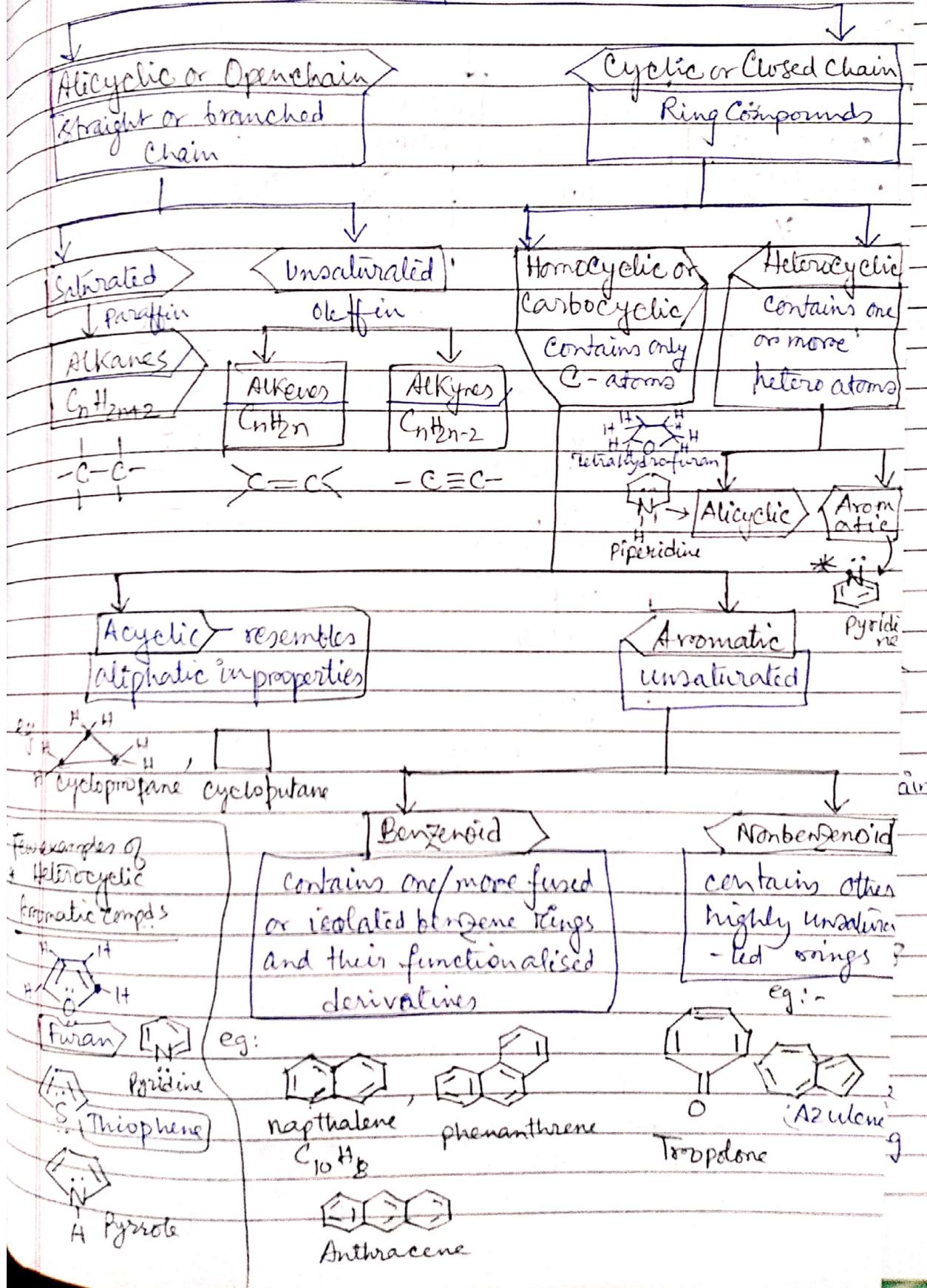


Some Basic Principles of Organic Chemistry

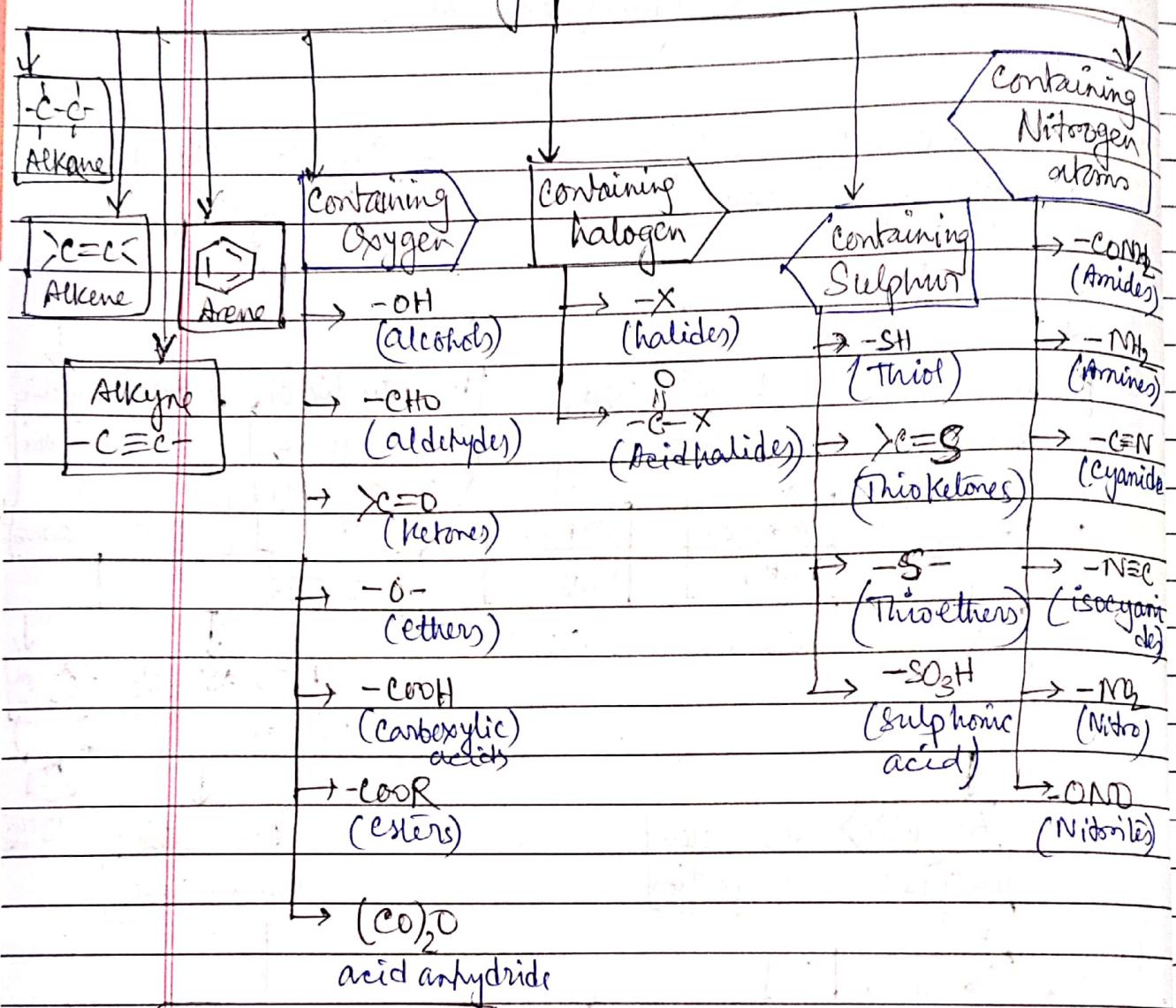
Classification of Organic Compounds :-

Organic Compounds



Classification of Organic Compounds based on function

Organic Compds



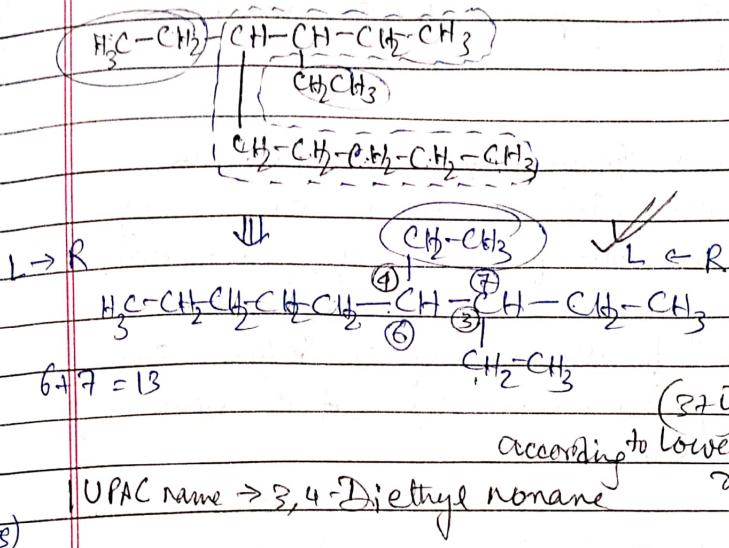
Rules for IUPAC

- (i) The longest continuous chain of C-atoms, which may or may not be straight is selected.
- (ii) The largest carbon chain is numbered as 1, 2, 3, 4 etc. starting from that end which gives the smallest possible number to the substituents, in case the parent has two or more substituents, numbering must be done in such a way that the sum of the locant-

Alkane - H = Alkyl
 Alkene - H = Alkenyl
 Alkyne - H = Alkynyl

Prime Merit
 Page No. _____
 Date _____

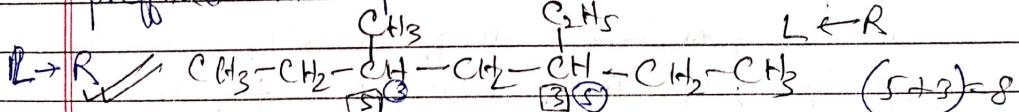
on the parent chain is the lowest possible number (lowest sum rule).



(iii) If case 2 alkyl groups are present on the identical positions in relation to the ends of the chain, numbering must be done as to give simpler side chain, the minimum number.

(iv) The name of the substituent is preferred to the name of the parent hydrocarbon and its position on the main chain is indicated by writing the locant before the prefix.

(v) If case two or more (Alkyl) groups at (side chain) are attached to the parent chain, these are prefixed in alphabetical order



- (a) The sum of locants is same i.e. 8 from ends.
 (b) Since, methyl (CH_3) group is smaller than the ethyl (C_2H_5) group, the former should be preferred in giving the lower numbers.

5-Ethyl-3-methyl heptane.

(vi)

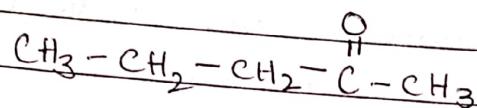
If a substituent is present two or more times, this is indicated by the prefix : - di-, tri-, tetra-, penta etc are added to the substituents.

(vii)

If functional group is present, then the largest C-chain is selected in such a way as to include the functional groups. Further numbering of C-chain is done in such a way that functional group(s) is (are) given minimum possible number even if it violates the lowest sum rule.

(viii)

The positional number of the functional group may be represented in either of the three ways



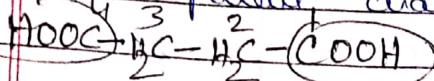
2-Pentanone, Pentan-2-one,
Pantanone-2

(ix)

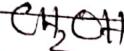
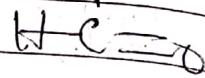
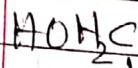
In case the compound contains two or more different functional groups (including, >C=O and $\text{-C}\equiv\text{C-}$), the principal group forms the suffix of the name while the other functional groups are considered as the substituents. The decreasing order of seniority among the principal groups is arranged in the following table.

<u>Order of Preference</u>	<u>Prefix</u>	<u>Suffix (ending)</u>
1. $-SO_3H$	Sulpho	Sulphonic Acid
2. $-COOH$	Carboxy	-oic acid
3. $-COOR$ (ester)	Alkoxycarbonyl	Alkyl Alkanate
4. $-COX$ (acid halide) $X = (F, Cl, Br, I)$	Haloformyl	-oyl halide
5. $-CONH_2$ (acid amide)	Carbamoyl	-amide
6. $-C\equiv N$ (cyanides or nitriles)	Cyano	-Nitrile
7. $-N\equiv C$ (isocyanide or isonitrile)	Isocyano	-isonitrile or carbylamine.
8. $-CHO$ $\geq C=O$	Formyl / aldo Keto / oxo	-al -one
9. $-OH$	Hydroxy	-ol
10. $-SH$	Sulphonyl	Thiol
11. $-NH_2$	Amino	-amine
12. $\geq C=C \backslash$	-	Ene
13. $-C\equiv C-$	-	-yne
14. $-O-$ (ether)	Epoxy / Alkoxy	-
15. $-NO_2$	Nitro	-
16. $-X$ (I_2, Br)	Halo	-
17.		

(x) When two carbon containing functional groups are present at the two ends of the chain and if these are similar both must be counted in the parent chain.

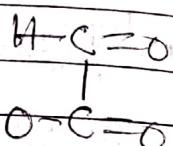


Butan-1,4-dioic acid



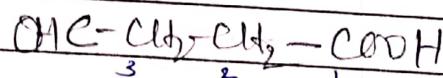
Ethan-1,2-diol.

Ethan-1,2-diol.



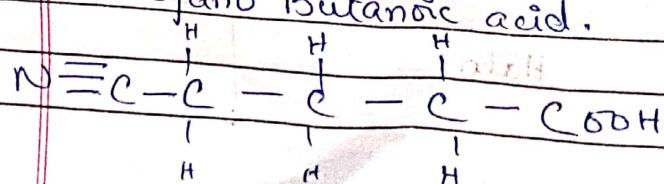
Formyl methanoic acid.

(xi) However if the two terminal carbon bearing groups are different, then one is selected as primary functional group and other (secondary) as substituent on the basis of their seniority. The substituent could not be counted in the parent chain.

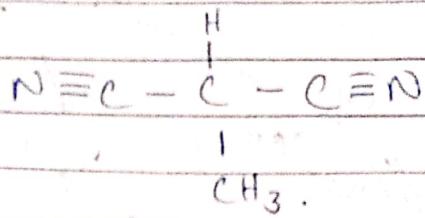


3-Formyl propan-1-oic acid.

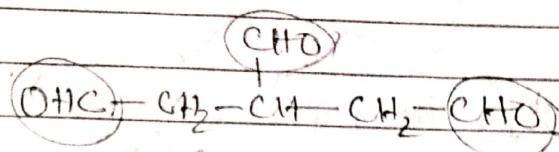
4-cyano Butanoic acid.



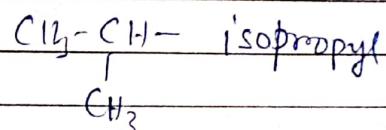
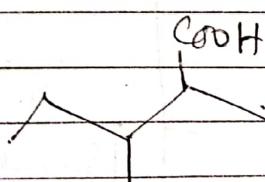
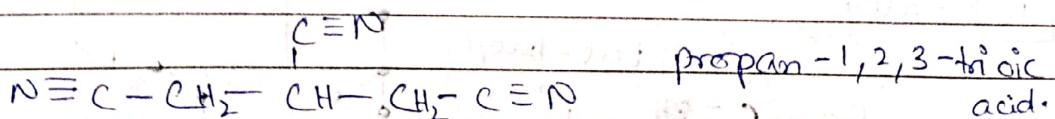
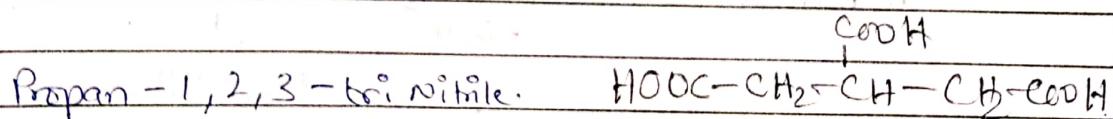
2-methyl Propan - 1, 3-dinitile.



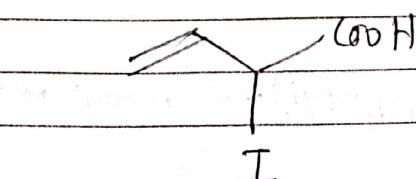
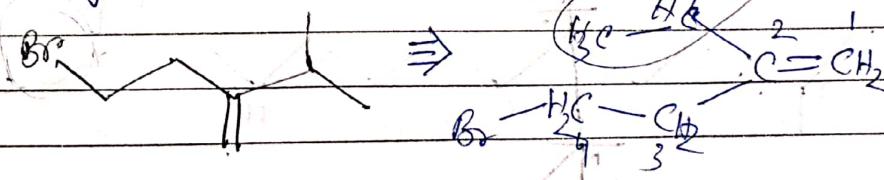
(xii) If a straight C-chain has more than 2 carbon containing functional groups, the functional groups are not counted in the C-chain, but these are named in suffix.

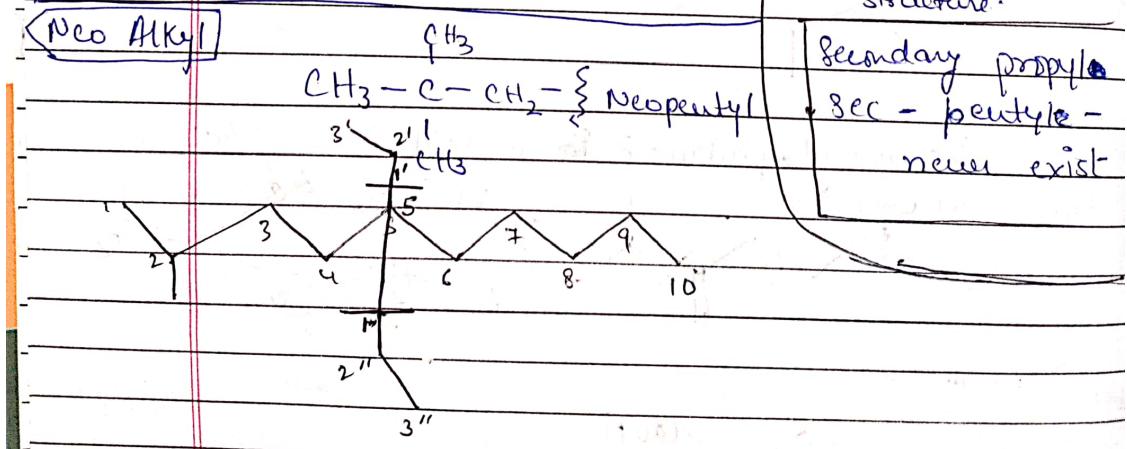
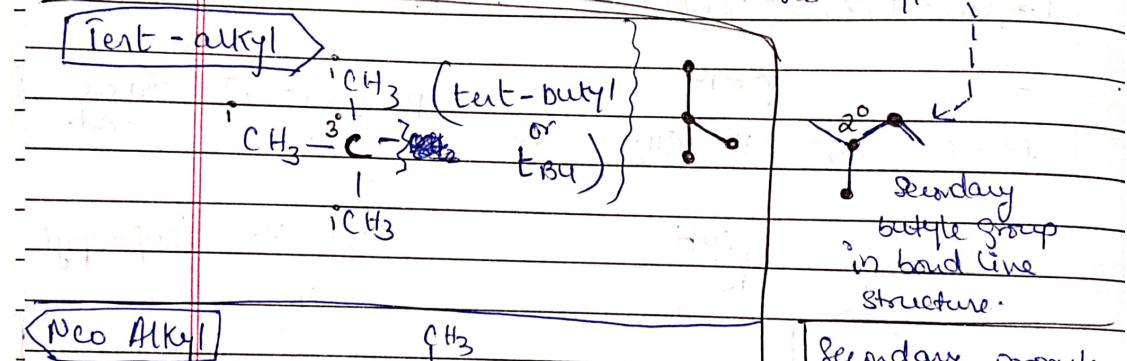
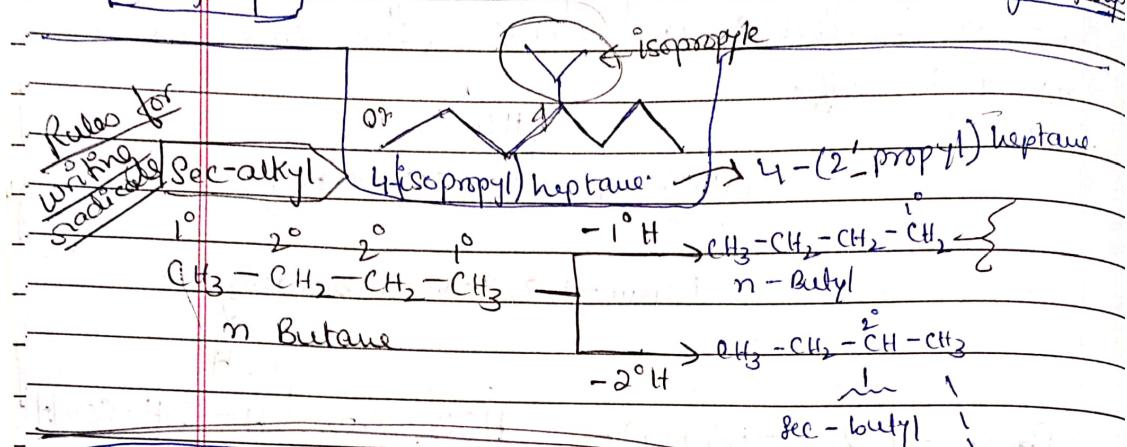
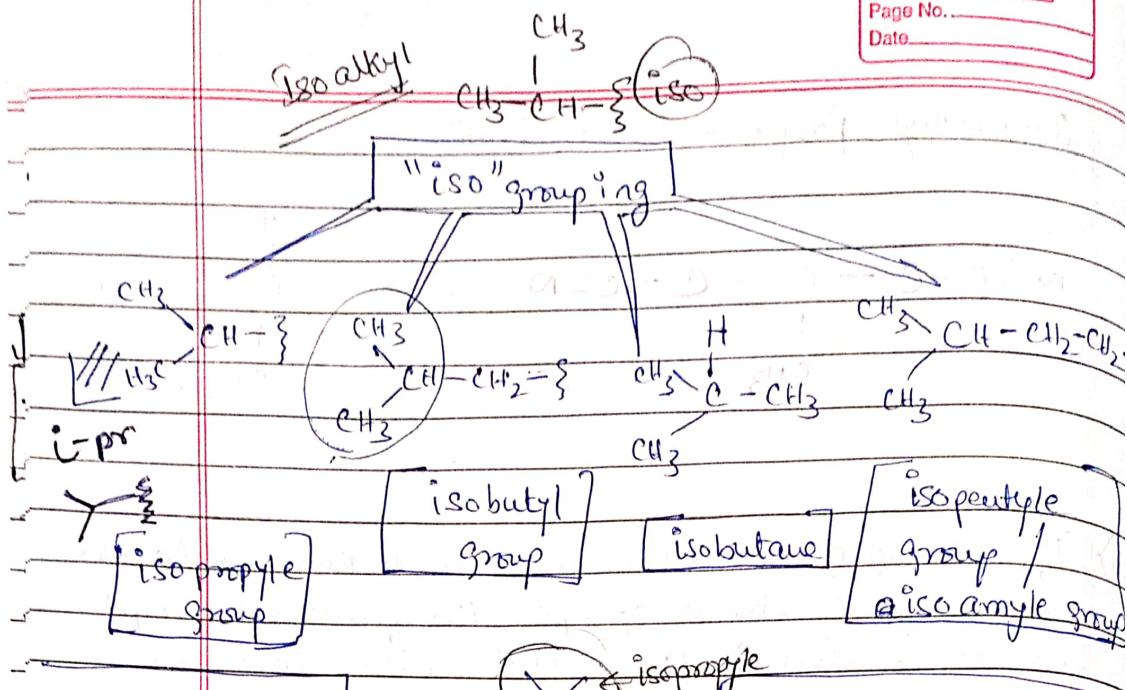


Propan - 1, 2, 3-tri carbaldelyde.

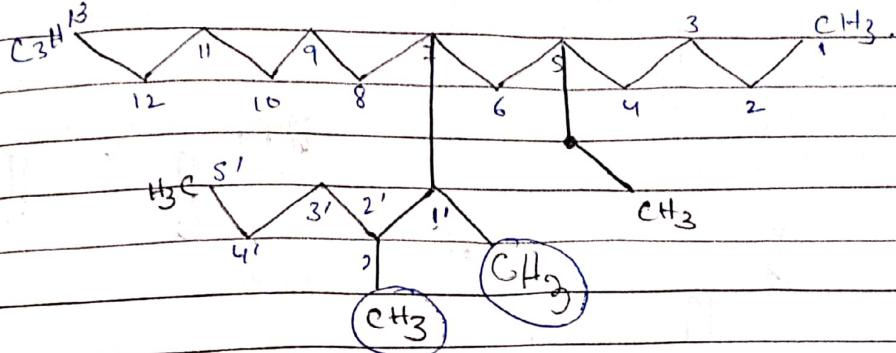


3-methyl pentan - 2 - carboxylic acid.

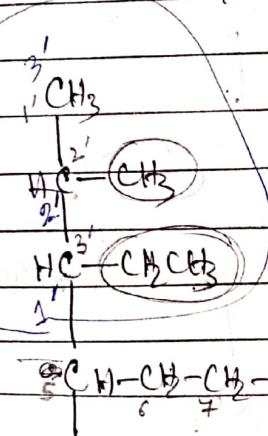




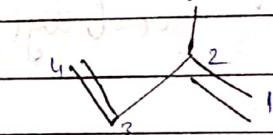
5,5-bis(1,1-dimethylpropyl)-2-methyl decane.



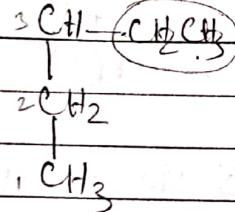
7-(1,2-dimethyl pentyl)-5-ethyl-3-methyloctane.



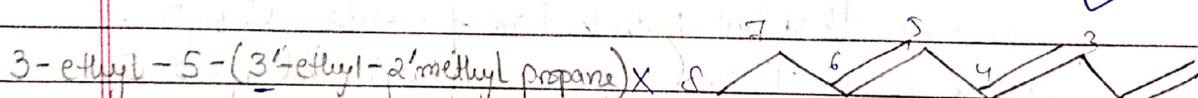
5-Methyl hex-1-ene-2-ol



2-methyl But-1,3-diene

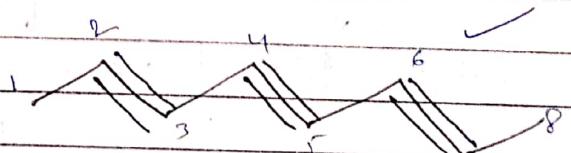


hepta-2,4-diene



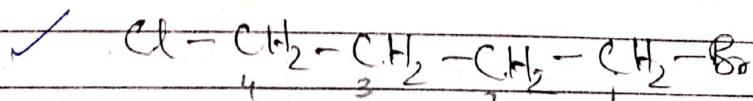
3-ethyl-5-(1'-ethyl-2'-methylpropane) nonane

Octa-1,3,5-triene

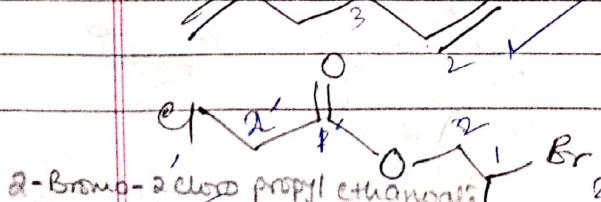


1-Bromo-4-chloro Butane

Octa-2,4,6-triyn



3-methylhexa-1,5-diene

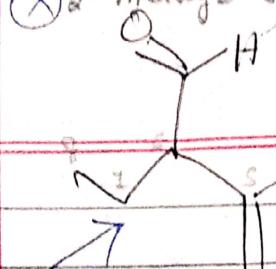


CO_2H

$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H}$

1-Carboxyhept-2-en-1,7-dioic acid

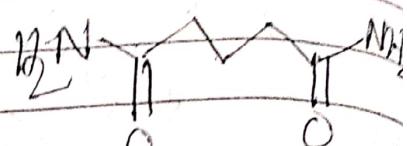
2-Bromo propyl-2'-chloro ethanoate



CEN

1,5-diaminopentane-1,5-dione

6-Formyl-5-Keto
-2-methyl Octanenitrile



pentane-1,5-diamide

3,4-diketopentanal

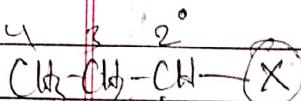
5-Hydroxy Pentan-2,3-one

CEN CEN

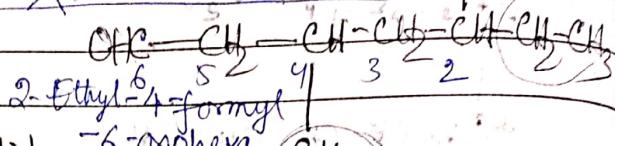
~~Pentan-2,3,4-tricarbonyl~~

Pentan-2,3,4-tricarbo
nitrile

~~(X)-ethyl-~~(X)~~-5-diformyl-penta-Nitrile~~

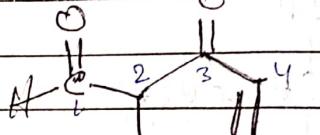


sec-butyl halide



-6-oxohepta
-nitrile

CHO



2-methyl-3-keto-hex-4-en-1-ol.

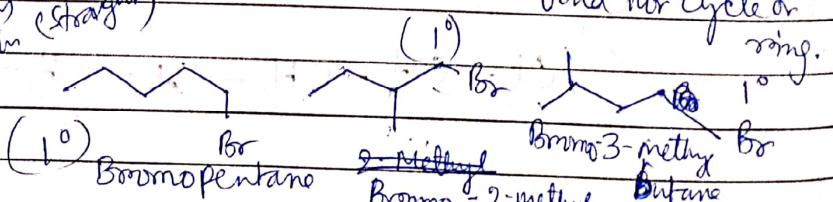
Draw the structures of all the 8 structural isomers that've molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system & classify them as 1° , 2° or 3° bromide.

$$C_5H_{11}Br, DU = \frac{1}{2}[2 + 2a - b + c - e]$$

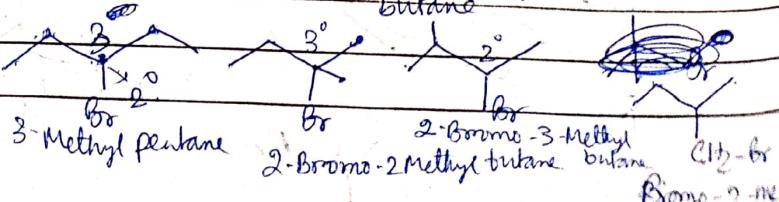
$$= \frac{1}{2}[2 + 10 - 11 - 1] = 0 \rightarrow \text{neither } \text{A} \text{ nor } \text{B}$$

bend nor cyclic or ring.

When 5 atoms (straight)
are in the chain



When 4 carbons
are in the straight
chain



19/12/20
 $\sum \text{C} = \text{H}_2 - \text{H}_2 = \text{H}_2$

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(PU) Degree of Unsaturation (or Index Hydrogen Deficiency)

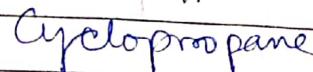
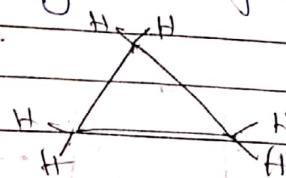
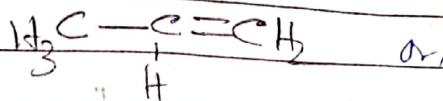
or IHD :-

$\text{C}_n\text{H}_{2n+2}$ = alkane (saturated hydrocarbon)

C_nH_{2n} = alkene (unsaturated ")

e.g. C_3H_6 , what structures may come from this formula?

Ans



- IHD — Known as "units of unsaturation" and several other similar names, its account of how many molecules of H need to be added to a structure in order to obtain the corresponding saturated, acyclic species.

- Hence, the IHD takes account of how many rings and multiple bond is present in the structure, so the IHD can also be thought as (multiple bonds + rings)

or $\text{IHD} = \pi + \text{rings}$

$\text{IHD} = \pi + \text{ring}$, for neutral organic molecules it must be a positive integer.

$$\Delta \text{U} (\text{IHD}) = \pi + \text{rings} = \frac{\text{C} - \text{H}}{2} + \frac{\text{N}}{2} + 1.$$

- There are two ways by which IHD / DU can be applied.

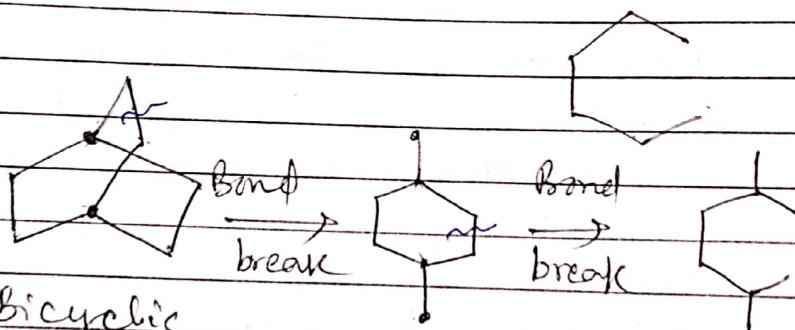
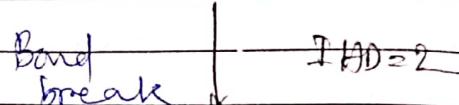
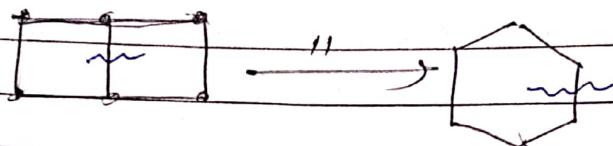
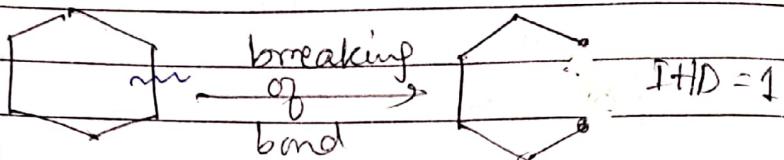
i) From a drawn structure :- from a drawn structure count the number of π bonds or rings present (i.e. $\pi + \text{rings}$) (but take care not to count any ring twice).

When counting π bonds, π bond containing heteroatoms (e.g., ~~O~~ O, N; S... etc.) can be counted in exactly the same way as C, π bonds.

Thyl butane

- Each double bond has π bond and therefore counts 1, each triple bond has 2π bonds and therefore counts 2.

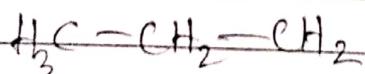
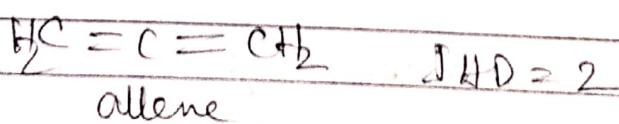
- Count the number of bonds you need to break to make an acyclic structure. (Chain structures).



Bicyclic
or Bridgehead
Compd.

IHD = 2

When DU (or IHD) is 1 - then deficiency of 2 H atoms.



Step ② From the molecular formula

Say an organic compd. $\text{C}_{a,b} \text{H}_{c,d} \text{N}_{e,f} \text{O}_{g,h} \text{X}_i$

$$(IHD_a) D_u = \frac{1}{2} [2 + 2a - b + c - e]$$

organic compound.

• We never count the number of oxygen in DU.
or we can ignore the number of oxygen and sulphur attached in O.C., but count the number of H-atoms attached to them.

• Whenever you will find double bond in O.C.
 $O.C = \text{add } 1 \text{ in DU}$

(b) If you have a triple bond add 2 in DU.

(c) if you have a ring in organic compound add 1.

① Find DU in C_3H_6 ?.

$$DU = \frac{1}{2} [2 + 2a - \frac{H}{2}]$$

$$DU = \frac{1}{2} [2 + 2a - b + c - e]$$

$$= \frac{1}{2} [2 + 2 \times 3 - 6 + 0 - 0]$$

$$= \frac{1}{2} [8 - 6]$$

$$= \frac{1}{2} \times 2 = 1.$$

Find DU in $O=C-C_6H_5$ How many H atoms



acetophenone

are deficient?

$$\underline{DU = 5}$$

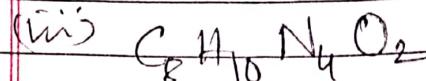
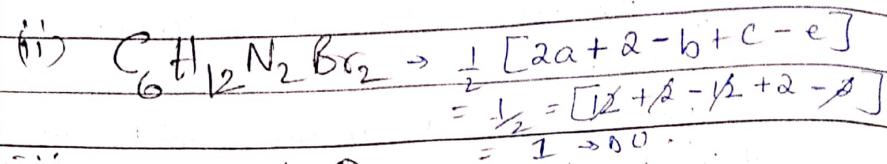
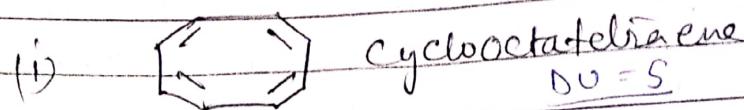
$$DU = 1 + (1+1+1) + 1$$

ring π bond for
 for another π bond.
(C=O)

$$DU = 5.$$

which means there are 10 hydrogen atoms deficient, since due to a π bond $2 - H$ atoms are deficient and since there a 5π bond, $\therefore H$ -atom less = $5 \times 2 = 10$ H-atoms.

Find DU in the following compds.



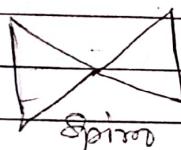
$$\frac{1}{2} [2 + 2a - b + c - e]$$

$$\frac{1}{2} [2 + 16 - 10 + 4 - 0]$$

$$+ 6 \rightarrow DU$$

possibilities \rightarrow 1 ring, 5 double bonds
 \rightarrow 2 rings, 4 double bonds
 \rightarrow 1 ring, 1 triple bond, 3 double bonds

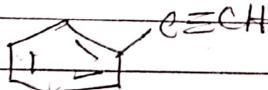
(iv)



$$IHD = ?$$

$\Delta V = 2$ (since 2 cycles)

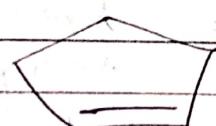
(v)



$\Delta V = 6 \rightarrow$ (ring, triple bond, & 3-bonds)

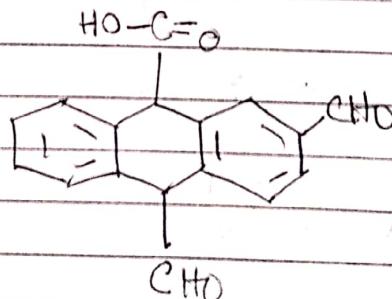
Styrene

(vi)



$$\Delta V = 2$$

(vii)



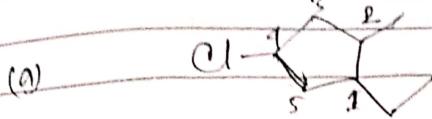
$$\Delta V = 12$$

Naming of alicyclic Compds

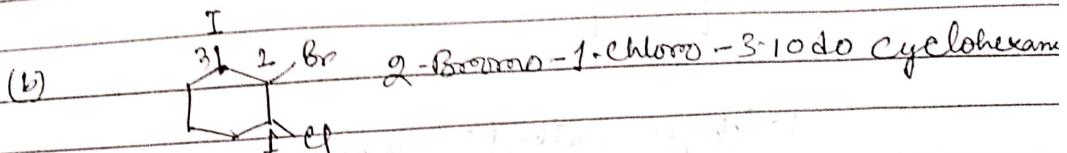
Rule 1:

(Prefix = cyclo)

i.) Numbering as per lowest set of locants rule

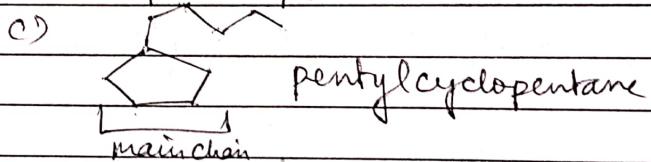
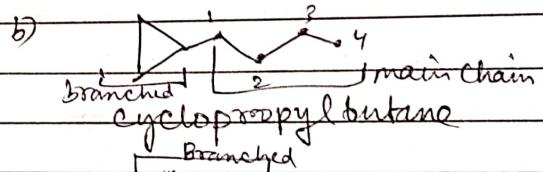
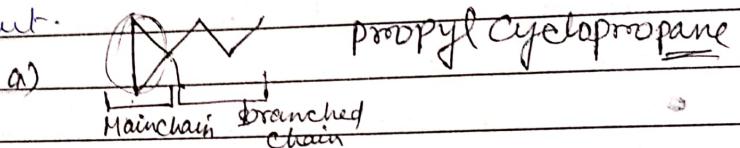


1-Chloro - 1-ethyl - 2-methyl cyclopentane



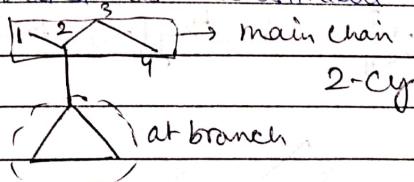
Rule 2

When the ring contains more or equal numbers of C-atoms than the alkyl groups attached to it, then it is named as derivative of Cyclo Alkane and the alkylic group is treated as substituent.



Rule 3

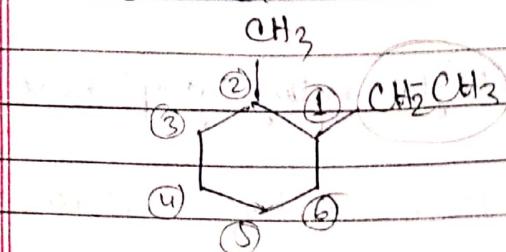
The alkane chain contains greater number of C-atoms than present in the ring. Then the compound is considered as derivative of alkane and ring is designated as substituent.



Rule 4

While numbering C-atoms of the ring

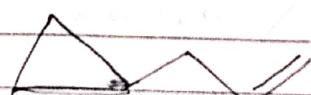
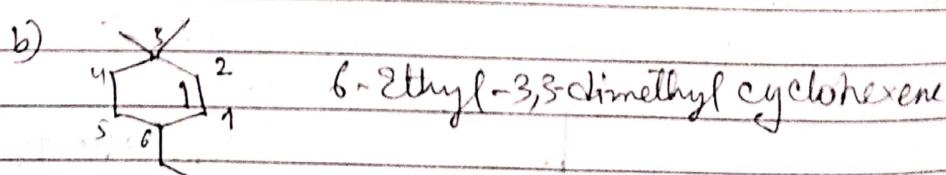
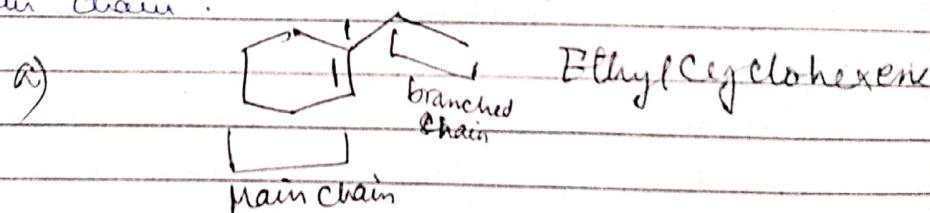
the substituent which comes first in alphabetical order is given the lowest number provided that it does not violate the & lowest sum rule.



1-Ethyl-2-methylcyclohexane.

Rules :

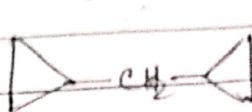
- If ring has unsaturation and side chain is saturated. Then ring is considered as main chain.
- If the side chain has unsaturation and ring is a saturated. Then side chain is selected as main chain.
- If cycle has both have unsaturation, the chain with maximum unsaturation will be selected as parent chain.
- If equal unsaturation, then top longest chain is selected as parent chain.
- If unsaturation and no. of atoms, both are equal, then ring is selected as main chain.



Rule 6: If more than 1 ~~one~~ aromatic alicyclic ring is attached to a single chain.

Then the compound is named as a derivative of alkanes and the ring is treated as a substituent.

Examp:

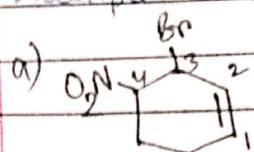


Dicyclopropylmethane



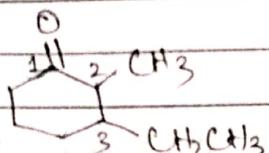
1,2-dicyclohexyl
ethane

Rule 7: If a multiple bond and some other substituents are present in the ring, a numbering is done in such a way that the multiple bond gets the lowest number.



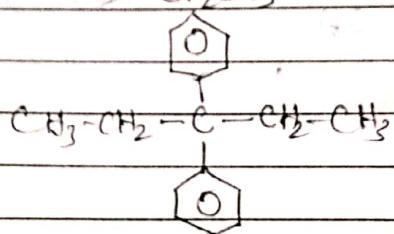
3-Bromo-4-Nitro Cyclohex-1-ene

b)



3-Ethyl-2-methyl Cyclohexanone

c)

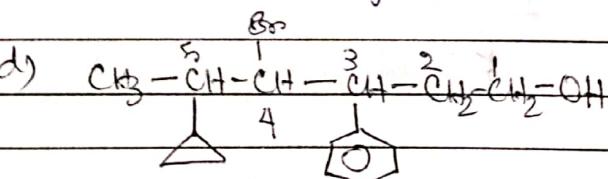


[If the aromatic compound has an open chain attached to benzene ring, then this chain gets the main status and ring is treated as substituents]

3, 3-di phenyl pentane.

chain gets the main status and ring is treated as substituents]

d)



treated as substituents]

4-bromo-3-phenyl-5-cyclopropyl Hexanol.

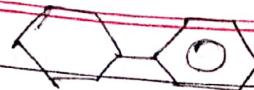
Rule 8

If a compound contains an alicyclic ring directly linked to the benzene ring, it is named as derivative of Benzene.

$\text{Me} = \text{-CH}_3$, $\text{C}_2\text{H}_5 = \text{Et}$

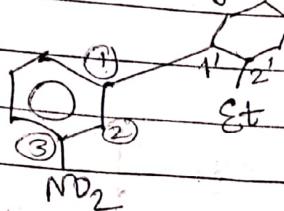
Prima Marita
Page No.
Date

a)



cyclohexylbenzene

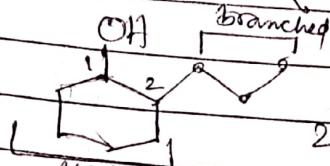
b)



3-Nitro-1-(2'-Ethylcyclohexyl)benzene

Rule - 9

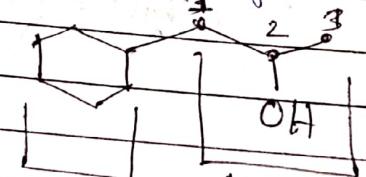
a)



2-propylcyclohexanol

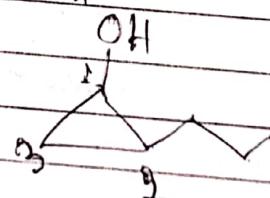
If functional group is present in cyclic compounds, then the main chain is taken in which principal functional group lies, if the principal functional group is present in the ring the main chain will be taken for the maximum number of C-atoms.

b)



1-Cyclohexylpropan-2-ol

c)

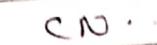
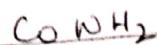
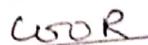
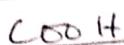
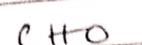


2-Cyclopropyl-2-propylcyclopropanol

Rule 10

When chain terminating functional group is directly attached with ring. Then ring is taken as parent chain and special suffix is used for these functional groups.

Functional Group



Suffix:

carbaldehyde

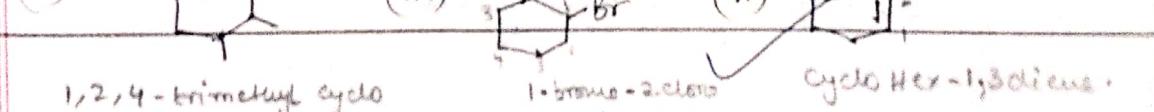
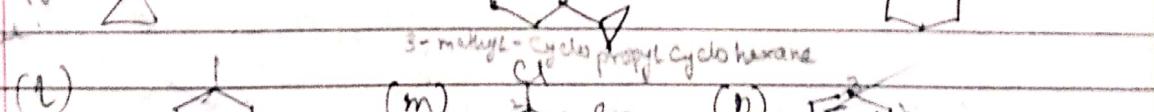
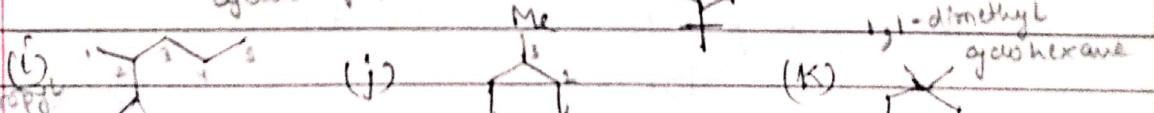
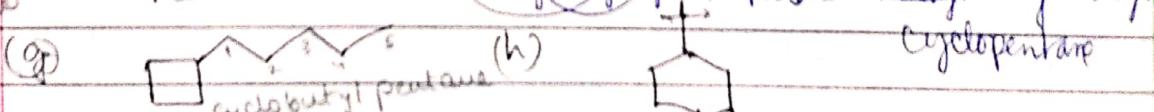
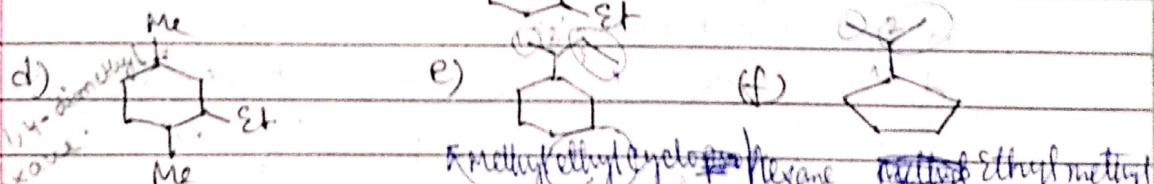
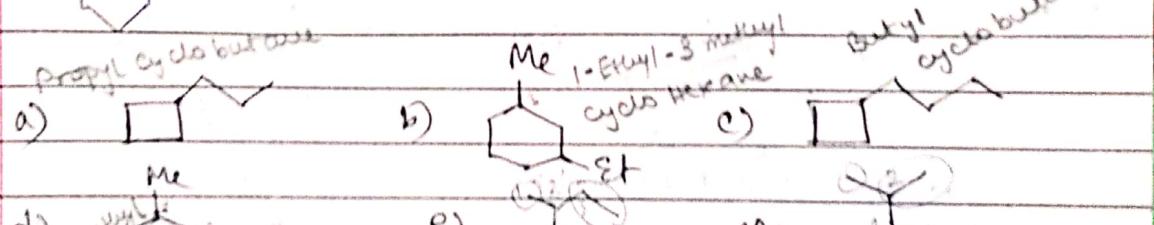
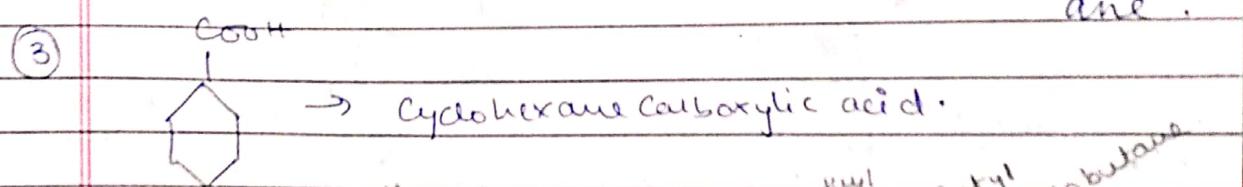
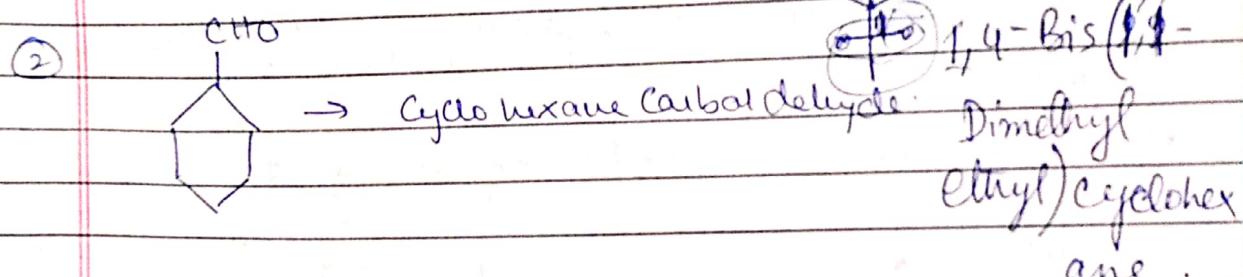
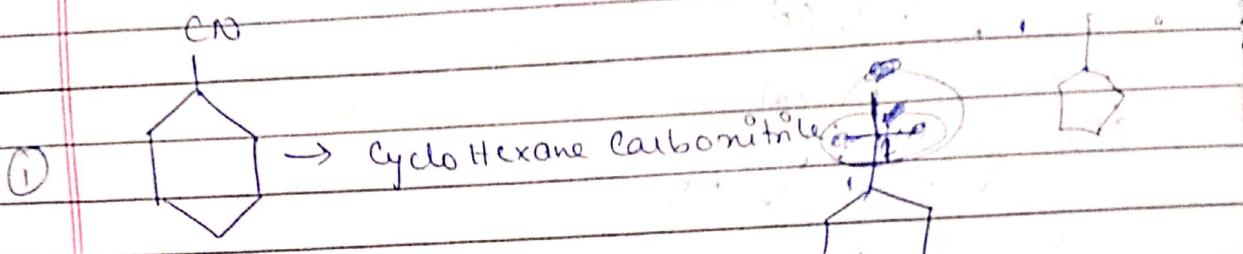
carboxylic acid

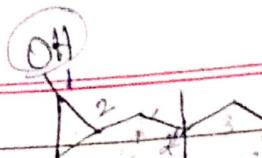
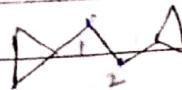
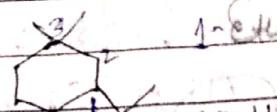
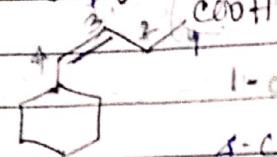
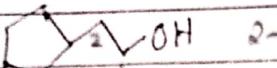
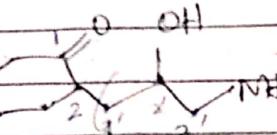
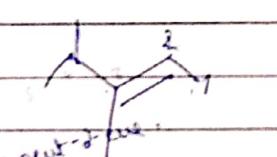
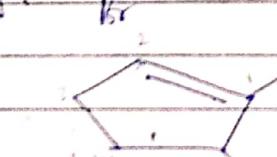
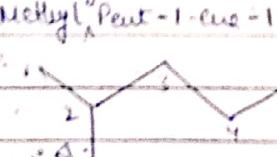
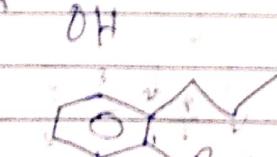
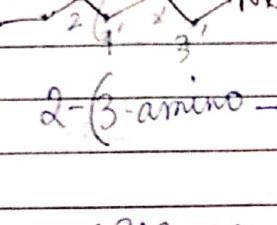
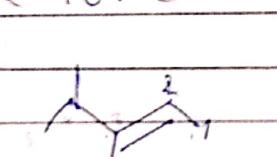
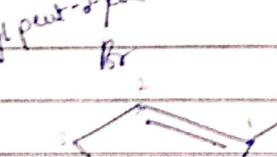
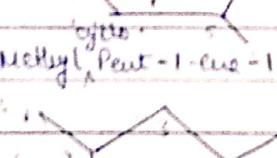
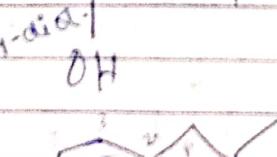
carbonyl halide

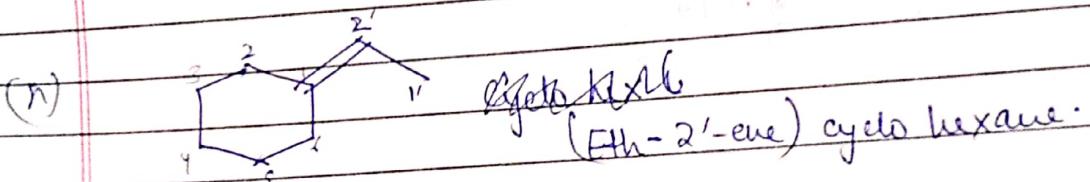
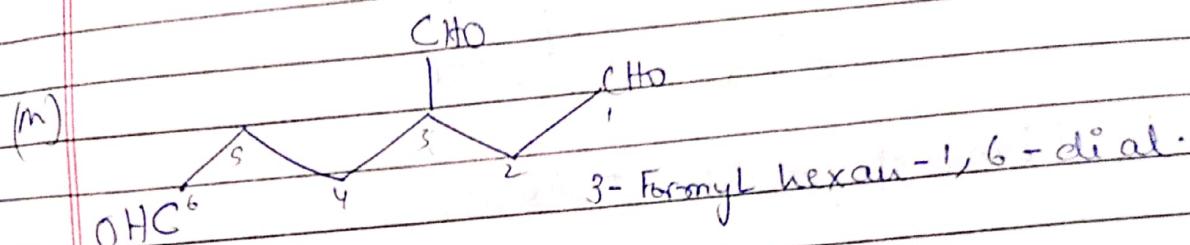
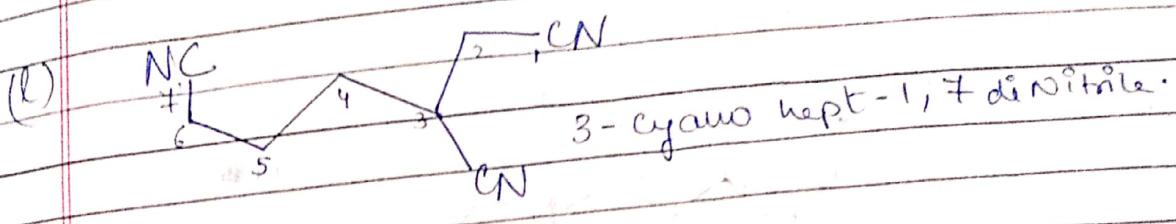
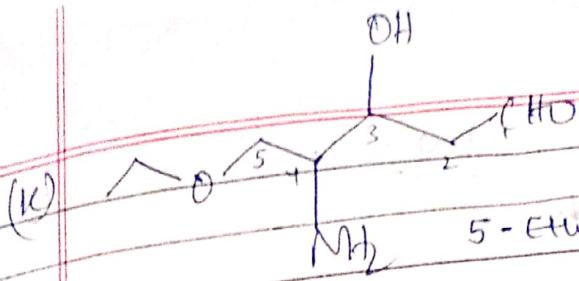
Alkyl carboxylate

carboxamide

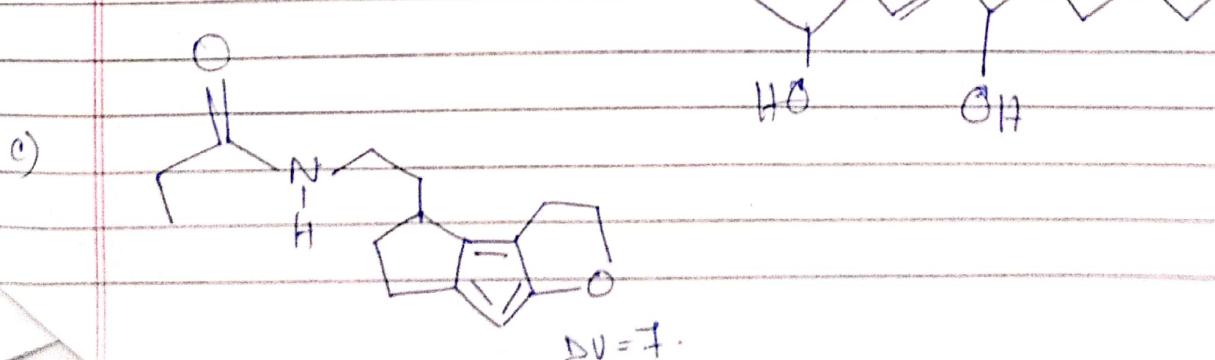
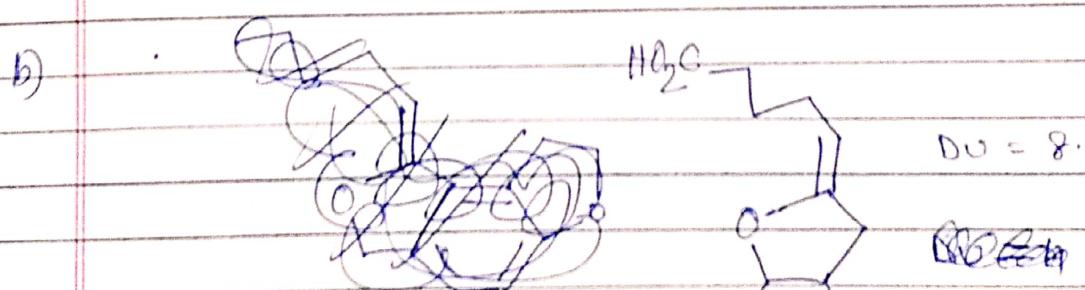
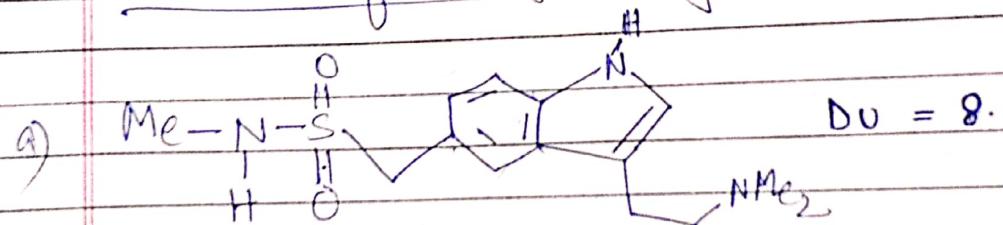
carbonitrile



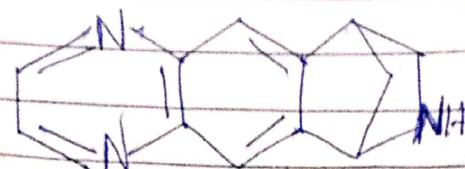
- (O)  2-(2',2'-dimethyl Butyl)cyclopropanol
- (P)  1,2-Dicyclopropylethane
- (Q)  1-Ethyl-3,3-dimethyl cyclohexane
- (R)  1-cyclohexyl But-1-en-4-oic acid.
3-cyclohexyl but-3-enoic acid
pentyl
- (S)  2-cyclohexyl ethanol
- (T)  2-(3-amino-2-hydroxy propyl) cyclohexanone.
- Q1
Give IUPAC names for the following structures :-
- a)  3-Bromo-4-methyl pent-2-ene
- b)  5-Methyl Pent-1-ene-1-ol.
- c)  Butan-2,4-diol
- d)  2-(2'-Hydroxy)-1-Bromo Benzene.
- e)  3-Hydroxy-4-formyl Benzonic acid
- f)  Methoxy Ethane
- g)  2-Methoxy Propane
- h)  1,3-Dihydroxy-2-propanone
- i)  2,4-Dihydroxy-3-pentenoic acid
- j) 



~~Q. 2.~~ Find DU of the following compds :-

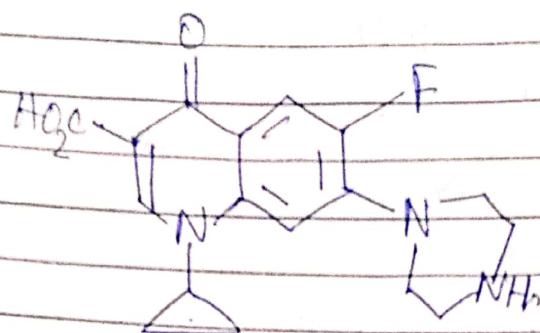


d)



DU = 9.
Bases.

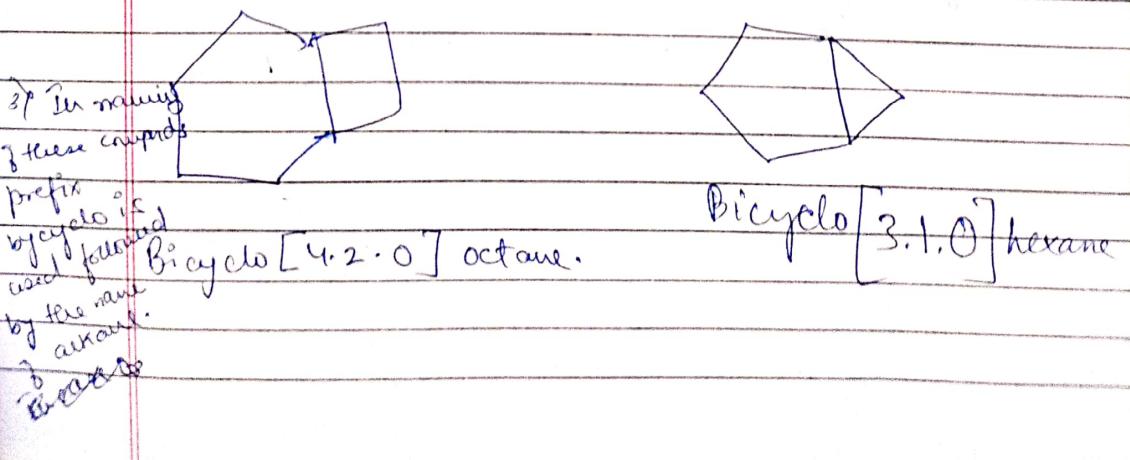
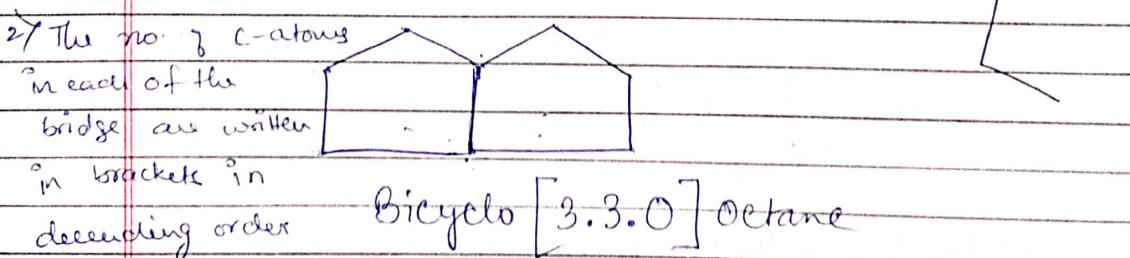
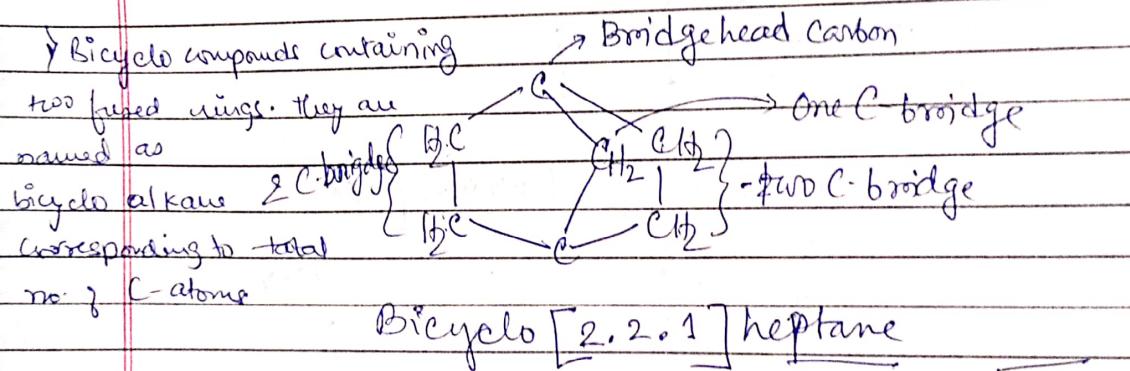
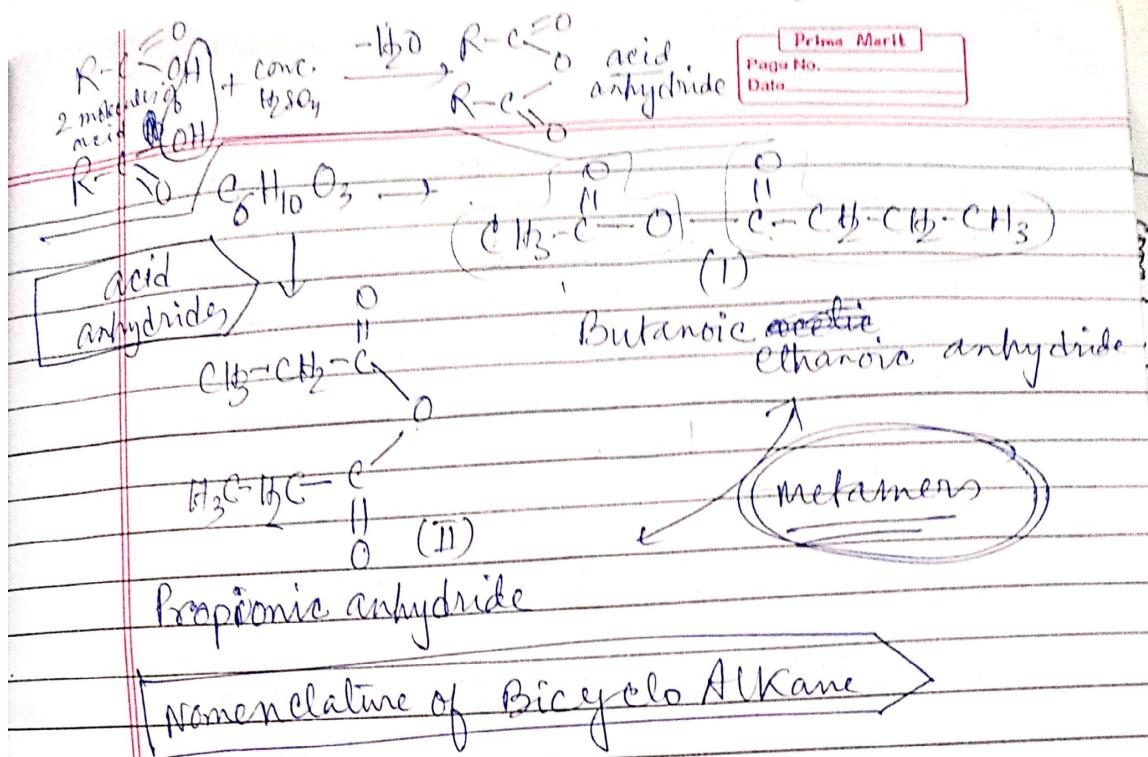
e)



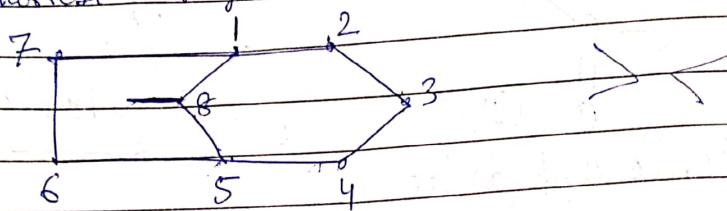
DU = 11.

f) Draw 9 possible structures

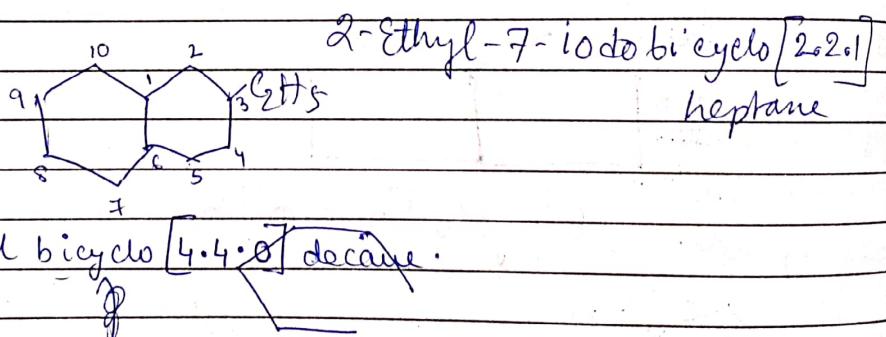
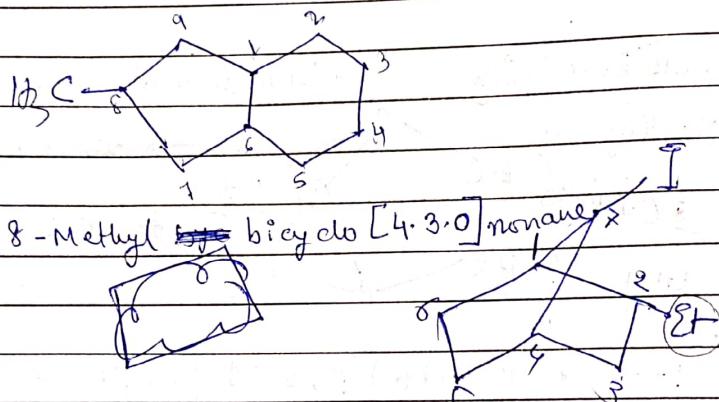
for C_2H_3N ?



4) In case of Substituents present in bicyclo compounds, no numbering of chain is done from the longest bridged ring beginning at one bridge head. The numbering is the next longest bridge and hence shortest bridge is numbered at last.



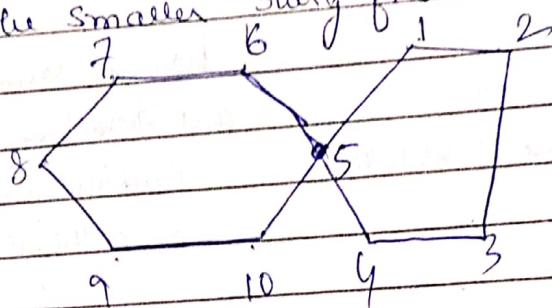
8-Methyl bicyclo [3.2.1] Octane



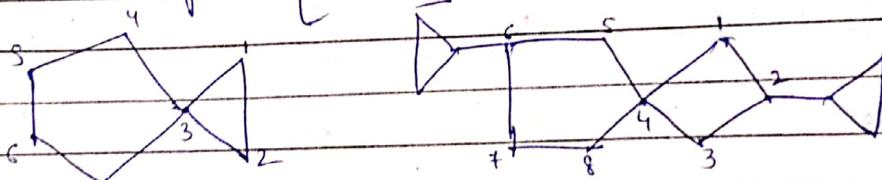
Nomenclature of Spiro Compounds

If two rings are joined by spiro carbon atom at the apex then they are preffixed by the word spiro followed by containing total c-atoms in each ring & both side of common point in ascending order and then in the name of parent hydrocarbon containing total number of c-atoms in the two rings.

The numbering starts from the atom next to the spiro atom (atom joining the rings) and proceed through the smaller ring first.

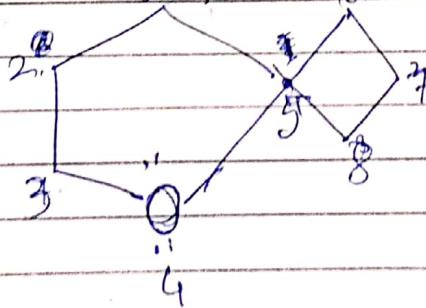


Spiro [4.5] decane



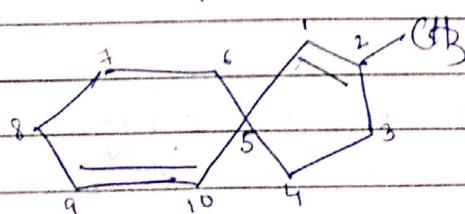
spiro [2.4] heptane. 2,6-dicyclopropyl spiro

2,6-dicyclopropyl spiro [3.4] octane



4-Oxo spiro [3.4]

heptane.



2-Methyl spiro [4.5] dec-1,9 diene.

ISOMERISM

Q. What do you mean by isomerism?

It's the phenomena of existence of two or more compounds having same molecular formula but different physical and chemical properties. These compounds are called isomers.

Isomerism

Structural Isomerism

Having same molecular formula but different structures

(a) Chain or Nuclear Isomerism

(b) Position Isomerism

(c) Functional Isomerism

(d) Melaomerism

(e) Tautomerism

Stereoisomerism

Having same molecular formula and structure but different configuration, i.e. arrangement of their atoms in space.

Geometrical Isomerism

cis/trans

E-Z

Optical Isomerism

d, l-isomerism

Conformational Isomerism

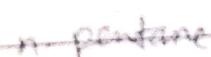
Chain Isomerism :- Having different carbon skeletons.

There should be a minimum of 4 C-atoms in the chain.

nanobots

General formula is

i) C_6H_{12} \rightarrow



no. of possible isomers

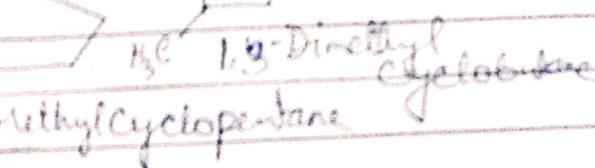
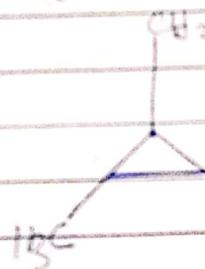
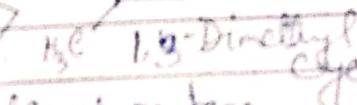


ii) C_6H_{12}

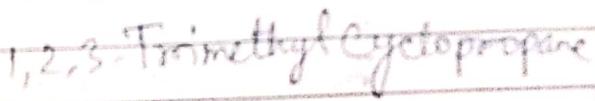


CH_3

CH_3



CH_3



Position Isomerism \rightarrow Having different positions of functional group on the C-chain, there should be a minimum of 3-carbon chain atom.



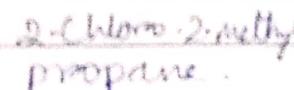
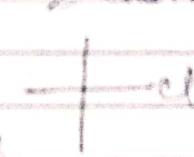
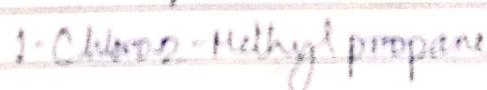
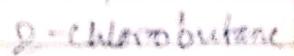
General formula

No. of possible isomers

ii) $C_4H_9Cl \Rightarrow$



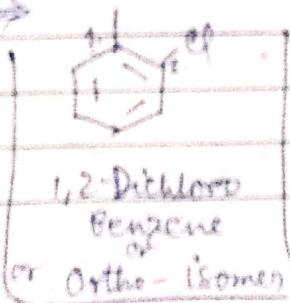
Cl



iii) $C_6H_5Cl_2 \Rightarrow$

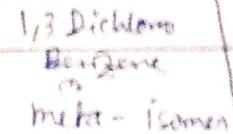
Cl

Cl



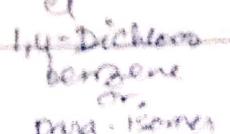
Cl

Cl



Cl

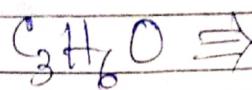
Cl



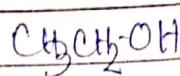
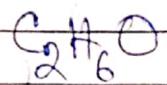
③ Functional Isomers > are those having different functional groups.

General formula

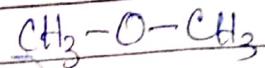
No. of possible isomers



IUPAC name → propanal propan-2-one 2-Methyloxiran
 Common name → ~~propanal~~ - acetone or epoxy propane



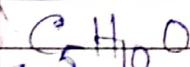
Ethanol



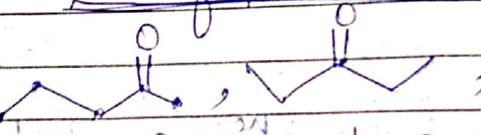
Dimethyl ether

④ Metamerism > Compds having same molecular formula but different alkyl chains on either side of the functional group, are metamers.

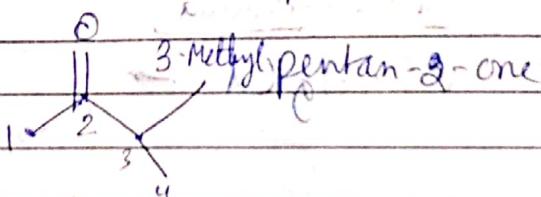
CARBONYL COMPODS



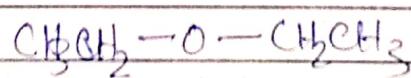
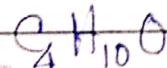
No. of possible isomers



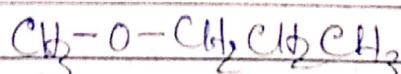
Pentan-2-one pentan-3-one



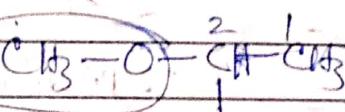
Ethers



Ethoxy Ethane

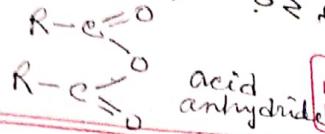


Methoxy propane



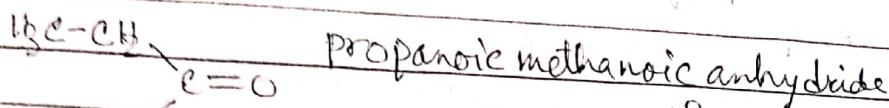
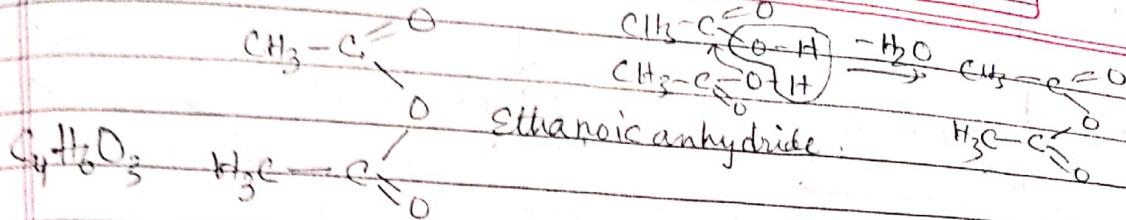
2-Methoxy propane

Acid anhydrides

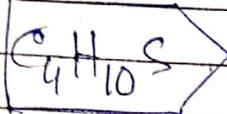


acid
anhydride

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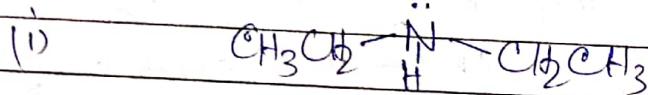
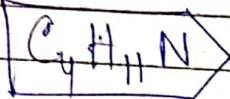


Thioethers

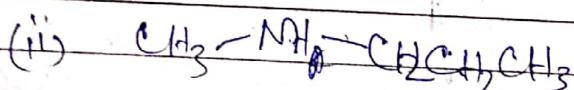


3 possible isomers.

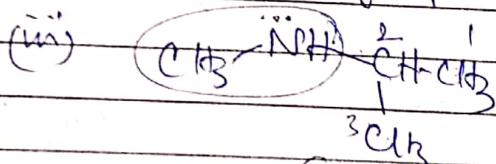
Q'amine



N-Ethyl ethanamine



N-Methyl propanamine



2-(N-methyl)propanamine

Tautomerism : Tautomers are structural isomers / ^{constitutional isomers} chemical compounds that ~~readily~~ interconvert due to a wandering nature of α -hydrogen from 1 to 3 position within a molecule, which can exist in dynamic equilibrium representing two compounds. This phenomenon is called tautomerism / desmotropism.

Classification of Tautomerism

Open System of Tautomerism

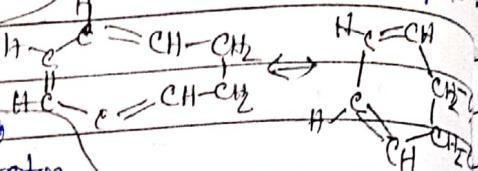
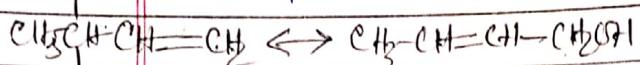
Ring chain tautomerism

Valence Tautomerism

If occurs when the movement of the proton is accompanied by a change from an open structure to a ring. It's an type of functional isomerism. Here the compds have same molecular formula but isomers have open chain structure and cyclic structure.

It involves processes in rapid motion of bending tautomerism. In valence two forms differ in the position of the valence example: of the valence for

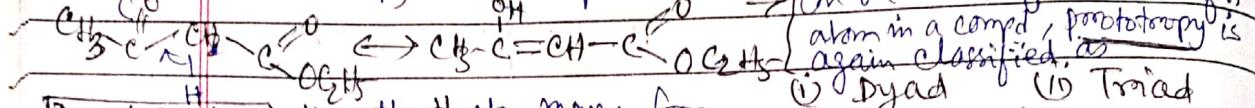
- Anionotropy** When the 2 tautomeric forms differ in the position of an atom/group capable of forming a stable anion, the phenomenon is known as anionotropy.
- This is mainly associated with allylic compds. For example



- OH**

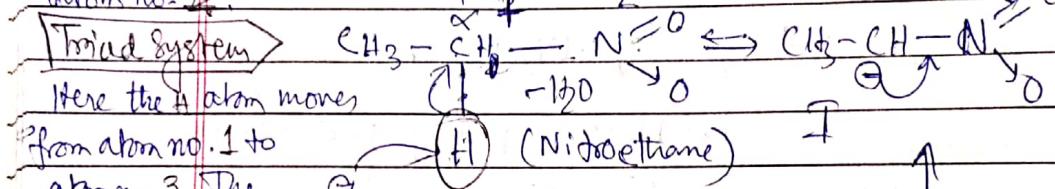
- Cationotropy** When the 2 tautomeric forms differ in the position of ~~an atom/group~~ capable of forming a stable cation, the phenomenon is

Known as cationotropy. For example -



- Dyad
- Triad

Dyad system Here the H-atom moves from atom no. 1 to atom no. 2.



Triad system Nitro-Aci-Nitro Tautomerism

Involves the migration of

H-atom from This can be shown

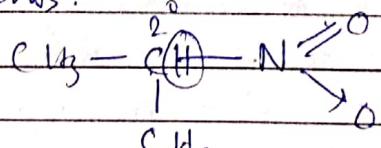
and to either only in 1° & 2° nitro compds (aci-form)

C, O or N. In 3° nitro compd. no α -H

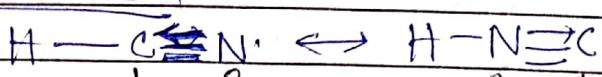
Various types presents.

of triad systems are

Keto-enol tautomerism



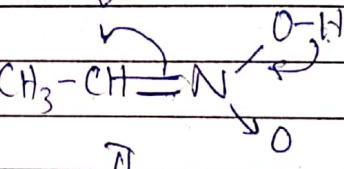
Nitroso-Oxime tautomerism



Imine-enamine tautomerism

Tautomers

Nitro-acifitro tautomerism

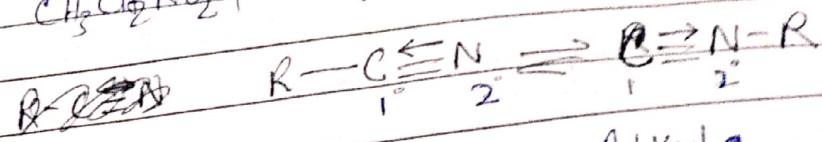


Istnitroethane

Lactum - Lactim tautomerism

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Tautomer in the following is a dyad system?
 (i) $\text{CH}_3-\overset{\text{C}=\text{O}}{\underset{\text{CH}_3}{\text{C}}} \text{H}_3$ (ii) $\text{CH}_3\text{CH}_2\text{NO}_2$ (iii) $\text{CH}_3-\overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}} \text{H}_3$



(iv) $\text{HC}\equiv\text{N}$

cyano Alkane

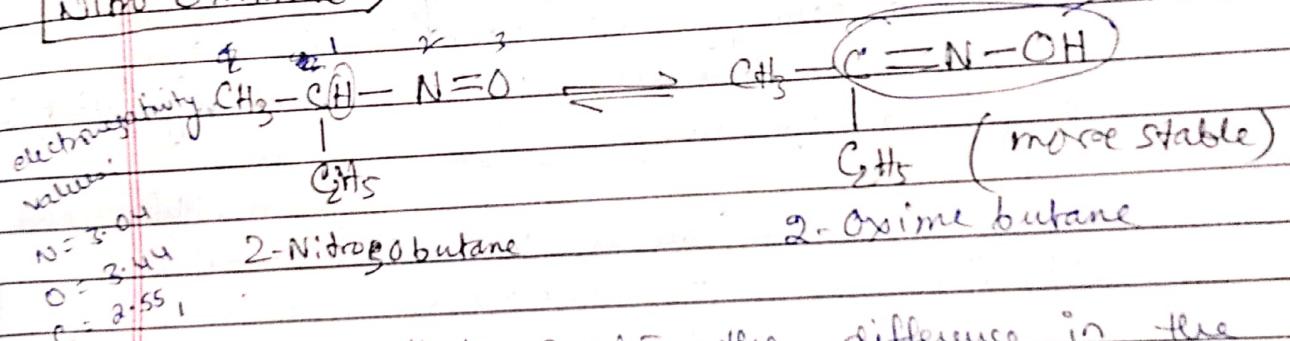
Alkyne

isocyanide

If the H-atom oscillates between two polyvalent atoms, linked together, the system is a dyad.
 If the H-atom travels from 1st to 3rd atom in a chain, the system is triad

Triad system involves migration of H-atom from 1 to 3 atoms:
 (i) Nitro-Oximino (Nitroso-isonitroso)
 (ii) Lactum-Lactim
 (iii) Keto-enol tautomerism.

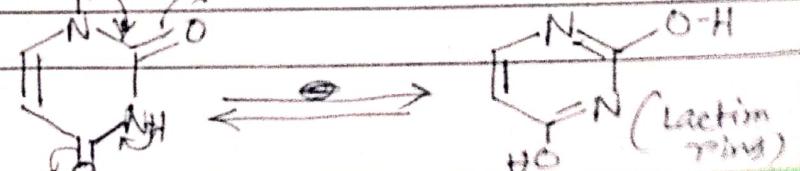
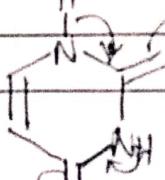
Nitro Oximino

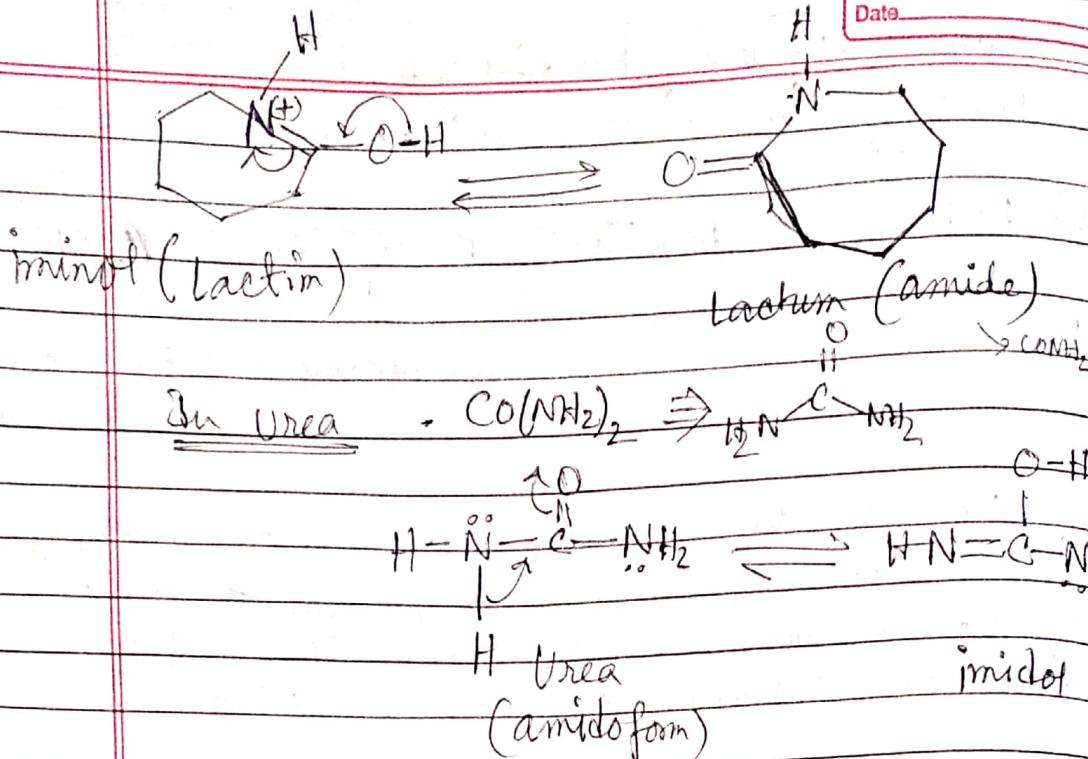


We know that greater the difference in the electronegativity values, stronger is the bond. This property makes the Nitrogen-carbon double bond stronger. Hence making oxime more stable than 2-nitrobutane.

Lactum-Lactim: A form of tautomerism occurs in Lactum-Lactim interconversion as a result of migration of H-atom ~~from~~ between the Nitrogen atom and the oxygen atom, it represents a special case of Amido-Imido tautomerism.

(Uracil) Lactum





④ Ket-enol tautomerism

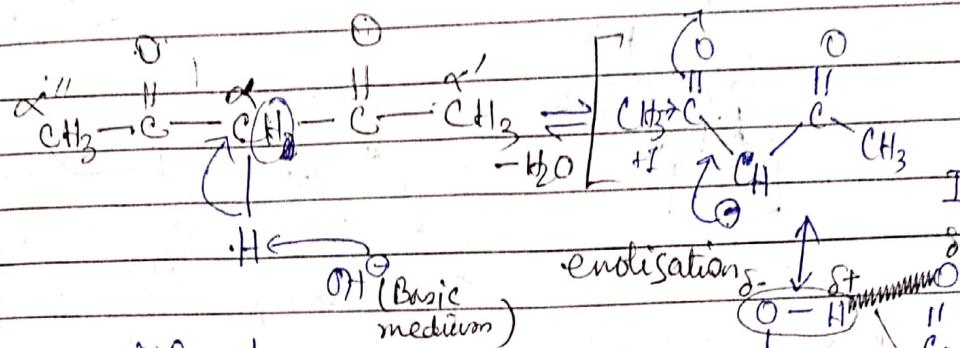
→ In organic chemistry, keto-enol tautomerism refers to a chemical equilibrium between a keto form (a ketone/aldehyde) and an enol (an alcohol), when a carbonifl (aldehyde) compound containing α -Hydrogen atom is treated with either acid or basic medium, this type of isomerism occurs, the interconversion (keto to enol) / (enol to keto) involves the movement of α -Hydrogen atom and the reorganisation of bonding electrons, then the isomerism qualifies as tautomerism.

It is also known as catiohotropy because this arises due to the exchange of H-atom between two polyvalent atoms, present in the molecule.

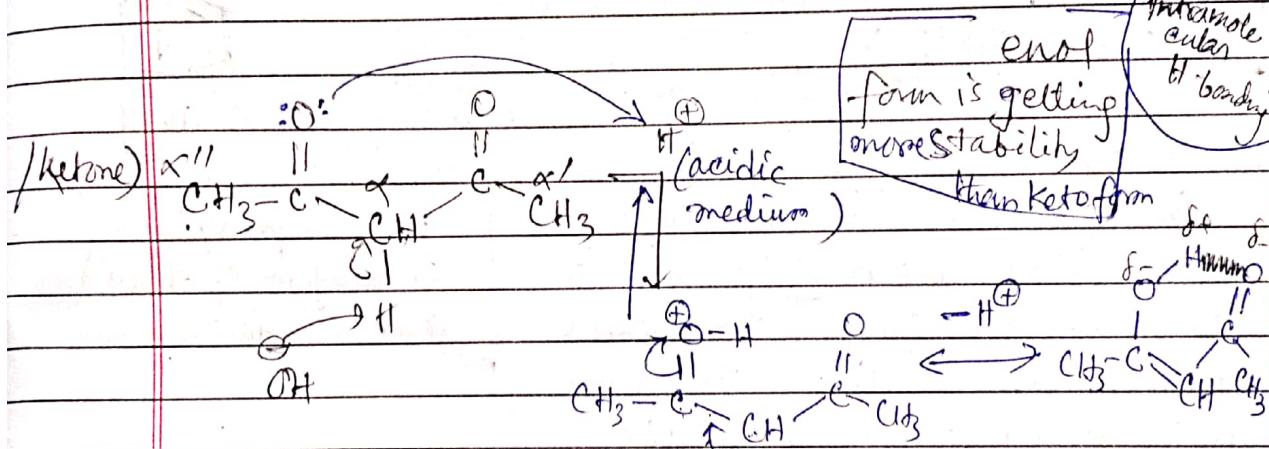
- It is a reversible intramolecular change.
- Separation of tautomeric forms is a bit difficult due to the dynamic equilibrium between two forms.
- However they can be separated by special methods

nature & temp.
→ The factors like solvent, pH, steric hindrance, presence of Ester & Enol etc effects the stability of these two tautomeric forms.

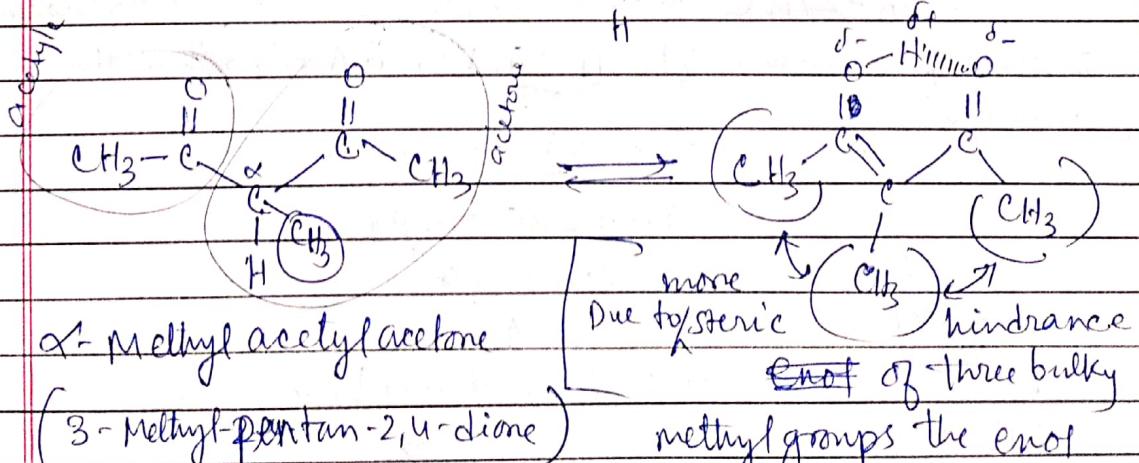
→ The conversion of Keto form into enol form is known as enolisation.



In acetyl acetone
(2,4-pentanedione)



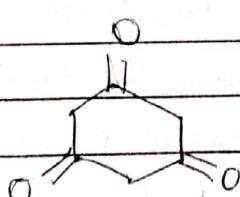
enol
-form is getting
less stability
than keto form



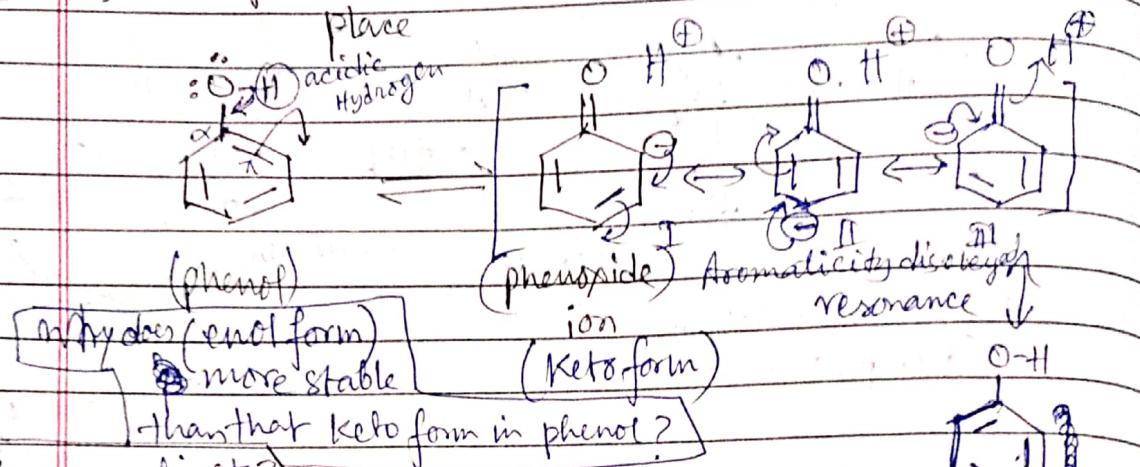
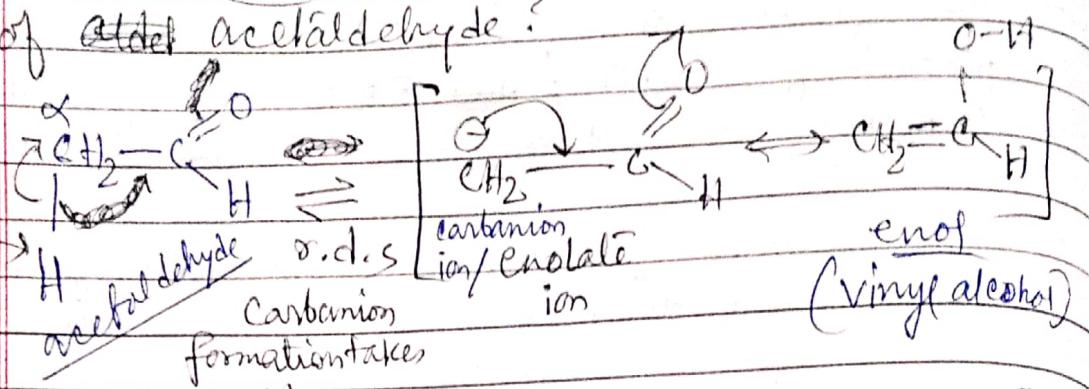
Due to steric
hindrance
enol of three bulky

methyl groups the enol
form ~~become~~ is
destabilised than

that of in case of acetyl
acetone



What's the name & structure of keto-enol tautomerism of aldehyde acetaldehyde?



What's aromaticity?

In enol form of phenol it obeys in Hückel's rule.

A cyclic, planar system in which delocalisation of electron cloud takes place due to conjugation (or resonance) and obeys Hückel's Rule for aromaticity i.e. the system which is aromatic must contains

$$(4n+2)\pi e^- \text{ where } n = 0, 1, 2, 3, 4, \dots \text{ etc. always a true whole no.}$$

In case of benzene, C_6H_6 , has $6\pi e^-$ s within the molecule, i.e.

$$(4n+2)\pi e^- = 6\pi e^-$$

$$4n+2\pi e^- = 6\pi e^-$$

$$\text{When, } n = 2$$

$$4n = 4\pi e^-$$

$$10\pi e^-$$

$$n = 1$$

$$n = 3$$

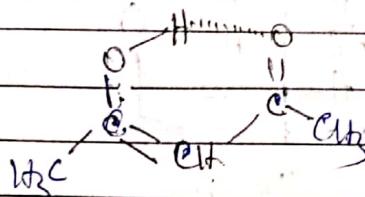
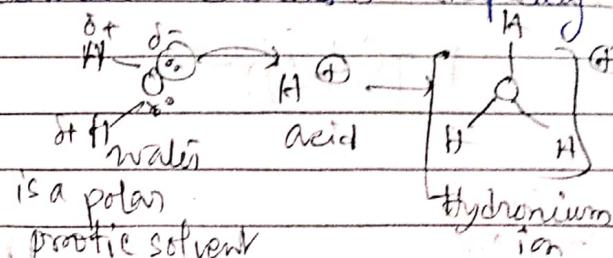
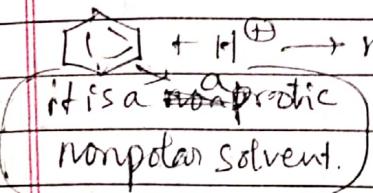
That's benzene has only one ring.

$$14\pi e^-$$

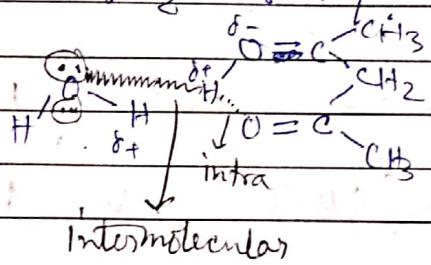
such as - (CN, -NO₂, -COOH, -CH₃, -COOR etc.)

Presence of **EWG** increases the stability of enol, but due to presence of **EDG** like group R (-CH₃, -CH₂, -OH, -NH₂, -Cl, -X, -NR₂, -COOH etc.) stability of enol decreases.

Solvent effect: Solvents can also play an important role in the relative stability of the enol form. For example in Benzene, the enol form of 2,4-pentanedione predominates in a 94:6 ratio over the keto form, whereas the number is almost reversed completely in water i.e. (6:94).



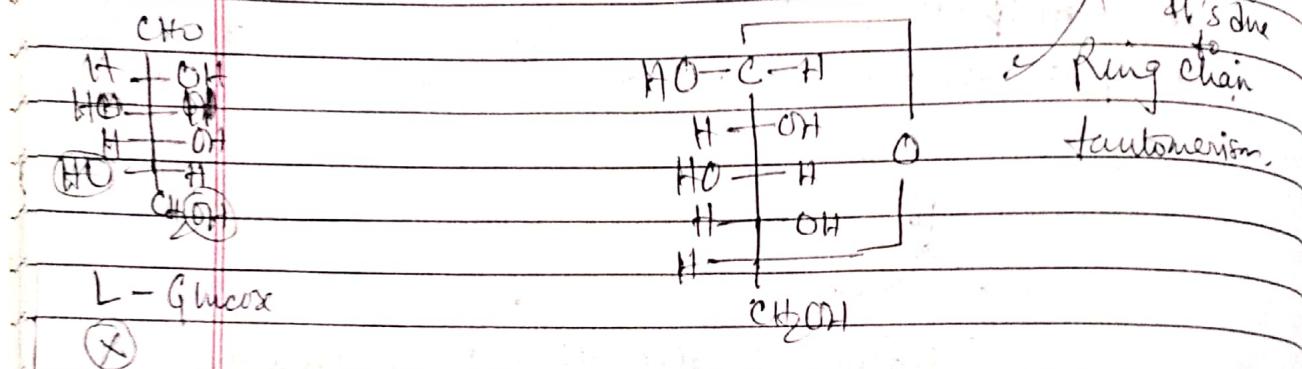
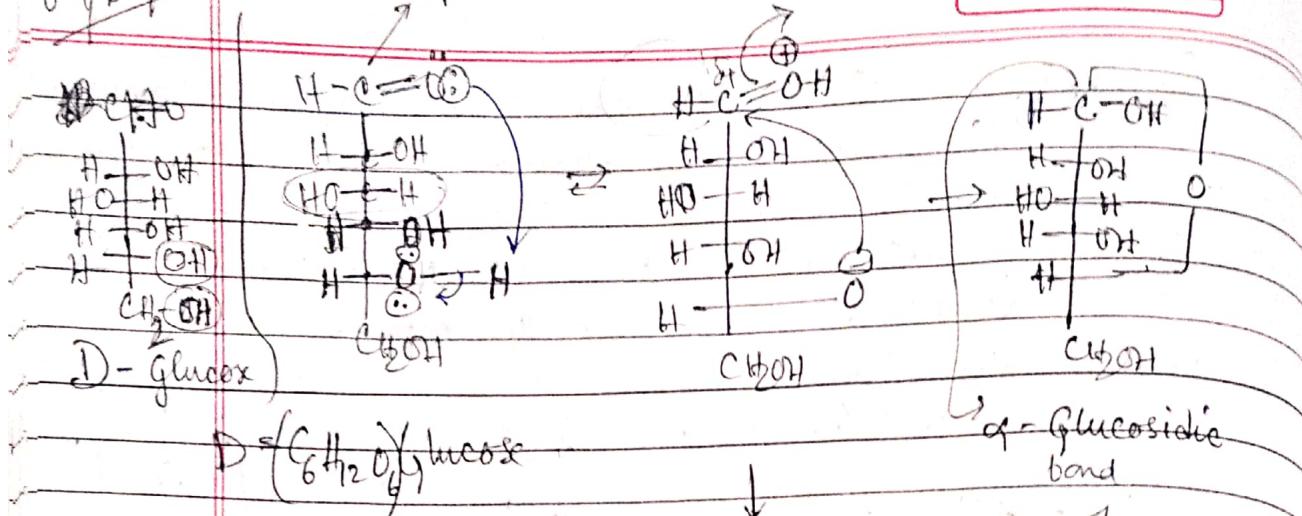
Enol form of 2,4-pentanedione is less stable in water than in benzene. Why?



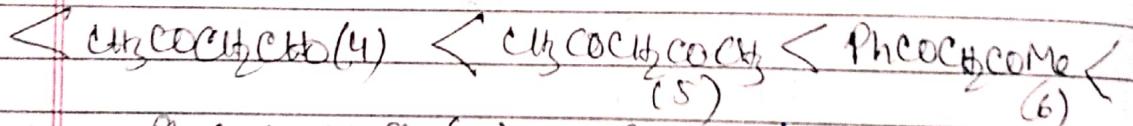
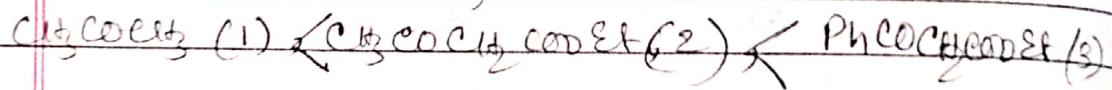
In a polar protic solvent like water, the lone pair will be involved in H-bonding with the solvent making it less available to H-bonding.

In a polar protic solvent like water, the lone pair will be involved in H-bonding with the solvent making them less available to H-bonding with the enol form.

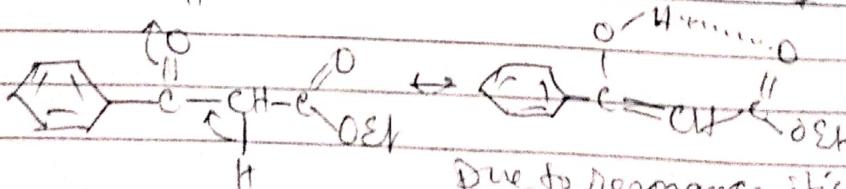
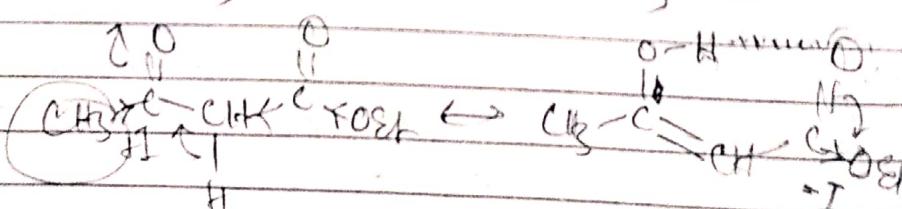
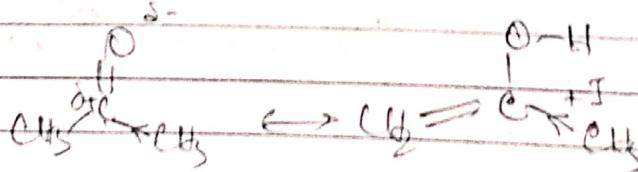
Q/DI/2)

sp² β -Glucosidic bond

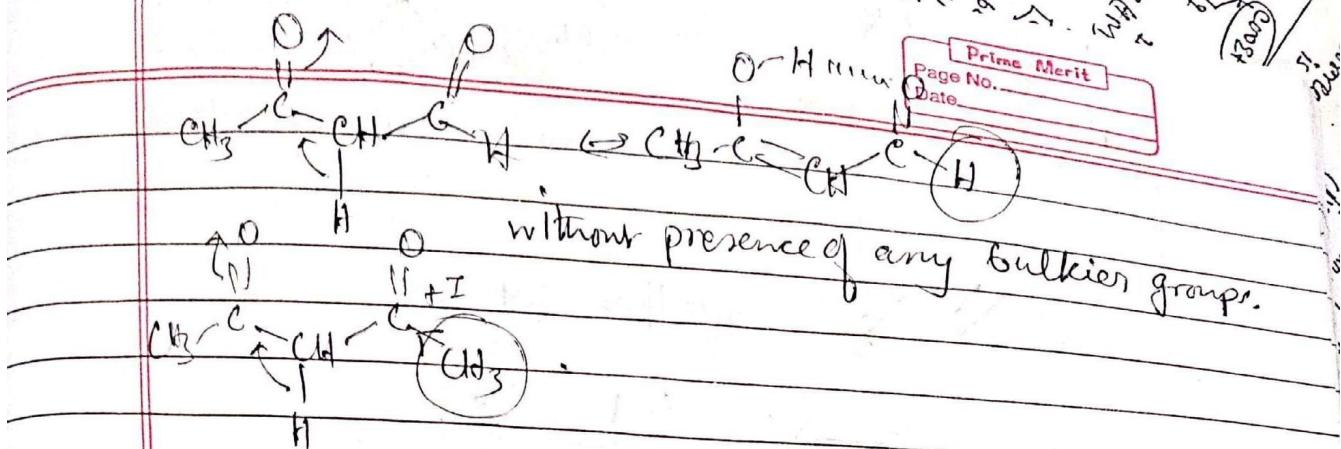
In Keto-Enol tautomerism, Enolisation is in the order



$\text{PhCOCH}_2\text{COPh}$ (7) — Reason for such order of enolisation is because of (Buck effect) of the group as follows: $-\text{COOH} < -\text{COR} < -\text{COCl}_2 < -\text{CHO}$



Due to resonance it's more stable.

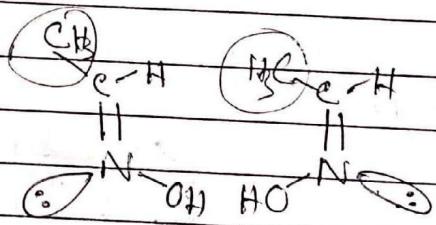
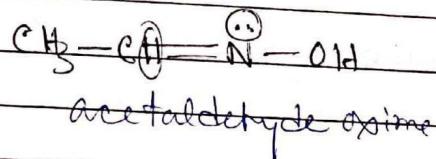


Types of Stereo isomerism

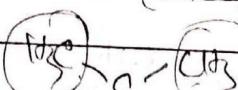
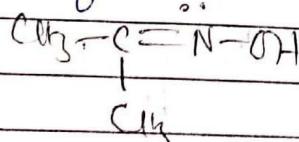
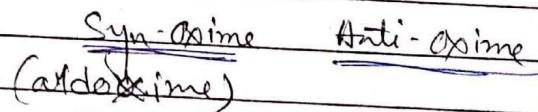
■ Geometrical Isomerism → They've the same structural formula but they differ in the spatial arrangement of atoms or group of atoms, about ($C=C$, $C=N$, $N=N$) double bond.

cis-trans Notation

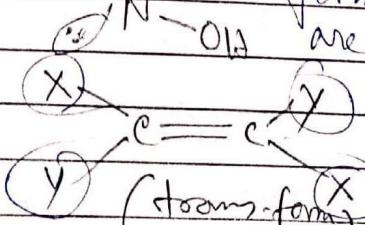
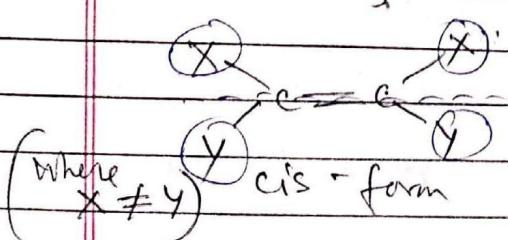
Since free rotation about the double bond is restricted, the cis- and trans-forms aren't interconvertible (except under extreme conditions) & hence can be separated from each other.



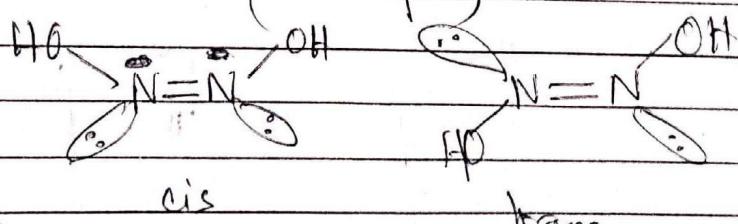
But there is
NO cis/trans isomerism
in case of Ketoxime.

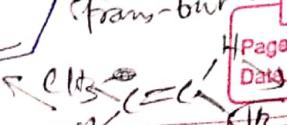
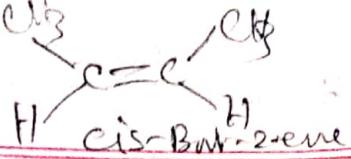


it exists only in one form as 2 CH_3 groups are at the same C -



In azo Compds



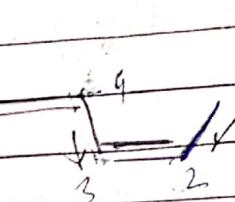
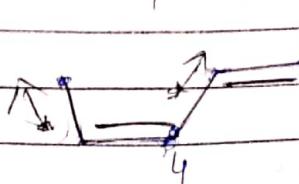


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Geometrical isomerism is also exhibited by dienes and cyclic compounds.



2Z,4E

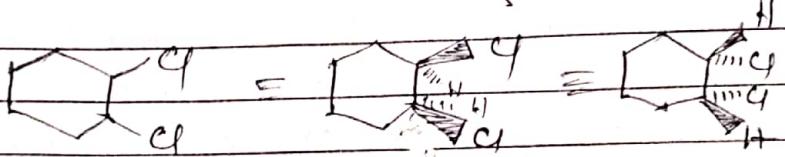
Z = zusammen

E = Entgegen

1 trans

trans

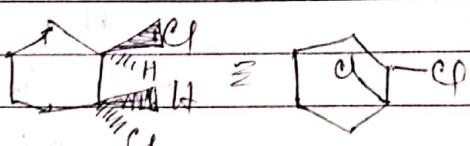
cis



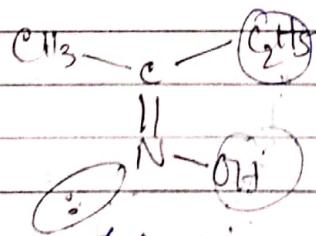
cis-1,2-Dichloro Cyclohexane

$\text{C}=\text{N}-\text{OEt}$

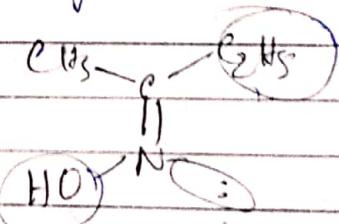
oxime



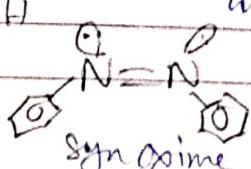
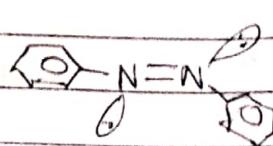
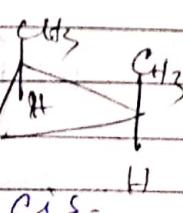
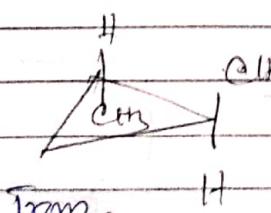
Trans - 1,2-Dichloro Cyclohexane



w.r.t. to ethyl group



w.r.t. to ethyl group



Property

- Stability: cis < trans

- Reactivity: trans < cis

- Dipole moments (μ):

trans ($\mu = 0$) < cis.

- Polar: trans < cis.

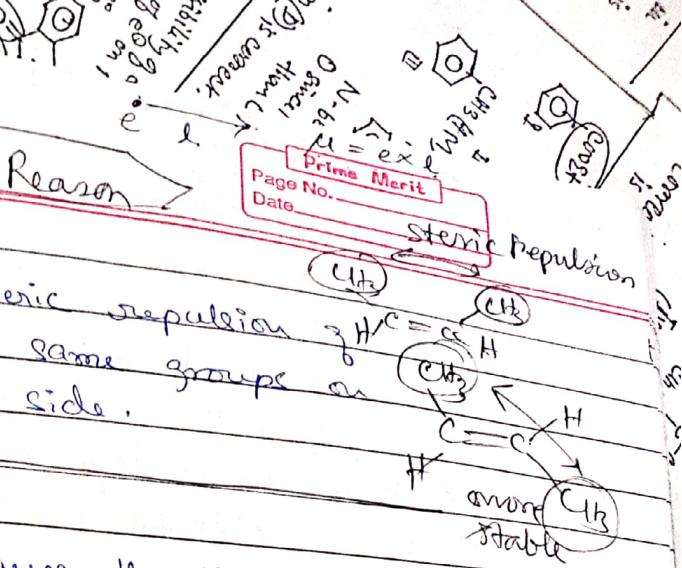
- Melting points:

cis < trans.

- Solubility, viscosity and refractive index:

trans < cis.

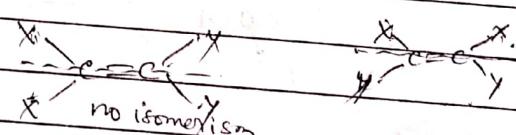
- Boiling points:



Because the dipole moments cancel in trans. $H \delta^+ + \delta^- Cl$
 $\delta^- Cl + \delta^+ Cl \quad \mu_{net} = 0$
 $\delta^+ C=C \quad \mu_{net} = 0$
 $\delta^+ C=C \delta^- + \delta^- Cl \text{ trans. } H \quad \mu_1 = \mu_2 = 0$
H more H dipole moment

trans has stronger intermolecular forces of attraction as it fits more closely in the crystal lattice due to its symmetry.

Molecules of cis are weakly held in crystal lattice.

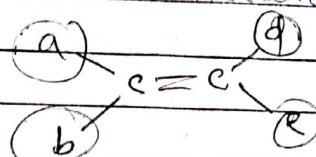


As cis has higher dipole moment (more polar).

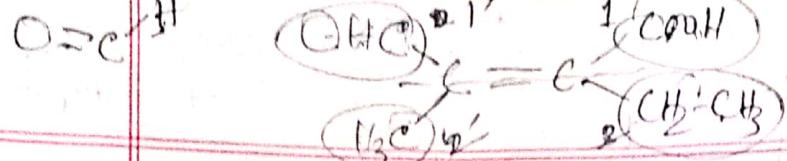
E-Z System of Nomenclature

For highly substituted alkenes having 4 different atoms or groups attached to C=C bond, cis and trans designations cannot be used.

In such cases E-Z notation is used.



Priority System was developed by Cahn, Ingold, & Prelog (CIP)



Which is used to assign E-Z nomenclature. According to this system

$-I > -Br > -Cl > -O > -N > -C > -H$ (Priority ↓ as atomic number ↑)

→ In case of isotopes of the same element, mass no. to be considered e.g., ${}^2D > {}^1H$,
 (Deuterium) (Protium)

$Cl^{37} > Cl^{35}$ etc.
 (a) (a)

$\rightarrow -Br > -SO_3H > -OH > -NH_2$

$-C_6H_5OH$ In the groups, priority is decided

decided on the basis of atomic no. of first atom of the group. But if the first atom is same in the groups, then the second atom or the subsequent atoms of the group are considered.

$-COOH > -CH_2-CH_3 > -CH_3$



$> C=O$

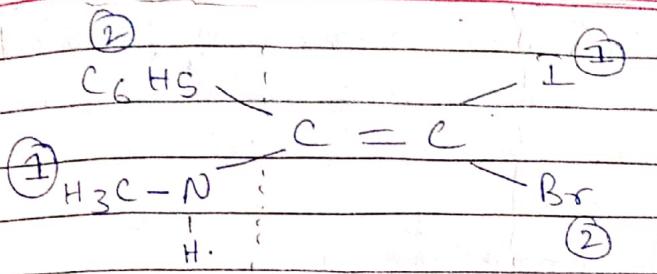
$-C\equiv N$

$> C-O$

$\begin{array}{c} NO \\ | \\ -C-N \\ | \\ N \end{array}$

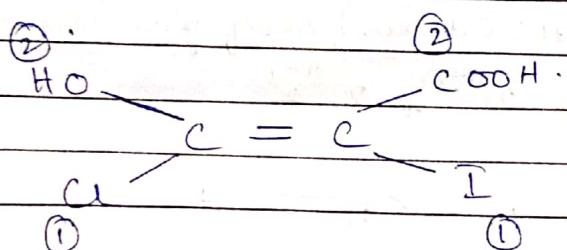
A doubly or triply bond atom is considered equivalent to 2 or 3 such atoms.

E from German word, Entgegen (means across or opposite) is assigned to an isomer in which high priority atoms or groups are on the opposite side.



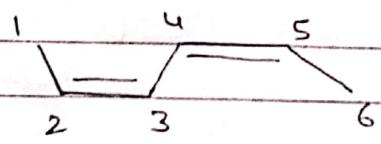
E - isomers.

→ 2 form German word, zusammen (meaning together) is assigned to an isomer in which high priority atoms or groups are on the same side.

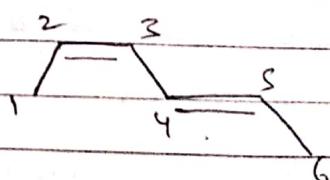


Z isomers

In case of dienes, positions are also mentioned eg:



(2Z,4Z)-isomer

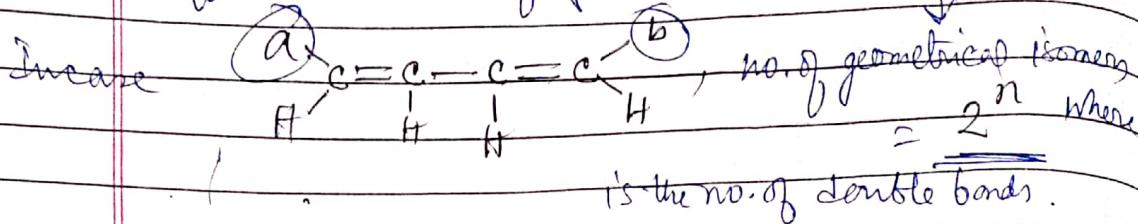


(2Z,4E)-isomer

N.B : No. of geometrical isomers = 2^n in polyenes. Here $n = 2$, so no. of geometrical isomers = $2^2 = 4$.

Case I

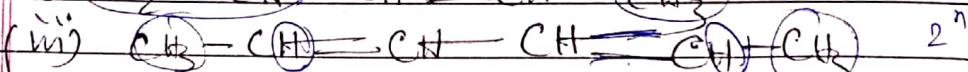
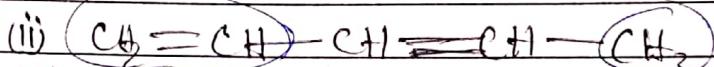
How can we find (or determine) the no. of geometrical isomers
if a compd has 2 double bonds in which the 2 ends are different then no. of geometrical isomers



Case II: if $a=b$ identical elements in both ends
then no. of geometrical isomers

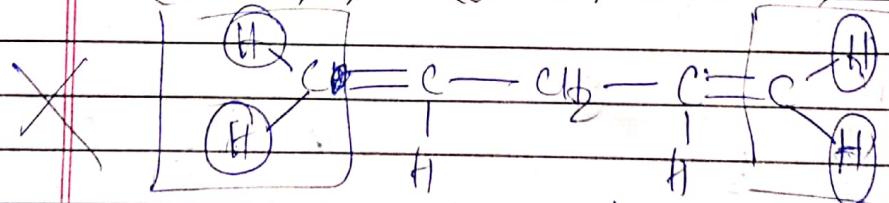
$$(i) 2^{n-1} + 2^{\frac{n-1}{2}-1} \text{ when } (n = \text{even no.})$$

(ii) for $n = \text{odd no.}$, no. of geometrical isomers (iii) $2^{n-1} + 2^{\frac{n-1}{2}}$

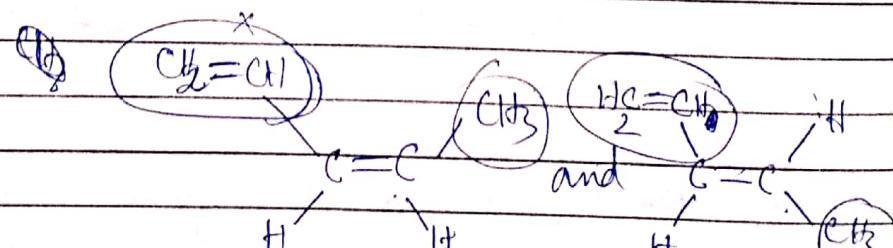
~~HW~~

The no. of possible geometric isomers for the above compds respectively are :-

- (a) 0, 2, 4 (b) 2, 2, 4 (c) 0, 3, 3 (d) 0, 2, 3



no geometrical isomers possible



$$2^1 + 2^{\frac{1-1}{2}} = 2^1 + 2^0 = 2$$

$$= 1 + 1 = 2$$

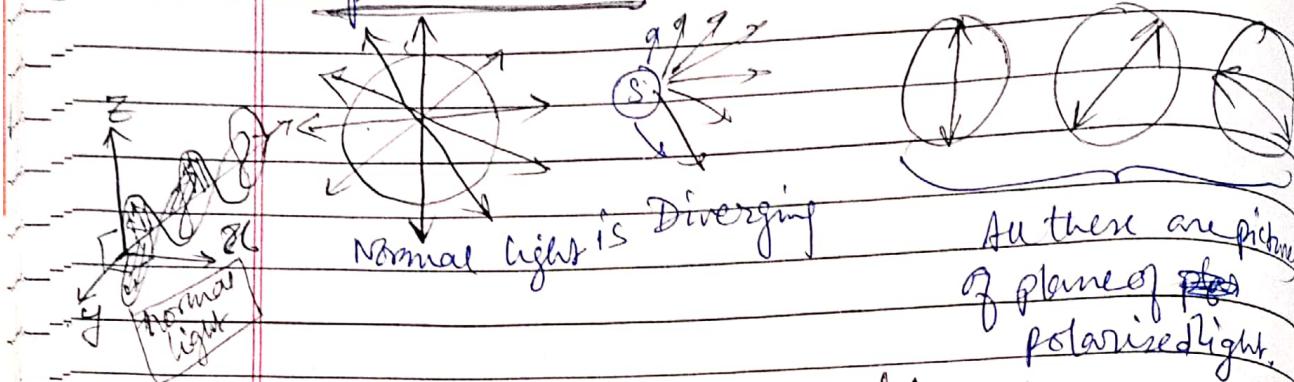
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Optical Isomerism

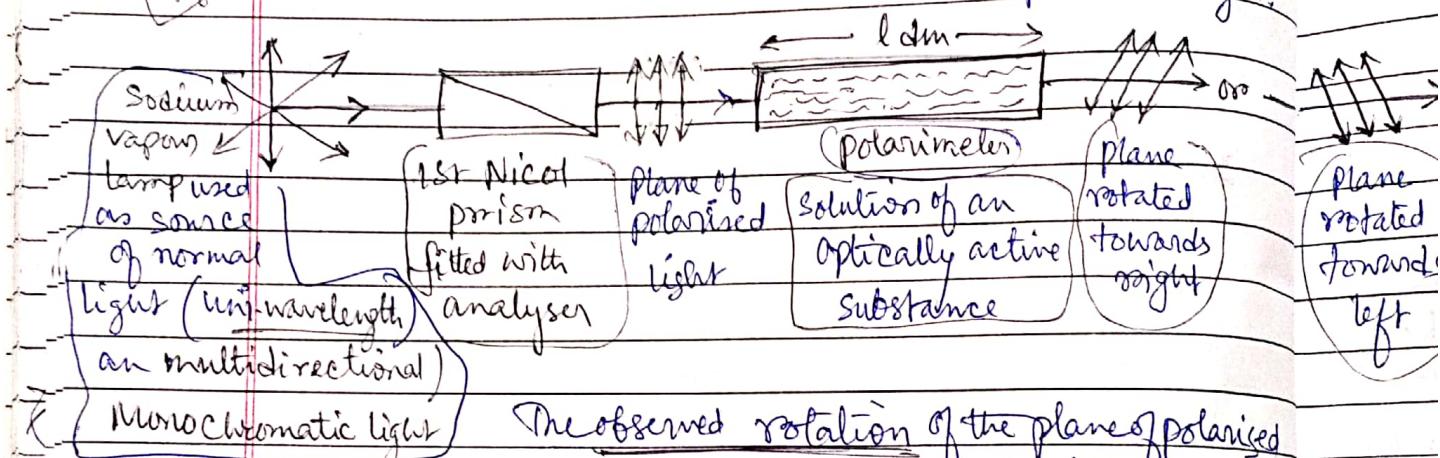
certain substances possess the property to rotate the plane of polarised light, such substances are called

optically active substances & this phenomenon is called optical activity.



Normal light is Diverging

All these are pic. of plane of pol. polarized light.



Monochromatic light The observed rotation of the plane of polarized

light determined with the help of polarimeter produced by a solution depends on :-

- The amount of the substance in tube
- On the length of the solution examined
- The temp. of the experiment.
- The wavelength (λ) of the light used.

The measurement of optical rotation is expressed in terms

of specific rotation $[\alpha]_D^t$, this is given by the following relation :

$$[\alpha]_D^t = \frac{\alpha_{\text{observed}}}{l \times C}$$

where

α = Observed angle of rotation

$[\alpha]_D^t$ = Specific rotation determined at $t^\circ\text{C}$, using D line of Sodium light.

l = length of solution in decimeters
 c = concentration of the active compd. in g/m³

e.g.: The specific rotation of amyl alcohol (2-methylbutanol) at 25°C for D-line of sodium light is given by

$$[\alpha]_D^{25^\circ} = -5.756^\circ$$

(-) Negative sign indicates that the rotation sign is towards the left, while (+) positive sign means the direction of rotation is towards right. The rotation may be different in different solvents and this needs to be mentioned while reporting the specific rotation.

Thus

$$[\alpha]_D^{25^\circ} = (+) 24.7^\circ \text{ (in chloroform)}$$

or (CHCl₃)

Plane rotated forwards left

Condition for Optical activity

The (minimum) condition for a compd. to show optical activity is molecular dissymmetry i.e. absence of symmetry like -

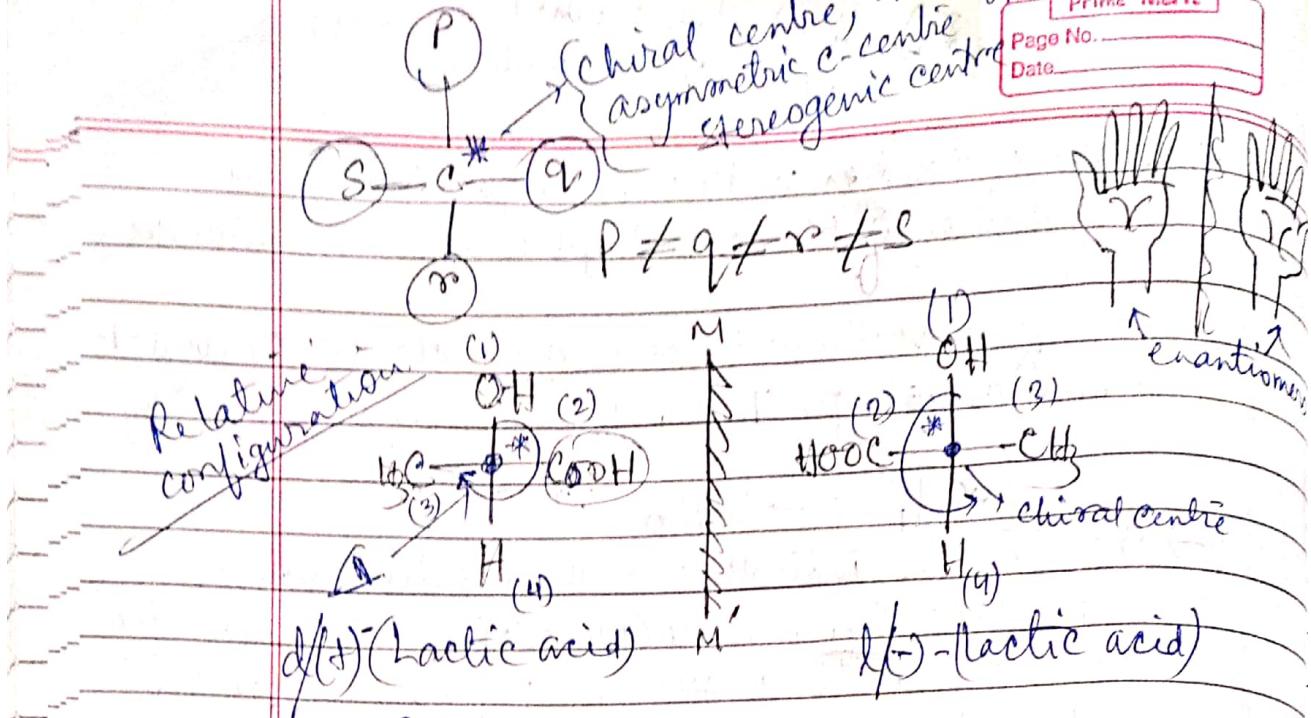
- (i) plane of symmetry
- (ii) alternating axis of symmetry
- (iii) centre of symmetry
- (iv) simple axis of symmetry

A molecule which doesn't possess any σ is called asymmetric.

A molecule which doesn't have plane of symmetry (σ plane) and centre of symmetry is called dissymmetric.

What is Chirality? A compound which is non superimposable to its mirror image is called chiral while a compd. which is superimposable to its mirror image is called achiral.

All dissymmetric (or asymmetric) compds. are chiral & vice-versa.

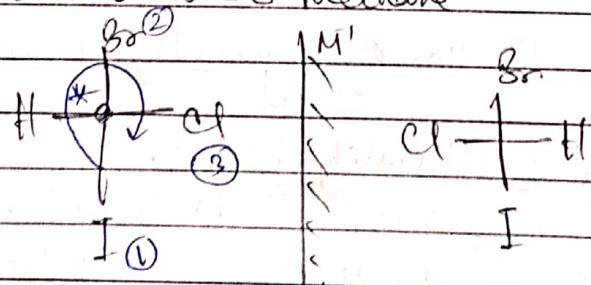


enantiomers
enantiomorphs

These two are known as enantiomers =
Non-superimposable mirror image relationship
Optical isomers are known as enantiomers]

certain organic compds when their solutions are placed in the path of a plane polarised light, have the remarkable property of rotating its plane through a certain angle which may be either to the left (l) to the right. This property of a substance of rotating the plane of polarized light is called Optical activity and the substance possessing it is said to be optically active.

Bromo Chloro Iodo methane -



D or (+) \rightleftharpoons Bromochloro iodomethane

According to Van't Hoff's rule total no. of optical isomers should be 2^n , where n is the no. of chiral centre.

All the physical & chemical properties of enantiomers are same except two factors :

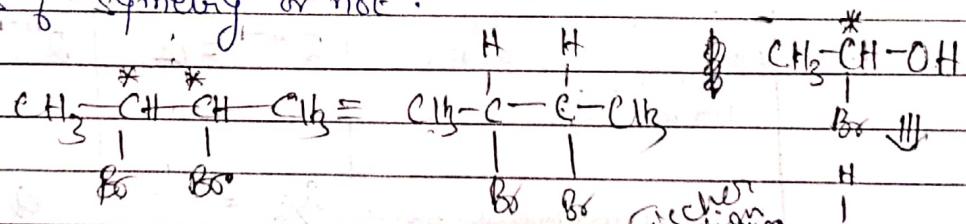
(i) They rotate PPL to the same extent but in opposite direction. One which rotates PPL in clockwise direction is called (dextro rotatory) and is designated by (+) or (d).

and the one which rotates PPL in anti clockwise direction is called laevo rotatory (left) and is designated by (-) or (l).

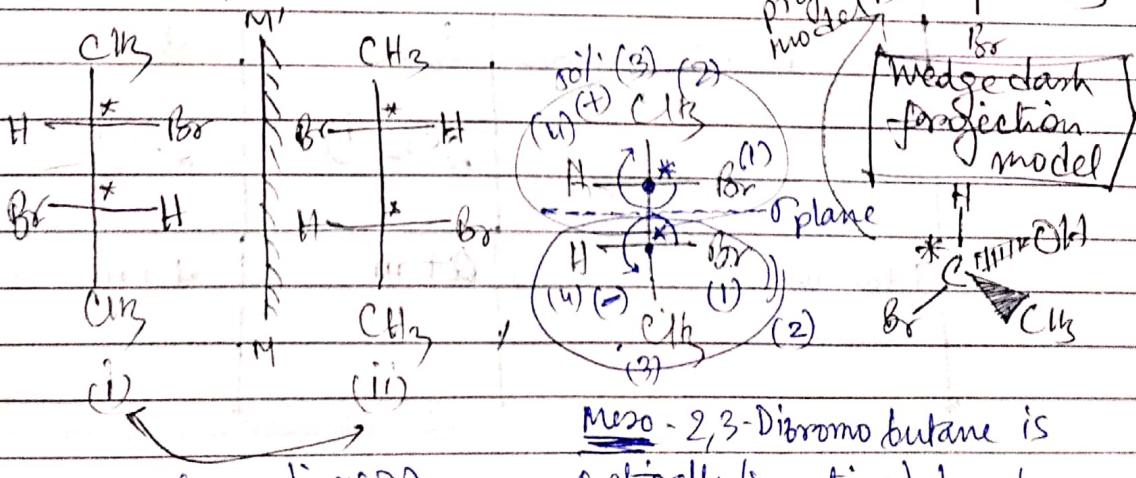
(ii) They react with optically active compounds with different rate.

Q Optical Isomerism in compounds having more than one chiral centres.

If an organic molecule contains more than one chiral carbon, then the molecule may be chiral or achiral depending whether it has elements of symmetry or not.



2,3-Dibromobutane



Meso-2,3-Dibromo butane is optically inactive due to planar symmetry or (O-plane) which makes an internal compensation.

Formula to calculate the number of optical isomers :

(i) When the molecule is asymmetrical

Chiral molecules have n number of asymmetric carbon atoms and is not divisible into two equal values.

- Number of optically active forms = $2^n = a$.

- Number of enantiomeric pairs = $\frac{a}{2}$

- Number of racemic mixtures = $\frac{a}{2}$

- Number of meso-forms (m) = 0.

- Total number of optically active isomers = $a + m$.

When the molecule is symmetrical

No. of optically active forms (a)

No. of enantiomeric forms

No. of racemic mixtures

No. of meso-forms (m)

Total no. of configurational isomers

Case I

(n = even no.)

$$2^{n-1} = a$$

Case II

(n = odd no.)

$$2^{n-1} - 2^{\frac{n-1}{2}} = a$$

$$\alpha_2 =$$

$$\alpha_2$$

$$\alpha_2 =$$

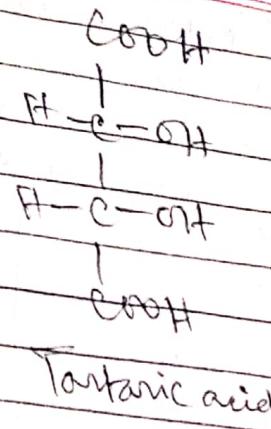
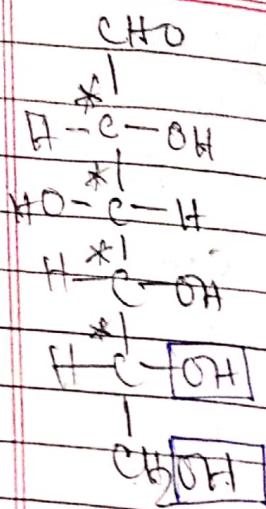
$$\alpha_2$$

$$2^{\left(\frac{n}{2}-1\right)} =$$

$$2^{\frac{(n-1)}{2}}$$

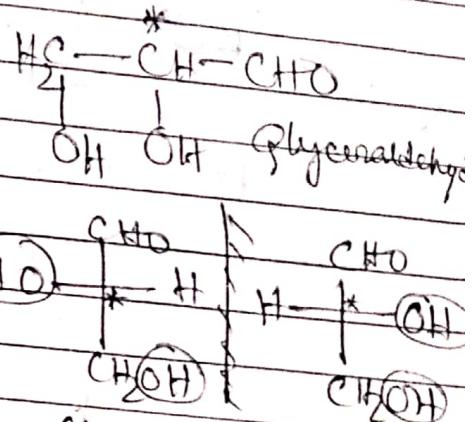
$$a+m$$

$$a+m$$



$\text{C}_6\text{H}_{12}\text{O}_6$

D-Glucose has 4 chiral carbon atoms, then total no. of optically active isomers of glucose = $2^4 = 16$.



L-Glyceraldehyde D-Glyceraldehyde

(a) Relative Configuration

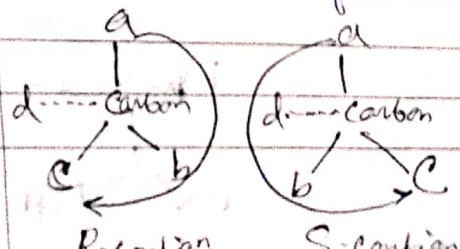
Experimentally determined orientation map between the configuration of two molecules, ~~we also~~ even though we may not know the absolute configuration which is also a 3-D either. Relative configuration is determined by D-L system. This configuration or nomenclature system relies on the fact that the 3-dimensional structures

of glyceraldehyde are arbitrarily given the stereochemical description D-L respectively.

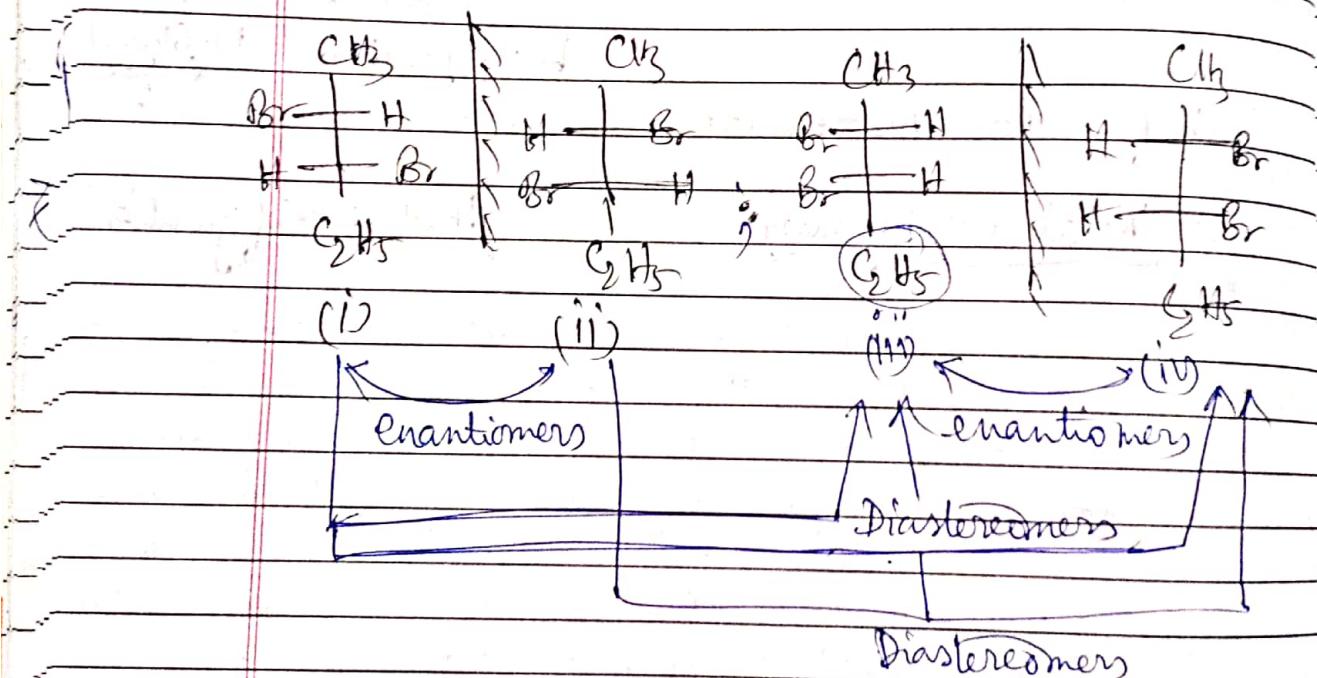
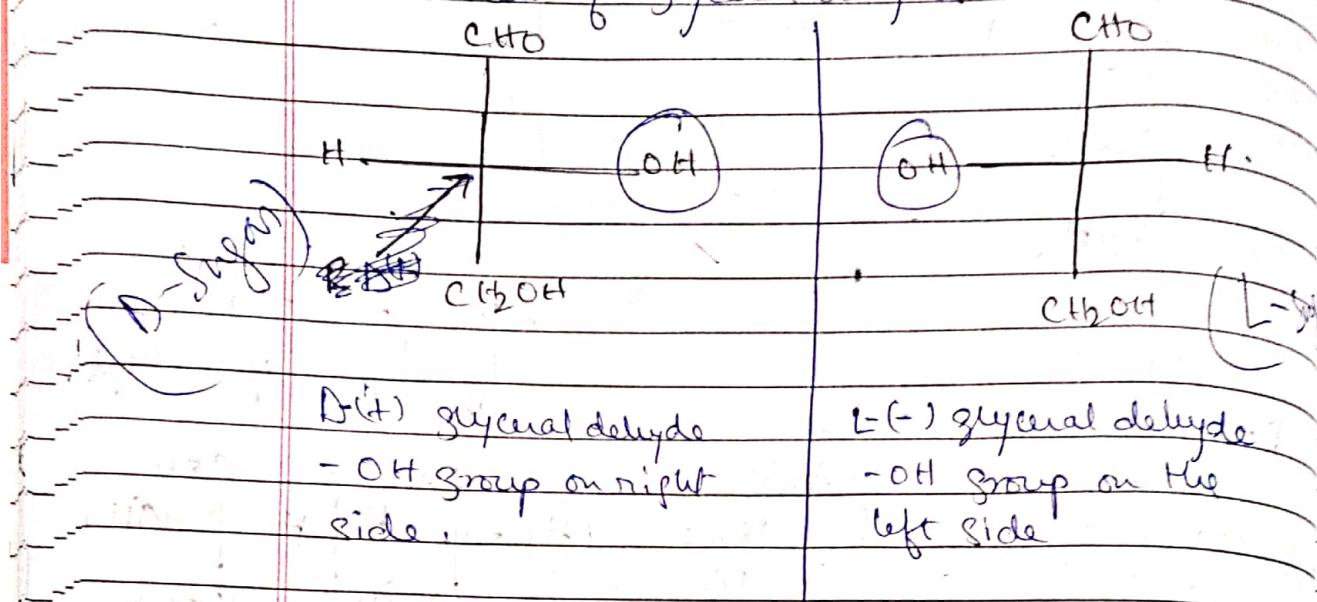
(b) Absolute Configuration

The detailed stereochemistry picture of a molecule, including how the atoms are arranged in space which is also a 3-D dimensional representation of optically active compounds, also said to be R-S system.

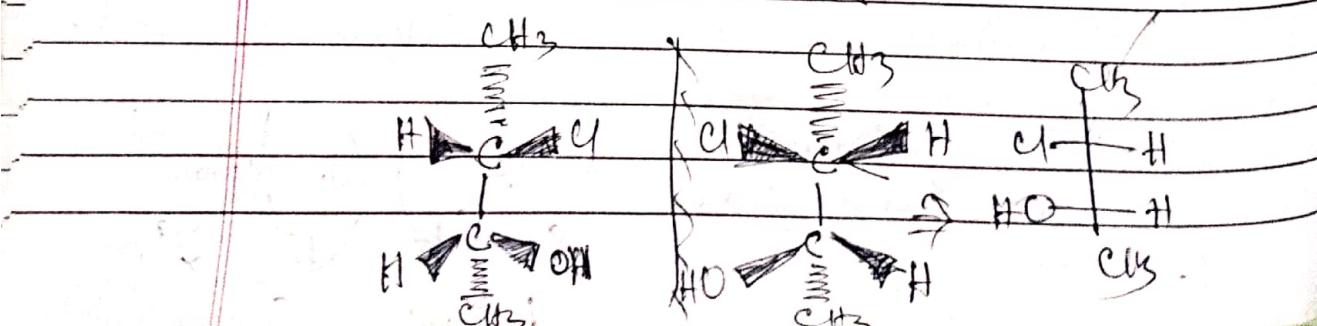
R → Rectus or Right handed.
S → Sinister or left handed.



D-L system (Relative configuration) This method is used to relate the configuration of Sugars and amino acids by the help of Enantiomers of Glyceraldehyde.



Diastereomers are - no mirror image relationship of optical isomers are called diastereomeric.



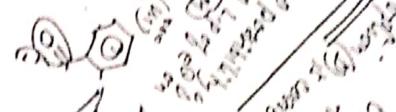
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Nomenclature

Symmetry

Ponemic

Racemic mixture.

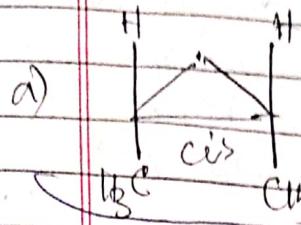


Boat form

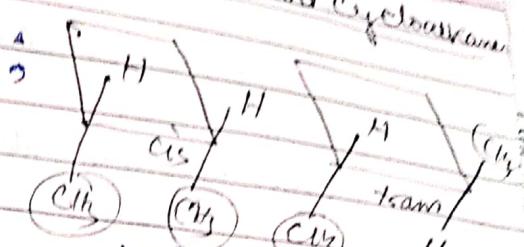
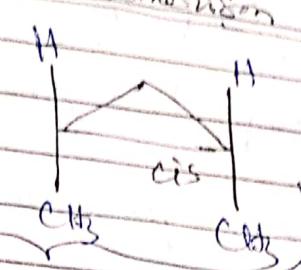
Petroleum ethers
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Geometrical isomerism

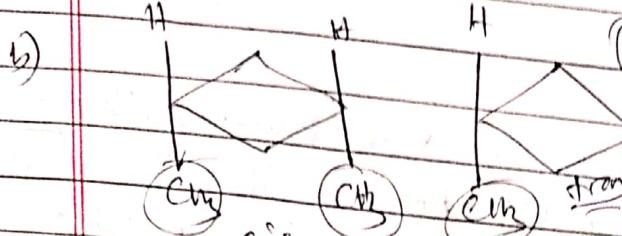
for 1,2-dimethylcyclohexane



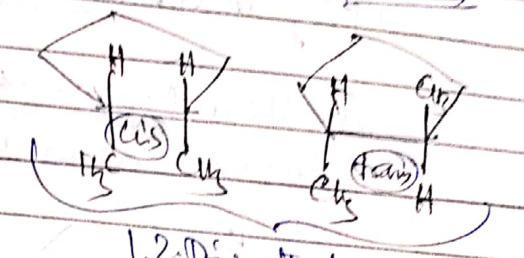
1,2-Dimethylcyclohexane



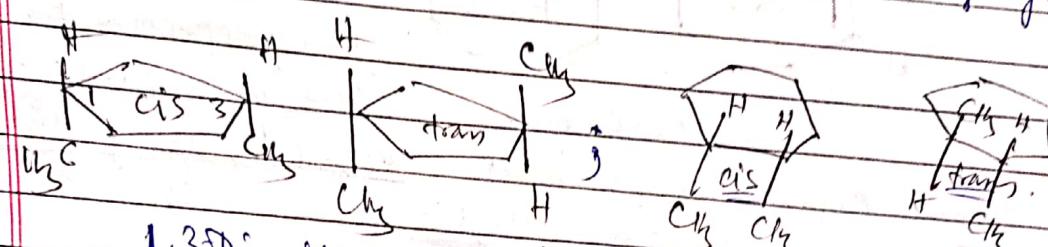
1,2-Dimethylcyclohexane



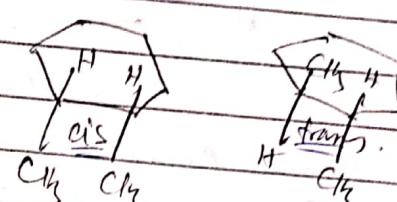
1,3-Dimethylcyclohexane



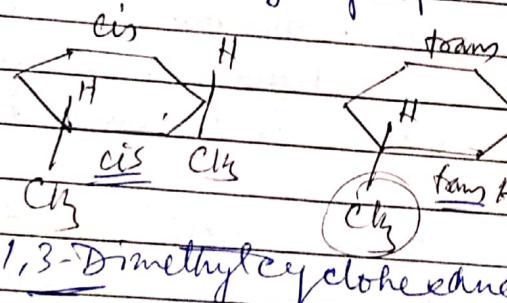
1,3-Dimethylcyclohexane



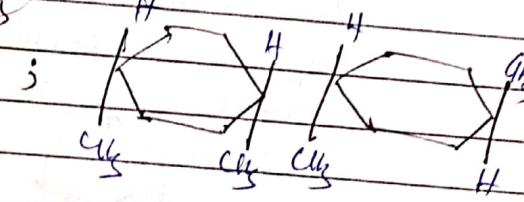
1,4-Dimethylcyclohexane



1,4-Dimethylcyclohexane

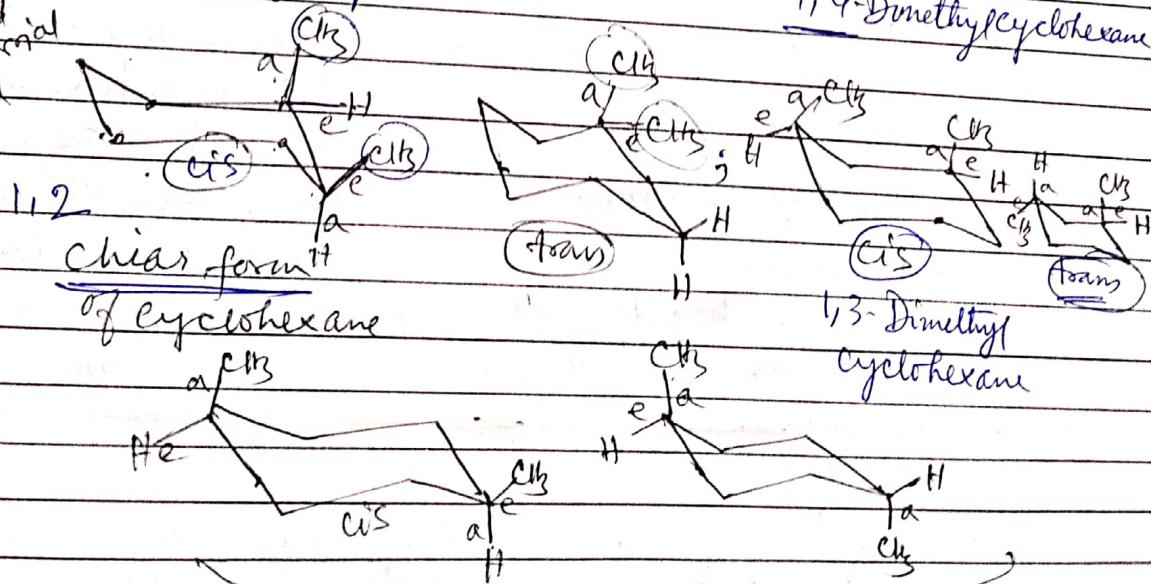


1,2-Dimethylcyclohexane



1,2-Dimethylcyclohexane

a axial bond
an equatorial bond

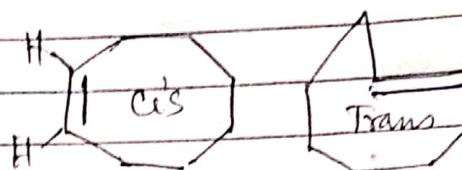


1,4-Dimethylcyclohexane

- Disubstituted Cyclopropane has only 1 pair of geometrical isomers
- Cyclobutane & cyclopentane show 2 pairs of isomers
1,2 & 1,3
- Cyclohexanes show 3 pairs of geometrical isomers
1,2; 1,3 and 1,1

(ii) Cycloalkenes

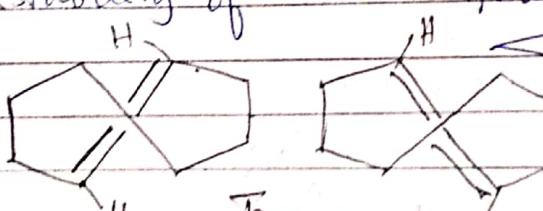
Smallest cycloalkene that can exist, either as the cis-trans-isomer is Cyclooctene. It is the smallest cycloalkene in which the trans-isomer is stable at room temp. (compared to cyclopropene for cis)



Cyclooctene

trans-Cycloalkenes have a longer bridging distance between the two allylic carbons than their respective cis-Cycloalkenes.

As a result, 8-carbons is the minimum ring size required to form trans-Cycloalkene without incurring severe angle strain, which is the cause for the instability of smaller trans-rings.



transcyclopentene

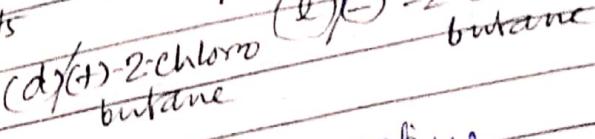
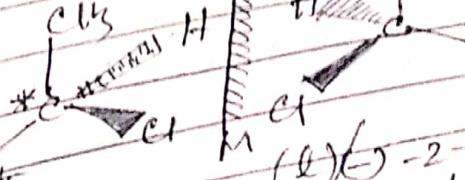
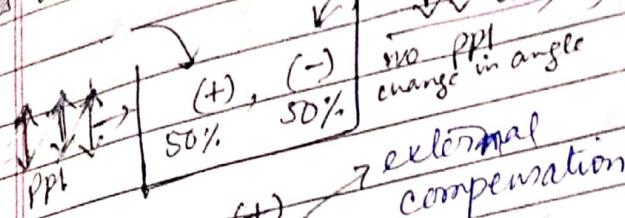
and trans cyclohexene can exist but they're very unstable at room temp.

Most stable trans-conformation is shaped like the 8-C equivalent chair conformation of cyclohexene. Cis-is more common & its most stable stereoisomer adopt various conformation most stable one being shaped ribbon



Resolving agent is separated and recovered pure enantiomers [R,R] and [S,S] from the racemate are separated

What's a racemic mixture?



Racemic mixture
equimolar mixture of two optically active compounds which cannot rotate PPL due to mutual cancellation is known as a racemic mixture.

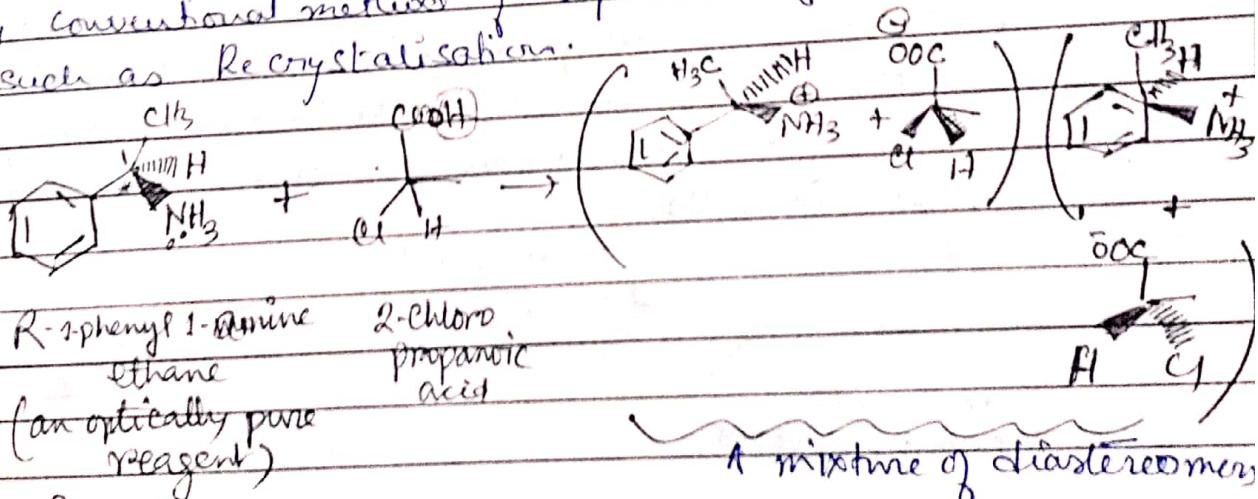
Resolution of Racemic Mixture

Resolution refers to the method of separating a racemic mixture into its enantiomeric constituents.

~~method of separating constituents~~ Chemical method

Mechanical method is Racemic mixture is to react with an enantiomer of another compound, this changes a racemic form into a mixture of diastereomers which have different melting and boiling points and solubilities.

These can be separated from one another by conventional method of separation of compounds such as Recrystallisation.



Separation of R and S isomers of

2-chloropropanoic acid by chemical methods

Separation by an appropriate method e.g. (Recrystallisation)

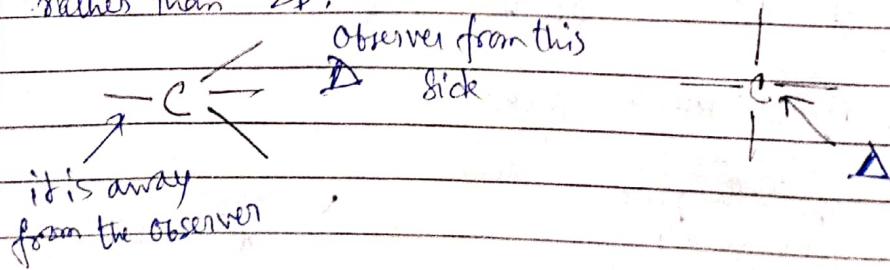
R-S System of Nomenclature (Absolute Configuration)

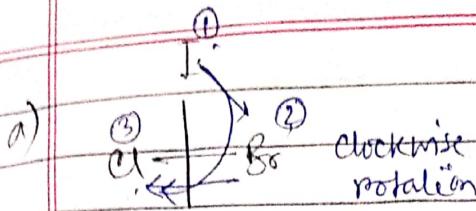
Prime Merit
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Date

This nomenclature was proposed by Cahn, Ingold and Prelog (CIP) this follows the below given sequence rule:

- 1) Atoms directly attached to the chiral atom Carbon are arranged in decreasing atomic no.
- 2) The lowest priority group is brought to the bottom of Fischer projection of two or even simultaneous exchange.
- 3) Then an arrow is drawn from first priority group to second priority group to third priority group.
- 4) If the sequence $1 \rightarrow 2 \rightarrow 3$ traces a clockwise turn, configuration is R.
- 5) If the sequence $1 \rightarrow 2 \rightarrow 3$ traces an anticlockwise turn, configuration is S.

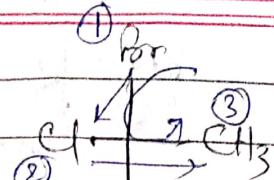
Now before assigning R,S - config. we must ensure that the lowest priority group must be directed away from the observer. The positioning of the lowest priority group down & away from the observer can be assumed easily in 3D rather than 2D.





F
④ (R)

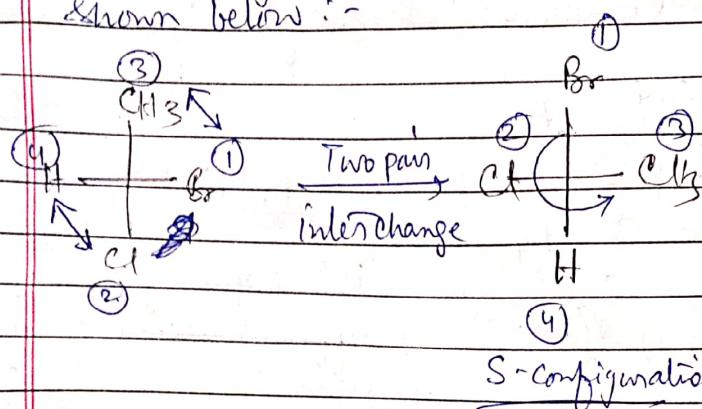
least priority group
is away from the observer



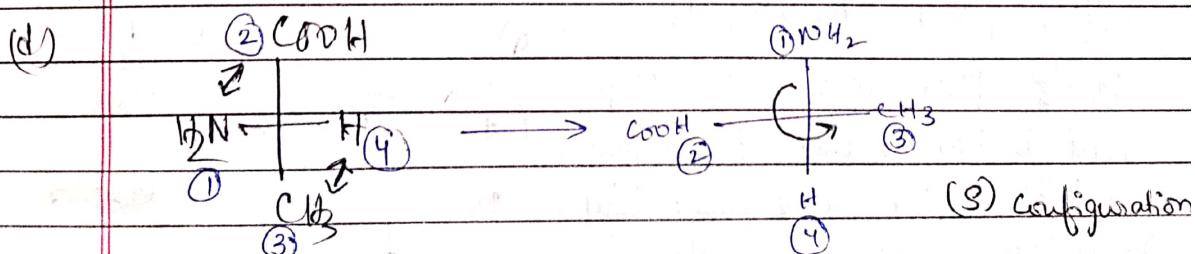
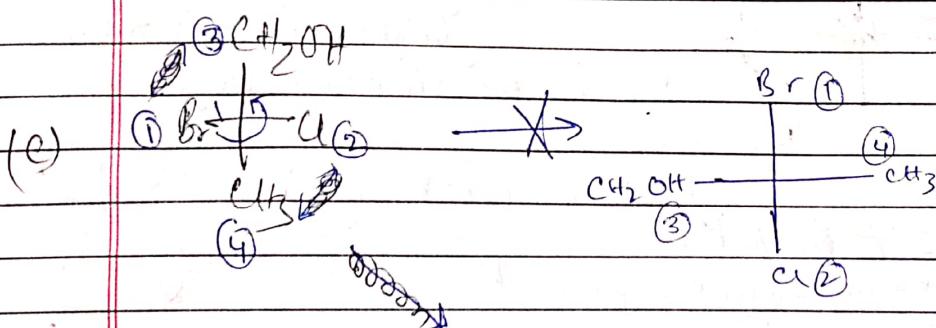
H
④ (S)

lowest priority
group is away from the
observer

(b) When the least priority group isn't away from observer we've to follow the two pair interchange rule as shown below :-

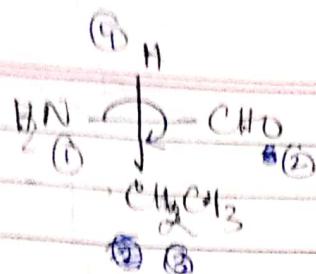


S-configuration



Note :-

The lowest priority group/atom will always be in the vertical (up or down) axis.



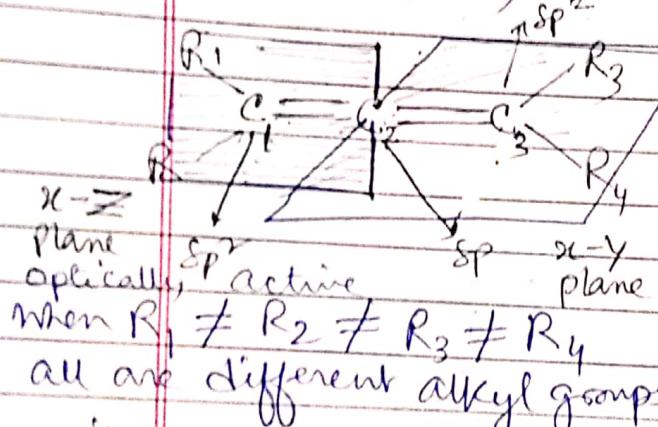
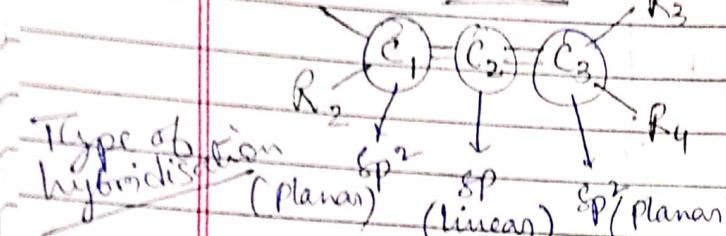
R configuration:

Optically active compds having no asymmetric carbon.

The compds even if they don't have the optically active carbon can still show optical activity.

e.g.: Alkenes, Cumulenes, Biphenyls, Spiro etc.

a) R₁ alkene R₂



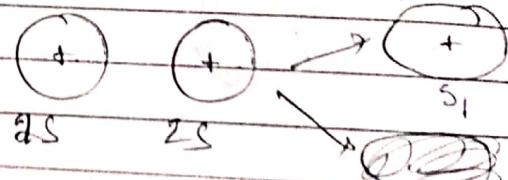
if $R_1 = R_2 = R_3 = R_4$ then

σ -Z plane within the compd will bisect it into two equal halves. So σ -Z plane will be the plane of symmetry & optically inactive.

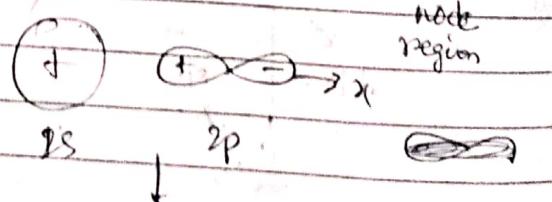
Hybridization

(chemical bonding)

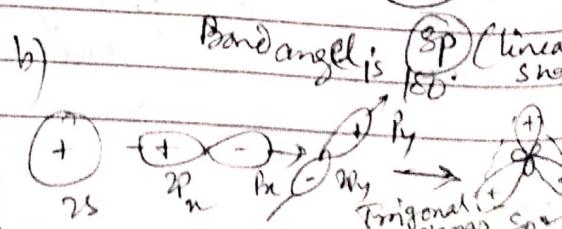
If it's a mixing of ~~same~~ same or different atomic orbitals of each other having ~~completely~~ completely energies to form a new hybrid (or mixed) orbital of ~~the~~ similar energy.

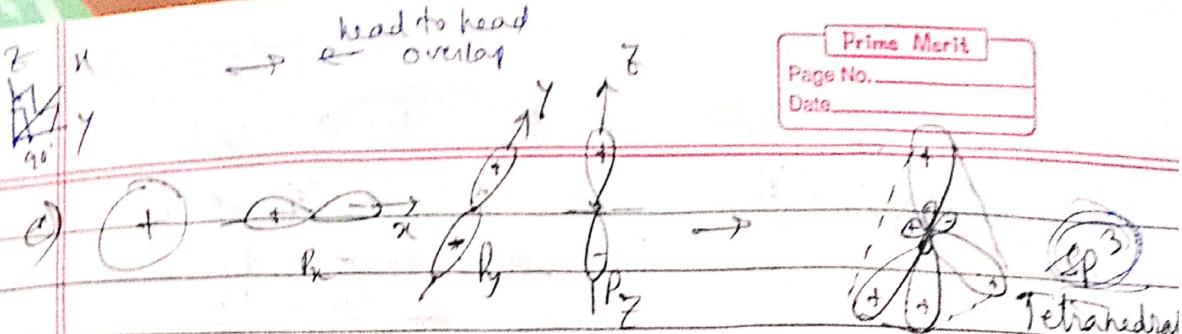


a)

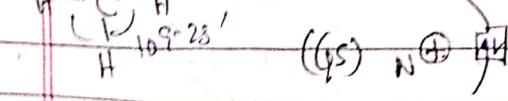
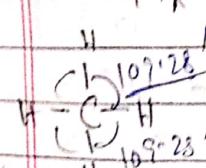


b)

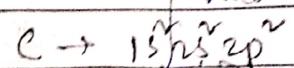




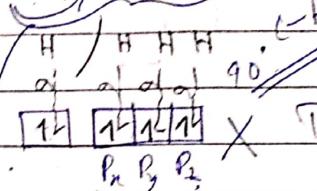
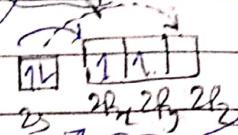
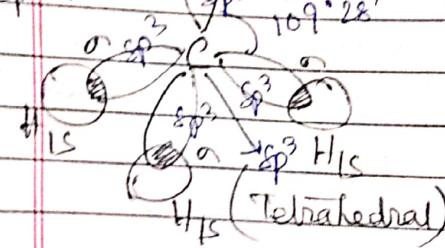
Central C

In CH_4 , C is sp^3 

Valence

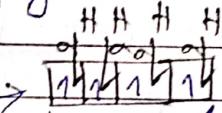


Bond angle

 $109^\circ 28''$ 

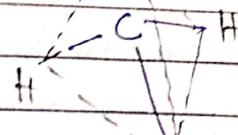
without hybridization
This can't be possible

Mixing of 2s & three 2p orbitals
to form a completely new type
of hybrid orbital sp^3



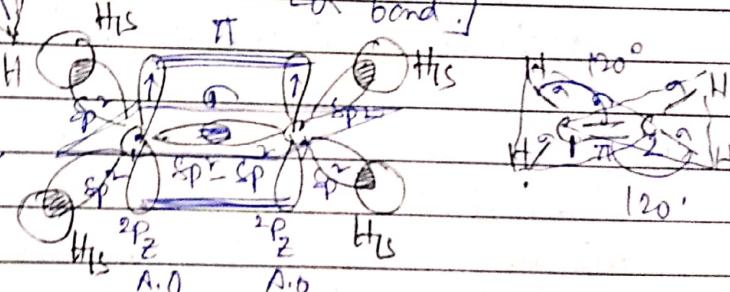
sp^3 hybridized

each C-H bond length is same



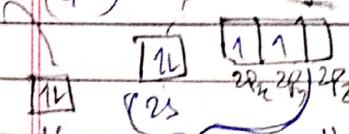
[π bond is weaker than that of
 σ bond]

In Ethene $\text{CH}_2=\text{CH}_2$

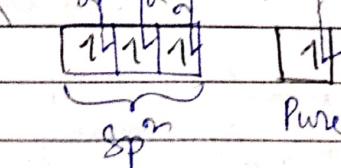


C_1 (G.S)

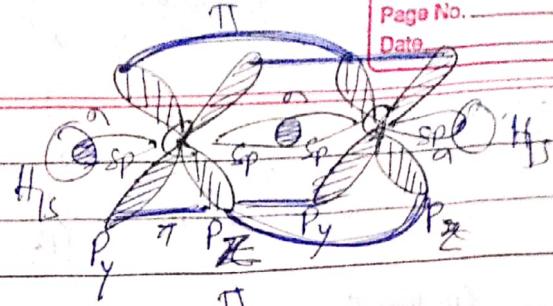
(+)



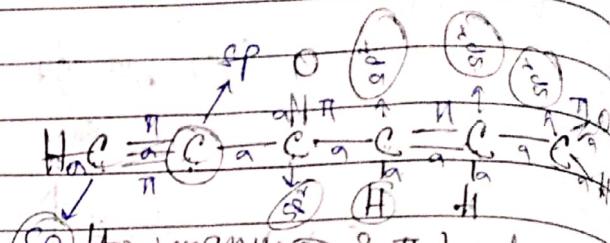
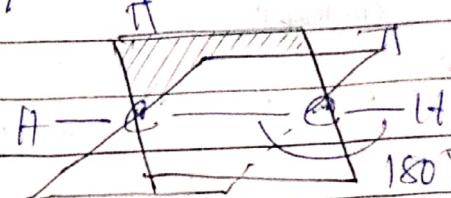
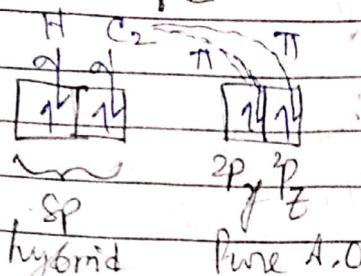
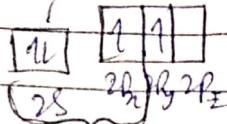
Side by side or
lateral overlapping



(Trigonal planar)

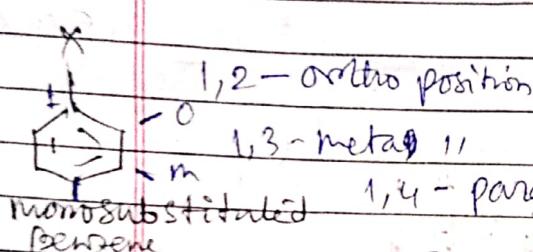


(G.S)

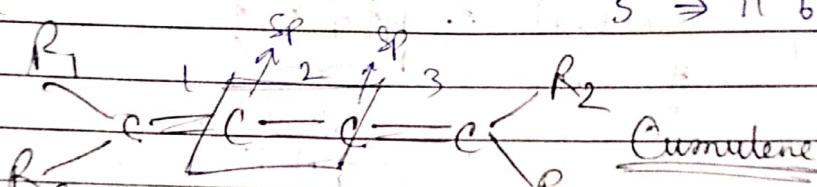


(sp) How many σ & π bonds

present, what are the hybridisation
of each C atom within the
molecule?

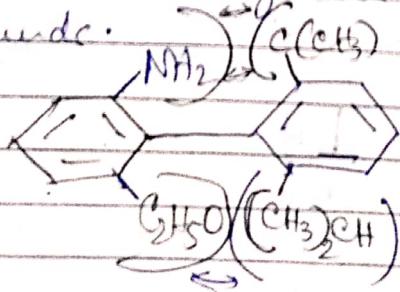


$\pi \Rightarrow \sigma$ bond
 $5 \Rightarrow \pi$ bonds



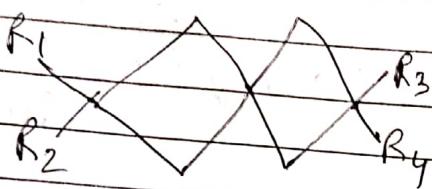
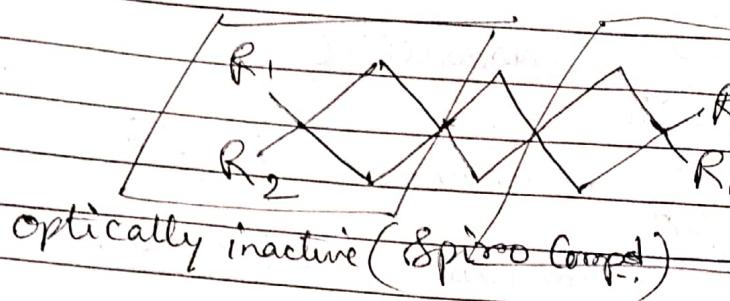
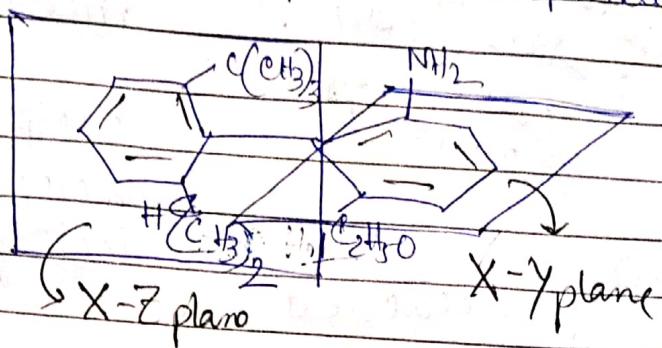
for the cumulative π odd no of double bonds
2 different terminal groups will never show
optical activity due to plane of symmetry.

(C2) for biphenyl compounds having all sp^2 hybridised C-atoms if the ortho substituents are very bulky, then to relieve steric strain, the rotation around C=C bond axis takes place causing loss of planarity of the compound.



Here as the ortho-groups are very bulky, biphenyl rings change their planarity as shown,

now the bulky groups are situated at 90° angle apart, hence now $x-y$ and $x-z$ are the plane of symmetry. Therefore the compound is optically active.

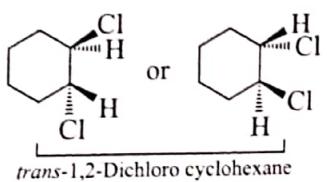
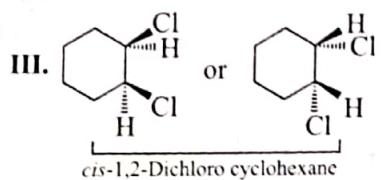
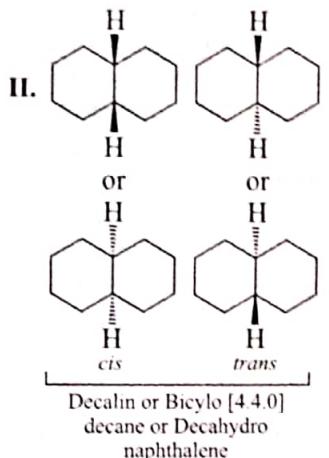
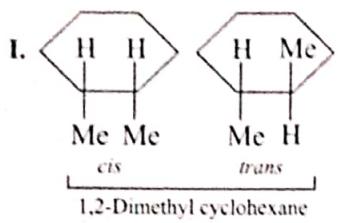


Here as the terminal wings are in the same plane, crest is symmetric therefore the compound will be optically inactive. Although terminal groups are different.

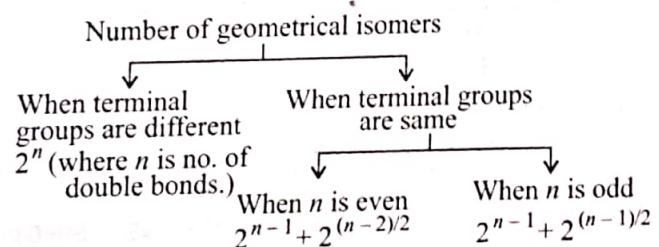
Optically active due to absence of plane of symmetry or centre of symmetry.

3.3.9 GEOMETRICAL ISOMERISM IN CYCLIC COMPOUNDS

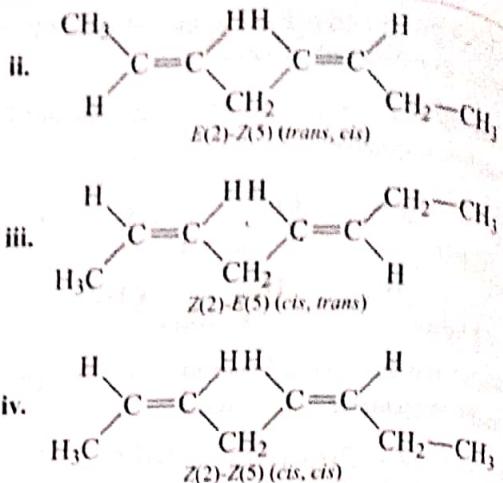
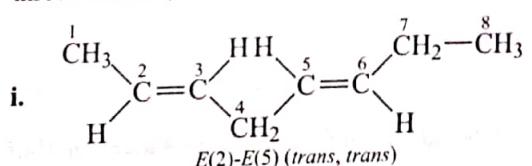
Disubstituted cycloalkanes also show geometrical isomerism. For example:



Geometrical isomers containing more than one double bond are given by the following formula:



For example: 2,5-Octadiene shows four isomers ($n = 2$, terminal groups are different, whereas 2,5-heptadiene shows three isomers ($n = 2$, even, same terminal groups)).



Geometrical isomers of 2,5-heptadiene:

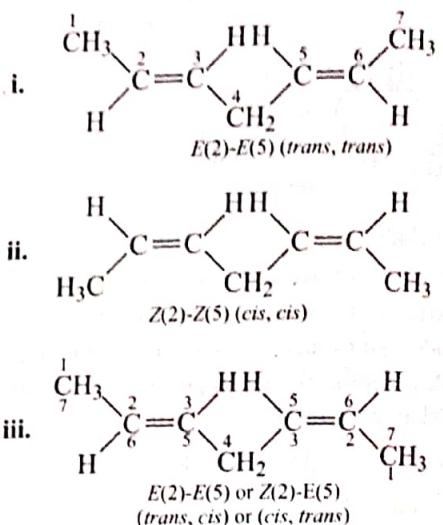
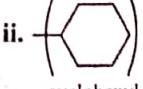
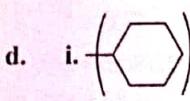
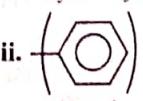
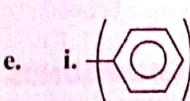


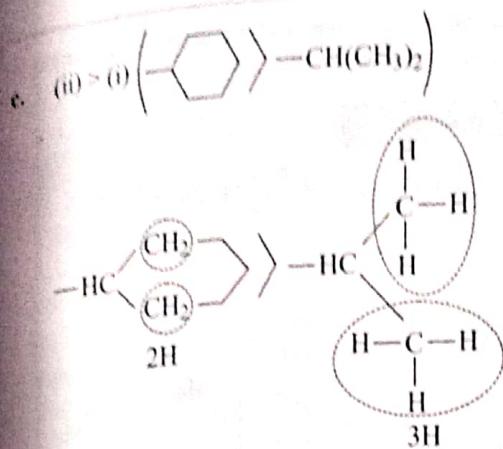
ILLUSTRATION 3.15

Arrange the following ligands in the decreasing order of priority:

- | | |
|--|---|
| a. i. —OH | ii. —COOH |
| iii. —CH ₂ OH | iv. —CH(OH)CH ₃ |
| b. i. —NH ₂ | ii. —C≡N |
| iii. —NO ₂ | iv. —CH ₂ NH ₂ |
| c. i. —CH(CH ₃) ₂ | ii.  |
| d. i.  | ii.  |
| e. i.  | ii. —C(CH ₃) ₃ |

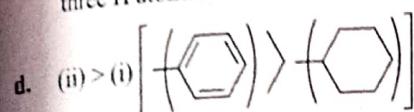
Sol.

- a. (i) > (ii) > (iv) > (iii) ($-\text{OH} > -\text{COOH} > -\text{CH}(\text{OH})\text{CH}_3 > -\text{CH}_2\text{OH}$)
- b. (iii) > (i) > (ii) > (iv) ($-\text{NO}_2 > -\text{NH}_2 > -\text{C}\equiv\text{N} > -\text{CH}_2\text{NH}_2$)



In cyclohexyl, ($-\text{CH}$) is joined to two (CH_2) groups and is further joined to another ring C atom.

In (i), ($-\text{CH}$) is joined to two (CH_3) groups each having three H atoms.



Phenyl C is doubly bonded and counted as attached to three C atoms.

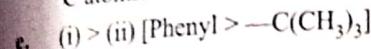
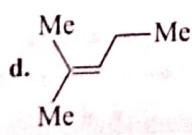
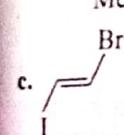
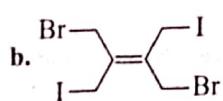
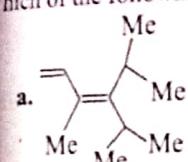
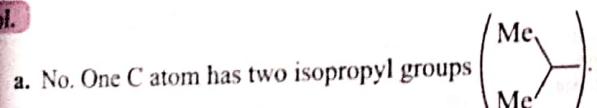


ILLUSTRATION 3.16

Which of the following alkenes have diastereomers?



Sol.

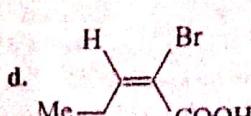
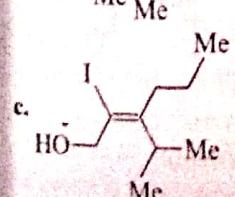
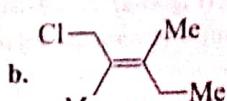
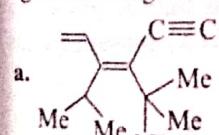


b. and c. Yes. Each C atom has two different groups.

d. No. One C atom has two Me groups.

ILLUSTRATION 3.17

Assign E-Z configuration to each of the following:

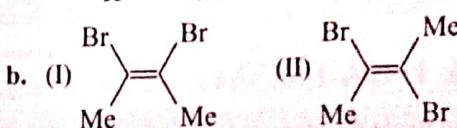
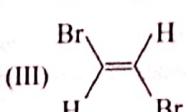
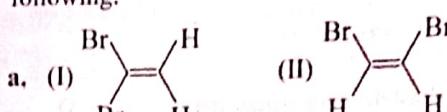


Sol.

- (Z) Priority of $\text{HC}\equiv\text{C} > -\text{CMe}_3$ and priority of $\text{CH}_2=\text{CH} > -\text{CHMe}_2$. So two higher priority groups on same side, hence Z-configuration.
- (E) Priority of $-\text{CH}_2\text{Cl} > \text{Me}$, and $\text{CH}_3 > \text{CH}_2 > \text{Me}$. So two higher priority groups on opposite sides, hence E-configuration.
- (E) Priority of $\text{I} > \text{CH}_2\text{OH}$ and $-\text{CHMe}_2 > \text{CH}_3\text{CH}_2\text{CH}_2$. So two higher priority groups on opposite sides, hence E-configuration.
- (E) Priority of $\text{Br} > \text{COOH}$ and $\text{CH}_3 > \text{H}$. So two higher priority groups on opposite sides, hence E-configuration.

ILLUSTRATION 3.18

Give the decreasing order of net dipole moments of the following:



Sol.

- I > II > III

I. (I) has a smaller angle of separation between two Br atoms than in (II) and (III), resulting in more net dipole moment (μ).

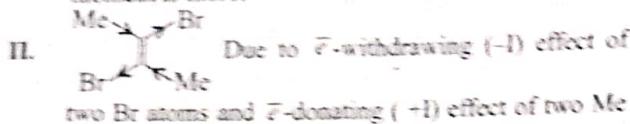
II. (II) has a large angle of separation between two Br atoms; therefore, net (μ) is less than (I).

III. In (III), two Br atoms and two H atoms have equal and opposite bond moments; therefore, net μ is zero.

- I > II.

I. $\xrightarrow{\text{net}}$ Due to $\bar{\sigma}$ -withdrawing (-I) effect of two Br atoms and $\bar{\sigma}$ -donating (+I) effect of two

Me atoms in the same direction, net resultant dipole moment is more.

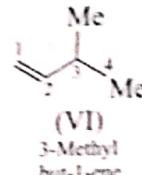
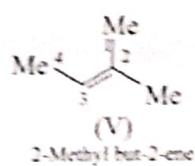
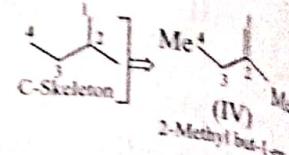
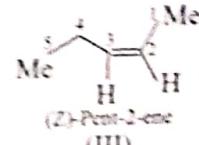
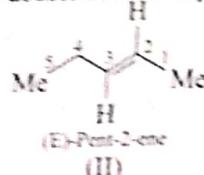
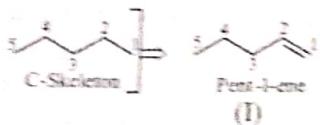


Hence net resultant is zero.

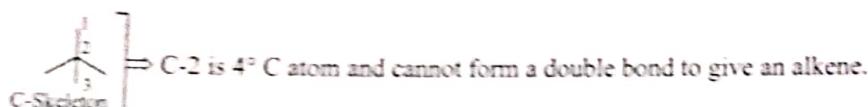
ILLUSTRATION 3.19

Give the structural and diastereomers of pentene.

Sol. Write the C-skeletons and introduce double bond. The possible structures are:



(II) and (III) are diastereomers (geometrical isomers).



3.4 OPTICAL ISOMERISM

Substances which can rotate the plane-polarised light are called optically active substances and the property of a substance to rotate plane-polarised light is called optical activity (Fig. 3.1).

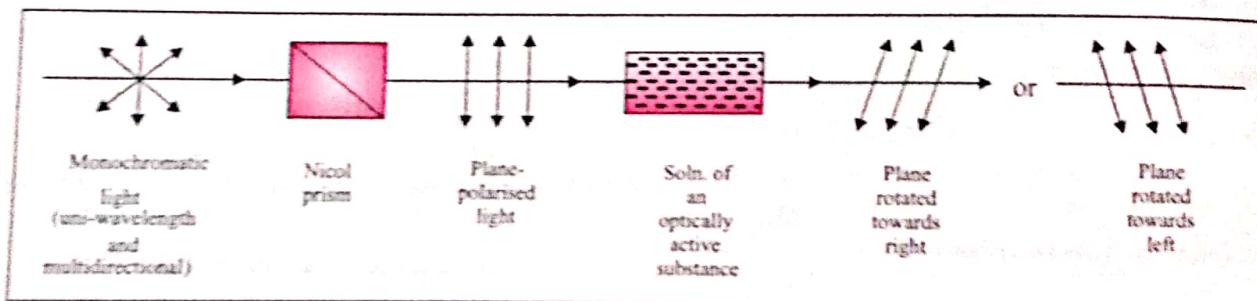


Fig. 3.1 Plane-polarised light and its rotation

A substance which rotates the plane-polarised light towards right (in the clockwise direction) is called **dextrorotatory** (Latin: dexter = right) and is usually represented by the prefix *d* or (+). On the other hand, a substance which rotates the plane-polarised light towards left (in the anticlockwise direction) is called **laevorotatory** (Latin: leaves = left) and is usually represented by the prefix *L* or (-).

The instrument used for measuring the optical rotation is called a *polarimeter* (Fig. 3.2). It consists of two Nicol prisms, one called the *polariser* (near the light source) and the other called the *analyser* (near the eye). Between the polariser and the analyser, a glass containing the solution of an optically active compound is placed.

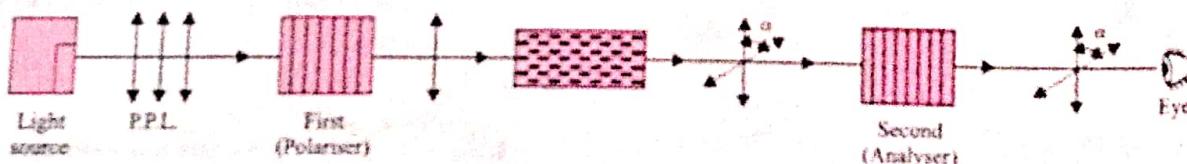


Fig. 3.2 Schematic representation of a polarimeter (solid lines before rotation, broken line after rotation)

Chirality of molecules and objects: An inspection of the molecular structures of optically active compounds indicates that all these compounds have Chiral* (or dissymmetric) molecules.

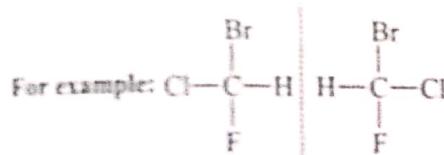
A molecule (or an object) is said to be chiral or dissymmetric, if it is not superimposable on its mirror image, and the property of non-superimposability is called chirality.

On the other hand, a molecule (or an object) which is superimposable on its mirror image is called achiral (non-dissymmetric or symmetric).

Specific rotation: $[\alpha]_D = \frac{\theta}{l \times C}$, where θ is the optical rotation, l is the length of the tube in decimetre, C is the concentration of the solution in g mL^{-1} , D is the wavelength of sodium light, and t is the temperature.

Conditions for optical activity:

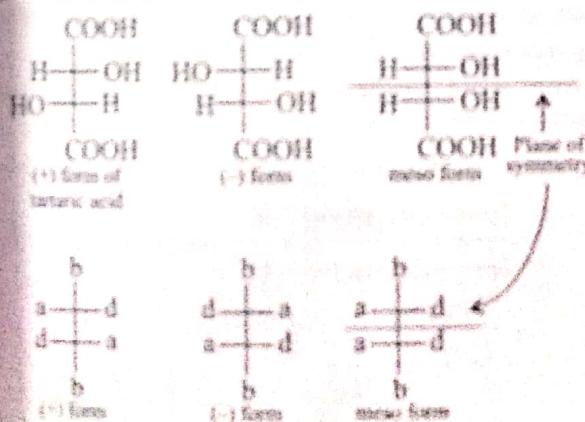
- It must have an assymmetric C atom or the chiral C atom which is attached to four different atoms or groups is called an assymmetric C atom or the chiral centre or stereogenic or stereocentre.



- It must have non-superimposable mirror image.
- It should not contain any element of symmetry, i.e.,
 - Plane of symmetry or (mirror plane or σ -plane).
 - Centre of symmetry or centre of inversion.
 - Alternating axis of symmetry.

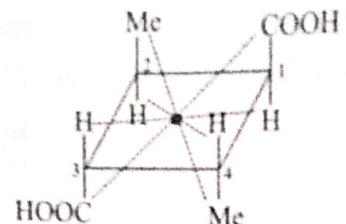
3.4.1 PLANE OF SYMMETRY OR MIRROR PLANE OR σ -PLANE

It is defined as an imaginary plane which divides the molecule into two equal parts such that one part of the molecule is a mirror image of the other part. For example:



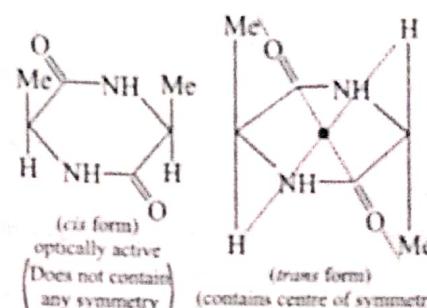
3.4.2 CENTRE OF SYMMETRY (OR CENTRE OF INVERSION)

It is defined as a point from which lines when drawn on one side and produced to an equal distance on the other side will meet several points in the molecule. For example:



2,4-Dimethyl cyclobutane-1,3-dicarboxylic acid

It possesses a centre of symmetry, which is the centre of the ring and is therefore optical inactive



Total stereoisomers = 3

Dimethyl di keto piperazine

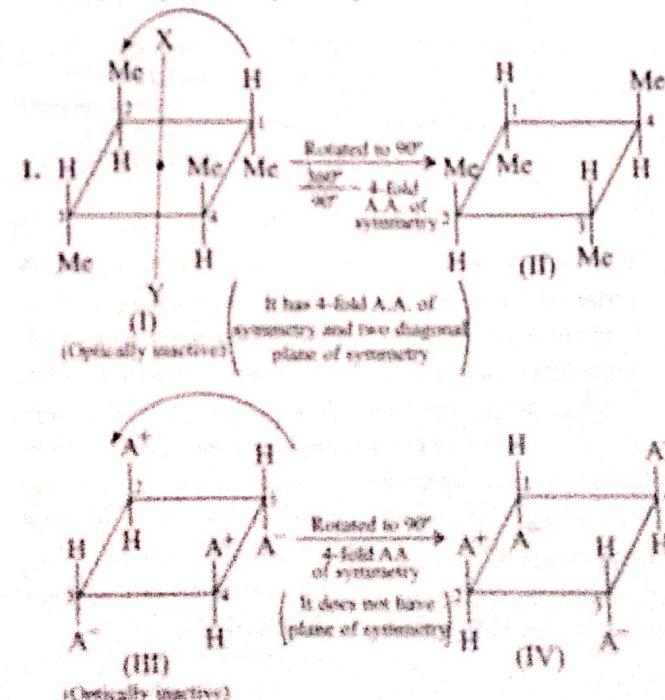
(Does not contain any symmetry d and l forms)

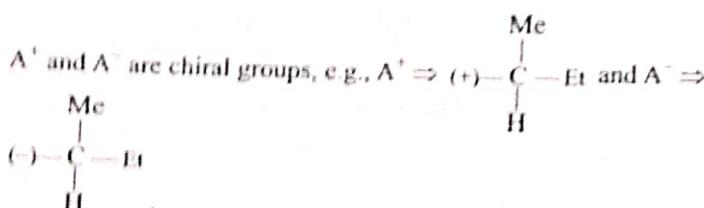
(contains centre of symmetry) (Optically inactive) (meso form)

3.4.3 ALTERNATING AXIS OF SYMMETRY

A molecule possesses an n -fold alternating axis (A.A.) of symmetry. When rotated through an angle of $360^\circ/n$ about this axis, followed by reflection in a plane perpendicular to this axis, the molecule is identical to the original molecule.

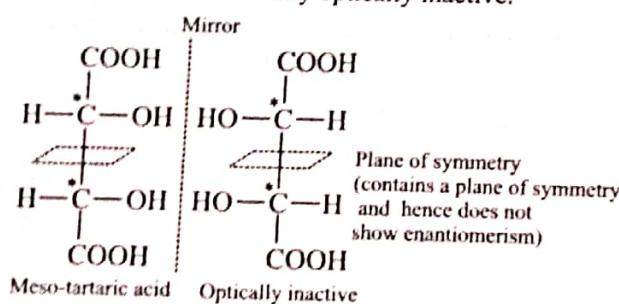
For example, 1,2,3,4-tetramethyl cyclobutane (I) contains four-fold alternating axis of symmetry. Rotation of (I) through 90° about axis XY, which passes through the centre of the ring perpendicular to its plane, gives (II) and reflection of (II) in the plane of the ring gives (I). This situation arises n times in the molecule; (I) has two diagonal planes of symmetry.





3.4.4 CONDITIONS FOR ENANTIOMERISM

- All the optically active compounds exist in two or more isomeric forms, which differ from one another in the relative spatial arrangement of atoms or groups.
- These stereoisomers which resemble one another in their chemical reactions and most of the physical properties but differ only in their behaviour towards plane-polarised light are called **optical isomers** and the phenomenon is called **optical isomerism**.
- Optical isomers which are non-superimposable mirror images of each other are called **enantiomers** and the phenomenon is called **enantiomerism**. The enantiomers have identical physical and chemical properties but rotate the plane of polarised light in opposite directions but to the same extent.
- It may be noted that the necessary and sufficient condition for a molecule to exhibit enantiomerism (and hence optical activity) is chirality or dissymmetry of molecule, i.e., molecule and its mirror image must be non-superimposable. It may or may not contain chiral or asymmetric carbon atoms.
- Usually, the presence of one or more chiral carbon atoms causes the molecule to show enantiomerism and hence optical activity but certainly it is not the necessary and sufficient condition. For example, meso-tartaric acid contains two chiral carbon atoms (marked by asterisks) but does not show enantiomerism and is actually optically inactive.



This is because it contains a plane of symmetry which divides the molecule into two equal halves so that one half of the molecule is a mirror image of the other. As a result, meso-tartaric acid and its mirror image are superimposable. In other words, meso-tartaric acid is an achiral or non-dissymmetric or symmetric molecule and hence it does not show enantiomerism or optical activity. Thus, the optical inactivity of meso-tartaric acid is due to **internal compensation**, i.e., the rotation caused by one half of the molecule is exactly cancelled by an equal and opposite rotation caused by the other half of molecule.

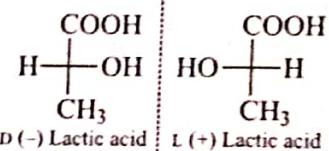
3.4.5 FORMULA FOR THE NUMBER OF OPTICAL ISOMERS

Optical isomers	
When terminal groups are different	When terminal groups are same
2^n (where n is the no. of asymmetric C atoms)	
	When n is even
	$2^{n-1} = \text{No. of O.A.}$
	$2^{\frac{(n-2)}{2}} = \text{No. of O.I.A. isomers}$ (i.e., meso form)
	$2^{n-1} + 2^{\frac{(n-2)}{2}} = \text{Total forms}$
	When n is odd
	$2^{n-1} = \text{Total forms}$
	$2^{\frac{(n-1)}{2}} = \text{No. of O.I.A. (i.e., meso form)}$
	$2^{n-1} - 2^{\frac{(n-1)}{2}} = \text{No. of O.A.}$
$\frac{2^{n-1}}{2} = \text{No. of racemic form}$	$\frac{\text{No. of O.A.}}{2} = \text{No. of racemic forms}$

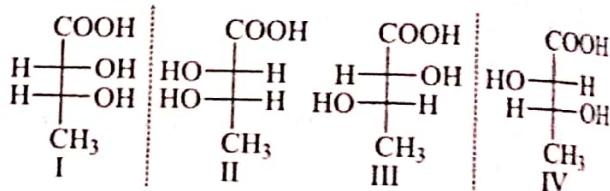
(O.A. \Rightarrow Optically active isomers, O.I.A. \Rightarrow Optically inactive isomers)

For example:

- ($n = 1$), different terminal groups (two isomers; one racemic)

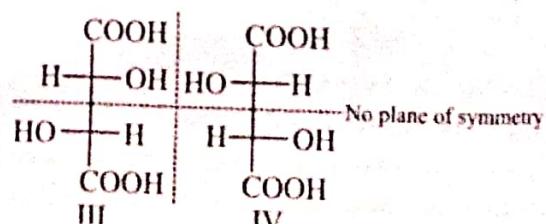
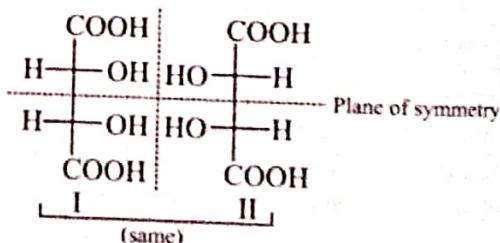


- When ($n = 2$), different terminal groups (for example, 2,3-dihydroxy butanoic acid).



I and II, III and IV are enantiomers; I and III, II and III and IV, II and IV are called diastereomers. Diastereomers are optical isomers but not enantiomers. They have different physical but same chemical properties.

- When $n = 2$, having same terminal groups (for example tartaric acid).



I and II are same and are optically inactive due to the plane of symmetry and are called 'meso form', whereas III and IV are enantiomers. I and III, I and IV are called diastereomers.

3.4.6 MESO AND RACEMIC

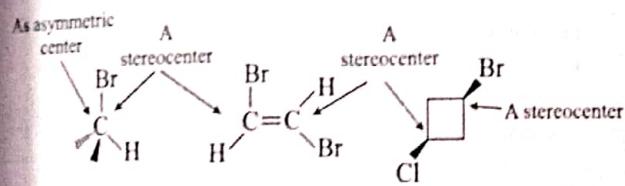
Meso form is O.I.A. due to the internal compensation or symmetry in the molecule or the presence of any symmetry in the molecule or superimposable mirror image or if the specific rotation is zero. Racemic (*r*) or (\pm) or *dl* or *Dl*, is also O.I.A. due to the external compensation and its specific rotation is also zero.

3.4.7 DIFFERENCE BETWEEN *d*, *l* AND *d*, *l*

d and *l* represent the optical rotation; *d* or (+) is called dextrorotatory and rotates the P.P.L. towards the right, whereas *l* or (-) is called laevorotatory and rotates the P.P.L. towards left.

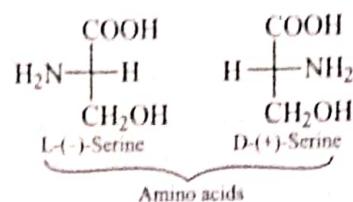
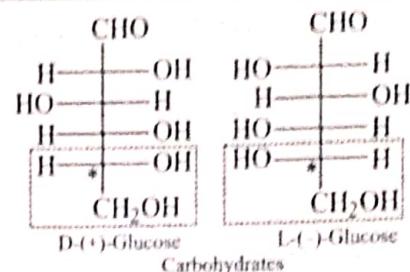
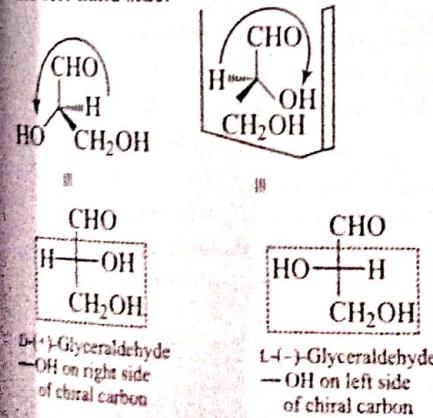
3.4.7.1 Difference Between Chiral Center and Stereocenter

Those centers in a molecule which can show optical or geometrical isomerism are called stereocenters. One chiral center showing optical isomerism means one stereocenters and one π bond showing geometrical isomerism means two stereocenters. Thus stereocenters include both (i) asymmetric centers, where the interchange of two groups produces an enantiomer, and (ii) the sp^2 carbons of an alkene or the sp^2 carbons of a cyclic compound, where the interchange of two groups converts a *cis* isomers to a *trans* isomer of vice versa. This means that although all asymmetric centers are stereocenters, not all stereocenters are asymmetric centers.



3.4.8 *d*, *l* CONFIGURATION DESCRIPTORS (RELATIVE CONFIGURATION)

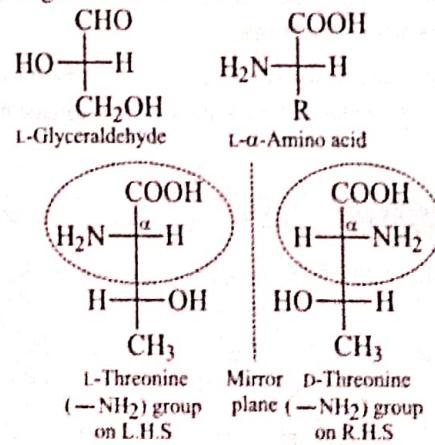
D and **L**: Symbols **D** and **L** refer to the relative configuration of the (—OH) group at the penultimate carbon w.r.t. glyceraldehyde taken as standard. **D** refers to the (—OH) group which lies on the right-hand side and **L** refers to the (—OH) group which lies on the left-hand side.



All molecules which can be chemically related to *D*-glyceraldehyde are assigned the *D* configuration and those related to *L*-glyceraldehyde are all designated *L* configuration. It may be noted here that there is no direct relation between *D* and *L* configurations with *d* and *l* or (+) and (-) notations.

The *D,L* system is commonly used in assigning the stereochemistry to carbohydrates and amino acids. For amino acid, (-)-serine has been used as a configurational reference compound, because there is a configurational similarity between *L*-glyceraldehyde and (-)-serine.

In drawing the Fischer projections while assigning *D*, *L* configuration, the Fischer projection of the molecule is drawn in such a way that the main longest chain becomes vertical with carbon-1, the most highly oxidised carbon at the top. For α -amino acids, the configurational arrangement of —NH₂, —COOH, R, and H groups at the C_α atom is related to that of —OH, —CHO, —CH₂OH, and H groups, respectively, of glyceraldehyde (2,3-dihydroxy propanal). Thus, *L*-glyceraldehyde and *L*- α -amino acids are said to have the same relative configurations.



3.4.9 PROPERTIES OF OPTICAL ISOMERS (ENANTIOMERS)

The important properties of enantiomers are given below:

- They have identical physical properties such as melting points, boiling points, densities, solubilities, refractive indices, etc. They only differ in the direction of rotation of the plane-polarised light: one rotates the plane-polarised light

towards the right and the other towards the left (but to the same extent).

- b. Enantiomers have identical chemical properties except towards optically active reagents.

The chemical reactions of enantiomers of any optically inactive reagents (achiral reagents) such as HBr, H_2SO_4 , CH_3COOH , etc., are not only same but occur at the same rate also. For example, the two enantiomers of 2-butanol not only give the same alkene, i.e., 2-butene, on treatment with conc. H_2SO_4 but the rates of these reactions are also identical.

On the other hand, the reactions of enantiomers with optically active reagents (chiral reagents) proceed at different rates. For example, if we separately esterify the enantiomers of 2-butanol with (-)-lactic acid, the rates are found to be different.

- c. Enantiomers have different biological properties. In biological systems, all reactions are catalysed by enzymes which themselves are optically active compounds. The reactions of enantiomers with enzymes are so stereospecific that quite often the reaction with one of the enantiomers does not take place at all. For example, we eat a lot of (D)-(+)-glucose in the form of carbohydrates daily. This is metabolised in the body to produce CO_2 and H_2O and a lot of energy is generated. We use this energy for our day-to-day work. However, if we eat (L)-(-)-glucose, it is metabolised and is excreted as such through urine.

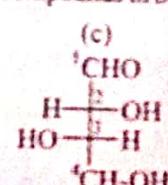
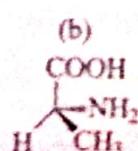
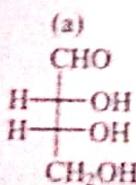
Examples:

- (-) Penicillin is an antibiotic but (+) Penicillin is not. (It was isolated by Alexander Fleming from *Penicillium notatum*.)
- (-) Chloromycetin or (-) Chloramphenicol is an effective drug against typhoid fever but (+) is not. It was isolated by Park and Davis from the fungus *Chloromycetes venezuelae*.

This difference in the reactivity of enantiomers is of great importance in biochemistry taking place in our body.

ILLUSTRATION 3.20

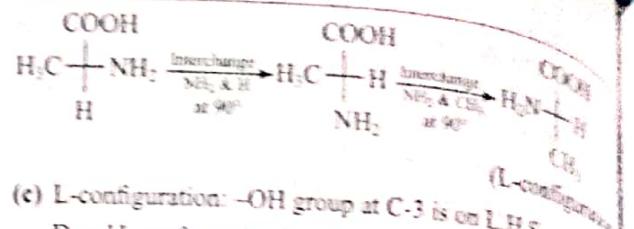
Specify the configuration of the following compounds in D or L.



Sol.

(a) D-configuration: Both OH w.r.t. H are on R.H.S.

(b) L-configuration: Convert into Fischer projection formula. COOH on vertical line, NH₂ on R.H.S. and CH₃ on L.H.S.



(c) L-configuration: -OH group at C-3 is on L.H.S.
D and L configuration is related to w.r.t. D(+) glyceraldehyde so the position of -OH at C-3 is considered.

3.4.10 ERYTHRO AND THREO DESIGNATION

Compounds with two adjacent chiral (stereogenic) C atoms are sometimes designated by prefix 'erythro' or 'threo' (name of C-2 epimeric aldotetroses).

These prefixes are used to distinguish between enantiomers containing two chiral C atoms when two pairs of substituents attached to each chiral C are the same while the third is different e.g., system of the type $[R-C(x)(y) — C(x)(y) — R']$ and $[R-C(x)(y) — C(x)(z) — R']$.

The stereoisomers in which the same groups are present on the same side of the Fischer projection are called erythro isomers while the stereoisomers in which these groups are present on the opposite sides are known as threo isomers.

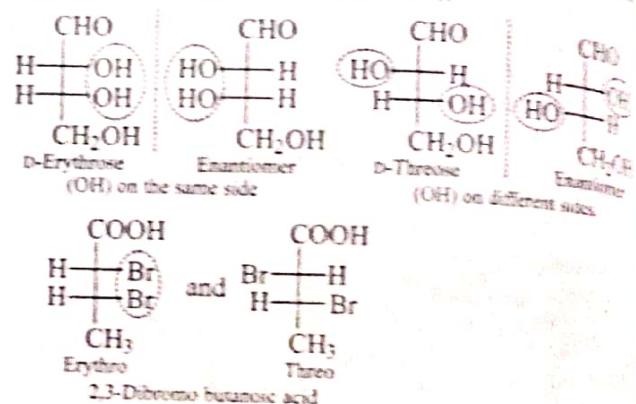


ILLUSTRATION 3.21

- The optical rotation of an optically active compound is +20°. The length of tube is 10 cm and the density of solution is 0.4 g mL^{-1} . The specific rotation of the compound is:
I. $+50^\circ$ II. $+500^\circ$ III. $+5^\circ$ IV. $+0.5^\circ$
- Which of the following are optically active compounds and why?
I. Butan-1-ol II. 2-Chlorobutane
III. Lactic acid IV. 3-Chloropentane
- Which of the following are optically active and why?
I. $CH_3CH(CH_3)CH_2CH_3$ II. $CH_3CH_2CH_2CH_2COOC_2H_5$
III. $CH_3CH_2CH(NH_2)CH_3$ IV. CH_3OHCH_2OH
- Which of the following are optically active and why?
I. Propan-1-ol II. Butan-2-ol
III. Heptan-4-ol IV. 3-Ammohexane
V. 2-Chloropentane VI. 2,2-Dichloropropane
- Mark (*) on the asymmetric carbon atom, if any, in the following compounds:
I. $CH_3—CHCl—CH_2—CH_3$ II. $CH_3—CHOH—CH_3$

Sol.

a. i. $10\text{ cm} = 1\text{ dm}$, $[\alpha] = \frac{+20^\circ}{1 \times 0.4} = +50^\circ$

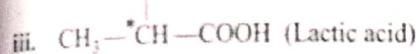
b. The structural formulas of the given compounds are as under:



Butan-1-ol is not optically active since it does not contain any asymmetric carbon atom. Hence the molecule is achiral.



2-Chlorobutane is a chiral molecule, since it contains an asymmetric carbon atom marked with an asterisk. Hence, it is optically active.



Lactic acid contains one asymmetric carbon atom and its molecule is chiral. Thus, it shows optical activity.



3-Chloropentane is a symmetrical molecule since it does not contain an asymmetric carbon atom. Hence it does not show optical activity.

c. (ii) and (iii) have asymmetric C atom.

d. (ii), (iv) and (v) have asymmetric C atom.

e. i. has asymmetric C atom, $\text{CH}_3-\overset{*}{\text{CH}}(\text{Cl})-\text{CH}_2\text{CH}_3$

ILLUSTRATION 3.22

Explain the following:

- What is stereocentre and how it is related to a chiral centre?
- What kinds of sp^2 -hybridised C atoms cannot be chiral centres?
- What kinds of sp^3 -hybridised atoms other than C atom can be chiral?

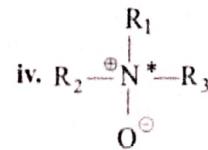
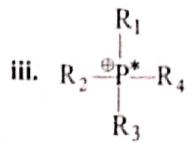
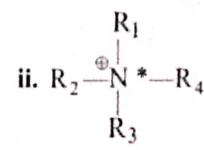
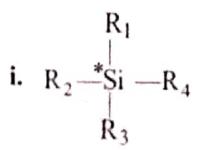
Sol.

a. If two groups (or ligands) attached to an atom are switched resulting in a new stereoisomer, the atom is called a stereocentre. If the new stereoisomer is an enantiomer, the stereocentre is a chiral centre. All stereocentres are not chiral centres, but all chiral centres are stereocentres.

b. sp^2 -Hybridised atoms have flat geometry and thus possess a plane of symmetry. So they cannot be chiral centres. Carbocation, ($\text{R}_1\text{R}_2\text{R}_3\text{C}^+$), free radicals ($\text{R}_1\text{R}_2\text{R}_3\text{C}^\bullet$), ($\text{C}=\text{O}$), acid, acid derivatives, ($\text{C}=\text{N}$) in imines and oximes, all have sp^2 -hybridised C atom and thus cannot be chiral.

c. sp^3 -hybridised Si, N, P, S can be chiral.

For example:



Trivalent S and P compounds, with lone pair of \bar{e} 's can be chiral.

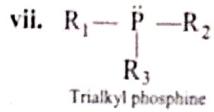
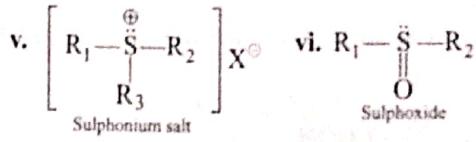


ILLUSTRATION 3.23

Write the name and structure of the following optically active compounds with lowest molecular weight.

i. alkane

ii. alkene

iii. alkyne

iv. unsaturated hydrocarbon

v. alkyl halide

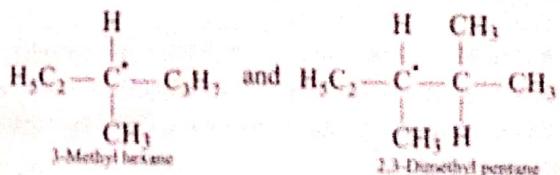
vi. alcohol

vii. acid

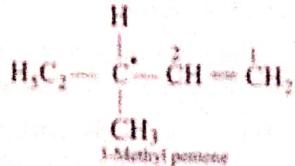
viii. amine

Sol.

i. Optically active alkane with lowest molecular weight:



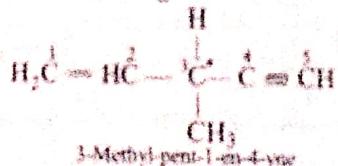
ii. Optically active alkene with lowest molecular weight:



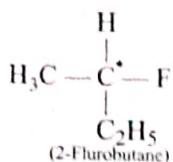
iii. Optically active alkyne with lowest molecular weight:



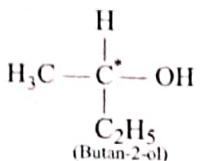
iv. Optically active unsaturated hydrocarbon with lowest molecular weight:



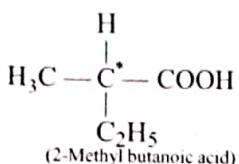
- v. Optically active alkyl halide with lowest molecular weight:



- vi. Optically active alcohol with lowest molecular weight:



- vii. Optically active acid with lowest molecular weight:



- viii. Optically active amine with lowest molecular weight:

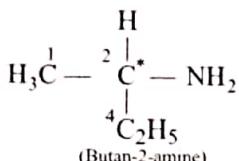
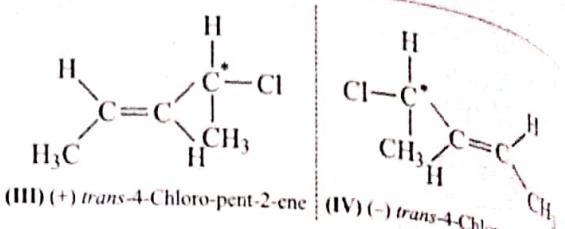
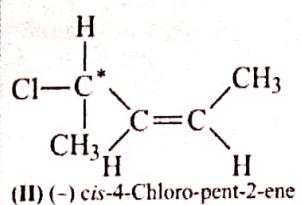
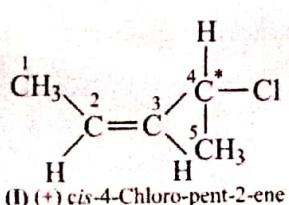


ILLUSTRATION 3.24

- How many stereoisomers are possible for the compound $\text{CH}_3\text{CH}=\text{CHCHClCH}_3$?
- How many stereoisomers are possible for the compound $\text{HOOCCH}_2-\text{COOH}$?
- Isopentane on monochlorination gives—isomers and out of them—are optically active.
- Which of the following compounds exhibit(s) geometrical isomerism?
 - $\text{C}_2\text{H}_5\text{Br}$
 - $(\text{CH})_2(\text{COOH})_2$
 - CH_3CHO
 - $(\text{CH}_2)_2(\text{COOH})_2$
- Write down the structures of stereoisomers of the following:
 - 2,3-Dihydroxybutane
 - 3-Phenyl-2-propenoic acid
- Write down the number of asymmetric carbon atoms in each optically active compound and report the number of isomers.
 - $\text{CH}_3(\text{CHOH})_2\text{COOH}$
 - $\text{COOH}(\text{CHOH})_2\text{COOH}$

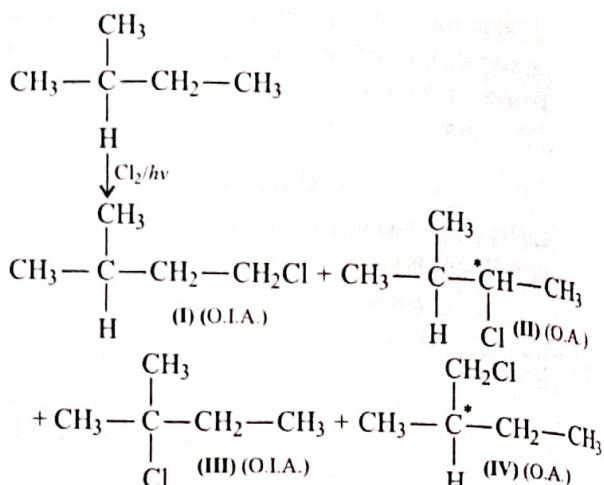
Sol.

- a. Four (one double bond, two G.I. and one asymmetric C atom, two optical isomers, total four).

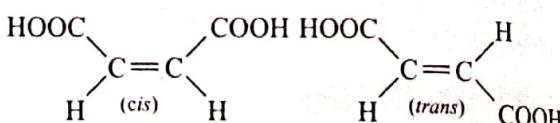


(I) and (II), and (III) and (IV) are enantiomers; (I) and (III), (II) and (IV), (I) and (IV), and (II) and (III) are diastereomers.

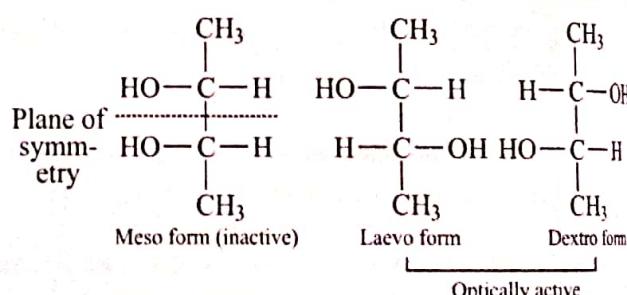
- b. Nil, since there is no asymmetric C atom.
c. Four, two



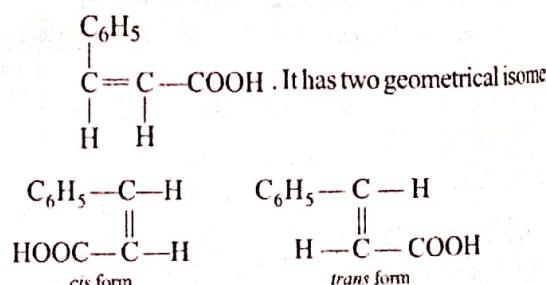
- d. ii.

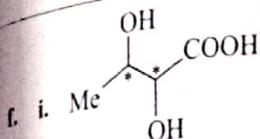


- e. i. 2,3-Dihydroxy butane; this name is wrong. It should be $\text{CH}_3*\text{CHOH}.\text{*CHOH.CH}_3$, where * shows asymmetric C atoms. Thus, the compound has optical isomers.



- ii. 3-Phenyl-2-propenoic acid:





Number of asymmetric C atoms = 2.
Different terminal groups: (—COOH) and (Me)

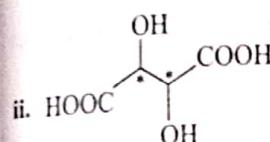
$$\text{Number of O.I.A.} = 2^n = 2^2 = 4$$

Number of meso forms = 0

$$\text{Number of (O.I.A.) racemic form} = \frac{4}{2} = 2 \text{ (racemate mixture)}$$

∴ Total optical isomers = 4

Optically inactive forms = 2.



Number of asymmetric C atoms = 2
Same terminal groups: (—COOH)

$$\text{Number of O.I.A.} = 2^{n-1} = 2^{2-1} = 2^1 = 2$$

$$\text{Number of (O.I.A.) meso form} = 2^{(n-2)/2} = 2^0 = 1$$

$$\text{Number of (O.I.A.) racemic form} = \frac{2}{2} = 1$$

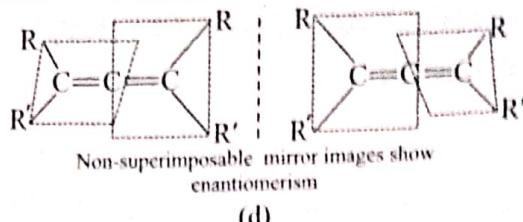
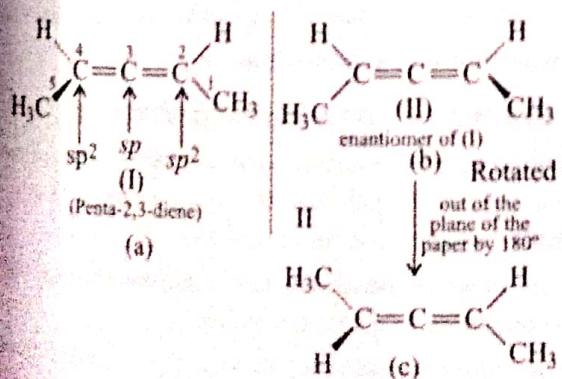
Total optical isomers = 2 + 1 = 3

3.5 STEREOCHEMISTRY OF C-COMPOUNDS NOT CONTAINING AN ASYMMETRIC CATOM (ALLENES)

The presence of an asymmetric C atom is not essential for optical activity. The essential requirement is the asymmetry of molecule as a whole (Fig. 3.3).

Allenes of the type $\begin{pmatrix} R_1 & & \\ & \diagdown & \diagup \\ & C = C = C \\ & \diagup & \diagdown \\ R_2 & & \end{pmatrix}$ are asymmetric and

are resolvable, e.g., penta-2,3-diene (I) has no chiral C atoms, yet it is a chiral molecule and has two enantiomers.

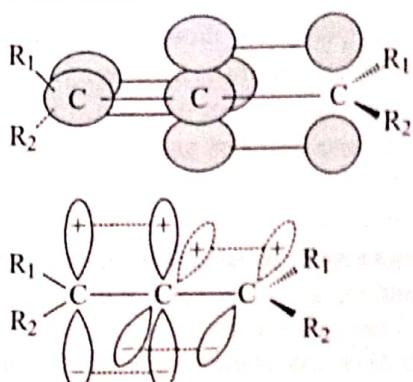


(d)

Fig. 3.3 (a-d) Stereochemistry of allenes

The planes of π -bonds of allenes are perpendicular to each other. This geometry of π -bonds causes the groups attached to the end C atoms to lie in perpendicular planes. The allenes with different substituents on the end C atoms are chiral. Such allenes do not show *cis-trans* isomerism.

- a. This is an example of a chiral molecule which has two stereocentres at (C^2 and C^4) but no chiral centres.

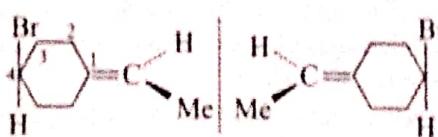


C^3 is sp -hybridised and has one p -orbital overlapping in the xy plane with the p -orbital of C^4 , and the other p -orbital overlapping in the xz plane with the p -orbital of C^4 to form two double bonds. The two groups (H and CH_3) attached to C^4 are, therefore, in the plane at right angles to the plane of two groups (H and CH_3) attached to C^2 . The mirror images are not identical as can be shown by rotating one of the structures, (II) [Fig. 3.3 (c)], 180° out of the plane of paper in order to superpose the H and Me groups in the plane of paper. The groups extending in front and back of the plane of paper will not match.

- b. 1,3-Dibromo allene also shows optical activity.



- c. 4-Bromoethyl cyclohexane also shows enantiomers by considering the ring to be flat.



- d. Penta-1,2-diene does not show enantiomers, since terminal C has two H atoms.

