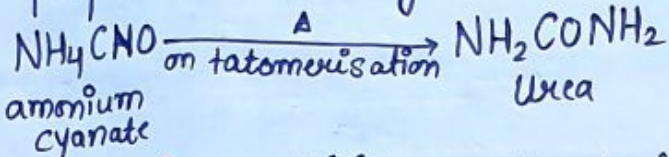


# Organic Chemistry - Some Basic Principles and Techniques..

## Introduction

- Urea is the first organic compound, prepared in lab by Wohler.



- Catenation** → Ability of carbon to form long chains / rings.
- Carbon → Highest catenation ability.

- E.N. of carbon with  $sp >$  carbon with  $sp^2 >$  carbon with  $sp^3$

## %s character & electronegativity of carbon

- Some Characteristic feature of  $\pi$  Bond -

- In  $\pi$  bond formation, parallel orientation of  $2\pi$  orbitals on adjacent atoms is necessary for a proper sidewise overlap

- In  $\text{H}_2\text{C}=\text{CH}_2$  molecule, The  $\pi$  orbitals mutually parallel and both the  $\pi$  orbitals are  $\perp$  to the plane of the molecule. Rotation about C-C double bond in  $\text{C}=\text{C}$  is restricted.

## Tetravalence Of Carbon...

### Structure and Bonding of Carbon in Carbon Compounds..

- Tetravalence of carbon and formation of covalent bonds by it are explained in terms of its **electronic configuration** and the hybridization of s and p orbitals.
- In organic comp. carbon atom undergoes  $sp$ ,  $sp^2$ , or  $sp^3$  hybridisation.

- Determination of Hybridisation in Organic Compounds..

### ① 1<sup>st</sup> method →

No. of $\pi$ bonds	types of hybridisation
0	$sp^3$
1	$sp^2$
2	$sp$

### ② 2<sup>nd</sup> method → Electron pair method.

$$ep = bp + lp$$

[ep = electron pair]  
[bp = bond pair]  
[lp = lone pair]

- Determination of bond pairs:  
No. of bp = no. of atoms present on central atom of the species

Hybridisation	Orbitals involved	% charac. of orbitals	Nature of bonds	Bond angle	Orientation of orbitals
$sp^3$	1s, 3p	S 25    P 75	all $\sigma$ , no $\pi$	$109^\circ 28'$	Tetrahedral
$sp^2$	1s, 2p	33.3    66.6	3 $\sigma$ , 1 $\pi$	$120^\circ$	Planar
$sp$	1s, 1p	50    50	1 $\sigma$ , 2 $\pi$	$180^\circ$	Linear

- Greater the s-character, lower the energy and thus near to the nucleus i.e. orbital is smaller.

- Order of size of different orbitals is  $p > sp^3 > sp^2 > sp > s$

- greater the s-character, of hybrid orbitals, greater is the electronegativity.

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## • Determination of lone pair of electrons →

No. of lp's can be determined as follows:

- If Carbon has  $\pi$  bonds / positive charge / odd electron, then lp on carbon will be zero.
- If carbon has negative charge, then l.p. will be equal to one.

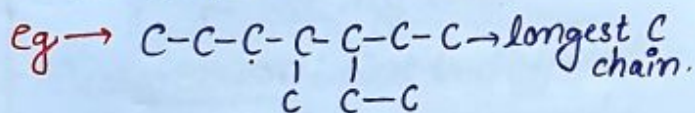
## No. of e<sup>-</sup> pairs tells us type of hybridisation as follows: →

ep	Hybridisation	ep	Hybridisation
2	sp	5	sp <sup>3</sup> d
3	sp <sup>2</sup>	6	sp <sup>3</sup> d <sup>2</sup>
4	sp <sup>3</sup>	7	sp <sup>3</sup> d <sup>3</sup>

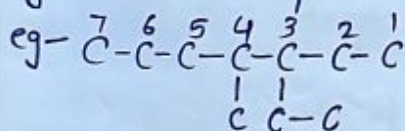
## Nomenclature

### Nomenclature of Branched chain alkanes.

- First of all, longest Carbon chain in the molecule is identified.



- The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atom at which branching takes place due to substituent of alkyl grp. in place of hydrogen atoms. Numbering is done in such way, that the branched carbon atom get the lowest possible numbers.



- Names of alkyl group attached as a branch are then prefixed to the name of the parent alkane and position

of the substituents is indicated by the appropriate numbers.

If different alkyl groups are present, they are listed in alphabetical order. eg → 3 → ethyl, and 4 → methyl.

- If two or more identical substituent groups are present, then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di(2), tri(3), tetra(4) ... are used.

While writing the name of substituents in alphabetical order, these prefix are not considered.

- If the two substituents are found in equivalent positions, lower number is given to the one coming first in the alphabetical listing.

- Branched alkyl groups can be named by following above mentioned procedures. However, carbon atom of the branch that attaches to the root alkane is numbered.

- In multi-substituted compounds, foll. rules may be remembered →

If there happens to be 2 chains of equal size, then that chain is to be selected which contains more no. of side chains.

- After selection of the chain, numbering is to be done from the end, closer to the substituent.

### Nomenclature Of Organic Compounds having Functional Groups →

- Longest chain of carbon atoms containing the functional group is numbered in such a way that the functional grp. is attached at the carbon atom possessing lowest possible number in the chain.



Order of decreasing priority of functional groups  $\rightarrow -\text{COOH} > -\text{SO}_3\text{H} > -\text{COOR}$  (R = alkyl group)  $> \text{COCl} > -\text{CONH}_2 > -\text{CN} > -\text{HC=O} > \text{C=O} > -\text{OH} > -\text{NH}_2 > \text{C=C} > -\text{C}\equiv\text{C}- > \text{X}$  (Halogen)

## ISOMERISM

Phenomenon shown by 2 or more organic compounds having same molecular formula but different properties.

### Isomerism

#### Structural Isomerism

Shown by compounds having same molecular formula but different structural formula.

$\rightarrow$  Chain Isomerism: Shown by compounds having same molecular formula but different carbon skeletons.

$\rightarrow$  Position Isomerism: position of substituent or functional groups are different on carbon skeleton.

$\rightarrow$  Functional Isomerism: Due to difference in nature or functional groups are different.

$\rightarrow$  Metamerism: Due to different nature of alkyl group around a polyvalent functional group.

$\rightarrow$  Tautomerism: single compound exist in 2 readily inter convertible structures that differ in relative position.

#### Stereo Isomerism

Shown by compounds having same molecular formula but different spatial arrangement.

$\rightarrow$  Geometrical Isomerism: Shown by compounds possessing same structural formula but differ in spatial arrangement of the groups around a doubly bonded carbon atoms.

Cis

Like atoms or groups at the same side of the double bond.

Trans

Like atoms or groups across the double bond.

#### Optical Isomerism:

$\rightarrow$  Arises from different arrangement of atoms or groups in 3-D space resulting in 2 isomers which are mirror images of each other..

#### Key Note $\rightarrow$

Tautomerism is not possible in  $\text{C}_6\text{H}_5\text{CHO}$  and  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$  because of absence of  $\alpha$ -Hydrogen.

• Geometrical isomerism due to  $-\text{N}=\text{N}$  bond

eg- a)  $\text{H}_2\text{N}_2\text{O}_2$   $\begin{matrix} \text{N}-\text{OH} \\ \parallel \\ \text{N}-\text{OH} \end{matrix}$   $\begin{matrix} \text{N}-\text{OH} \\ \parallel \\ \text{OH}-\text{N} \end{matrix}$  (anti-isomer)  
(syn isomer)

b) Azobenzene.

$(\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5)$

#### \* Condition for Tautomerism:

For any compound to show tautomerism  $\alpha$ -Hydrogen.

a) Compound should have electron withdrawing groups like

$\begin{matrix} \text{O} \\ \parallel \\ -\text{C}- \end{matrix}$ ,  $-\text{NO}_2$ ,  $-\text{C}\equiv\text{N}$  etc.

b) Compound should have at least one  $\alpha$ -H, i.e., H attached to  $\alpha$ -Carbon

$\text{H}-\text{O}-\text{N}=\text{O} \rightleftharpoons \text{H}-\text{N} \begin{matrix} \nearrow \text{O} \\ \searrow \text{O} \end{matrix}$  Nitro form  
Nitrite form



## Calculation of Number of Optical Isomerism →

- Number of optically active forms =  $2^n = a$   
Number of enantiomeric pair =  $\frac{a}{2}$   
Number of racemic mixture =  $\frac{a}{2}$   
Number of meso form = 0

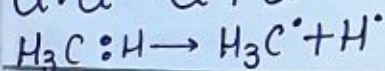
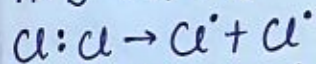
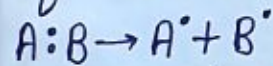
## Fundamental Concept Of Organic Reactions :→

- Fission of a Covalent Bond.  
Depending upon nature of given compound, the nature of attacking reagent and reaction conditions bond cleavage occurs in 2 different ways—

### i) Homolytic Cleavage—

(Equal cleavage of covalent bond)

- In homolytic bond fission, covalent bond is cleaved in such a way that each atom separates with one electron forming highly reactive entities called free radicals.



### ii) Heterolytic Fission —

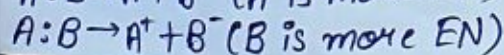
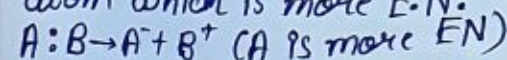
(Unequal cleavage of covalent bond)

- In Heterolytic bond fission, a covalent bond is cleaved in such a way that both the electrons of shared pair are carried away by one of the atoms leading to formation of negative and positive ion pair.

- $\oplus$  charge on Carbon, then cation formed is **Carbo cation**.

- $\ominus$  charge on Carbon, then anion is **Carbanion**.

- Electron pair is carried away by the atom which is more E.N.

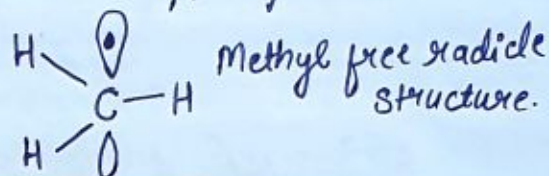


## \* Reaction Intermediates →

Free radicals, carbocations, carbanion, carbenes, nitrenes, benzyne.

## \* Characteristics of Free Radicals.

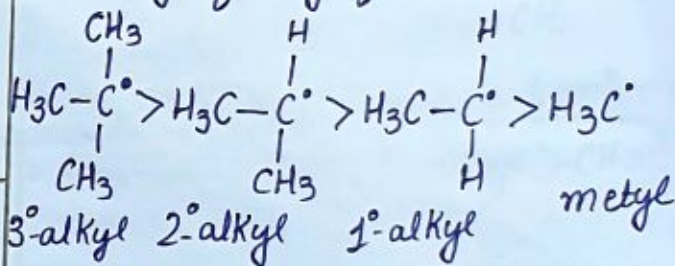
The free radicals are planar and the central carbon atom is in  $sp^2$  hybridisation. The unhybridised  $2p$  orbital of the central carbon atom contains the ~~up~~ unpaired electron.



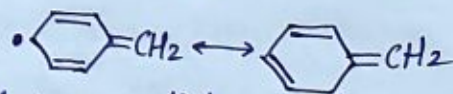
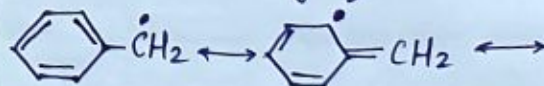
## \* Relative Stability of Free Radicals —

- Alkyl radicals are classified as primary, secondary and tertiary radicals on number of carbon atoms attached to radical.

- Stability of alkyl free radicals can be explained by hyperconjugation and number of resonating structures due to hyperconjugation. Decreasing order of stability of alkyl free radicals.



- Benzyl, allyl free radicals are resonance-stabilised, Hence, they are more stable than alkyl free radical.



Benzyl free radical resonance structure.  
 $H_2C=CH-CH_2^\bullet \leftrightarrow \dot{C}H_2-CH=CH_2$

Allyl free radical resonance structures.  
 $(C_6H_5)_3C^\bullet > (C_6H_5)_2CH^\bullet > (C_6H_5)CH_2^\bullet > H_2C=CH-CH_2^\bullet$

i) No. of resonating structures decreasing.

ii) Decreasing stability.



Both electron-withdrawing groups such as carbonyl, cyano, and electron-donating groups like methoxy and dimethyl amino have stabilising effect on a radical at an adjacent carbon due to resonance.

Stability of various free radicals in decreasing order  $\rightarrow$

$(C_6H_5)_3C^\bullet > (C_6H_5)_2CH^\bullet > (C_6H_5)CH_2^\bullet > H_2C=CH-C^\bullet > (CH_3)_2 > H_2C=CH-CH^\bullet-CH_3 > H_2C=CH-CH_2^\bullet > 3^\circ \text{ alkyl free radical} > 2^\circ \text{ alkyl free radical} > 1^\circ \text{ alkyl free radical} > \text{Methyl free radical}$

2) Carbocations (Carbonium ions)

$\rightarrow$  Stability of Carbonium ions.

Stability of alkyl carbocation is influenced by resonance, hyperconjugation and inductive effect.

Stability decreases as +I effect decreases.  
 $CH_3CH_2CH_2CH_2^+ > CH_3CH_2CH_2^+ > CH_3CH_2^+ > CH_3^+$

If  $\alpha$ -position with respect to carbocationic carbon has an atom with one or more lone pair of electrons, it strongly stabilises the carbocation due to resonance or delocalisation.  $(-NH_2)$  and alkoxy  $(-OR)$  groups are important substituents for such type of carbocations.

$CH_3$   
 $CH_3 \searrow \text{N}^+-CH_2$  and  $CH_3-\ddot{O}^+-CH_2$  are more stable than  $R_3C^+$ .

Allyl and benzyl carbocations are more stable due to resonance.

$H_2C=CH-CH_2^+ \leftrightarrow CH_2^+-CH=CH_2$  (Allyl)

Among allyl and benzyl carbocation, benzyl carbocation is more stable due to more resonating structures and

cyclopropyl methyl carbocations are more stable than benzyl carbocations. Their stability increases with additional cyclopropyl group.

\* Relative stability of carbocations are

benzyl  $>$  allyl  $>$  alkyl  $>$  methyl;  $3^\circ > 2^\circ > 1^\circ$ .

$(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ > (CH_3)_3C^+ > C_6H_5CH_2^+ > CH_2=CH-CH_2^+ > (CH_3)_2CH^+ > CH_3CH_2^+ > CH_3^+ > HC\equiv C^+$

3) Carbanion

$\rightarrow$  Stability of Carbanions.

Following factors  $\uparrow$  the stability of carbanions.

$\rightarrow$  M effect

$\rightarrow$  Delocalisation of negative charge.

$\rightarrow$  I effect.

$\rightarrow$  If  $\alpha$ -position of a carbanion has a functional group which contains multiple bond ( $C=C$ ,  $C=O$ ,  $C\equiv N$ ,  $NO_2$  etc) then carbanions are stabilised by resonance.

eg. of stability order  $\rightarrow$

$CH\equiv C^- > CH_2=CH^- > CH_3-CH_2^-$

\* Relative stability of Carbanions.

Aromatic  $>$  benzyl  $>$  allyl  $>$   $CH\equiv C^- > CH_2=CH^- >$  alkyl (pri  $>$  sec  $\rightarrow$  tert)

$(C_6H_5)_3C^- > (C_6H_5)_2CH^- > C_6H_5CH_2^- > HC\equiv C^- > H_2C=CH^- > CH_3^- > CH_3CH_2^- > (CH_3)_2CH^- > (CH_3)_3C^-$

Stability of carbanion increases with increase in s-character of orbitals.

$R-C\equiv C^- > R_2C=CH^- > R_3C-CH_2^-$  groups like  $-NO_2$ ,  $-CN$ ,  $-COOC_2H_5$ ,  $>C=O$  halogen and  $C_6H_5$  (electron attracting groups) increases the stability of carbanions.



# Types of Reagents:

## # Electrophiles —

- Electrophile means electron seeking species. Electrophiles are the reagents that attack a point of high electron density or negative site.
- Electrophiles are electron deficient species.
- They are either positively charged or neutral, and attack regions of high electron density in substrate molecule.
- They act as Lewis acids. eg-  $\text{H}^+\text{SO}_3$ .

## # Nucleophiles —

- Nucleophile means nucleus seeking or electron hating species. Nucleophiles are the reagents that attack a site of low electron density or positive centres.
- Nucleophiles are electron donating species. They are either negatively charged or neutral molecules with free electron pairs to donate.
- They act as Lewis bases. eg-  $\text{Cl}^-$ ,  $\text{C}_2\text{H}_4$

## # Electron displacement in Organic compounds →

Types of electronic displacement are:

Electron displacement in covalent bond

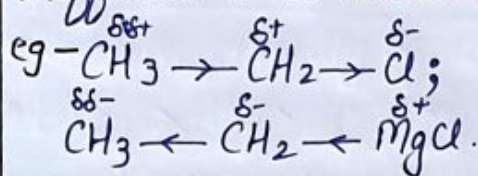
- 1) Inductive effect
- 2) Resonance effect
- 3) Mesomeric effect
- 4) Hyperconjugation
- 5) Electromeric effect (temporary effect).

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## 1) Inductive effect —

polarisation of  $\sigma$  bond caused by the polarisation of adjacent  $\sigma$  bond is referred to as **inductive effect**.

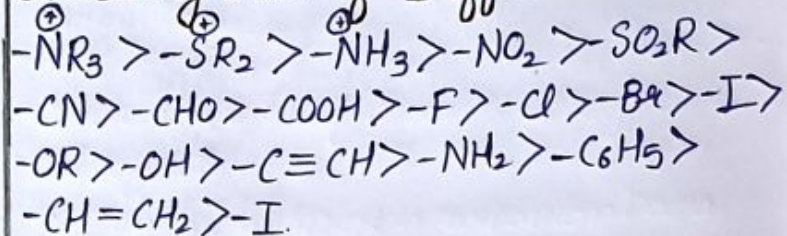


Inductive effects are of two types:-

### ① -I effect.

The atom or group which withdraws electron clouds is known as -I group and effect is called -I effect.

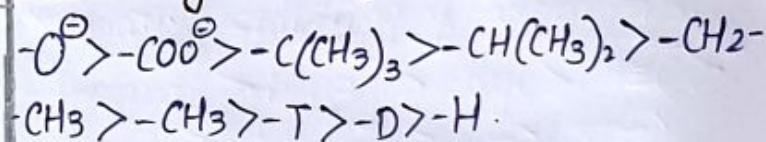
Decreasing order of -I effect:



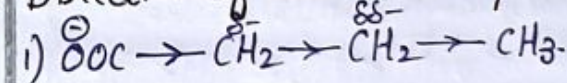
### ② +I effect.

The group which releases or donates electron clouds is known as +I group and effect is called +I effect.

Decreasing order of +I effect:



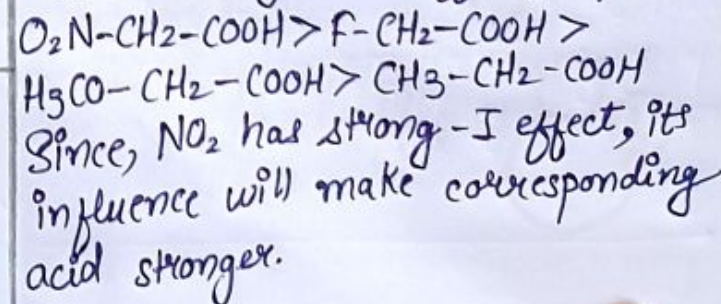
Direction of electron displacements.



## # Applications of Inductive effect:-

1) Acidic Strength: presence of -I groups increases acidic character.

Acidic strength -I effect groups.





## ii) Basic Strength:

Basic strength + I effect  
 $\text{CH}_3\text{-NH}_2 > \text{NH}_3$ ;  $\text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

## iii) Dipole moment: Greater I effects results in greater dipole moment.

$\mu = \text{CH}_3\text{NO}_2 > \text{CH}_3\text{COOH} > \text{CH}_3\text{F} > \text{CH}_3\text{OH}$

## (2) Resonance Structure

- Resonance structures are hypothetical and individually do not represent any real molecule.
- Difference in energy b/w the actual structure and lowest energy resonance structure is called **resonance stabilization energy**.
- +R effect: -halogen, -OH, -OR, -OCOR, -NH<sub>2</sub>, -NHR, -NR<sub>2</sub>, -NHCOR.
- R effect: -COOH, -CHO, >C=O, -CN, -NO<sub>2</sub>.

## (3) Electromeric Effect (E effect)

- Complete transfer of a shared pair of  $\pi$ -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.
- Positive electromeric effect (+E effect):  
In this effect,  $\pi$ -electrons of the multiple bond are transferred to that atom to which, the reagent gets attached.
- Negative electromeric effect (-E effect):  
In this effect,  $\pi$ -electrons of multiple bond are transferred to that atom to which, attacking reagent does not get attached.

## (4) Mesomeric Effect

- Electron pair displacement caused by atom or group along a chain by a conjugative mechanism is mesomeric effect of that atom. It is denoted by M.

## (i) +M effect.

- Groups that tend to increase the electron density of rest of molecule are said to have +M effect. These groups possess lone pair of electrons.
- Down the group, electron density decreases due to increase in size, as result +M effect decreases.  
-F > -Cl > -Br > -I;  
-OH > -SH > -SeH.  
-OR > -SR > -SeR.
- With decreasing the basic strength, electron releasing tendency, as result +M effect decreases.  
-NR<sub>2</sub> > OR > F,  
-NH<sub>2</sub> > -OH > -F;  
-O > -OR.

## (ii) -M effect.

- Groups that had to decrease the electron density of rest of the molecule are said to have -M effect.
- Group exhibiting -M effect possess multiple bond and -M effect can be compared, based on electronegativity.  
 $=\text{O} > =\text{NR} > =\text{CR}_2$   
 $=\text{NR}_2 > =\text{NR}$   
 $\equiv\text{N} > \equiv\text{CR}$   
NO<sub>2</sub>, >COOH, >CHO, >HSO<sub>3</sub> and >CONH<sub>2</sub> also have (-M) effect.
- Halogens have -I effect but with lone pairs they have +M effect. These two operate in opposite directions.

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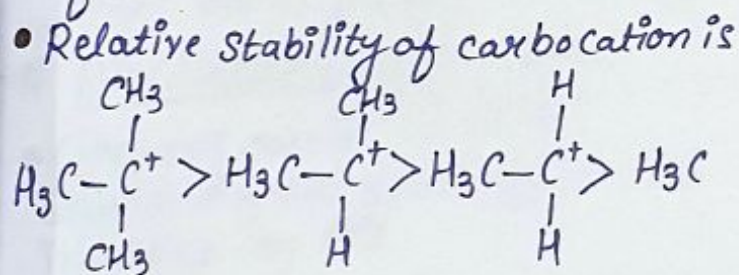
## ⑤ Hyperconjugation

- It involves delocalisation of  $\sigma$  electrons of C-H bond of an alkyl group directly attached to an atom of unsaturated system  $sp^2$  or to an atom with unshared p-orbital.
- $\sigma$  electrons of C-H bond of alkyl group enter into partial conjugation with attached unsaturated system  $sp^2$  or with the unshared p-orbital.
- Hyperconjugation is permanent effect.

∴ Condition for hyperconjugation.

- Compound should have at least one  $sp^2$ -hybrid carbon.
- $\alpha$ -carbon with respect to  $sp^2$ -hybrid carbon should be  $sp^3$ .
- $\alpha$ -carbon should have at least one hydrogen.

- Greater the no. of alkyl groups attached to a positively charged carbon atom, greater is the hyperconjugation interaction and greater is stabilisation of cation.



- Hyperconjugation is also possible in alkenes and alkylarenes

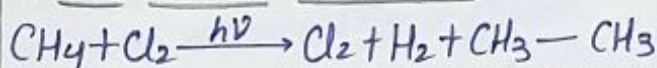
No. of hyperconjugative structures = No. of  $\alpha$ -Hydrogens + 1

notes by -  
Sasha ♡♡♡

## Types Of Organic Reactions

### ① Substitution Reactions.

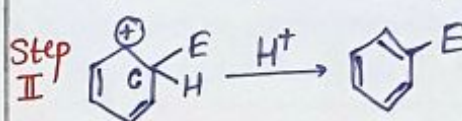
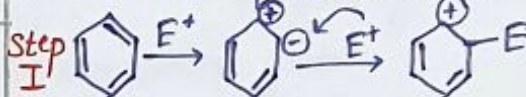
a) Free radical substitution.



b) Electrophilic substitution (Ring substitution).

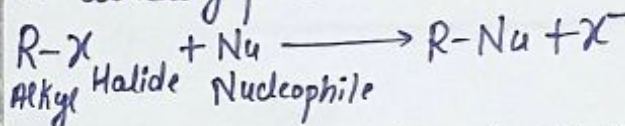
1) 2 step reaction

2) Carbocation formed as intermediate.



c) Nucleophilic Substitution.

Better nucleophile replaces the nucleophile already present.

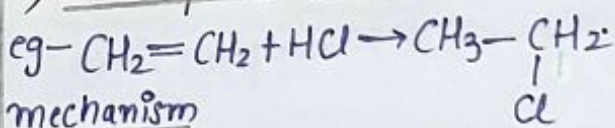


### Types of Electrophilic Substitution Rxn

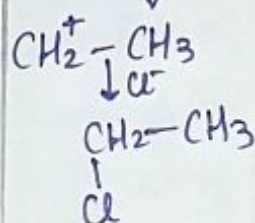
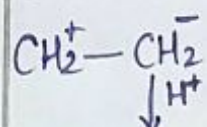
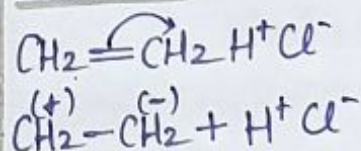
- Halogenation
- Nitration
- Sulphonation
- Friedel crafts reaction

### ② Addition Reactions (presence of multiple bond is required).

a) Electrophilic Addition reaction.



mechanism





eg-  $\text{C}^{(+)}=\text{O}^{(-)} + \text{H}^+\text{CN} \rightarrow \text{C}(\text{OH})(\text{CN})$

## Dehydrohalogenation

Alkyl Halide

$$\text{CH}_3-\underset{\text{Cl}}{\text{CH}_2} \xrightarrow{\text{KOH (Alcoholic)}} \text{CH}_2=\text{CH}_2 + \text{KCl} + \text{H}_2\text{O}$$

## Methods of purification of Organic Compounds

- Chloroform (b.p. 334K) and aniline (bp 457 K) are easily separated by the technique of distillation.

- Separate different fractions of crude oil in petroleum industry.

- Glycerol can be pressure separated from spent-lye in soap industry by this.

- Aniline is separated by this method from aniline water mixture.
- Steam distillation is applied to separate substances which are steam volatile and immiscible with water.

★ Adsorption Chromatography:  
diff. compounds are adsorbed on an adsorbent to diff. degrees.

Column Chromatography: Separate single chemical compound from a mixture dissolved in a fluid.

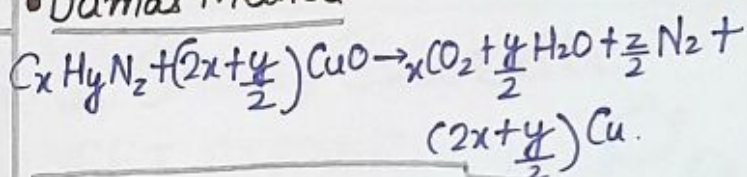
$R_f$  value = Distance moved by substance from baseline (x)

Distance moved by solvent from baseline (y)

- paper chromatography is an example of partition chromatography.

## Qualitative Analysis Of Organic Compounds

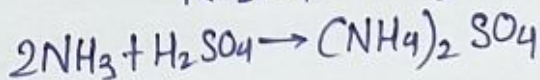
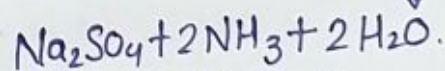
- Dumas Method



$$\% \text{ of Nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

$m$  = mass of organic compound.  
 $V$  = Vol. of nitrogen collected

Organic compound +  $H_2SO_4 \rightarrow (NH_4)_2SO_4$   
| 2NaOH



Vol. of  $H_2SO_4$  of molarity  $M$  taken =  $V$  ml.

Vol. of NaOH of molarity  $M$  used for titration of excess of  $H_2SO_4 = V_1 \text{ ml.}$

$$V_2 \text{ ml of NaOH of molarity } m$$

$$= \frac{V_1}{2} \text{ ml of H}_2\text{SO}_4 \text{ of molarity } m$$

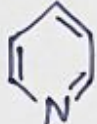


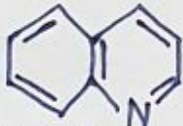
Volume of  $H_2SO_4$  of molarity  $M$   
unused  $= (V - \frac{V_1}{2}) \text{ mL}$ .

$$\% \text{ of N} = \frac{14 \times M \times 2 (V - \frac{V_1}{2})}{1000} \times \frac{100}{m}$$
$$= \frac{1.4 \times M \times 2 (V - \frac{V_1}{2})}{m}$$

### Key Note

Kjeldahl's method is not applicable to compounds containing nitro ( $-NO_2$ ), Nitroso ( $NO$ ), azo group ( $-N=N-$ ), azoxy compounds  $[-N=\overset{O}{N}-]$  and nitrogen

present in ring (pyridine ,

quinoline ) because nitrogen

present in these compounds is not quantitatively converted into ammonium sulphate.

My index finger got injured badly, as I wrote for 13 hours straight. 😞

Study Hard

### Some Important Formula

① % of Halogen =

$$\frac{\text{atomic mass of } X \times m_1 \times 100}{\text{mol. mass of } AgX \times m}$$

$X \rightarrow$  Halogen.

$m_1 \rightarrow$  mass of  $AgX$

$m =$  mass of organic compound

② % of Sulphur =  $\frac{32 \times m_1 \times 100}{233 \times m}$

$m =$  mass of organic compound.

$m_1 =$  mass of  $BaSO_4$ .

③ % of phosphorus =  $\frac{62 \times m_1 \times 100}{222 \times m} \%$

$m_1 =$  mass of ammonium phosphomolybdate

④ % of Oxygen =  $\frac{32 \times m_1 \times 100}{88 \times m} \%$

$m_1 =$  mass of  $CO_2$  produced

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