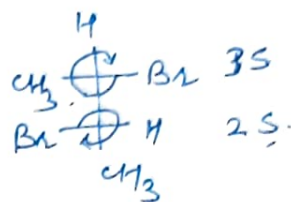
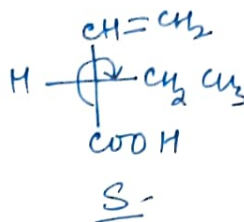
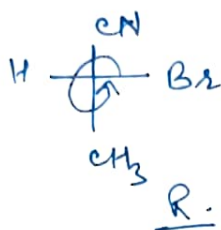
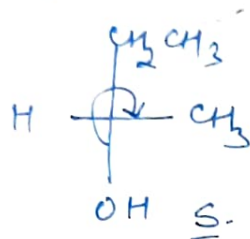
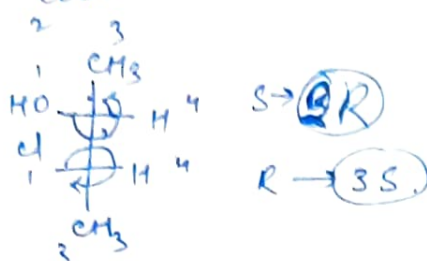
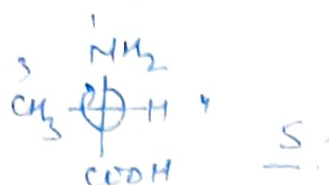
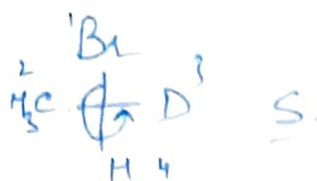
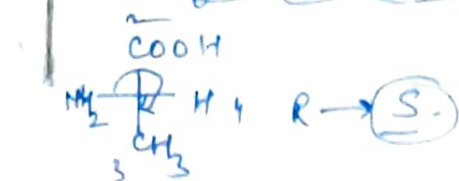


R/S System of Nomenclature from Fischer Projections (F.P.)



There is a very simple alternative way of predicting the conf. (R/S) from F.P.

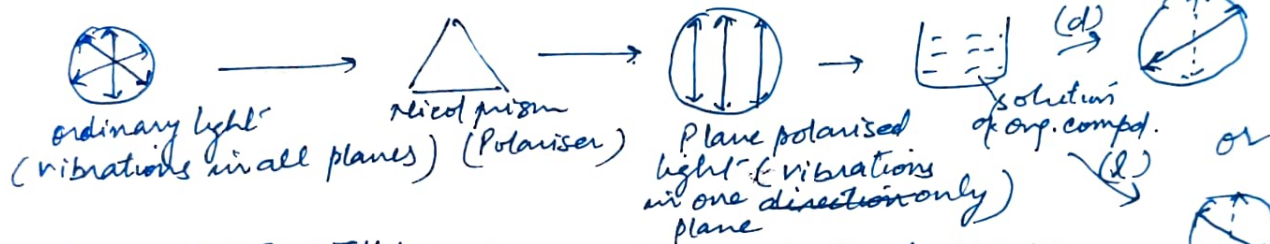
- Assign priorities to 4 atoms/groups on chiral C
- If atoms/groups of lowest priority occupies vertical position in F.P., $R \Rightarrow R$, $S \Rightarrow S$.
- If atoms/groups of lowest priority occupies horizontal position, $R \Rightarrow S$, $S \Rightarrow R$.
- $S \Rightarrow R \Rightarrow R$, i.e. change $R \rightarrow SS$ or $S \rightarrow RR$.

This gives the correct configuration.

NOTE: Priorities are assigned on the basis of Sequence Rules.

CHIRALITY, OPTICAL ISOMERISM.

Such type of light which has vibrations in only one plane is known as plane polarised light.



OPTICAL ACTIVITY:- When plane polarised light is passed through the solution of certain organic compounds, they rotate the plane polarised light either towards left or to right. Substances which rotate ppl. are known as optically active and phenomenon is called optical activity.

Depending upon the rotation of ppl, optically active compounds are

- Levorotatory → compounds which rotate ppl to left: l or $(-)$
- Dextrorotatory → " " " " to Right: d or $(+)$

(2)

SPECIFIC ROTATION! - The optical activity of a compd is expressed in terms of specific rotation. It is an inherent property of an enantiomer. S.P. Rotation is denoted by $[\alpha]_t^t$ and it depends upon \rightarrow temp ($^{\circ}\text{C}$), Solvent used & wavelength of light used (λ)

$$[\alpha]_{\lambda}^t = \frac{\alpha}{l \times c} \quad \text{where } \alpha = \text{Obsd. rotation}$$

$$l = \text{path length (dm)}$$

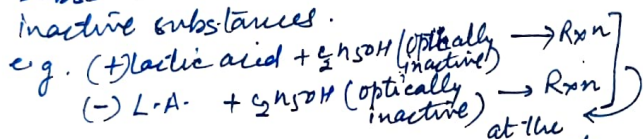
$$c = \text{conc}^n \text{ in g/cm}^3$$

OPTICAL ISOMERISM

Compds having similar chemical & physical properties and differ in their optical activity are known as optical isomers & the phenomenon is known as optical isomerism.

ENANTIOMERS

1. Optical isomers that are mirror images of each other are known as enantiomers.
2. They have identical physical properties (m.p., b.p., refractive index, density, solubility etc.).
3. Enantiomers are optically active and rotate p.p.l. to the same extent but in opposite direction.
4. The enantiomers have identical chemical properties. However, they differ in the rates of rxn towards the optically active substances but not towards optically inactive substances.



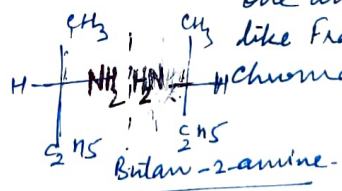
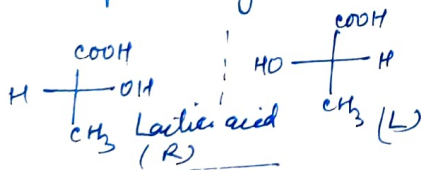
But they react with different rates with sec. butyl alcohol ($\text{CH}_3\text{CHOHCH}_2\text{H}_5 \rightarrow$ optically active) at the same rate

DIASTEREOMERS

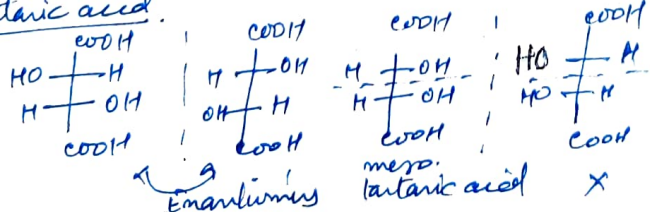
1. Optical isomers that are not the mirror images of each other are known as diastereomers.
2. They show different physical properties.
3. They may or may not be optically active (only geometrical isomers which are diastereomers are optically inactive).
4. They show similar but not identical chemical properties [e.g. are same \rightarrow similar positions are different \rightarrow not identical]

5. The equimolar mixture of two enantiomers (racemic mix.) can be separated by resolution

5. On account of the difference in their physical properties, they can be separated from one another through techniques like Fractional distillation, chromatography etc.

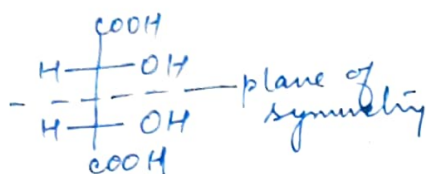


Tartaric acid



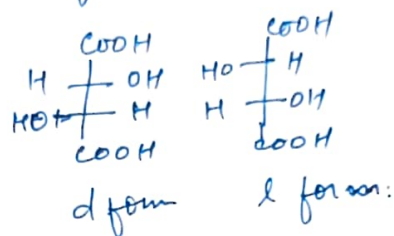
MESO COMPOUNDS

1. A compound, having two or more asym. c-atoms, which superimposes on its mirror image and hence is optically inactive.
2. Meso compd is optically inactive due to internal compensation.
3. It can not be resolved into optically active forms.
4. The molecule as a whole is not dissymmetric, as it has plane of symmetry.
5. e.g. eq. mix. of d & l tartaric acid



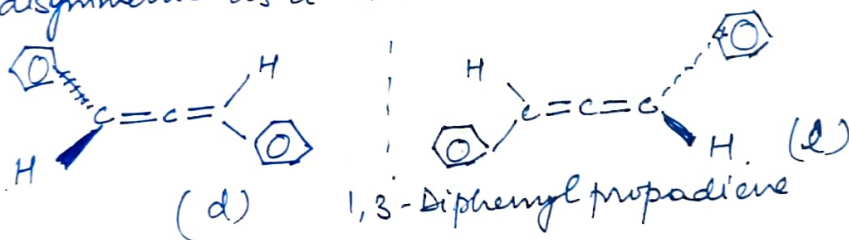
RECEMIC MIXTURE

1. Racemic mix. contains equimolar amounts of enantiomers.
2. Racemic mix is optically inactive due to external compensation.
3. It can be resolved in optically active forms.
4. Enantiomers which are part of a racemic mixture are dissym. in nature.
5. e.g. ^{equimolar mix of} tartaric acid d & l forms



CONDITIONS FOR OPTICAL ISOMERISM

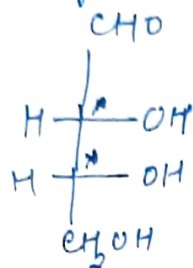
- 1- The compd containing asymmetrical carbon (chiral) must be present.
- 2- The structures of a molecule should not superimpose on its mirror image.
- 3- They must be devoid of any symmetry elements. (i.e. Plane of sym., Centre of sym., Alternating axis of sym.).
- 4- In case of no any chiral carbon, molecule should be dissymmetric as a whole.



④

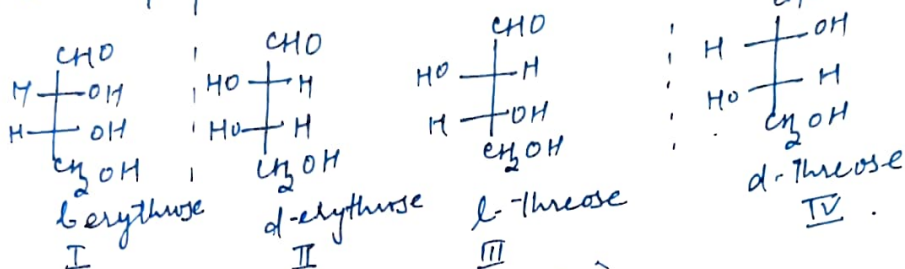
compds containing 2 or more dissimilar asym. c-atoms

e.g. Erythrose



No. of asym. c-atoms = $n = 2$

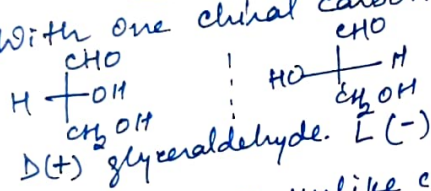
Total no. of optical isomers = $2^n = 2^2 = 4$.



All are optically active

No. of optical isomers for chiral molecules

(a) → With one chiral carbon. = 2 optically active form.
 $n = 1$
 $2^n = 2^1 = 2$



(b) With 2 or more unlike c-atoms
 eg. $n = 2 = 2^n = 4$ diff. configurations \Rightarrow e.g. Erythrose

(c) With 2 like chiral c-atoms.
 e.g. tartaric acid $2^n = 4$

chiral c = $n = 2$
 optically active forms = $2^{n-1} = 2^{2-1} = 2^1 = 2$ (d), (l)
 optically inactive forms = $2^{(n-2)/2} = 2^{2-2/2} = 2^0 = 1$ meso.

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

$$2^2 - 1$$

$$= 4 - 1$$

$$= 3$$

2 optically active $2^{n-1} = 2^{2-1} = 2^1 = 2$ (d, l)

1 optically inactive = $2^{n-2/2} = 2^{2-2/2} = 2^0 = 1$ (meso)

ATROPISOMERISM:

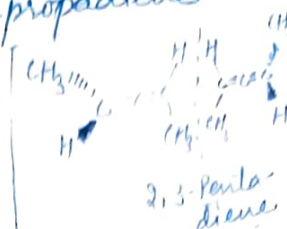
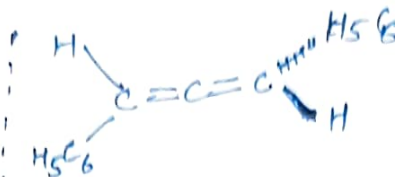
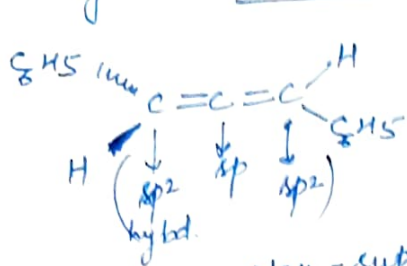
(1)

Optical isomerism without chiral centre

Compounds which do not possess an asymmetric carbon atom can also exist in optically active form provided that the whole molecule as a whole is dissymmetric.

This phenomenon is known as ATROPISOMERISM.

For e.g. (1) Allene Derivatives: - 1,3-diphenylpropadiene

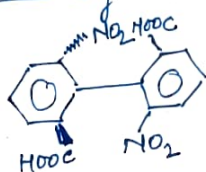
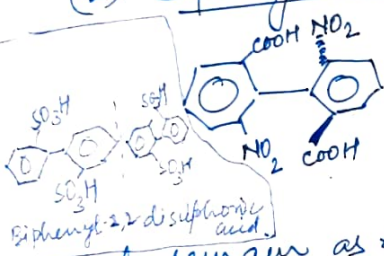


Non-superimposable mirror images
(Enantiomers \Rightarrow optically active)

The compounds in which a single carbon atom is connected to two other carbon atoms by double bonds are called as allenes. The allenes show optical isomerism if the two groups bonded to each terminal carbon atom are different.

As both the π bonds are perpendicular to each other, this special geometry makes the molecule asymmetric or chiral which is having no plane or centre of symmetry. They are in the form of non-superimposable mirror images of each other and hence are enantiomers i.e. optically active. (One form is $d(+)$ and other is $-l(-)$).

(2) Biphenyl Derivatives e.g. 6,6'-dinitrodiphenic acid

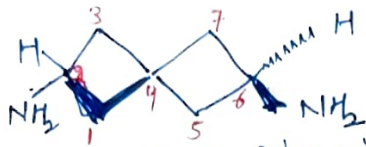


When bulky groups are present on the o-positions in biphenyl molecule, the groups tend to

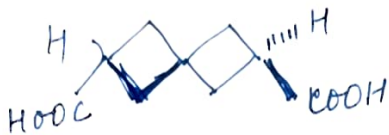
to remain as far as possible from each other ~~due~~ to minimize steric repulsion (steric hindrance), so as to attain such a conformation in which the aromatic rings will be ~~more~~ almost perpendicular to each other. Thus the molecule will become dissymmetric & optically active.

(2)

Spirans - Compounds having carbon atoms common to two rings are called as spirans. They may be considered as allenes in which both the double bonds are replaced by rings which are perpendicular to each other. Thus, they lack any type of symmetry and hence are optically active.



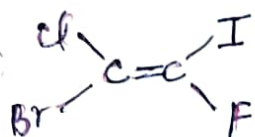
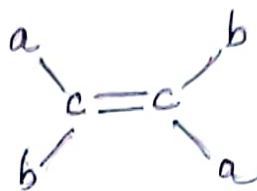
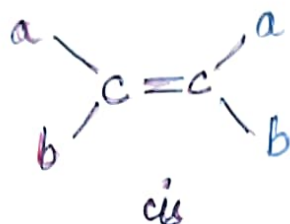
2,6-Diaminospirocycloheptane



Dicarboxyspirocycloheptane

(1)

Geometrical Isomerism (E/Z System)
 Same molecular formula but ^{different of nomenclature} spatial arrangement
 of gps about $C=C$.



cis or trans?

$\left[\begin{array}{l} Z = \text{Zusammen (together)} \\ E = \text{Entgegen (opposite)} \end{array} \right]$

E-Z System - If the two higher priority gps are on the same side of the double bond, the isomer is called Z (together) and if the two higher priority gps are on the opposite side of the double bond, isomer is called E (opposite).

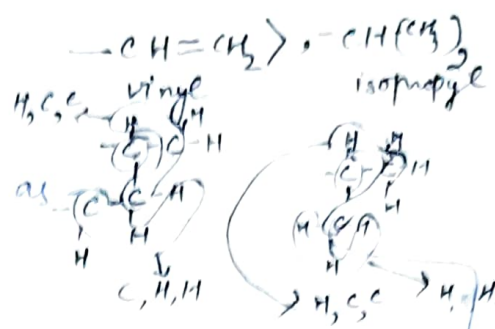
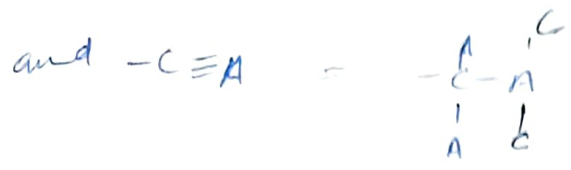
The priority can be assigned on the basis of following rules -

SEQUENCE RULES:-

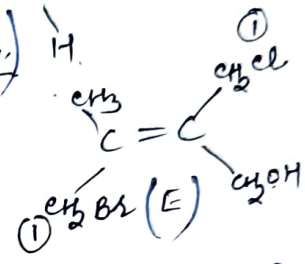
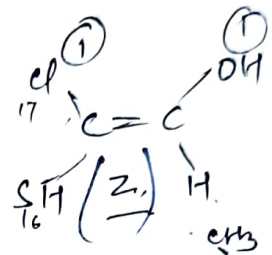
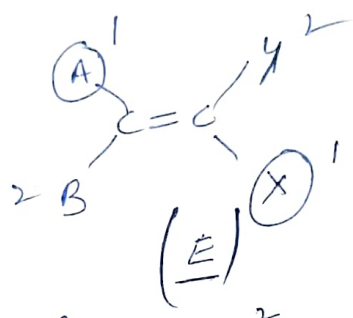
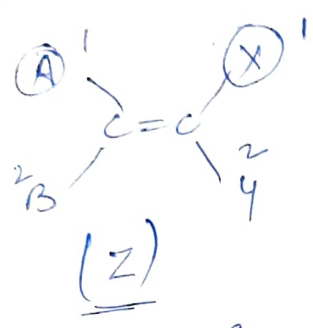
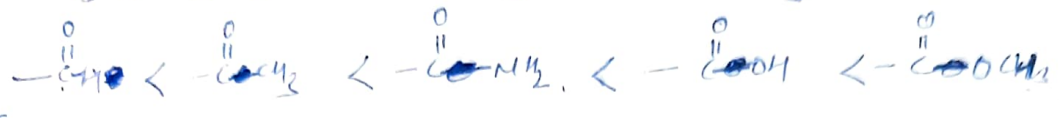
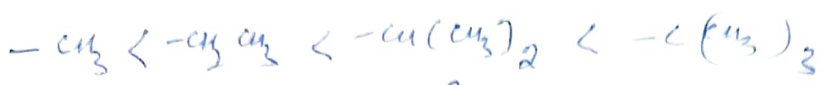
- ① Higher priority is given to atoms of higher at. no.
- ② If isotopes of the same element are ~~not~~, the isotope with higher atomic ~~wt~~ will have the higher priority.
- ③ If the priority can not be decided by this rule, it is determined by comparing the next atoms in the gp and so on.
- ④ A doubly or triply bonded atom is considered equivalent to 2 or 3 such atoms. For e.g.



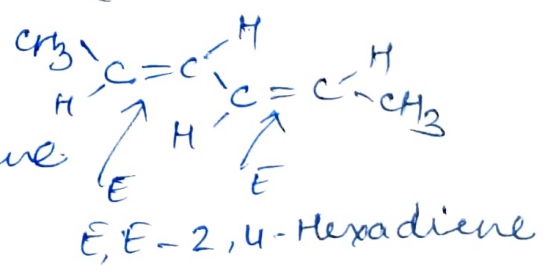
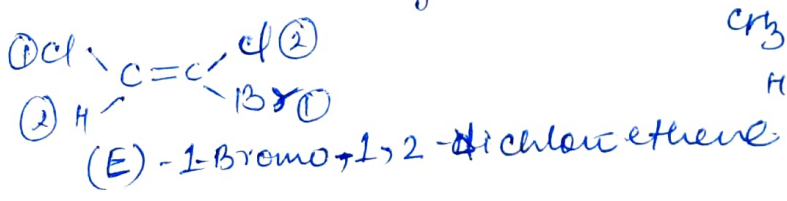
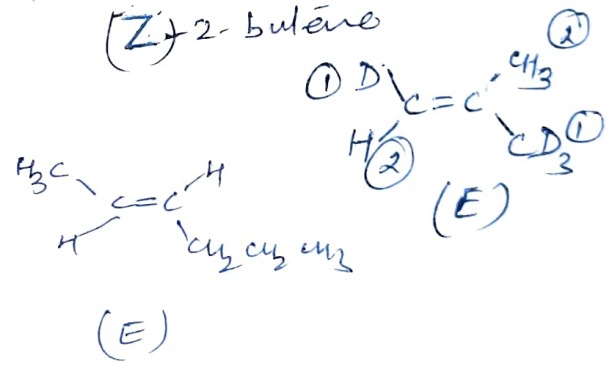
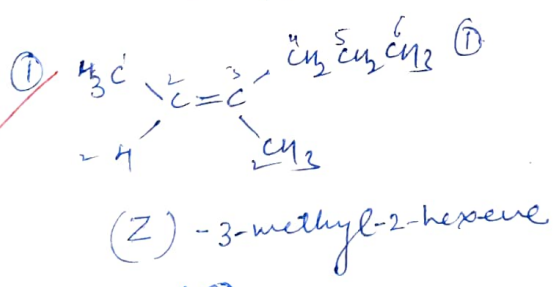
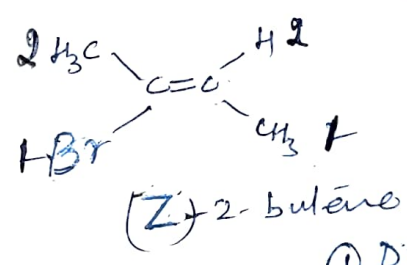
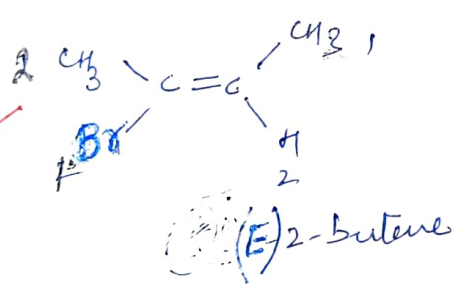
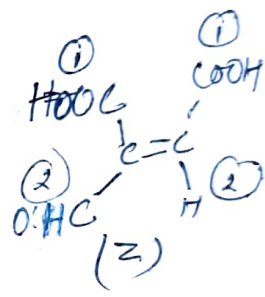
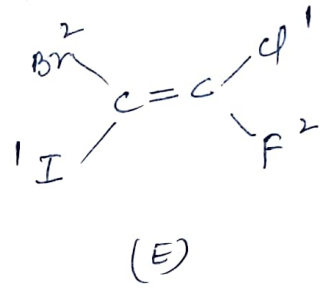
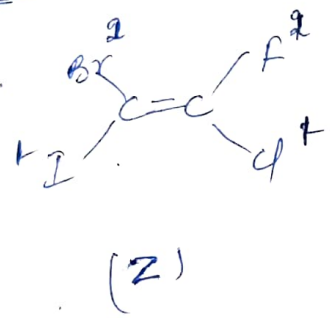
②



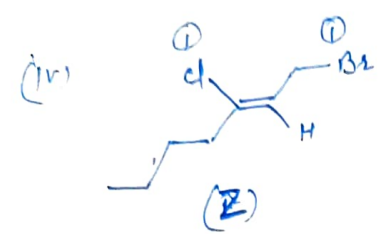
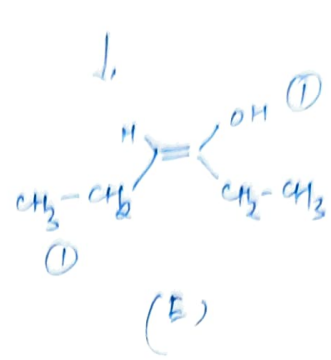
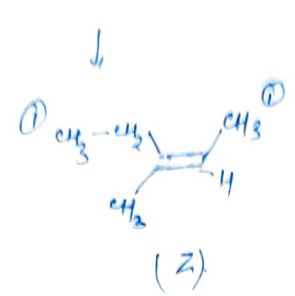
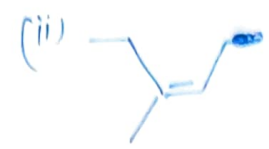
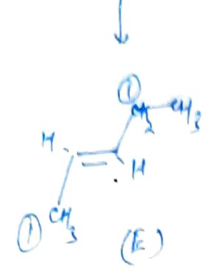
The priority order will be as

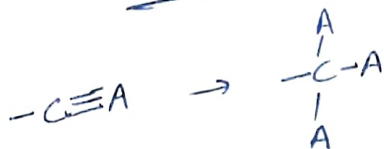


For e.g.



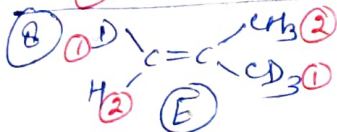
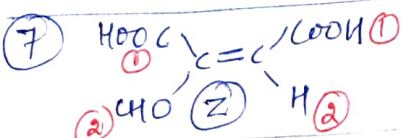
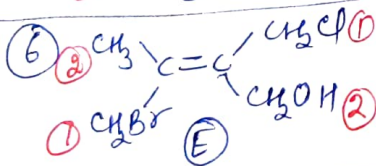
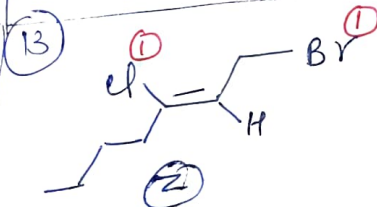
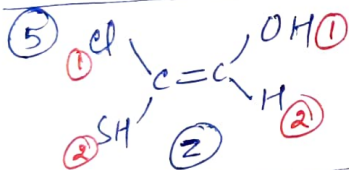
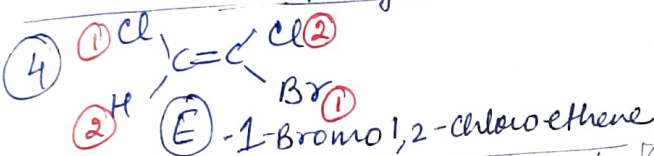
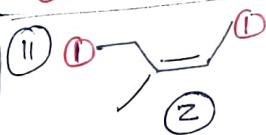
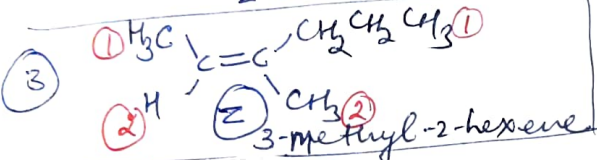
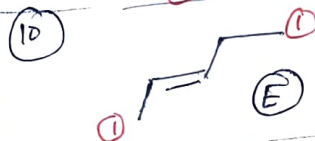
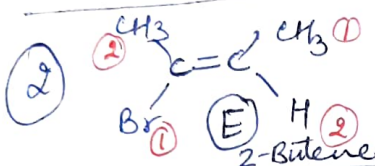
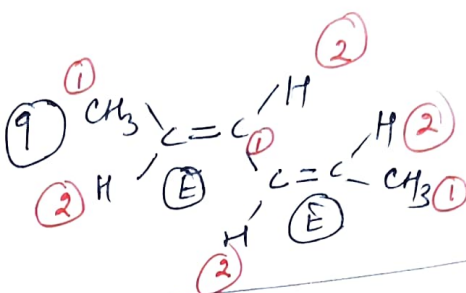
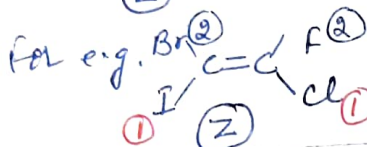
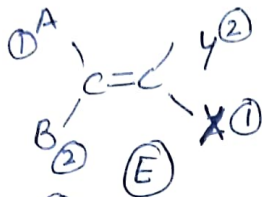
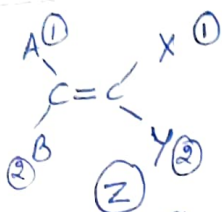
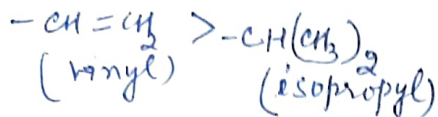
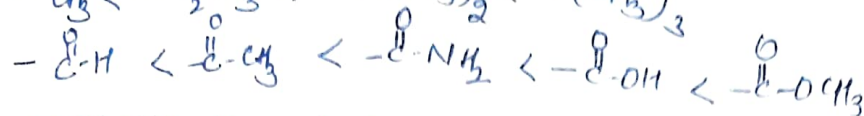
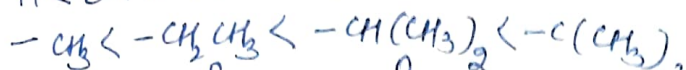
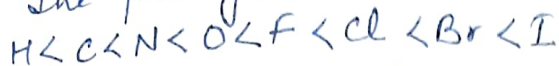
Write E/Z configuration of the following compounds:



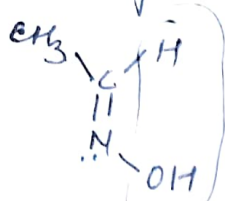


(2)

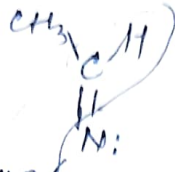
The priority order will be as :-



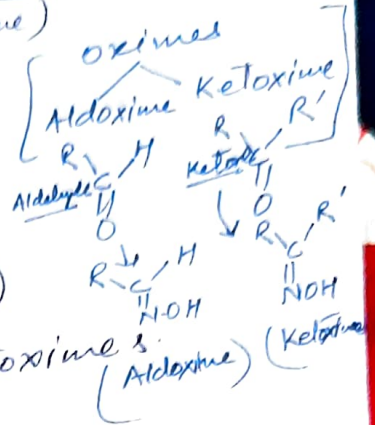
Geometrical isomerism is also shown by other compounds containing $C=N$ or $N=N$ bonds such as oximes & certain cyclic compounds:-



Syn
(Equivalent to cis)



Anti
(Equivalent to trans)



Syn & anti isomerism is not possible in ketoxime 3.

