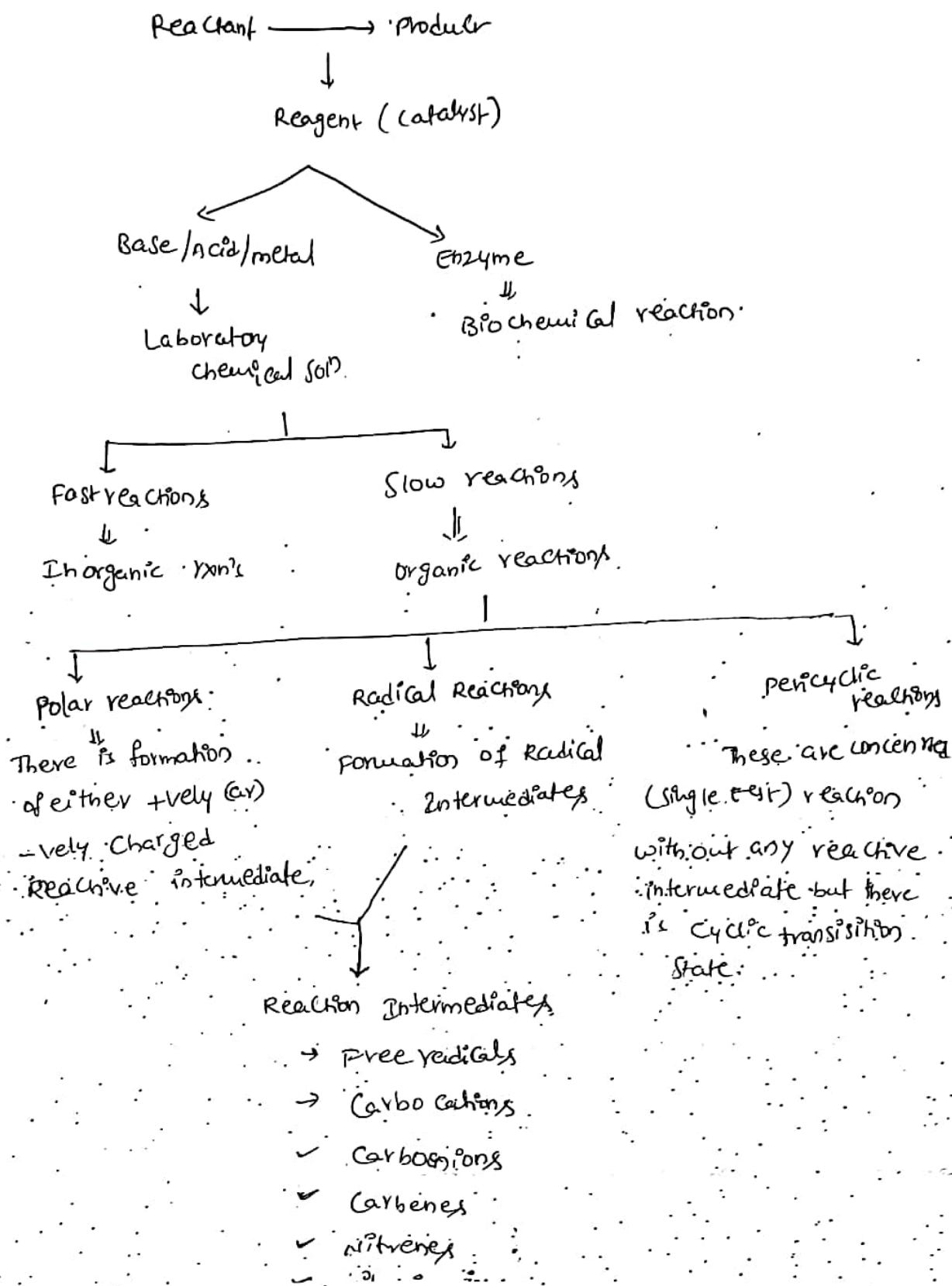


27/05

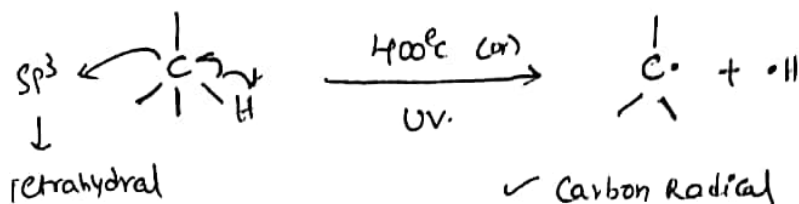
TYPES OF CHEMICAL REACTIONS

①



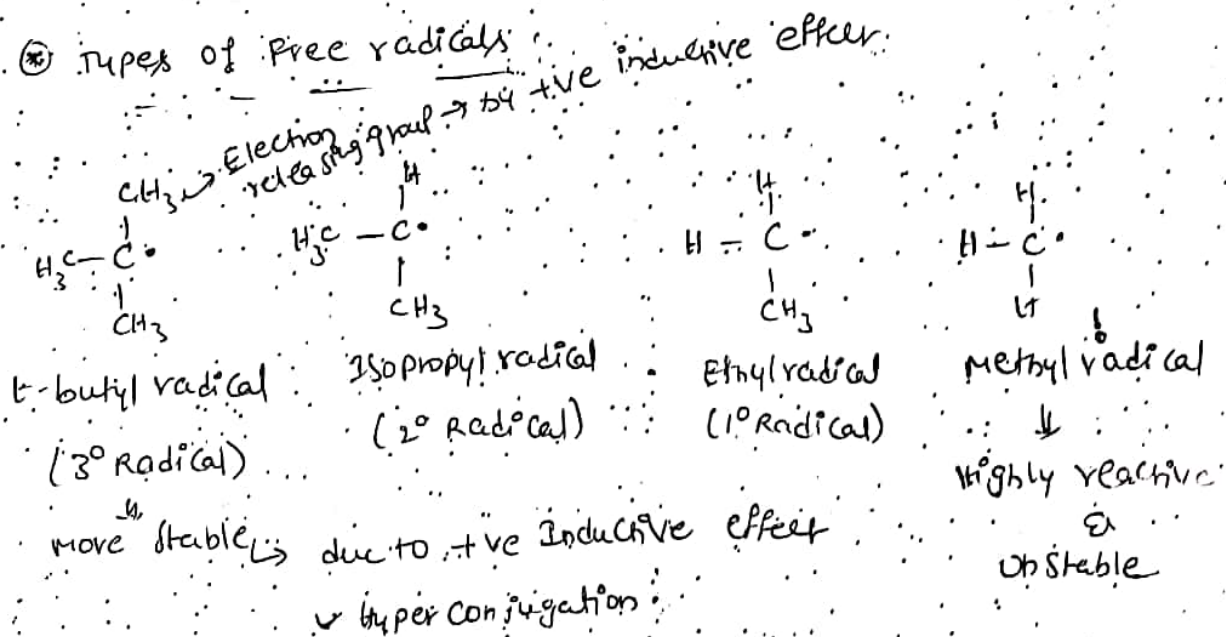
① Free Radicals :

Are formed by homolytic cleavage



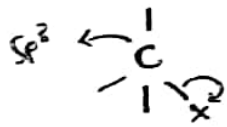
- ✓ Carbon Radical
- ✓ sp² hybridization
- ✓ Trigonal Shape
- ✓ Odd no. of electron (7e⁻)
- ✓ Electrically neutral (due to NO charge)
- ✓ Highly reactive (Unstable)
- ✓ Free radicals due to their high reactivity can interact with DNA cause mutations leading to cancer.
- ✓ Free radicals are paramagnetic as they are influenced by magnetic field due to presence of odd no. of electrons.
- ✓ Free radicals are detected by ESR - Electron spin resonance spectroscopy (or) EPR → Electron paramagnetic resonance spectroscopy

② Types of Free radicals :



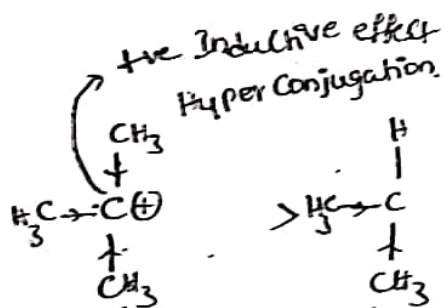
② Carbo Cation

②



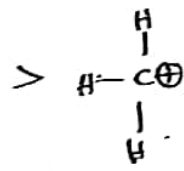
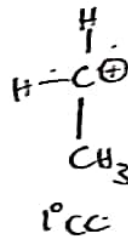
Carbo Cation \Rightarrow +vely charged species are decreased detected by Mass Spectrometry.

- ✓ sp^2
- ✓ Trivalent
- ✓ Planar
- ✓ Electron deficient
- ✓ Electrically not neutral.



3° CC

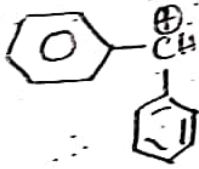
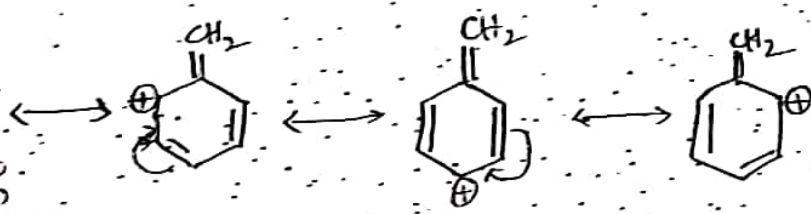
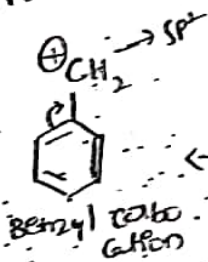
2° CC



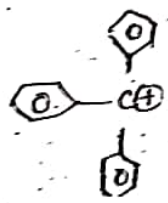
Methyl Carbocation

More reactive,
less stable

More stable

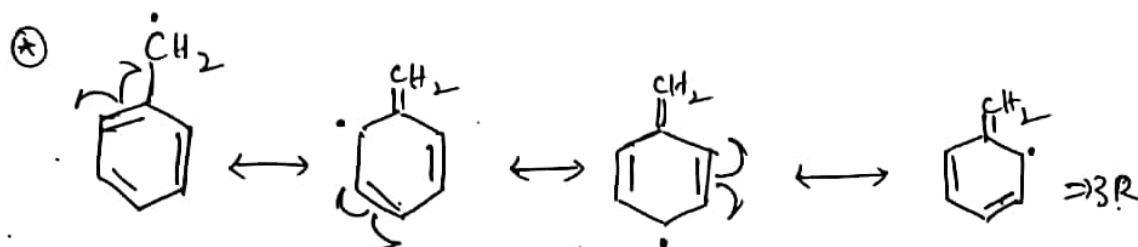


Diphenyl methane CC \Rightarrow 6-R

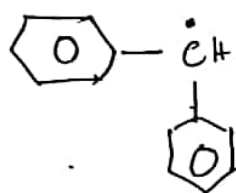


Triphenyl methane CC \Rightarrow 9 Resonances

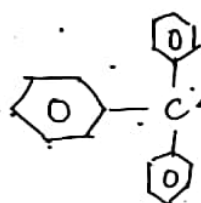
* Benzyl c.c, Diphenyl methane c.c, Triphenyl methane c.c as well as Benzyl radical, diphenyl methane radical, triphenyl methane radical are stabilised due to resonance



Benzyl radical (Less stable)



Diphenyl methane radical $\Rightarrow 6R$

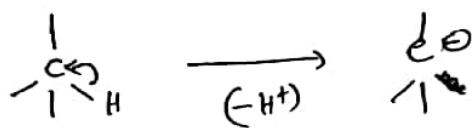


$\Rightarrow 9R \Rightarrow$ Triphenyl methane radical
More stable

3)

Carbanion:-

③

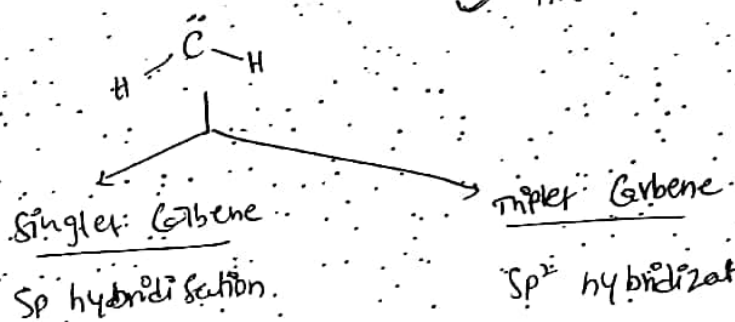
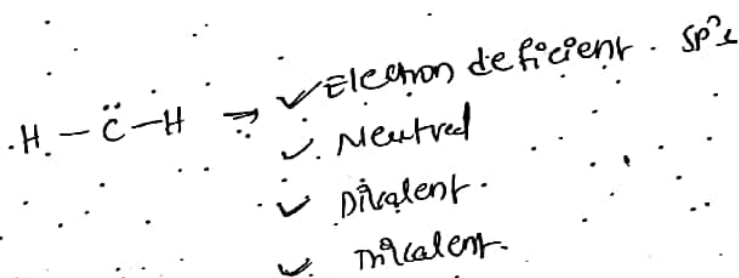


- ✓ trivalent
- ✓ electron rich
- ✓ pyramidal shape
- ✓ Influenced by the electrical field.

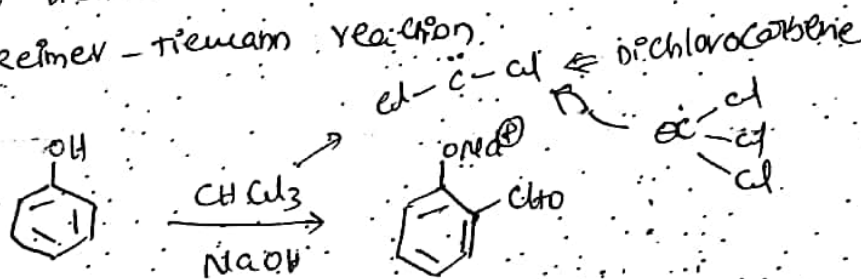
3° Carbanion < 2° Carbanion < 1° Carbanion < Methyl Carbanion
 (Less stable) (more stable)
 (more reactive) (least reactive)

* Carbanions will get stabilized by losing their electrons.

④ Carbenes:-



* Dichloro carbene is an reactive intermediate in Reimer-Tiemann reaction.



⑤ Nitrene:

- N: \leftarrow Electron deficient nitrogen
- Neutral
- \checkmark 2 lone pair of electrons

Nitrenes found as a reactive intermediate in Hofmann's, Curtius, and Lossen rearrangements.

Nitronium ion

NO_2^+ \Rightarrow By reaction of conc. $\text{HNO}_3 + \text{H}_2\text{SO}_4$
 \rightarrow Electrophilic aromatic Substitution Reaction.

Attacking agents

① Free radical

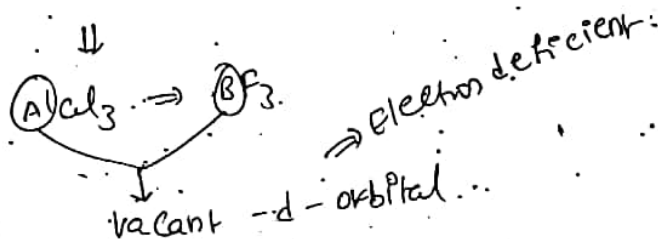
② Electrophile:

Strong electrophile \Rightarrow +ve charged

- Carbocation $\Rightarrow \text{C}^+$
- Chloronium ion $\Rightarrow \text{Cl}^+$
- Bromonium ion $\Rightarrow \text{Br}^+$
- Nitronium ion $\Rightarrow \text{NO}_2^+$

\checkmark It is an electron deficient species which loves e^- s.

$E =$ Neutral electrophile \Rightarrow weak electrophile



③ Nucleophile: \Rightarrow love +ve charge

\checkmark Electron rich species

$\text{Nu}^- \Rightarrow$ charged nucleophiles $\Rightarrow \text{Cl}^-, \text{Br}^-, \text{CN}^-, \text{OH}^-, \text{NH}_2^-, \text{amide ion}$

$\text{Nu} =$ Neutral nucleophile \Rightarrow They have lone pair of electrons

$\rightarrow \text{NH}_3, \text{H}_2\text{O}, \text{R-OH}, \text{R-NH}_2$ } used as solvents

Free radical Substitution \Rightarrow Alkanes

" " Addition \Rightarrow Alkenes

Electrophilic Substitution \Rightarrow Aromatic compounds

" " Addition \Rightarrow Alkenes

Nucleophilic " \Rightarrow Carbonyl compounds

31/05/19
27/05/19

Electron displacement effects ①

Migration of electrons within the same molecule.

Inductive effect
Mesomeric effect
Hyperconjugation effect } Permanent effects
Electromeric effect } Temporary effect.

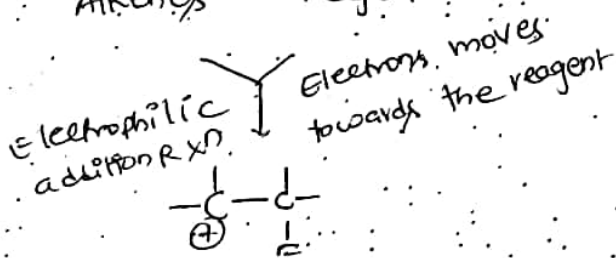
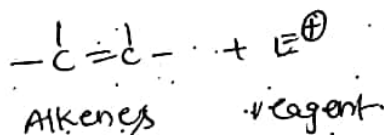
* permanent effects: They are operated continuously without the influence of any external reagent.

* Temporary effect: As this occurs only in the presence of a reagent.

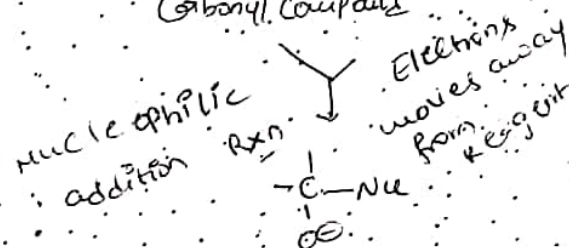
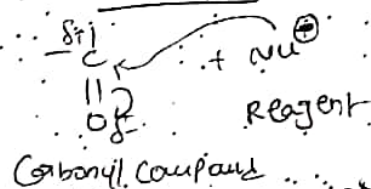
* Electromeric effect:

In this effect there is instantaneous and complete transfer of π -electrons in the presence of a reagent.

+E effect:

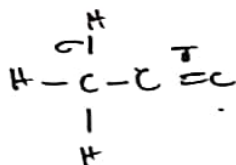


-VE Effect

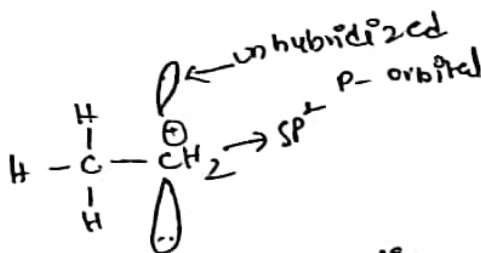


Hyper Conjugation / No bond Resonance:

Hyper Conjugation is the conjugation of $\sigma - C-H$ with

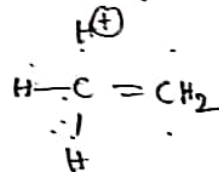
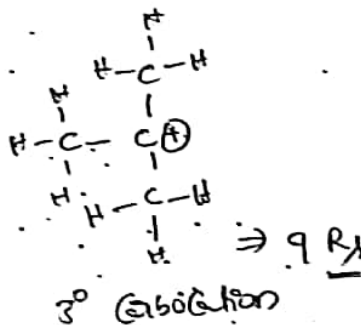
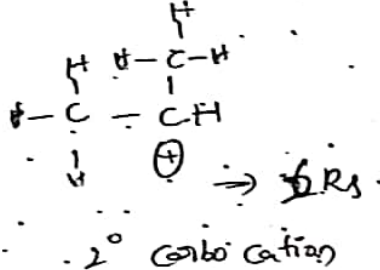
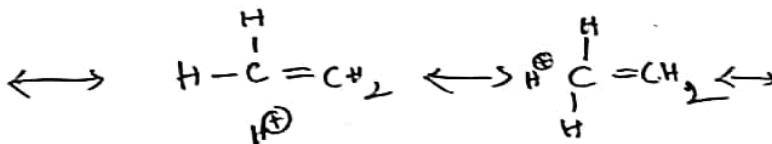
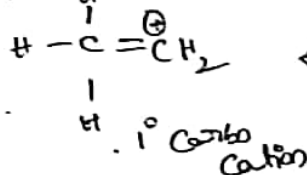


$\sigma - \pi$ Hyper Conjugation



$\sigma - p$ Hyperconjugation

$\sigma - p$ Hyper Conjugation



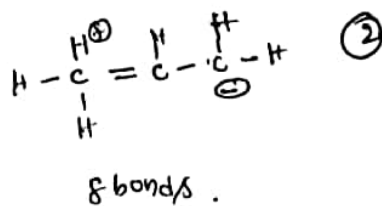
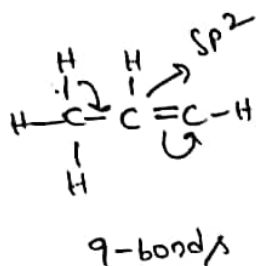
$CH_3^+ \Rightarrow$ No Hyper Conjugation

$CH_3 \Rightarrow$ Not Stabilised by $H-C$ (w) Inductive Effect

* Isovalent HC

Same no. of bonds in the Resonating structures

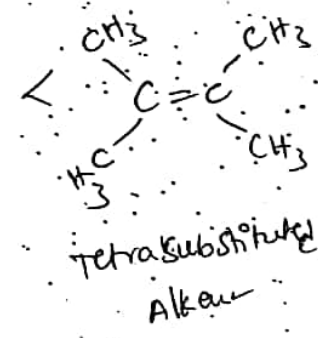
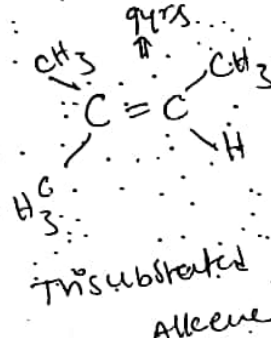
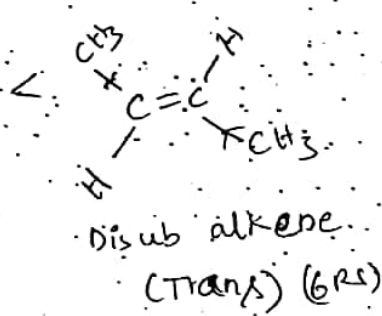
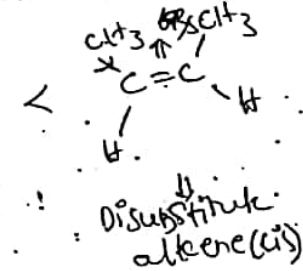
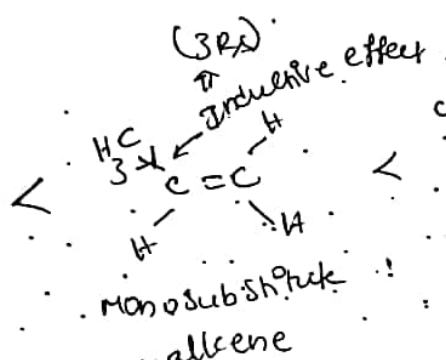
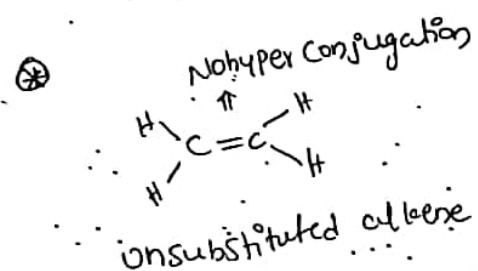
$\sigma - \pi$ Hyper Conjugation: It is a Sacrificial Hyper Conjugation



- ✓ Hyper Conjugation used to stabilize the alkenes.
- ✓ More substituted alkenes are more stable.



- ✓ $3^\circ \text{R} > 2^\circ \text{R} > 1^\circ \text{R}$



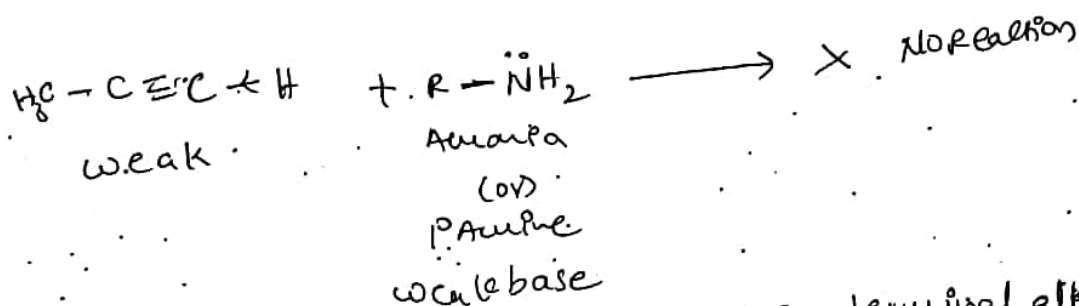
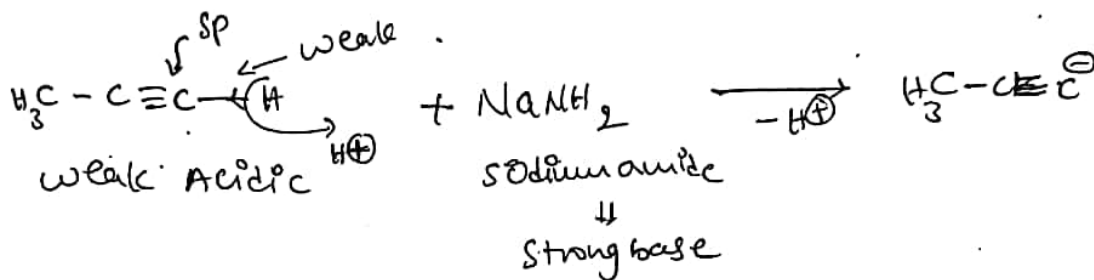
(12Rs)

* The stability of substituted alkene is due to

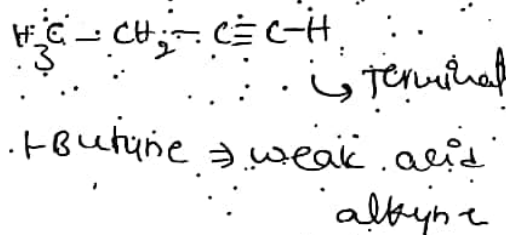
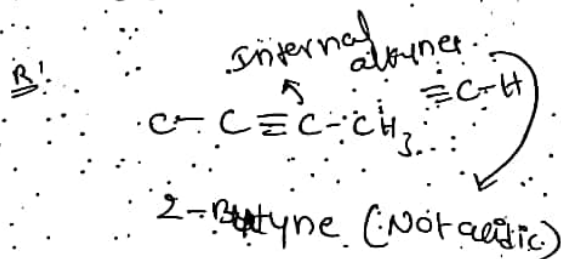
1. $\sigma-\pi$ hyper conjugation &
2. +ve Inductive effect

④ sp hybridisation containing alkynes are weak acids

✓ Compound containing sp hybridized C-atom bond hydrogen \rightarrow weak acids.



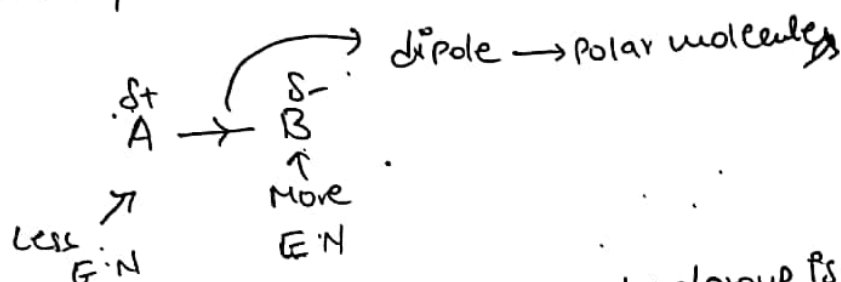
* Internal alkynes are not acidic, terminal alkynes are acidic.



* Inductive effect: (IE) ③

✓ It is the movement of σ -electrons toward atoms (or) group in covalent bonds.

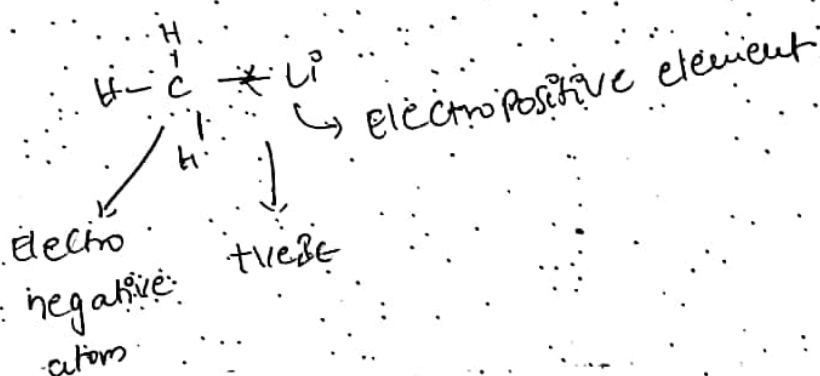
✓ Generally IE induces polarity in a molecule

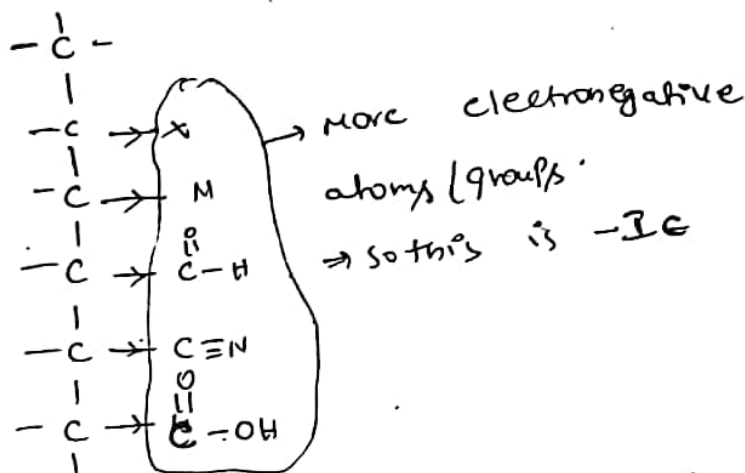


✓ I.E. $\left\{ \begin{array}{l} +IE \Rightarrow \text{seen when the atom/group is less electronegative than hydrogen.} \\ -IE \Rightarrow \text{seen when the atom/group is more electronegative atom than hydrogen.} \end{array} \right.$

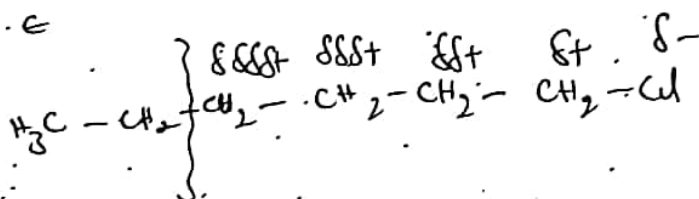
✓ $+IE$ is seen in alkyl groups (or) Electron releasing group and with electropositive elements.

Methyl Lithium:





⑧ Inductive effect operates upto 4th C-atom in a linear chain. Beyond that there will be no more influence of I.E.



Applications:

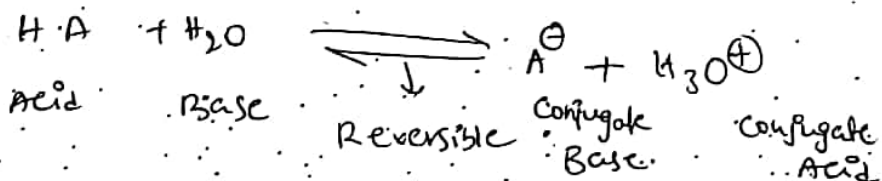
✓ I.E. explains stability of Carbo Cation and Carbon Radicals

✓ Strength of acids

✓ Acid is a substance which donates protons (H⁺)

✓ Acidic strength of an acid can be explained based on stability of a conjugative base.

✓ Basicity of amines



(3)(4)

A^-
conjugate
base

more stable
Then the acid
is strong
acid

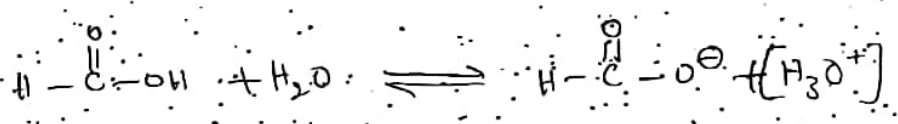
less stable
then the acid is
weak acid.

It is more stable
the increase
in conc. of H_3O^+
 \downarrow
less $pH \Rightarrow$ strong acid

$$pH = [-\log [H_3O^+]]$$

hydrogen ion

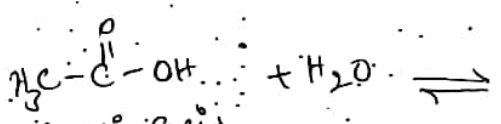
✓ stronger acids have stable conjugated base & vice versa



Formic acid

Formate
anion

more stable as
there is no

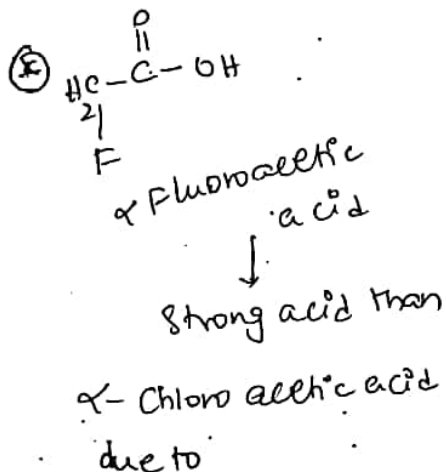
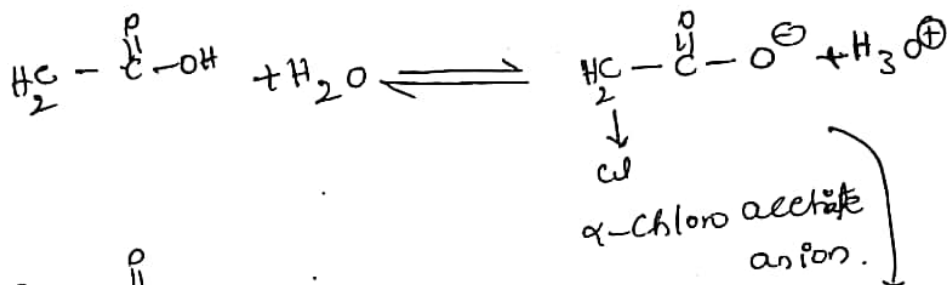


Acetic acid

Acetate
anion

Inductive
effect
less stable
due to ~~the~~ Inductive
effect

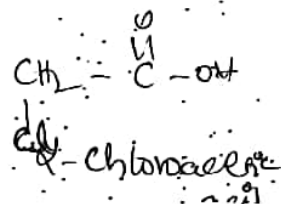
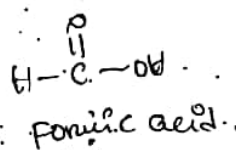
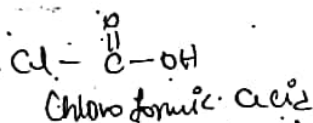
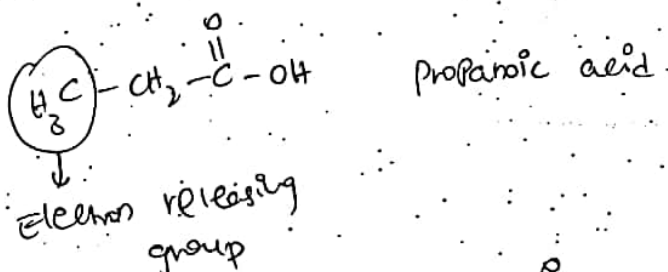
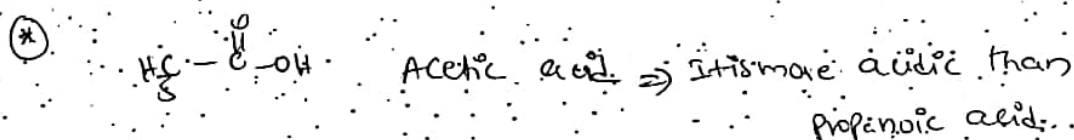
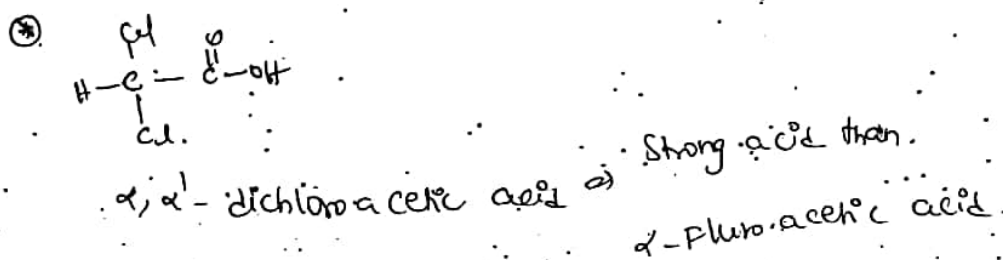
(*) So Formic acid is strong acid than Acetic acid.

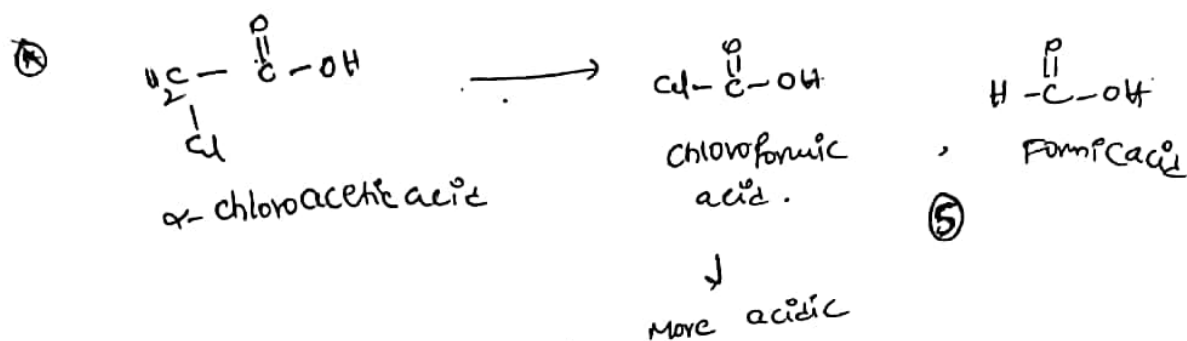


-ve Inductive effect

\downarrow
 So it is more stable than
 formate anion

\downarrow
 Hence α -chloro acetic acid
 is strong acid than formic
 acid





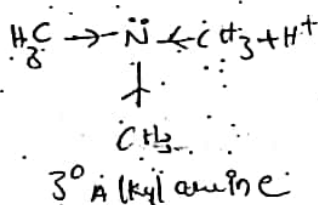
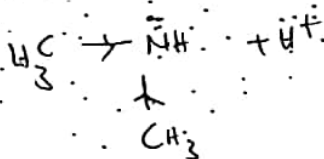
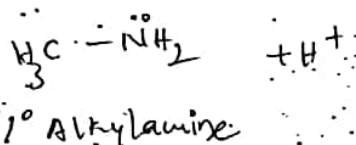
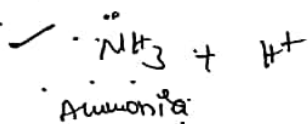
✓ Base is substance which donates lone pair of e^- s and accepts the proton (or) Base is the substance which can donate hydroxide ion.

✓ Amines are ^{organic} bases which donate the lone pair of e^- s

✓ Amines react with acids and they form ammonium ion.

✓ More is the stability order is $3^\circ > 2^\circ > 1^\circ \text{ amines} > \text{NH}_3$

↓
more basic
↓
due to +ve Inductive effect
↓
less basic



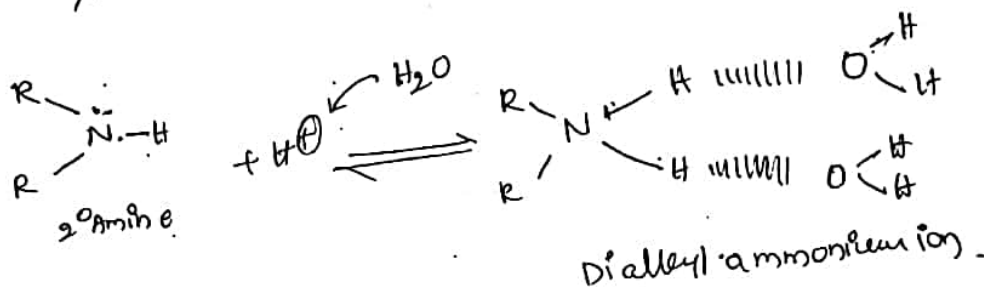
(More density) \Rightarrow due to +ve Inductive effect.

Actual Basicity order

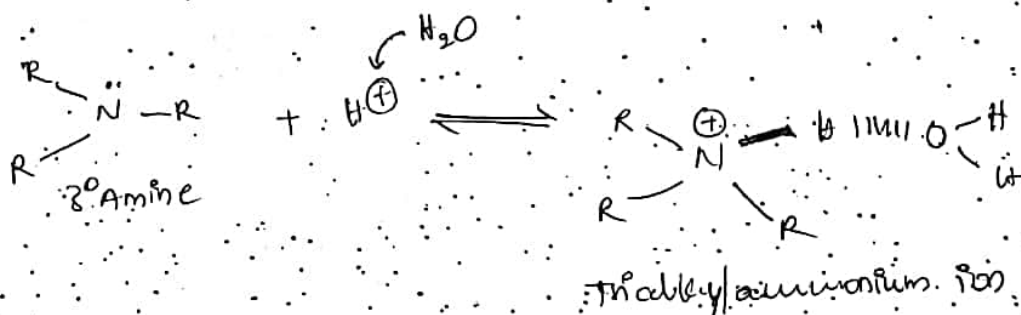
$2^\circ \text{ amine} > 3^\circ \text{ amines} > 1^\circ \text{ amines} > \text{NH}_3$

↓
Explained by steric hindrance as well as the stability of conjugated acid.

* 3° Amine due to presence of 3° bulkier Alkyl group sterically hinders the attack of proton on the nitrogen despite of presence of electron density. These strong shows that steric factor is predominant over +ve I.E making 3° amine less basic than 2° amines

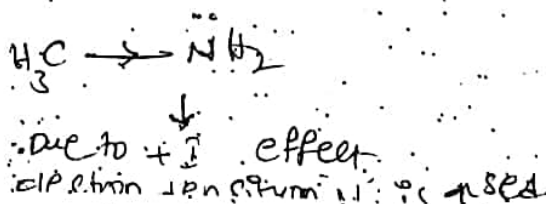
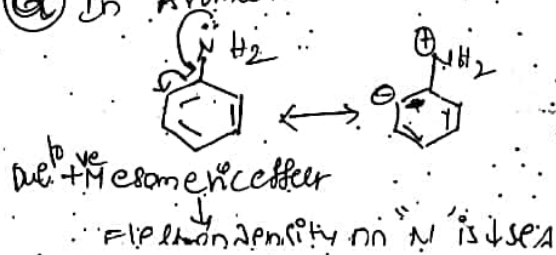


Dialkyl ammonium ion is more stable than trialkyl ammonium ion due to twice of 2 hydrogen bonds. Hence 2° amines are strong basic than 3° amine.



Here number of hydrogen bonds ↑ & More Basic

② In Aromatic amines vs aliphatic amines which is more basic.

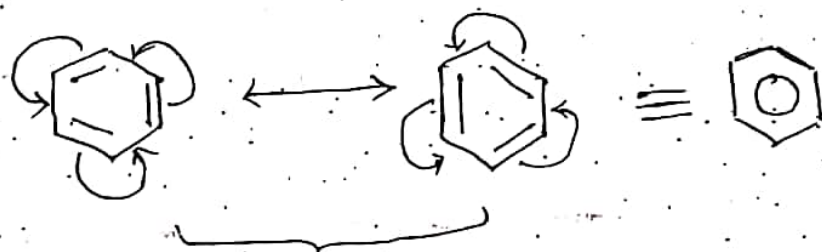


* So Aliphatic amines are strong bases than Aromatic amines. ⑥

Electron density is more then Basicity is more.

Resonance / Mesomeric Effect:

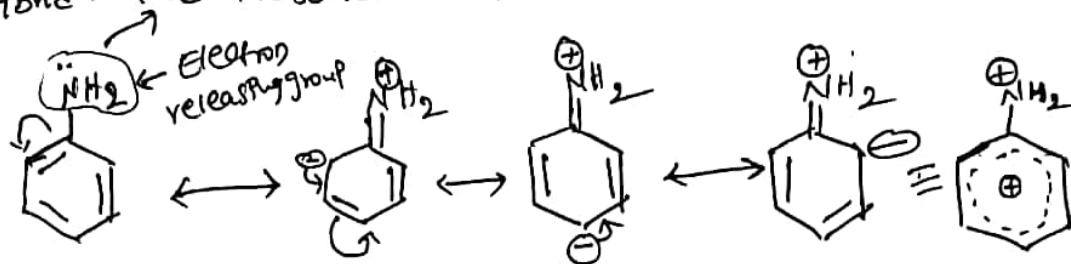
- * It involves the delocalisation of either purely (or) πe^- s (or) delocalisation of πe^- s in association with lone pair of e^- s
- * Due to delocalisation of the energy of the molecule will reduce leading to the stability of the molecule.
- * More is the that is utilised for the delocalisation process is called as delocalisation (or) Resonance energy.
- * More is the delocalisation energy more will be the stability of a molecule.
- * Due to delocalisation molecule will exist in more than one form these forms are called as Resonance forms (or) Resonance structures.



Resonance structure (or)

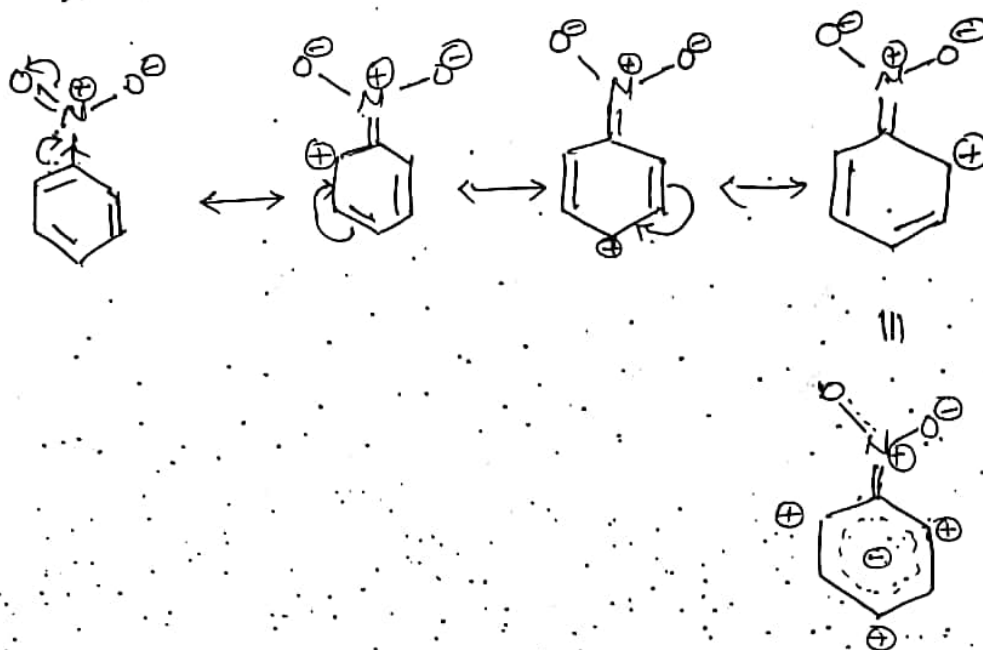
Can Canonical Structure

The hybrid of all these structures is called resonance hybrid. +ve Mesomeric effect / +R effect.



* Electron releasing groups are +M/+R effect.

⊗ -M/-R effect \Rightarrow Due to electron withdrawing groups

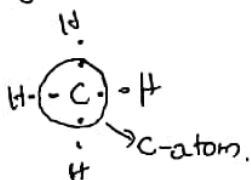
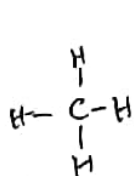


09/05/19

ORGANIC CHEMISTRY

①

- * Study about hydrocarbons and their functional derivative
- * Organic compound possess covalent bond \Rightarrow cooperative to satisfy their valency sharing of electrons.

Valency of Carbon is 4

- * An orbital contain 2 electrons, H - contain 1 orbital & 1 electron

STEREO CHEMISTRY

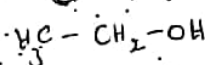
Isomerism in organic compounds

Isomers are the compounds with same molecular formula but different functional - arrangements of atoms (or) groups.

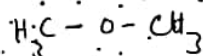
Basically Isomers are divided into 2 types.

Structural/Constitutional

- * They have different structure (or) constitution (or) composition.

Eg: $\text{C}_2\text{H}_6\text{O}$ 

Ethanol



Dimethyl ether

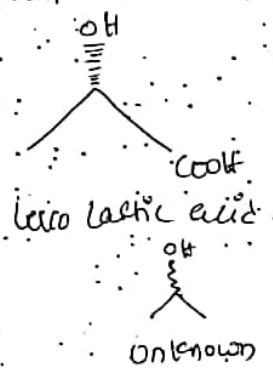
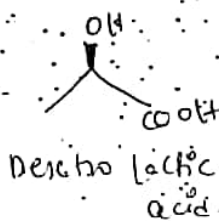
functional group isomers

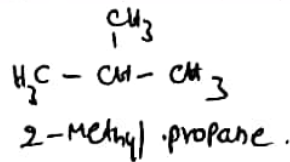
⑩ Types of Structural Isomerism

- ① Chain Isomers: These are the isomers with same molecular formula but different alkyl chains

Stereoisomers - 3D structure

- * Same structure different in spatial arrangement.

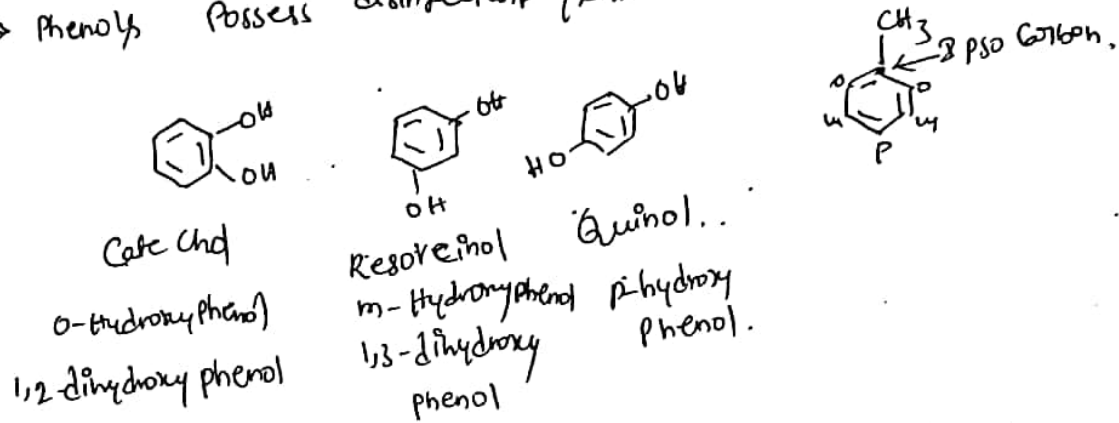




② ~~Metamers~~ / Positional group isomers / Regio isomers -

The 4 have same functional groups but different position of functional groups.

→ Phenols possess disinfectant / antimicrobial property.



* Quinol possess more disinfectant property as the functional groups are differ in their distance and they are free & free from intermolecular hydrogen bond.

* * Phenol Coefficient: Determination of disinfectant (or) Antiseptic property of new compound is - comparison with phenol

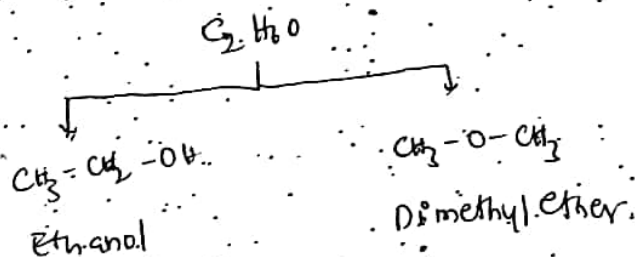
It contains - 2 tests

1) Riedel - Walker coefficient

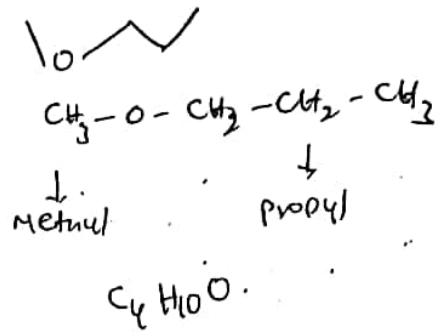
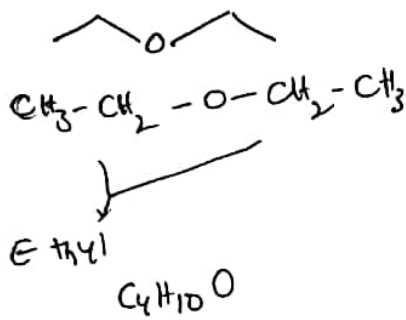
2) Chace - Martin coefficient

③ Functional Group Isomerism!

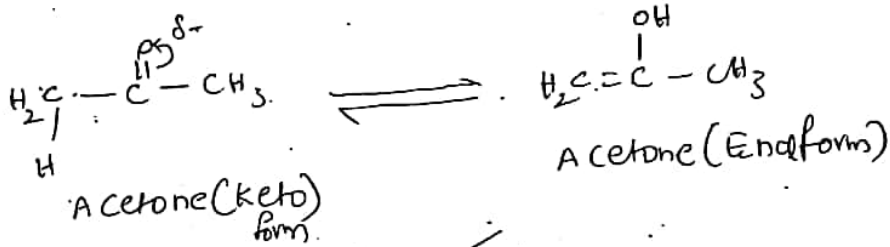
Same molecular formula but different functional group.



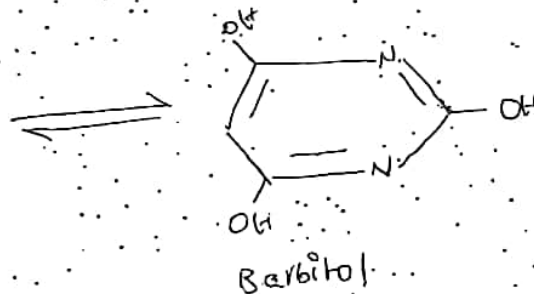
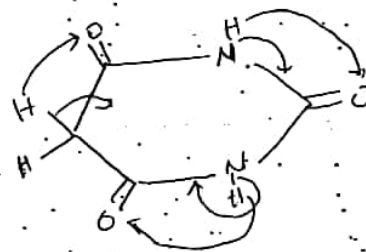
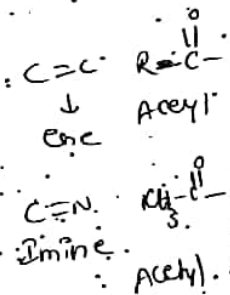
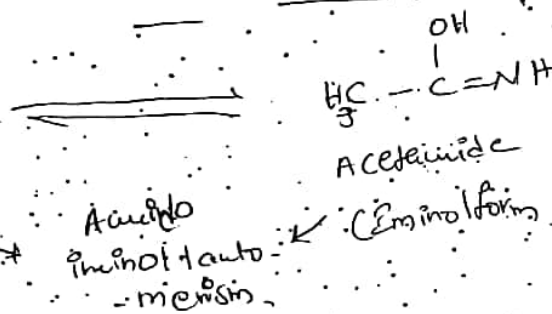
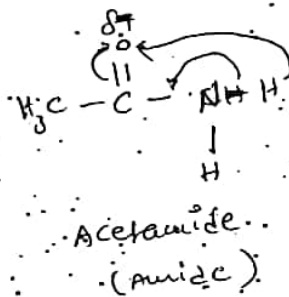
4) Metamers: Metamers Possess same functional groups with different alkyl chains.



5) Tautomers: It is a type of Isomerism which arises due to migration of proton from one region of the molecule to other region.



Keto-enol Tautomerism



Barbitone (Lactam form)

Lactam

(Lachim form) \Rightarrow Cyclic Iminol