of π-ē take place towards the attacking reagent or electrophile, the effect is called +E effect:

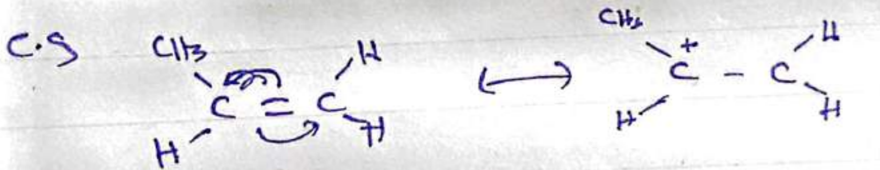
اگر آنے والی چیز میاں اٹیک کریں یہاں ē شفٹ ہو رہے ہوں تو اس کو (+E) کہیں گے۔



Note:

* If both group are same it can be form any side
* If Both the group are differet it is favoured by +I effect favouring direction:

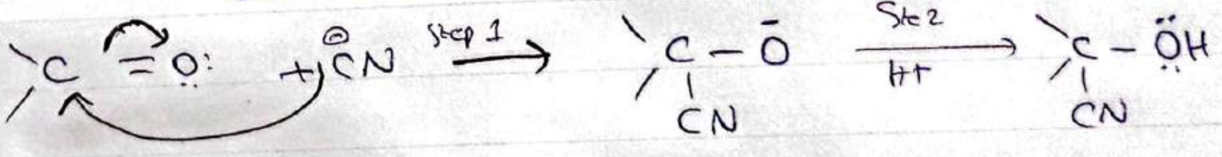
e.g

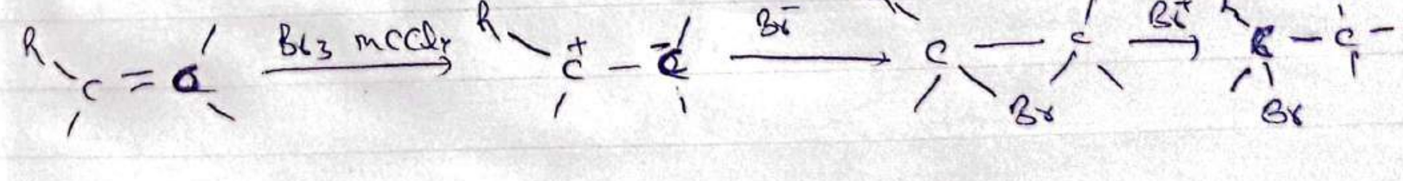


-E effect

~~Here~~ when transfer of ē take place away from attacking reagent then it is called -E effect.

Addition of HCN

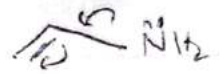




* Helpful to explain mechanism of electrophilic and nucleophilic addition reaction.

## Localized and Delocalized Bond

→ Robinson and Ingold

| Localized Bond | Delocalized Bond |
|---|---|
| ⇒ Those bonds in which the overlapping orbitals are almost in fixed positions are called localized Bonds. | Those bonds in which the overlapping orbitals are ~~almost~~ not in fixed position but in resonance or in conjugation are called delocalized bond. |
| e.g<br>$CH_3-CH_2-CH_3$, $CH_2=CH_2$, $CH\equiv CH$<br>$H_2\ddot{O}:$, $H_2S$, HCN etc.<br>Donot participate in resonance<br> | $C=C-C=C$<br>Participate in resonce<br> |

Some Basic terms.

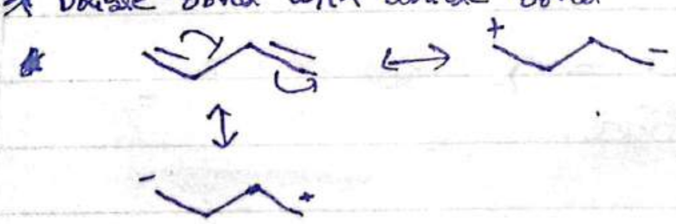
Conjugation:

Alternate single and double bond

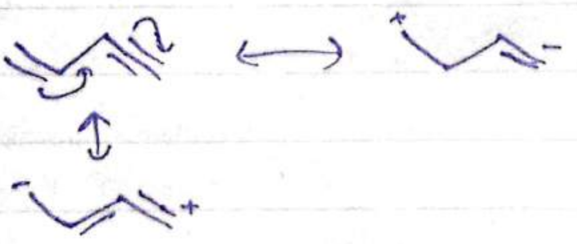
For example $A\boxed{=}B\boxed{-}C\boxed{=}D\boxed{-}E\boxed{=}F$

Conjugation rules

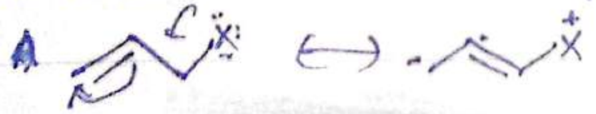
* Double bond with double bond



* Double bond with triple bond

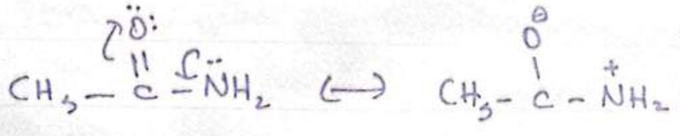


* Double bond with with Lone pair



$CH_2=CH-\underset{..}{\overset{..}{Cl}}: \longleftrightarrow \overset{\ominus}{C}H_2-CH=\underset{..}{\overset{\oplus}{Cl}}:$

Vinyl Chloride



$CH_3-\overset{\ddot{O}:}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{\overset{\ominus}{O}}{\overset{|}{C}}-\overset{+}{N}H_2$

Acetamide

* Douple bond conjugation with (+) charge

$A=B-\overset{+}{X} \longleftrightarrow \overset{+}{A}-B=X$

* A Double bond in congugation with (−) charge

$CH_2=CH-\overset{-}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH_2$

* A Double bond in conjugation with (·) Radical

$\dot{A}-B=C \longleftrightarrow A=B-\dot{C}$

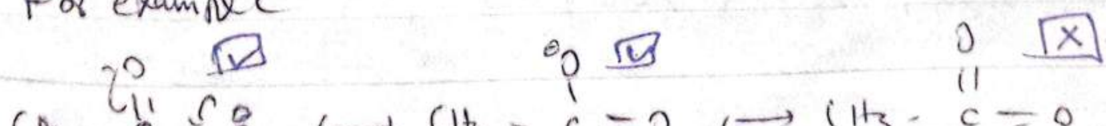
## Resonance Effect:

Decrease in electron density at one position correspond to increase in ē density on other position is called Resonance effect

* Rule for resonance:

→ All contributing structure should follow Lewis Structure

For example

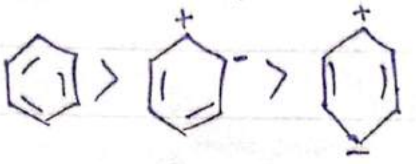


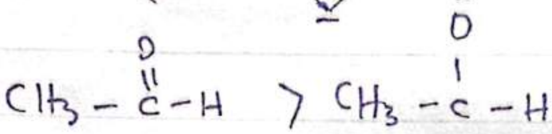
$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\ \boxed{\checkmark} \longleftrightarrow CH_3-\overset{\overset{\ominus}{O}}{\overset{|}{C}}=O\ \boxed{\checkmark} \longleftrightarrow CH_3-\overset{O}{\overset{\|}{C}}=O\ \boxed{X}$

Numbers of covalent bond H - one Oxygen two Nitrogen - 3
Carbon - 4

* Non-polar structure are always more stable the a polar structure

or Neutral R.S > Charge R.S



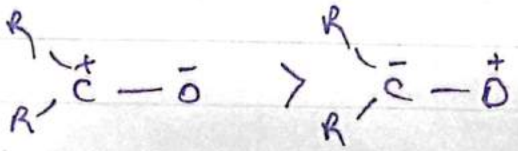


$CH_3-\overset{O}{\overset{||}{C}}-H > CH_3-\overset{\bar{O}}{\overset{|}{C}}-H$

* Greater the covalent bond greater the stability

$CH_3-C\equiv\overset{+}{O} > CH_3-\overset{+}{C}=O$

* Positive charge in on positive atom and negative charge on negative atom is more stable



* Canonical structure in which each atom has octet state is more stable one.

$CH-C\equiv O > \overset{+}{C}H-C=O$

* If the same ~~structure~~ charge are closer, structure will be unstable

$\bar{N}=\overset{+}{N}=O \longleftrightarrow N\equiv N-\ddot{O}:$

$\Updownarrow$ most stable

$N-\overset{+}{N}\equiv\overset{+}{O}$

unstable.

(+, +), (xx, xx) (xx, -) (-, -)

## Criteria of Resonance

- charge bond length

For example
In benzen C-C = 1.39 Å   E C-C = 1.54 Å, C=C = 1.34 Å

Resonance Energy = Energy of most stable Conical structure — Resonance Hybrid energy. (or actual molecule)

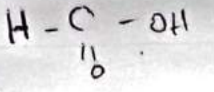
- Resonance Energy ∝ Number of Canonical structure

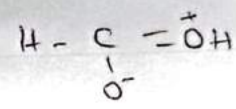
R.E ∝ Stability

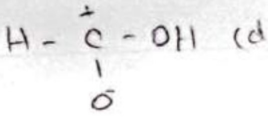
$R.E \propto \frac{1}{Reactivity}$

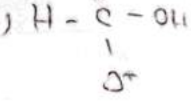
- Benzene   36 K.Cal/mole
- $CO_2$   154.9 KJ/mole

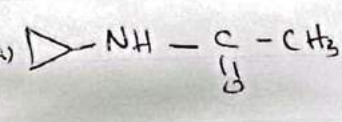
Example:

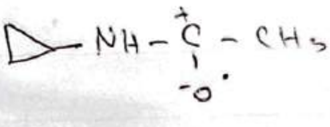
1) (a)

$H-\underset{\overset{\|}{O}}{C}-OH$

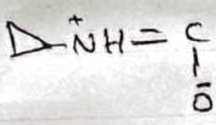
(b)

$H-\underset{\overset{|}{O^-}}{C}=\overset{+}{O}H$

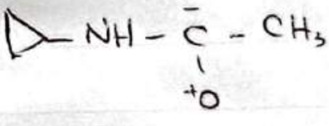
(c)

$H-\underset{\overset{|}{\bar{O}}}{\overset{+}{C}}-OH$

(d)

$H-\underset{\overset{|}{O^+}}{\bar{C}}-OH$

2) (a)

$\triangleright-NH-\underset{\overset{\|}{O}}{C}-CH_3$

(b)

$\triangleright-NH-\underset{\overset{|}{^-O}}{\overset{+}{C}}-CH_3$

(c)

$\triangleright-\overset{+}{N}H=\underset{\overset{|}{\bar{O}}}{C}$

(d)

$\triangleright-NH-\underset{\overset{|}{^+O}}{\bar{C}}-CH_3$

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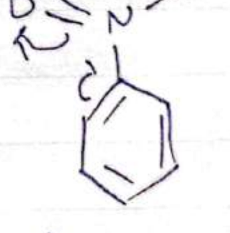
Note


+R (EDa)


-R (EWG)

Activating group
2,4. Directing Groups
Ortho-Para directing
↑ ē density
(OH, NH$_2$, R)

Deactivating
Meta Directing
↓ ē density
Reactivity
Carbonyl Cyano Nitro
Aldehyde Nitro Ethod

## (4) Mesomeric Effect:

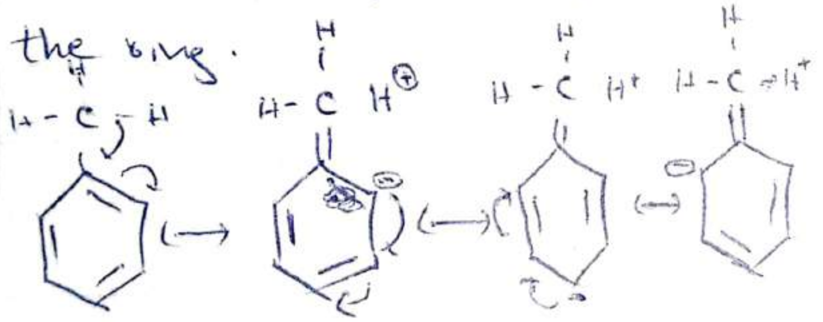
It involves complete transfer of pi-electr. or lone pair of electrons towards more electronegative species.

Types

+M effect

The electron are transferred towards the conjugate system by electron eleasing (+M) groups.

- * Central atom has lone pair of ē to donate. e.g $-\ddot{O}R$, $-OH$, $-\ddot{N}H_2$, $-NHR$, $-NR_2$, $-O-$, $CO-R$, X $-$ (Cl, Br, I)
- * When these groups are attached to Benzene ring the increase the rate of electrophillic substitution reaction.
- * They increase electron density at ortho and para position by activating the ring.

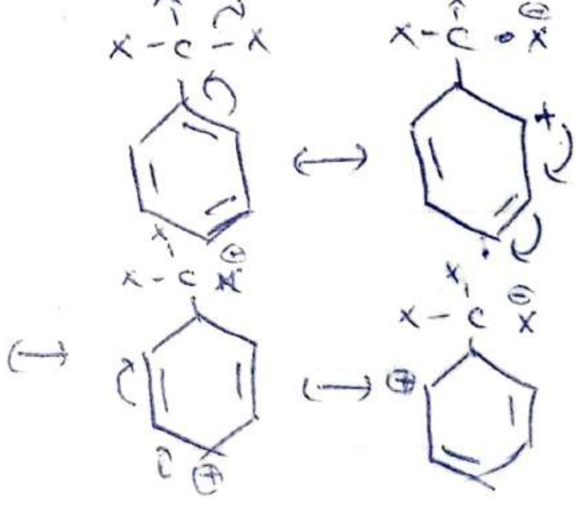


−M effect

The electrons are attracted from conjugate system by the electron withdrawing −M group. Here in −M group central atom is electron deficient and surrounded by more electronegative atoms with multiple bonds.

e.g

$-NO_2$, $-SO_3H$, $-CN$, $-CX_3$, $-COOR$, $-COOH$, $-CO$ etc



Here at meta-position electron density is not effected so electrophilic substitution can take place here

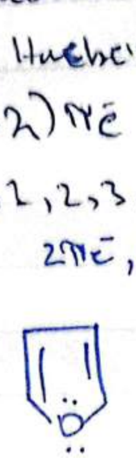
## Aromatic Compound

- * Cyclic
- * Complete conjugation or delocalization of ē -
- * Obey Huckel's rule.

$(4n+2)\pi\bar{e}$

n = 0, 1, 2, 3, 4, 5 etc.

e.g. 2πē, 6πē, 10πē, 14πe⁻



Cyclic ✓
Conjugated ✓
Planer ✓
$(4n+2)\pi\bar{e}$ ✓ $\boxed{6\pi\bar{e}}$

C, C, P 6πe⁻

C, C, P 6πē

6πe⁻
C, C, P Aromatic

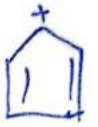
## Anti Aromatic

- * Cyclic
- * Complete conjugation or delocalization of ē.

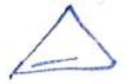
$(4n)\pi\bar{e}$.

n = 1, 2, 3, 4 etc

4πē, 8πē, 12πe⁻ etc.



Cyclic but ~~not~~ ~~conjugation~~. 4πē
so Anti aromatic



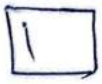
4πē → Anti Aromaz

## Non-Aromatic

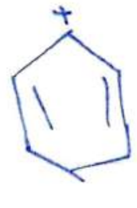
Other compounds which are neither aromatic nor Anti Aromatic they are called non-aromatic.

e.g.

,



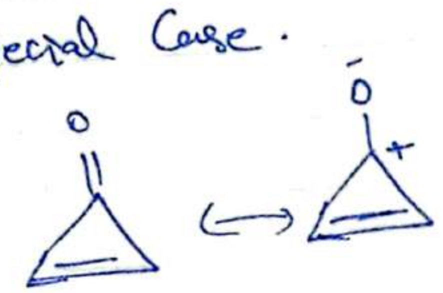
$CH_4$ $CH_3Cl$
$CH_3OH$



not conjugated

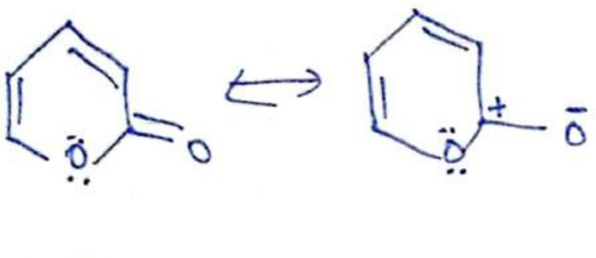
no conjugated

Special Case.



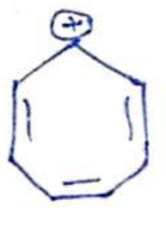
C, C, P $2\pi e^-$

Aromatic



C, C, P

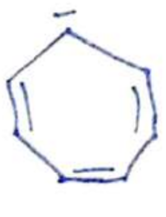
$6\pi e^-$



C, C, P

$6\pi e^-$

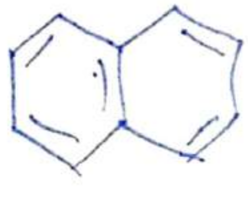
Aromatic



C, C, P

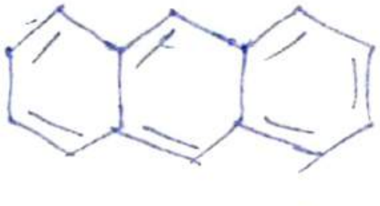
→ Anti aromatic

Stability Aromatic > Non-Aromatic > Anti-Aromatic



C, C, P

$10\pi e^-$ aromatic



C, C, P $14\pi e^-$

Aromatic

~~$12\pi e^-$~~

Highly Stable / ~~Anti aromatic~~

each ring will be aromatic