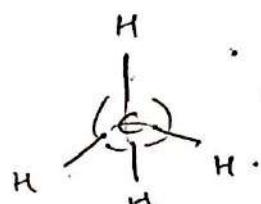


GENERAL ORGANIC CHEMISTRY

Q) How many $109^{\circ}28'$ Bond angles are present in methane?

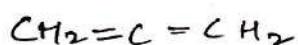
A) 6



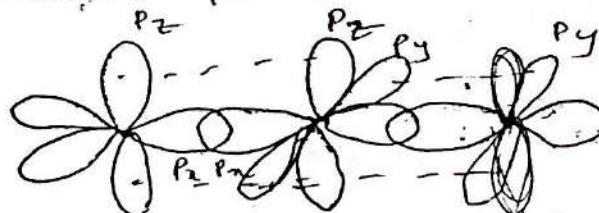
B) Molecular plane: All the atoms of a molecule lie on the plane.

→ Nodal plane of π , bond in ethene and its molecular plane are same plane.

Allene: C_3H_4 (acyclic compound), which possess 2 double bonds



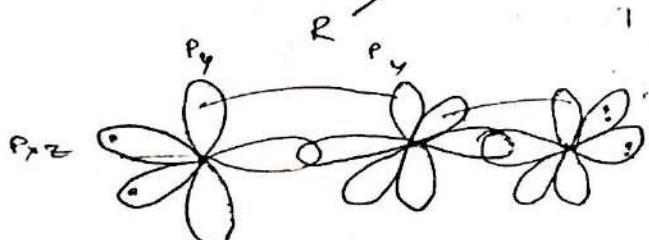
→ Doesn't possess molecular plane.



No. of atom in same plane = 5

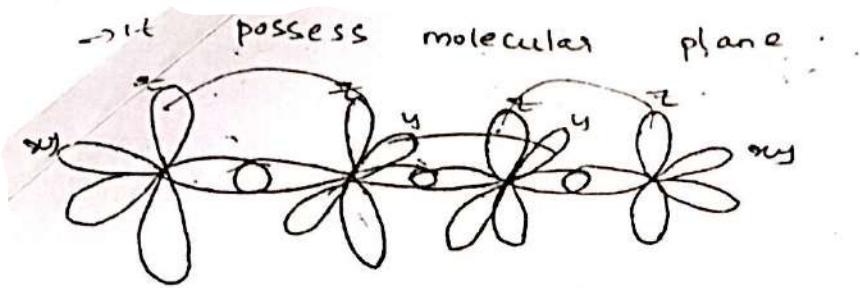
Same line = 3

Ketene = $R-C=C=O$. has molecular plane.

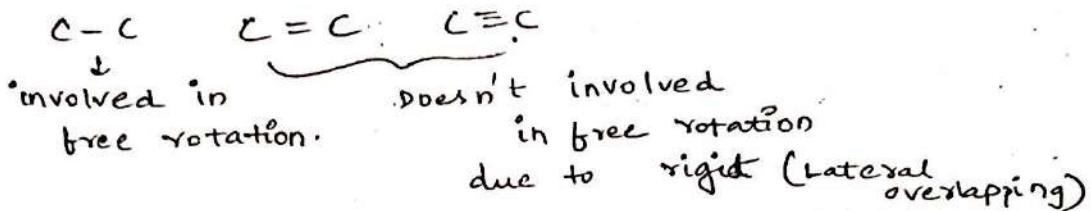


cummine: if 3 or more double bonds continuously present in a cyclic compound

..... situated bond.



→ At Room temperature.



→ BE of C-C; C=C; C≡C. in Kcal/mole.

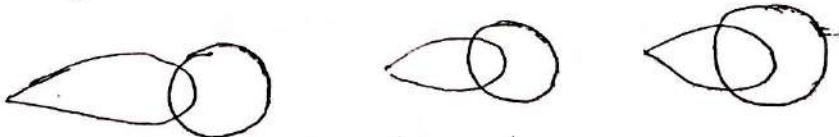
$$C-C : \approx 100 \text{ kcal (85)}$$

$$C=C : \approx 150 \text{ kcal}$$

\downarrow C≡C : $\approx 2200 \text{ kcal}$.
Reason: because of electron cloud repulsions.
($C_2^{nd} \pi$ bond is weaker)

→ % S \propto spherical characters $\propto \frac{1}{BL} \propto$ B. strength

B. v. order: $\geq C-H > =C-H > \equiv C-H$

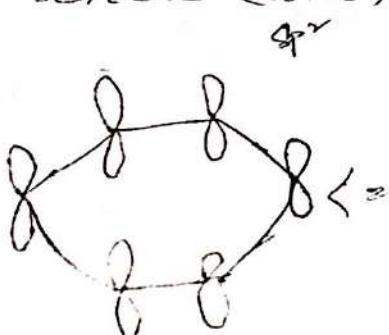


→ Ratio of P.O: H.O present in H-C≡C-H

$$P.O = 2(\text{no. of } \pi\text{-bonds}) + \text{Hydrogens} = 6.$$

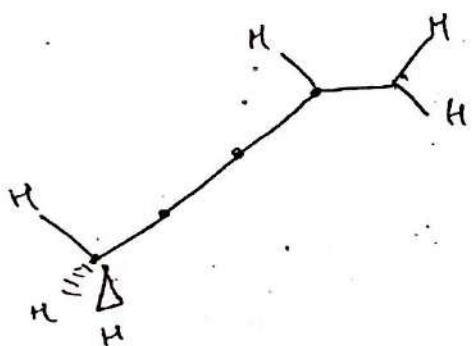
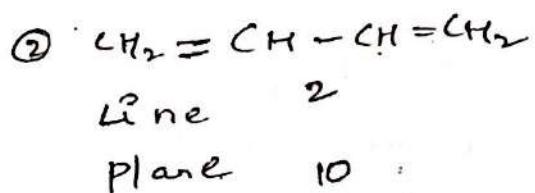
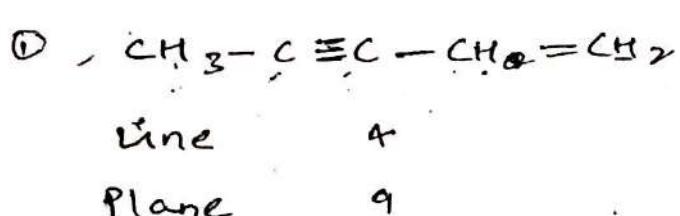
$$6:4 = 3:2$$

→ Benzene (C₆H₆)



$$\begin{aligned} P.O &= 12 \\ H.O &= 18 \\ 12:18 & \\ -2 &= 3 \end{aligned}$$

→ Max. no. of atoms in the plane; in the line?



→ Urea is the 1st organic compound prepared in the lab.

→ Carbon is innumerable due to:

① Max. catenation.

② Tetravalency.

③ Isomerism.

④ tendency to form multiple bonds.

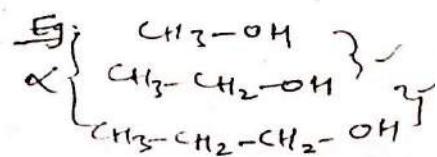
→ Greater the s-character, smaller the orbital size

$$S\% \propto \frac{1}{\text{size of orbital}}$$

→ % s-character \propto EN of carbon.

HOMOLOGOUS SERIES:-

→ They are series of compounds possessing same functional group differed by $-\text{CH}_2-$ unit.



Classification of organic Compounds:

Acyclic/open chain

Aliphatic.

* may be linear (or)

branched

Saturated

c - c

Unsaturated

C=C, C≡C

Condns for aromatic:

→ cyclic, planar

→ Hückel rule: $(4n+2)\pi e^-$

→ all should involve in sp^2 hyb.

Alicyclic

Aromatic

→ They are aliphatic → They are aliphatic

→ They may (or) → They may (or) may not have may not have saturation.

→ Homocyclic compounds.

[Same atoms in ring]

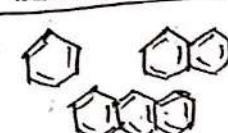
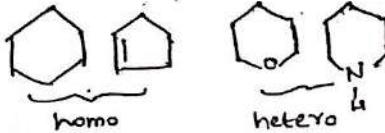
→ They may be heterocyclic. i.e other elements like O, N

Heterocyclic compounds.

[Hetero atoms in ring].

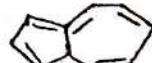
→ They are benzenoid and non-benzenoid.

Benzenoid:



Non-Benzenoid:

Azulene



Classification of Cyclic Compounds:-

Monocyclic:



Classification of Bicyclic compounds

Spiro-bicyclic Compounds

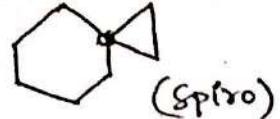
→ compounds formed by joining of 2 rings sharing one carbon

Fused-bicyclic Compounds

→ 2 rings are joined by 2 carbons

Bridged bicyclic

→ Bridged head carbons are connected to bridged carbonyls.

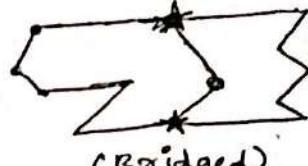


(spiro)

classification of carbon:



(fused)



(Bridged)

Primary (1°)

→ Carbon connected to no (or) only one carbon.

Secondary (2°)

→ carbon Connected to 2 carbons.

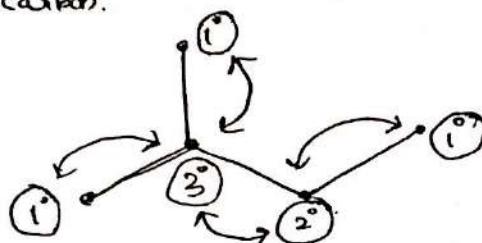
Tertiary (3°)

→ carbon connected to 3 carbons

Quaternary (4°)

→ carbon connected to 4 carbons.

Eg:



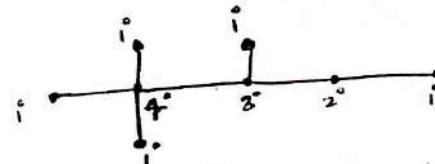
How many discrete carbons are present in the compound?

It means that how many carbons are in diff. envisioned.

Sol: ④

→ Hydrogens attached to primary, secondary, tertiary and quaternary are termed as $1^\circ, 2^\circ, 3^\circ, 4^\circ$ hydrogens.

Eg:



1° hydrogens = 15

2° hydrogens = 2

3° hydrogens = 1

→ If $-OH$ is attached to 1° carbon, it is primary alcohol and same for all others.

→ If $-X$ is attached to 1° carbon, it is primary halide and same for all others.

→ Amines are classified into 3.

1° Amine



2° Amine



3° Amine



→ Unlike alcohols, alkyl amines are classified in different by taking them as ammonia derivatives.

VINYLC CARBON: [IUPAC name: ethenyl]

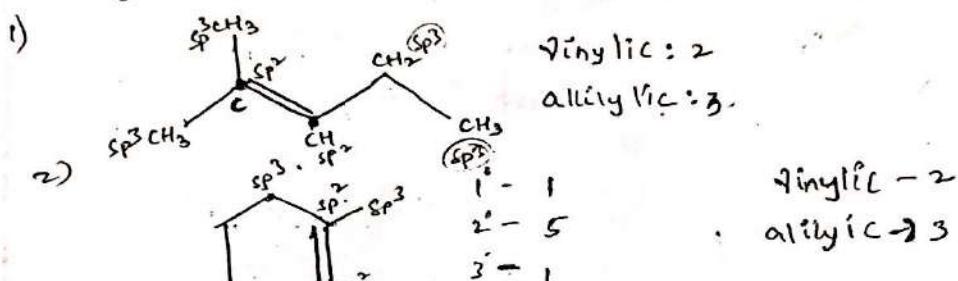
→ sp^2 carbons which are directly connected to sp^2 of alkeneic carbons.

Vinylic Group: $-CH=CH_2$

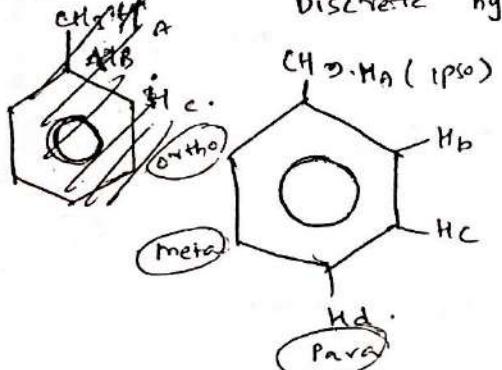
ALLYLIC CARBON: [IUPAC name: propenyl]

→ sp^3 carbons which are directly connected to sp^2 of alkene.

allylic group: $-CH_2-CH=CH_2$

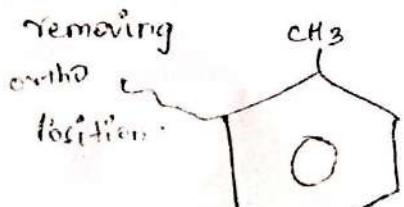
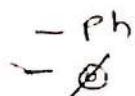
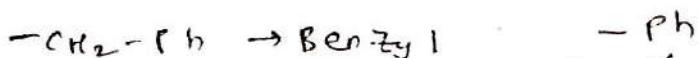


3) Toluene.



→ Benzene have only one-type of H.

removing H → Phenyl (C_6H_5).

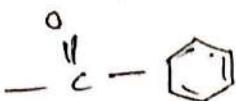


orthotolyl

metatolyl } removing at meta

paratolyl } removing at para

BENZYL: $\text{C}_6\text{H}_5\text{CH}_2\text{CO}$

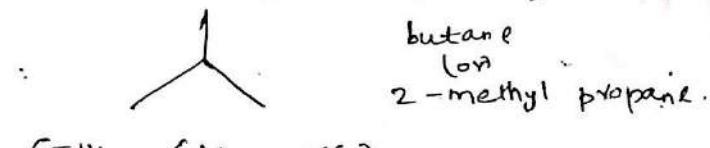
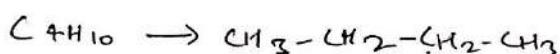
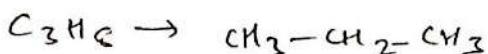
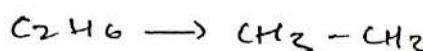


saturated acyclic alkane G.M.F: $\text{C}_n\text{H}_{2n+2}$

CH_4
Common name:
Marsh gas
↓
Poisonous

IUPAC name: Prefix + Root word + suffix

C_1	meth
C_2	eth
C_3	prop.
C_4	but
C_5	pent
C_6	hex
C_7	sept
C_8	oct
C_9	nove
C_{10}	dec



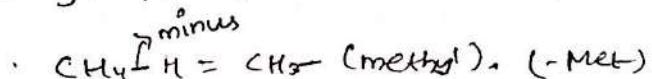
C_5H_{12} : Isomers.



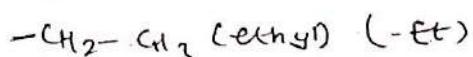
Alkyl group:

Def: (Alkane - H) is alkyl

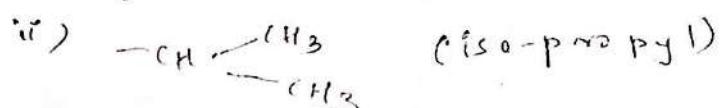
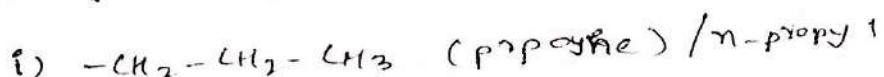
① Alkyl groups possible for methane.



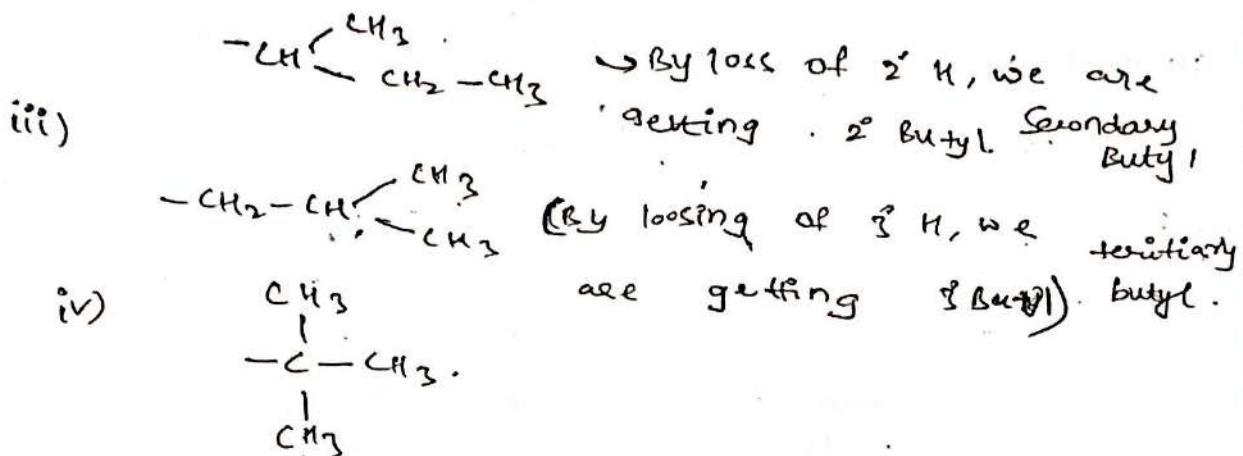
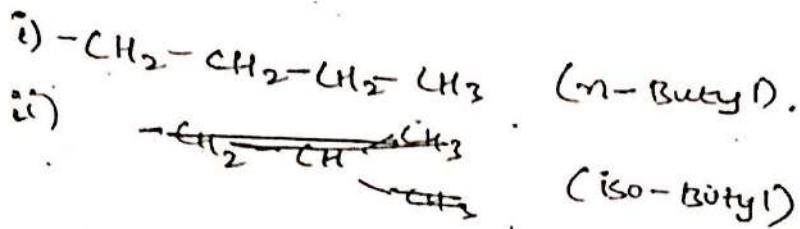
② Alkyl groups possible for ethane.



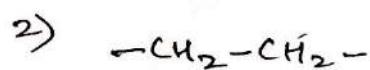
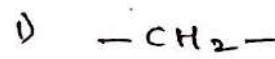
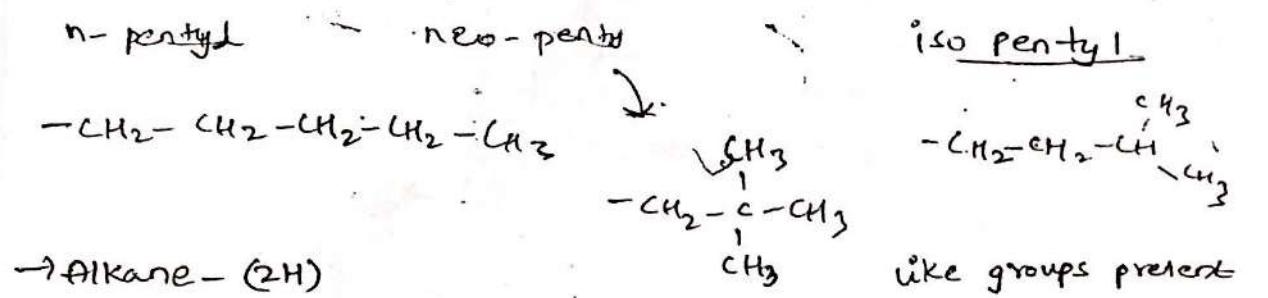
③ Alkyl groups for propane



iii) Alkyl group in Butane.



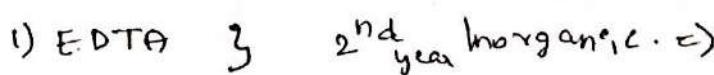
$C_5H_{12} \rightarrow$ Total 8 isomers.



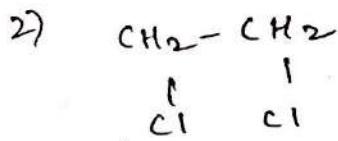
methylene
Ethylene

Like groups present
on adjacent atoms
viciinal compounds

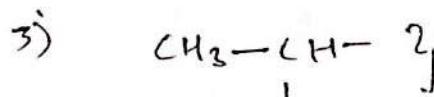
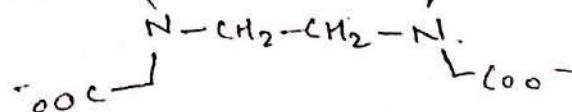
Eg:



Ethylene di amine
tetra acetate



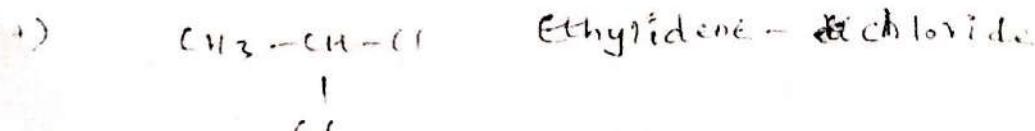
(Ethylene di-chloride)



Ethyldene

Like groups present
on same terminal compound atoms

Eg:



* $=\text{CH}_2 \rightarrow$ methylidene.

* $=\text{CH}-\text{CH}_3 \rightarrow$ ethylidene

DEGREE OF UNSATURATION: (DU)

(by)

Double bond equivalents (DBE).
(by)

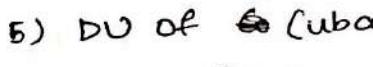
Index of Hydrogen deficiency (IHD)

$$\Rightarrow \text{DU} = (\text{No. of carbons} + 1) - \left(\frac{\text{Hyd.} + \text{Halogens} - \text{Nitrogens}}{2} \right)$$

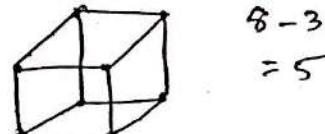
Eg: 1) C_6H_{12} 2) C_4H_6 , 3) $\text{C}_4\text{H}_{10}\text{O}$.

A) $\text{DU} = 7 - 6 = 1$ DU = 2 DU = 0.
(no π bond)

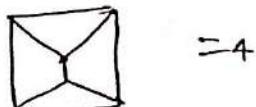
1 DU indicates one
cyclic (or) one π bond.

4) DU of $\text{C}_5\text{H}_5\text{N}$ 5) DU of  (cubane):

A) $6 - 5 = 1$ ✓



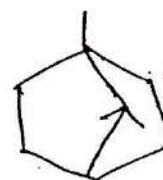
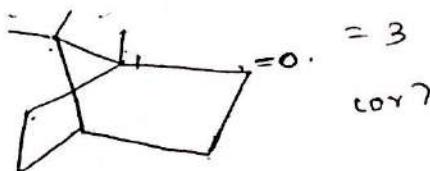
6) DU of prismane 7) DU of $\text{C}_3\text{H}_3\text{Cl}_3$.



= 1

→ if DU is fractional
that means that
comp. doesn't
exist

8) DU of camphor: $\text{C}_{10}\text{H}_{16}\text{O}$



Alternative method:

1) $\text{C}_{10}\text{H}_{16} \times$.

(10 H_2 , alkane)

$$\text{DU} = \frac{22 - 16}{2} = 3$$

2) $\text{C}_5\text{H}_5 \times$

$$\begin{matrix} \text{~} \\ \text{~} \\ \text{~} \\ \text{~} \end{matrix} \text{H}$$
$$(5 + 4) \\ \text{C}_5\text{H}_{12}$$

$$\frac{12 - 4}{2} = 4$$

3) $\text{C}_6\text{H}_5 \times$

$$\begin{matrix} \text{~} \\ \text{~} \\ \text{~} \\ \text{~} \end{matrix} \text{H}$$
$$\text{C}_6\text{H}_6 \\ \text{C}_6\text{H}_{14}$$

$$\frac{12 - 6}{2} = 4$$

* → How many cyclic structures are possible for C_4H_6 ? (5)

A) DO: $5 - \frac{6}{2} = 2 \rightarrow$

$2\pi, 0$ cyc.
 $1\pi, 1$ cyc.
 $0\pi, 2$ cyc.

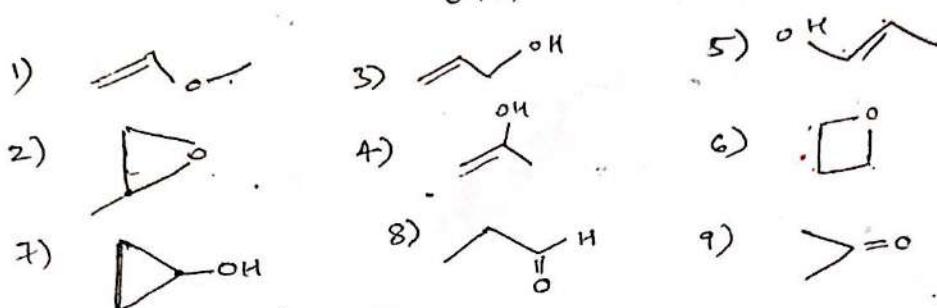


→ C_3H_6O all structures

D.U. = $4 - 3 = 1$

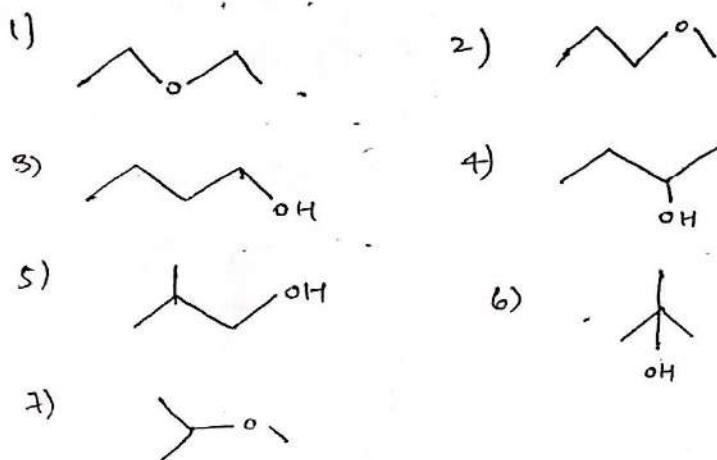
$1\pi, 0$ cyc.
 $0\pi, 1$ cyc.

(9)

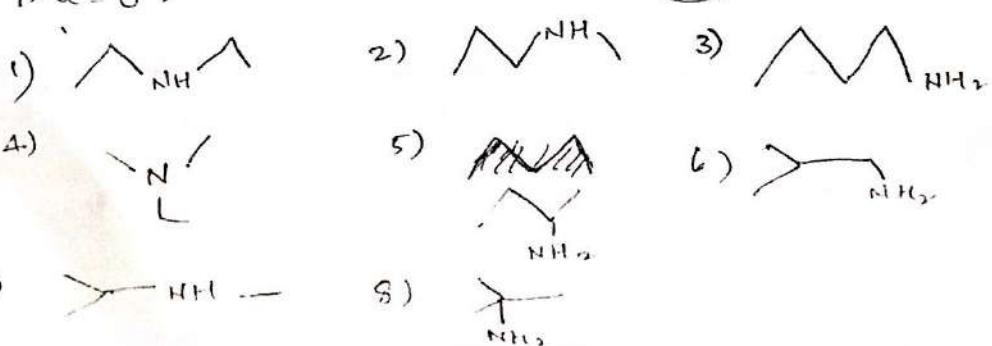


→ C_4H_{10} No. of structures.

D.U. = 0. (6) + 1 = 7

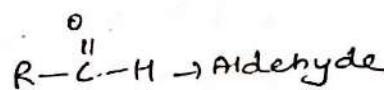
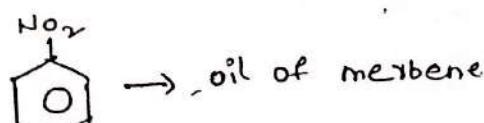
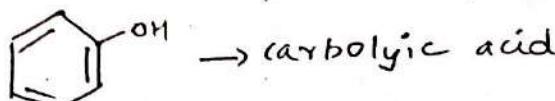
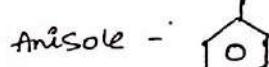
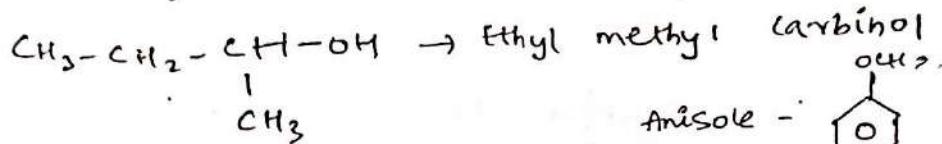
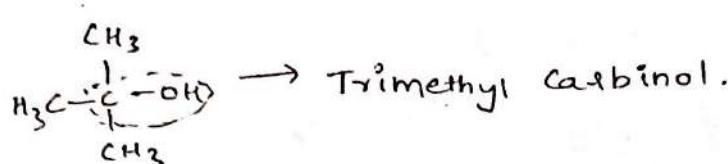
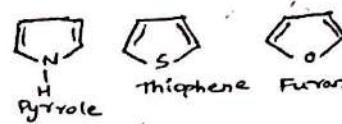
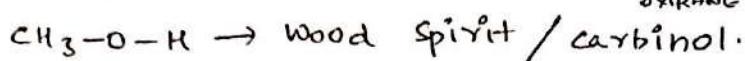
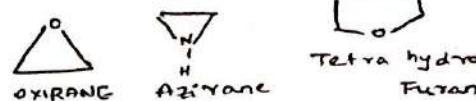
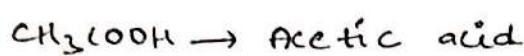
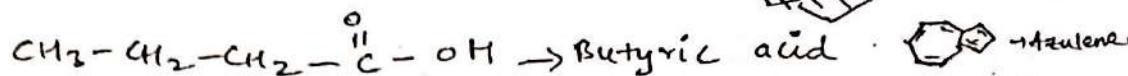
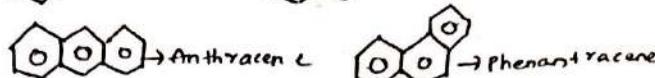
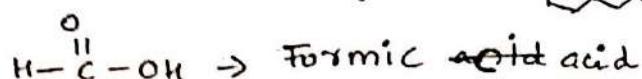


→ $C_4H_{11}N$ No. of structures (8)



IUPAC NAMING :-

Common names :



$\text{C}_1 \rightarrow$ Form

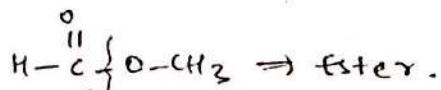
$\text{C}_2 \rightarrow$ Acet

$\text{C}_3 \rightarrow$ Propionic

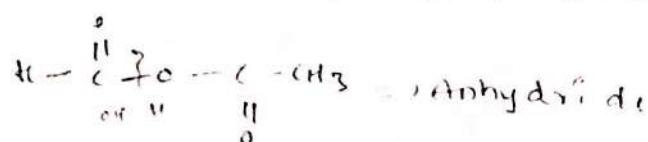
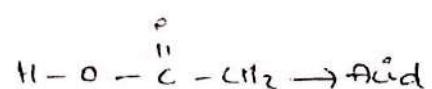
$\text{C}_4 \rightarrow$ Butyric

$\text{C}_5 \rightarrow$ Amyl / Valero

$\text{C}_6 \rightarrow$ Capro

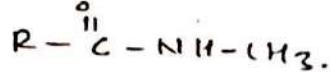
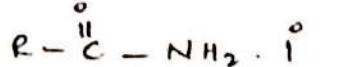
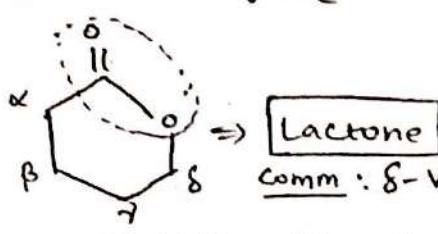


\rightarrow on addn. of water to Ester,
we get acid & alcohol.



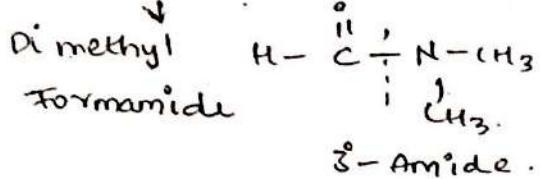
Acid & Acid.

Ester when cyclic

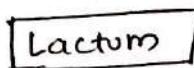
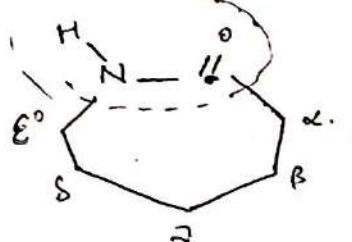


Comm: δ° -Valero lactone. 2°

D.M.F. is derivative of Formic acid

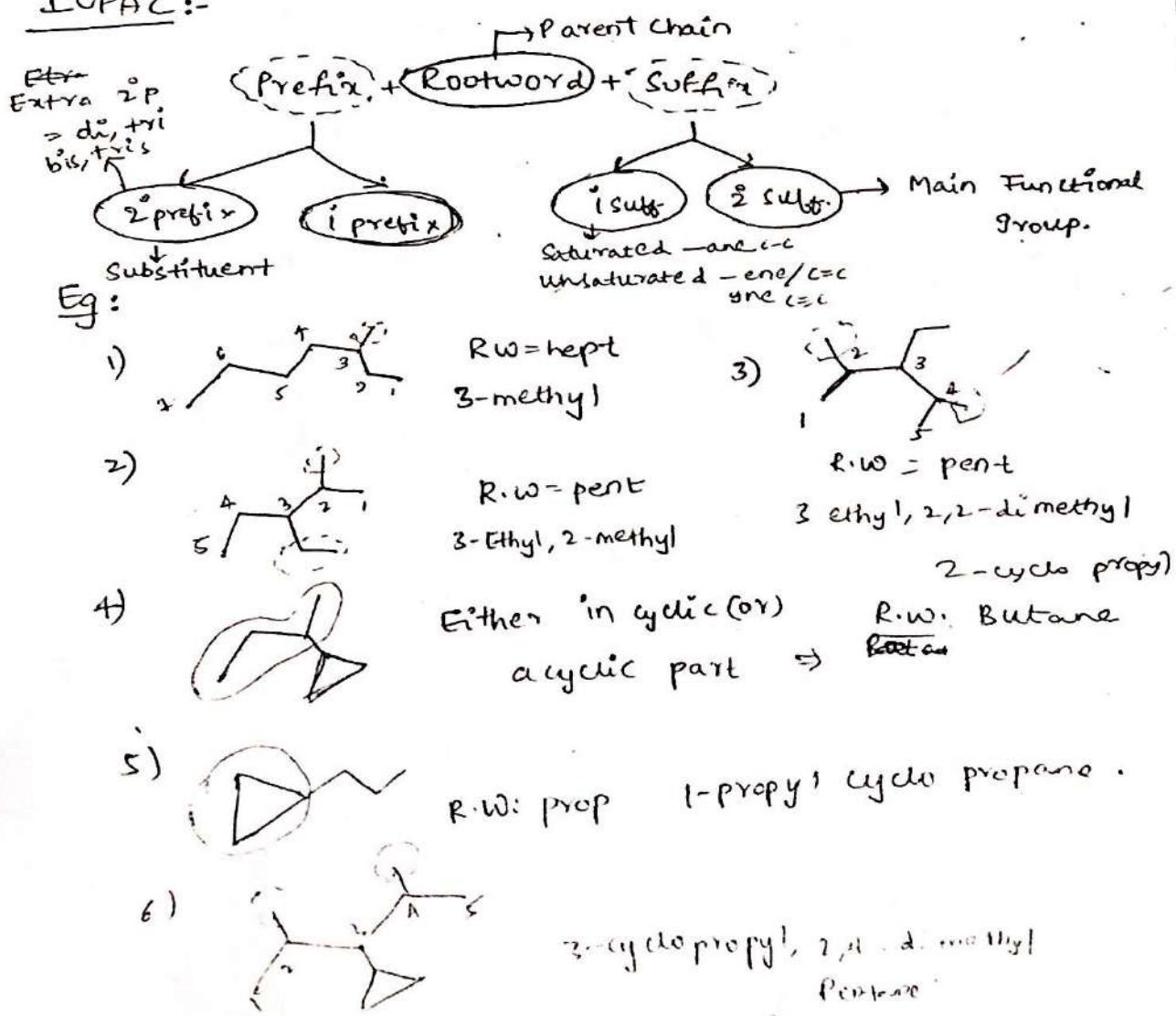


cyclic amide.



Comm: ϵ° -Capro lactam.

IUPAC :-



Q)



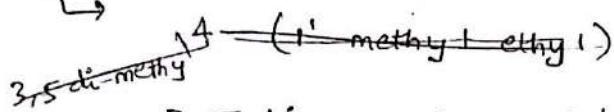
4-isopropyl

3,5-di methyl

heptane.

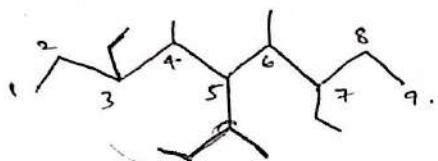
di v
tri neo
bis cyclo
tris alphasets.

Also ⇒ One organic compound will have only one specific IUPAC Name.



3,5 di-methyl 4-(1-methyl ethyl) heptane.

2)

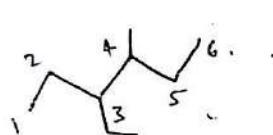


5-isobutyl

3-ethyl
4,4-dimethyl

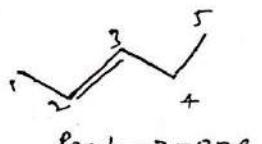
nonane.

3)



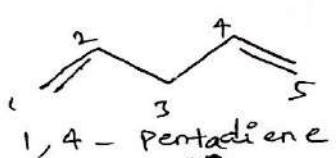
3-Ethyl,4-Methyl hexane.

4)



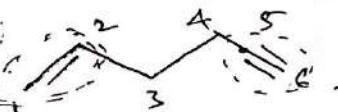
Pent-2-ene
2-pentene.

5)

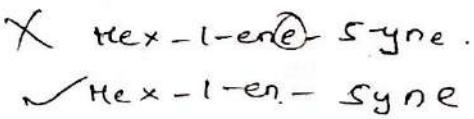


1,4-Pentadiene.

6)



7)



Hex-1-ene-5-yne.

Hept-5-en-1-yne.

Functional group :- An atom (or) group of atoms which decides the characteristic and chemical property of the substance.

Priority order of Functional group groups :-

-COOH > -SO₃H > -CO-O-OC > -C≡O > -COCl > -CONH₂ > -CN > -CHO >
-C=O > -OH > -SH > -NH₂

Naming For alkyl halides, Ethers & Nitro Comp.

(i) Neopentyl chloride

only 2 prefixes.

(ii) Allyl chloride

(iii) Secondary Butyl Ethyl Ether

(iv) Allyl Vinyl Ether.



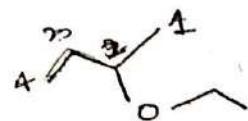
1-Chloro 2,2-dimethyl propane.

2)



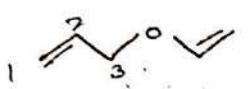
3-chloro propene.

3)



2-Ethoxy butane.

4)



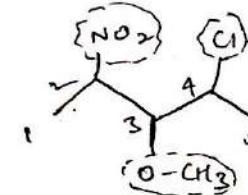
3-Ethenyl oxy propene.

5) Iso butyl methoxy propyl Ether.



1-Propoxy, 2-methyl propane.

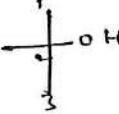
6)



4-Chloro, 3-Methoxy,
2-Nitro butane hexane.

Naming of alcohols & Amines:

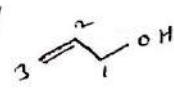
i) tertiary butyl alcohol



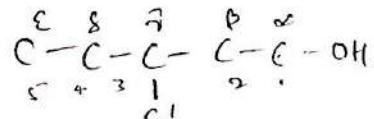
ii) Allyl alcohol

2-methyl propan-2-ol

iii) ~~γ-hydroxy~~ chloro amyl alcohol

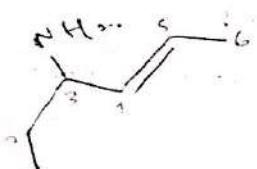


Prop-2-en-1-ol

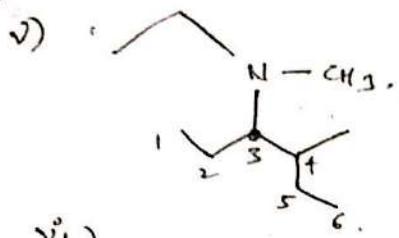


3-Chloro pentan-1-ol

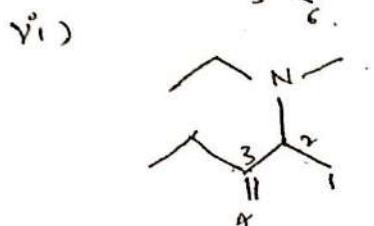
iv)



Hex-4-enyl-3-amine



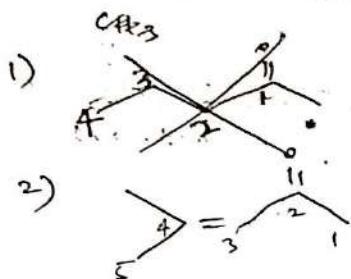
N-Ethyl-N-methyl-4-methyl
hex-3-amine.
(or)



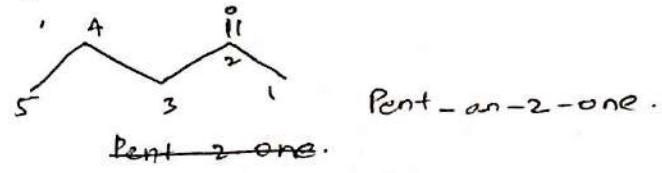
N-Ethyl-N,4-dimethyl hex-
an-3-amine.

N,3-diethyl N-methyl
But ~~prop~~-3-en-2-amine.

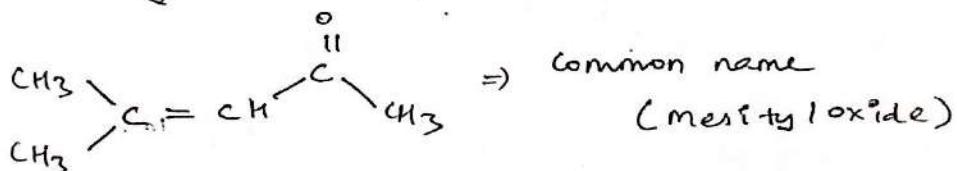
III) KETONES:- (Exceptions)



→ Just gives least solant

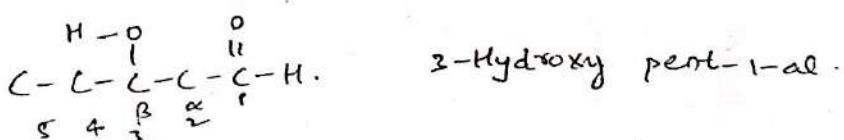


↓
4-Methyl pent-3-en-2-one.



IV) -COOH, -CHO, -CN:

1) β -hydroxy valeraldehyde.



2)



Vinyl aldehyde.

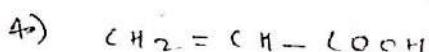
(or)

Acraldehyde (or) $\text{CH}_3\text{CH=CHOH}$ (or) Acroleine.

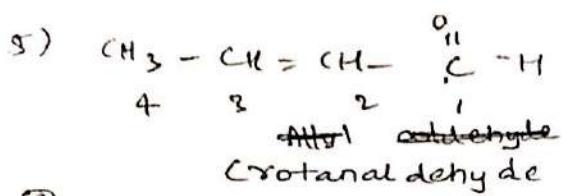


Acrylic nitrile.

Prop-2-en-1-nitrile



Prop-2-en-1-carboxylic acid

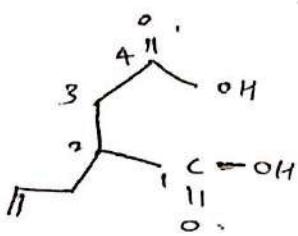


but-2-enal

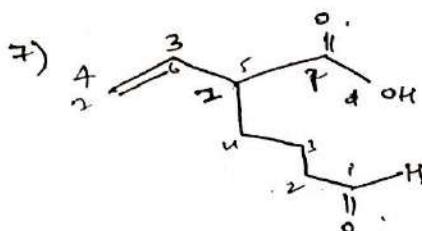
6)



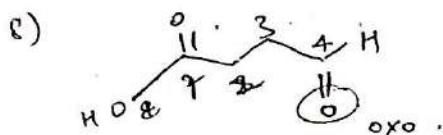
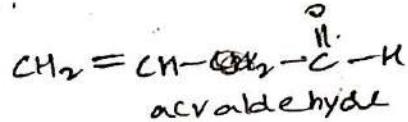
6)



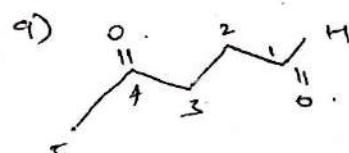
like functional group \Rightarrow boxes are imp.



unlike groups, unsaturation
is imp.

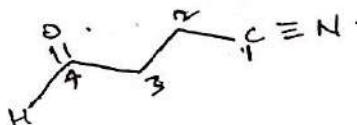


4-oxo butanoic acid



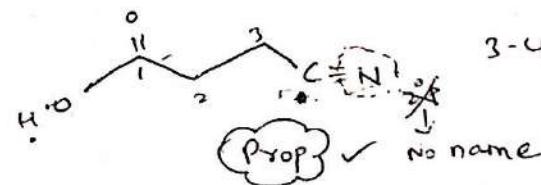
4-keto pentanal

10)



4-oxo-Butan-nitrile

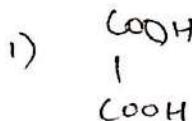
11)



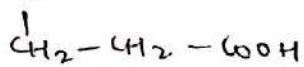
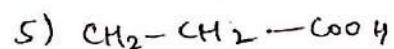
3-cyano Propanoic acid.

Prop ✓ no name

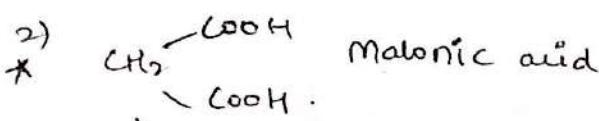
12) Common names of acids:



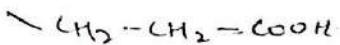
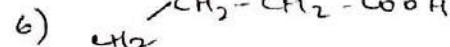
oxalic acid



(Adipic)

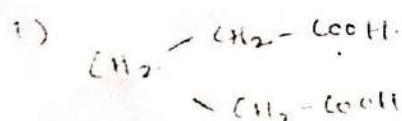


Malonic acid

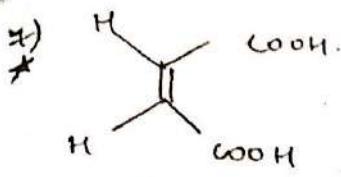


Succinic acid

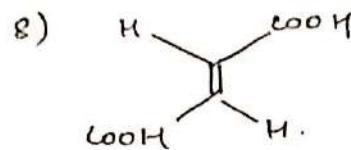
Pimelic



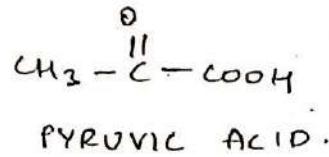
Glutaric acid



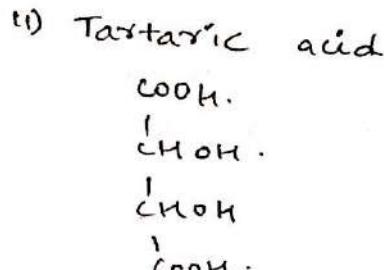
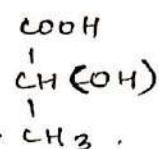
cis (Z)
Maleic acid



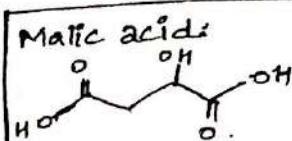
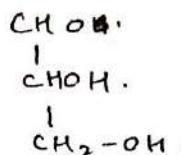
trans (E). Trans (E)
Fumaric acid.



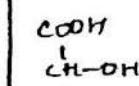
10) Lactic acid



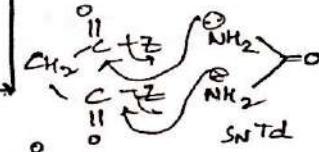
12) Glyceraldehyde



Mandelic acid:



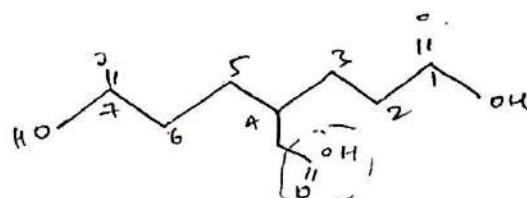
Barbituric acid:



Propane 1,2,3-tricarboxylic acid.

Pent 2-dicarboxy pent 1,2-dioic acid.

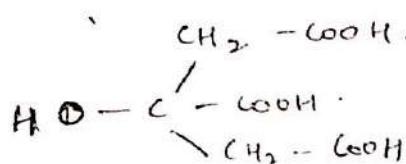
2)



~~4-methyl~~

4-Carboxy methyl heptan-1,7-dioic acid.

13) IUPAC Name of Citric acid.



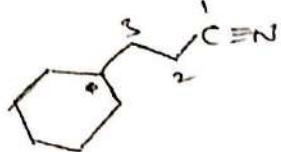
Himanshu Pandey:

3-Carboxy; 3-hydroxy.

Pentane dicarboxylic acid.

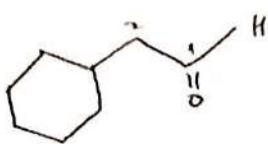
2-hydroxy propane 1,2,3-tricarboxylic acid.

14)



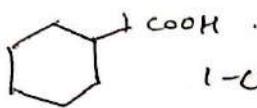
3-cyclohexyl propan-1-nitrile

15)



2-cyclohexyl

16)



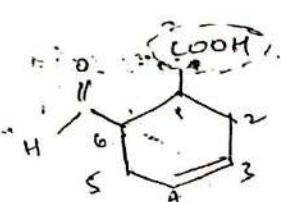
1-cyclohexyl (methanoc acid) X

only its directly connected.

X carboxylic acid X

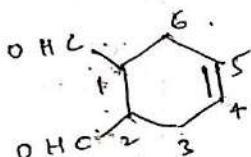
cyclohexane carboxylic acid.

17)



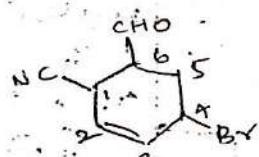
6-formyl cyclohex-3-ene-2-carboxylic acid.

18)



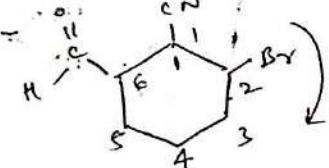
cyclohex-4-ene-1,2-di carbalddehyde.

19)



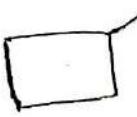
cyclohexylidene methanone.

20)

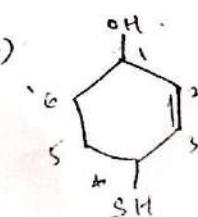
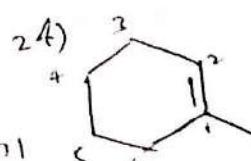


alphabetical order

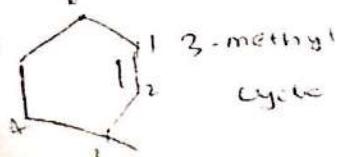
21)

1-cyclo...
butyl ethene i.1-cyclo...
Pentyl
methanol

23)

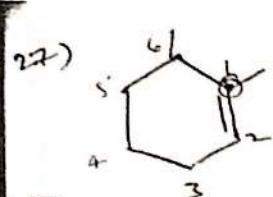
4-mercapto
cycle hex-
-2-en-1-ol1-methyl
cyclohex-1-ene

25)

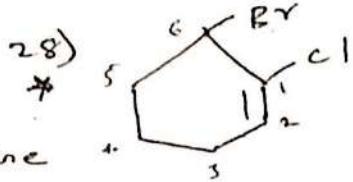
3-methyl
cyclohexene

26)

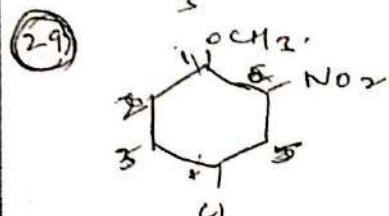
1,3-dimethyl
cyclohexene



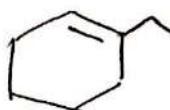
1,6-dimethyl
cyclo hexene



6-Bromo
1-Chloro
cyclo-hexene.

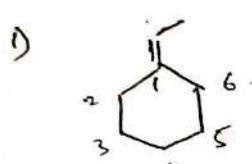


30)

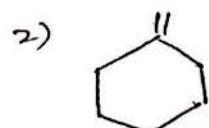


1-Ethy
cyclo hexene.

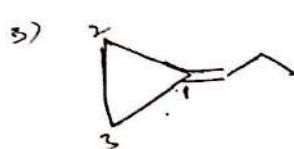
→ 1b unsaturation is part of both. Select Parent chain from the one which contains more no-of carbons. (Parent-chain-saturated).



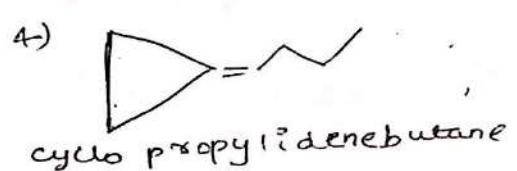
1-Ethylidene
cyclo hexane



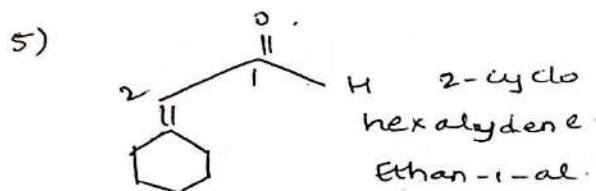
1-methylidene
cyclo hexane.



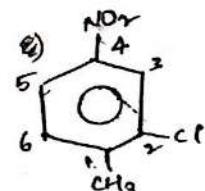
1-propylidene
cyclo propane



cyclo propylidenebutane.

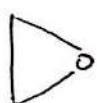


2-cyclo
hexaldehyde
Ethan-1-al.



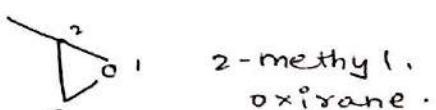
2-chloro, 1-methyl, 4-Nitro
Benzene.

EPOXIDES: (Naming)



Epoxide/Ethylene oxide.

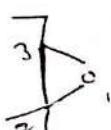
1)



2-methyl
oxirane.

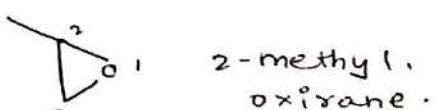
Cyclic Oxirane:

2)



3-Ethyl
2,2-dimethyl
Oxirane

3)

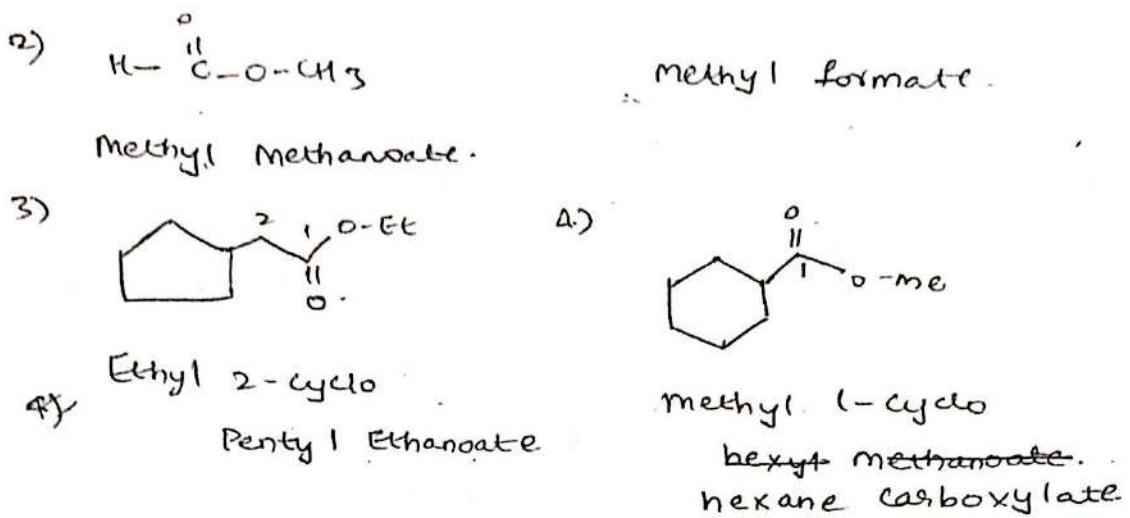


Esters:

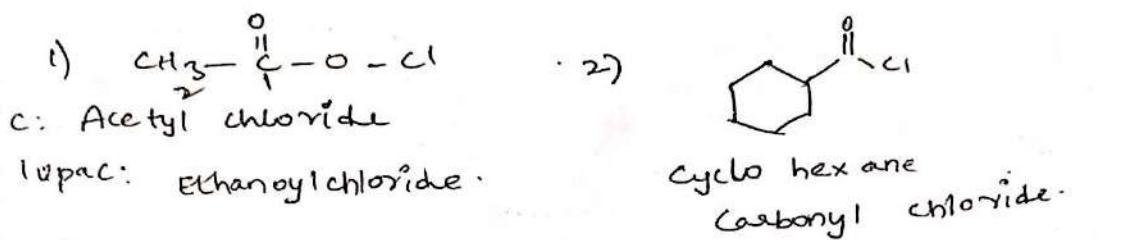


Common: Ethyl
acetate

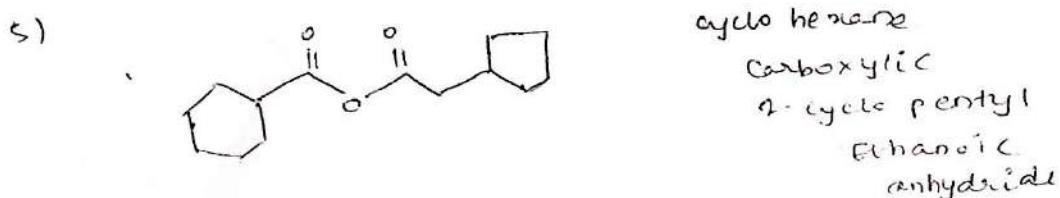
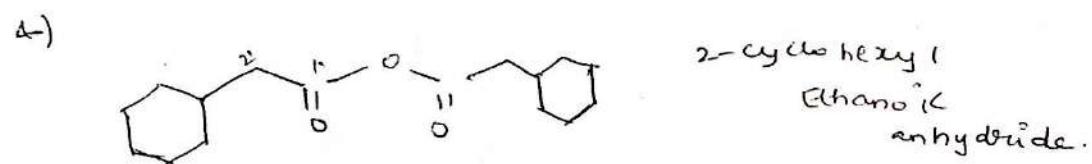
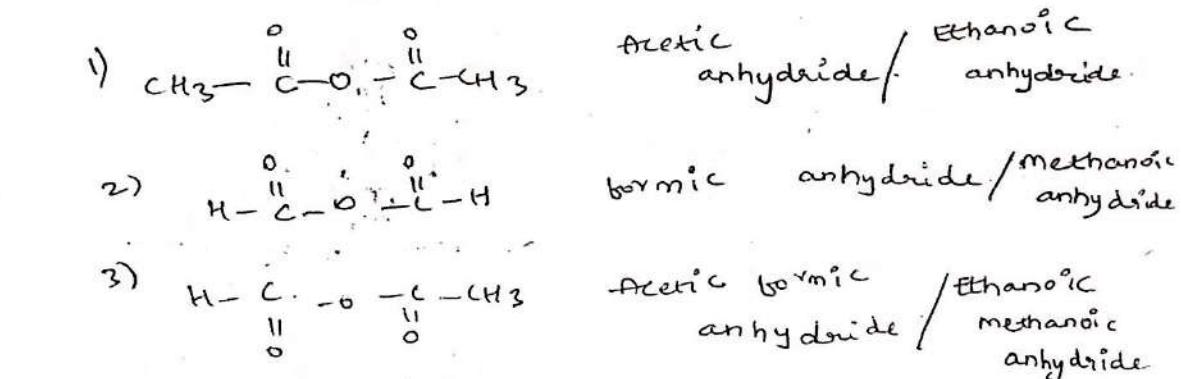
Ethyl Acetate



ACID HALIDES:-

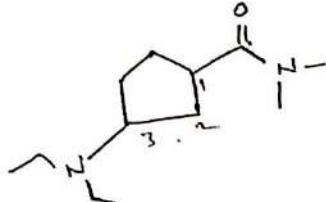
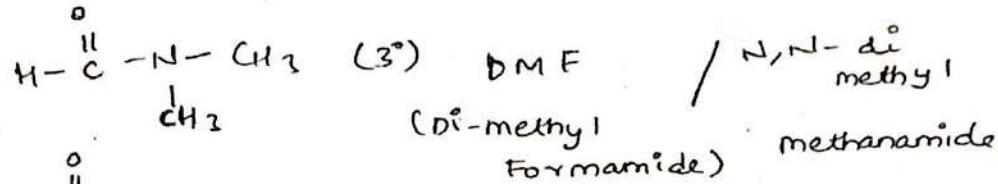
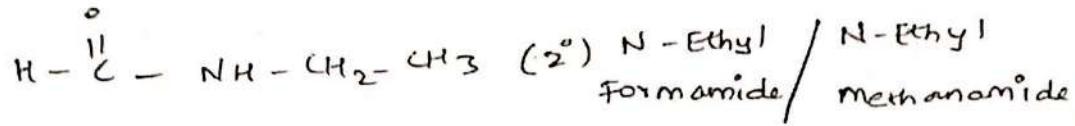
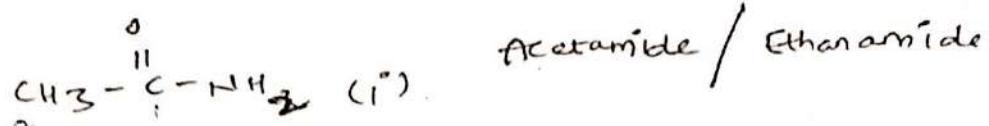


* Anhydride Anhydrides:



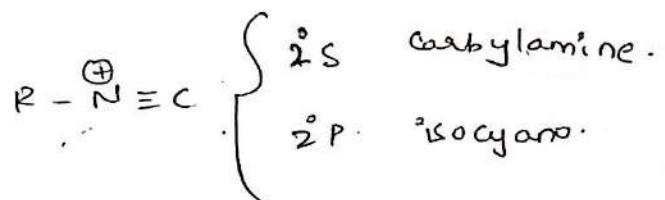
→ If all are substituents then we have to go in alphabetical order.

AMIDE:



N,N-dimethyl-
3(N,N-dimethyl ammine)
cyclo pentane carboxy amide

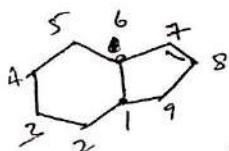
ISO-CYANIDES:-



BICYCLO COMPOUNDS:- (N^* & Olympiad)

Not in JEE.

①



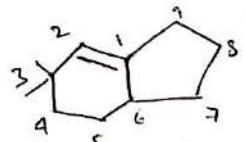
Bicyclo [4,3,0].

non-2-ene.

^2P ^1P .

bicyclo (4,3,0).

②

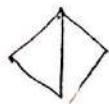


3,3-dimethyl.

bicyclo (4,3,0).

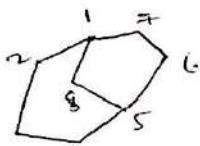
- non - $\Delta^{(1,2)}$ - ene

③



bicyclo [1,1,0] butane.

④



bicyclo [3,2,1]

octane

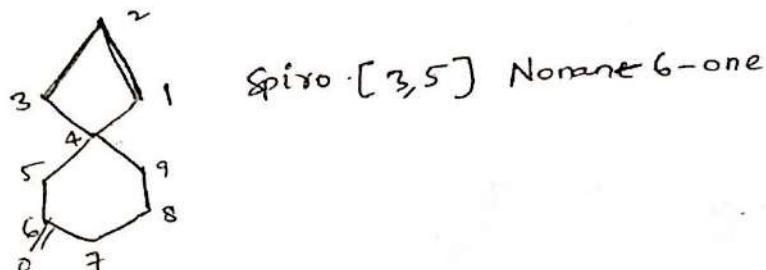
② Camphor:



1,7,7-trimethyl Bicyclo[2.2.1]

heptan-2-one.

SPIRO COMPOUNDS:



IUPAC NAME OF AROMATIC COMPOUNDS:

① Benzene:

	COMPOUND + STRUCTURE	COMMON NAME	IUPAC NAME
1) Benzene		Benzene	Benzene
2)		oil of Mirene / Nitro Benzene	Nitro Benzene
3)		Chloro Benzene	Chloro Benzene
4)		Toluene	Methyl Benzene

Note: For most of the aromatic compounds IUPAC is accepted, their common names as IUPAC names.

Structure	Common name	Pref. IUPAC	Syst. IUPAC
1)	para chloro toluene	4-chloro toluene.	(1-chloro, 4-methyl) benzene.
2)	Benzyl Chloride.	1-chloro-1-phenyl methane.	NOTE: Even though halo groups are substituents but one comp. contains benzene ring & halo groups; where the halo grp. is present from that you should select parent chain.
3)	2,3-dibromo-1-phenyl pentane.		
4)	Benzal chloride.	1,1-dichloro-1-phenyl methane.	
5)	Benzo chloride.	1,1,1-trichloro-1-phenyl methane.	
6)	DDT	1,1,1-trichloro-2-bis(4-chlorophenyl)ethane.	
7)	o-xylene	1,2-dimethyl benzene	
8)	m-xylene	1,3-dimethyl benzene	
9)	p-xylene	1,4-dimethyl benzene	

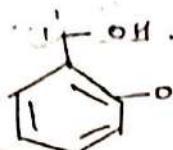
10)		mesitylene	1,3,5-trimethyl benzene
11)		Cumine	2-phenyl iso propyl Benzene
12)		Styrene.	1-Phenyl Ethene
13)		Stilbene	1,2-diphenyl Ethene
14)		Ortho chloro toluene	1-Chloro, 2-methyl benzene 2-chloro toluene
15)		meta chloro toluene.	(-chloro 3-methyl benzene) (or) 3-chloro toluene.
16)		Carboxylic acid	Benzanol (or) Phenol ✓
17)		<u>O-cresol</u>	2-methyl phenol
18)		<u>M-cresol</u>	3-methyl phenol
19)		<u>P-cresol</u>	4-methyl phenol
20)		Catechol	Benzene - 1,2-diol
21)		Resorcinol	Benzene - 1,3-diol
22)		Quinol (or) <u>Hydroquinone</u>	 Benzene - 1,4-dio

22)

→ Phenol is preferred more than alcohol

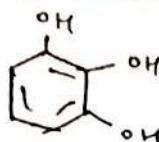
(iii)

Eg:



OH
 $\text{OH} \cdot 2\text{-}(\text{hydroxy methyl}) - \text{phenol}$

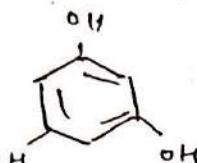
23)



Pyrogallol

Benzene-1,2,3-triol

24)



phloroglucinol

Benzene-1,3,5-triol

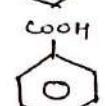
25)



Benzaldehyde

Benzene carbaldheyde
(or)
Benzaldehyde

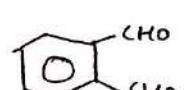
26)



Benzoic acid

Benzene carboxylic
acid
(or)
Benzoic acid.

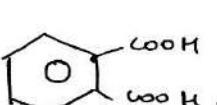
27)



Phthalaldehyde

Benzene 1,2-di
carbaldehyde

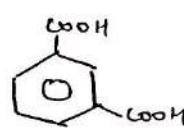
28)



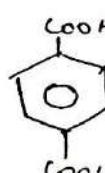
Phtalic acid

Benzene 1,2-di
carboxylic acid

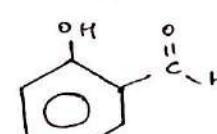
29)

Iso pthalic
acidBenzene 1,3-di
carboxylic acid

30)

Ter pthalic
acidBenzene 1,4-tri
carboxylic acid

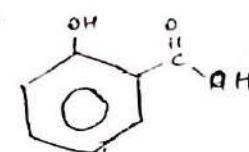
31)



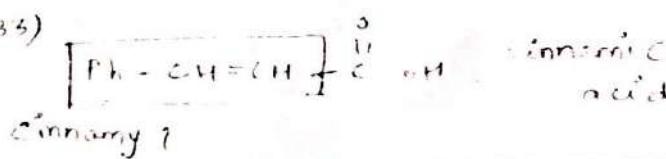
Salicylaldehyde

2-hydroxy benzal
-dehyde

32)

Salicylic
acid2-Hydroxy
benzoic acid

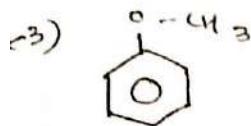
33)



Cinnamyl

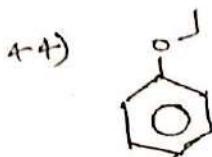
Intrinsic
acid β -phenylProp-2-en-1-
-ol acid

34)		Aspirin	2-acet oxy Benzoic acid
35)		methyl Salicylate (or) oil of winter green	methyl 2-hydroxy benzoate.
36)		Phenyl Salicylate (or) Salol	Phenyl 2-hydroxy Benzoate.
37)		Picric acid.	2,4,6-tri nitro phenol
38)		TNT (Tri Nitro Toluene)	2-methyl 1,3,5-trinitro benzene. (or). 2,4,6 - tri NO ₂ toluene.
39)		O-toluenoic acid	2-methyl benzoic acid
40)		chloral	2,2,2-trichloro Ethanol
41)		HCB (hexa chloro benzene)	1,2,3,4,5,6- hexa chloro benzene.
42)		BHC (benzene hexa chloride) Grammerane (or) Lindane (or) 666 (triple 6)	1,2,3,4,5,6- hexa chloro cyclo hexane



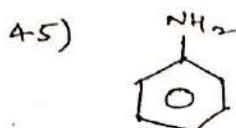
Anisole

methoxy benzene
(or)
Anisole ✓



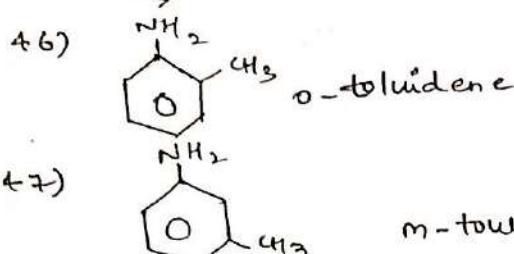
Phenetole

Ethoxy benzene



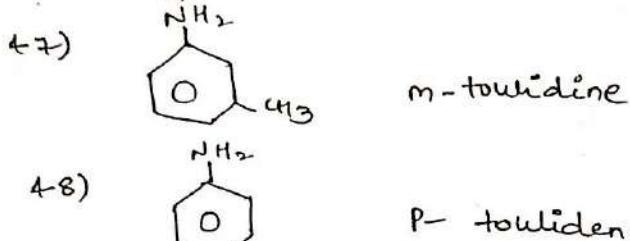
Aniline

Benzene Amine
(or)
Aniline ✓



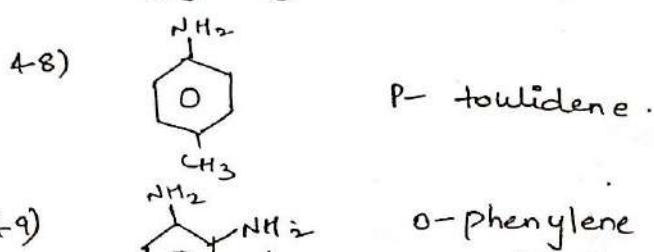
o-tolidine

2-methyl
benzene Aniline



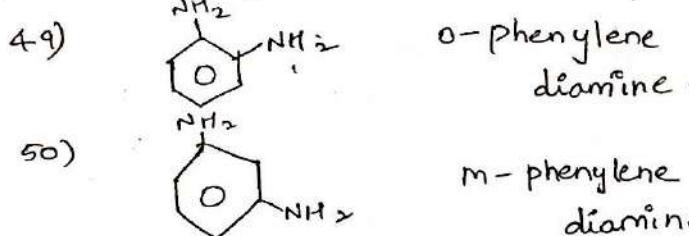
m-tolidine

3-methyl
Aniline



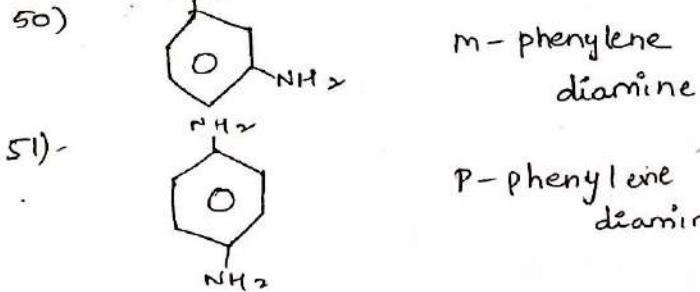
p-tolidine

4-methyl
Aniline



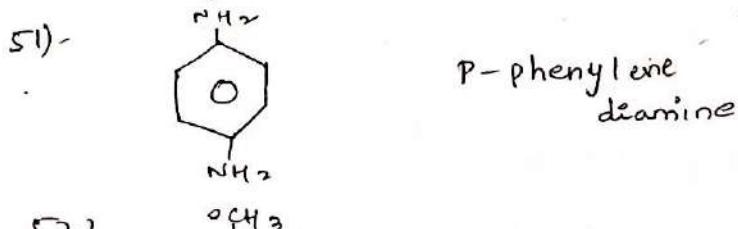
o-phenylene
diamine

Benzene-1,2-
diamine



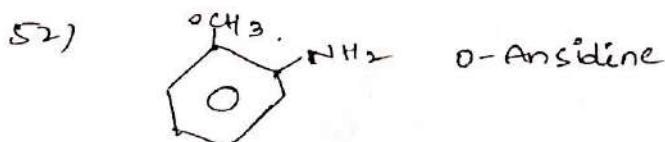
m-phenylene
diamine

Benzene-1,3-
diamine



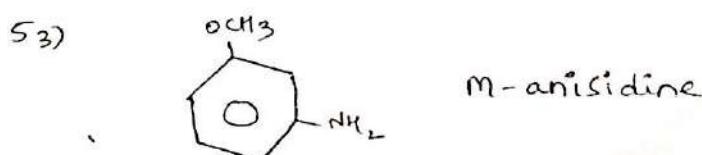
p-phenylene
diamine

Benzene-1,4-
diamine



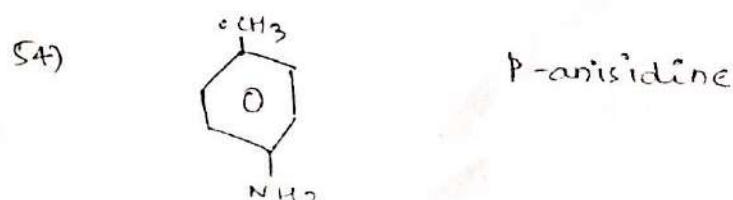
o-Anisidine

1-methoxy
aniline



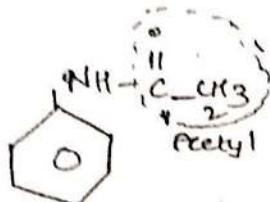
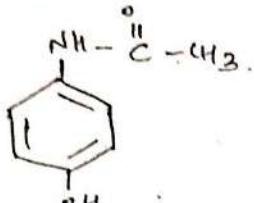
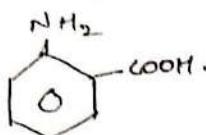
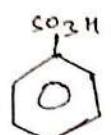
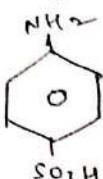
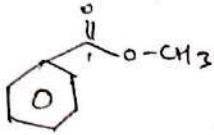
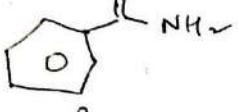
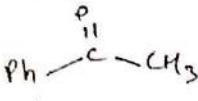
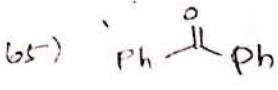
m-anisidine

2-methoxy
aniline



p-anisidine

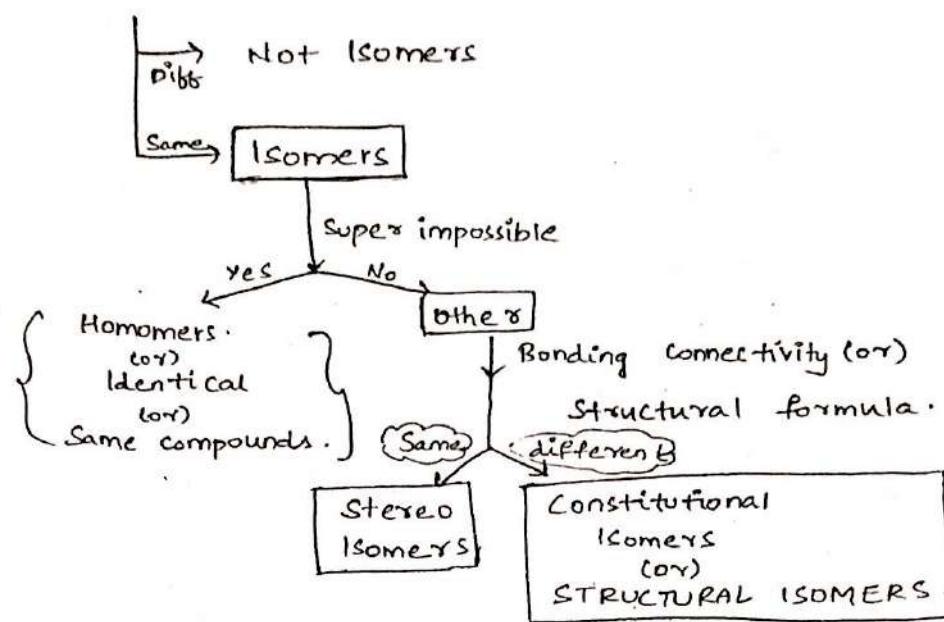
3-methoxy
aniline

55)		(not directly connected to benzene) Aliphatic i amine	Benzyl amine	1-phenyl methanamine.
56)			Acetanilide.	N-phenyl Ethanamide.
57)			Paracetamol	N-(hydroxy phenyl) Ethanamide
58)			Anthranilic acid	2-amino. benzoic acid.
59)			Benzene sulphonic acid	Benzene sulphonic acid
60)			p-Sulphanilic acid	4-amino. benzene-1-sulphonic acid.
61)			Methyl benzoate	phenyl. methanoate
62)			Benzoyl chloride	
63)			Benzamide.	
64)			Acetophenone	
65)			Benzophenone	

STEREO - CHEMISTRY

W.M.

Molecular formula.

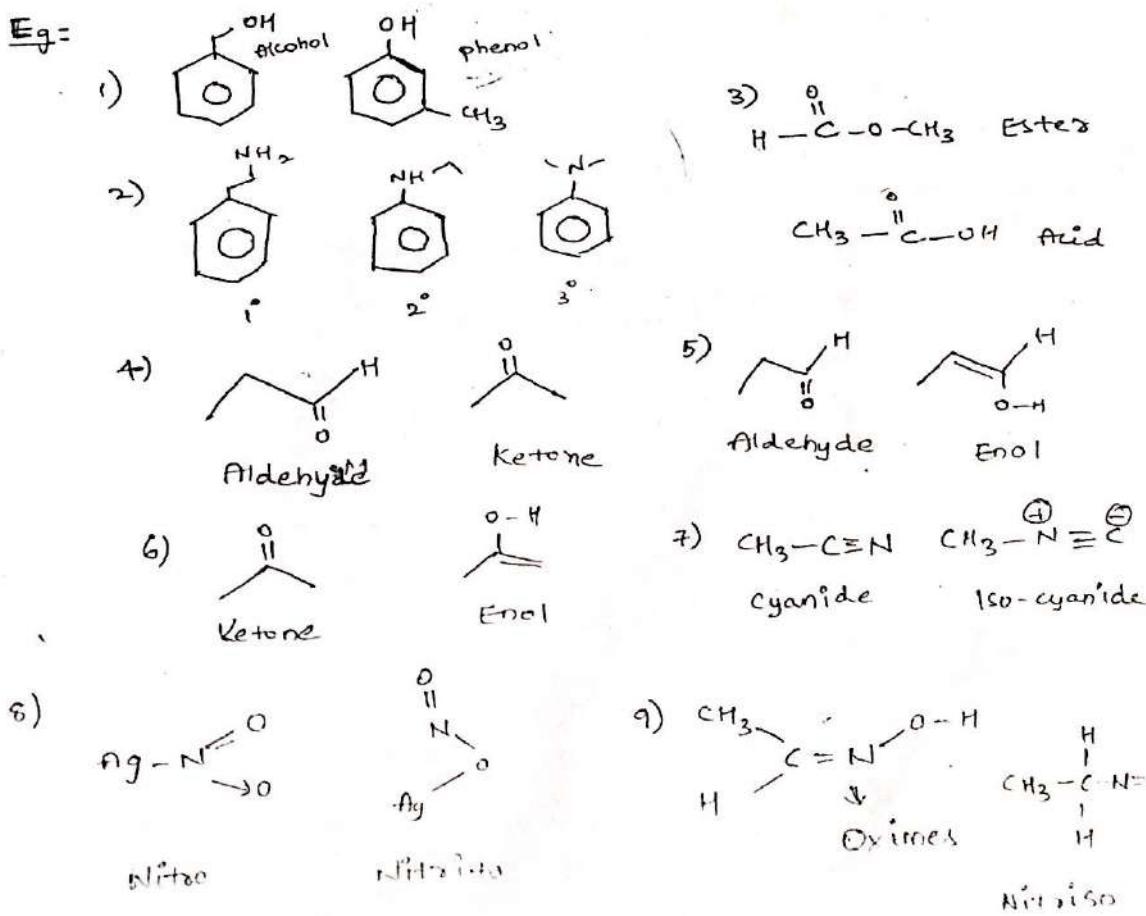


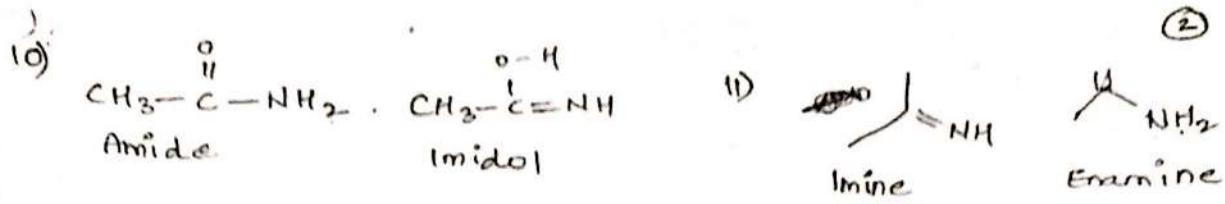
CONSTITUTIONAL ISOMERS (or) STRUCTURAL ISOMERS :-

i) Functional Isomerism:

→ possesses different functional groups.

Eg:-

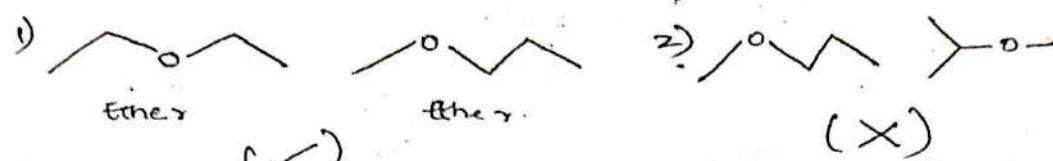




2) Metamerism :-

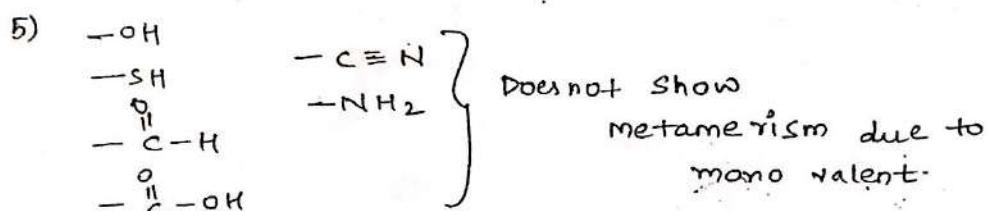
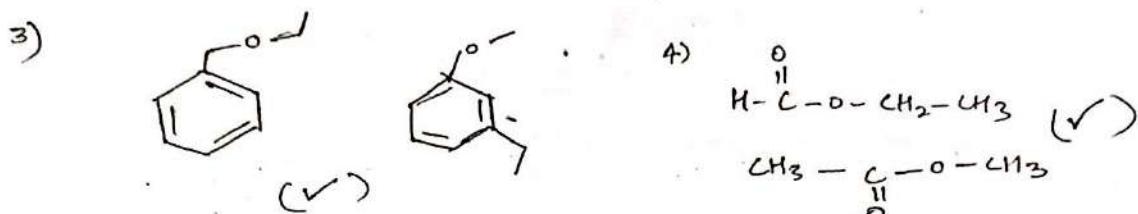
→ Exchanging groups upon same functional groups.
Together

Eg:



→ Both the sides are changed.

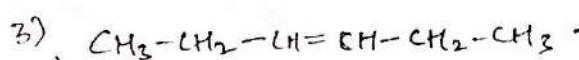
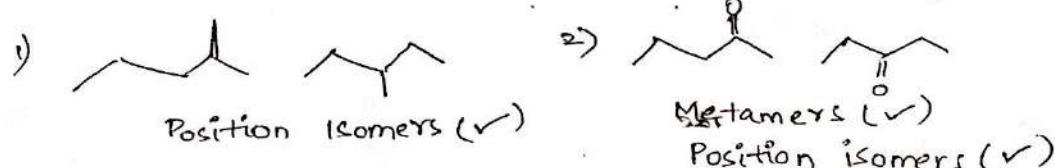
→ only one side was changed



3) Position Isomerism :-

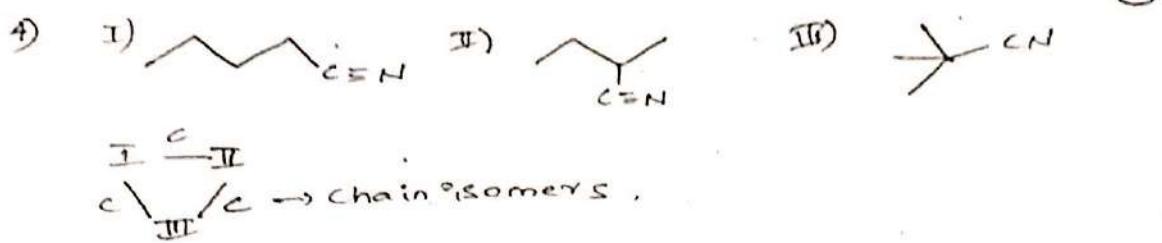
→ With same root word; position of secondary prefix (or) secondary suffix are changed.

Eg:



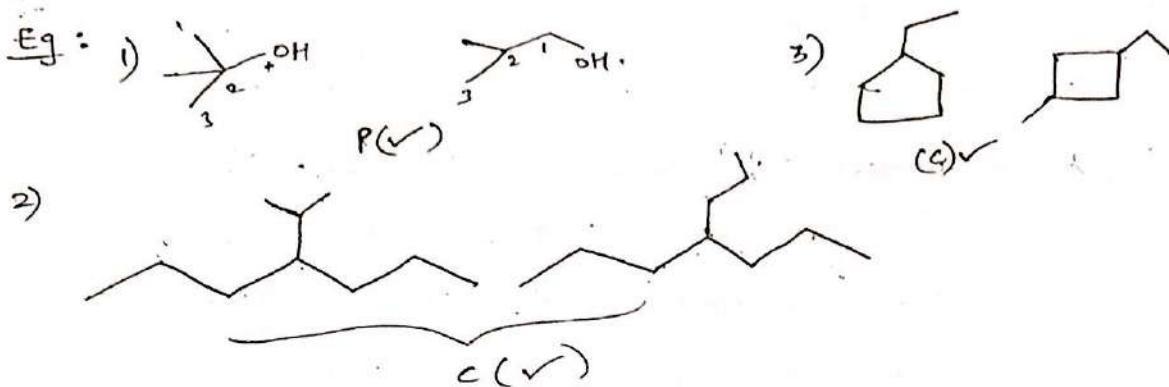
P(✓) M(X)

- vinylene & yne; Metamerism is not defined.



4) CHAIN ISOMERS:-

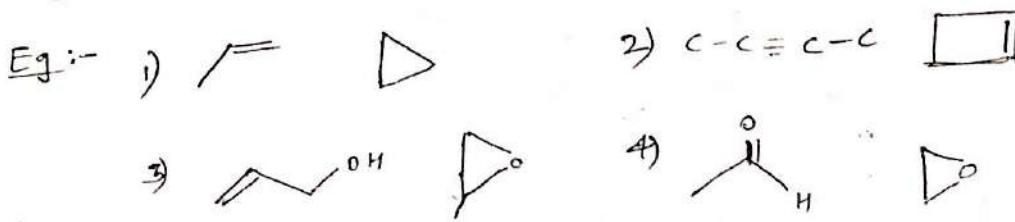
→ changing in the root word either in main chain (or) in side chain (or) both.



- Chain, position together doesn't exist.
- Once, it is Functional, no need to check whether it is chain (or) positional.
- Once it is metamer, no need to check chain, position except in case of Ketones. (Few)

5) RING-CHAIN ISOMERISM:

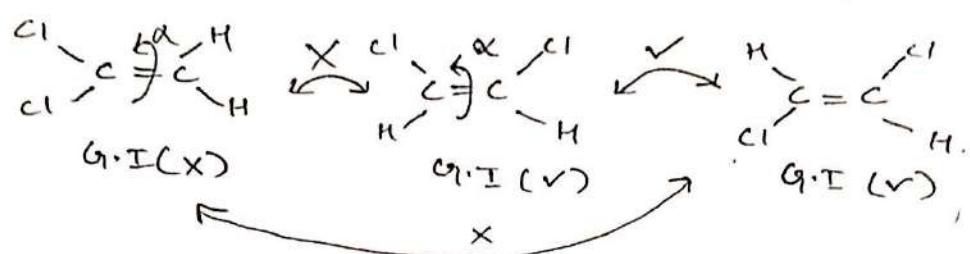
→ All Ring chain isomers are functional isomers.
and vice-versa Not true.



NOTE: All structural isomers possesses

- same molecular formula ✓
- same structural formula ✗
- same physical properties ✗
- same chemical properties ✗

GEOMETRICAL ISOMERS / CONFIGURATIONAL ISOMERISM :-



→ All Geometrical Isomers are Stereo Isomers

→ Without changing structural formula, spatial exchanging of groups (or) group of atoms on RRS (Restricted Rotational System), if results different potential energetic forms, then they are called Geometrical Isomers. The phenomenon is known as Geometrical Isomerism.

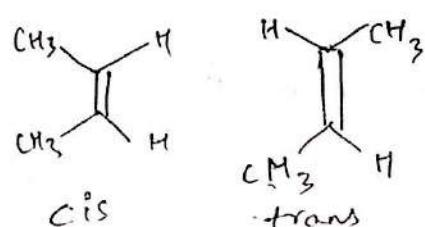
→ Pair of Geometrical Isomers does not interact inter exchange at room temperature. ($25^\circ - 22^\circ C$)

Eg:

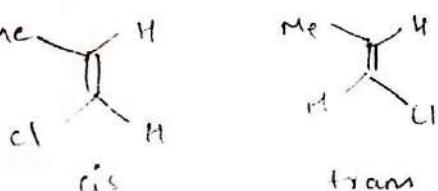
- 1) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ ✓
- 2) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ ✗
- 3) $\text{CH}_3-\text{CH}=\text{N}-\text{OH}$ ✓
- 4) $\text{CH}_3-\text{CH}=\text{NH}$ ✓
- 5) $\text{CH}_3-\text{N}^{\oplus}=\text{N}^{\ominus}-\text{CH}_3$ ✓
- 6)

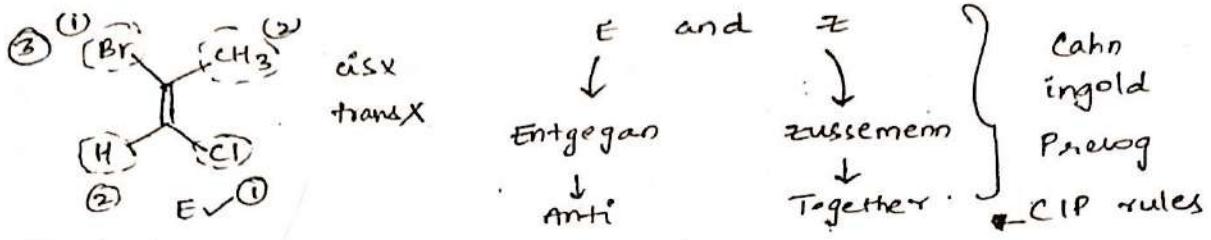
NAMING OF GEOMETRICAL ISOMERS:-

①



②

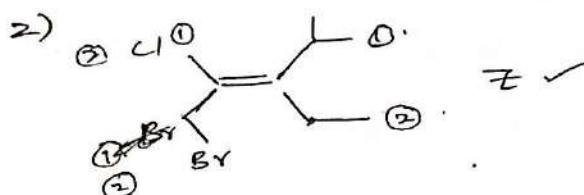
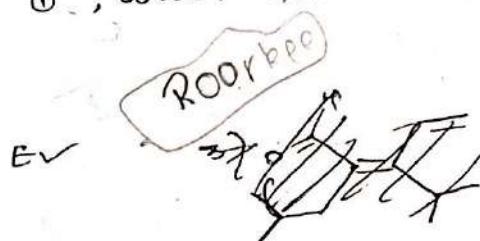
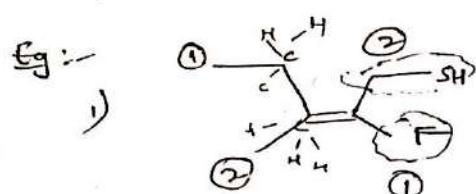




→ Individual numbering should be made.

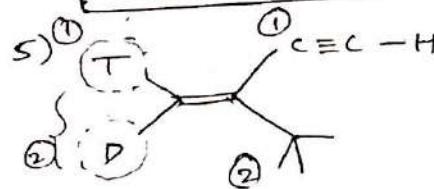
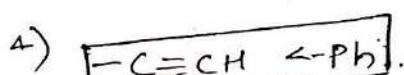
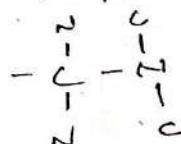
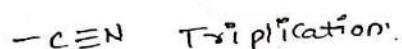
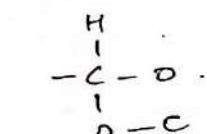
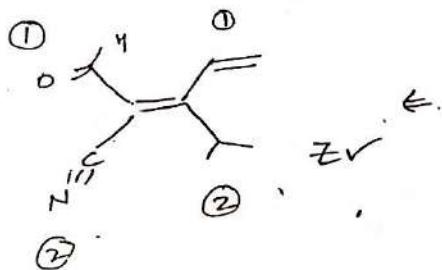
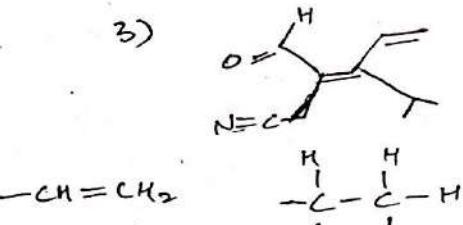
→ Based on the directly connected atomic number assign 1, 2, ~~3, 4~~.

→ Higher at.no receives ①, lower at.no → ②



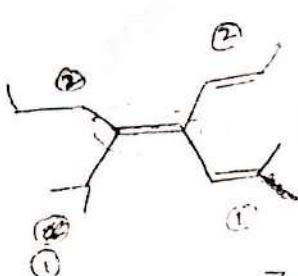
z ✓

3)



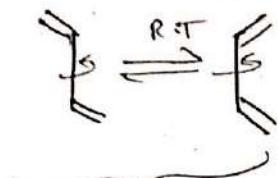
If At.no are same
mass should be taken

5)



→ All cis alkenes possess 'z' configurations (or) all trans alkenes possess 'e' configuration. [False]

Eg : 1) S-cis S-trans.

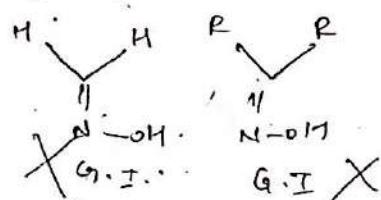


Not Geometrical Isomers

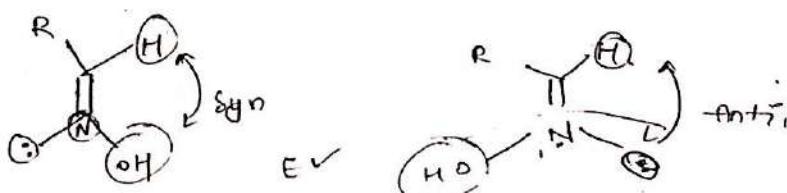
NAMING FOR OXIMES:

→ The oximes which are obtained from symmetrical carbonyl compounds does not exhibit geometrical isomers.

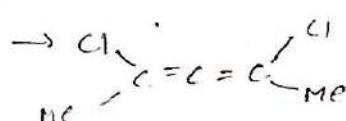
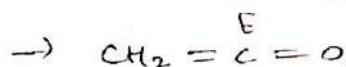
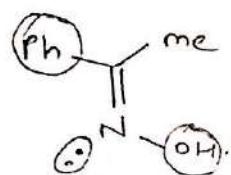
→ The oximes which are obtained from unsymmetrical carbonyl compounds does exist geometrical isomerism.

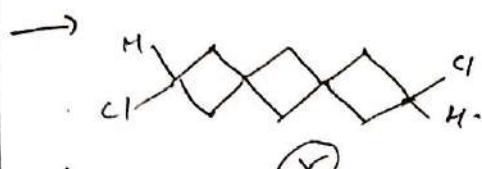
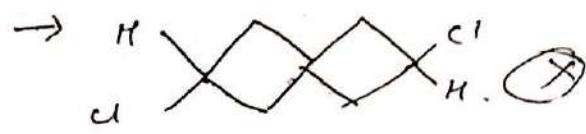
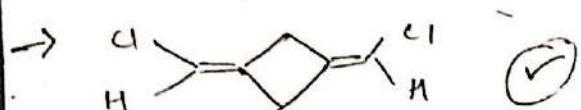
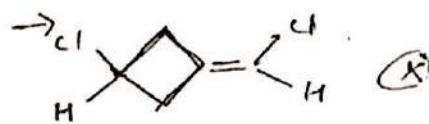
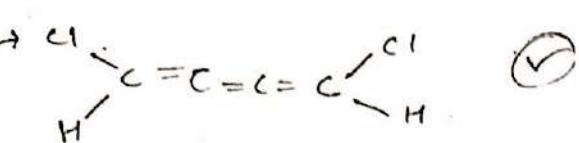


→ In case of aldoximes, if H & OH are same side, syn. If H & OH are opp. side, anti. Naming is preferable.

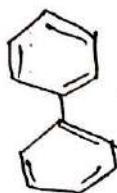


→ In case of ketoximes, assign only E & Z ✓

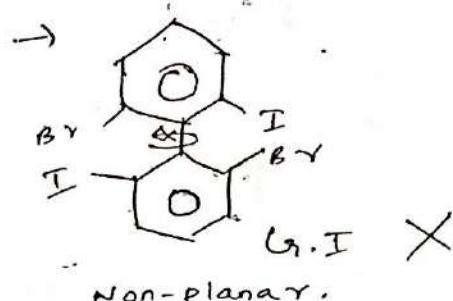




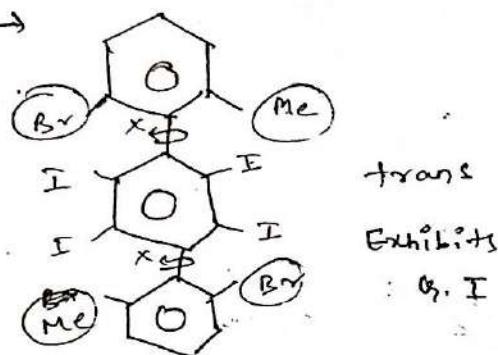
BIPHENYL:



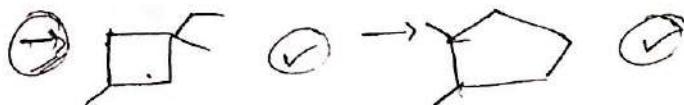
Planar ✓



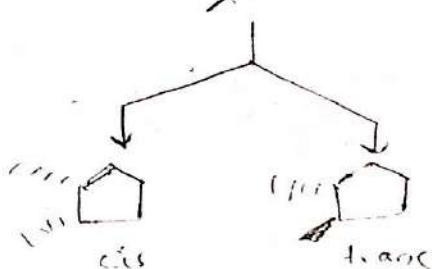
Non-planar.



NOTE: Take 3, 4, 5 membered ring C-C bonds are planar.



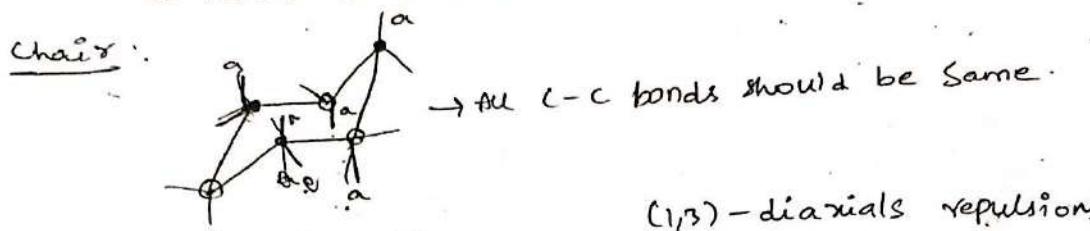
→



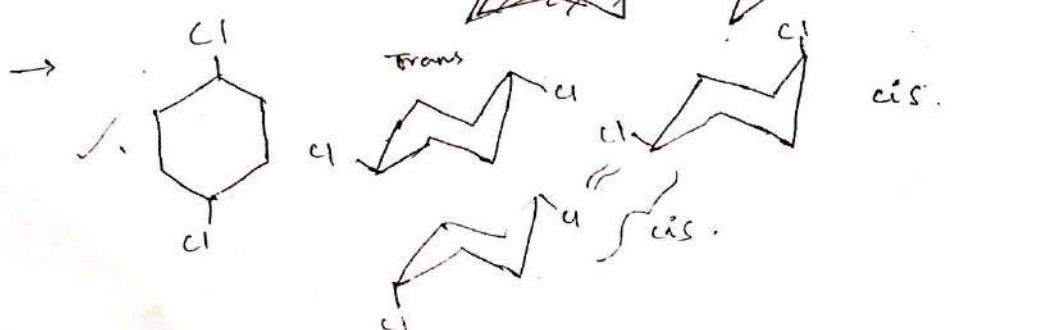
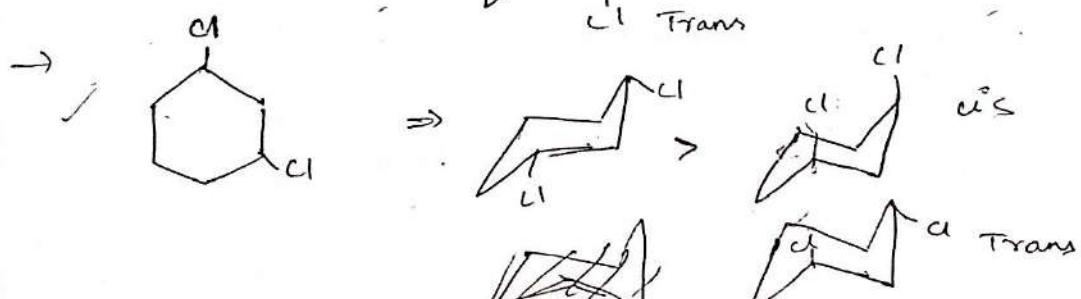
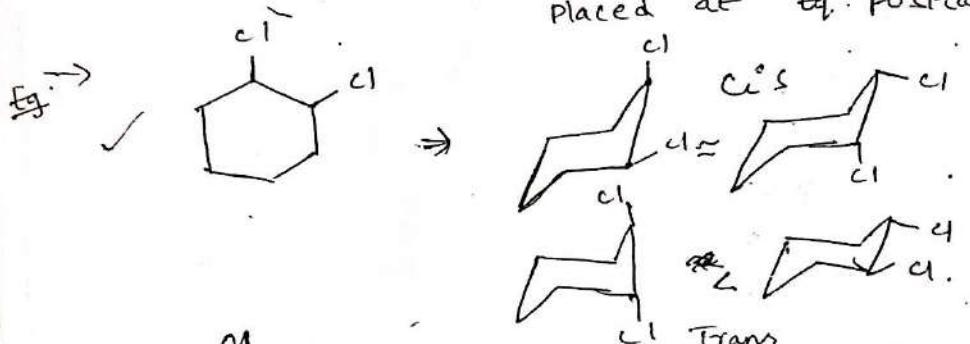
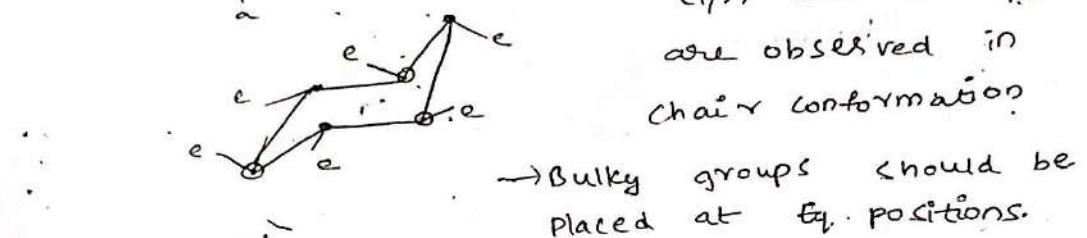
CYCLO HEXANE:

- Non-planar. is to be considered
- Exists in diff. forms

- ① Chair
- ② Boat
- ③ Half chair
- ④ Twist boat etc--

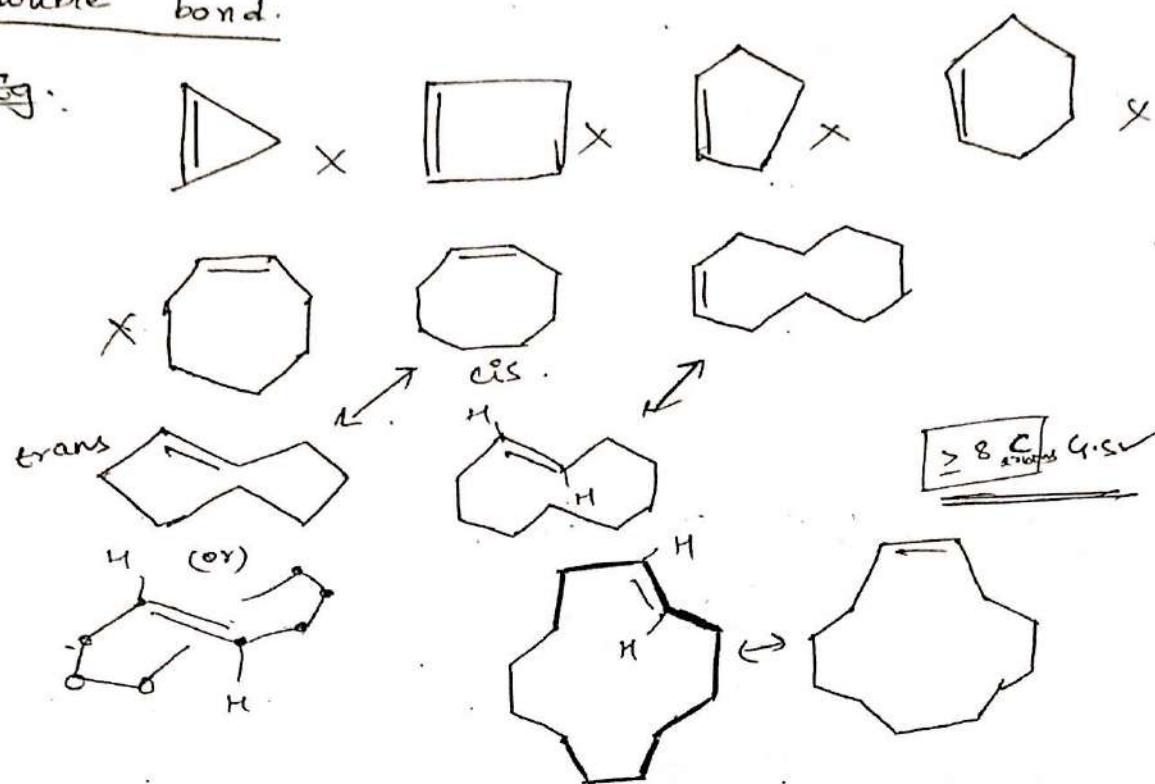


(1,3)-dioxials repulsions
are observed in
chair conformation?



→ Geometrical Isomerism in cyclo alkenes w.r.t
its double bond.

Eg:-



→ STABLE CONFIGURATION FOR cis-3-chloro-cyclo hex-1-ol is

A)



Diaxial.

Properties of Geometrical Isomers :-

cis

Trans



i) Stable : II > I

ii) μ : I > II

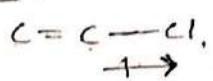
iii) Soluble : I > II (more polar, more soluble \Rightarrow more μ)

iv) BP : I > II (strength-Hydrogen bonding / δ/δ vander waal's force of inter)

v) MP : II > I (packing π)



Hence:



1) Dipole moment : trans > cis (II > I)

2) Stability : II > I

3) Solubility : II > I

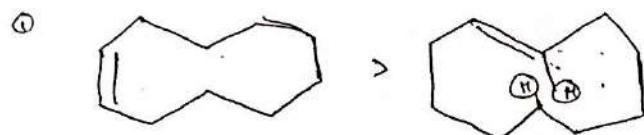
4) BP : II > I

5) MP : II > I

Fact:

→ In case of cycloalkenes (cyclo octene, cyclo nonene, cyclo decene and cyclo undecene (!)) cis isomer is more stable than trans.

Reason: Hydrogen-Hydrogen Repulsions in trans.



→ In case of cyclo dodecene trans is more stable than cis.

No. of Geometrical Isomers:-

No. of geometrical isomers:

1)

0

2)

2

3)

2

4)

0

5) $CH_2 = C = O$

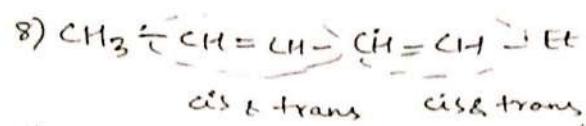
0

6) $CH_2 - CH = C = CH - CH_3$

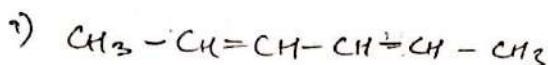
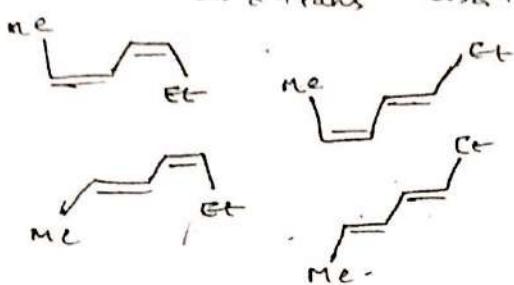
0

7) $CH_2 - CH = C = C = CH - CH_3$

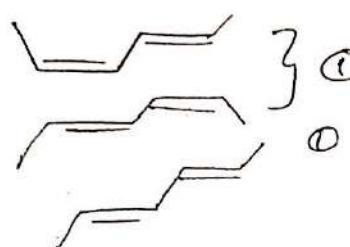
2



(4)



(5)



{ ① overlapping of
these both gives same.

→ If 'n' no. of RRS systems which exhibits geometrical isomerism, then G.I. = ?

$$= 2^n \text{ if } n \text{ is unsymmetrical}$$

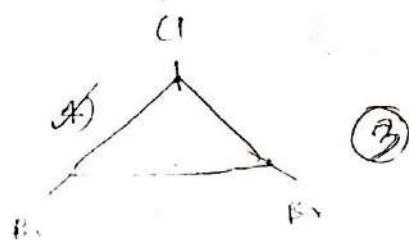
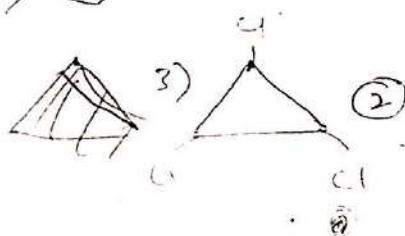
$$= 2^{n-1} + 2^{p-1} \text{ if } n \text{ is symmetrical}$$

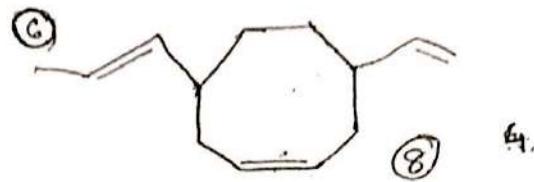
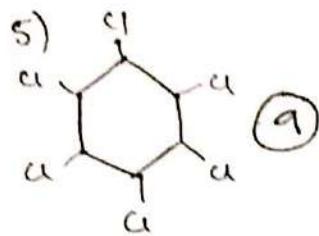
$$p = \frac{n}{2} \text{ (Even)}$$

$$= \frac{n+1}{2} \text{ (Odd)}$$

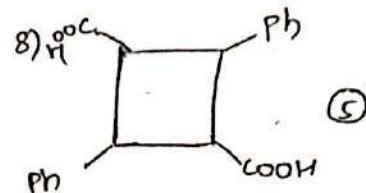
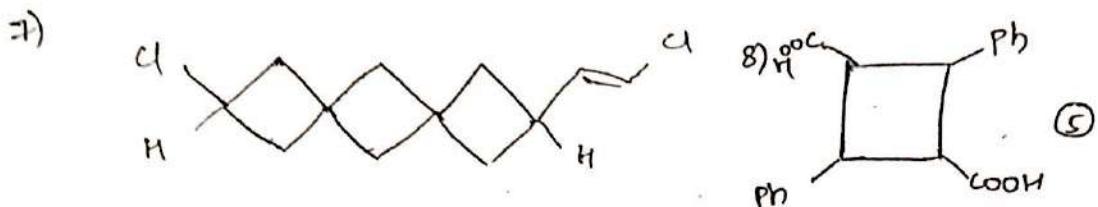
n	Sym	Unsym
1	2	2
2	3	4
3	6	8
4	10	16
5	20	32

Eg





4.

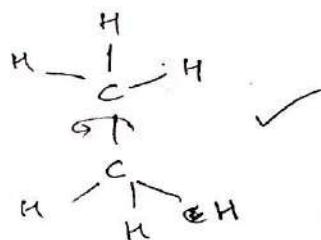


CONFORMATIONAL

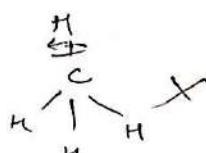
ISOMERISM : (or) Rotamerism :-

- Infinite no. of potential Energetic Forms are formed by internal rotation about 'σ' bond are called Conformations.
- Out of infinity conformations, which are corresponding to minimum potential energy are called Conformers.
- In General, isomers can be separated, but conformers cannot be "isolated" (separated) since they are rapidly interconvertable at room temperature

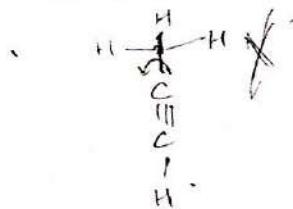
Eg: Ethane:



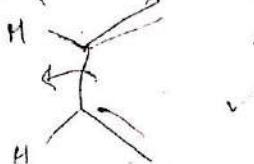
Methane



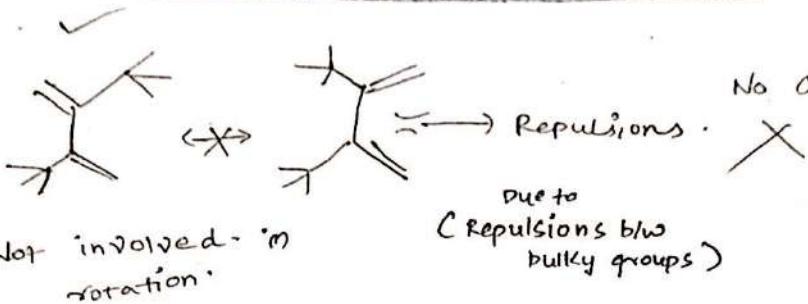
Propyne:



1,3-Butadiene



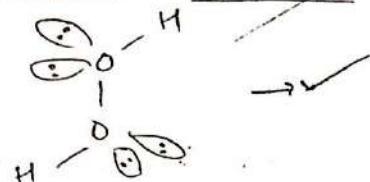
→ 2,3-di-tertiary Butyl 1,3-butadiene 



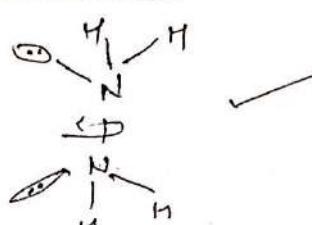
No Conformation

Due to
(Repulsions b/w
bulky groups)

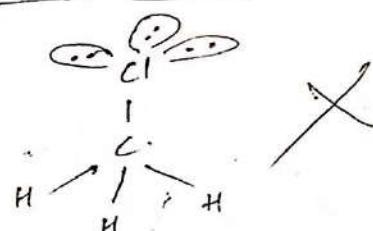
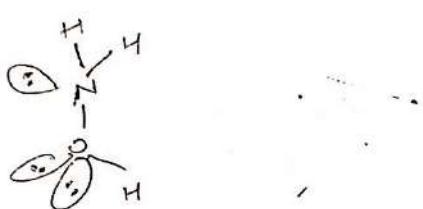
→ Hydrogen peroxide:



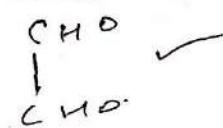
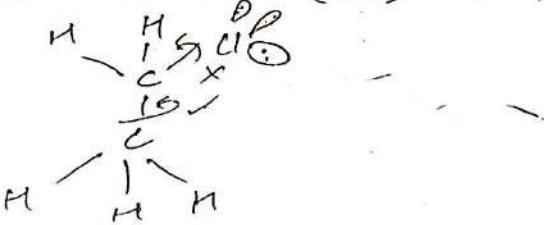
→ Hydrazine: (NH₂-NH₂)



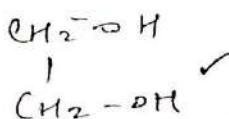
→ Hydroxy amine: (NH₂-OH) → ? Methyl chloride (CH₃Cl)



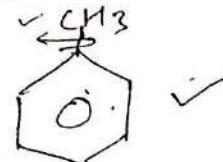
→ Ethyl chloride: (CH₃-CH₂-Cl) → Glyoxal:



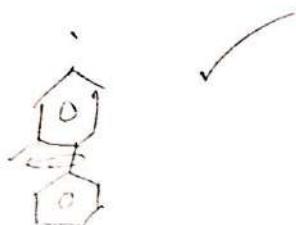
→ Glycol: (or) Ethylene diol:



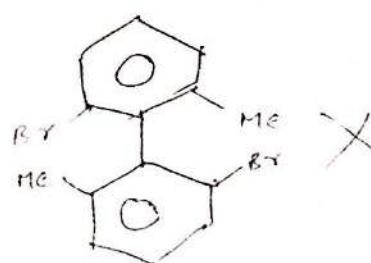
→ Toluene:



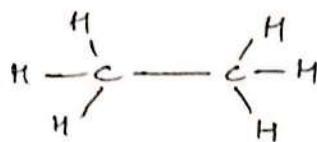
→ Biphenyl?



→



① Conformations of Ethane:



' ∞ ' no. of conformations

Representation:

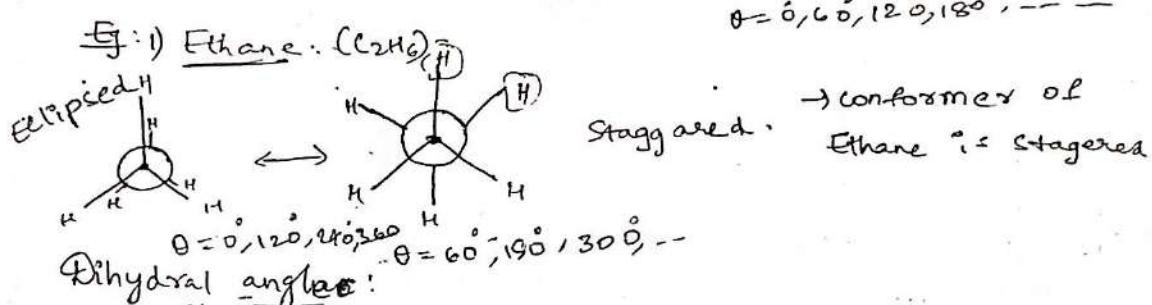
Ethane is,

① Newmann projection:

② Saw horse projection.

Rules to write Newmann projection:

→ Select (imaginary axis C-C bond) ^{which is directly} connected by 2 atoms in which 1st atom always represented with '•' and 2nd one always represented with circle.



Dihedral angles:

→ The angle b/w 2 groups (or) gap. of atoms which are joined on adjacent atoms. It is denoted with ' θ '.

→ Conformational changes in Ethane leads to change in torsional angle but not B.A (or) B.L

Stability: Staggered > Skew > Eclipsed.

↓

→ Less Vanderwaal repulsions. (or) (repulsions between the steric strain) → More Vanderwaal repulsion.

(cyclic groups)

→ More eclipsed

→ Less Eclipsed strain (or)

strain (observed only at 60°)

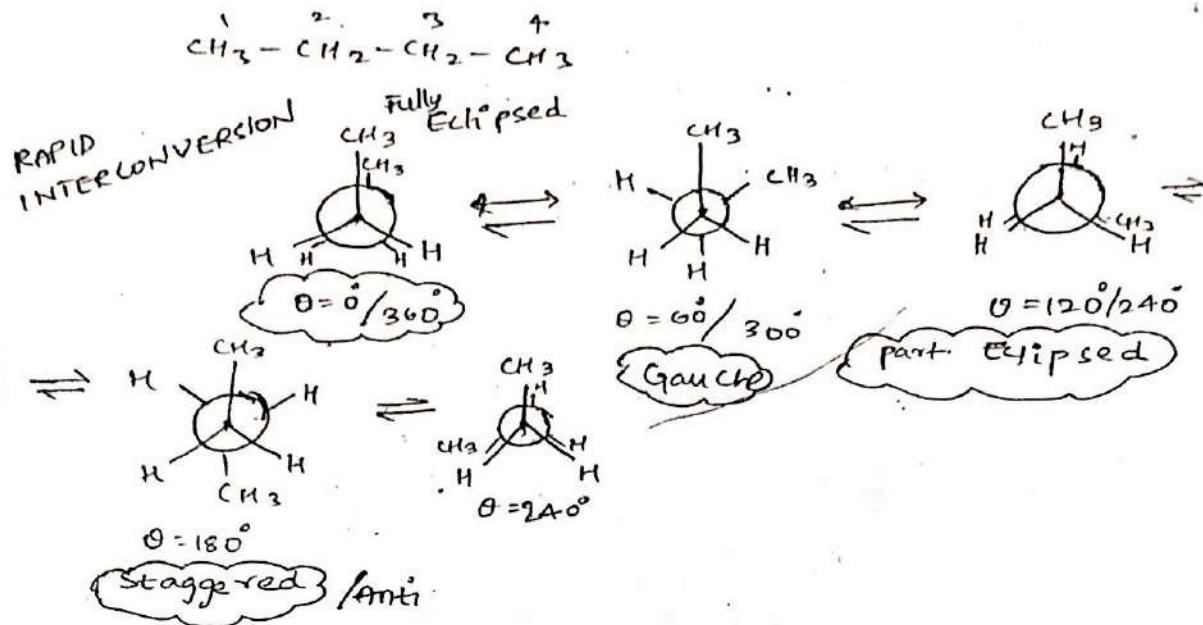
Torsional strain (or)

Pitzer strain

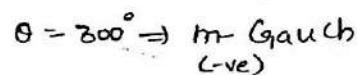
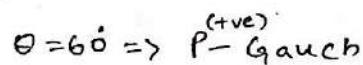
→ Vanderwaal repulsion (max. at 0°) decreases by increasing angle.

(A) Staggered Conformer is more stable than eclipsed conformer about $12 \text{ kJ/mole} \approx 2.9 \text{ kcal/mol}$

2) n-Butane (C_2-C_3 axis)



No. of Gauche conformations possible = 2

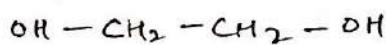


Stability: Staggered/Anti > Gaucher part-eclipsed > Fully eclipsed.

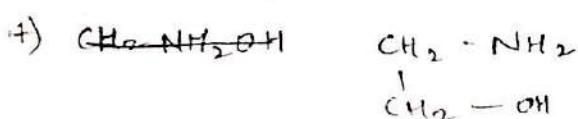
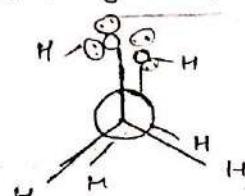
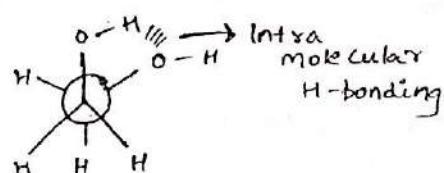
→ 3) Ethylene Glycol (or)

Glycol (or)

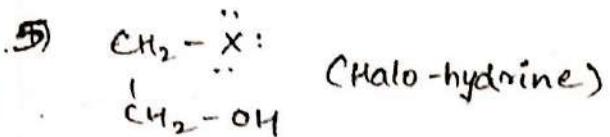
Ethane 1,2-diol (w.r.t C-C)



Stability: Gaucher Anti > Part-Eclipsed > Fully Eclipsed.



Stability: Gaucher Anti > part. > Fully Eclipsed



Stability: Gauche > Anti > part. > Fully Eclipsed. (Fluorine)

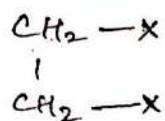
→ If chlorine

Gauche > Anti > part. > Fully.

Bromo/Iodine

Anti > Gauche > P.E > F.E

6) Vicinal dihalides:



→ If X is iodine. $\begin{array}{c} \text{CH}_2 - \text{I} \\ | \\ \text{CH}_2 - \text{I} \end{array} \xrightarrow{\text{I}_2} \text{CH}_2 = \text{CH}_2$

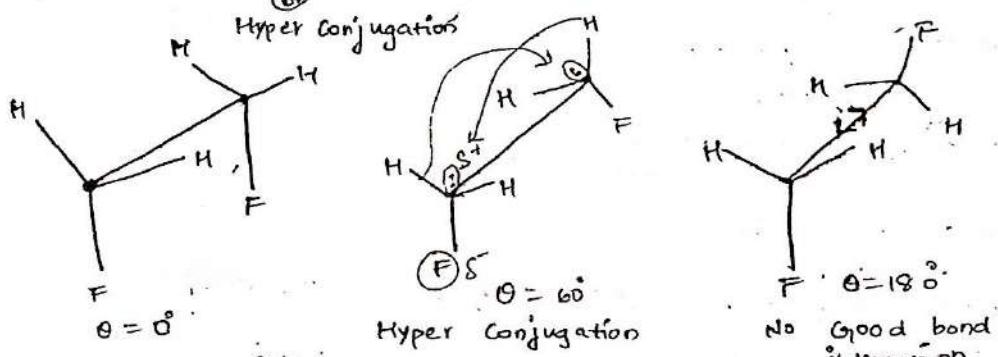
(doesn't exist
due to severe repulsion)

→ X-Cl : Anti > Gauche

- Br : Anti > Gauche

X-F : Gauche > Anti

(Good-bond interaction)

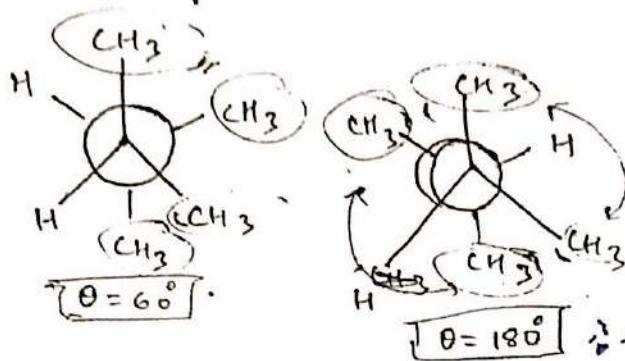


7) $\begin{array}{c} \text{CH}_2 - \text{COOH} \\ | \\ \text{CH}_2 - \text{COOH} \end{array}$ (succinic acid) in basic medi soln. $\rightarrow \begin{array}{c} \text{CH}_2 - \text{COO}^- \\ | \\ \text{CH}_2 - \text{COO}^- \end{array}$.

⇒ Anti > Gauche

N*

Nx → NOT IN VLE - -



→ Because in $\theta = 60^\circ$, there is van der waal repulsions but in 'Anti' due to repulsions Bond angles get compressed.

Stability: Gaucher Anti [$60^\circ > 180^\circ$]

→ compressing in bond angle is succession of B.A.

CONFORMATIONS OF CYCLO-ALKANES:-

1) Cyclo-hexanes:-

→ It is non-planar (i-C bonds in cyclo-hexane)

→ It may exist in the following conformations:

① CHAIR \rightleftharpoons Half Chair \rightleftharpoons Twist Boat \rightleftharpoons Boat

Stability: (cyclo hexanes)

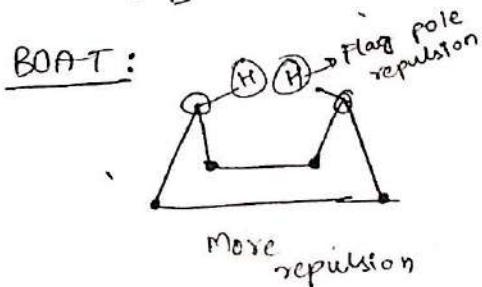
Chair > twist boat > boat > half chair (skew)

Energy differences:

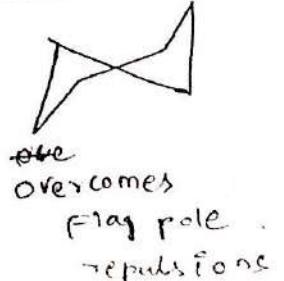
Chair - T.B 23KJ

Chair - half Chair 45KJ

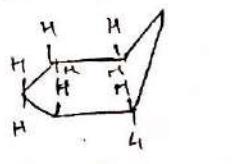
T.B - Boat 4KJ



Twist Boat:

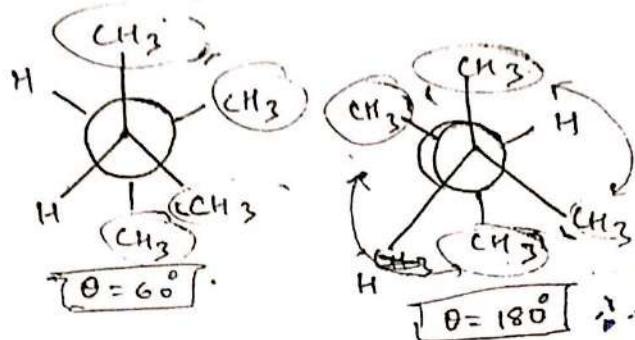


Half Chair:



∴ Stability: Chair > Twist boat > boat > half chair

N* → NOT IN V.L.



→ Because in $\theta = 60^\circ$, there is van der waal repulsions but in $\theta = 180^\circ$ due to repulsions bond angles get compressed.

Stability: Gaucher Anti [$60^\circ > 180^\circ$]

→ compressing in bond angle is succisiong of B.A.

CONFORMATIONS OF CYCLO-ALKANES:-

1) Cyclo-hexanes:-

→ It is non-planar (i-C bonds in cyclo-hexane)

→ It may exist in the following conformations:
is existed

① CHAIR \rightleftharpoons Half Chair \rightleftharpoons Twist Boat \rightleftharpoons Boat

Stability: (cyclo hexanes)

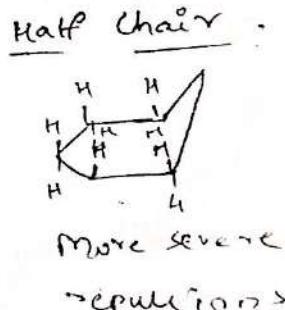
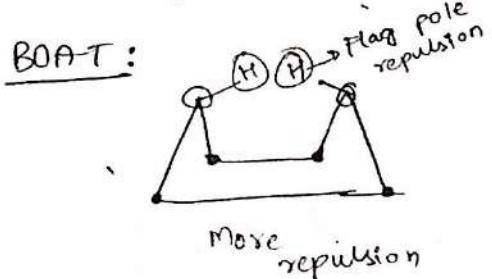
Chair > twist boat > boat > half chair (skew)

Energy differences:

Chair - T.B 23KJ

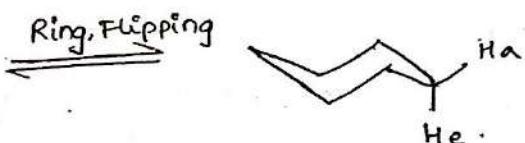
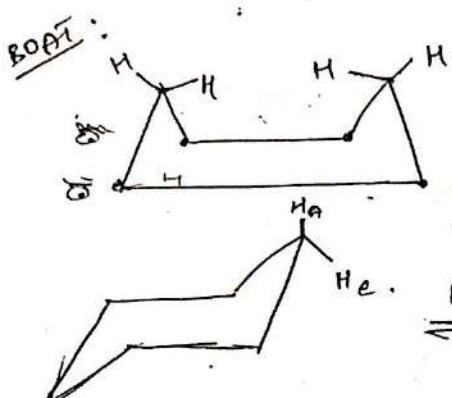
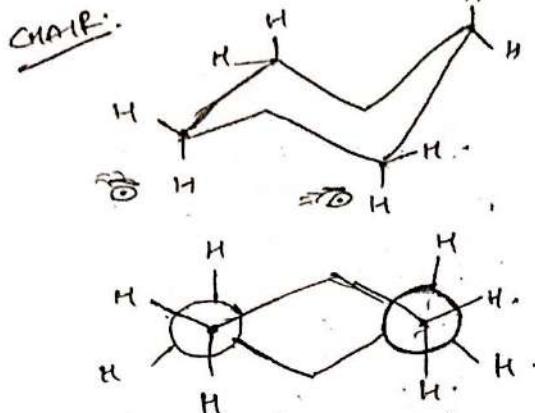
Chair - half chair 45KJ

T.B - Boat 4KJ

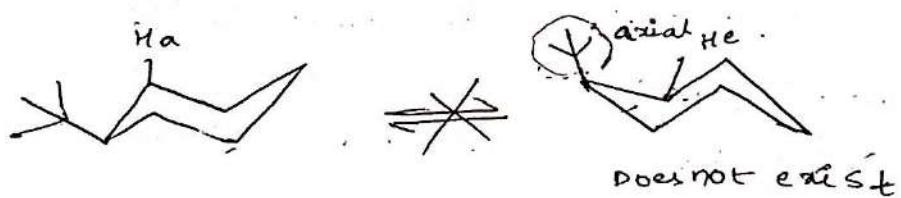


∴ Stability: Chair > Twist boat > boat > Half chair

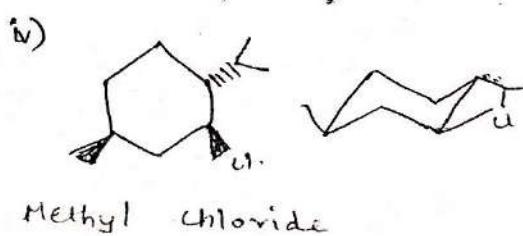
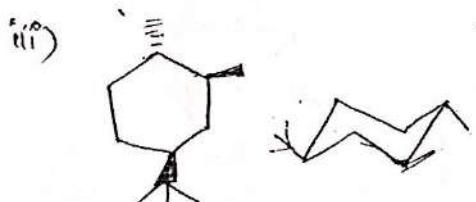
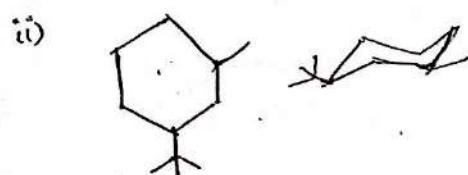
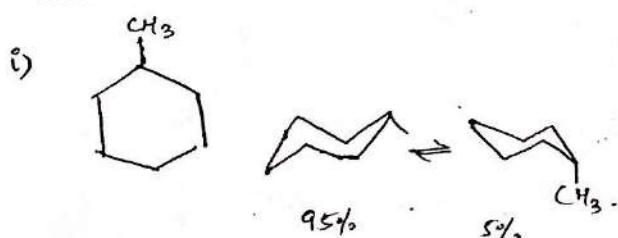
New-mann projection for chair conformation:-

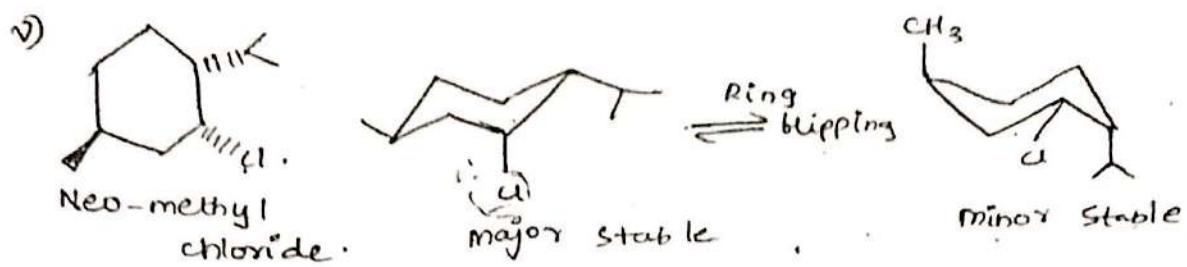


→ Due to high strain tertiary butyl does not exist at axial.

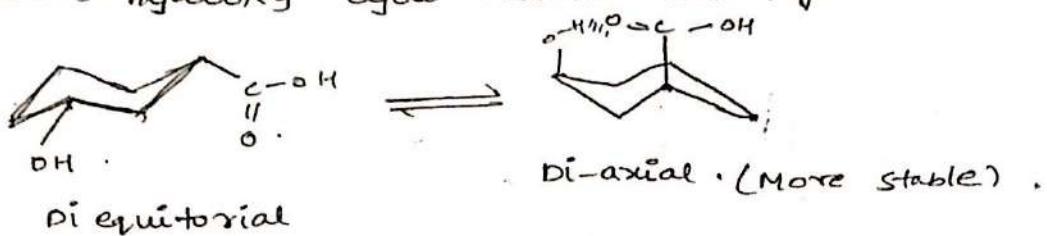


stable conformers for the following compounds:

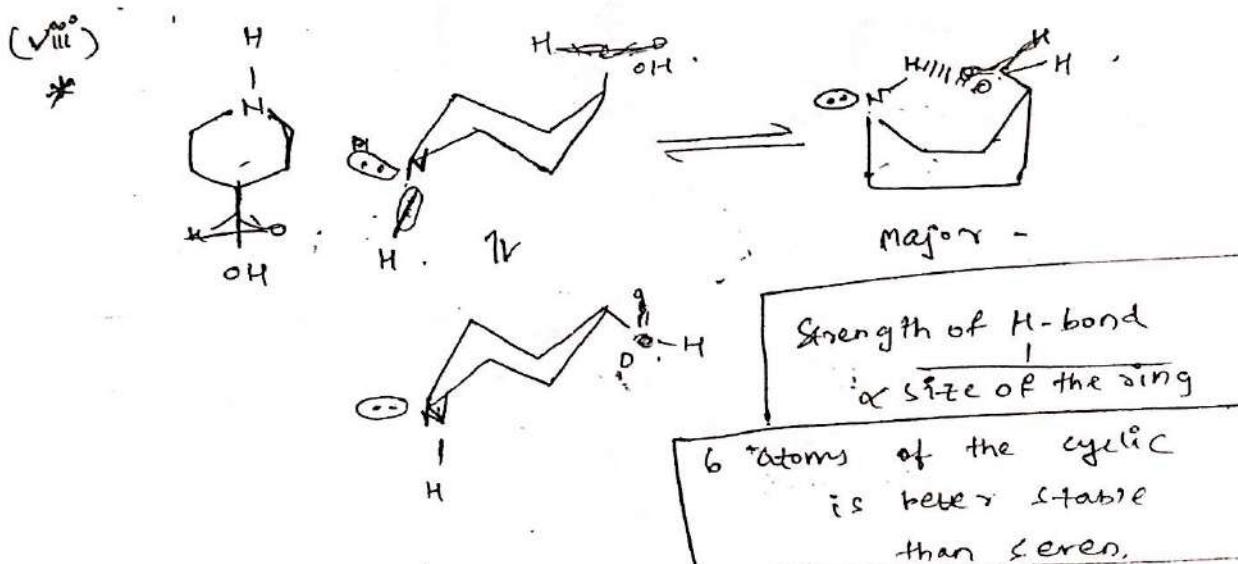
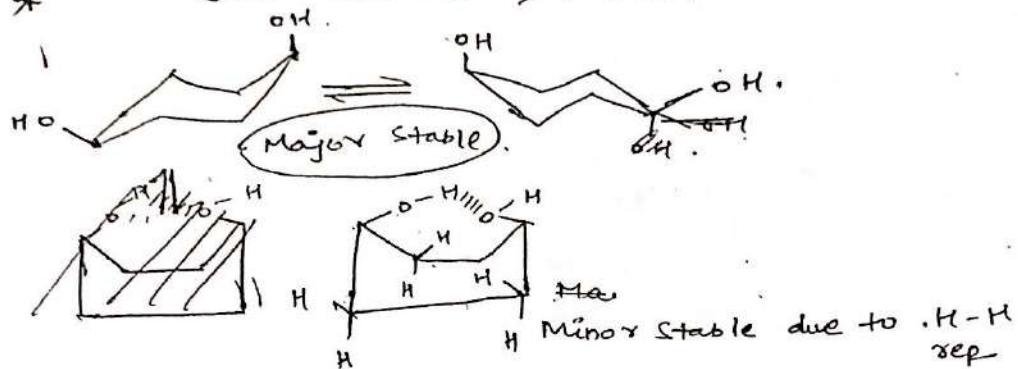




vi) Cis-3-hydroxy cyclohexane carboxylic acid.

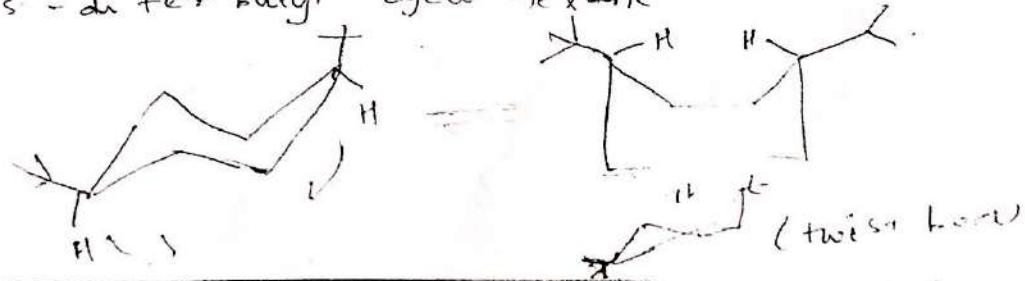


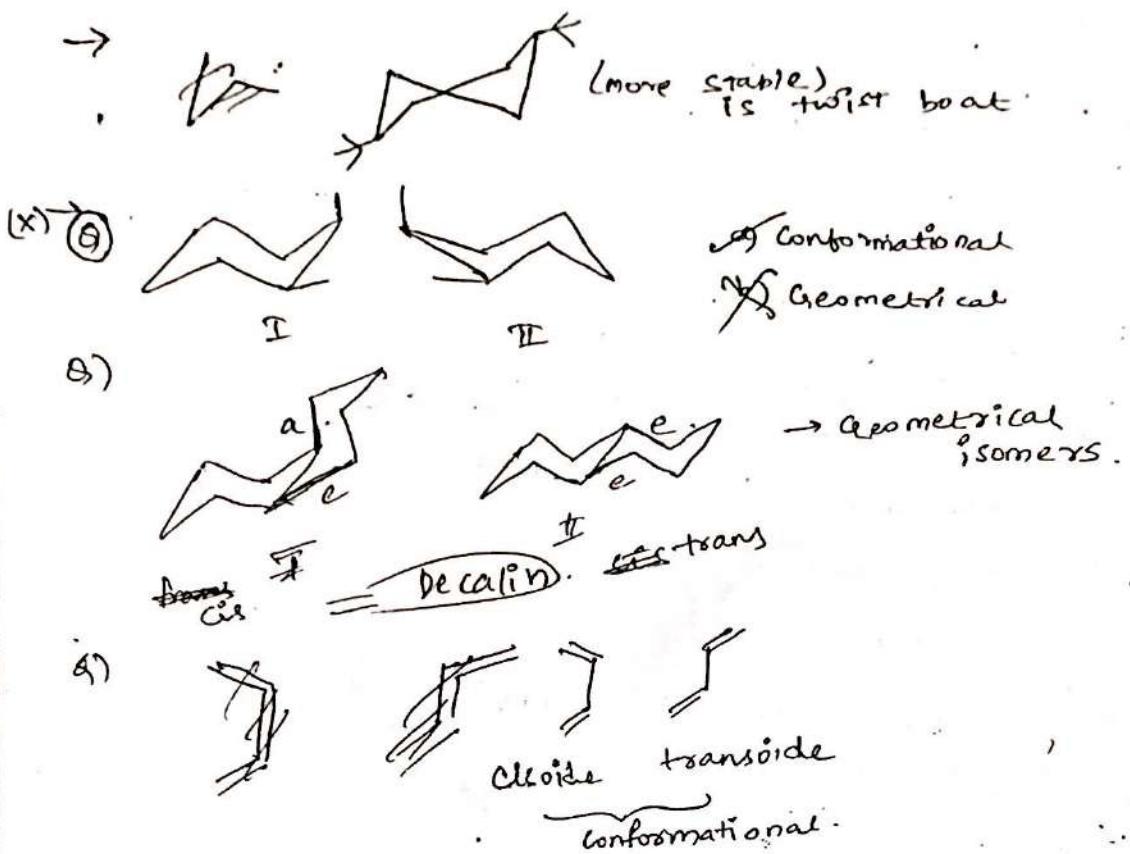
vii) * cis cyclohexane 1,4-diol



→ So, it predominantly exist in boat.

(ix) cis-di-tert-butyl cyclohexane



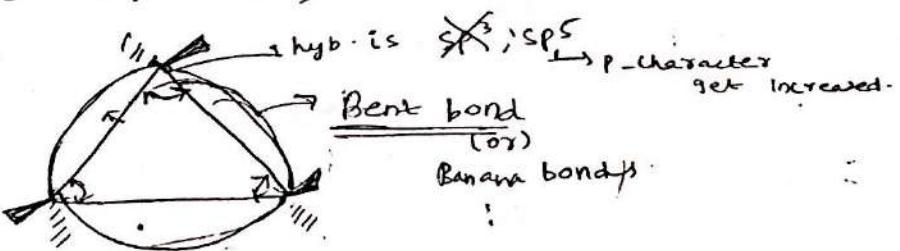


→ CONFORMATIONS FOR CYCLOPROPANE.

→ It is a planar molecule [C-C bonds] but due to are in one plane

high strain b/w C-C bonds

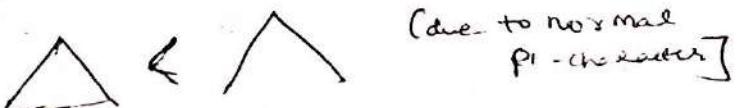
↳ Due to high strain, C-C bonds are bent.



C-C bond length order

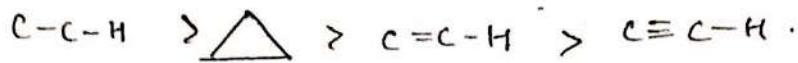


* b) C-H B.L is more in.



NOTE:

1) C-H bond length

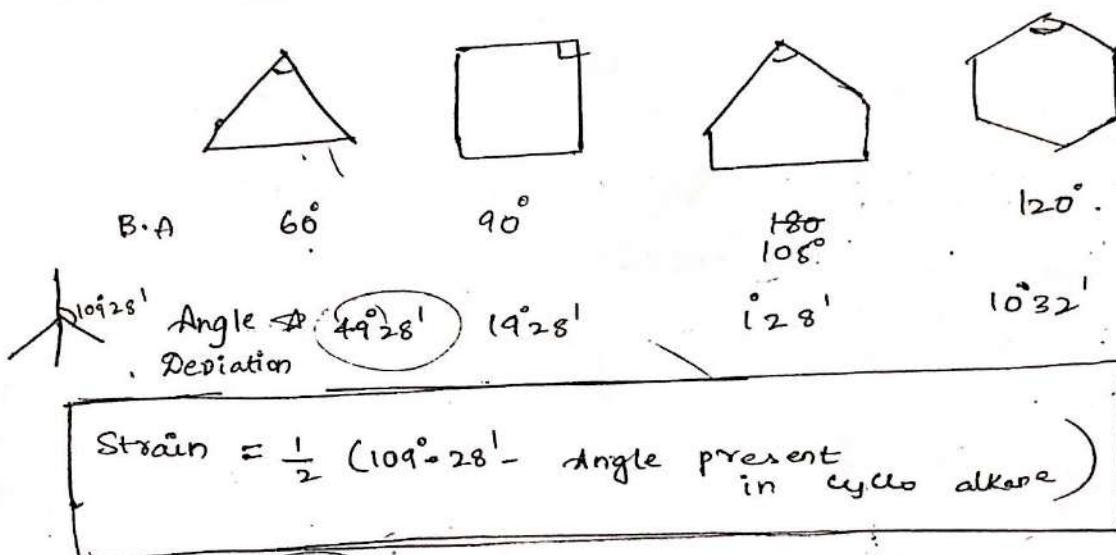


1) \rightarrow cyclo butane adjusted in butterfly structure.
 \rightarrow Stable form is butterfly.

2) \rightarrow cyclo pentane adjusted in envelope.

STABILITY OF CYCLO-ALKANES:-

\rightarrow Baeyer's STRAIN THEORY: (1885)

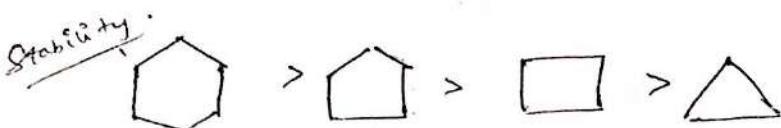


strain: ~~24.44'~~ 24.44' 9.44' 8.4' 5°26'

More is the strain, less is stable.

cyclo pentane > cyclo hexane > cyclo butane > cyclo propane

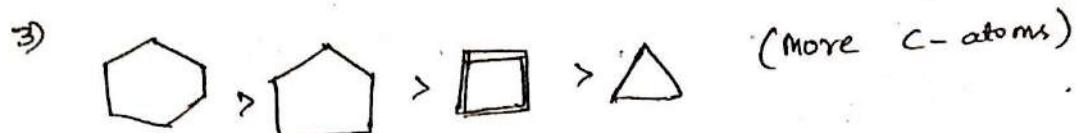
\rightarrow According to heat of combustion and Spectroscopic studies, we got the following result:



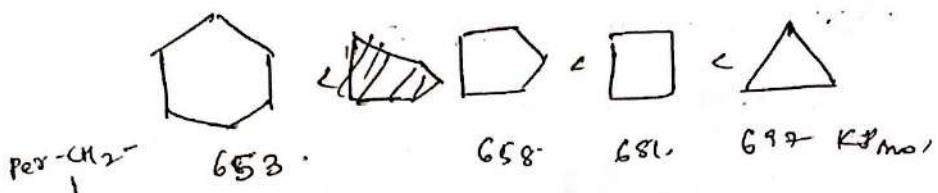
(Q) Arrange the following comp. in increasing order of heat of combustion.



$$\Delta H_c \propto \frac{1}{\text{stability}}$$



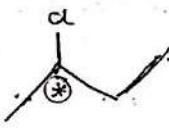
4) Heat of Comb. per (CH_2) is



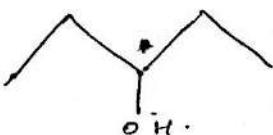
FISCHER PROJECTION: (1891)

- Identify asymmetric atom/assymmetric center/chiral atom/chiral centers.
- Atom (or) Element which possess 4 different groups.

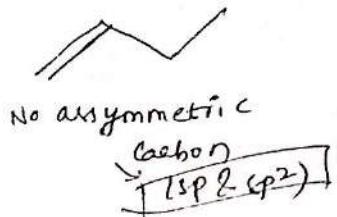
Eg: 1) 2-chloro butane.



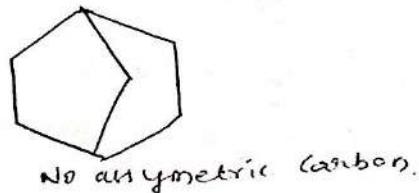
2) pentan-3-one



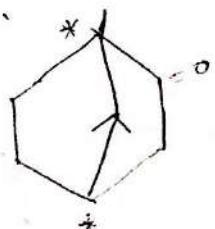
3) 1-Butene.



4)

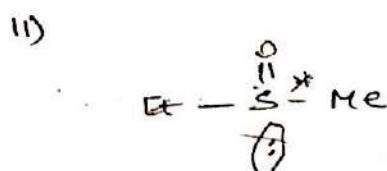
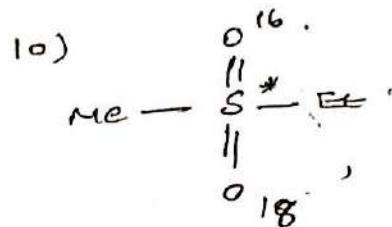
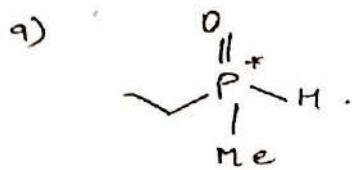
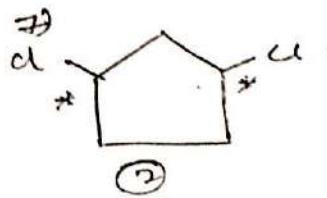


5)

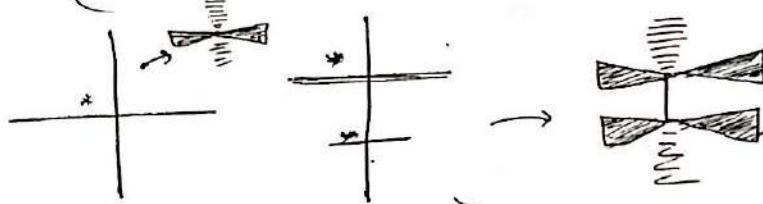


6)





→ Generally asymmetric atom(s) are indicated with
 (1 vertical line & 2 more hor. lines)

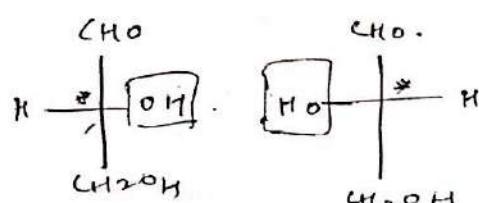
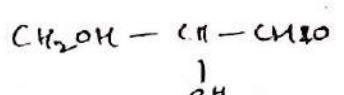


Naming:

① D & L Naming: (Relative Naming)

→ He took Glyceraldehyde as a reference molecule and implemented D & L.

→ It exists in 2 stereo isomeric forms.

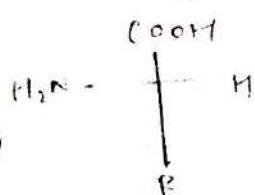


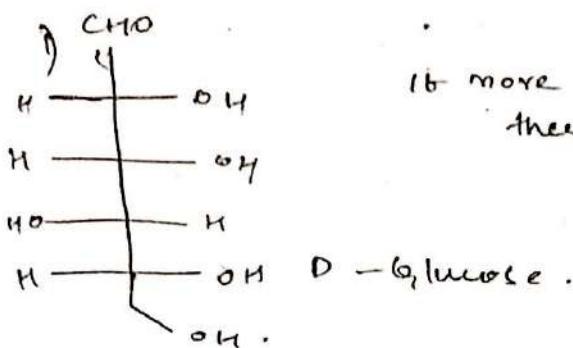
→ Later he complemented D & L Naming for Carbo-hydrates and ~~not~~ α -Amino acids.

↓
Poly hydroxy

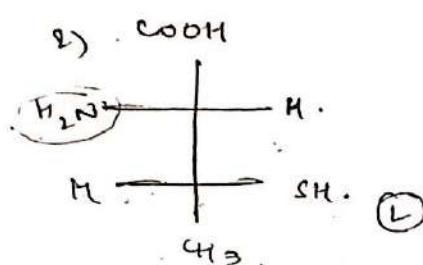
carboxylic comp.

(ketones/fatty acids)

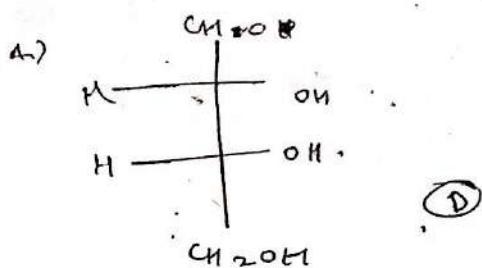
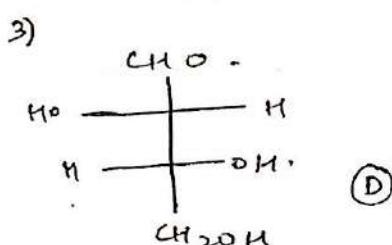




If more than 1 carbon is there, take last carbon in consideration



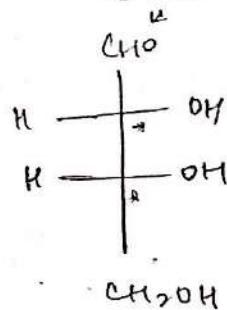
In case amino acids, configuration of amine is important



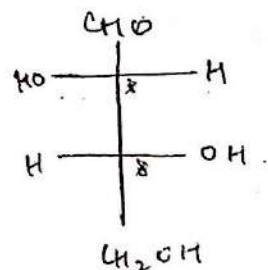
Second Naming:-

→ ERYTHRO & THREO nomenclature :-

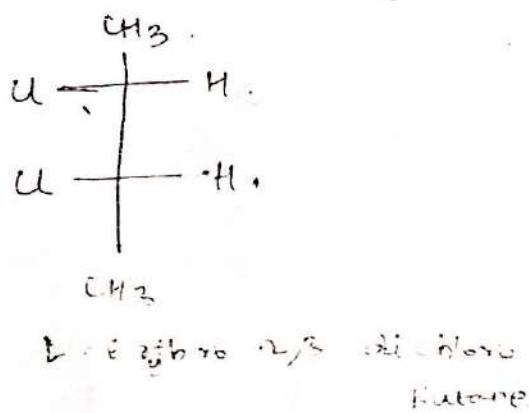
(Based on Erythrose & Threose)



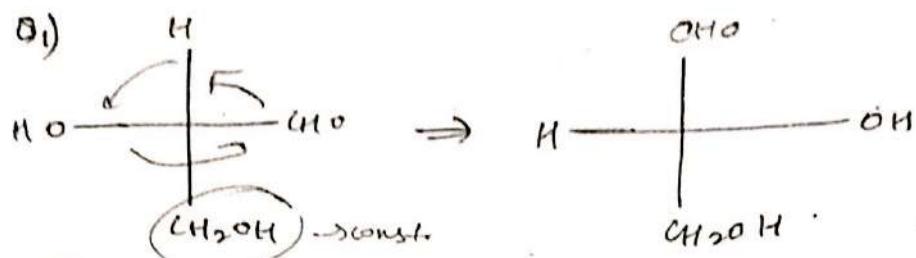
D - Erythrose



D - Threose

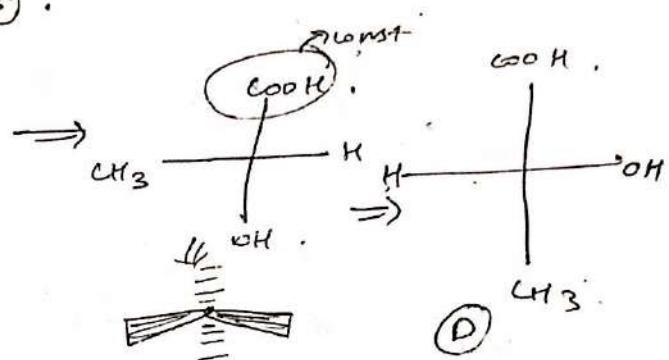
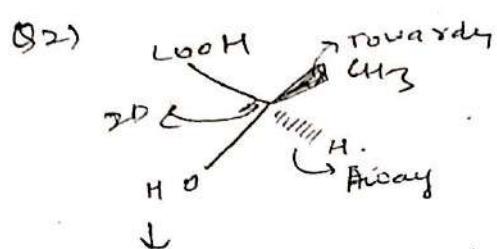


NOTE: Fischer implement 'D & L' nomenclature as well as Erythro, Threo naming on real Fischer projections

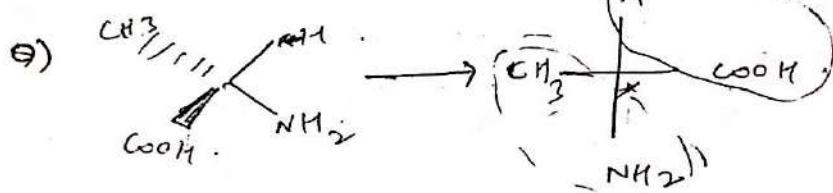


Fischer implemented real Fischer projections

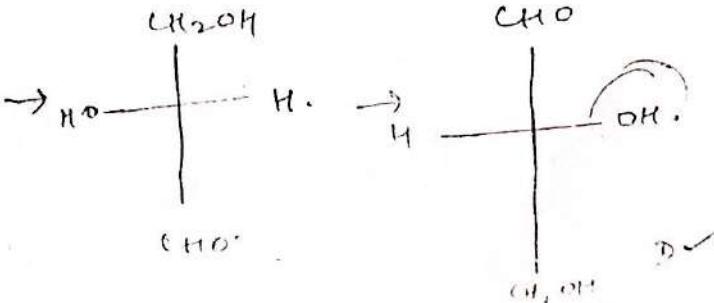
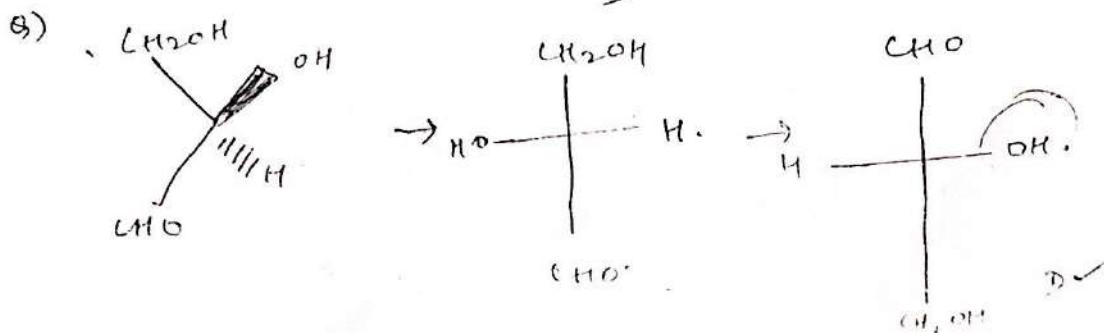
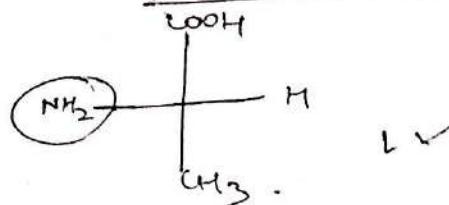
- ↓
- Max. No. of carbons should be present on vertical line in which the carbon with highest O.S. should be top.
- we have to keep one constant and rotate other (3).

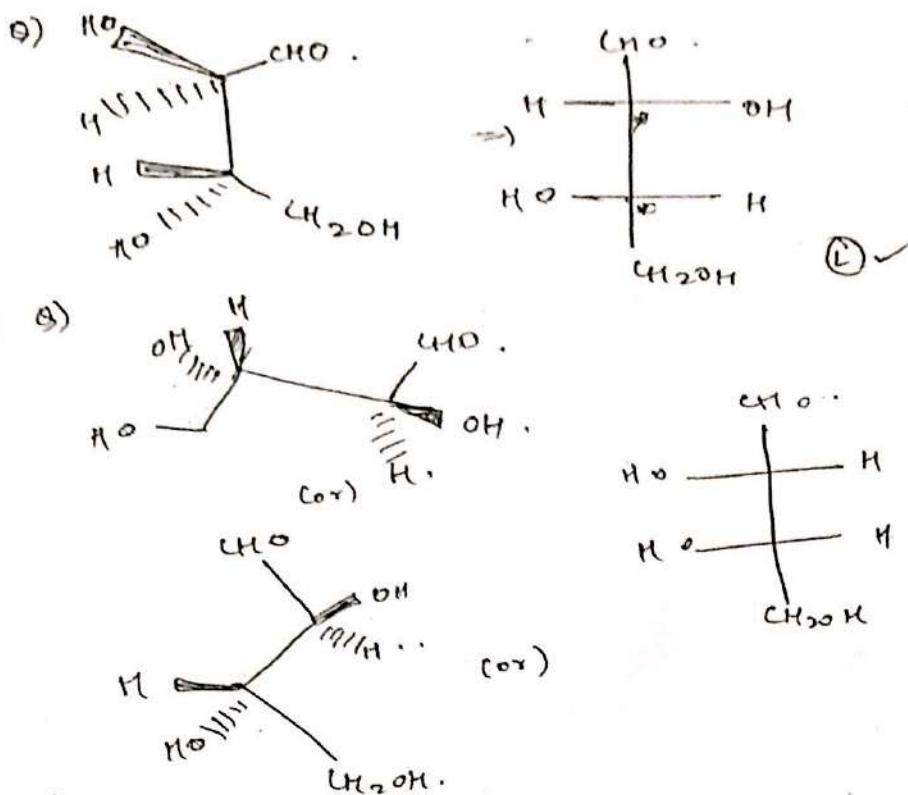


(Wedge-dash (or)
Flying-wedge
projection)



Rule 2: Select any 2 pairs and exchange them on same asymmetric carbon.



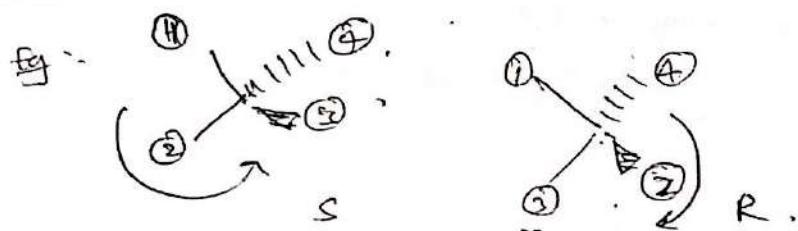


R & S FOR NOTATIONS: (Absolute configurations)

Rectus Sinister
(L.W) (A.L.W)

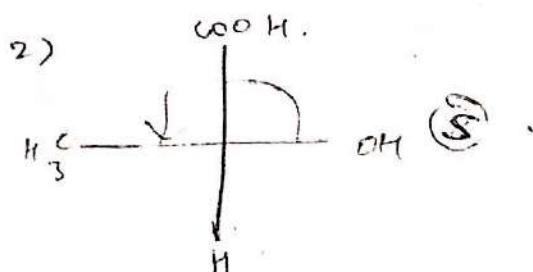
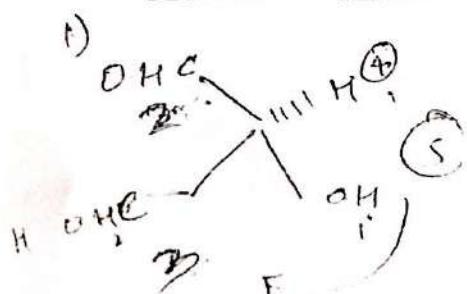
→ ④ should be opposite of the viewer

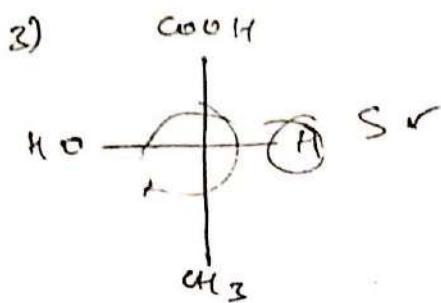
→ Identify the asymmetric atoms and assign the order of priority ①, ②, ③, ④ according to C.I.P rules



→ ④th priority should be away to viewer.

Eg.: Assign R & S:

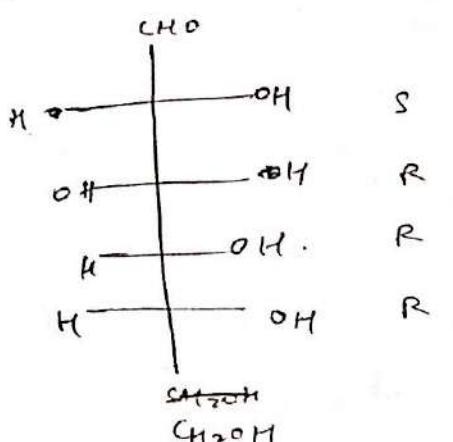
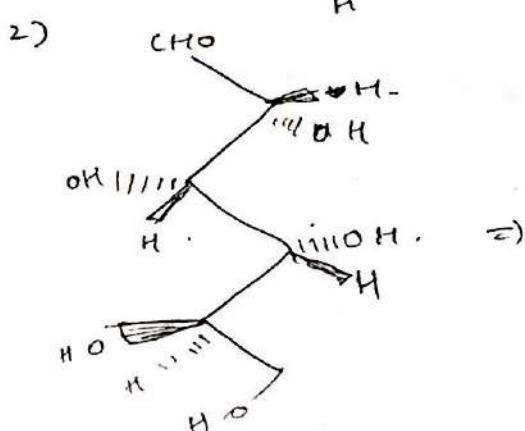
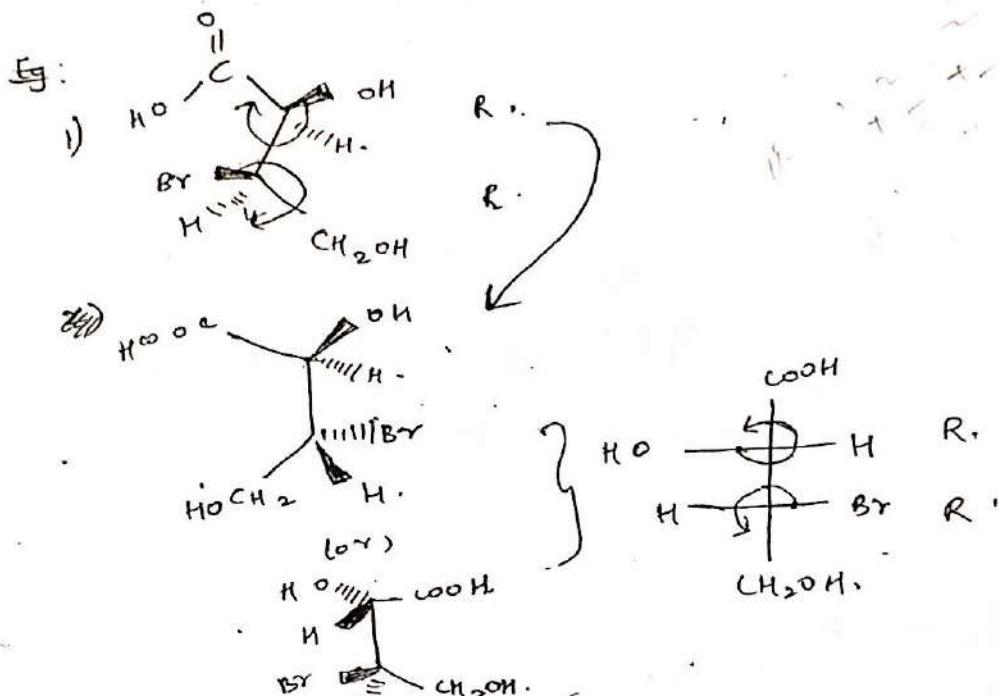


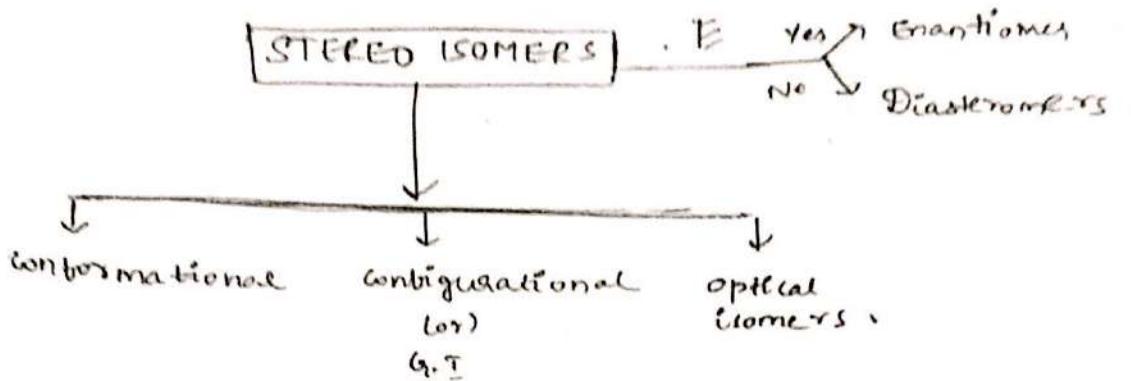


→ If 4th is vertical we can give S/R

→ If 4th is horizontal give R to S &

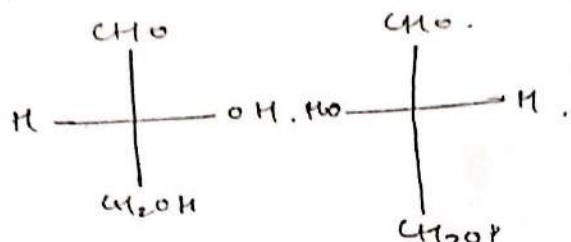
S to R





ENANTIOMERS: Non super-impossible mirror images.

Eg:

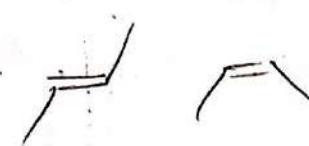


→ Physical properties are same.

Diastereomers: Non-super-impossible non-mirror images.

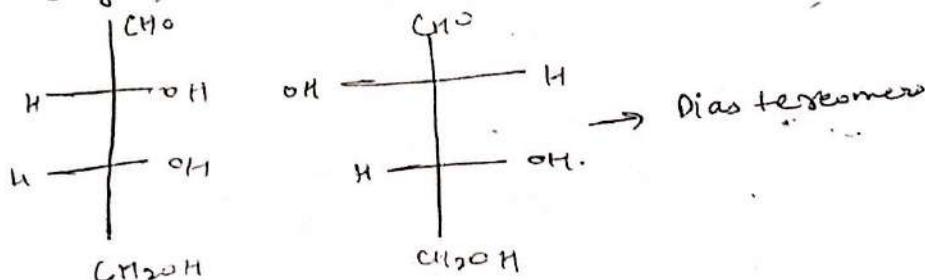
→ Physical properties are different.

Eg:



Other Examples:

1) D-Erythroose & L-threose.



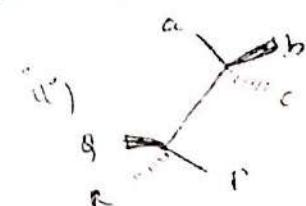
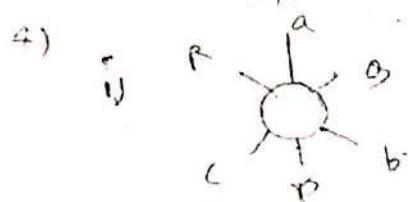
→ Diastereomers

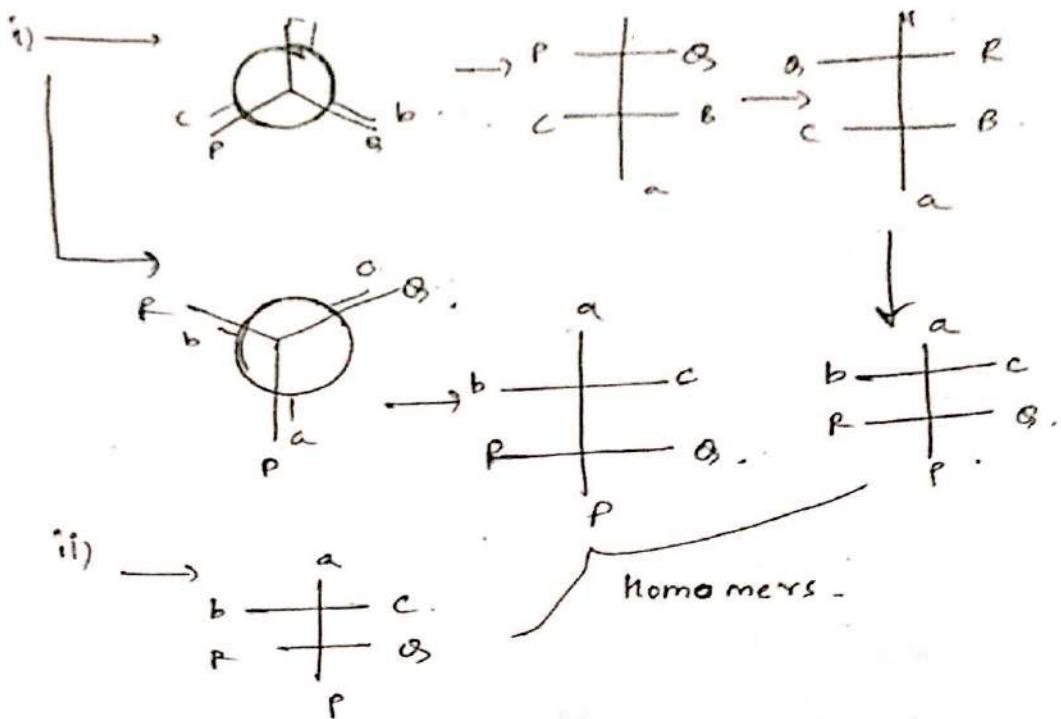
2) M-Gauche (n-butane) P-Gauche (n-butane)

→ Enantiomers

3) Gauche (n-butane) anti (n-butane)

Diastereomers





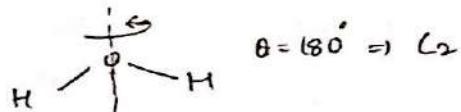
SYMMETRY ELEMENTS:

i) Axis of Symmetry / n-fold axis of symmetry: [Cn].

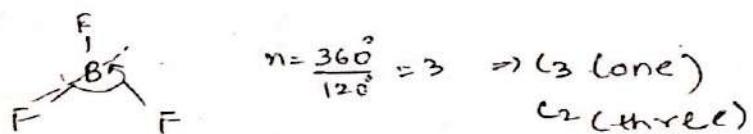
→ Rotate the entire molecule through an imaginary axis to get identical structure [min. angle of rotation except 360°).

$$n = \frac{360^\circ}{\theta} (n \neq 1)$$

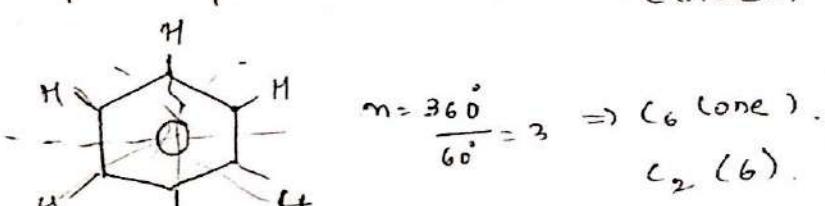
Eg: 1) H₂O



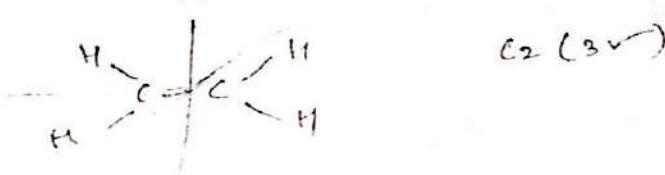
2) BF₃

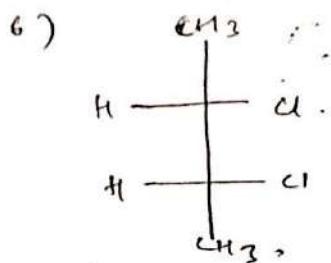
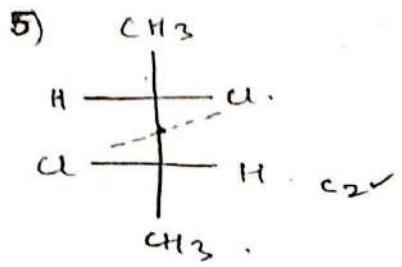


3) Benzene

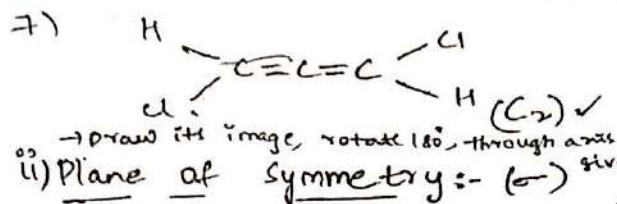


4) Ethene





No m (due to diff orientation)



→ Most of the optical active have C_2

ii) Plane of Symmetry :- (σ) gives identical one.

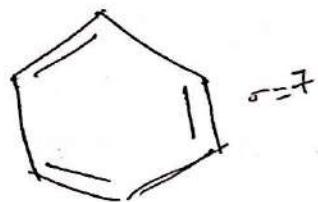
→ Plane passing through an object such that the part one side of plane is exact reflection of other.

Eg:- 1) H_2O



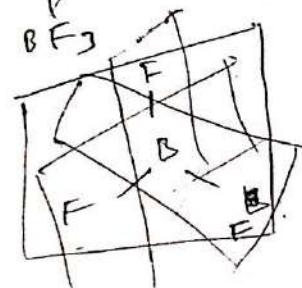
$\sigma = 2$

3) C_6H_6



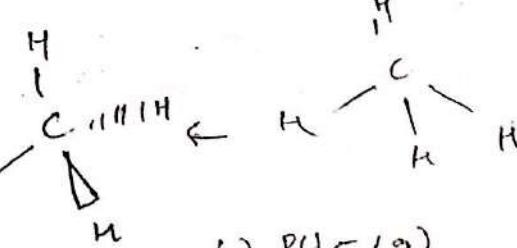
$\sigma = 7$

2) BF_3



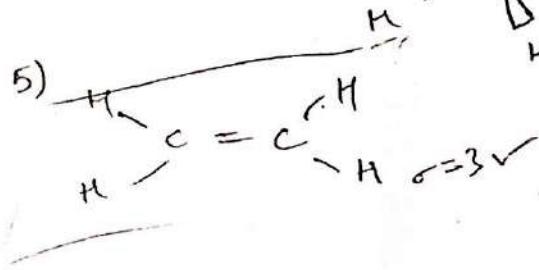
$\sigma = 4$

4) CH_4



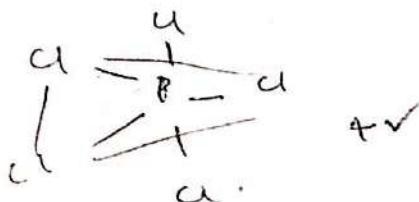
$\sigma = 6$

5)



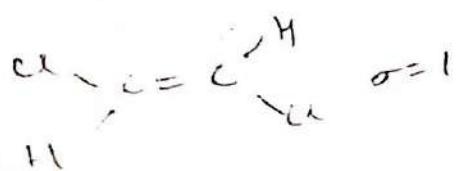
$\sigma = 3$ ✓

6) $PCl_5(g)$



✓

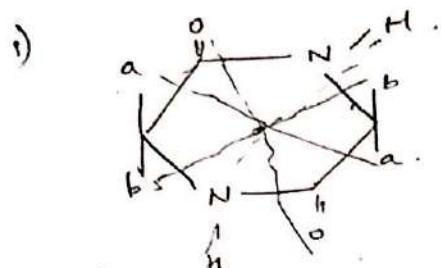
7) Trans-dichloro Ethene



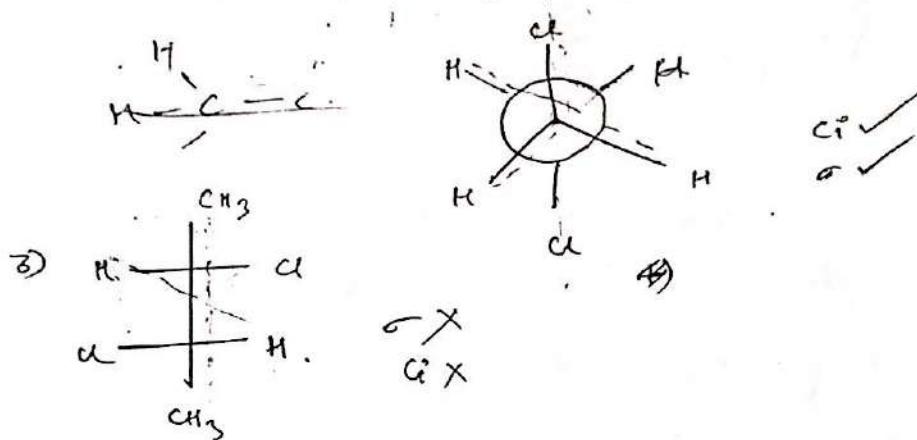
$\sigma = 1$

(iii) Center of Inversion / Inversion centre / Point of inv. / Point of centre (ci)

→ All the lines passing through the centres meet equal atoms through equal distances.

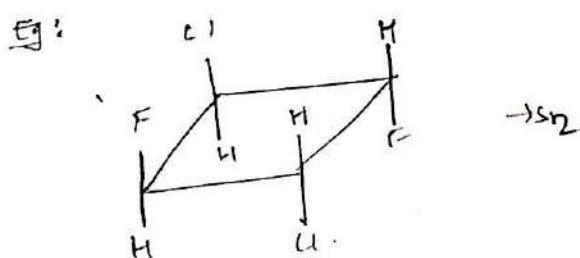


2) Anti-wiñformers of t,t -dichloro ethane



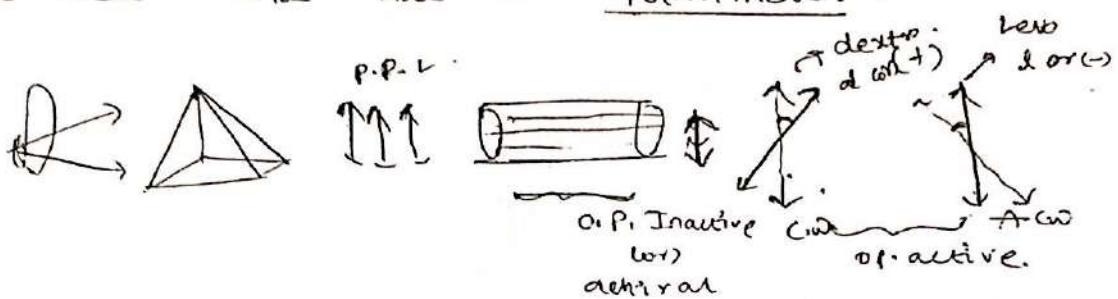
(iv) Alternating axis of symmetry (s_n):

→ A Molecule is rotated through 90° about an axis passing through the molecule, and then rotated 180° about the same axis. If the molecule is reflected in a mirror that is perpendicular to the axis of rotation, if gives an arrangement identical (or) superimposable to the original.



OPTICAL ISOMERISM:

- It is a physical property like length, volume, density etc... - op
- Optical rotation (or) absorbed rotation is also an physical behaviour of that compounds.
- To measure opt. rotation, instruments should be used and that is "Polarimeter".



→ The resultant rotation is 'd' and known as optical rotation (or) absorbed rotation.

→ Not constant always. depends upon:

- ① Conc. of soln.
- ② Temperature.
- ③ Nature of solvent
- ④ Wave length of light.
- ⑤ Length of sample tube.

→ The standard measurement for optical rotation is known as specific rotation $[\alpha]_T^\lambda = \frac{\alpha}{c \cdot l}$

α - observed rotation.

c - conc. (g/ml)

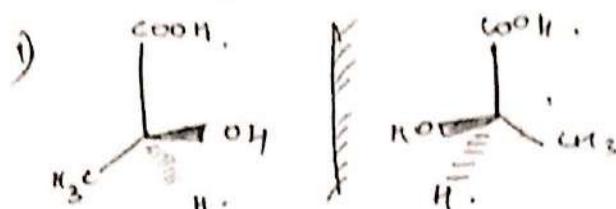
l - length (dm)

→ To become optically active, object should obey the following conditions.

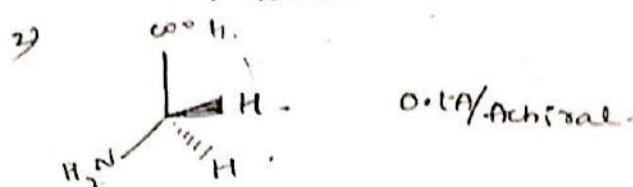
* CHIRALITY:

→ object should possess non-superimposable mirror image.

Eg:

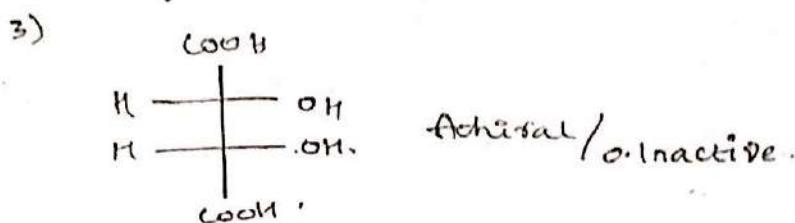


Given is O.A / chiral.



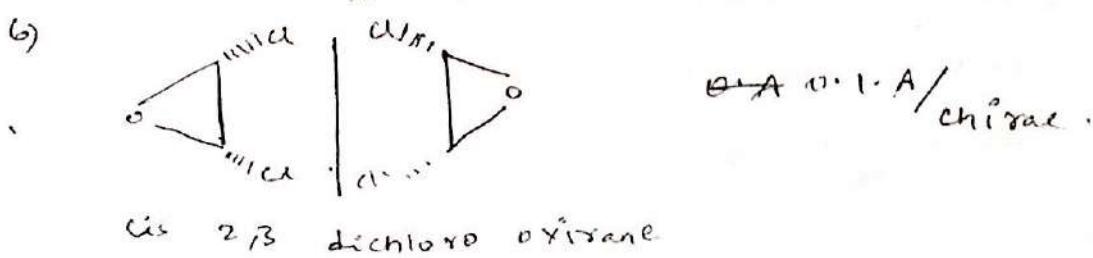
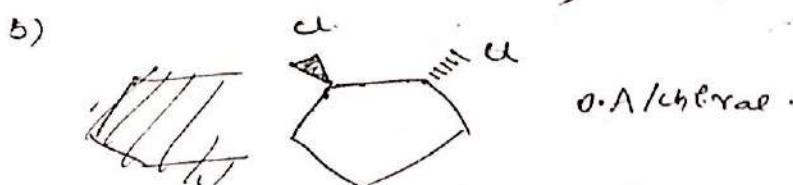
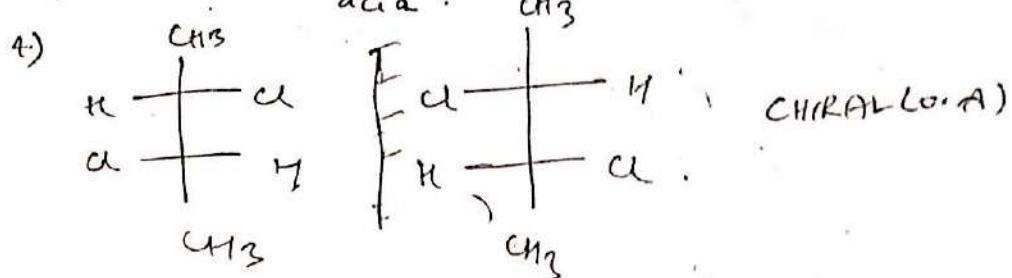
O.L.A / Achiral.

Glycine.



Achiral / O.inactive.

D-Erythro tartaric acid:



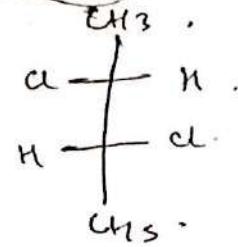
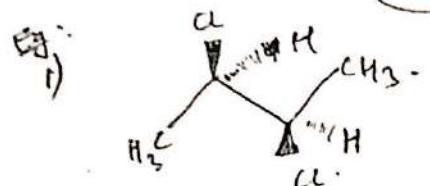
→ To become chiral, it should possess dissymmetry.

(ex) Asymmetric condition

$C_n X - O - C_i X S n X$

No comment $O \oplus$

$C_n X$



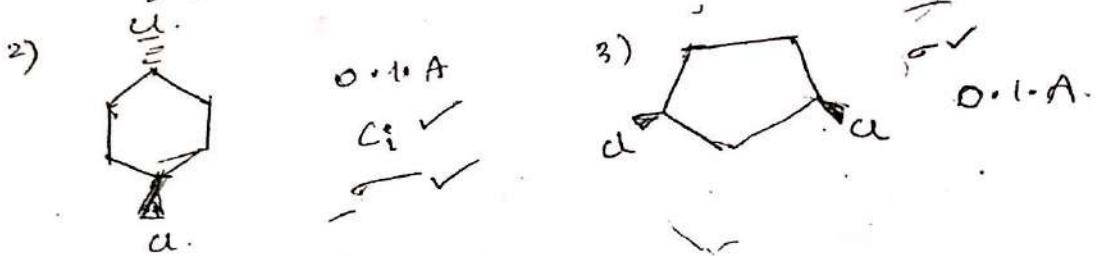
a) Chiral ($O \cdot A$)

b) $O - (X)$

c) $C_i (C_X)$

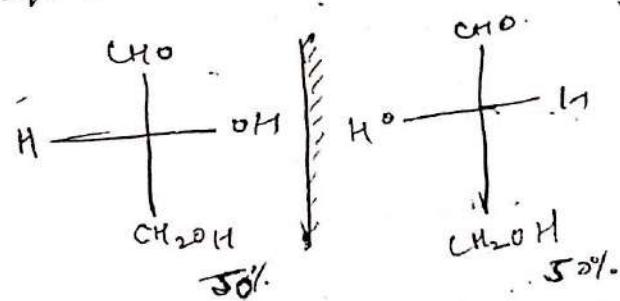
d) $C_n C_2 (\checkmark)$

* → If the comp. is optically inactive, $\Sigma \alpha$ should be definitely zero.



4) RACEMIC MIXTURE:-

→ Equal molar mixture of pair of enantiomers (\pm)



→ Racemic mixture is optically inactive due to External compensation with same magnitude and opp. direction.

MESO COMPOUNDS

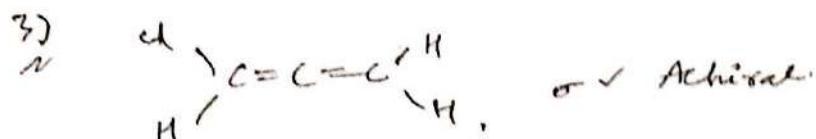
CHIRAL / ACHIRAL :-



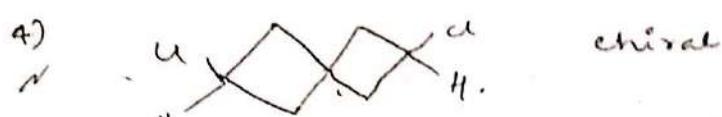
✓



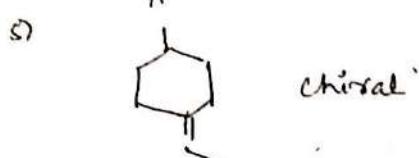
✗



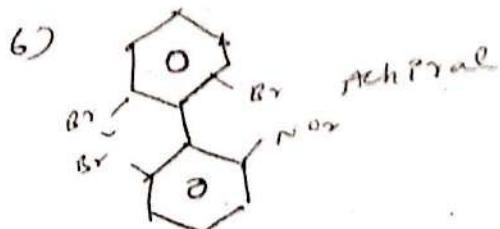
✓ Achiral



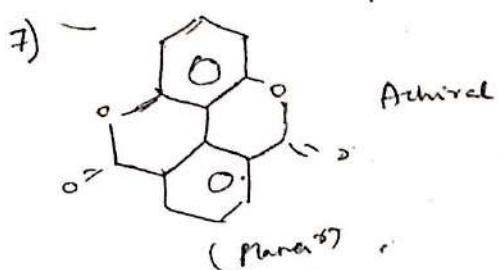
chiral



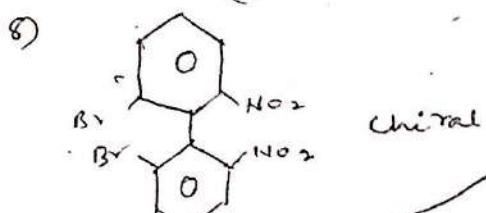
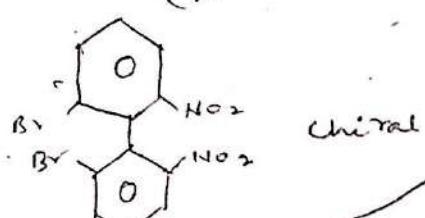
chiral



Achiral



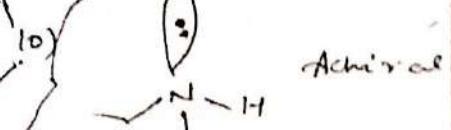
Achiral



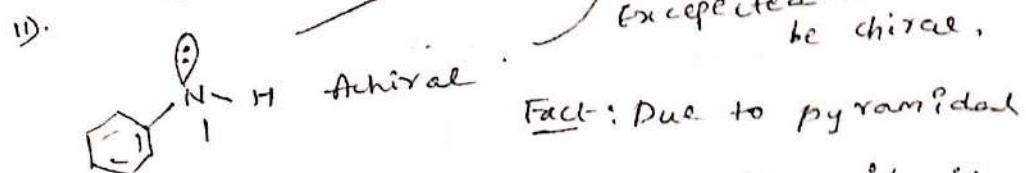
chiral



Achiral



Achiral



Achiral

Expected to be chiral.

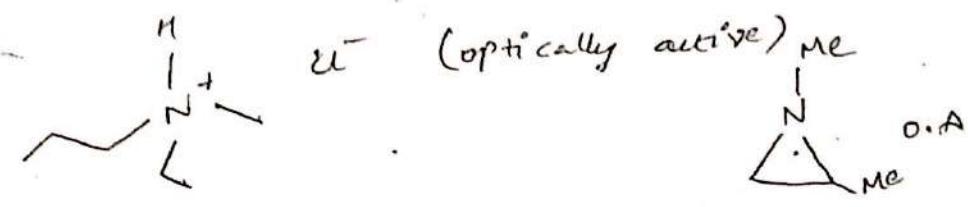
Fact: Due to pyramidal

shape, among the RP, LP repulsions, it is doing pyramidal inversion dance more than 10,000 times per second

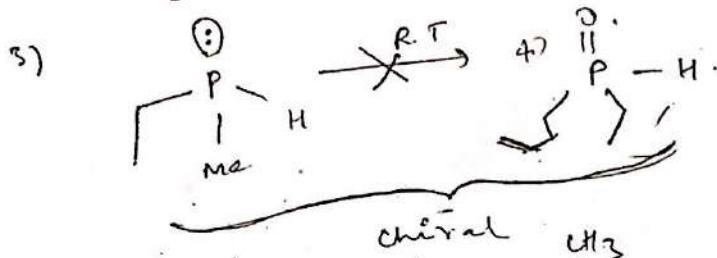
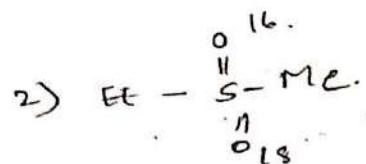
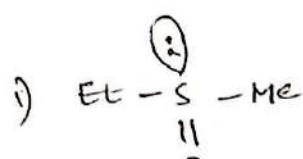
transitions s-state sp^2



These are called as non-resolvable, racemic mixtures.

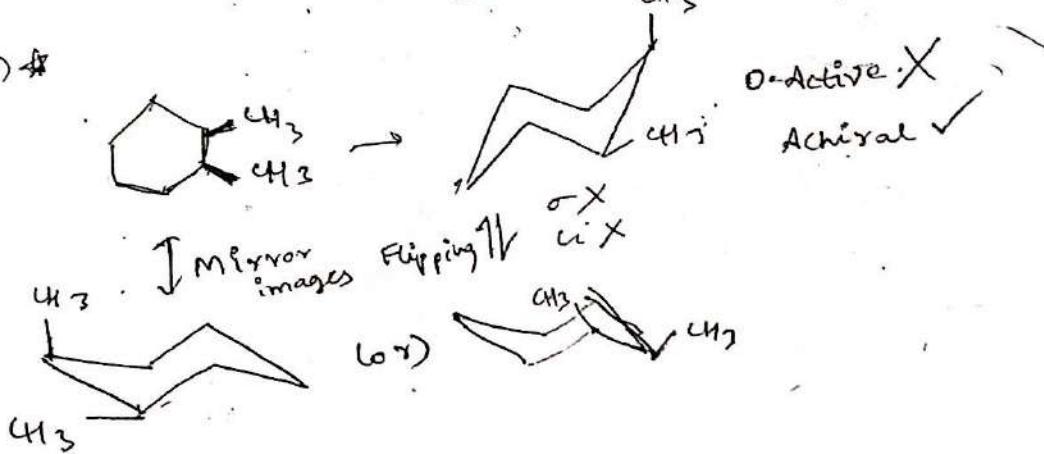


Eg:-



chiral CH_3

5) *



No-of ISOMERS:-

No-of structural

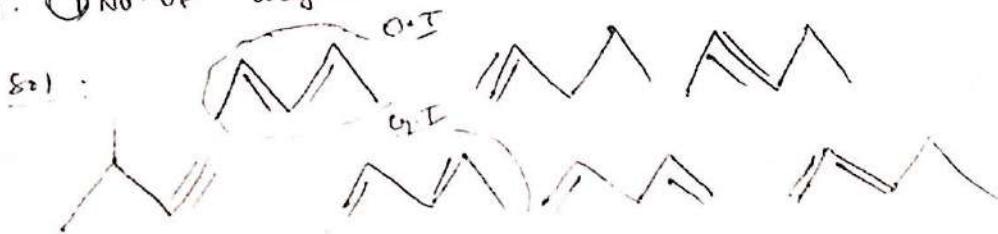
+
No-of G.I

+
No-of O.I

+
No-of Stereo Isomers

No-of Isomers
(Total)

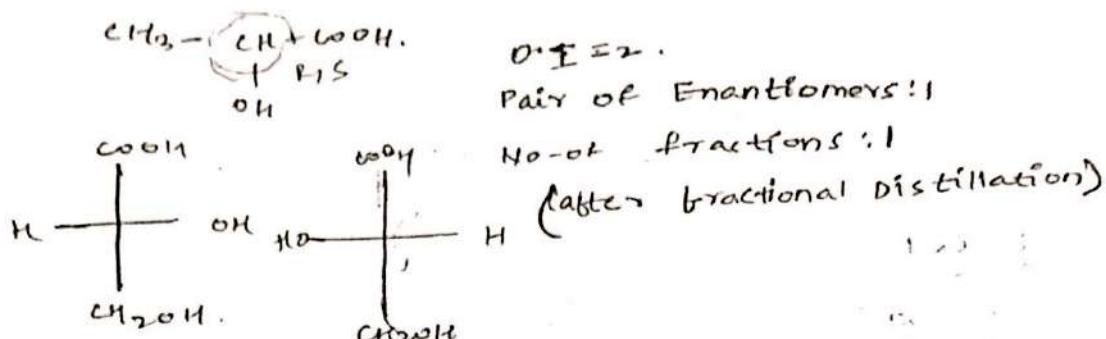
Eg: ① No-of acyclic structural isomers for C_5H_8



Y-1 Y-1 ⑨

Total acyclic isomers of $C_5H_8 = 11$

Q) No. of optical isomers:

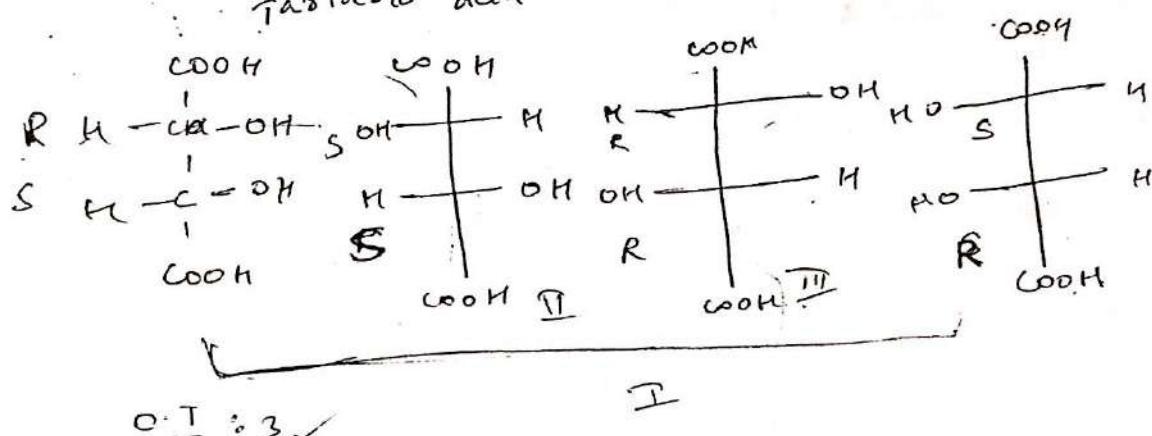


8) $\text{CH}_2\text{OH} \rightarrow \begin{cases} \text{CH} & -\text{H} \\ \text{R,S} & \text{OH} \end{cases} - \begin{cases} \text{H} & -\text{CHO} \\ \text{D,H} & \text{R,S} \end{cases}$

$O: 1 : 4$ $O: 1 : A: O$
 $O: A: 4$ Enant: 2

Diastereomers: 4
 Fractions: 2

- RR
- RS
- SS
- SR



$$0 \cdot A = 2$$

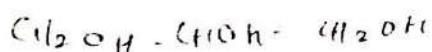
$$c_{\perp} A = 1 \checkmark$$

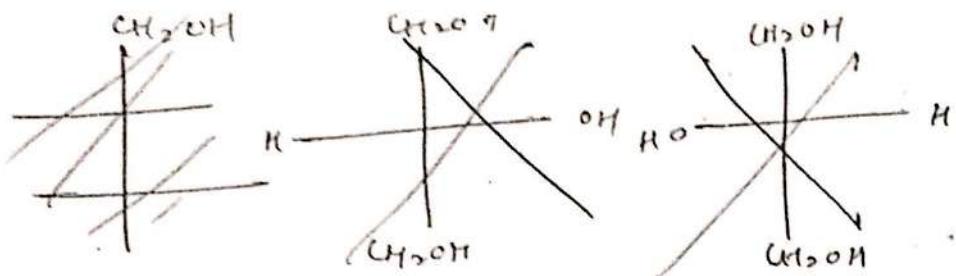
$$E_{\text{PA}} = 2$$

$$DIA = 3$$

Fractions: 2

8) Glyceral (or) glycerine

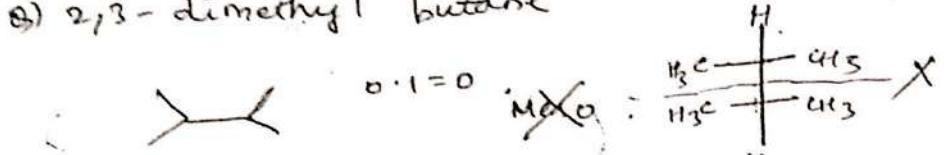




No-chiral centres

$$\text{D} = 0 \cdot \text{L} = 0$$

(b) 2,3-dimethyl butane

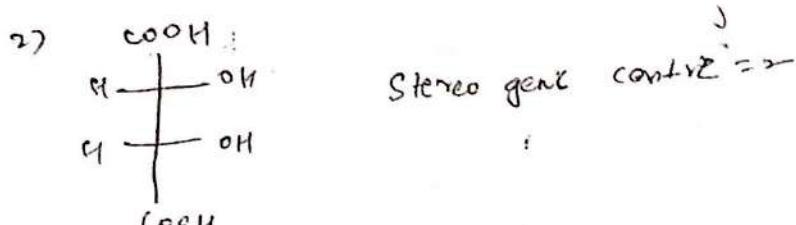
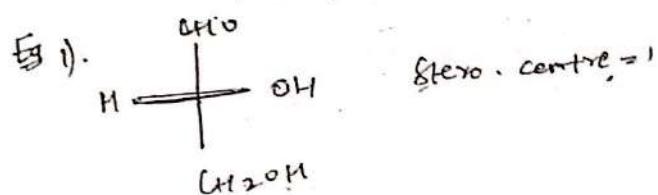


MESO COMPOUNDS:

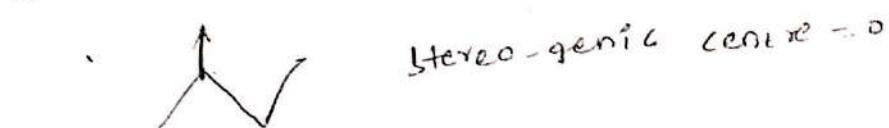
→ the one which possess plane of symmetry and also contains atleast one-active isomer with the same structural formula. → optically inactive due to internal compensation

STEREOGENIC ATOM (or) STEREOGENIC CENTRE:

→ After spatial exchanging of 2 groups (or) group of atoms at any centre if results new stereo isomer, that center is termed as stereogenic center (optical/geometrical)



3) 2-Methyl butane



4) Iso-butene



5) 2-Butene



(2)

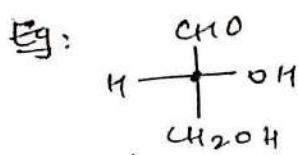
6)



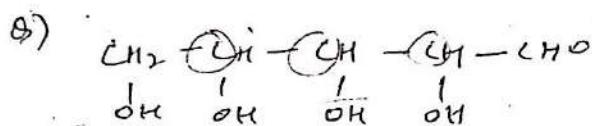
(2)

→ Stereo genic Unit (or) ENTITY:

→ The boundary of group of atoms (or) the Proper arrangement of group of atoms responsible for stereo isomerism (Optical/Geometrical)

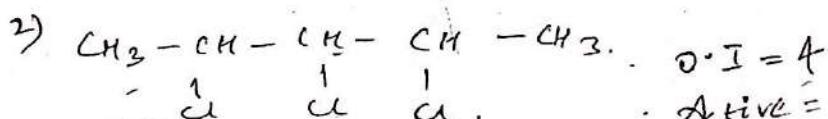


NOTE: All asymmetric (or) chiral carbons (or) stereogenic atoms (or) centers. (vice-versa not true)

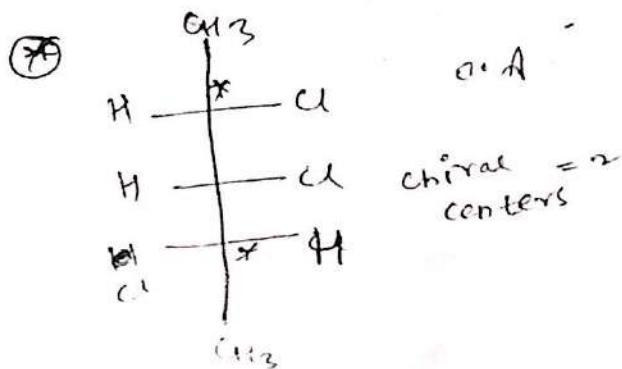
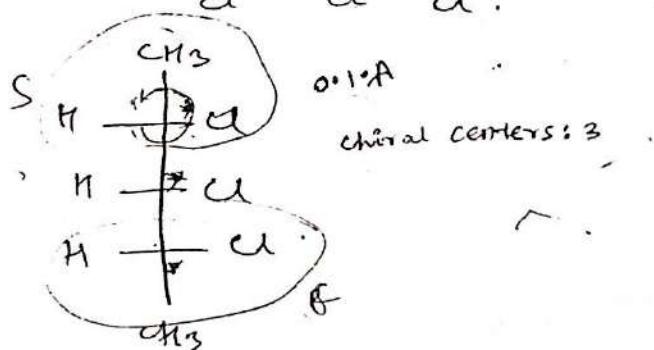


O.I = ? - RRR
RRS
RSR
RSS
SSR
SRR
SRS
SSS

Sol: 1) O.I: 8



O.I = 4
Active = 2
(n-active) = 2



O.I = ?
chiral centers = 2

No. of optical isomers = 2^n (All are O.A)

n = no. of different stereogenic entities.

n = no. of same stereogenic units.

$$\left\{ \begin{array}{l} \text{Even } 2^{n-1} + 2^{\frac{n-1}{2}-1} \\ \text{Odd } 2^{n-1} \end{array} \right.$$

$$O.A = 2^{n-1}$$

$$O.I.A = 2^{\frac{n-1}{2}-1}$$

$$O.A = 2^{n-1} - 2^{\frac{n-1}{2}}$$

$$O.I.A = 2^{\frac{n-1}{2}}$$

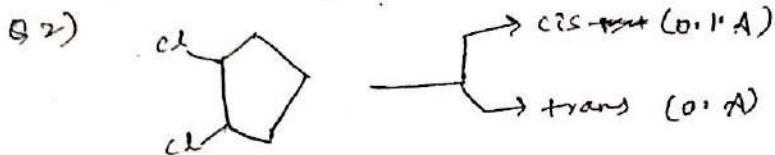
→ No. of stereo isomers (G.I + O.I)

Q1)



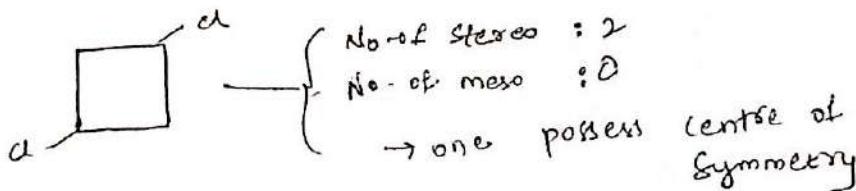
cl T → 2

Q2)

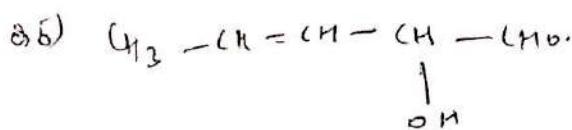
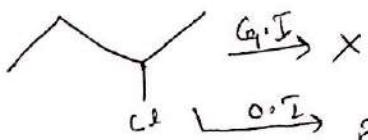


Total = 3.

Q3)



Q4)

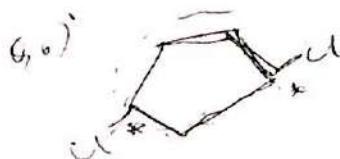


chiral carbons: 1

Stereogenic atoms: 3

Stereogenic Entities: 2

Stereo ~~ge~~ isomers: 4



Stereogenic units = 2

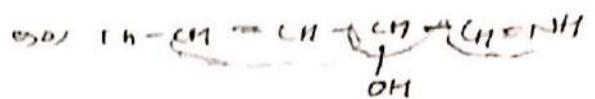
No. of stereo isomers = 3

meso: 1

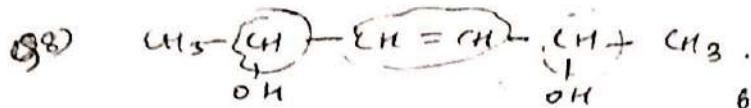
Q7)



(2)



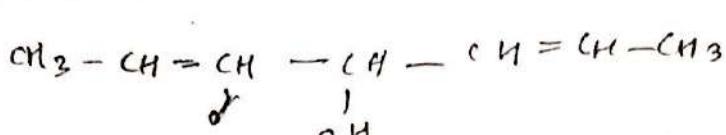
(8) = stereoisomers.



✓

RTS ? Super impossible
STR ? Super impossible RC S. Super impossible
SC R

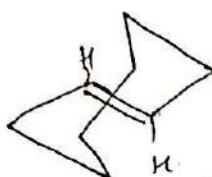
(10)



(4)
2 O.A
2 O.A

(11) Cyclo octene:

(3)

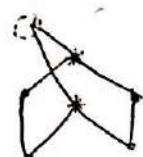
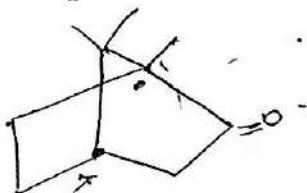


trans is existing with
no plane of symmetry/ centre of
symmetry \rightarrow optically active

(12) which conformer of cyclohexane is optically active.

Ex 1: Twist boat.

(13) No. of stereo isomers for camphor.

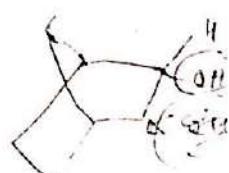
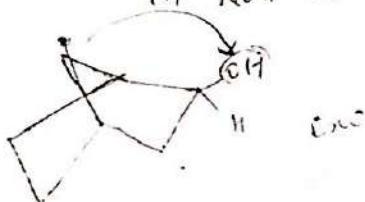


NOTE: Exo & Endo nomenclature

i)



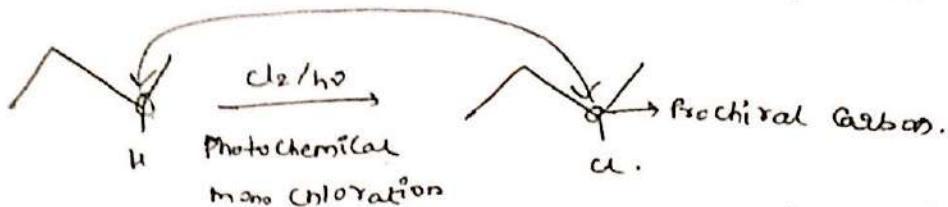
ii) Bridged bicyclic compounds are existed
in Non-Boronyl skeletons.



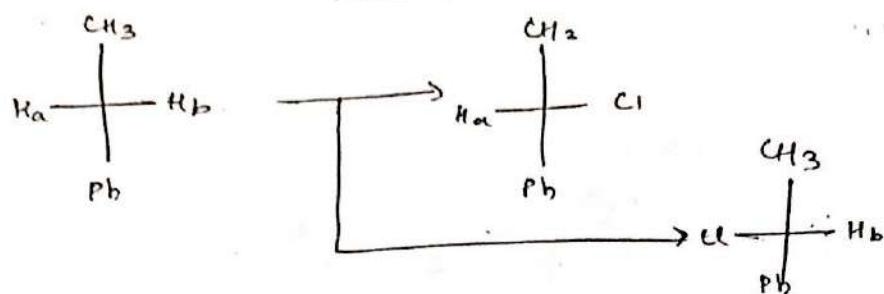
Endo

Asymmetric Induction:-

→ Converting achiral to chiral carbon is prochiral carbon.



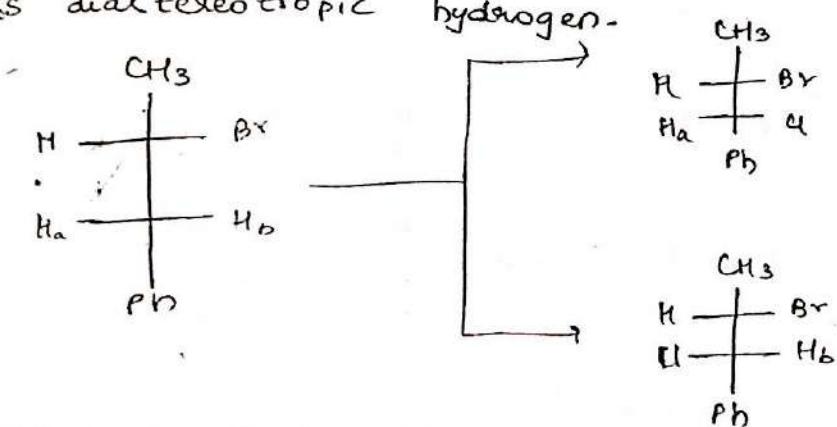
Enantiotropic hydrogens :-



→ After asymmetric induction if we get pair of enantiomers, it is Enantiotropic -hydrogen.

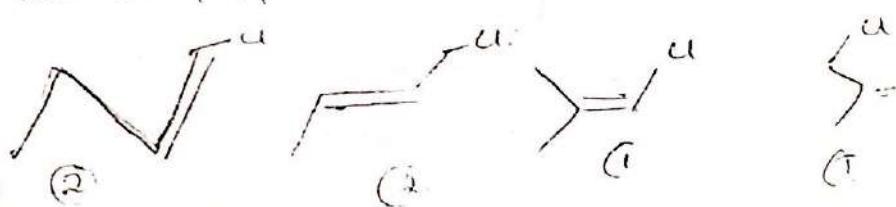
DIASTEROTROPIC HYDROGENS :

→ If we get pair of diastereomers, then it is diastereotropic hydrogen.



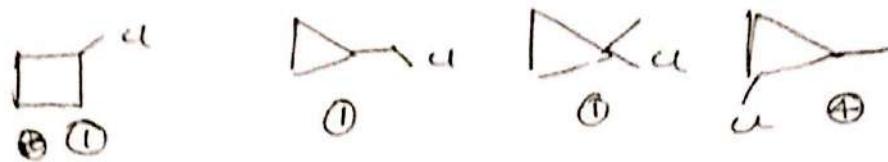
Total No-of Isomers:-

Eg: i) C_4H_7Cl . → one double bond
one (or)
one sing
 $DU = 5 - 4 = 1$

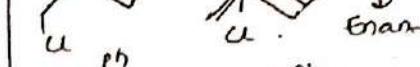
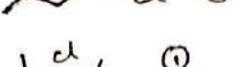




Total - (19)



→ Find the no. of products & Fractions upon photochemical mono chlorination of:



Prod: (3) Frac: (2)

Prod: (6)

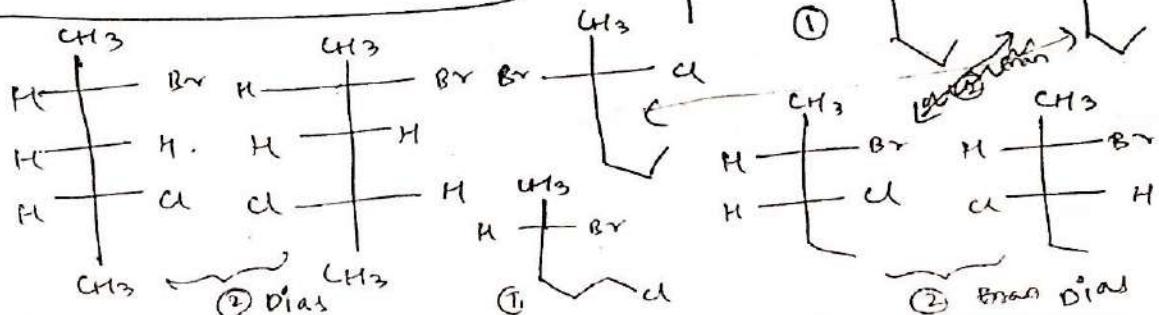
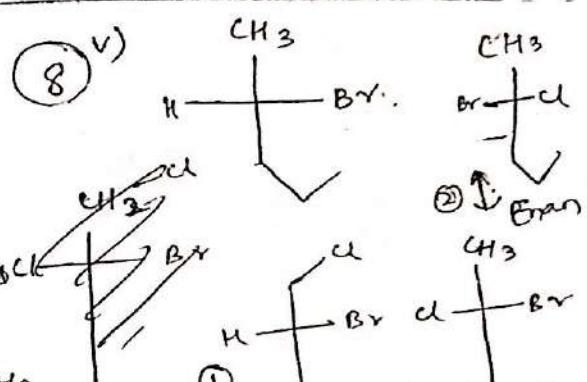
Frac: (5)

iv)



Tot: (8)

Prod: (6) Frac: (4)



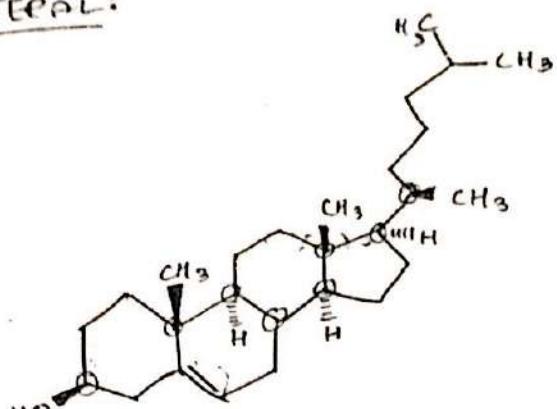
NOTE : For (iii) eg.

Photo chemical halogenation does not occur unless

place on sp^2 carbon (i.e.) sp -carbon.

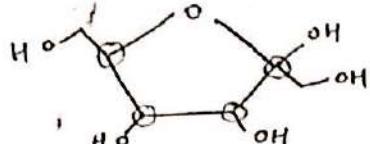
Q) How many stereo isomers can be possible for cholesterol?

CHOLESTEROL:

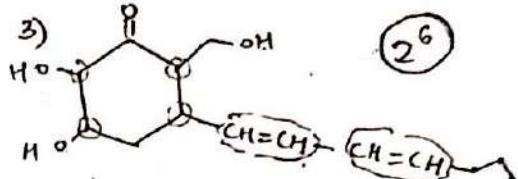


$$\text{No. of stereo isomers} = 2^8.$$

2)

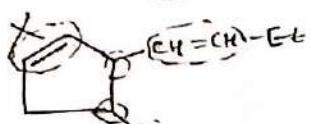


(2⁴)



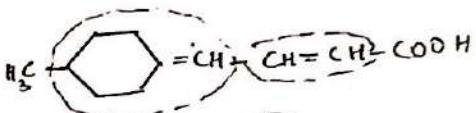
(2⁶)

4)



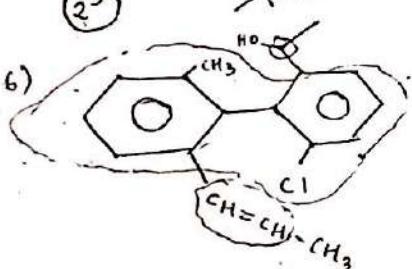
(2⁵)

5)

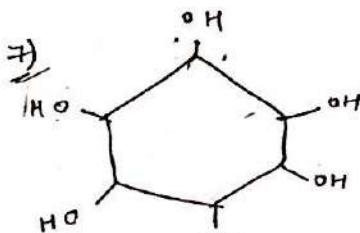


(2²)

6)



(2³)

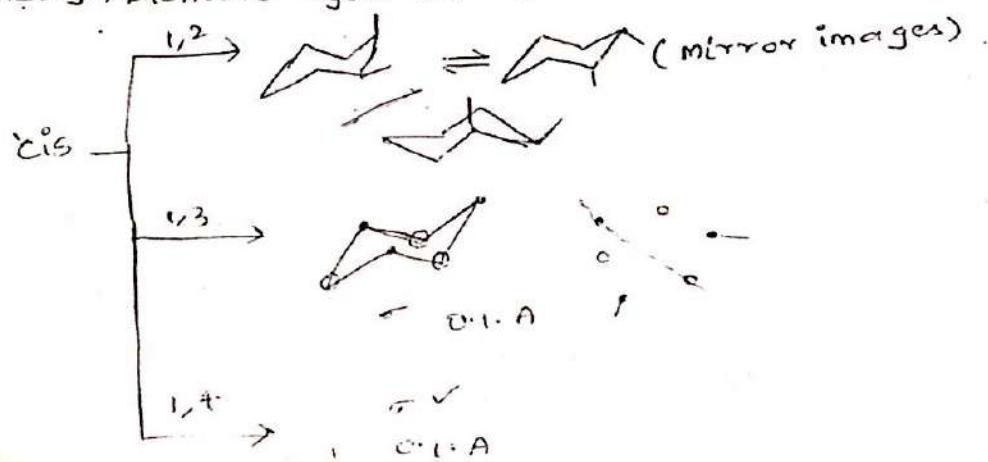


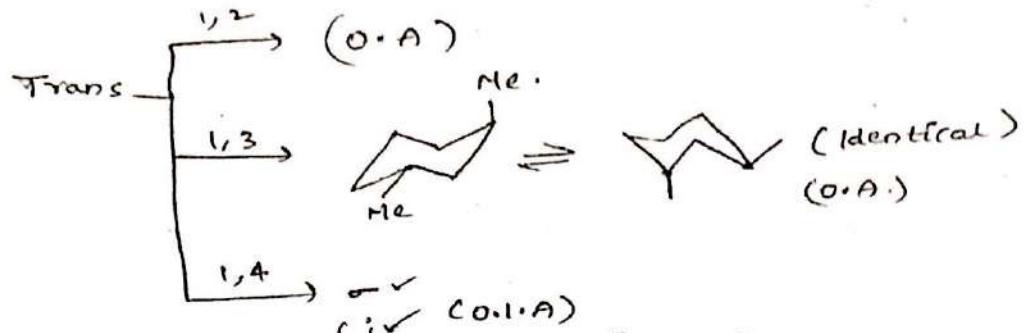
Stereo isomers: 9

Geometrical: 8

Meso: 7

8) Dimethyl dichloro Cyclo hexane:





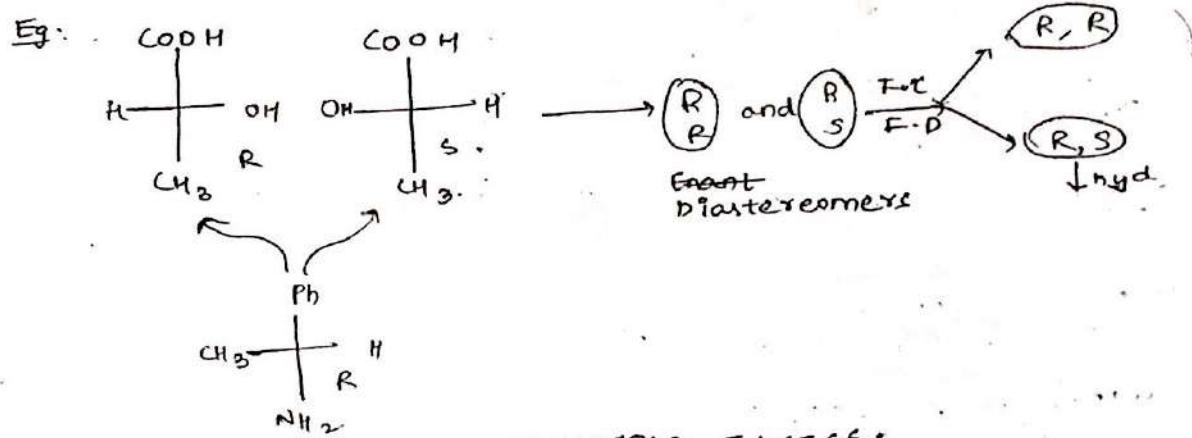
RESOLUTION:-

$$\frac{[A] - [B]}{[A] + [B]}$$

→ Separation of Racemic mixtures into individual forms.



→ By Using optically pure compound.



OPTICAL PURITY (OR) ENANTIOMERIC EXCESS:

→ How much one enantiomer is excess of racemic mixture.

Q) The observed rotation of $2g$ of compound in 10mL soln in a 25cm long polarimetric tube is $+13.4^\circ$. Then find the specific rotation.

Sol:- Specific rotation $[\alpha]_D^2 = \frac{\alpha}{c \times l} = \frac{13.4}{2 \times 10 \times 25} = 26.8^\circ$

E) A sample of Butan-2-ol has an observed rotation of -19.77° . The optical rotation of

Pure leaves is -13.6° . Calculate the % composition of mixture.

Sol:

$$\text{optical purity} = \frac{[\alpha]_{\text{observed}}}{[\alpha]_{\text{max}} (\text{Pure enantiomers})} \times 100$$

$$= \frac{[d] - [l]}{[d] + [l]} \times 100$$

PMS:

ELECTRONIC EFFECTS:

Permanent effects (3)

- ① Inductive effect (I) ① Electromeric effect (E)
 ② Hyper Conjugation (H)
 ③ Resonance (R) or
 Mesomeric effect (M)

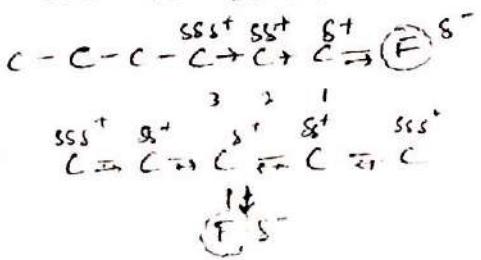
INDUCTIVE EFFECT:-

→ partial transfer of $-e^-$ towards most EN element.
(w.r.t Hydrogen)

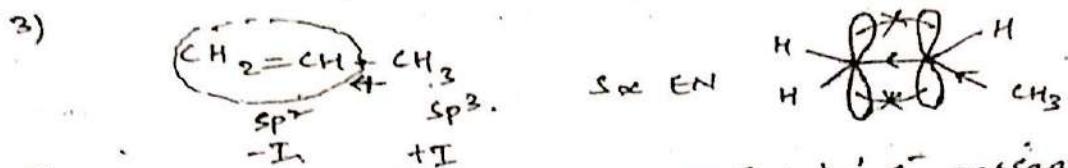
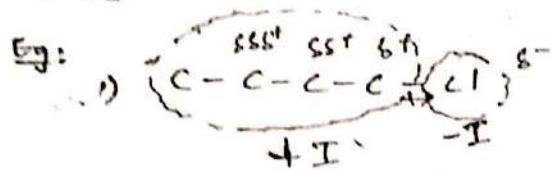
(non-polar) ($\mu = 0$).

→ In alkanes, among C & H, I-effect is not taking place.

→ I. Effect is dist. dependent effect proceeds max upto 3 covalent bonds

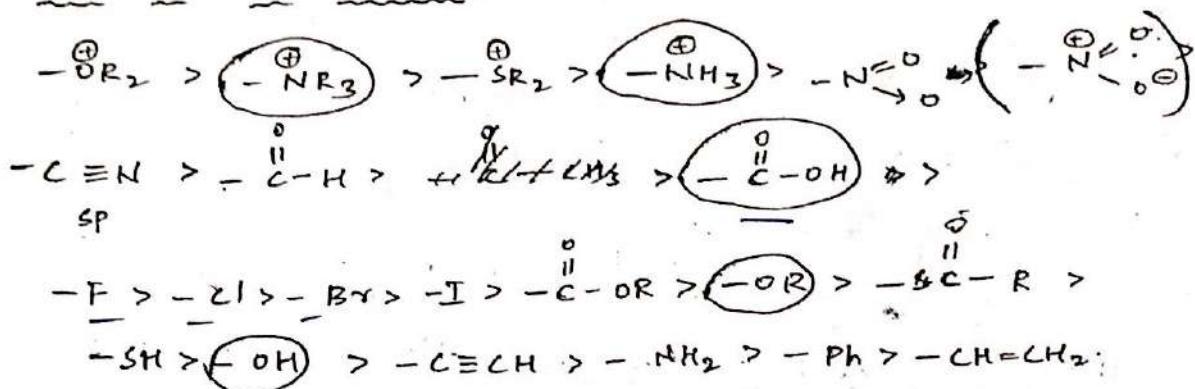


- The groups which are taking e^- are called $[-I]$ (2)
- The groups which are releasing e^- are called $[+I]$

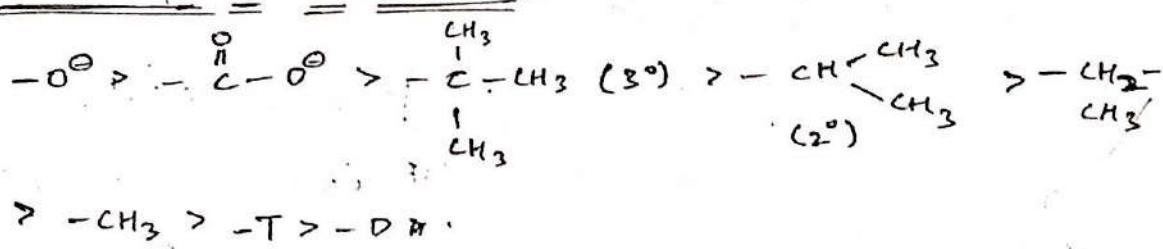


→ During Inductive effect only, partial ' σ ' e^- passage is observed.

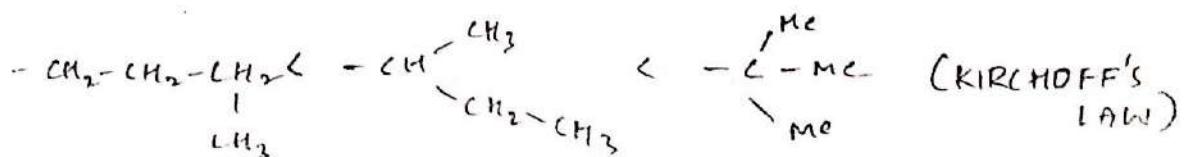
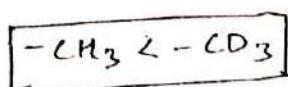
LIST OF $-I$ EFFECT:-



STRENGTH OF $+I$ EFFECT:-



B) $+I$ EFFECT:

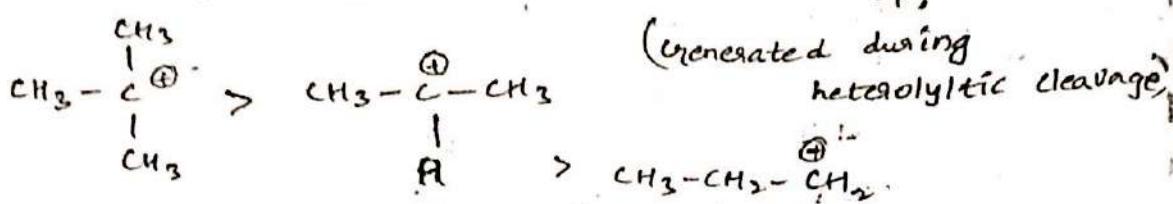


Applications of Inductive effect:

(3)

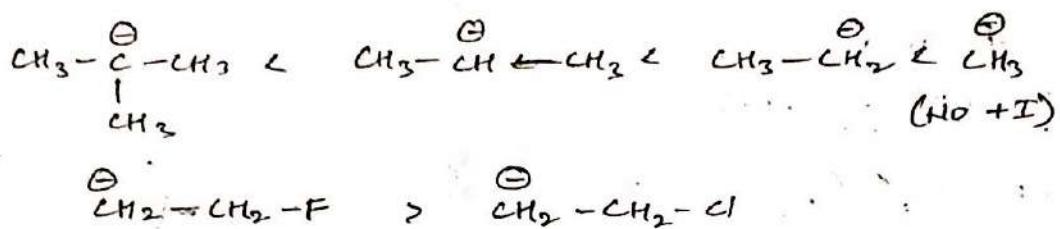
- ① Used to predict stability of carbo-cation:

(Trivalent, e⁻ deficient, 6e⁻ in its valence shell, sp²)

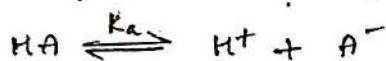


- 2) To measure stability of carbocation:

(Generated by heterolysis, sp³, pyramidal, (similar to ammonia), Trivalent, 8e⁻ in its valence shell, e⁻ rich)

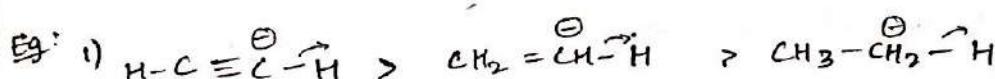


- 3) To measure acidic strength:

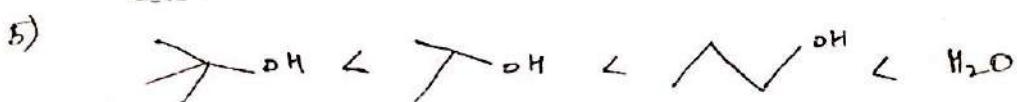
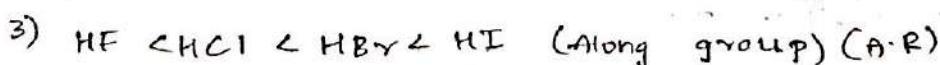
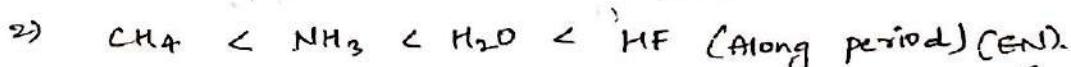


$$K_a \propto \text{stability of anion} \propto \frac{1}{pK_a}$$

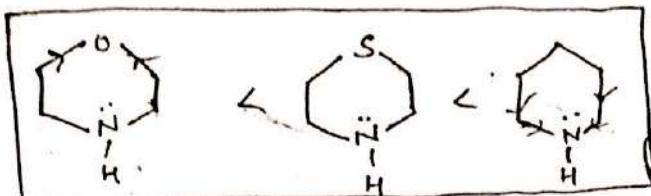
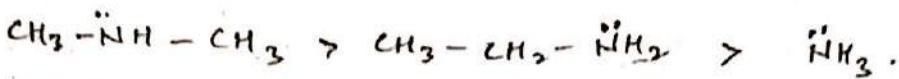
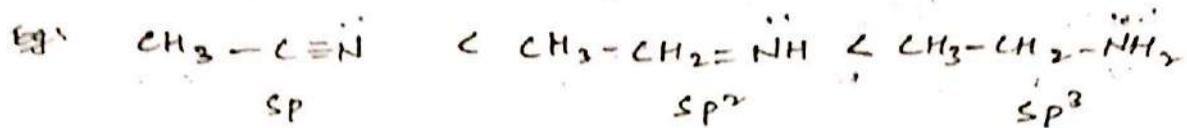
→ The one which can readily form stable anion.



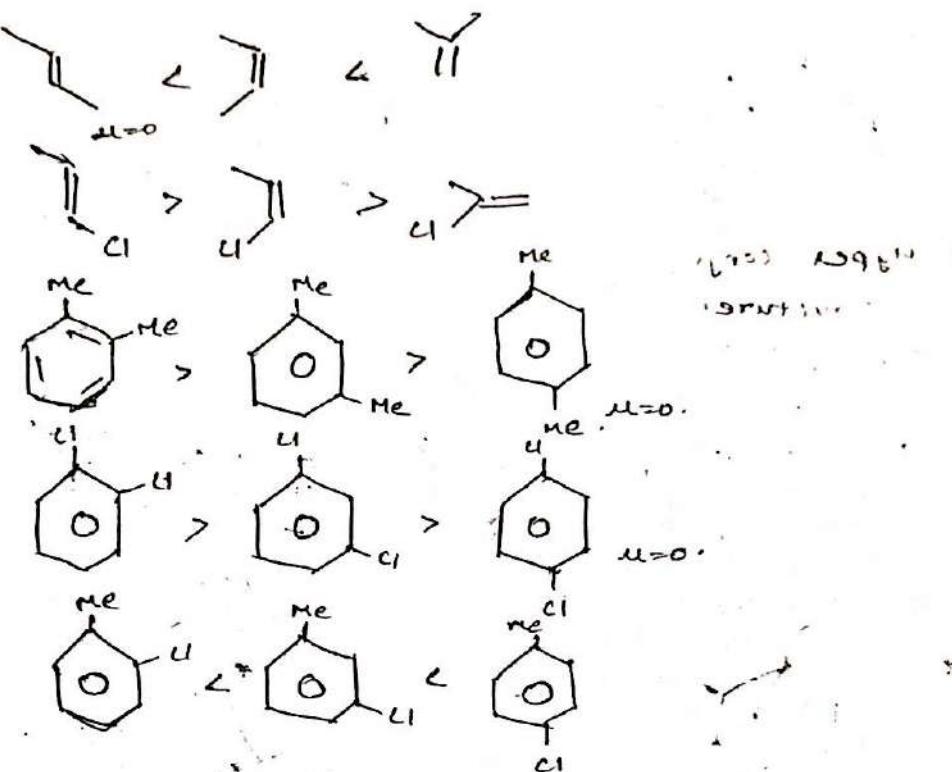
$$[\text{EN} \propto \% \text{ s} \propto -\text{I}]$$



4) To measure Basic strength:



5) To measure dipole moment:



2) HYPER CONJUGATION: / (NO BOND RESONANCE) /

BAKER-NATHAN EFFECT:

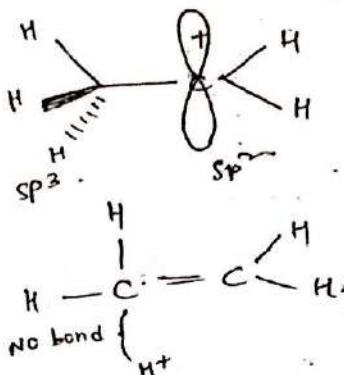
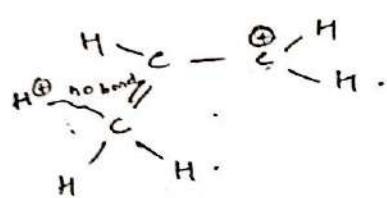
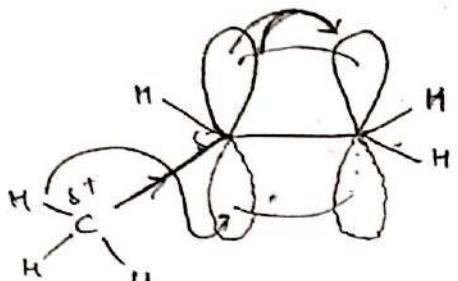
→ σ or SP^3 σ bond { SP^3 C-H
 SP^3 C-D
 SP^3 C-T } overlapped with

adjacent 'p' orbital either empty / filled or SP/SP^2
carbon is Hyper Conjugation

($\leftarrow \rightarrow p$)

- If one bond is decreased, that is sacrificial hyper conjugation
- If no. of bonds are same, it is isovalent hyper conjugation.

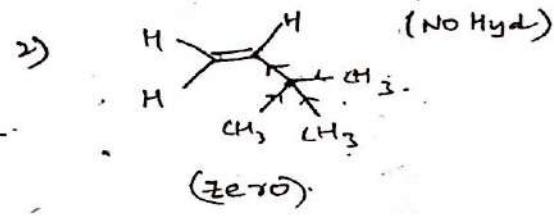
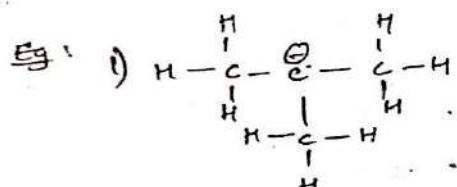
(α -hyd. participate in hyp. conjugation)



(Isovalent).

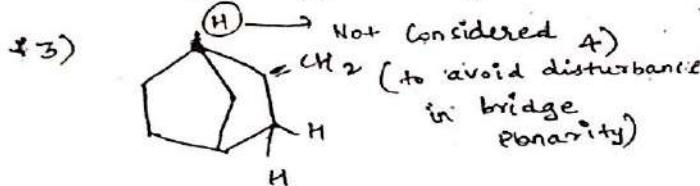
3 Hyper conjugation structures.

(Sacrificial)

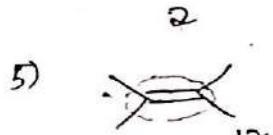
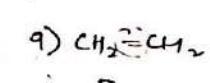
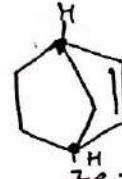


(No Hyd)

zero (carbanium)

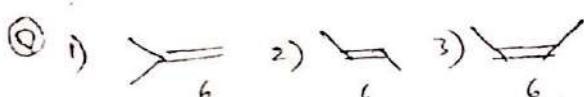


(zero).



a) Stability: ⑤ > ⑥ > ⑦ > ⑧ > ⑨

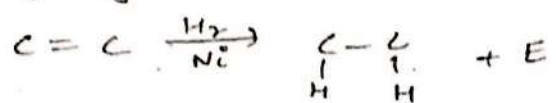
b) C=C B.L: ⑤ > ⑥ > ⑦ > ⑧ > ⑨ (Very more the times the π bond get lifted)



Stability: 1 > 2 > 3

Heat of Hydrogenation:

(G) B

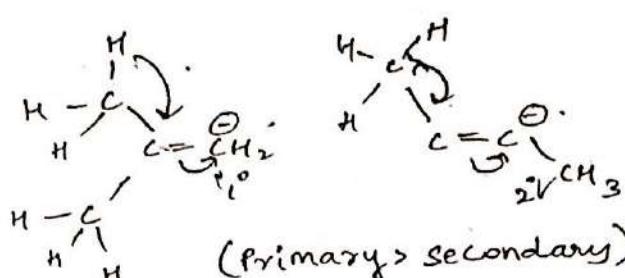


(No of C & π -bonds are same) $\Rightarrow \Delta H_h \propto \frac{1}{stab}$.

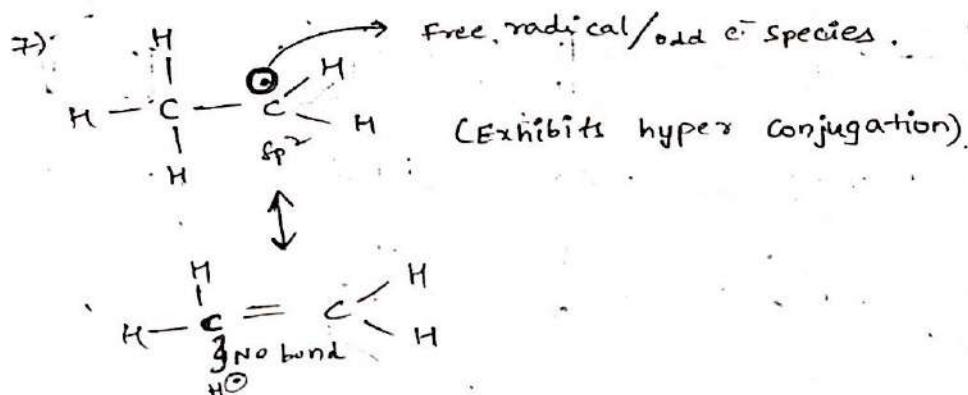
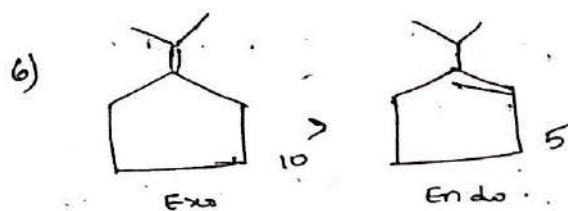
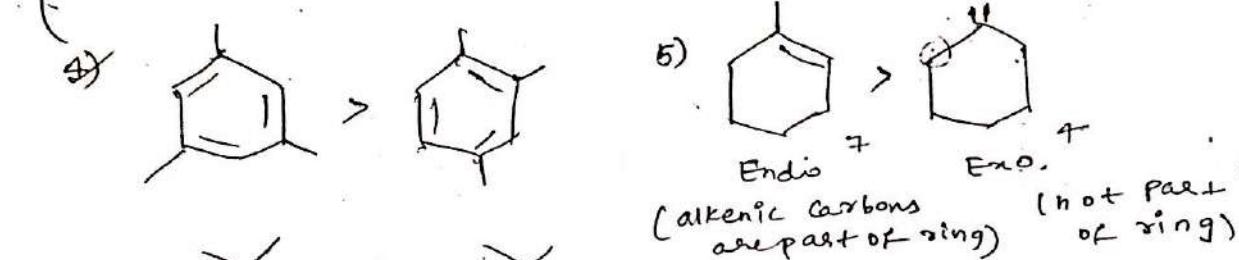
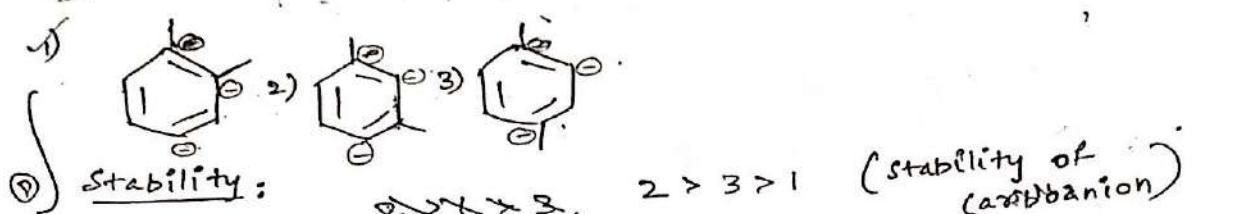
Expt: $\Delta H_C : 3 > 2 > 1$ ($3 > 1 > 2$)

$\Delta H_C : 3 > 2 > 1$

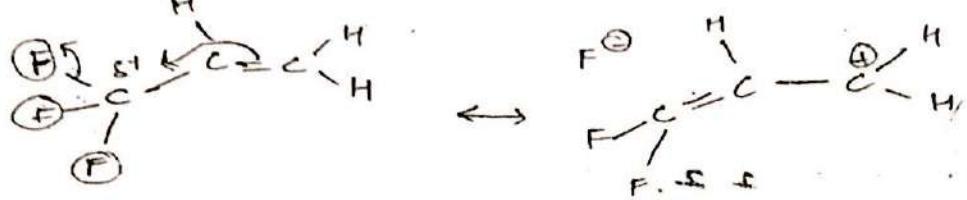
Hyperconjugation:



Ex:



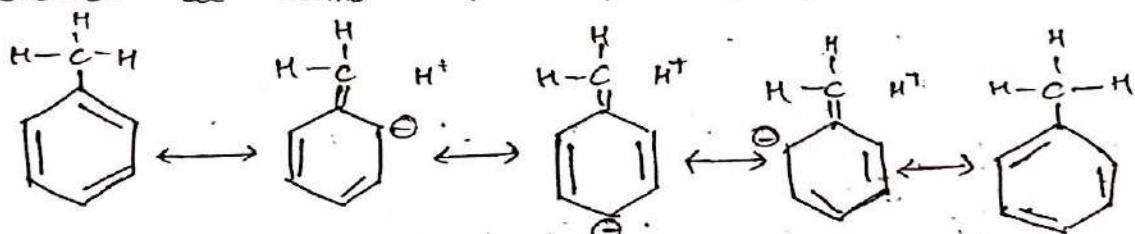
REVERSE HYPER CONJUGATION:



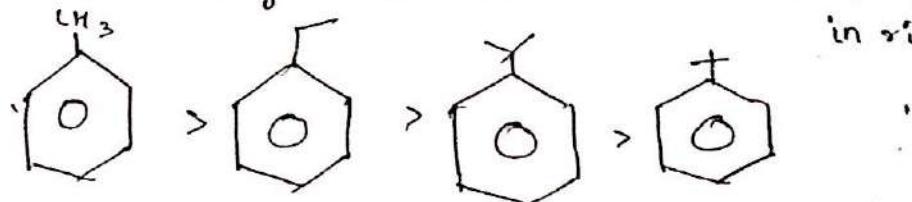
→ observed with $-CF_3$ & $-CCl_3$.

<u>SYSTEM</u>	<u>TYPE OF OVERLAPPING</u>
1. $CH_3\overset{\oplus}{-}CH_2$	$\pi \rightarrow p$ (empty) (UV spectroscopy)
2. $CH_3-CH=CH_2$	$\pi \rightarrow \pi^*$
3. $F-B-F$	$n(LP) \rightarrow p$ (empty)
4. $CH_3-N-\overset{\oplus}{C}-H$	$n(LP) \rightarrow p$ (empty)
5. $O-H-C-H$	$n(LP) \rightarrow \pi^*$
6. $*F-C-F-CH=CH_2$	$\pi \rightarrow \pi^*$

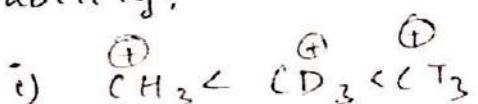
→ In Toluene, due to hyper conjugation, electron density increases at ortho & para position.

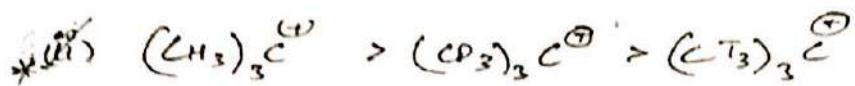


④ In which ring max. Electron density is present in ring

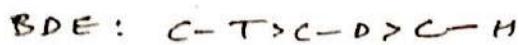


a) Stability:

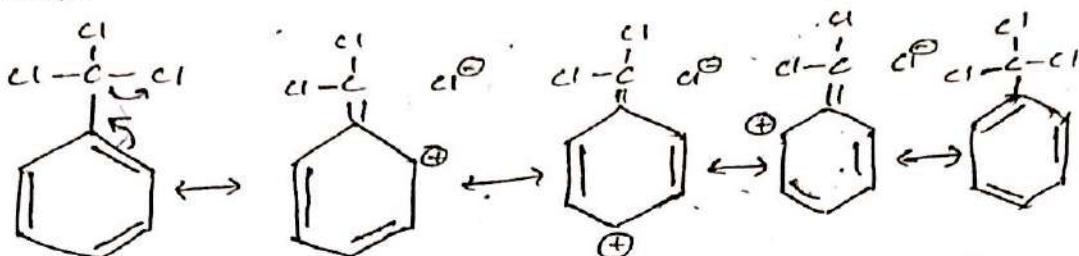




(B)

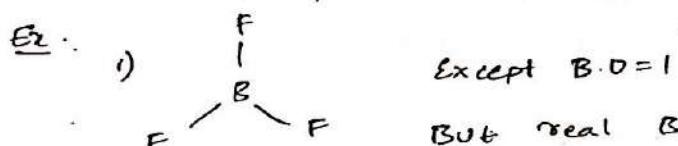


→ Due to Reverse Hyperconjugation, in tetrachloro toluene
the charge is developed at ortho & para positions

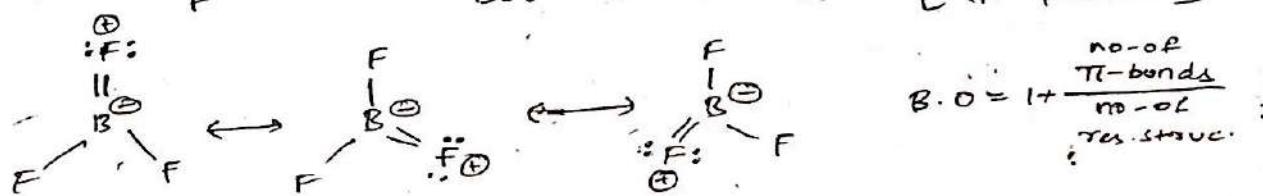


RESONANCE (R) OR MESOMERIC EFFECT (M) :-

→ Some times, (in some cases) Single Lewis dot structure is not sufficient to explain the real properties of the molecule.

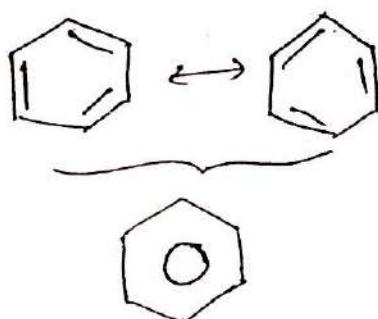


But real B.O = 1.33 [observed in IR spectrum]



$$B.O = 1 + \frac{\text{no. of } \pi\text{-bonds}}{\text{no. of } \sigma\text{-bonds}}$$

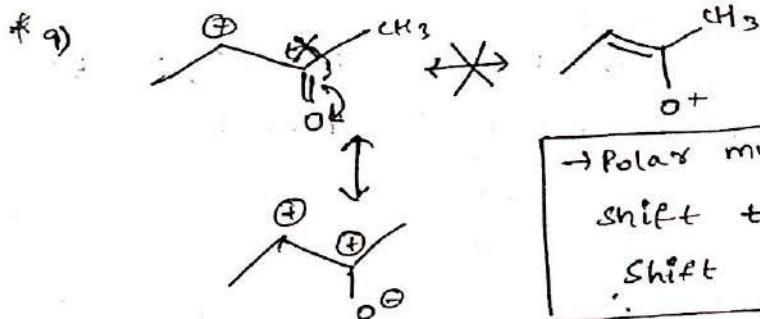
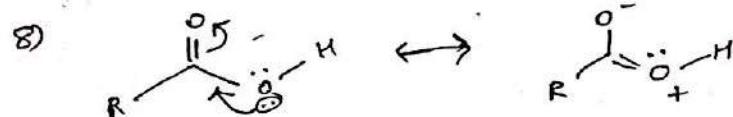
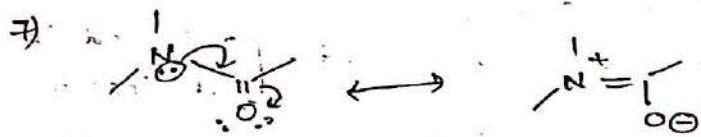
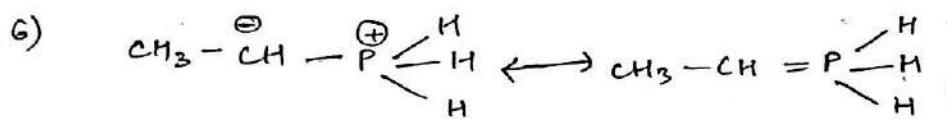
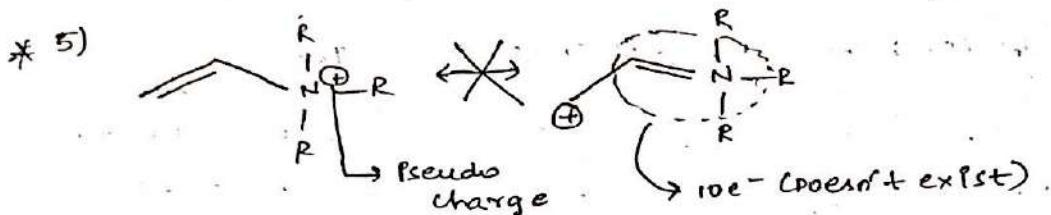
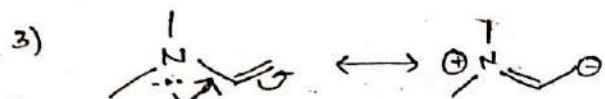
2) The C-C bond length in Benzene is unique from C-C & C=C B.L. All the B.L in Benzene are (1.34) (1.34) same. i.e 1.39 \AA .



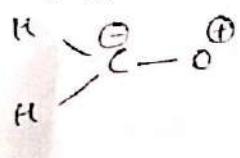
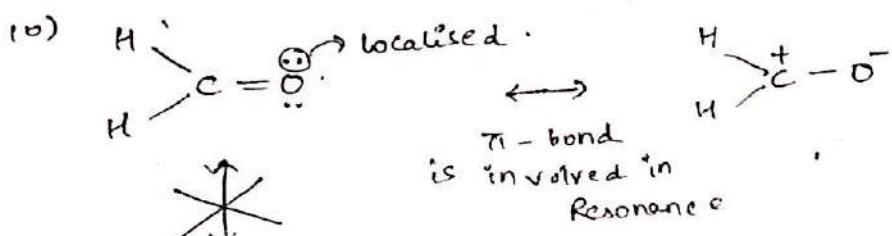
Def:- -ve charge (or) L.P (or) π -electrons (or) odd- e^- overlapped with its adjacent p/d orbital is

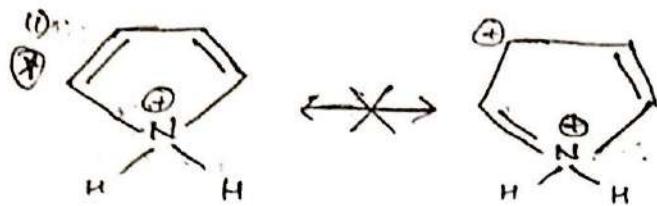
Known as Metameric effect.

①



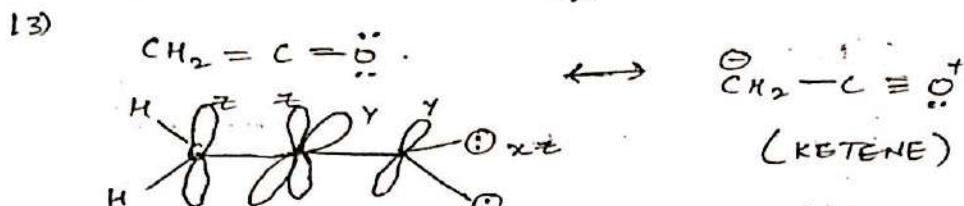
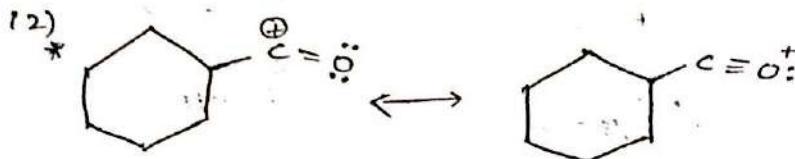
$\text{C}=\overset{\delta}{\text{O}}$



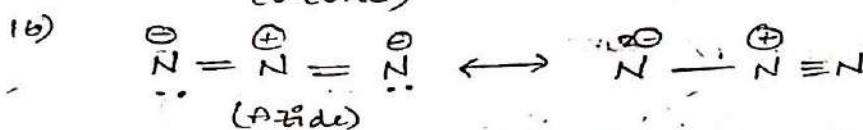
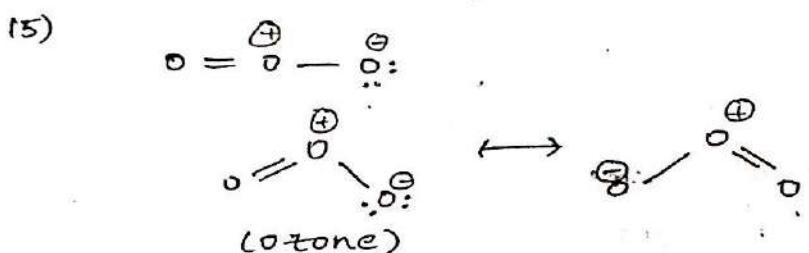


(16)

(Pseudo charge does not take e^-)

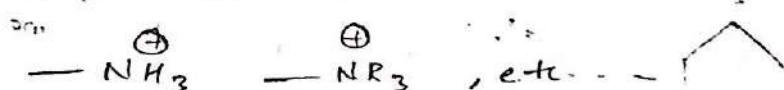


(Diazomethane)

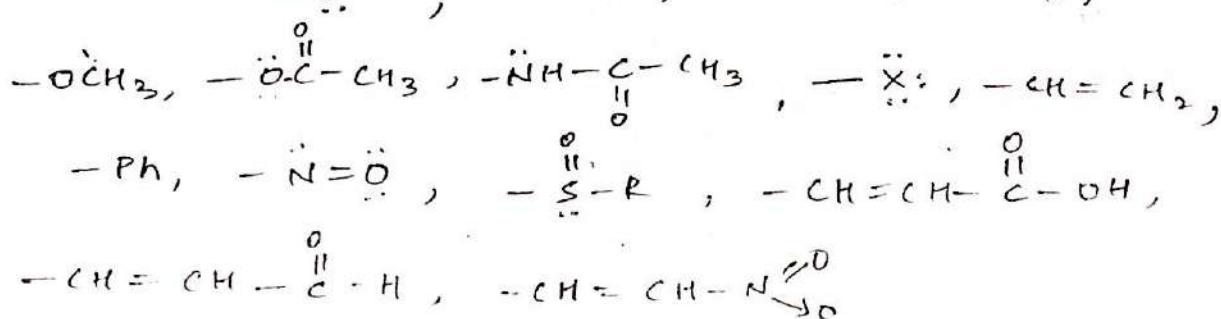


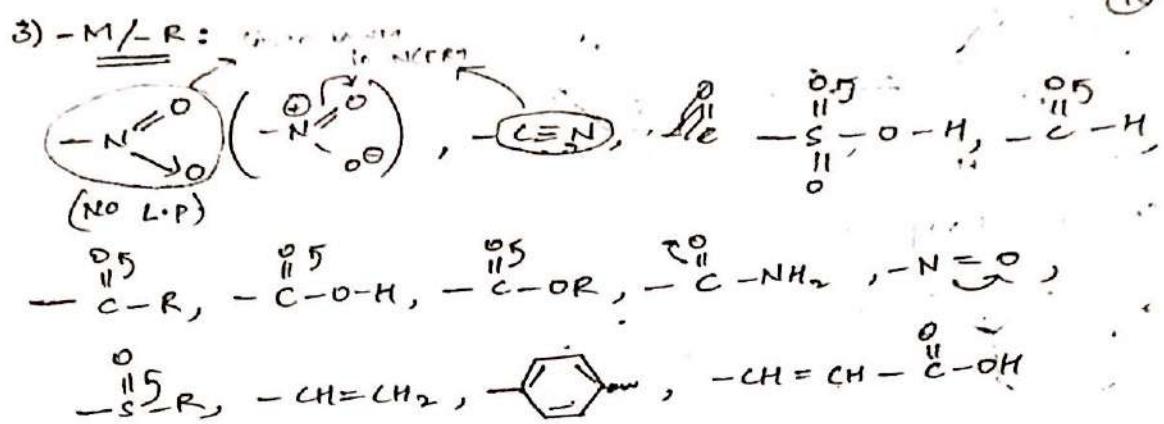
CLASSIFICATION OF GROUP'S:-

1) Neither $+M$ nor $-M$:

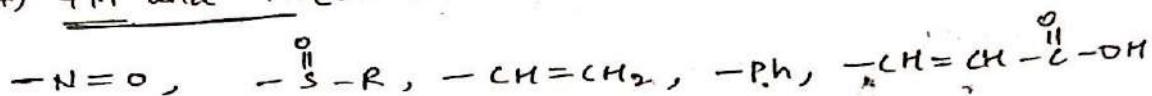


2) $+M/-R$: ---O^- , ---NR_2 , ---NHR , ---NH_2 , ---OH





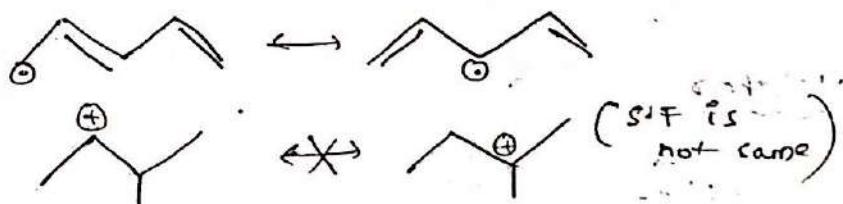
4) $+M$ and $-M:$ (Both +n)



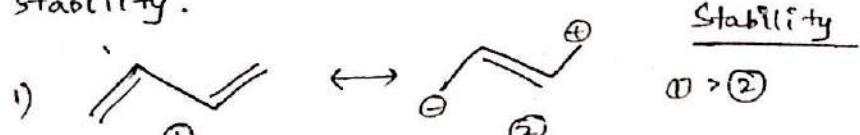
RESONANCE RULES:-

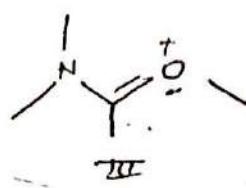
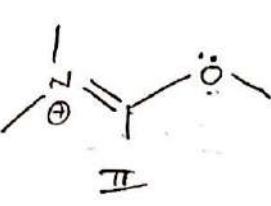
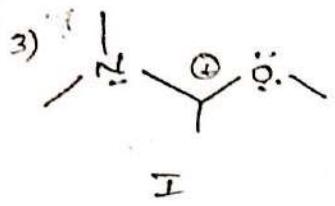
→ To become canonical structures, they should obey the following conditions:

- * M.F same
- * S.F same
- * Total no-of e⁻ should be same.
- * Net charge should be same.
- * No-of odd e⁻ should be same.

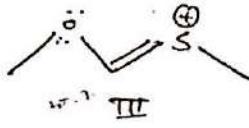
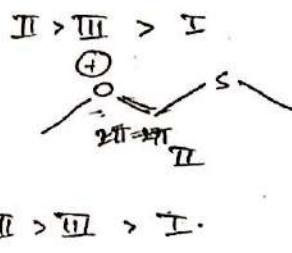
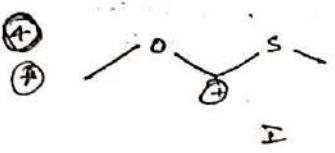


→ More is the No-of Covalent bonds, more will be the stability.



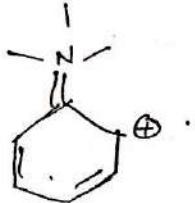
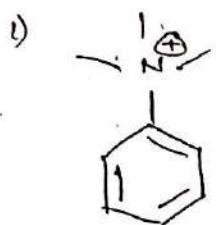


(12)

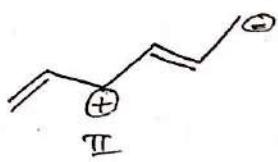
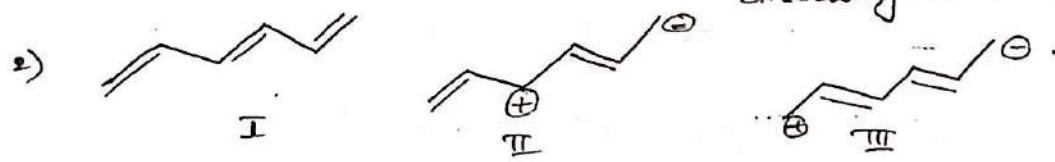


$\text{II} > \text{III} > \text{I}$

→ 2nd period Element never exceed octet

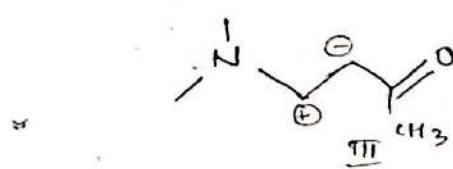
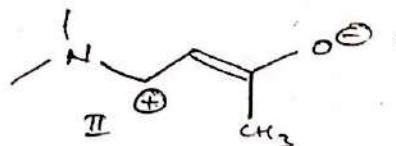


Dienonof" exist (due to 2nd grp element exceeding octet)

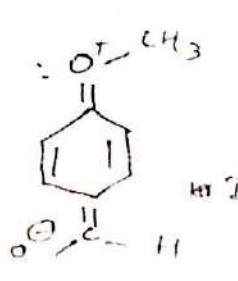
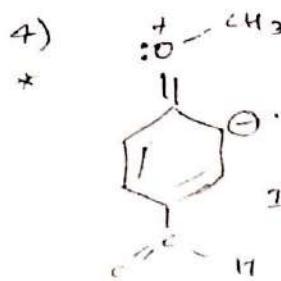


$\text{I} > \text{II} > \text{III}$

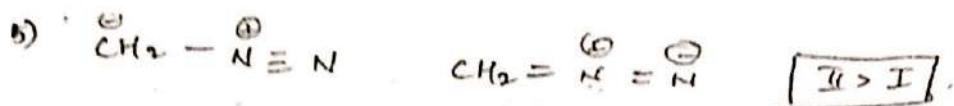
→ According the coulomb's law of Force of attraction more the dist b/w OPP. charges, less is the stability (if charges are on same atoms)



$\text{I} > \text{II} > \text{III} \rightarrow \text{I} > \text{II} > \text{III}$

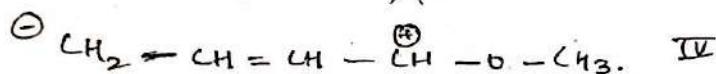
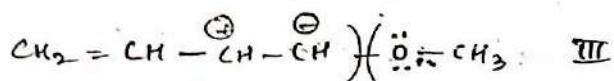
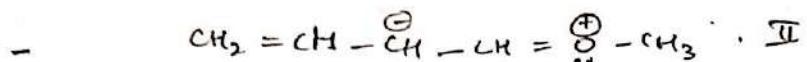
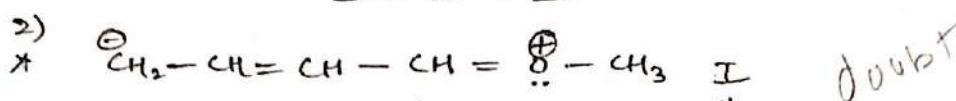
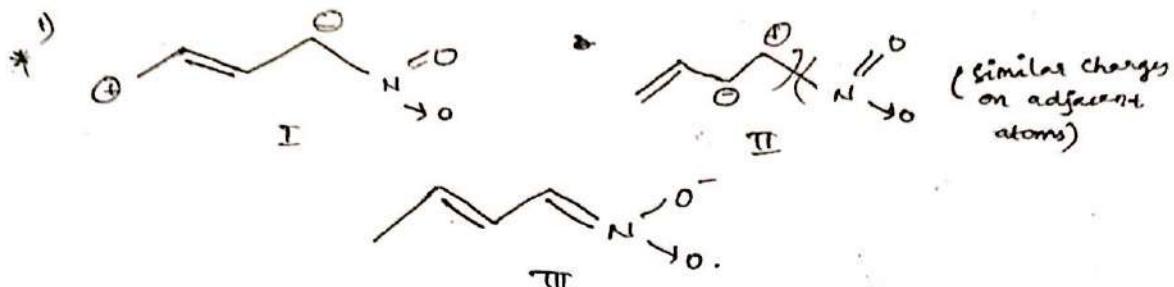


$\text{II} > \text{I}$



(1)

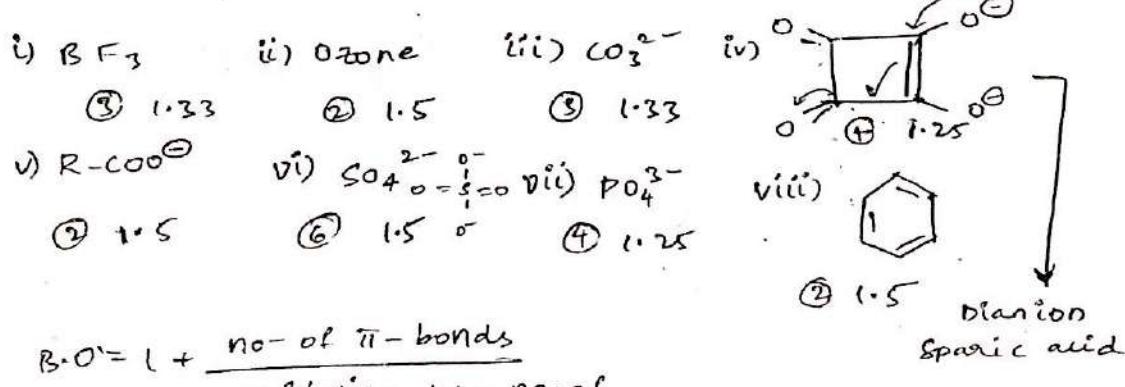
→ Similar charges on adjacent atoms are highly unstable.



→ All resonance structures are hypothetical and exist only on paper. (Doesn't exist in nature)

→ Resonance hybrid is Real.

1) How many Res. Structures are possible.

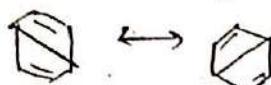


RESONANCE ENERGY:

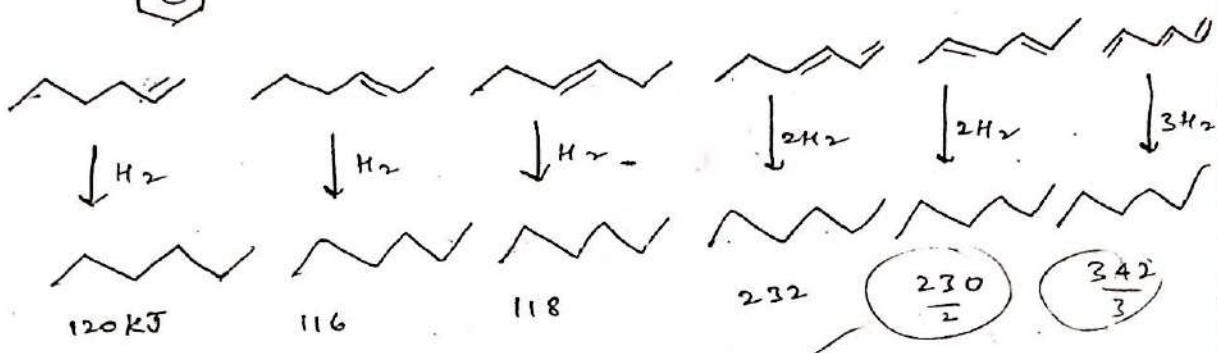
(4)

→ The Energy difference b/w Resonance hybrid and its most stable canonical structure.

(+ve)



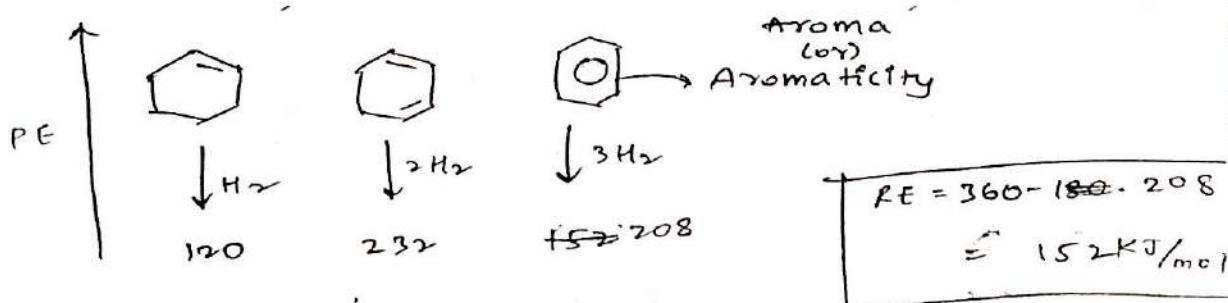
$\uparrow \downarrow$ 152 KJ/mol. (or) 36 kcal/mole



stability: 6 > 5 > 1 (peak)

$$R.E = (120 \times 3) - (342)$$

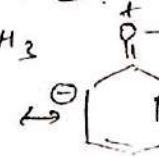
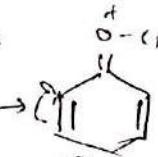
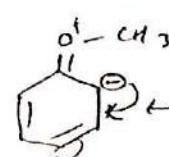
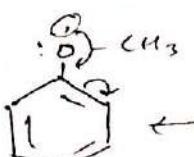
Heat of Hyd: 6 > 5 > 1



* Write the Res. structures for anisole?



Sol:



stability of structures:

$$\text{I} - \text{V} > \text{II} - \text{IV} > \text{III}$$

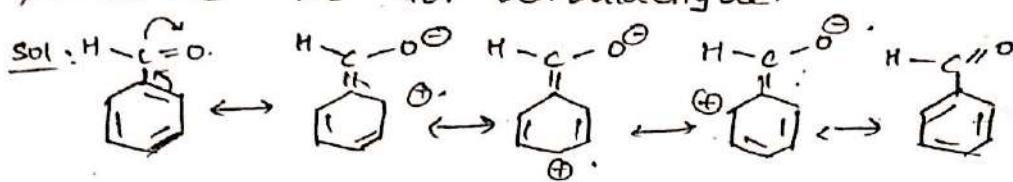


NOTE:

(15)

→ +M groups increases electron density at ortho and para positions.

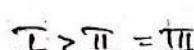
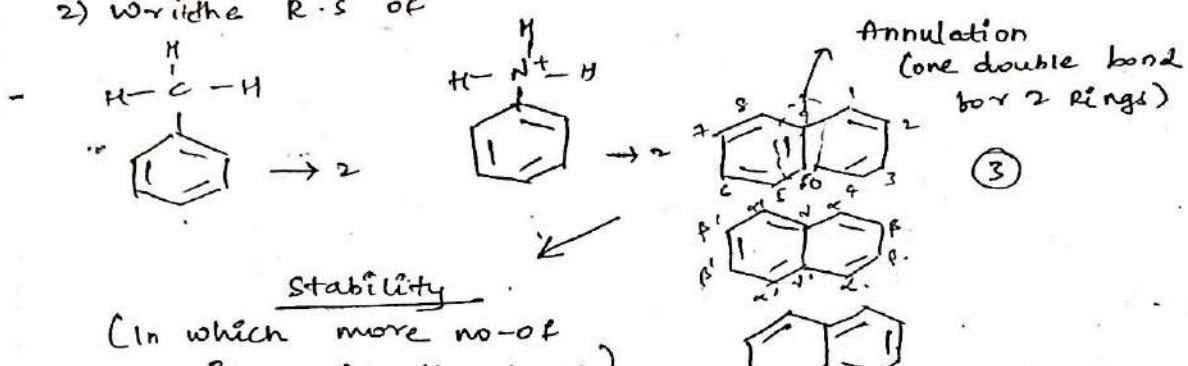
1) Write the R.S. for Benzaldehyde.



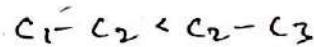
NOTE: stability: $\text{I} = \text{II} > \text{III} = \text{IV} > \text{V}$

→ -M groups decreases electron density at ortho and para positions.

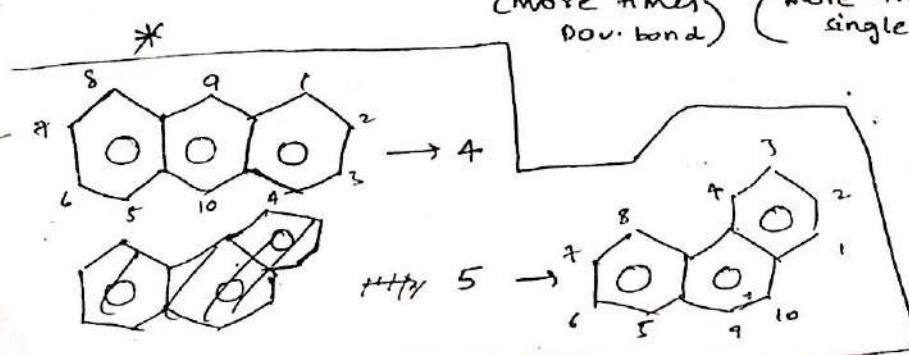
2) Write the R.S. of



C-C Bond Length:



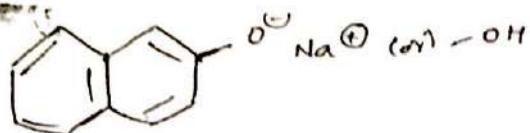
(more times double bond) (more times single bond)



→ In anthracene, middle ring has more diene character

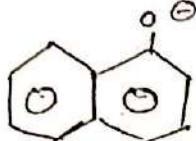
→ In Phenanthrene, C_9-C_{10} has more diene character double bond

(16)



2-Naphthal (or) p-Naphthal

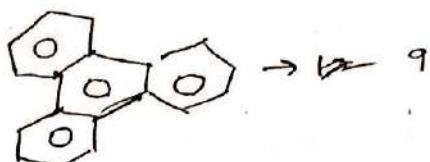
No. of R.S = 9



R.S = 10

(or) o-Naphthal

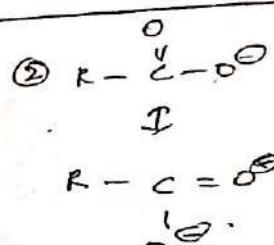
→ which possess No. of RS of



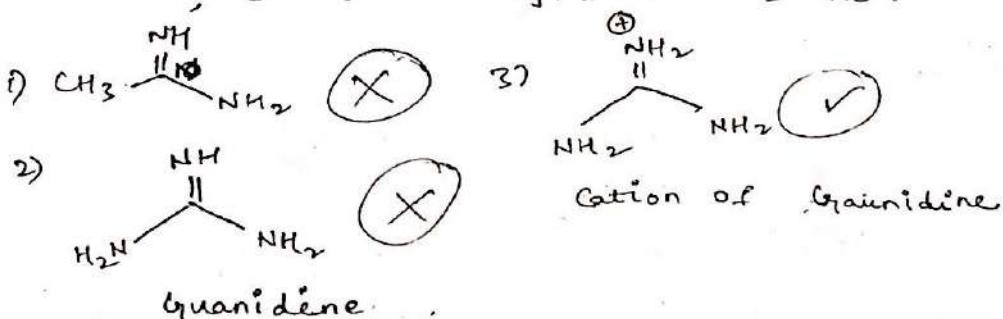
→ In which compound C-O bond length are same.

- ① $R-COOH$ ④ H_2CO_3
 ② $R-COO^- \checkmark$
 ③
 (only ②)
 ⑤ $R-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{H} \leftrightarrow R-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}=\overset{+}{\text{O}}-\text{H}$

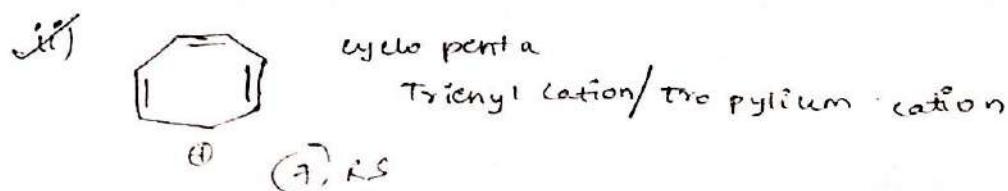
Fact
 → If RE-structures
 are like, B.L
 are same.

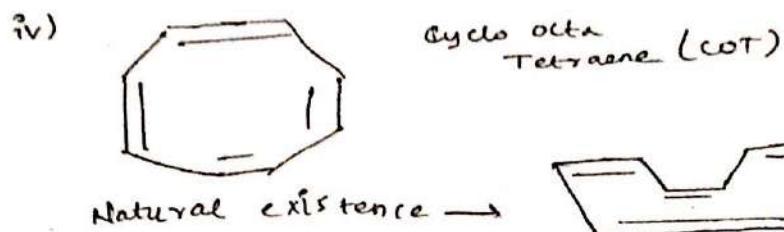
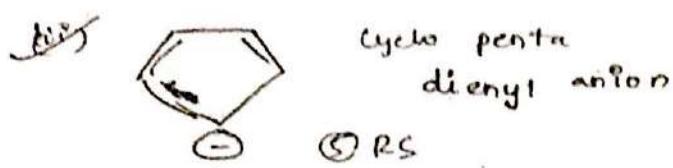


→ In which CN bond lengths are same:

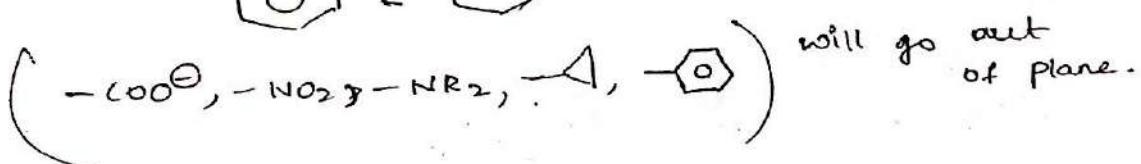
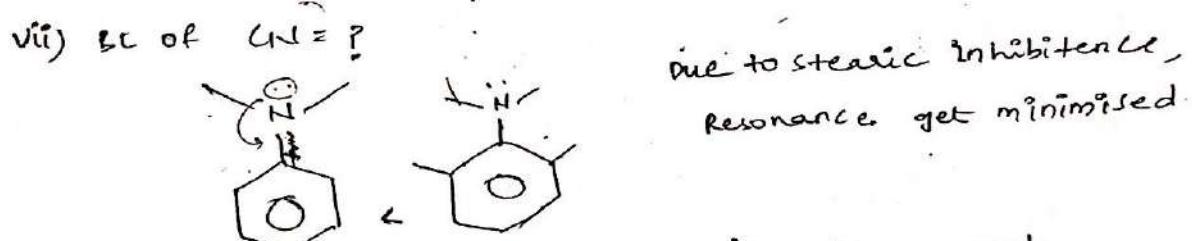
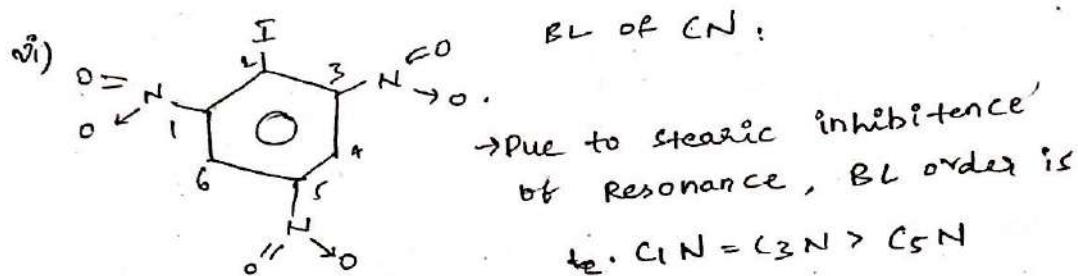
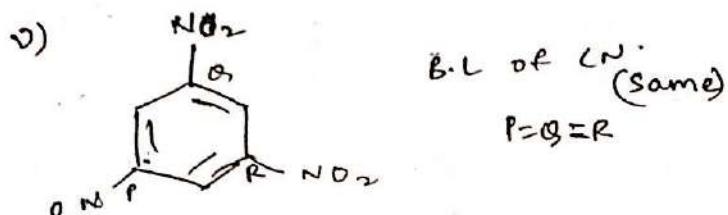


→ In which CC bond lengths are same.

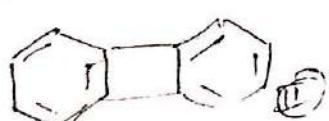
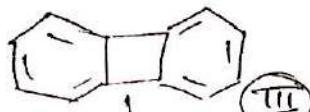
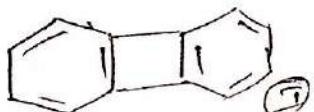




→ Resonance takes place in conjugated system (π -bonds alternative)



STABILITY:

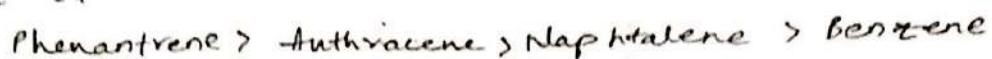


(double bond in 4-membered ring are highly strained)

No Strain III > II > I

Stability of

(18)



86

85

65

36 kcal/mol

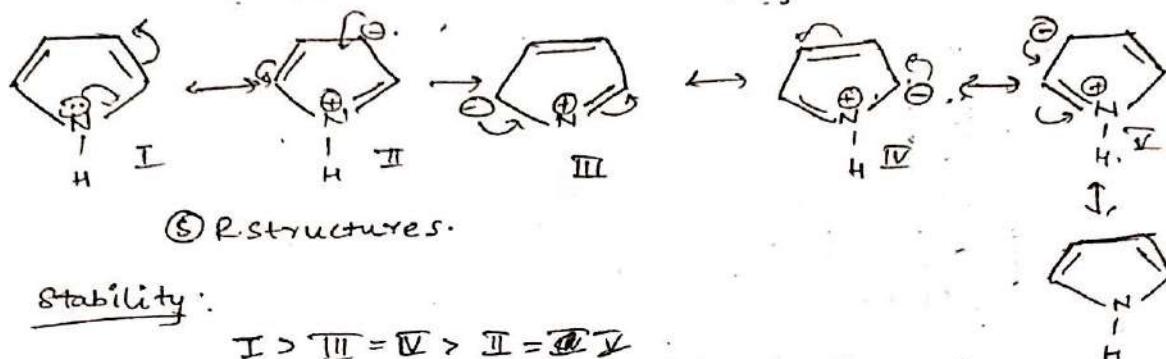
→ More is Benzenoid character, more is stability.

Stability: (RE per ring)

A < P < N < Benzene

[Benzene > N > A] , [P > A]

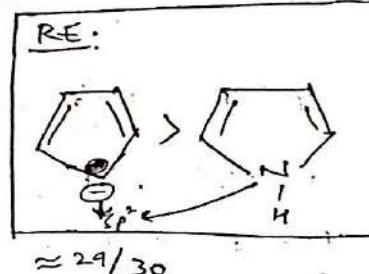
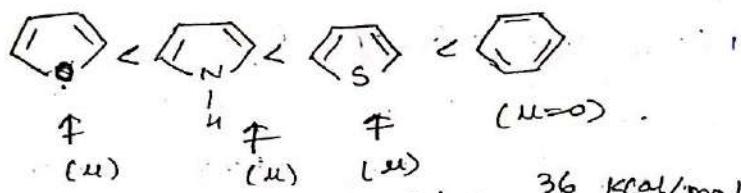
Q) Resonance structures for Furan/Pyrrole :-



Stability:

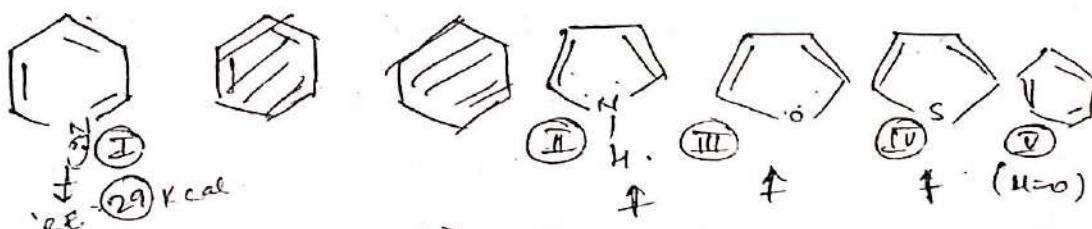
I > III = IV > II = ~~VII~~ VI

Order of Resonance Energy :-



More than 5 R.S
(due to availability
of d-orbitals)

→ In which ring electron density is maximum?

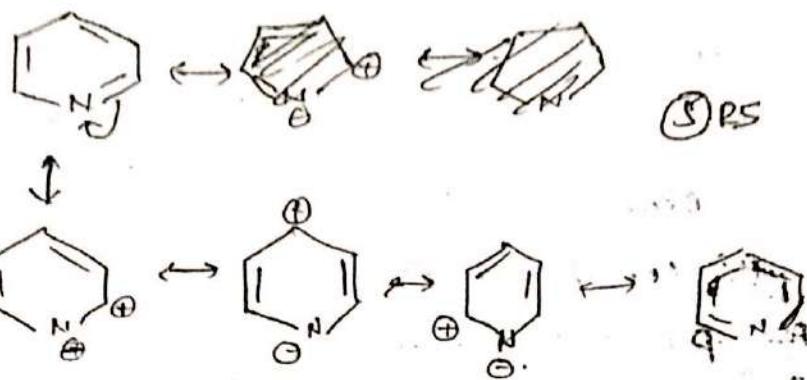


(II) > (III) > (IV) > (V) > (I)

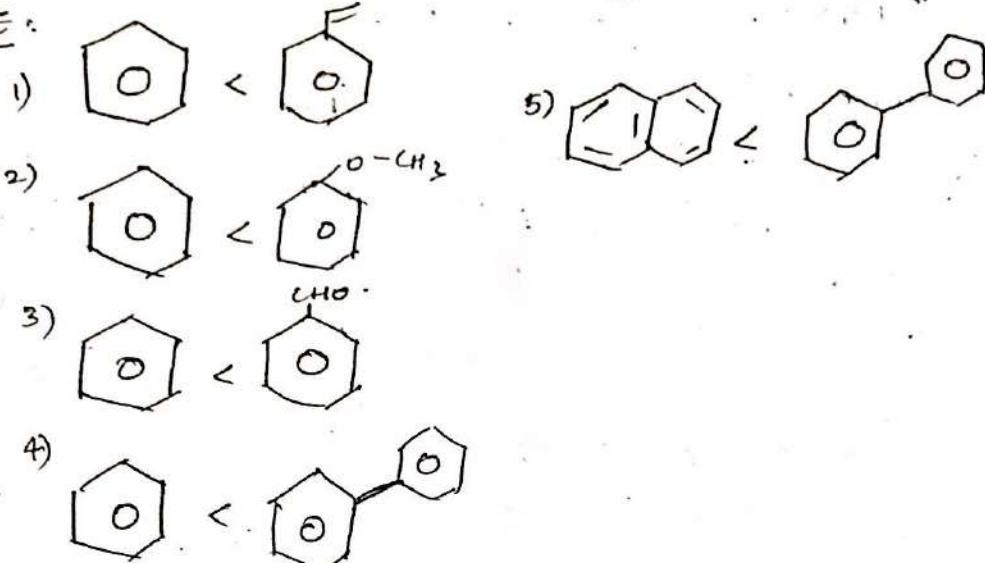
Pyrrole Furan Thiophene Benzene Pyridine

→ Any -ve charge (or) LP is involved in Fully delocalized ionicization and part of ring are sp^2 .

Pyridine:



RE:



ACTIVATING AND DE-ACTIVATING GROUPS:-

→ Electron density is more available in a substituted phenyl ring when compared to simple Benzene, then that particular substituent is called Activating group.

Eg: All $+M$ groups, (Except halo groups)

All $+I$ groups

Alkyl groups which exhibits hyperconjugation.

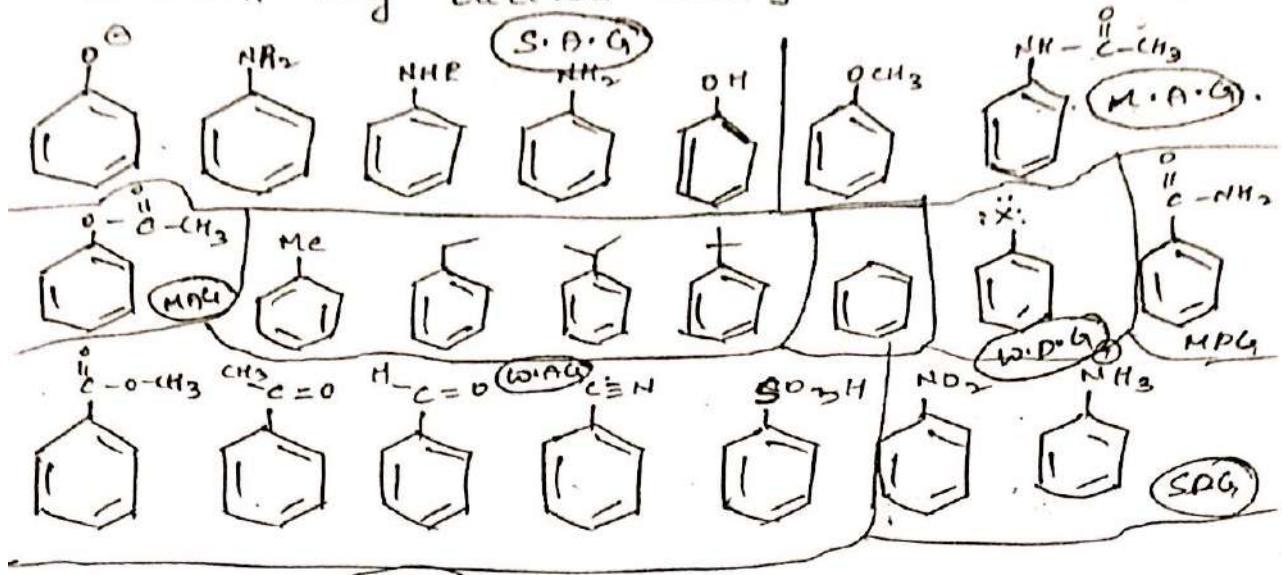
→ Electron density is ~~more~~ less available in ^{'Substituent'} phenyl group ~~compared to substituent~~ when compared to simple Benzene, then that particular substituent is called Deactivating group.

Eg: All $-M$ groups

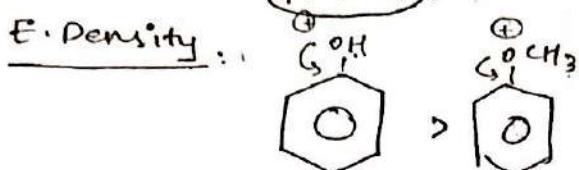
Halo groups

$-(F_3, -CCl_3, -NF_3^+, +NH_3^+)$ etc.
(Reverse hyp wi) (Neither $+M$ nor $-M$)

→ In which ring Electron density is more available?



E. Density : (M.D.G.)



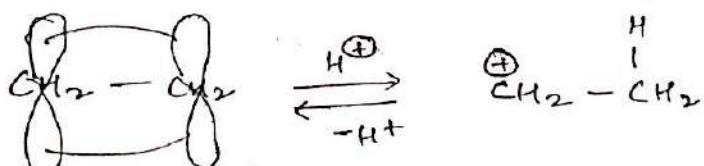
Reason : After $\begin{cases} \text{donating} \\ \downarrow \end{cases}$ $\begin{cases} \text{LP, they get +ve charges.} \\ \downarrow \end{cases}$
More polar less polar

→ For all activating groups, net ~~net~~ dipole is ~~out~~ into the ring.

For all deactivating groups, net dipole is ~~out~~ of the ring.

ELECTRO MERIC EFFECT

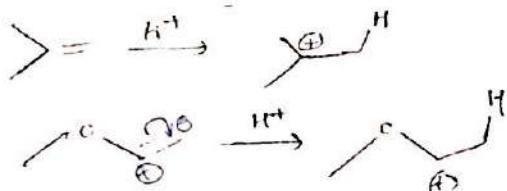
→ Transfer of π -electrons in presence of suitable reagent is called Electromeric effect [E]

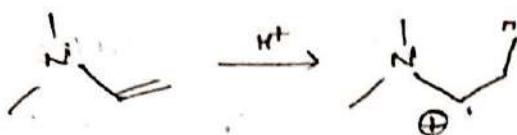


Addn of reagent & Removing of reagent.

(+E) effect:

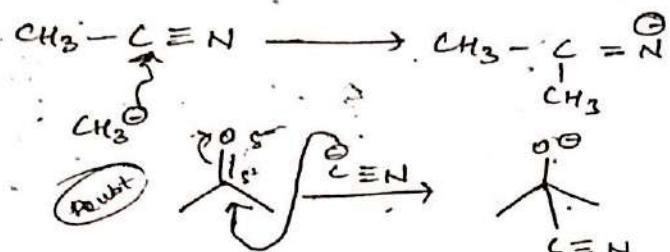
→ π -electrons transferred towards the reagent





(-E) effect:

→ π -electrons are transferred away from the reagent.



Rate of Electromeric effect: (w.r.t. electrophile)

1) i) $\text{C}_6\text{H}_5\text{CH}_2^- > \text{ii}) \text{CH}_2=\text{CH}_2 > \text{iii}) \text{CH}_2=\text{CHCOO}^-$ (^{More hyper} conjugation)

2) $\text{C}_6\text{H}_5\text{CH}_2^- > \text{CH}_2=\text{CH}_2$ (all are attached to one carbon)

3) $\text{C}_6\text{H}_5\text{CH}_2^- < \text{CH}_2=\text{CHCOO}^- < \text{CH}_2=\text{CH}-\text{NH}_2$

4) $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{CH}_2^- > \text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{CH}_2^- > \text{C}_6\text{H}_5\text{OOC}_6\text{H}_4\text{CH}_2^-$

AROMATICITY:

→ cyclic delocalisation of π -electrons if establishes extreme stability, that phenomenon is known as Aroma, those compounds are called Aromatic Compounds.

→ To become Aromatic,

a) Should be cyclic

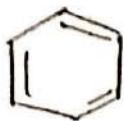
b) Should be planar (all ring atoms are sp^2 /sp)

c) Should be Conjugated.

d) After if obeys the above 3 conditions, then check Hückel's rule.

HUCKLE'S RULE: $(4n+2)\pi e^-$ rule. $n = 0, 1, 2, 3, \dots$ (2)

Eg:

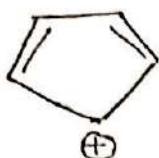


- a) ✓
- b) ✓
- c) ✓
- d) ✓ $(4n+2 = 6 \Rightarrow n=1)$

Aromatic ✓

→ If not obeying Hückel's Rule, then check $4n\pi e^-$ rule; $n=1, 2, 3, \dots$

Eg:



- a) ✓
- b) ✓
- c) ✓
- d) $4n+2 = 4 \Rightarrow n=1 \times X$

$4n\pi = 4$ $\boxed{n=1} \checkmark$

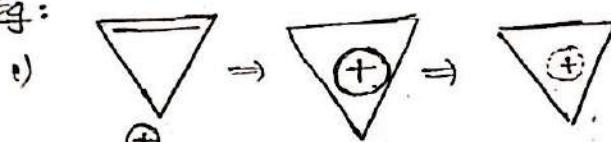
Anti-Aromatic \times

→ If obeying $4n\pi$ rule, it is anti-aromatic.

→ To become non-aromatic,

- Should be cyclic.
- Non-planar & no conjugation

Eg:



$n=0 \checkmark$
Aromatic.

2)

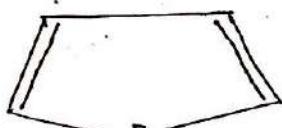


→ Anti-Aromatic.

→ L.P. e^- are considered to be $\pi-e^-$ since they are part of delocalisation.

+/-L.P involved in delocalisation do not get considered in hybridisation.
 $\therefore N \text{ is } sp^2$.

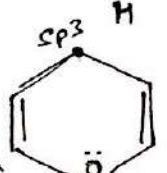
3)



→ Anti-Aromatic.

→ Boron allows for delocalisation.

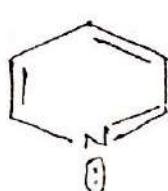
4)



→ Non-aromatic.
(sp^3 -carbon)

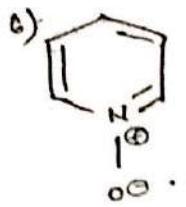
PYRANE

5)

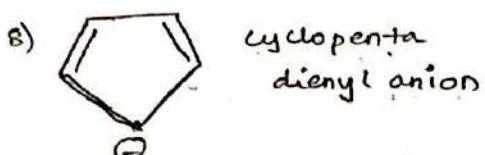
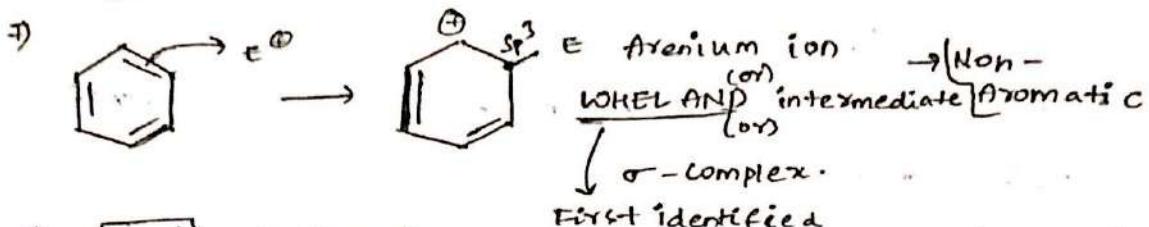


→ Aromatic.

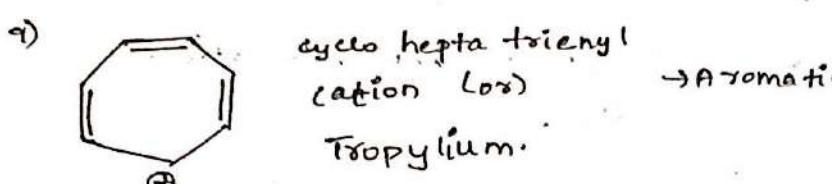
PYRIDINE



→ Aromatic
Pyridine - N-oxide.



→ Aromatic



→ Aromatic

I) Annulens :

→ Cyclic Compounds possesses equal no-of carbons, π -e⁻ & Hyd. are called. Annulenes.

Eg: [4]-annulen. → → Anti-Aromatic

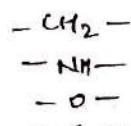
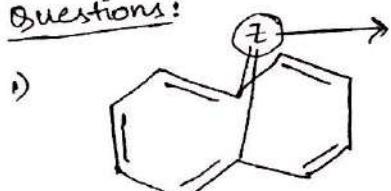
[6]-Annulen. → → Aromatic

IT-JEE
[8]-Annulen. → → Non-aromatic (Non-Planar)

[10]-Annulen. → → Non-aromatic (Non-Planar)

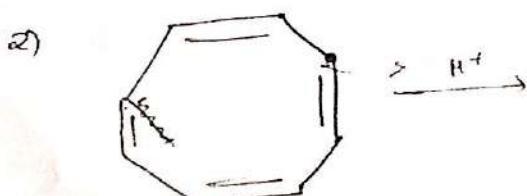
N* { [12], [14], [16], [18] }
Annulens aromatic Non- aromatic
Anti-Non-aromatic aromatic aromatic

Questions:

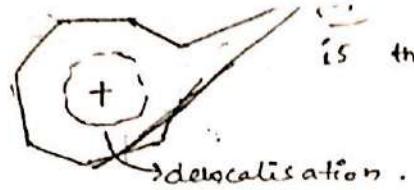


Really
Homo-aromatic.
but in exam, it
is : aromatic

Homo-aromatic: By ignoring some part, if it is aromatic.



Really
Homo-aromatic
⇒ Aromatic.

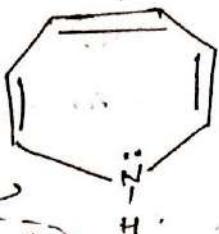
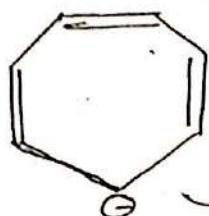


is the existence of
the above product -

(4)

→ delocalisation.

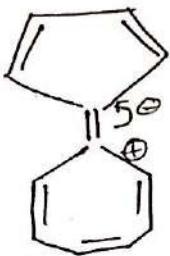
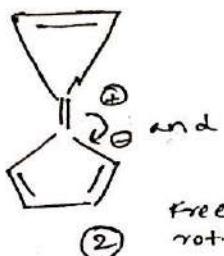
3)



(→ it is slightly
(Deviates from
plane))

Non-aromatic

II) Fulvens :-



and



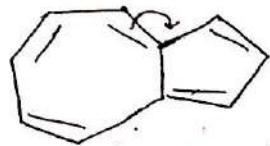
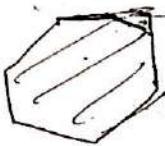
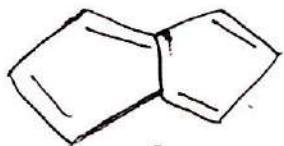
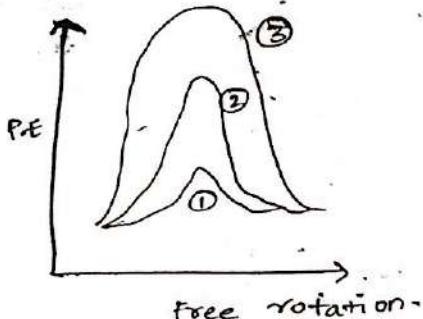
called
Fulvens.

No free
rotation

a) Dipole moment: $\textcircled{1} > \textcircled{2} > \textcircled{3} (\mu=0)$

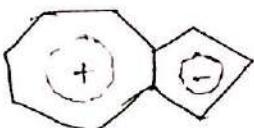
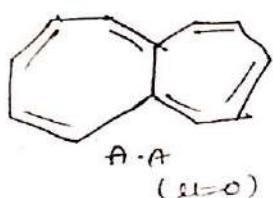
b) $\textcircled{1}, \textcircled{2}$ are aromatic :-

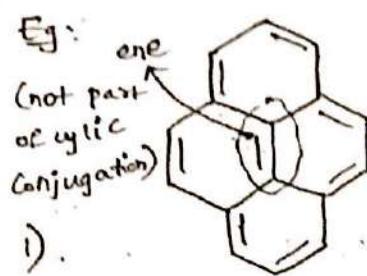
c)



→ Aromatic

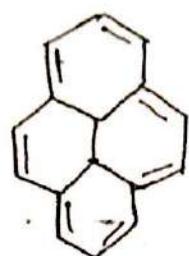
↓ Azulene ($\mu=0$)
→ Polar.



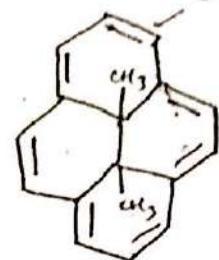


1).

PYRENE
→ Aromatic



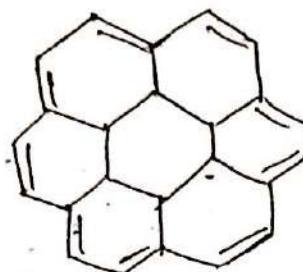
→ Aromatic



→ Aromatic

(b)

$$(4n+2)\pi e^-$$

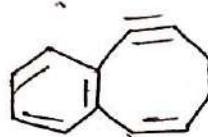


→ Aromatic

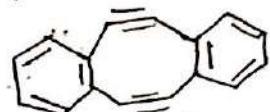
2) Biphenylene



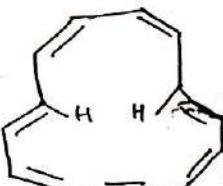
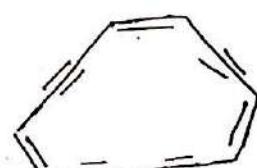
→ Aromatic (due to
high strain on
cyclo butane)



Anti-Aromatic



3)



→ out of triple
bond, only 1
is involved in
cyclic delocalisation

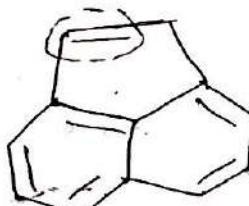
→ Aromatic

5)

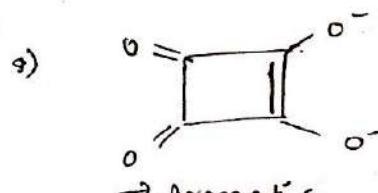


→ Aromatic

6)

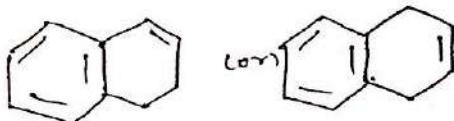


→ Benzyne.



→ Aromatic

7)

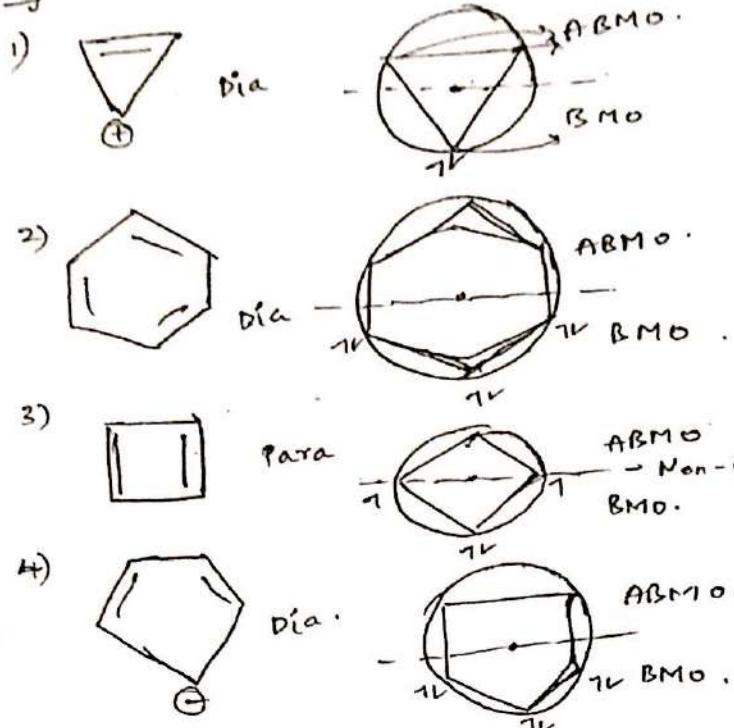


→ Aromatic

Foost diagrams / MOT:

→ To explain magnetic behaviour of these compounds.

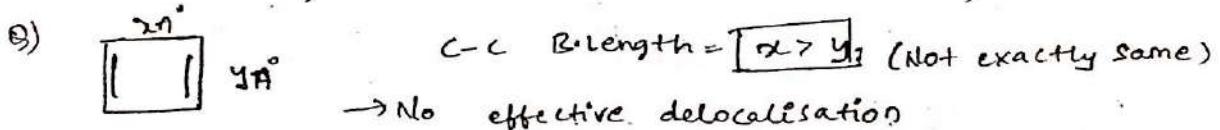
→ all the 'C' should be in circle (touch)
and one vertex down.



Liesg
 → Liesg above to
 Imaginary axis. are
 Anti-Bonding Molecular
 orbitals
 → below are 'bonding'
 M.O.
 → on the line are
 non-bonding M.O.

Conclusion:

- Not all anti-aromatic compounds are para magnetic but vice-versa not true.
- If unpaired e^- are present in non-bonding orbitals (or) anti-bonding orbitals, their C-C bond lengths are not equal due to non-degeneracy, they are not effectively involved in delocalisation.



Anti-Aromatic → Some are in Antibonding, Non-bonding.

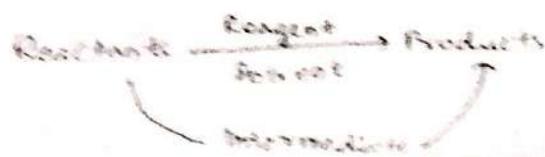
BOND CLEAVAGE:

A & B → Homolytic $\xrightarrow{\text{Reagents}}$ A^{\bullet} and B^{\bullet} and $\text{A}^{\bullet\bullet}$ and $\text{B}^{\bullet\bullet}$ discharged
and $\text{A}^{\bullet\bullet}$ and $\text{B}^{\bullet\bullet}$ are neutral

NOTE: More energy is consumed for Heterolytic cleavage.
 $E_{\text{exotherm}} > E_{\text{homolytic}}$

Reactions:

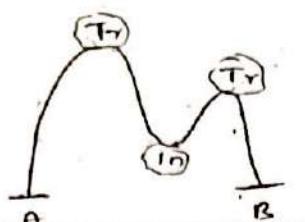
→ Reactants are converted into products under suitable reaction conditions



Transition state: High energy active mass barrier (2)
 → Not possible to isolate
 → Hypothetical.

Intermediate:

- Highly unstable, but isolated species.
- Life span: $(\tau_{1/2}) = 0.001\text{sec}$ to 0.1sec
- Formed in b/w the Reaction course.



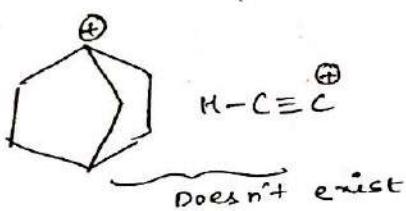
Tr - Transition state.
 In - Intermediate.

n intermediates: $(n+1)$ transition states.

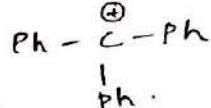
i) CARBO CATION: (CH_3^+)

- Trivalent
- Positively charged species
- possess 6 valence e⁻.
- sp^2 (Trigonal planar)
- Diax Diamagnetic.
- Electron deficient.

Ex:



Shape of



→ Propeller (non-planar)

Hyp:

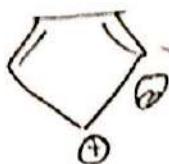
- 1) $\text{CH}_2 = \text{CH}_2 \rightarrow \text{SP}$



STABILITY:-

- i) $\text{CH}_3^+ < \text{CO}_3^+$
- ii) $\text{CH}_3-\overset{\oplus}{\text{C}}-\text{CH}_3 > \text{CD}_3-\overset{\oplus}{\text{C}}-\text{CD}_3$ [Hyper conjugations
 $\text{BDE of } \text{C}-\text{D} > \text{C}-\text{H}$]
- iii) $< \text{CH}_2=\overset{\oplus}{\text{C}}=\text{CH}_2 < \text{Ph}-\overset{\oplus}{\text{C}}\text{H}_2$

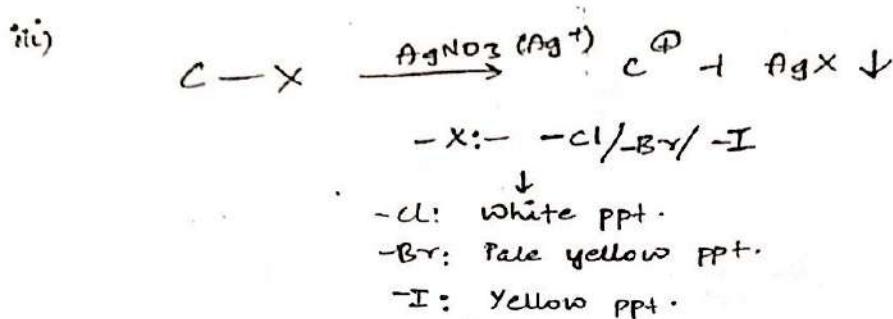
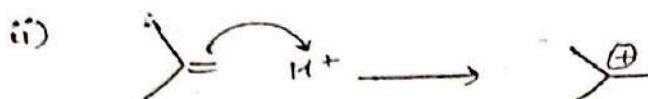
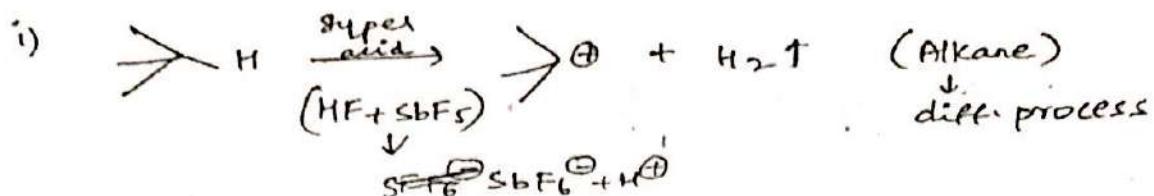
1)



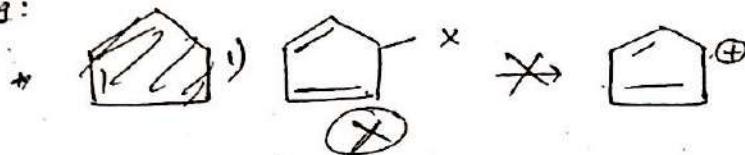
2 > 1 > 3

anti aromatic

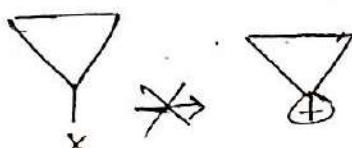
2)

GENERATION:

Ex:

 $\rightarrow \text{X}^-$ will not go due to Anti Aromaticity.

2)



(due to increase in strain)

3)

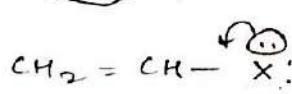


4)



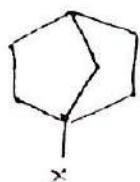
$(+M$ groups, (double bond character)
 $\text{Energy} +)$

5)

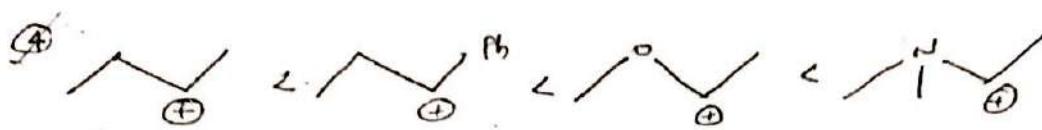


(cleavage doesn't take place)

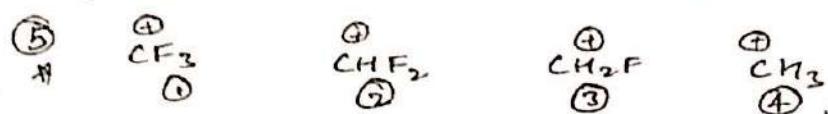
6)



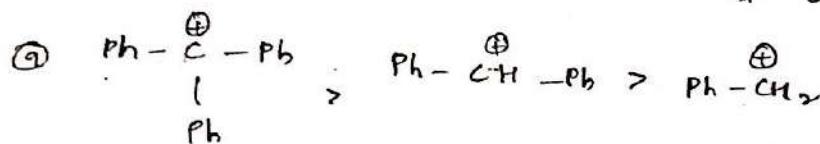
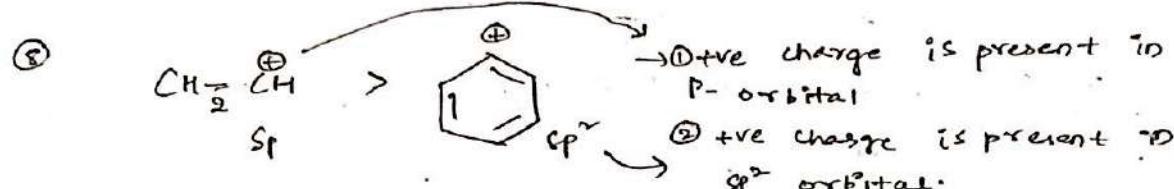
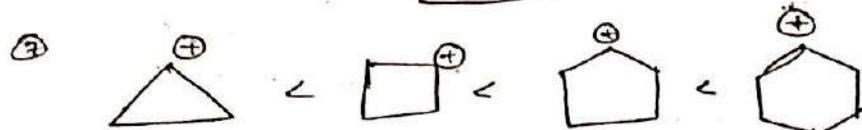
(double bond character doesn't exist at bridged carbon)



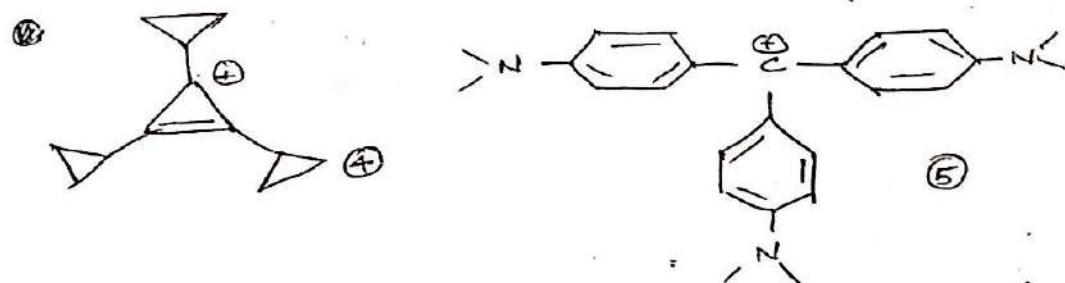
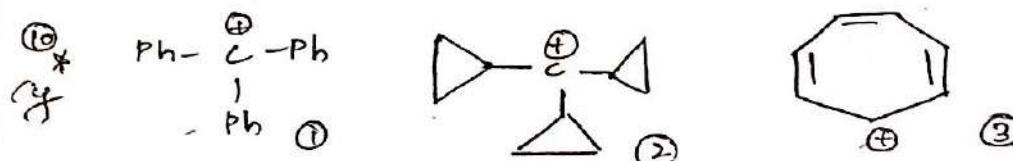
(2)



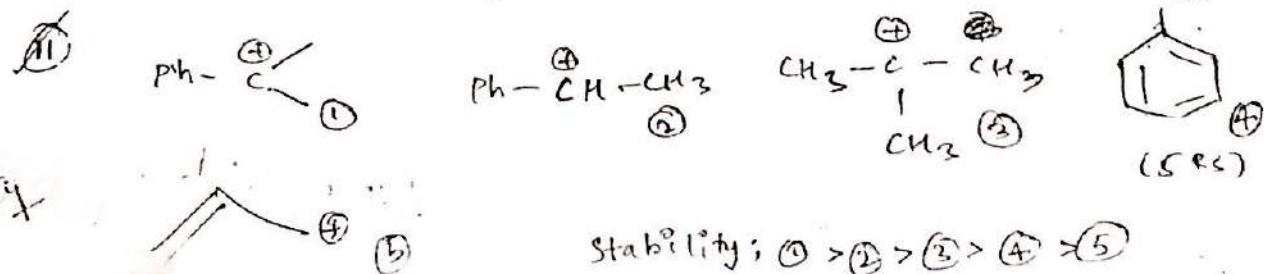
2 > 3 > 4 > 1 (use -I)



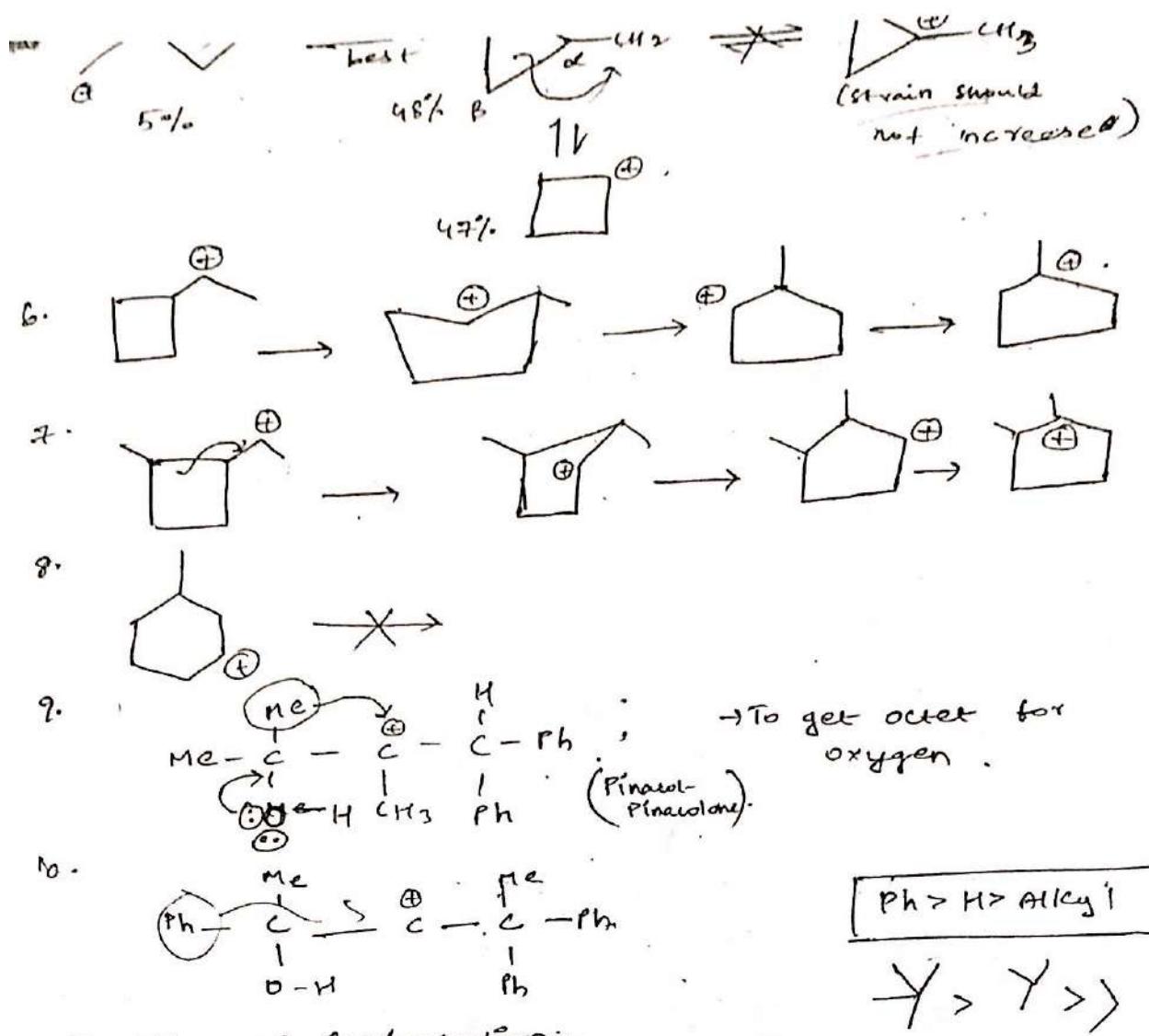
Tritile
Carbocation



*Stability: ④ > ⑤ > ③ > ② > ①

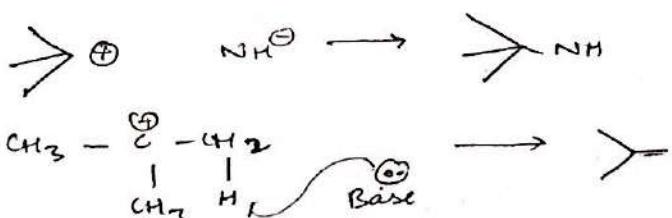


Stability: ① > ② > ③ > ④ > ⑤



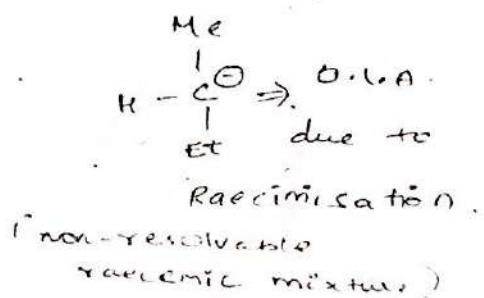
Reactions of Carbocation:

→ May react with nucleophile (or) may react with base.



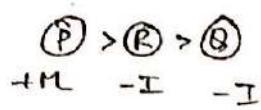
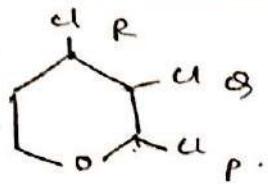
ii) CARBANION:

- trivalent
- -ve charged
- Be-
- sp^3 (Pyramidal)
- Diamagnetic



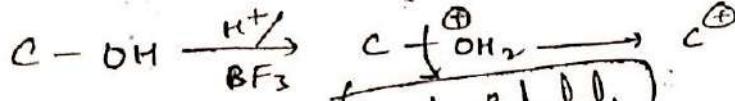
(b) Rate of Precipitation:

(5)



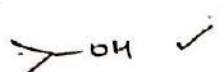
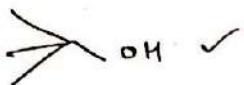
less $-I$ better than more $-I$

(iv)

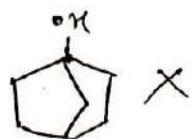


Eg:

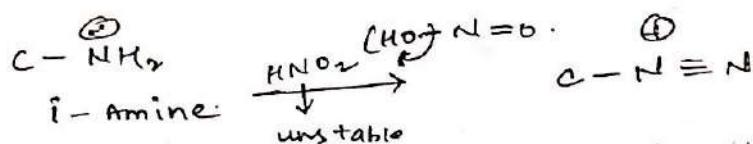
(a)



Except 1° alcohols



(v)

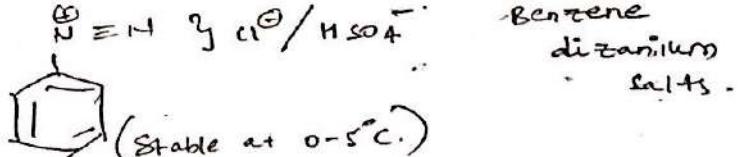


case (i): If CR_2 is aliphatic

by loss of N , we get C^\oplus

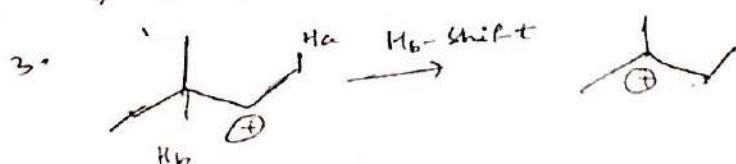
case (ii): If R is aryl (aromatic)

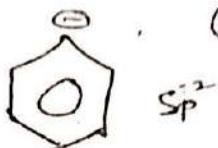
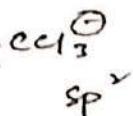
(b)



Fate of Carbocations:-

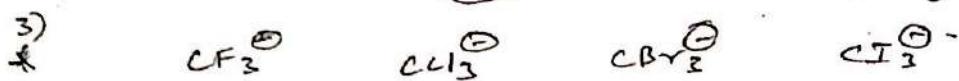
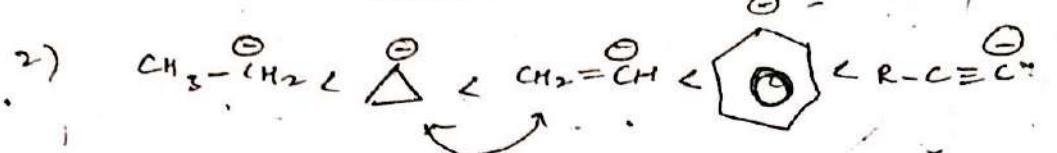
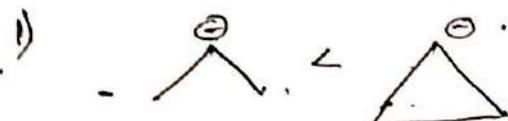
Eg:



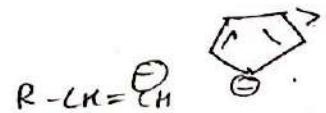
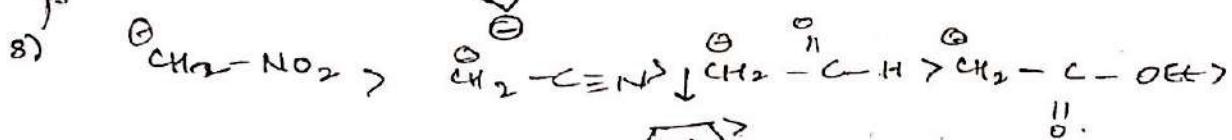
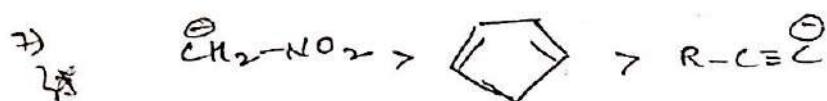
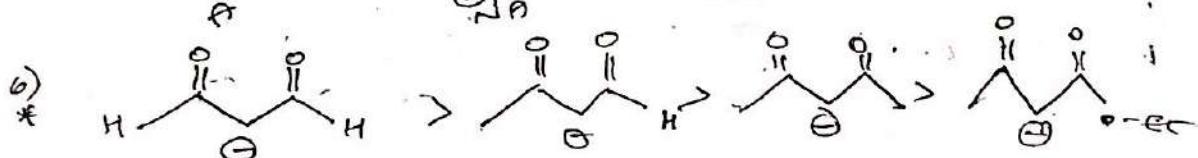
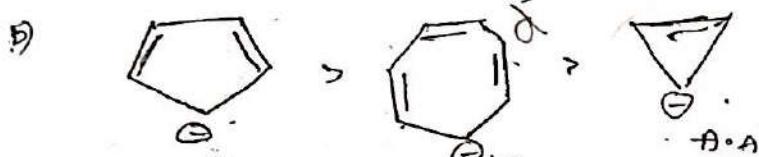
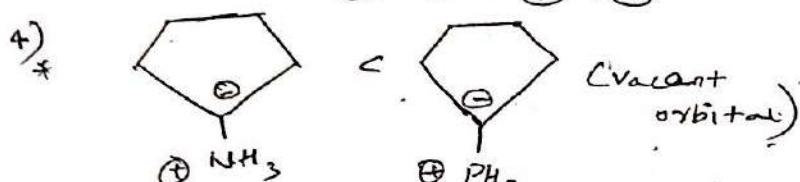


(7)

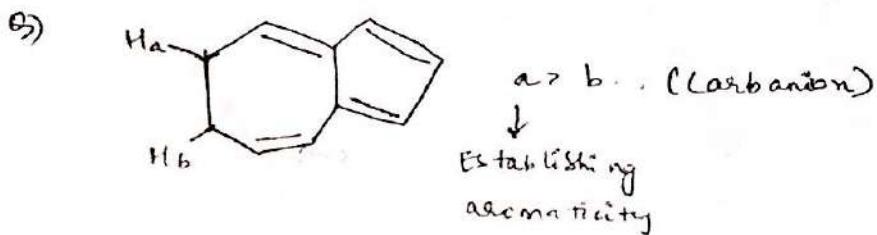
Stability:

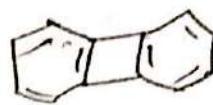
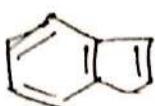
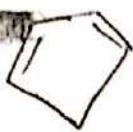


$\textcircled{2} > \textcircled{1} > \textcircled{3} > \textcircled{4}$



acidic strength \propto stability of carbanion.





(3)

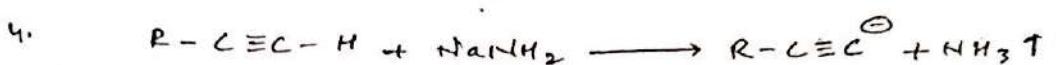
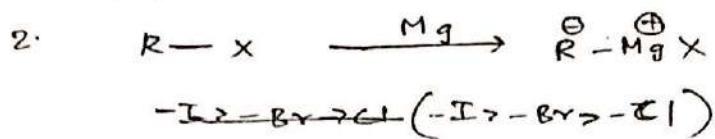
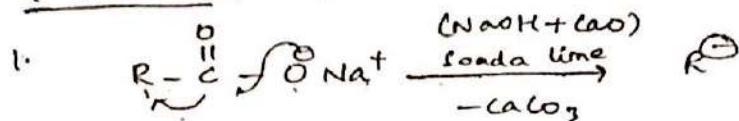
alone aromatic

annulation

(1) > (2) > (3)

Biannulation

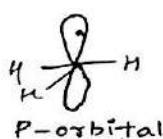
Generation:



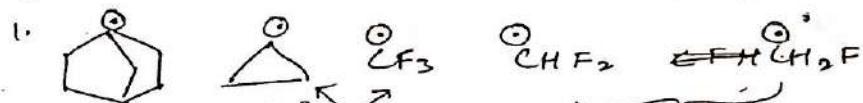
(iii) FREE RADICALS:-

$\rightarrow \dot{\text{CH}}_3 \rightarrow \text{Trivalent} \rightarrow \text{para-magnetic}$

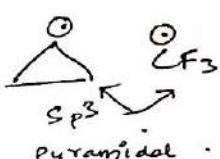
$\rightarrow \text{sp}^2 \rightarrow \text{Fe}^\bullet \rightarrow \text{Neither Electrophile}$
 nor nucleophile



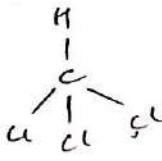
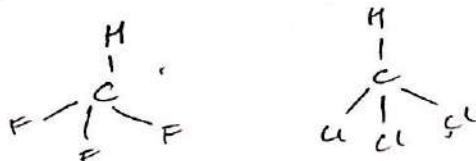
Eg:



Exist
sp³
Pyramidal



both non-planar &
non-pyramidal



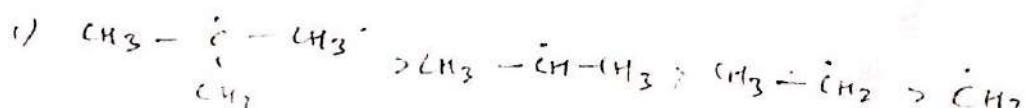
1. BDE: 106 > 96

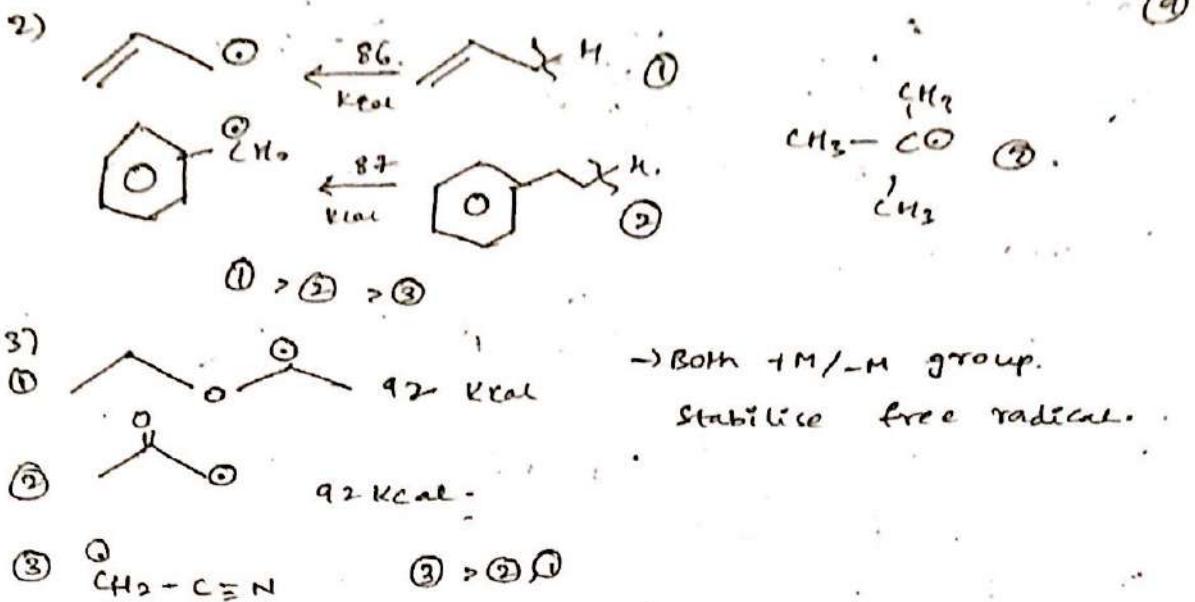
Stability: F₃C-H < Cl₃C-H

NOTE: → Radical stability depends on

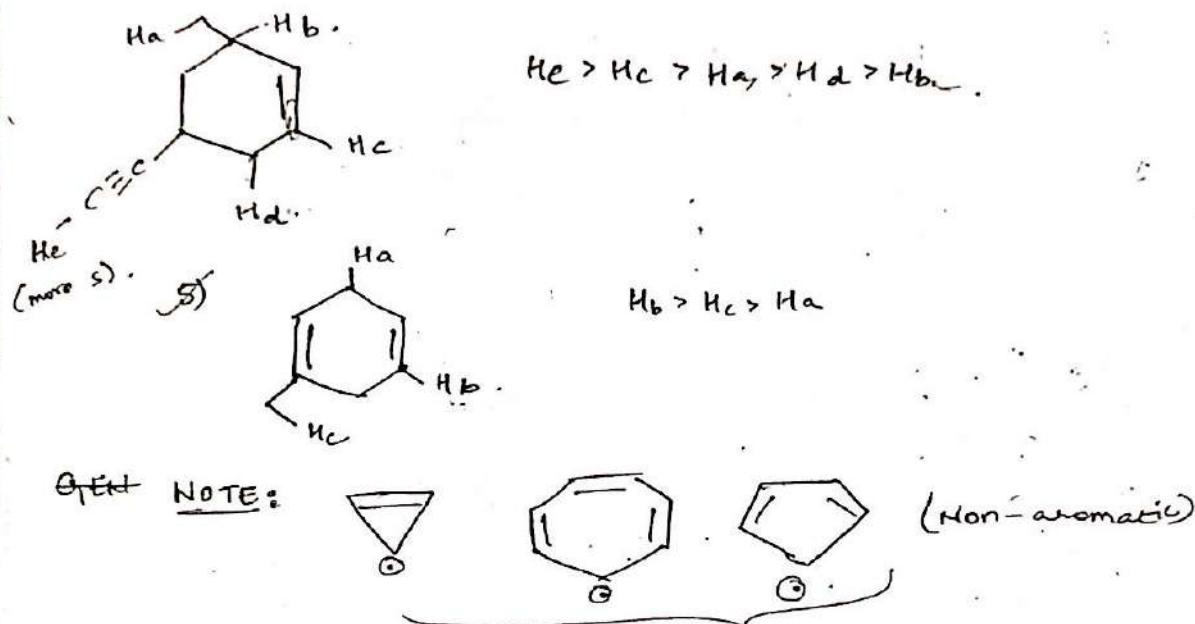
• Dance (Hyperconjugation & Resonance)

Eg.

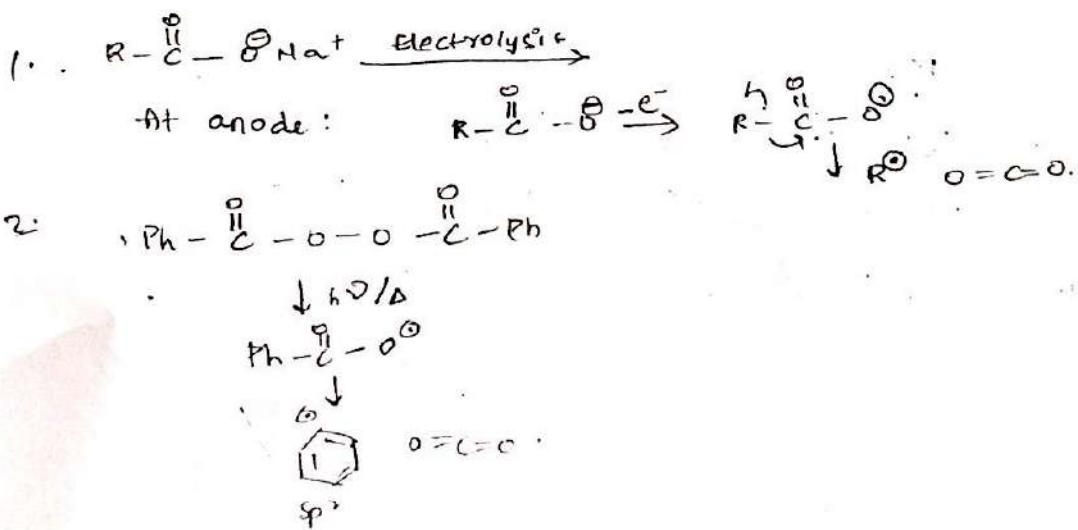




(4) BDE of C-H:



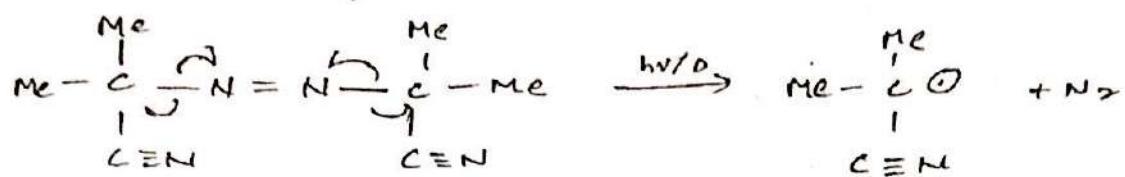
GENERATION:-



3. AIBN

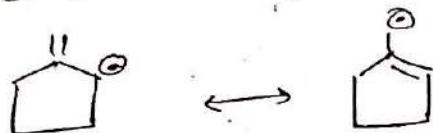
(14)

Azo Iso Butyro Nitrile (First prepared)



Fate:-

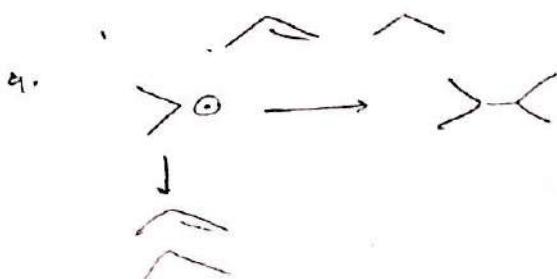
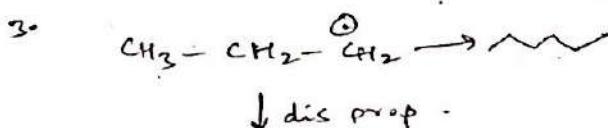
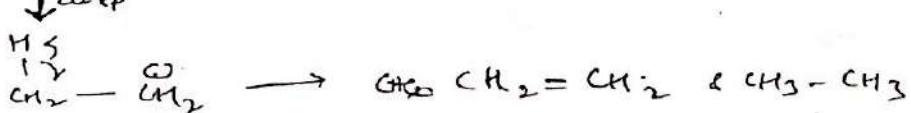
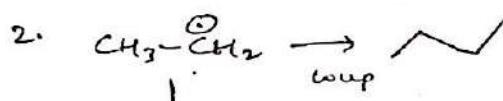
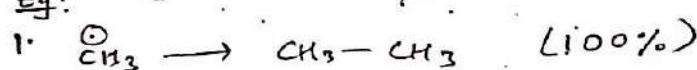
→ Rearrangements are most uncommon. (or) does not takes place except in case of allylic.



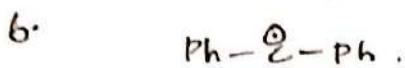
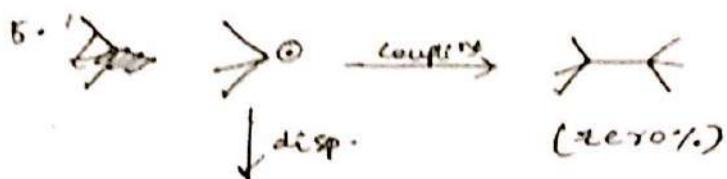
→ carbocation acts as both nucleophile and electrophile.
either (or)
Base

→ Free radical finally involved in may couple (or)
may disproportionate.

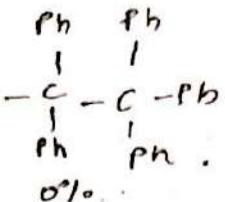
Eg:



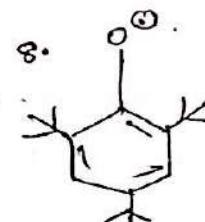
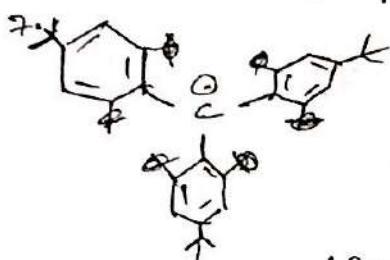
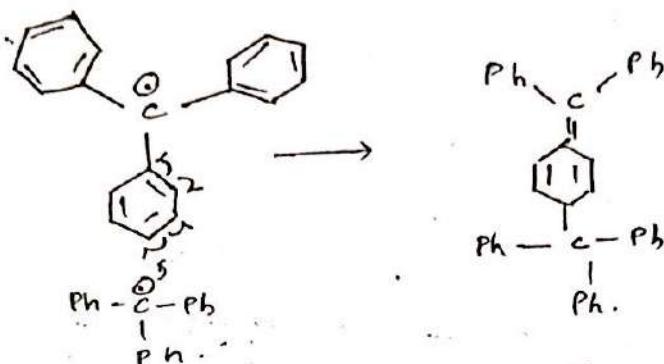
(11)



(propeller)



(undergoes dimerisation)



(Permanently exist as radicals in neutral soln).

iv) CARBENE(S)

→ Di/ Bi valent → $6e^-$ in valence shell.

→ Electrically neutral

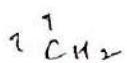
→ Based on 2 free e^- , carbenes are classified into 2 types according to Hund's maximum multiplicity rule:

$$2l+1$$



$$2l=0 \Rightarrow 1$$

singlet

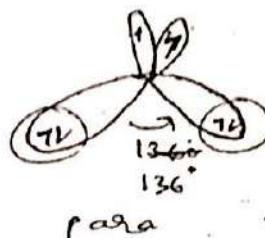
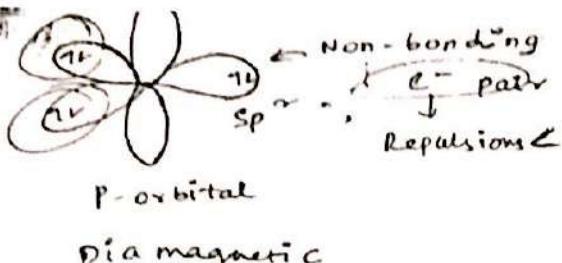


$$2l+1=1 \Rightarrow 3$$

triplet

$$\text{Rb: } \text{sp}^2$$

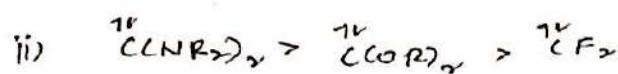
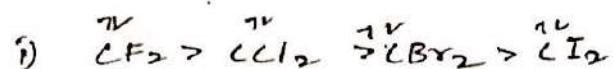
$$\text{sp}^2 > \text{sp}$$



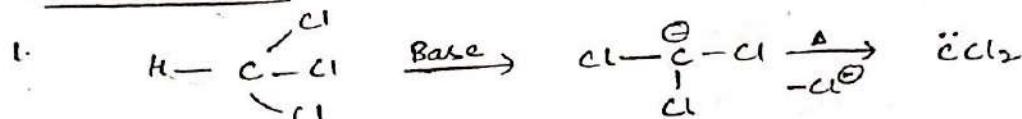
→ Both electrophile & nucleophilic (carbenes) [experimentally proved as Electro phile]

NOTE:

→ Halo carbenes & Carbenes are more stable in singlet state. due to back bonding.



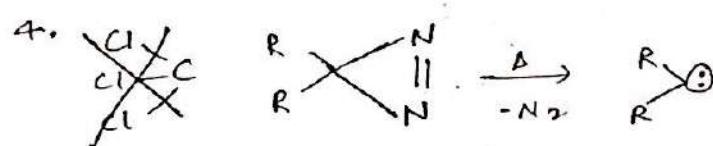
GENERATION:



2. Pyrolysis of Ketene.



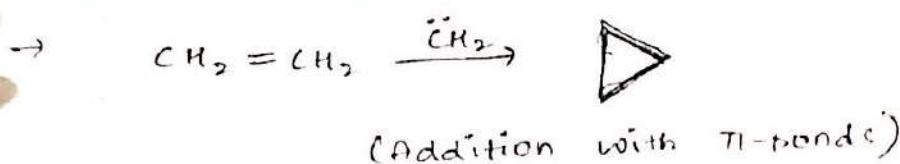
3. Pyrolysis of diazo-methane

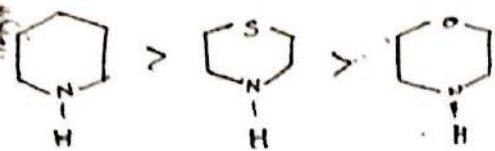


FATE:

→ Involved in Rearrangements

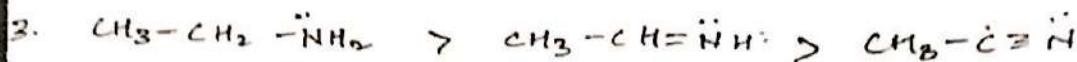
→ Acts as Electrophile





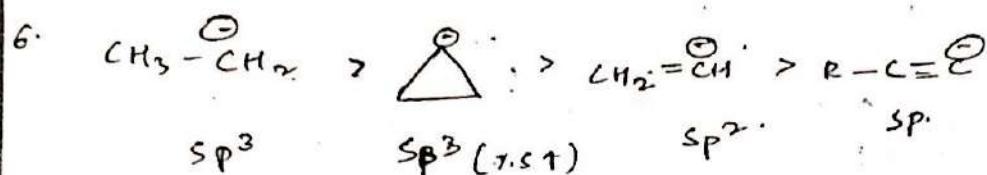
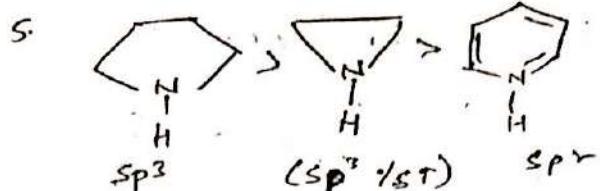
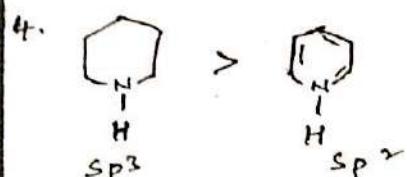
Reason: -I
-I \propto Basicity

(2) 21

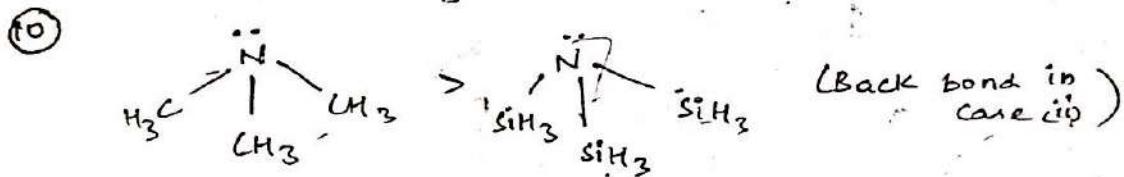
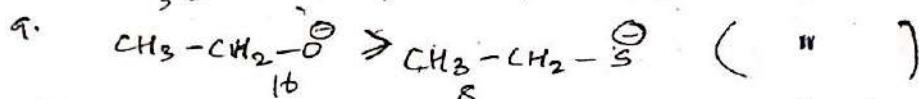
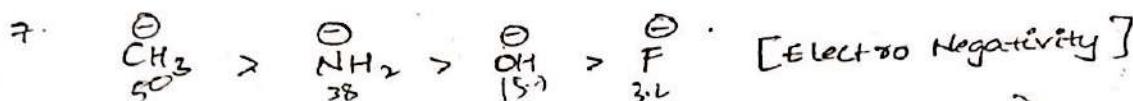


($\% \text{S} \propto \frac{1}{\text{Basicity}}$) only if:

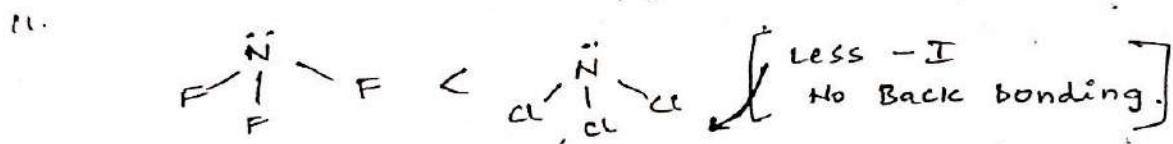
(Lone pairs are localised)



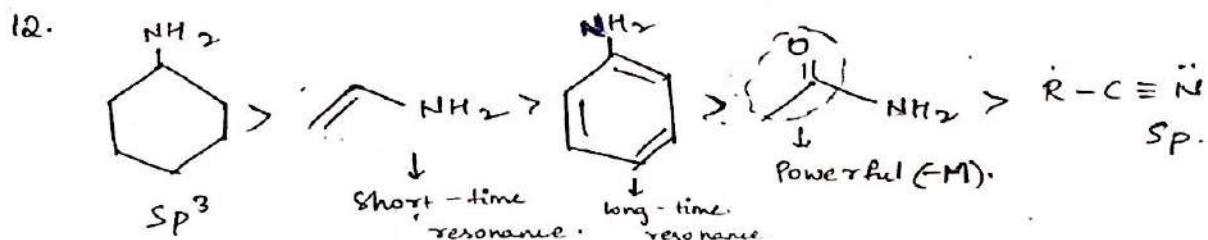
SP^3 SP^3 (7.5+) SP^2 SP



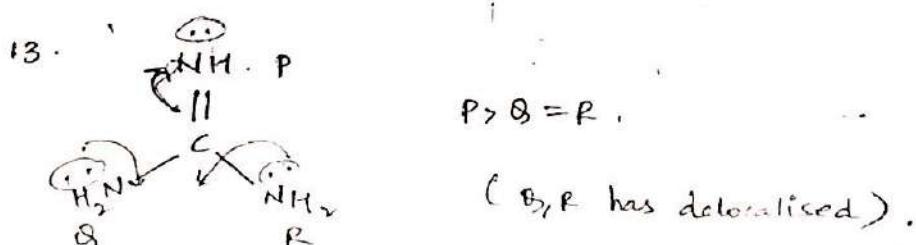
(Back bond in care of)



LESS - I
No Back bonding.



Powerful (-M).



$\text{P} > \text{Q} = \text{R}$.

(S, R has delocalised).

→ Involved in substitution reactions.

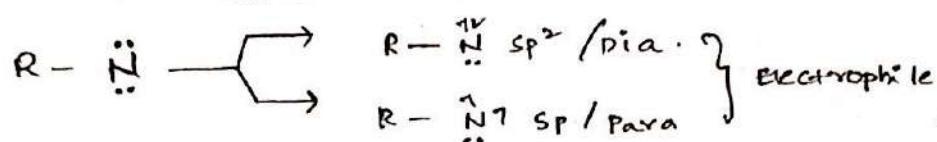


V) NITRENE:-

→ Monovalent.

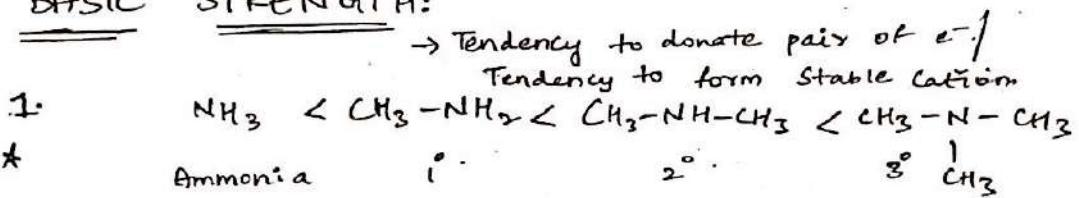
→ Electrically neutral.

→ Possesses 6e⁻ in its valence shell.



→ Undergoes rearrangement.

BASIC STRENGTH:

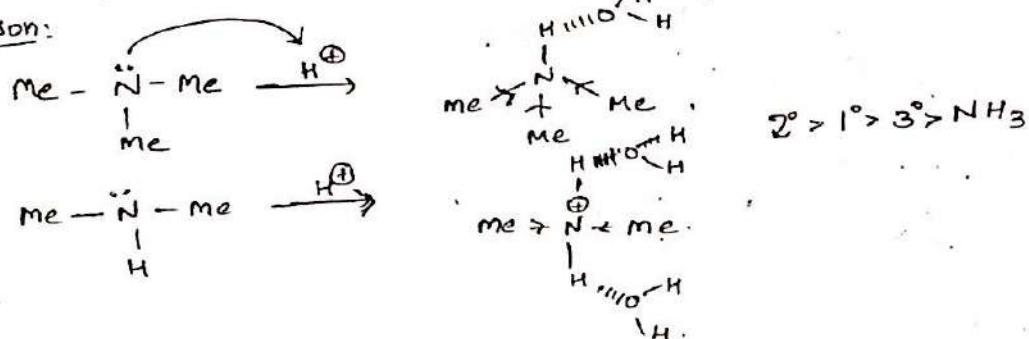


a) 3° > 2° > 1° > Ammonia (Gas phase / Non-polar solvent like CS₂/CCL₄ etc..)

b) 2° > 1° > 3° > NH₃ (Protic solvents
Eg: water, alcohol)

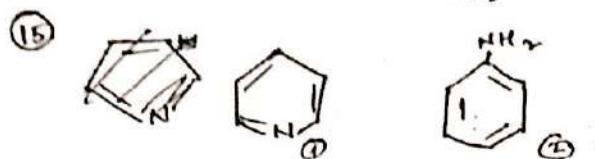
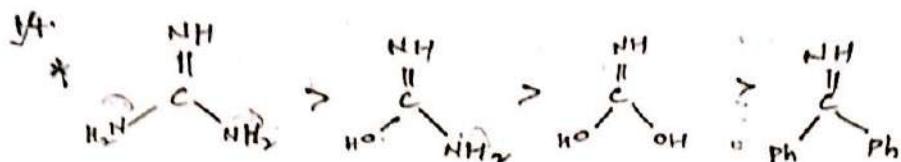
→ If nothing is mentioned answer should always be written in protic solvents.

Reason:



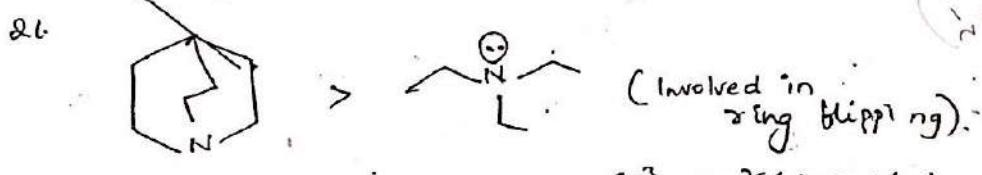
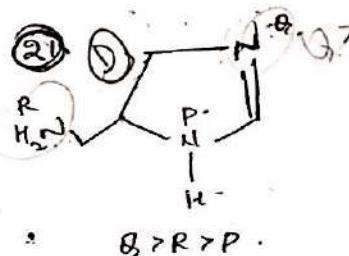
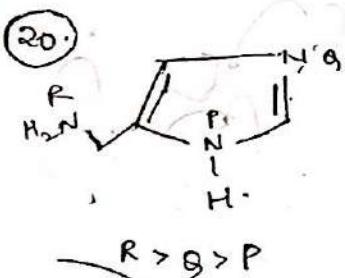
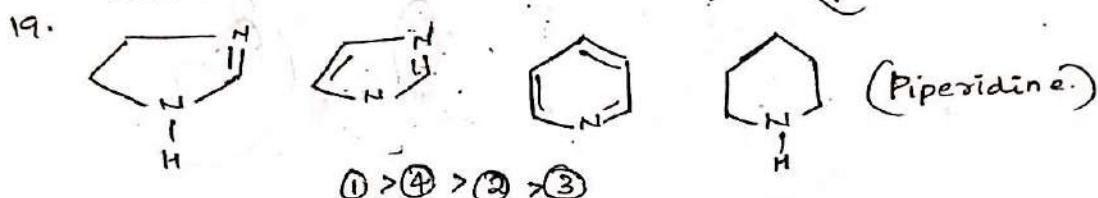
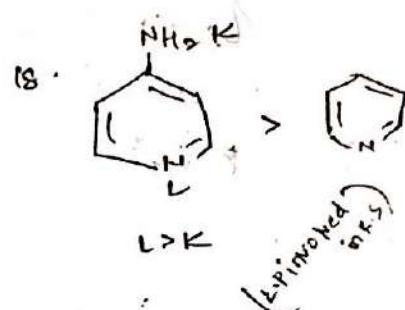
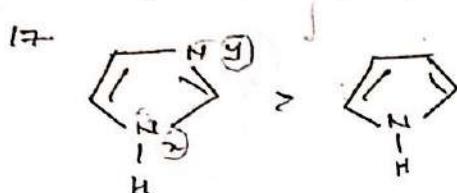
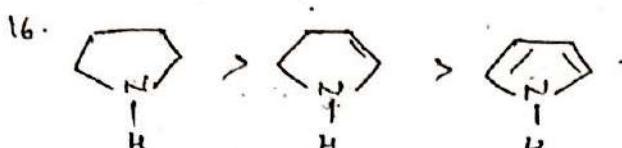
→ If -R is ethyl group

2° > 3° > 1° > NH₃. (Protic Solvent).

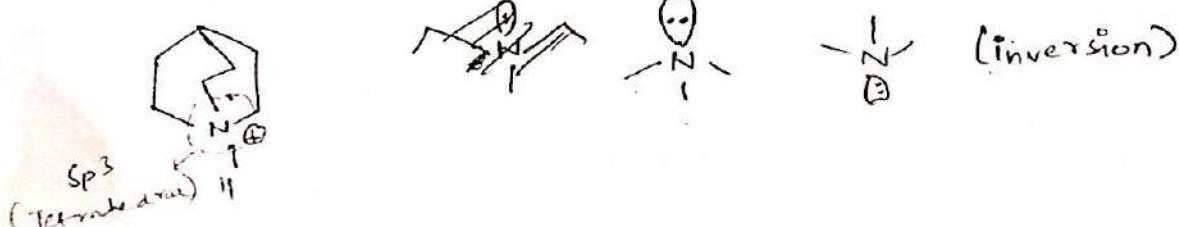


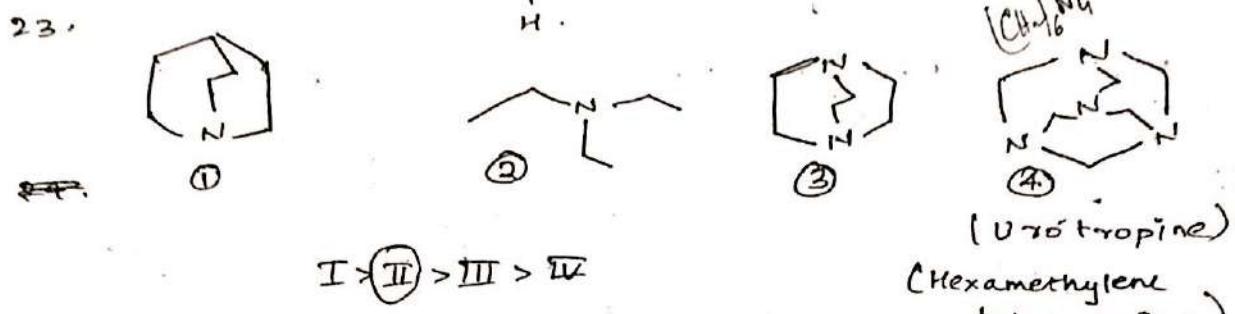
Hypb: $sp^2 > sp^3$ ($sp^2 \rightarrow sp^3$)

16. BASIC CHARACTER: ① > ②

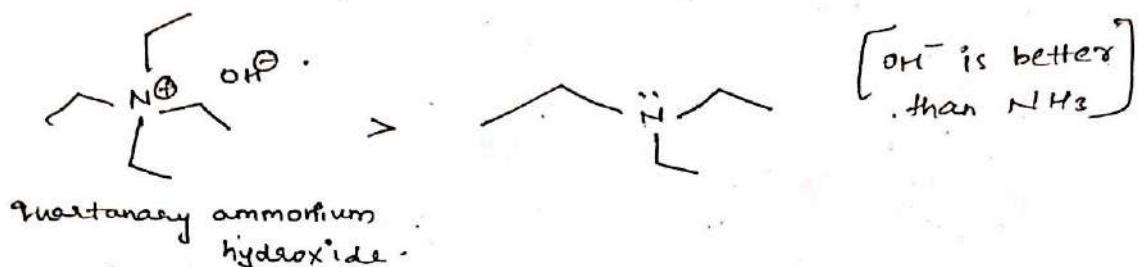


$sp^3 \rightarrow sp^2$ (transition state)

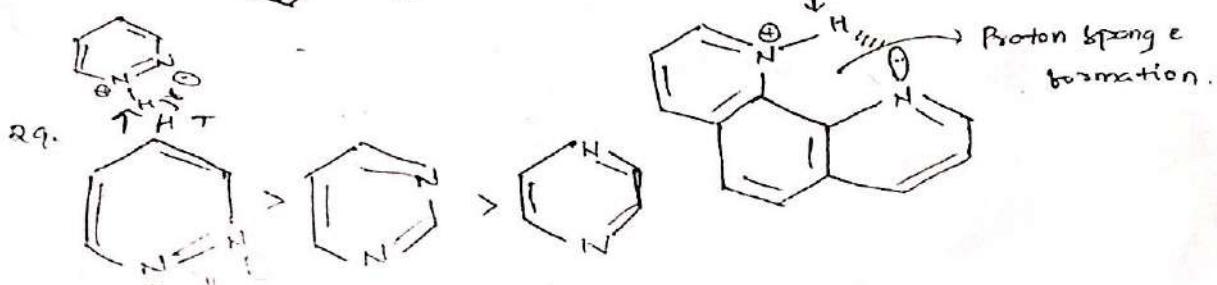
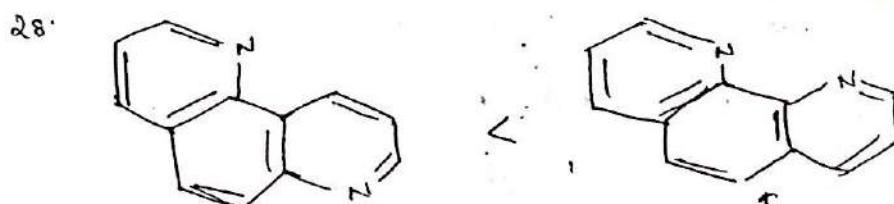
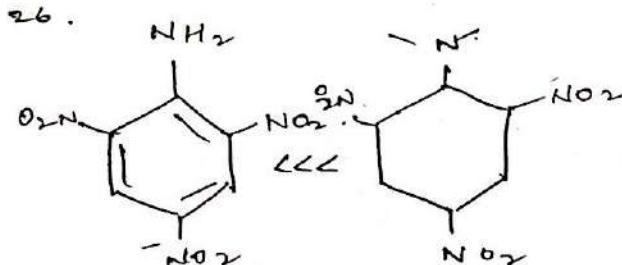
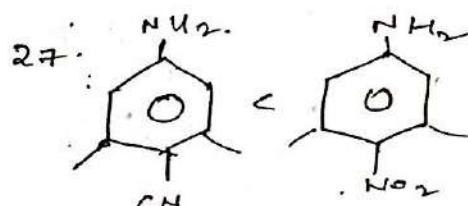
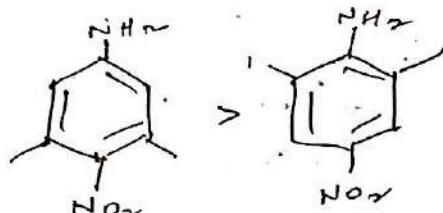




24. Nature of bond:

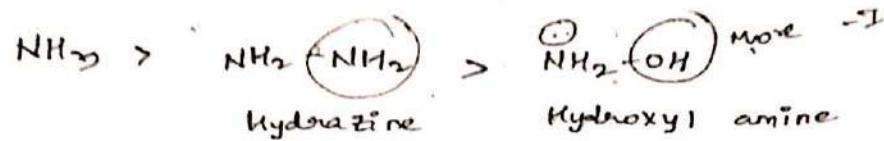


25. Steric Inhibition of Resonance (SIR)



(readily form cations to avoid LP repulsion.)

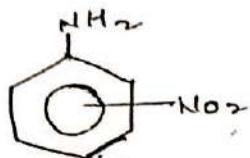
30.



⑤

BASIC STRENGTH OF SUBSTITUTED ANILINES:

1.



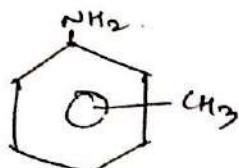
$-m \quad \} \quad m > (O \& P)$

$-I \quad \} \quad O > P$

$\Rightarrow m > P > O$

Unsubstituted aniline $>$ Meta $>$ Para $>$ Ortho

2.



Hyp: $O \& P > m$

+ I: $O > P$

$O > P > m > u$ (unsub- \times) $\leftrightarrow [P > m > u > O]$

3.

NOTE: (only for NH₂ grps)

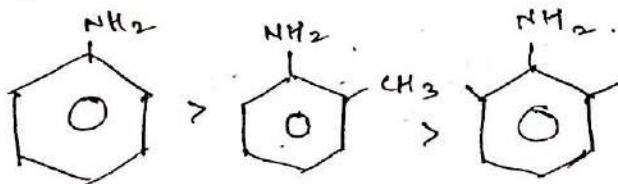
\rightarrow Para effect:-

* If activating group is present at para position, that should be most basic than ortho, meta, unsubstituted.

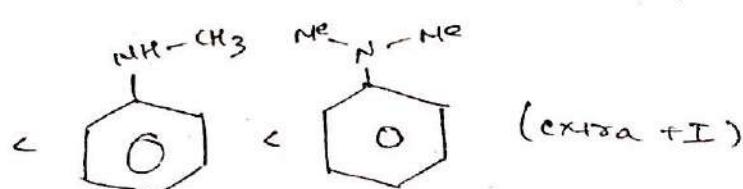
\rightarrow Ortho effect:

* Any hydrophobic (water repelling) group if present at ortho position that should be least basic compared to unsubstituted, para & meta.

⑥)

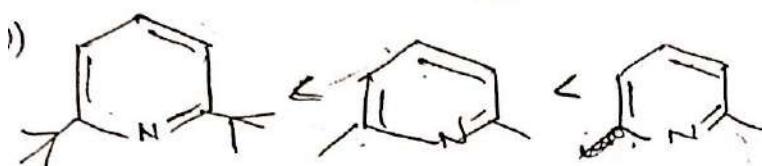
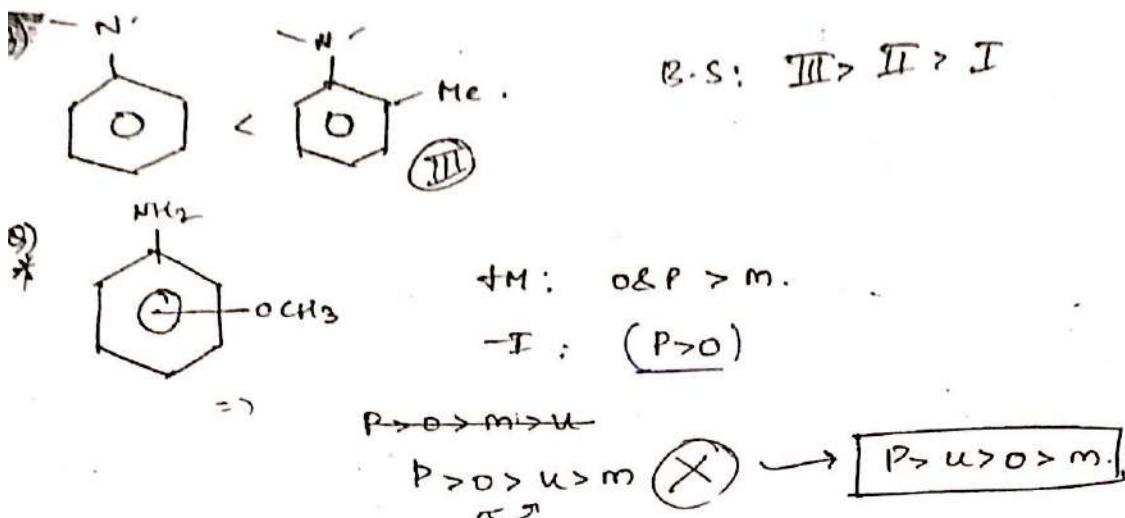


⑦)



⑧)





ELECTRO-PHILE :-

→ Pair of e^- acceptor / accept. 2 e^-

$$\text{Eq: i) } \text{H}^+ \quad \text{Cl}^+ \quad {}^+_1\text{NO}_2 \quad {}^+_1\text{CH}_3 \quad \text{R}-\text{C}\equiv{}^+_1\text{O} \leftrightarrow \text{R}-{}^+_1\text{C}=\text{O}$$

But not H_3O^+ , NH_4^+ (No pseudo charges)

ii) BE_3 , AlCl_3 , SbF_5 , ZnCl_2 etc - iv) carbene.

iii) $O=C=\overset{\circ}{O}$, $\overset{O}{S}=\overset{\circ}{O}$. (π -bond b/w unsym. atoms get polarized and accept e^- pair.)

NUCLEOPHILES:

~~... - to~~ loving group.

→ Nucleus lover is nucleophile (Pair of e⁻ donor)

Eg: i) H^- , OH^- , NH_2^- , CH_3^- etc -

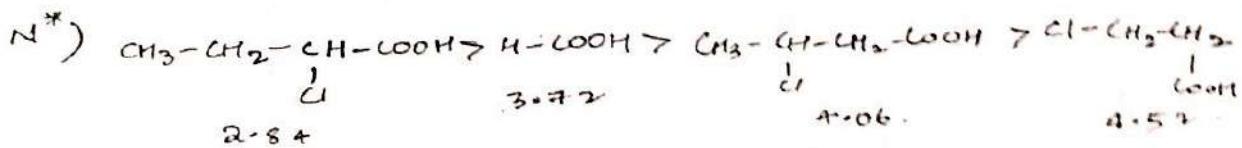
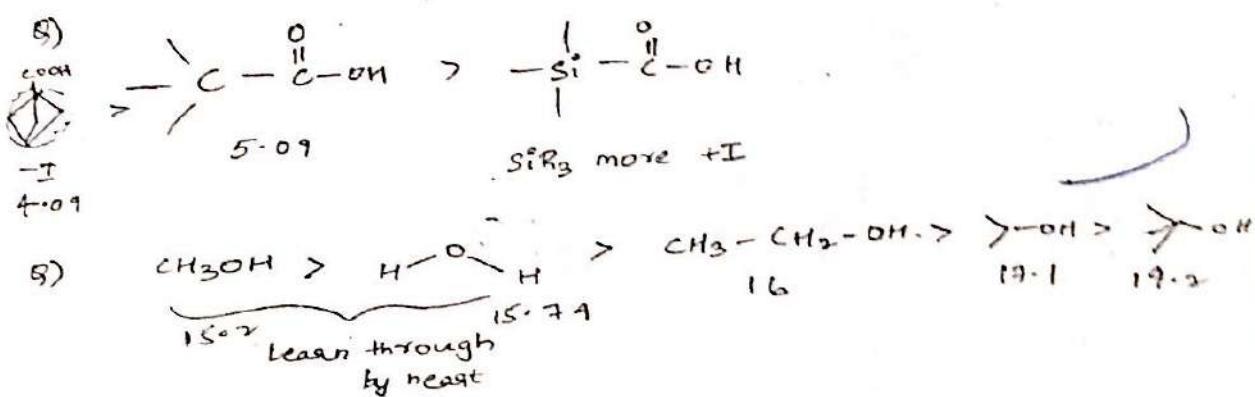
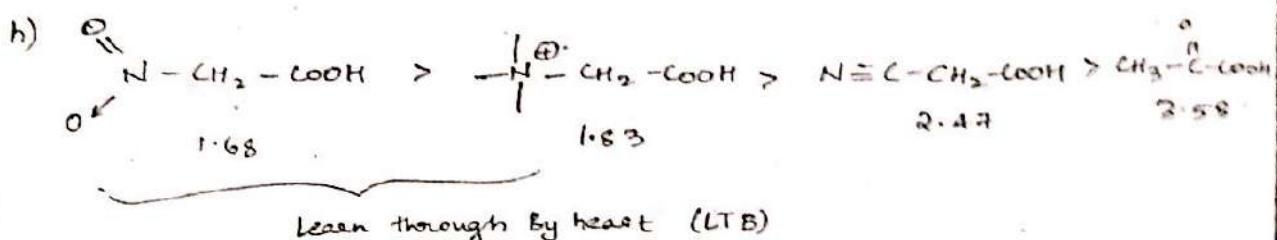
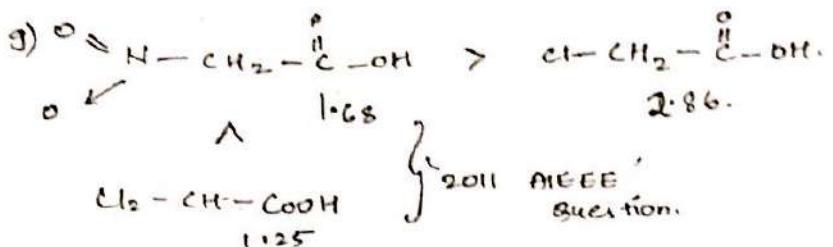
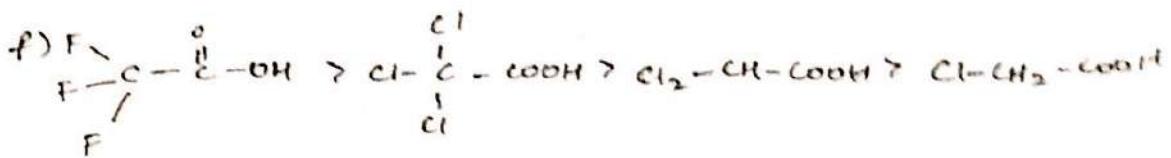
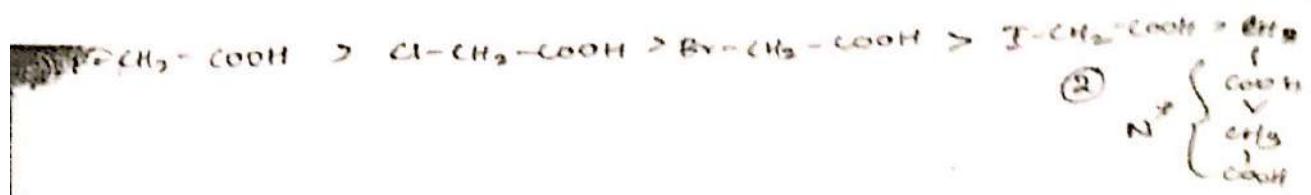
but not BH_4^-

ii) $\text{H}_2\ddot{\text{O}}$, NH_3 , $\text{R}-\ddot{\text{O}}-\text{H}$ etc.

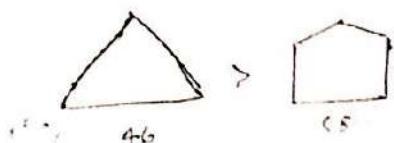
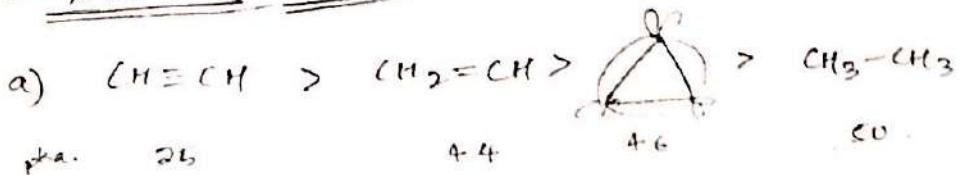
$$iii) \quad CH_2 = CH_2, \quad CR \equiv CR, \quad [O]$$

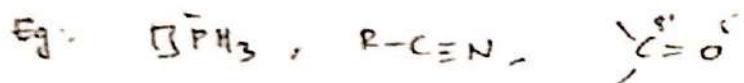
AMBIPHILES :-

→ Act as both electrophile & nucleophile.



④ % of S. Character :-





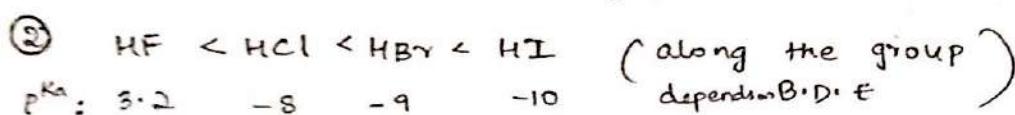
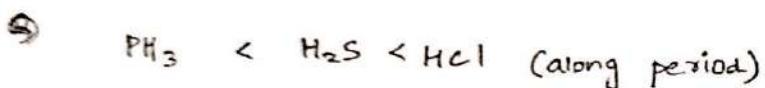
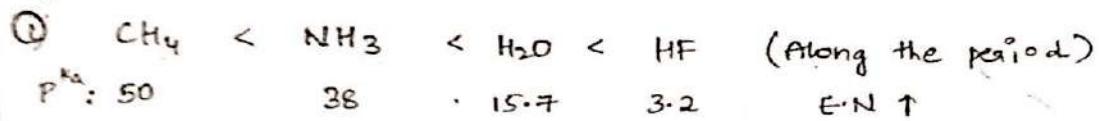
①

ACIDIC STRENGTH:

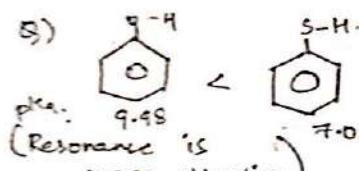
→ Acidic strength depends on stability of anion.

→ More the K_a , more is the acidic strength.

Eg:

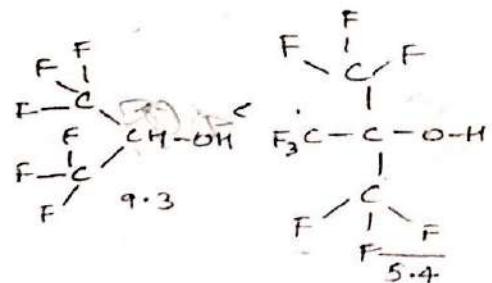
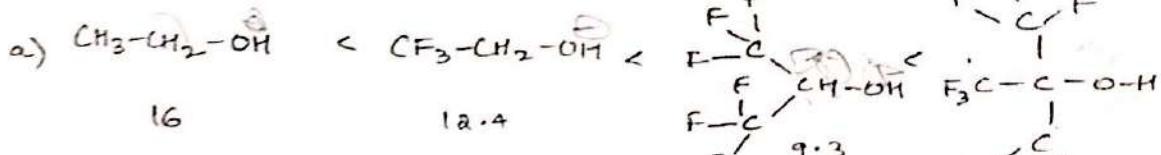


$pK_a: 16 \quad \sim 8$

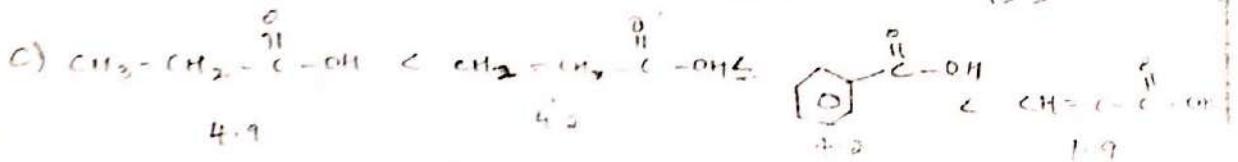
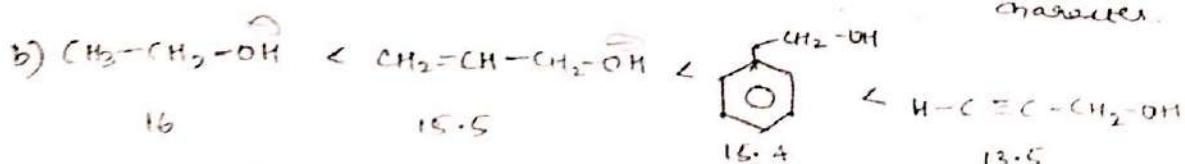


even though BDE plays imp. role
 if belongs to same grp.

⑥ Inductive effect:-

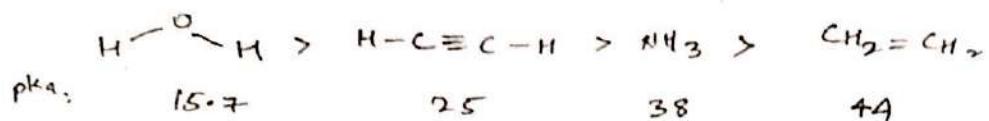


→ +I groups decreases and -I groups increases acidic character.

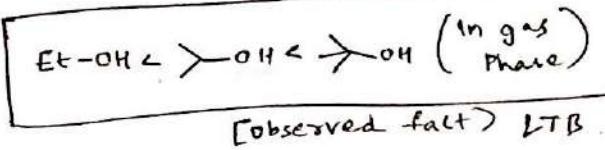
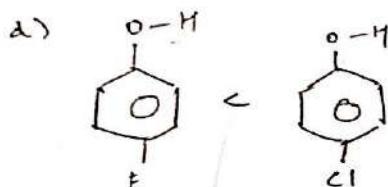
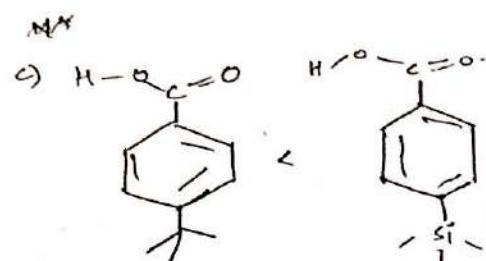
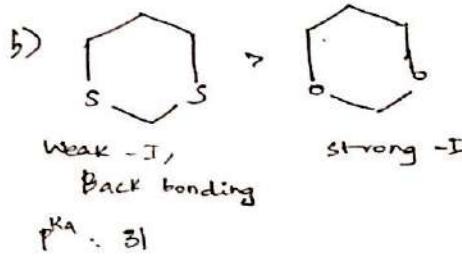
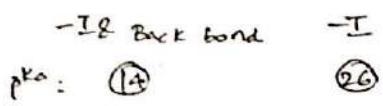


JEE-MAIN:

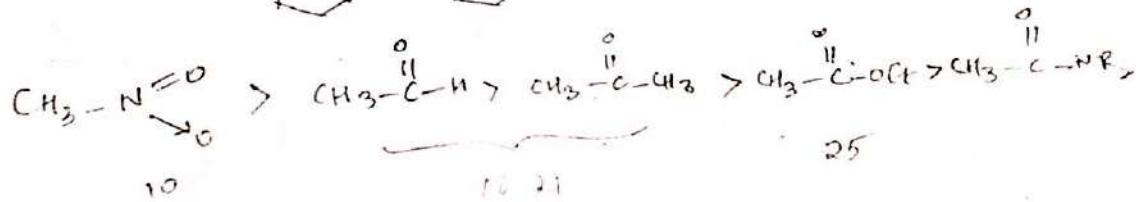
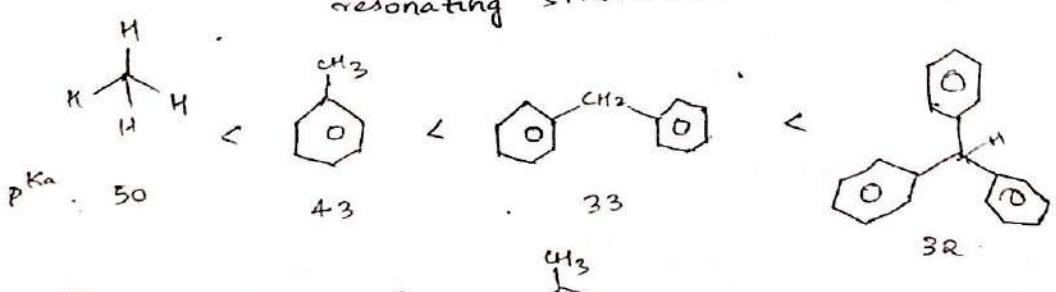
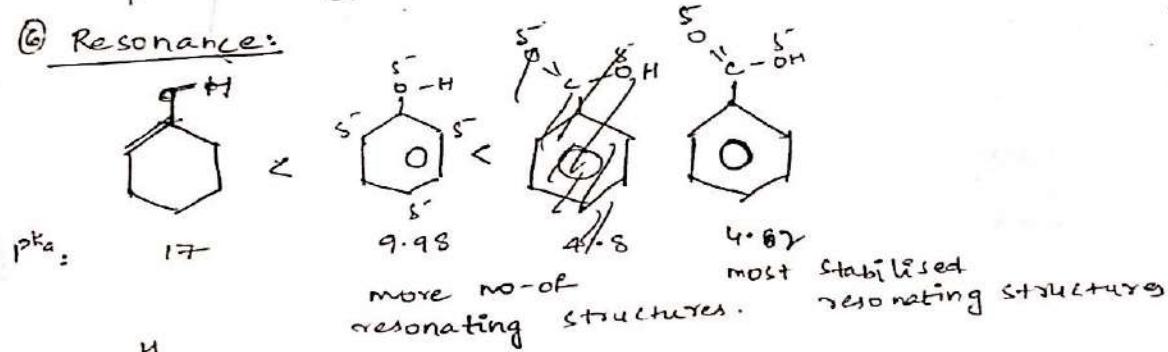
(B)

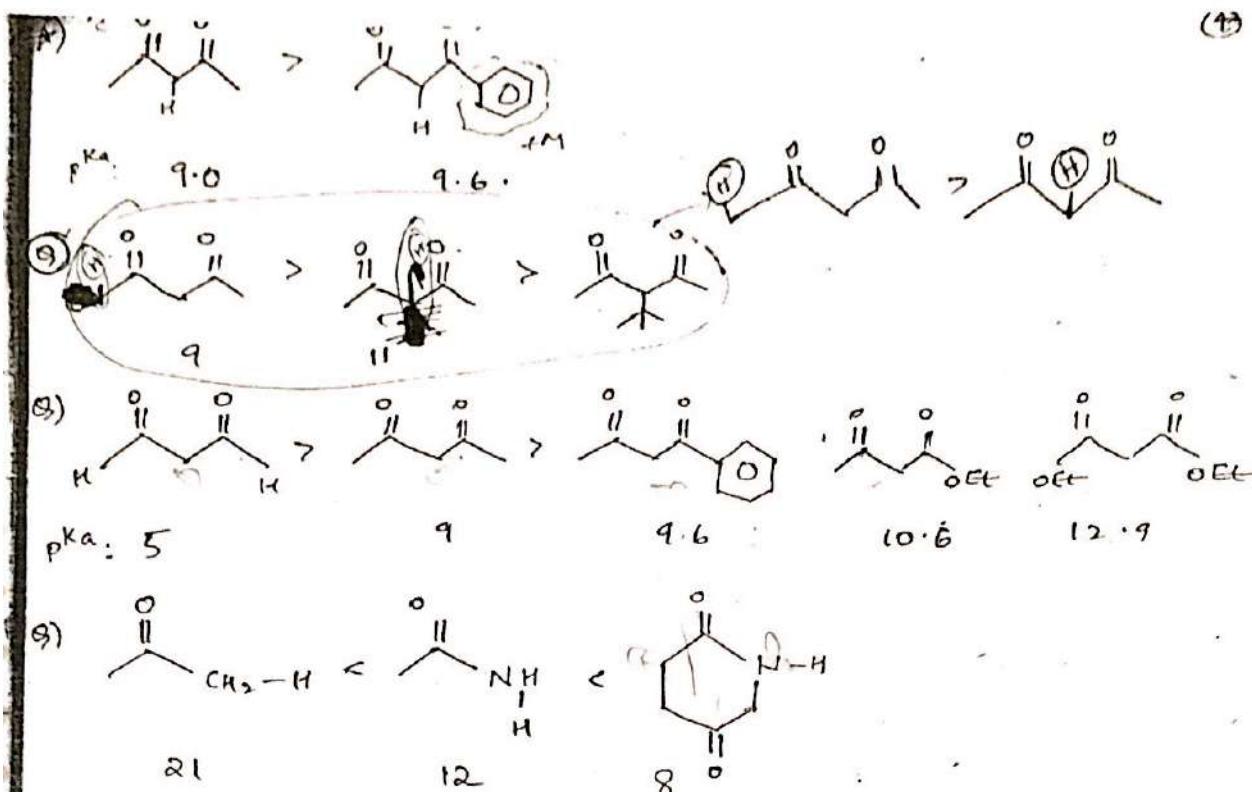


⑤ Role of d-orbitals:-

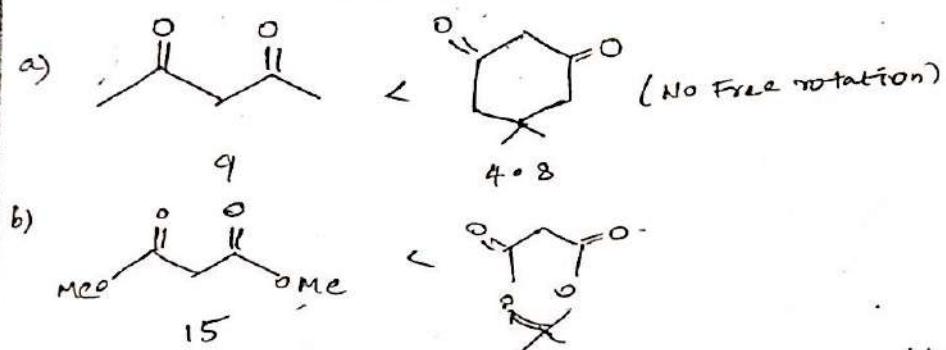


⑥ Resonance:-

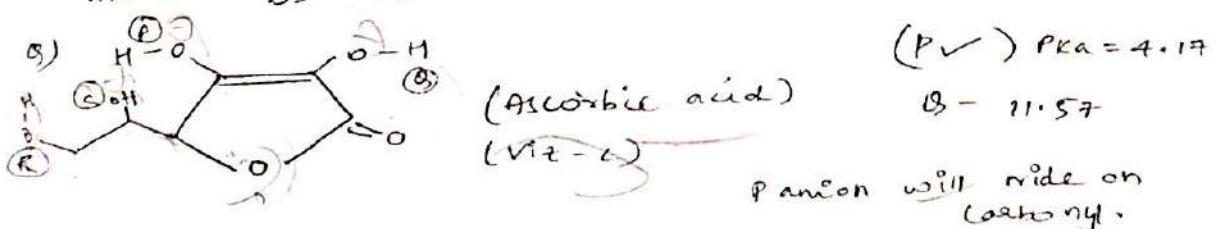




④ CYCLIC vs ACYCLIC:- (For same functional group).



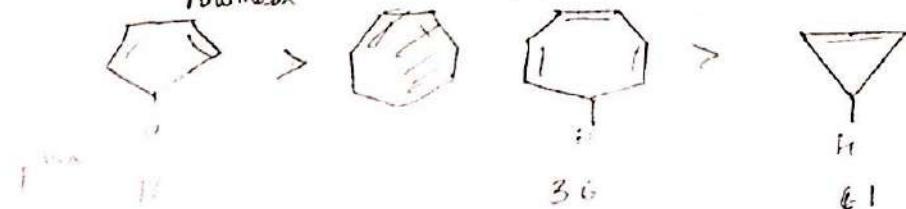
→ After formation of anion, that will ride on oxygen by which the free rotation of C-C decreases, more as is lost.



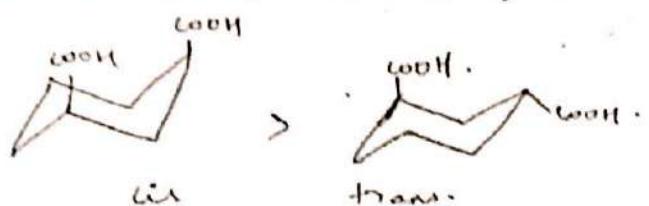
3. AROMATICITY:

Aromatic

Non-Aromatic

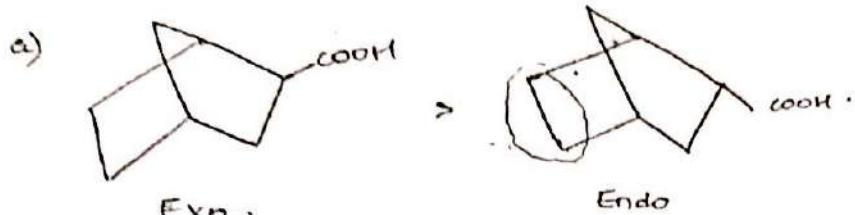


cis-1,2-hexane 1,3-dicarboxylic acid

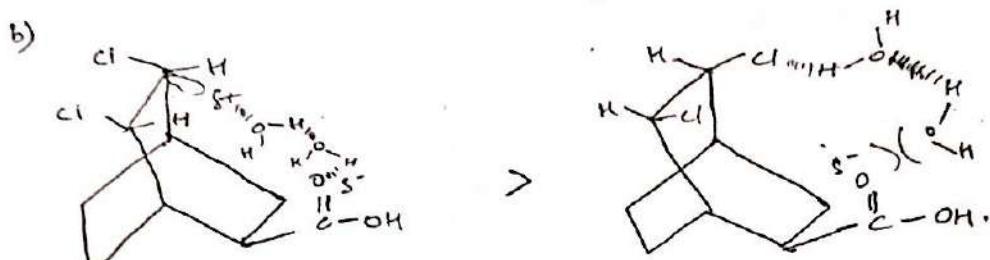


(Due to H-bonding after forming anion)

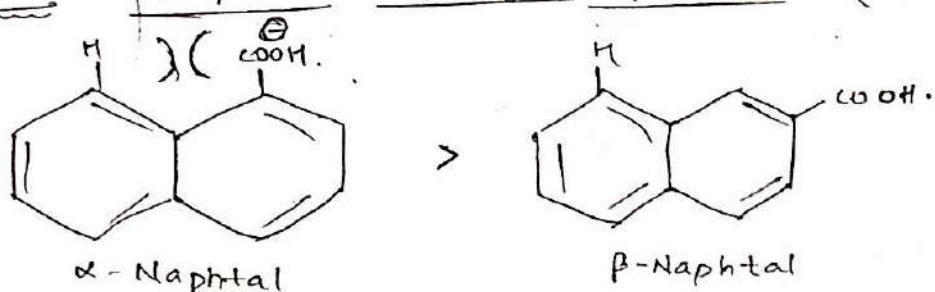
10) SOLVATION:-



→ More solvated due to less repulsion because COO^- is close to shorter bridge.

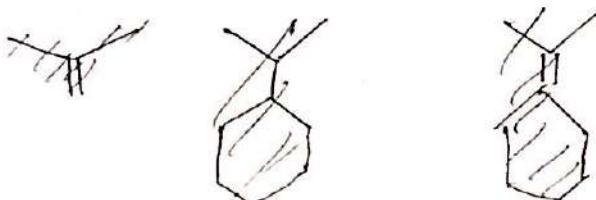


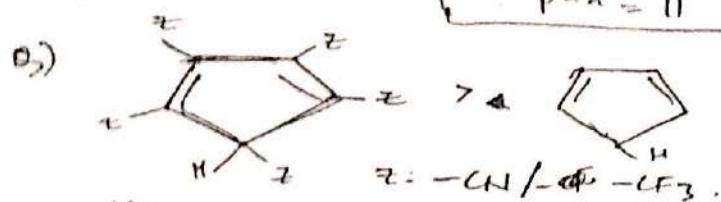
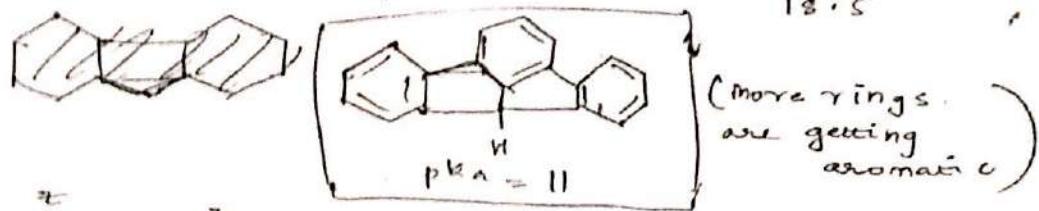
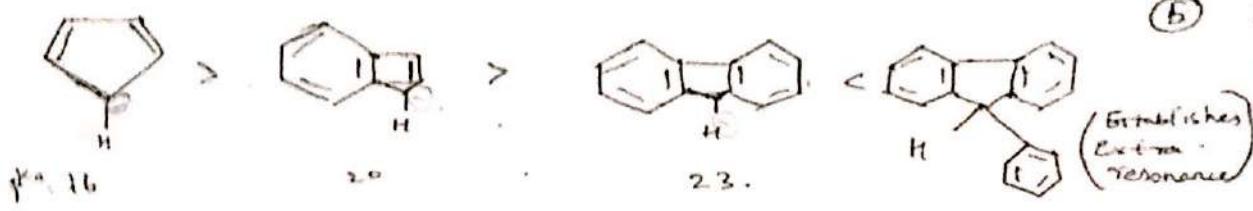
NOTE: Peripheral Hydrogen repulsions: (N^*)



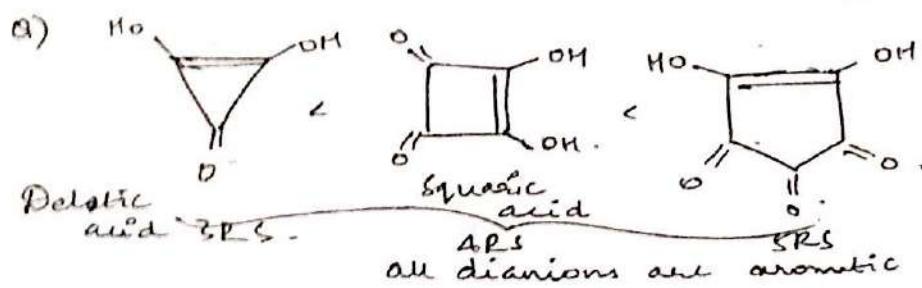
→ Easily become ion due to repulsions.

8)





pK_a : 16 \rightarrow 2 (HNO_3) 16 \rightarrow 22 (HNO_3) .

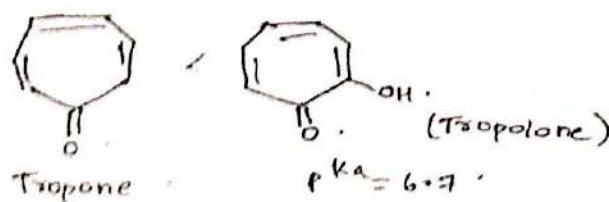


pK_{a1} : 2.57
 pK_{a2} : 6.03

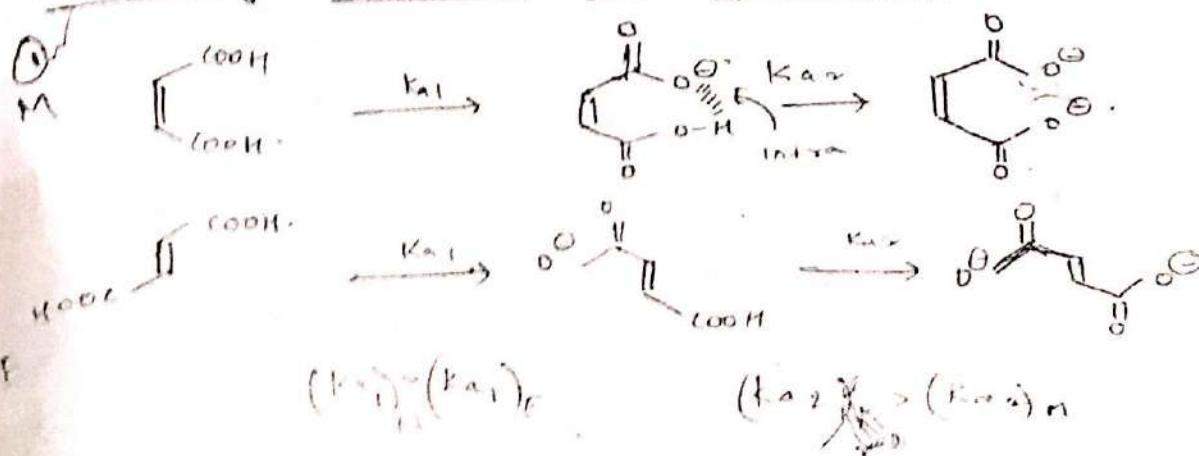
pK_{a1} : 1.7
 pK_{a2} : 3.5

pK_{a1} : 1.0
 pK_{a2} : 2.0

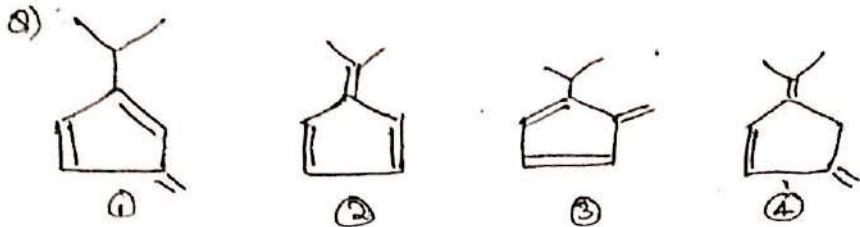
NOTE:-



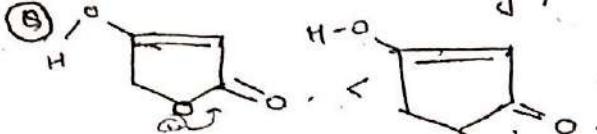
9) H-bonding influence on acidic strength.



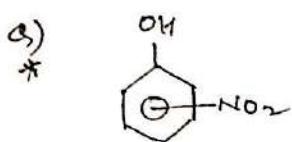
- If involved in H-bonding, difficult to ionise



$② > ④ > ③ > ①$
 attains aromaticity
 after losing proton.



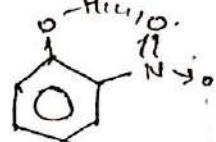
ACIDIC CHARACTER OF SUBSTITUTED PHENOLS:



-M: O < P > M

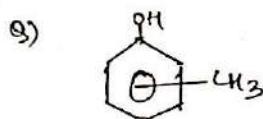
-I: O > P

Then



$P > O > M > u$

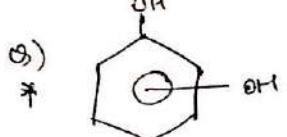
Ortho: due to intra molecular H-bonding, losing proton is harder.



→ Due to hyper conjugation: O, P < M.

+I. O < P.

$U > M > P > O$



+M: M > P > O.

-I: O > P.

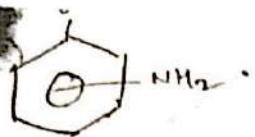
a) acidic character:
 $M > U > O > P$. X

$M > O > U > P$

due to establishes strong H-bond after ionisation.

b) Boiling point:

$P > M > O > U$
 inter intra Ienn wt

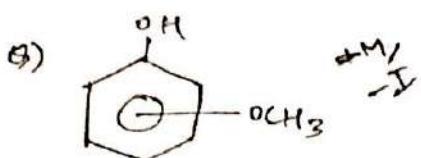


$M > U > O > P \times$

$\Leftrightarrow [O > M > U > P] \checkmark$

due to H-bonding after ionisation.

(B)

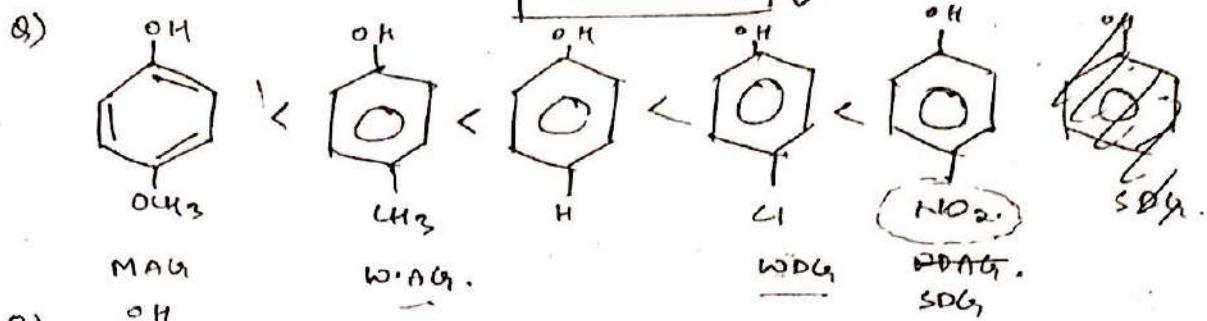


$\xrightarrow{+H_3O^+}$

$M > U > O > P. \times$

(or)

$[M > U = O > P] \checkmark$



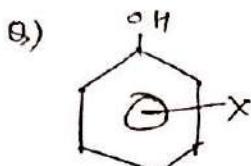
MAG

WAG.

WDG

WDG.

SDG.



$-U, -Br, -I \}$

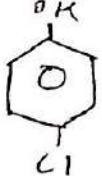
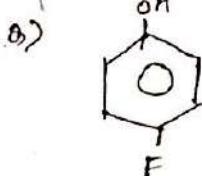
$\xrightarrow{+H_3O^+}$

$O > m > p > u (-I).$

(A)

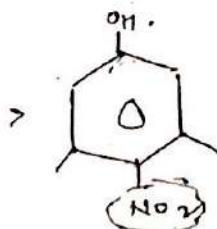
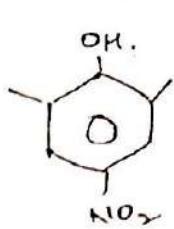
$-F \}$

$O > m > p = u$



Least acidic: $\text{IF } (1)$

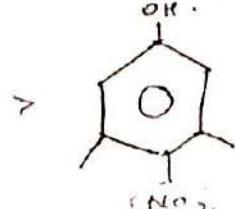
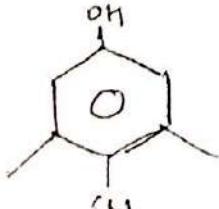
(Q)



(SIR)

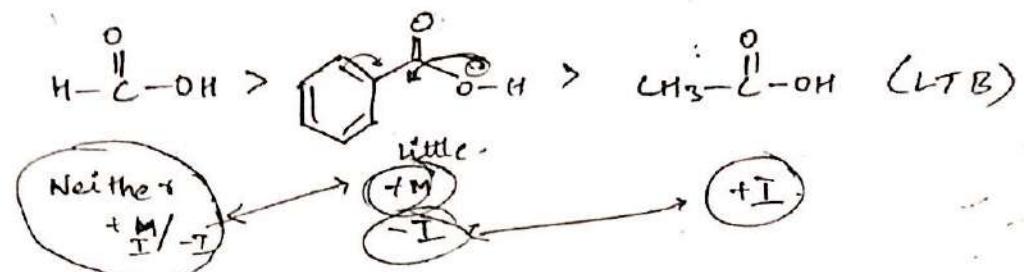
deviates from the plane \Rightarrow -M effect
not operated.

(B)

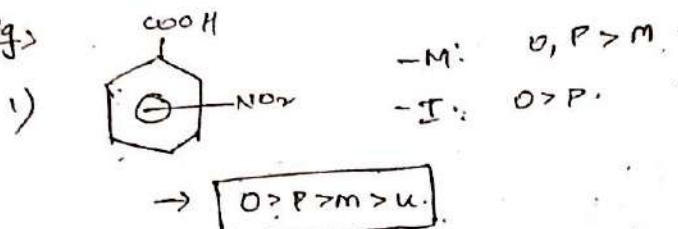


ACIDIC CHARACTER FOR SUBSTITUTED BENZOIC ACID:- ⑨

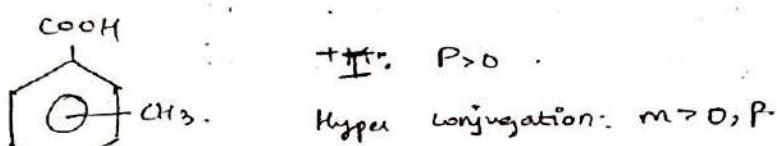
Q)



Eg,



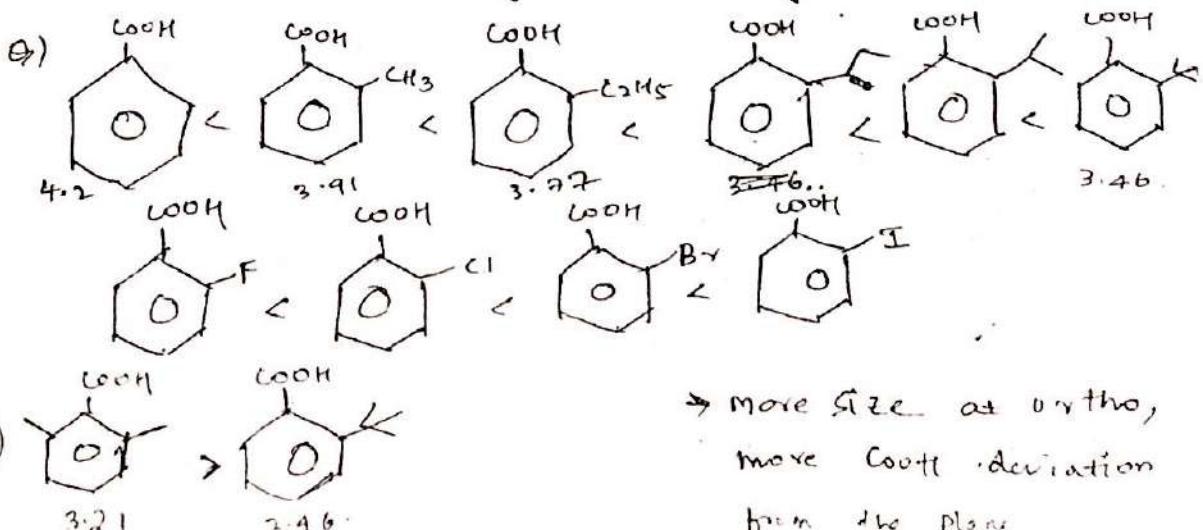
2)



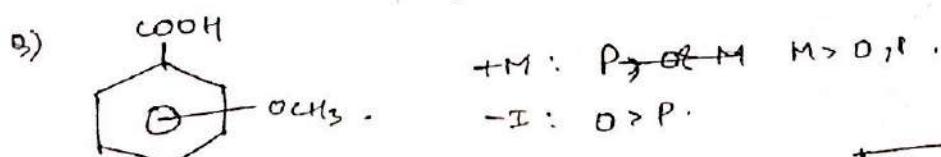
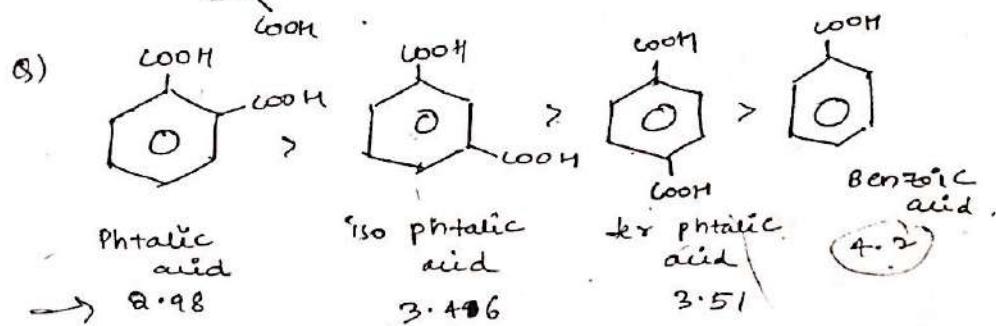
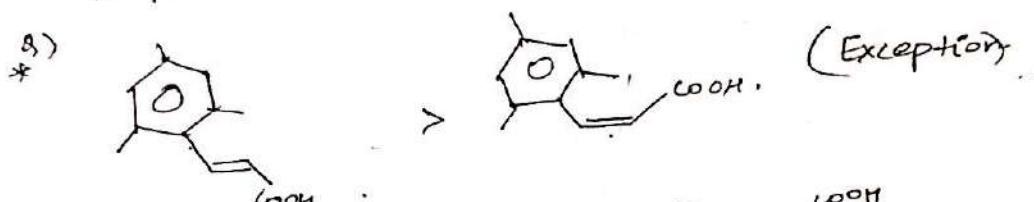
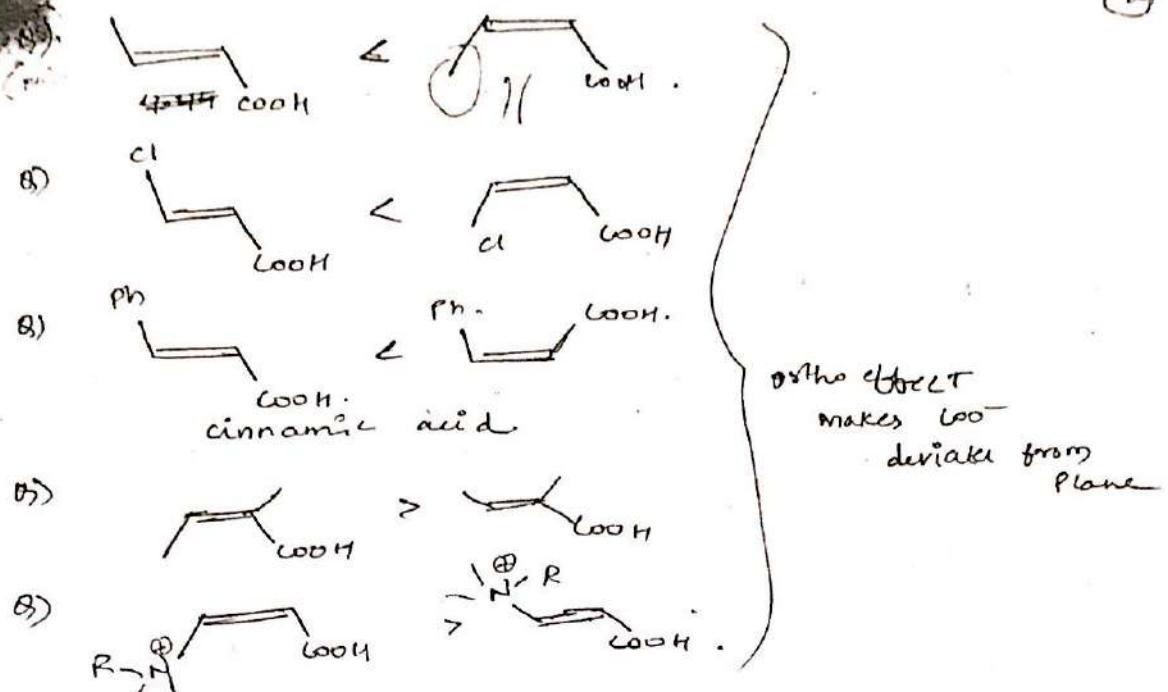
$$[\text{u} > \text{m} > \text{p} > \text{o}] \times \Rightarrow [\text{O} > \text{u} > \text{m} > \text{P}]$$

* Ortho effect: H except NH_2

→ any substituent at ortho position makes phenyl ring and COO^- non-planar. by which its $+M/-M$ of phenyl ring will not be operated (or) less operate on COO^- by which COO^- effectively establishing resonance.

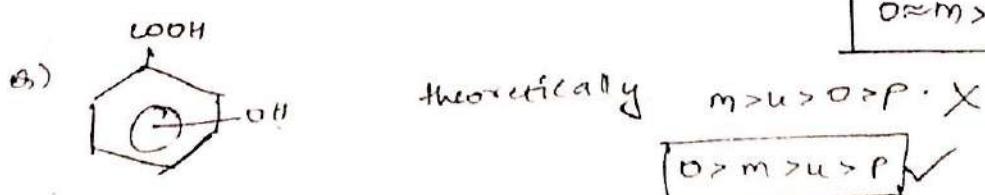


(17)



$$\Rightarrow M > O > P \quad \boxed{O > M > O > P} \quad \checkmark$$

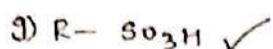
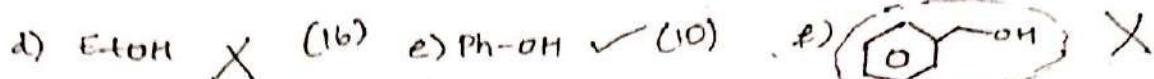
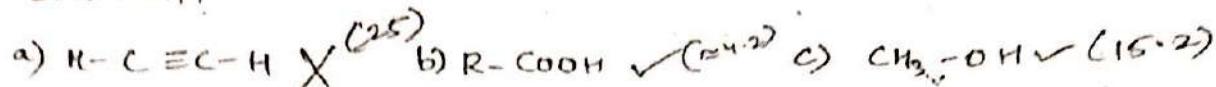
(or)
 $O > M > O > P$



$$\boxed{O > M > O > P} \quad \checkmark$$

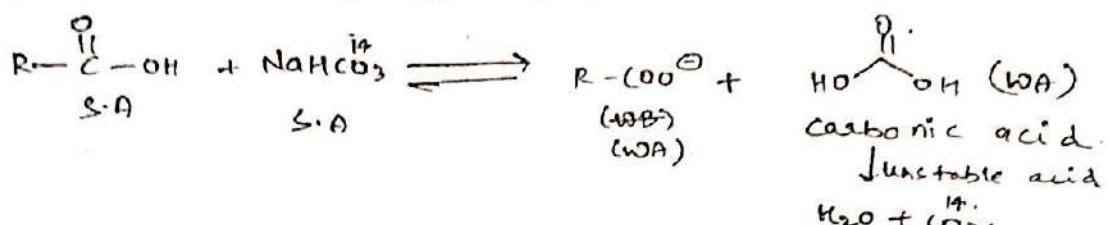
NOTE: Ortho is more acidic mainly due to π -bonding.

Q) How many of the following are soluble in NaOH solution? (12)

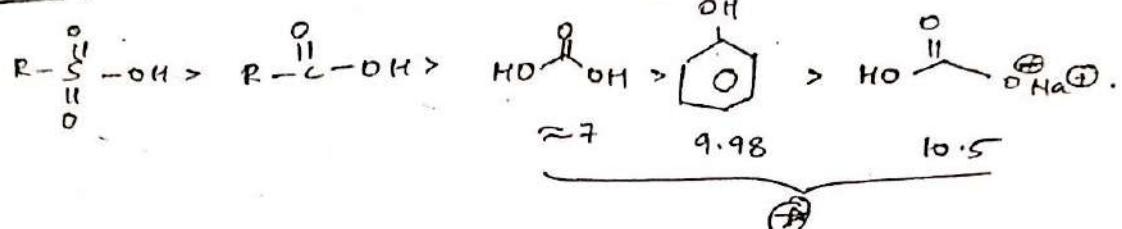


Its acidic character is little more than water but hydrophobic nature is more.

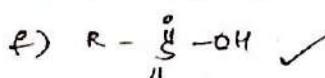
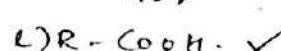
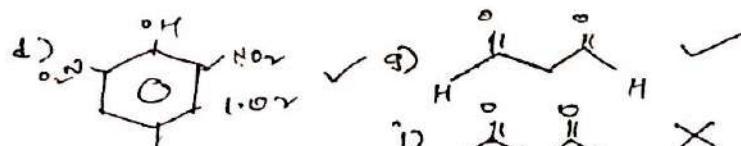
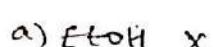
Q) K_{eq} const. for the below given is:



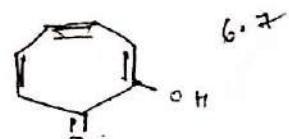
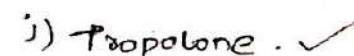
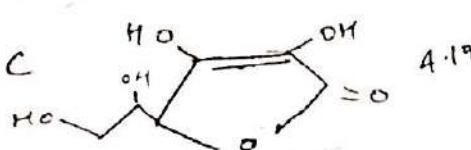
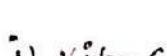
NOTE:



Q) How many of the following compounds gives effervescence with NaHCO_3 soln.

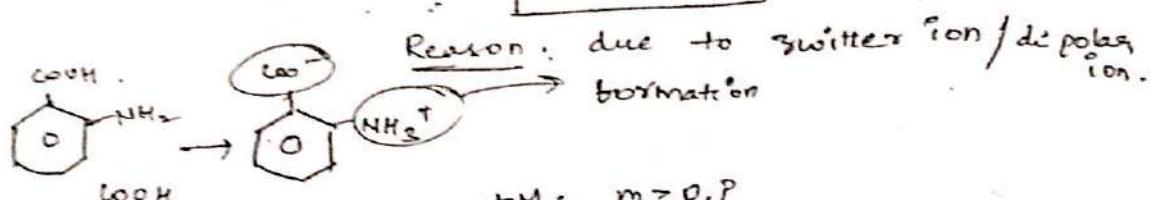
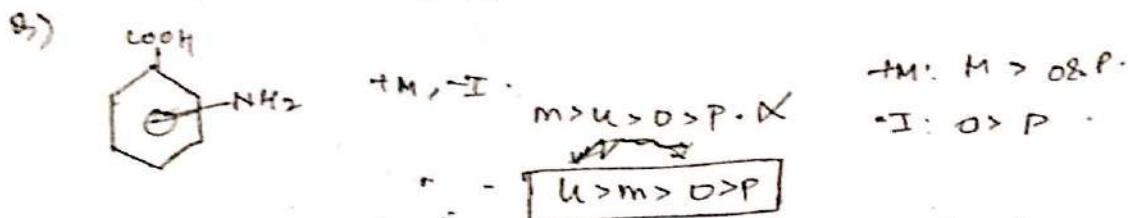
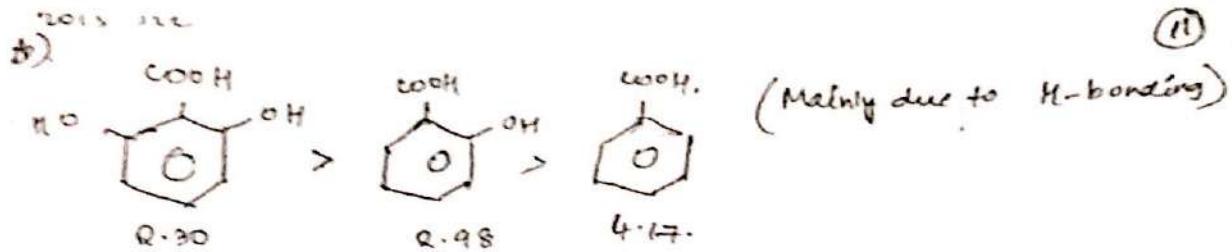


✓

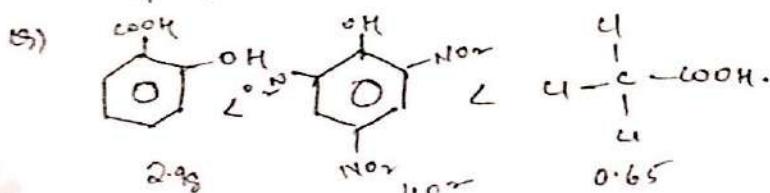
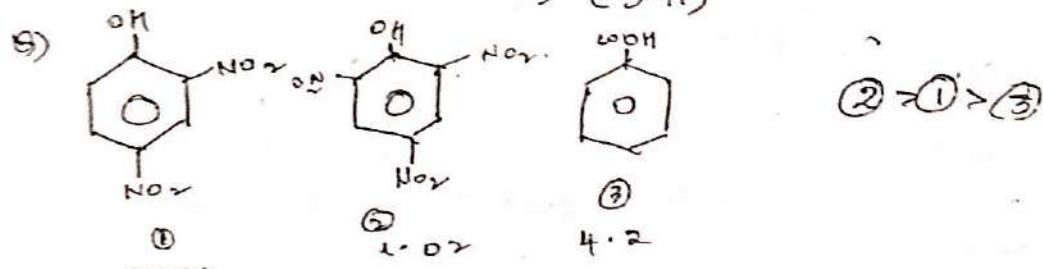
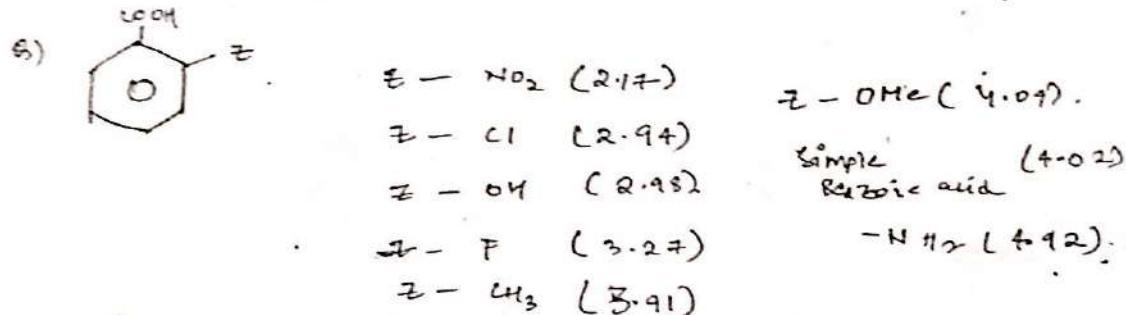


Q) How many of the following compounds give precipitate S_{m-II} with NaNH_2 .

(H_2N_2)

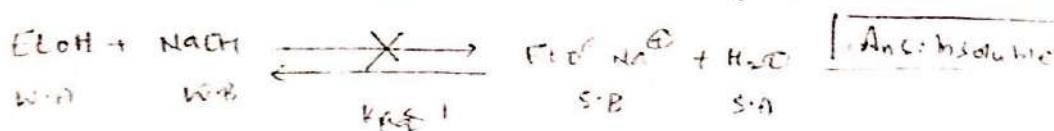


X = -F, -Cl, -OH, -NH₂, -CH₃, -OMe : O > M > P > u

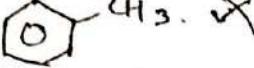


BROWNSTED-LOWRY ACID BASE THEORY.

Is ethanol soluble / insoluble in NaOH soln?



(13)

- a) $\text{CH}_3 - \text{CH}_3$ (so) X e) $\text{Ph} - \text{CH} - \text{Ph}$ ✓
b) $\text{CH}_2 = \text{CH}_2$ X (uu) f) $\text{H} - \text{C} \equiv \text{C} - \text{H}$ ✓ (25)
c)  X g) EtOH ✓ (16)
d) $\text{Ph} - \text{CH}_2 \text{OH}$ ✓

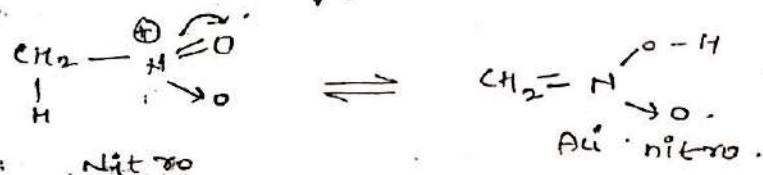
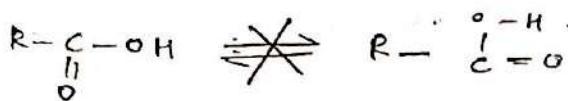
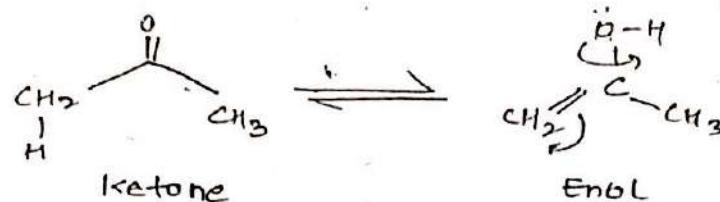
89

TAUTOMERISM:-

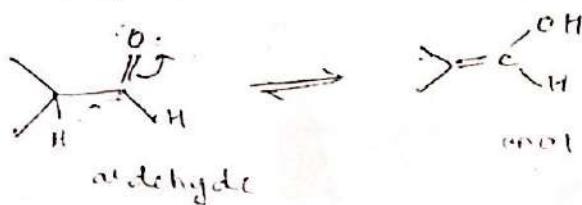
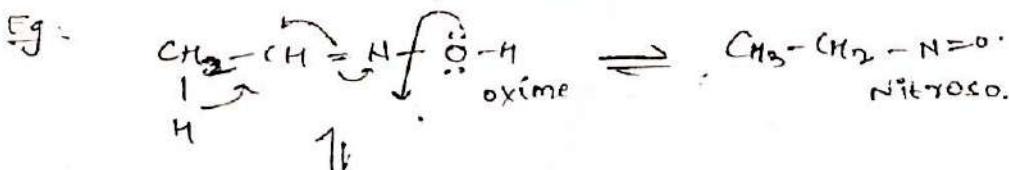
(1)

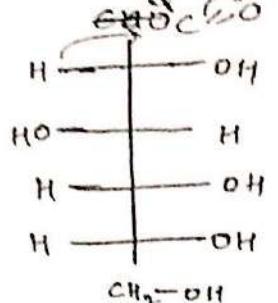
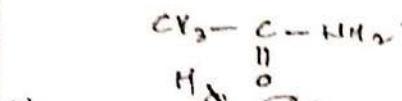
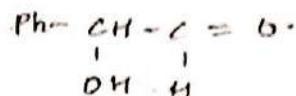
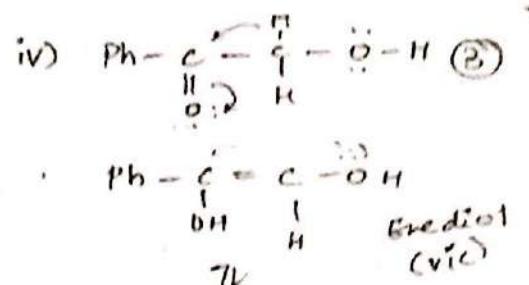
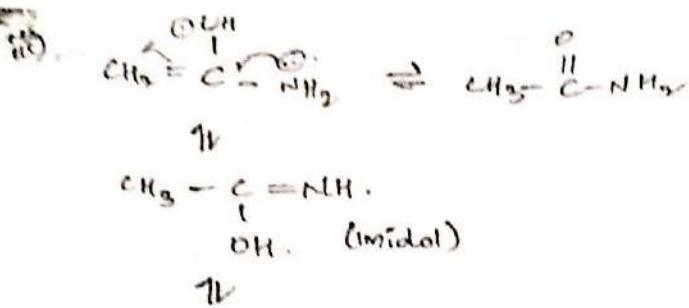
→ 2 (or) more different functional groups of the same molecular formula rapidly interconvert and existed in dynamic equilibrium at room temperature.

Eg:

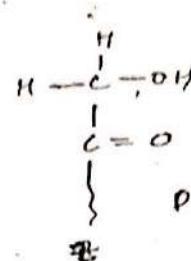
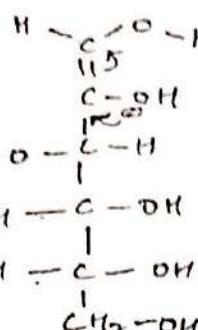


→ All tautomers are functional isomers.

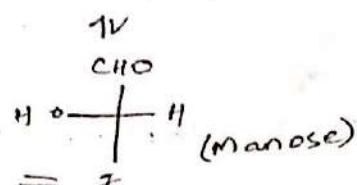




D(+) - Glucose

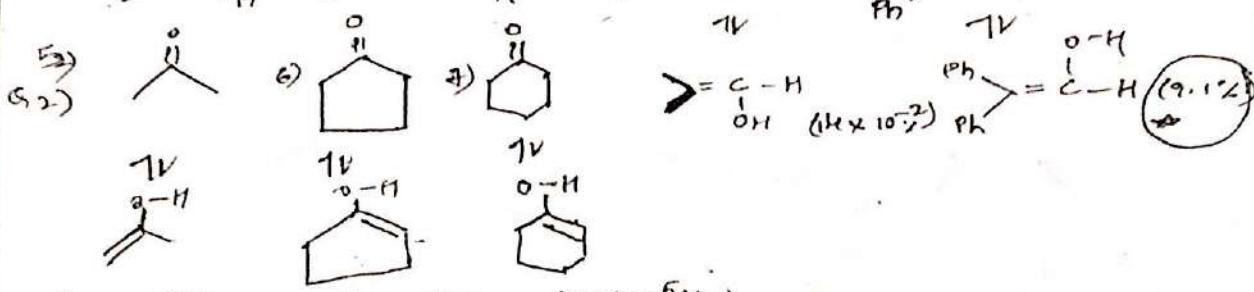
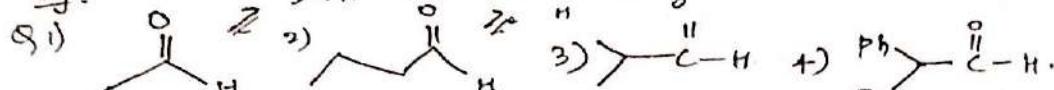
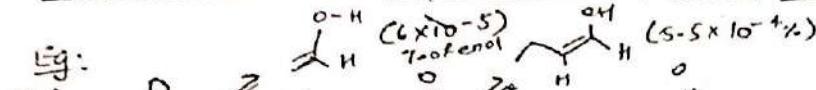


D(-) Fructose



(mannose)

Percentage of Keto form vs enol form :- (In Dynamic equilibrium)



Reason: Stability of π -bond increases \rightarrow % of enol increases.

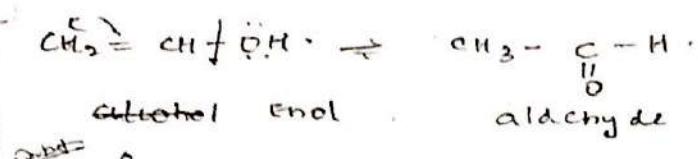
2) I^+ \rightarrow more as I^+ is more
2nd \rightarrow less as I^+ is less

6 membered ring more stable than 5 membered ring

3) % of enol is more in:

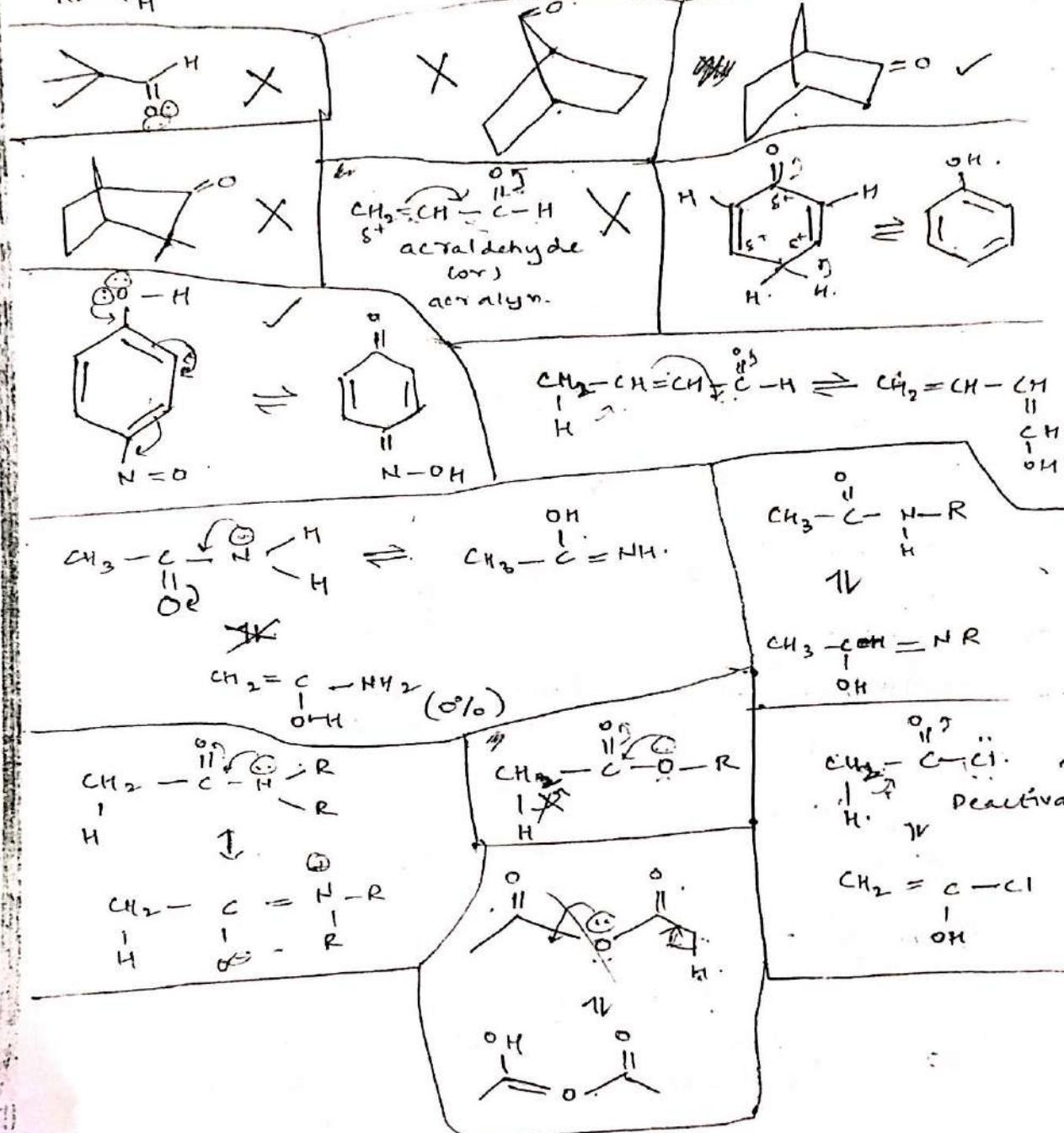


(a) resonance
more π electron density

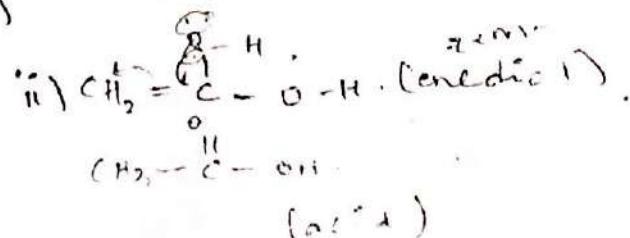
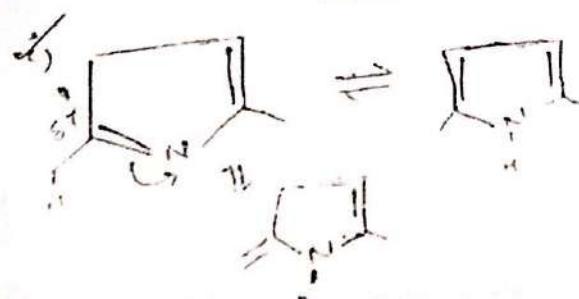


②

~~Does~~ $\text{H}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{H}$ does not exhibit Tautomerism

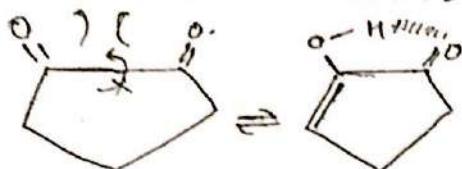


Write the enolic forms of the following compound?
(tautomeric forms)

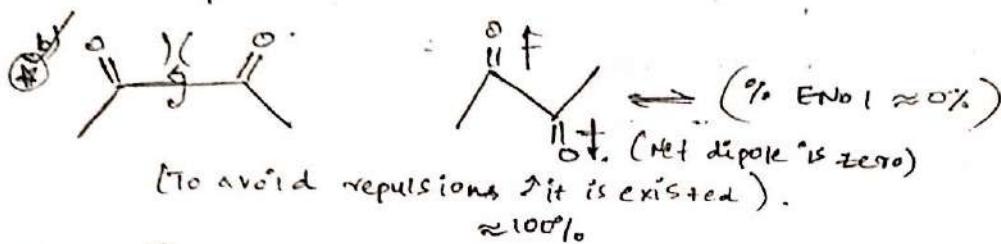


Conclusion: For all these above compounds keto form (4) is much more than enol contribution since thermodynamically keto form is more stable about 50 KJ/mole. (thermo chemistry observation)

2) $\alpha\beta$ CYCLIC 1,2-DICARBONYL COMPOUND

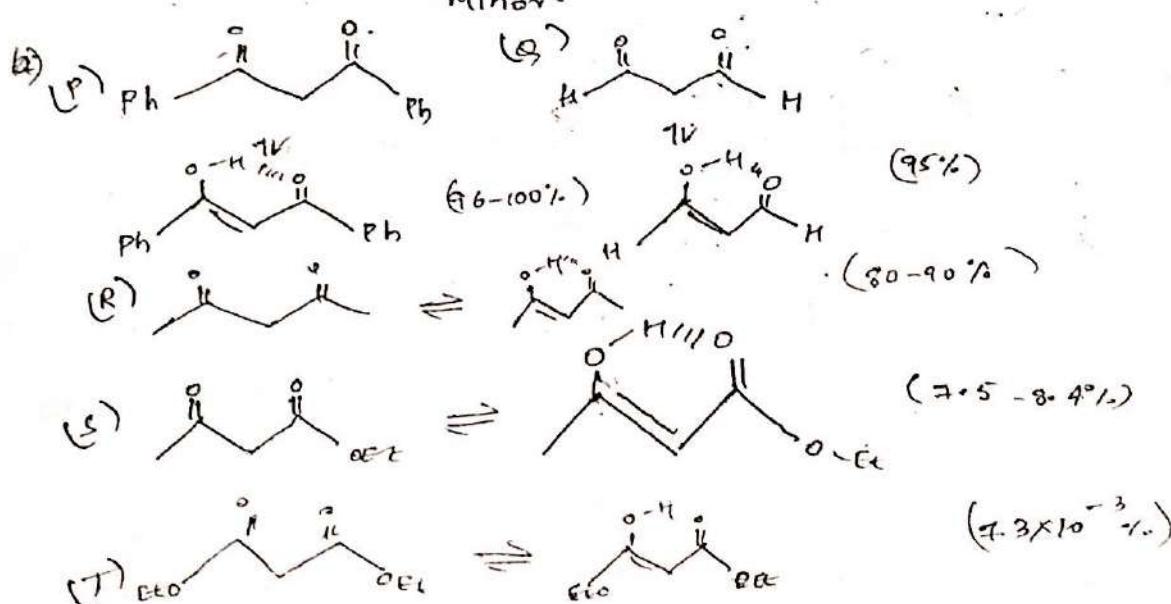
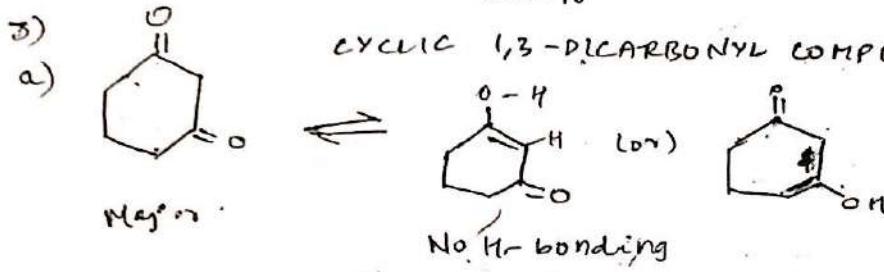


(To avoid repulsions) $\approx 100\%$



(To avoid repulsions it is existed). $\approx 100\%$

3) CYCLIC 1,3-DICARBONYL COMPOUND.



R_o > R, P > S > T

% of enol P > Q > R > S > T

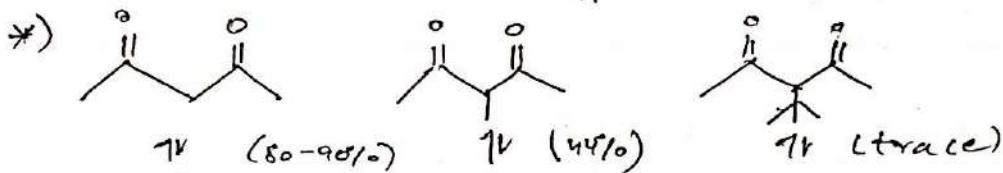
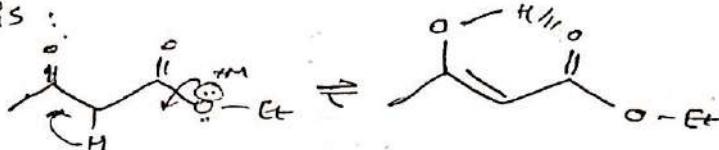
(5)

Names: R: Acetyl Acetone
 S: Ethyl aceto acetate (EAA) /
 Aceto Acetic Ester (AAE)

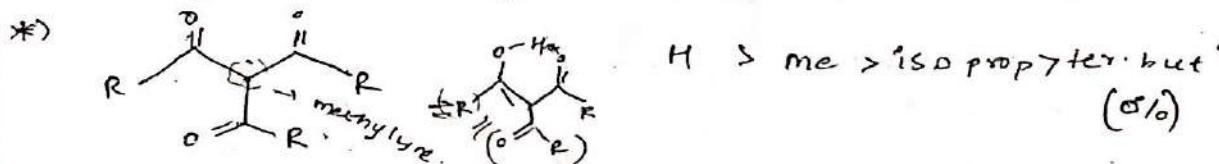
No. of enols for 'R' is: 3

terminal - 1
 middle - 2 (E & Z)

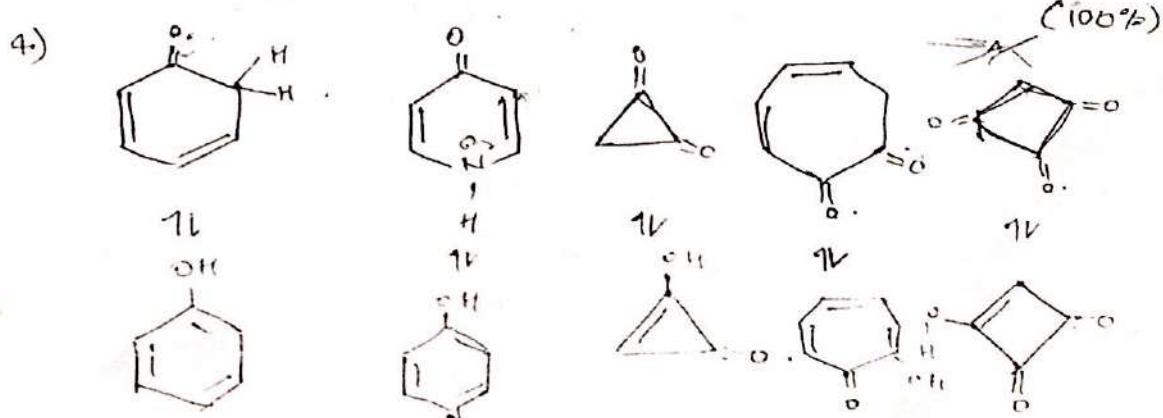
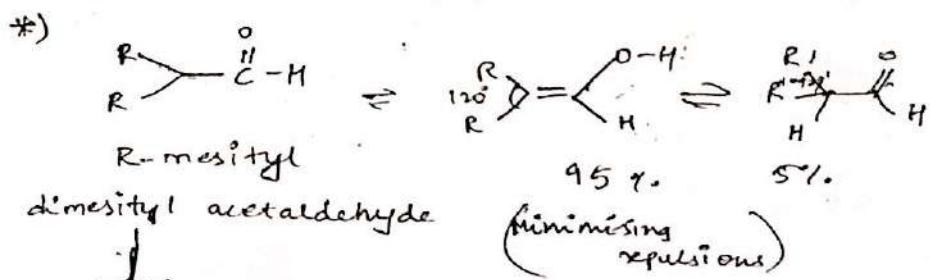
Major enol for 'S' is:

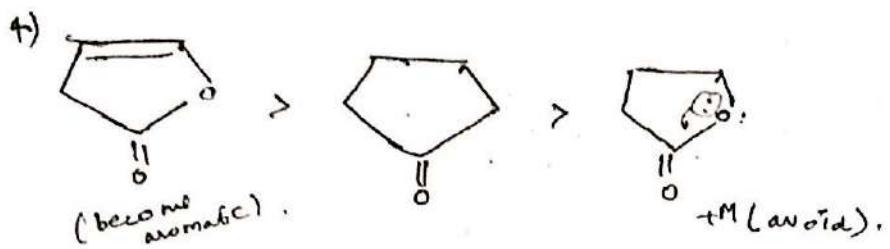


Z: (H > Me > Ter. butyl)

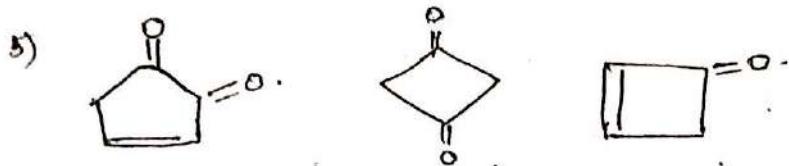


% of enol w.r.t R:





(6)



% of enol is 0% (because π-bond is part of aromatic ring)

NOTE: Factors influence on the given dynamic equilibrium



→ Compound should be either in liquid phase (or) gaseous phase shows tautomerism

→ In solid state, it does not show tautomerism

→ In gas phase: 92%

In n-hexane: 92%

$\text{CH}_3 - \text{C}\equiv\text{N} : 58\%$.

$\text{H}_2\text{O} : 15\%$

→ By ↑ in temperature, eq. shifted towards backward because H-bonding gets collapsed.

$22^\circ\text{C} \rightarrow 95\%$.

$68^\circ\text{C} \rightarrow 68\%$

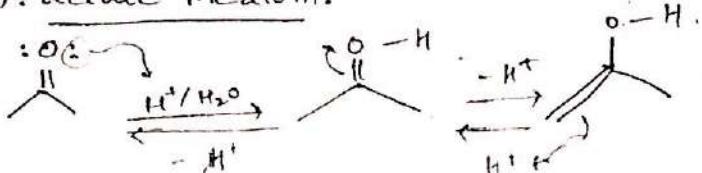
$275^\circ\text{C} \rightarrow 49\%$

→ in protic solvents, keto form is more than enol form since it is also establishing H-bonding with solvent.

NOTE:

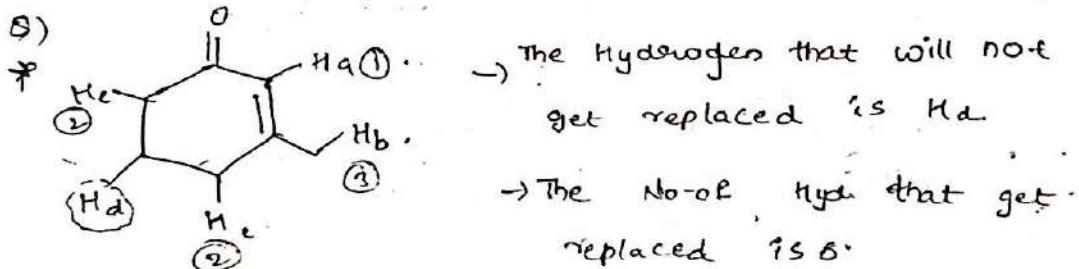
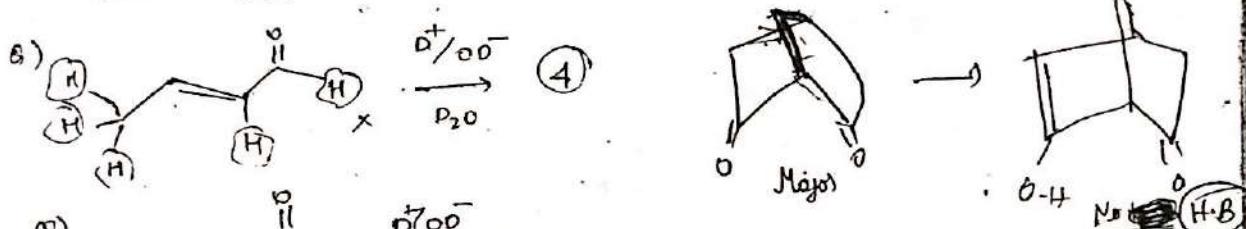
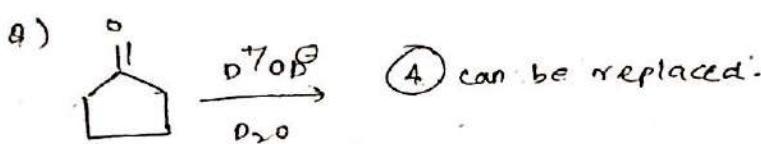
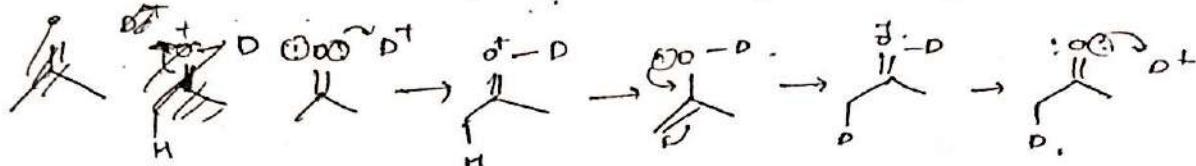
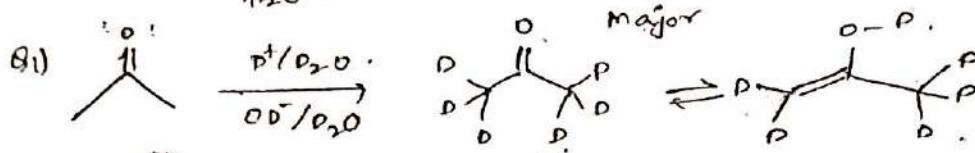
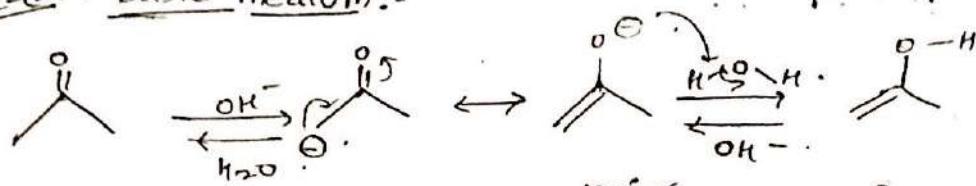
→ Tautomerism is the phenomenon which is catalysed either by means of acid or by means of base

Case (i): acidic medium:



(7)

Ques-(ii): Basic medium:-



→ enol content of ≈ 60%.

