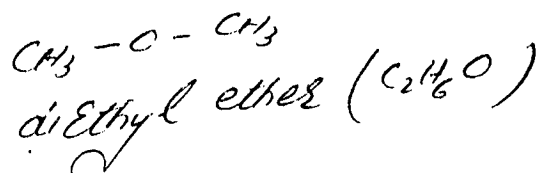
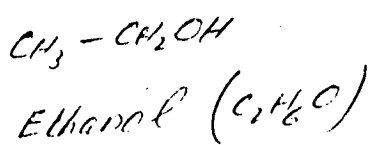


WHAT ARE ISOMERS? WRITE A BRIEF NOTE ON

CONSTITUTIONAL ISOMERS

Ans:- The compounds having same chemical formula but different structural formulae are called isomers and phenomenon is known as isomerism.

Let us consider simplest example of isomerism. Let there be a compound with formula C_2H_6O . It can have following structures.



These two have same chemical formula but these are two different compounds due to different structures.

TYPES OF ISOMERISM:-

Isomers are basically

divided into two categories.

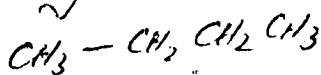
- (i) CONSTITUTIONAL ISOMERS OR STRUCTURAL ISOMERS.
- (ii) STEREO ISOMERS.

STRUCTURAL ISOMERS:- These are isomers which have same molecular formula but different connectivity i.e. they have different sequence of atoms.

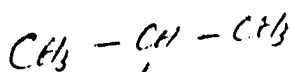
Constitutional isomers are further divided into following categories

CHAIN ISOMERS:- These are isomers which have same chemical formula, same functional group but different chain length.

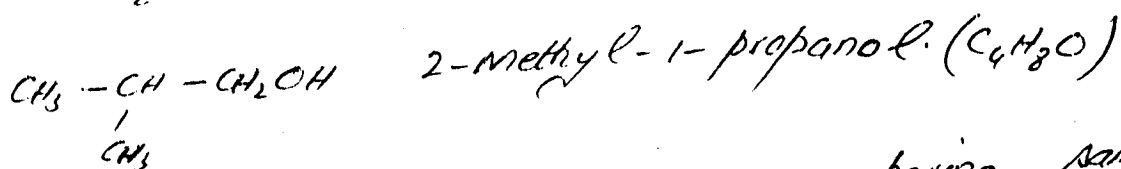
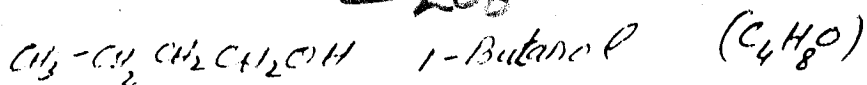
For example



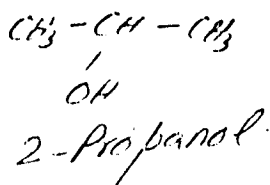
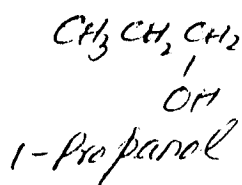
n-Butane (C_4H_{10})



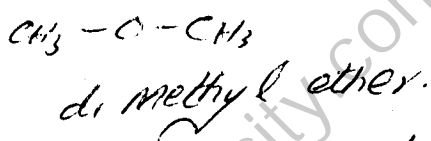
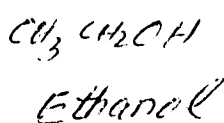
Isobutane (C_4H_{10})



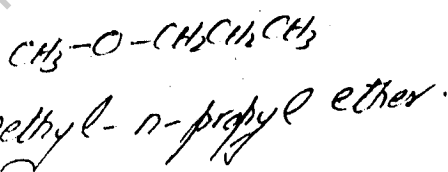
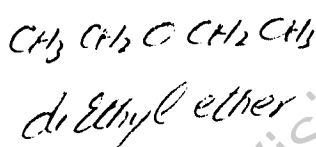
POSITIONAL ISOMERS:- These are isomers having same chemical formula, same functional group but different position of functional group. For example



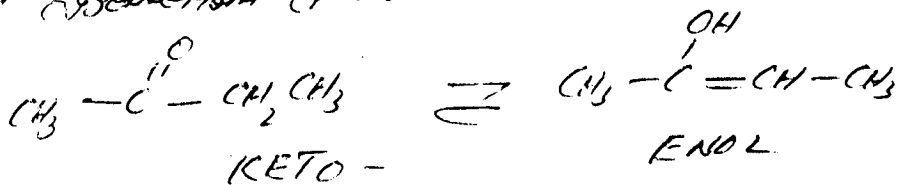
FUNCTIONAL GROUP ISOMERS:- These are isomers having same (functional group) molecular formula but different functional groups. e.g. $\text{C}_2\text{H}_4\text{O}$ can have following formula



METAMERS:- These are isomers which differ in alkyl groups attached to same multivalent atom. e.g.



TAUTOMERS:- These are isomers which differ in arrangement of proton on one atom or the other with the corresponding shift of double bond. The most common type of ~~isomerism~~ tautomerism is keto-enol tautomerism.



Constitutional Isomers are distinguishable by two dimensional structure

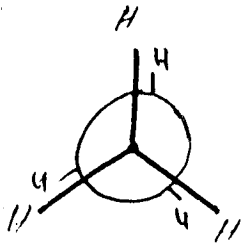
EXERCISE 1. WRITE ALL ISOMERS OF $\text{C}_5\text{H}_{12}\text{O}$ (HINT CHAIN, POSITION
2. WRITE CHAIN ISOMERS OF HEPTANE AND METAMERS)
AND WRITE NAMES OF EACH ISOMER.

STEREISOMERS:-

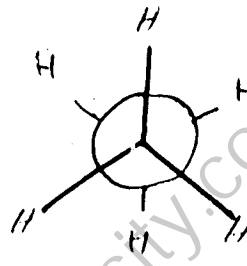
These are compounds which have same chemical formula, same connectivity but different arrangement of atoms in space. Stereoisomers can be distinguished by only three dimensional representation.

Stereoisomers are further divided into following categories

(i) CONFORMATIONAL ISOMERS:- These are isomers which are interconvertible by simple rotation around single bond. For example consider following isomers of Ethane in Fischer projection.



Fully Eclipsed



Skew Form (Gauche)

These are also called Rotamers

The conformational isomers differ slightly in energy. The study of conformations and energy changes is called Conformational Analysis.

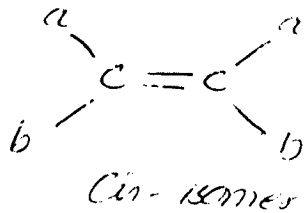
CONFIGURATIONAL ANALYSIS:- ISOMERS

These are isomers which cannot be interconverted by rotation about single bond. These can be interconverted by breaking and remaking of bonds. These are further divided into:-

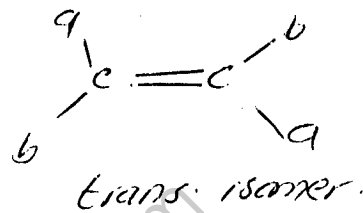
- (i) OPTICAL ISOMERS
- (ii) GEOMETRICAL ISOMERS.

OPTICAL ISOMERS: These are isomers which differ from each other by their behaviour towards plane polarized light. If one isomer rotates polarized light to left the other may rotate to right and vice versa. They are further divided into various types i.e. enantiomers, diastereoisomers, mesoisomers, epimers etc. (to be discussed later on).

GEOMETRICAL ISOMERS: These are configurational isomers which are produced due to restricted rotation around d.b. (especially $C=C$). These are also called cis-trans isomers. e.g.



§



WHAT ARE VARIOUS ELEMENTS OF SYMMETRY. DEFINE DISSYMMETRIC, ASYMMETRIC, CHIRAL AND ACHIRAL MOLECULES.

The symmetric, dissymmetric, asymmetric nature of an object (molecule) can be determined on the basis of elements of symmetry. Let us consider these elements of symmetry one by one.

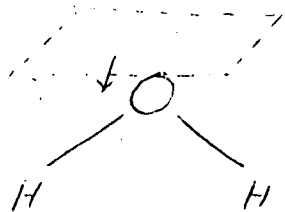
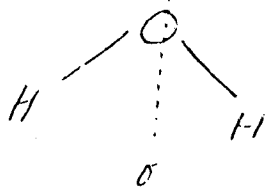
PLANE OF SYMMETRY (SIGMA PLANE) OR MIRROR PLANE.

It is an imaginary plane which bisects molecules into two identical half which are mirror images of each other. It is also called mirror plane or sigma plane. Conventionally a molecule having sigma plane, is called symmetric molecule. An object (molecule) having no sigma plane is said to be dissymmetric molecule. Planar molecules have at least one sigma plane. Let us consider some examples

BILATERAL SYMMETRY: - An object having one and only one sigma plane is said to possess bilateral symmetry. For example human body possess bilateral symmetry.

TWO AND THREE SIGMA PLANES:-

(i) WATER MOLECULE water molecule has two sigma planes perpendicular to each other these can be shown as follows

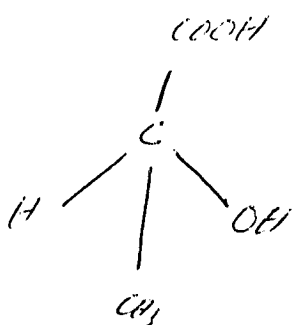


(ii) AMMONIA MOLECULE Ammonia molecule has three sigma planes each passing through one hydrogen. Similarly methane has a number of sigma plane each passing through two hydrogens.

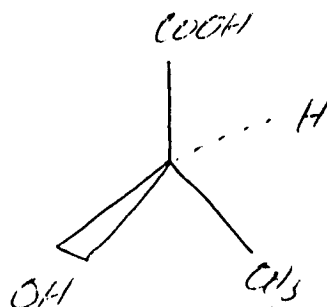
CYLINDRICAL SYMMETRY:- A cylinder has an infinite number of sigma planes along one axis (vertically) and one sigma plane perpendicular to its length. The molecules having infinite number of sigma planes are along one axis and one sigma plane perpendicularly, is said to possess cylindrical symmetry.

SPHERE:- A sphere has infinite number of sigma planes. Such objects are said to possess spherical symmetry.

DISYMMETRIC: The molecules having no ~~plane~~ sigma plane is said to disymmetric molecule. For example consider following molecules



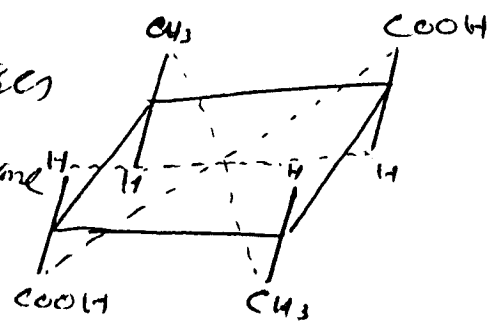
Lactic acid molecule.



CENTRE OF SYMMETRY

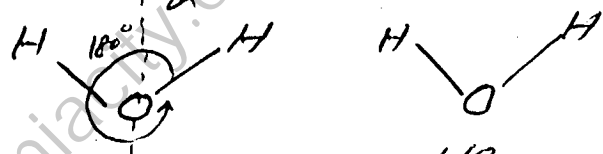
It is a point within a molecule from which if we draw a line ~~one~~ on one side and extend to an equal distance on opposite side, it encounters identical environment. This test can be easily applied in three dimensional structures.

For example 2,4-dimethyl cyclobutane-1,3-dicarboxylic acid. Only even numbered rings can exhibit this element of symmetry.



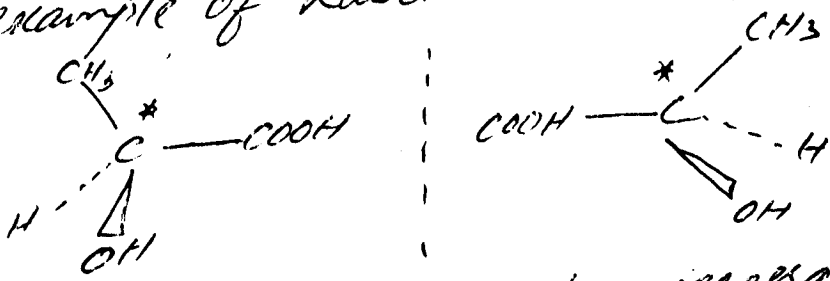
AN ALTERNATING AXIS OF SYMMETRY

A molecule possesses n-fold axis of symmetry if when rotated through an angle of $360^\circ/n$ about this axis, brings an indistinguishable form. For example water has two fold axis of symmetry because when rotated through 180° ($\frac{360}{2} = 180^\circ$) it brings indistinguishable form.



CHIRAL ATOM

When a molecule is nonsuperimposable on its mirror image it is said to be chiral. Compounds which have at least one carbon attached to four different substituents are non-superimposable on their mirror image. Such compounds are called chiral and such an atom is called CHIRAL ATOM. Consider an example of lactic acid.

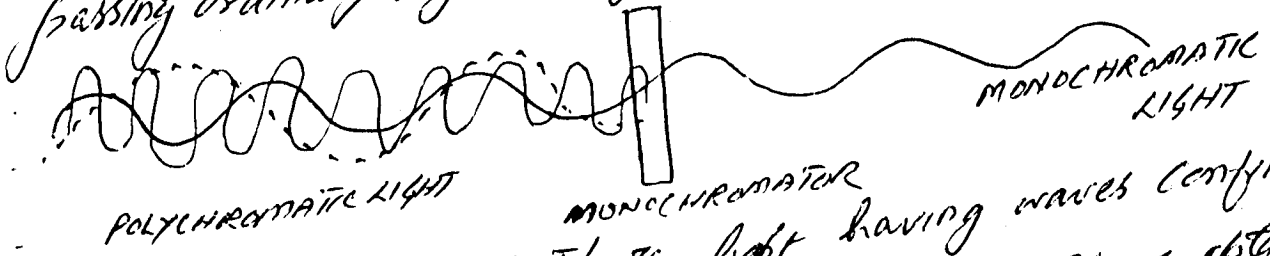


However a chiral atom is not a necessary condition of chirality. A molecule may not have a chiral atom but still it may be chiral. Only chiral compounds can rotate plane polarized light.

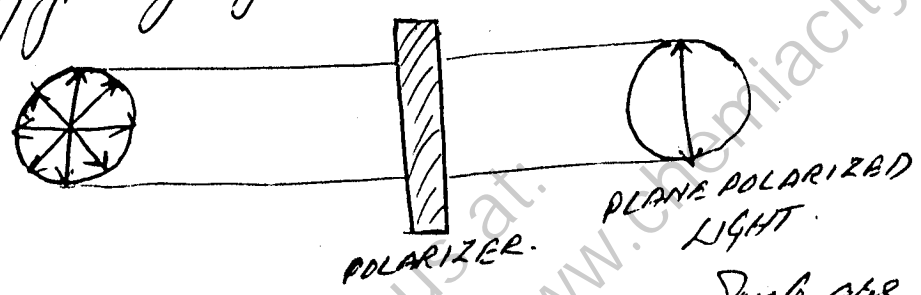
ASYMMETRIC MOLECULE / A molecule having no element of symmetry is called Asymmetric molecule. A classical example of asymmetric molecule is lactic acid.

DEFINE THE FOLLOWING

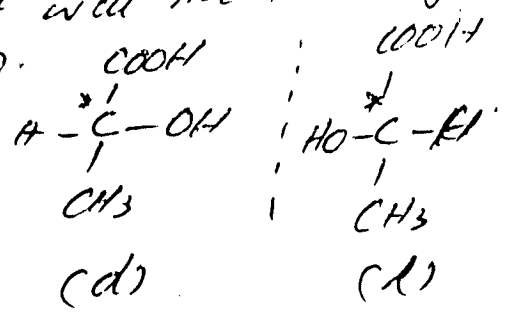
(i) MONOCHROMATIC LIGHT / Light having waves of a single wavelength is called monochromatic light. It is obtained by passing ordinary light through a monochromator.



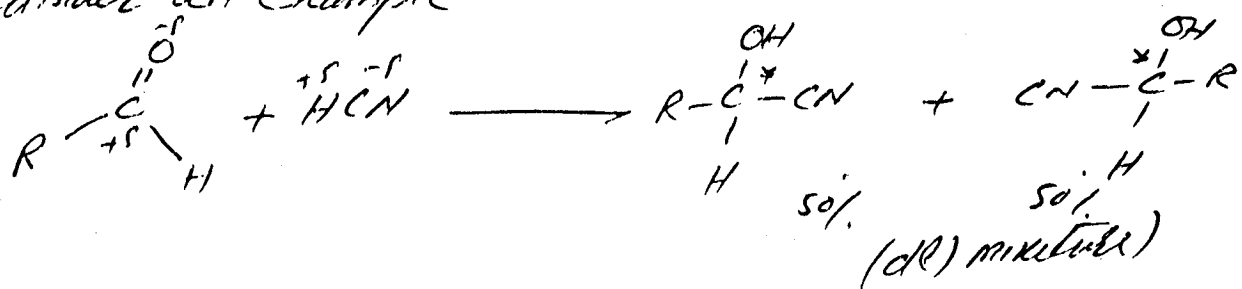
PLANE POLARIZED LIGHT / The light having waves confined to one plane is called plane polarized light. It is obtained by passing light through polarizer such as NICOL PRISM.



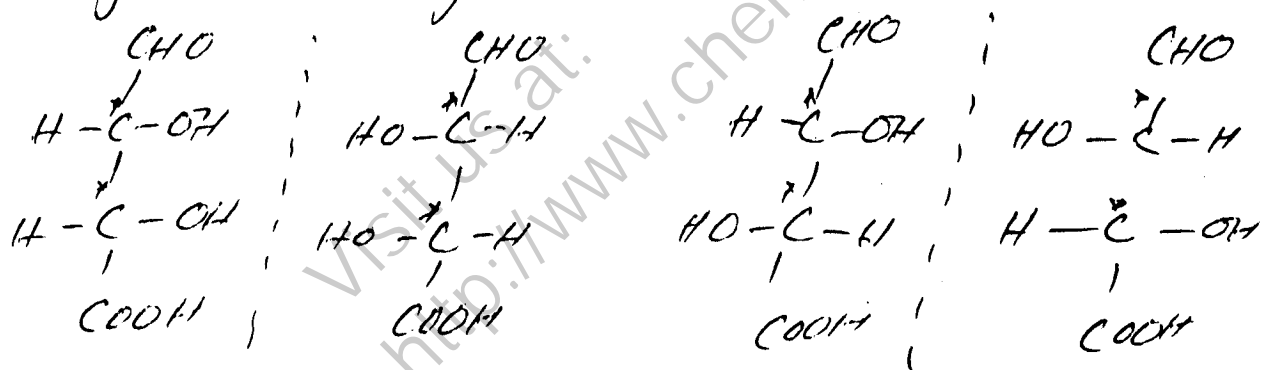
ENANTIOMERS / The stereoisomers which are related to each other as non superimposable mirror images of each other are called enantiomers. The enantiomers have same physical and chemical properties. They differ only in their behaviour towards plane polarized light. If one enantiomer rotates plane polarized light to left (l) the other will rotate it to right in equal ~~but~~ angle (d). The equal equimolar mixture of two enantiomers is called Racemic mixture. It will not rotate plane polarized light in any direction.



Since enantiomers have same physical and chemical properties therefore it is very difficult to separate pure enantiomers from racemic mixture. The separation of enantiomers from racemic mixture is called Resolution. Whenever an asymmetric centre is produced during a chemical reaction from a planar compound the two enantiomers are always produced in equal amount. Consider an example



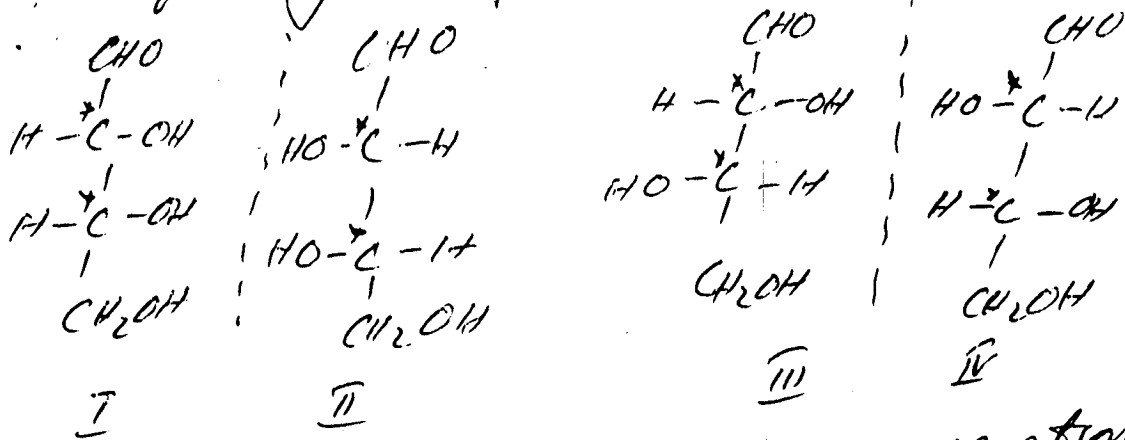
The maximum number of enantiomers produced by a compound is 2^n where "n" is number of asymmetric centres. i.e. a compound having 2 asymmetric centres will produce two pairs of enantiomers.



WRITE A NOTE ON DIASTEREOISOMERS.

DIASTEREOISOMERS / The stereoisomers which are not related to each other as non superimposable mirror images of each other are called DIASTEREOISOMERS. Diastereoisomerism is exhibited by compounds having more than one asymmetric atoms. The max. No. of diastereoisomers exhibited by a compound are (2^n) where "n" is number of asymmetric atoms.

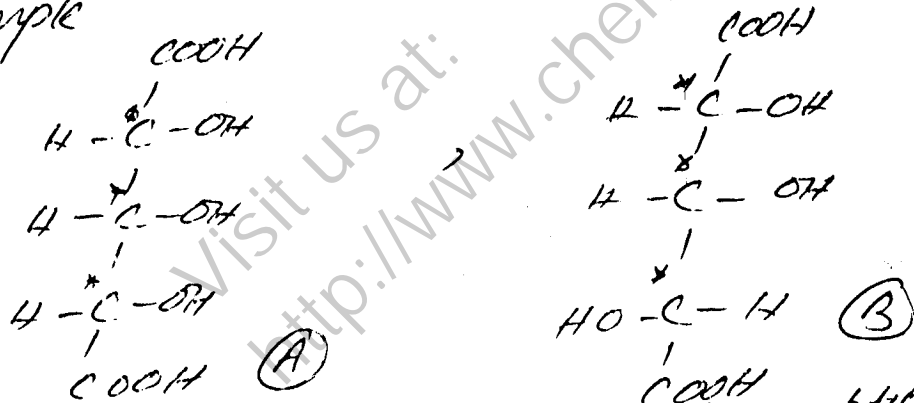
Consider following example - 213 -



I & II and III & IV are pair of enantiomers.
 But I & III, I & IV, II & III and II & IV are diastereoisomers of each other.

Diastereoisomers behave like different chemical comp. They have different physical and chemical properties reactivities. They also have different optical rotation.

One diastereoisomer may be optically active and other may be inactive or meso form. Consider following example

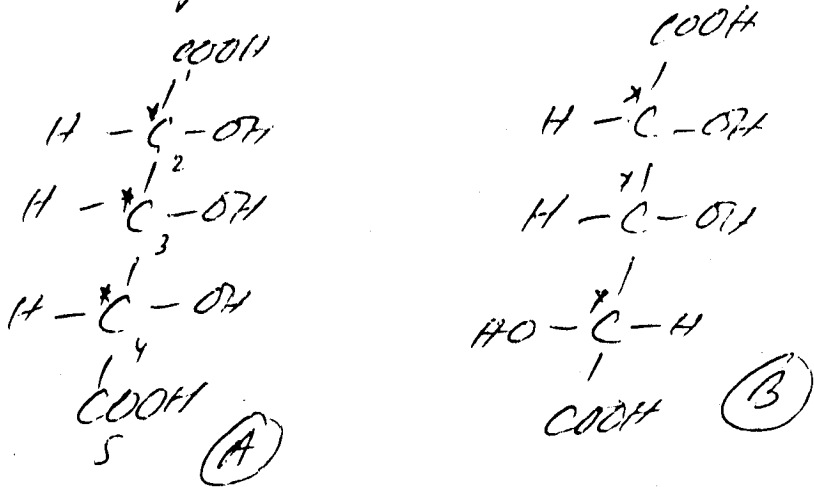


(A) and (B) are diastereoisomers. (A) is optically active due to plane of symmetry (meso form) while (B) is optically inactive.

Racemic mixture can be resolved by making diastereoisomers by reacting with an optically active compound.

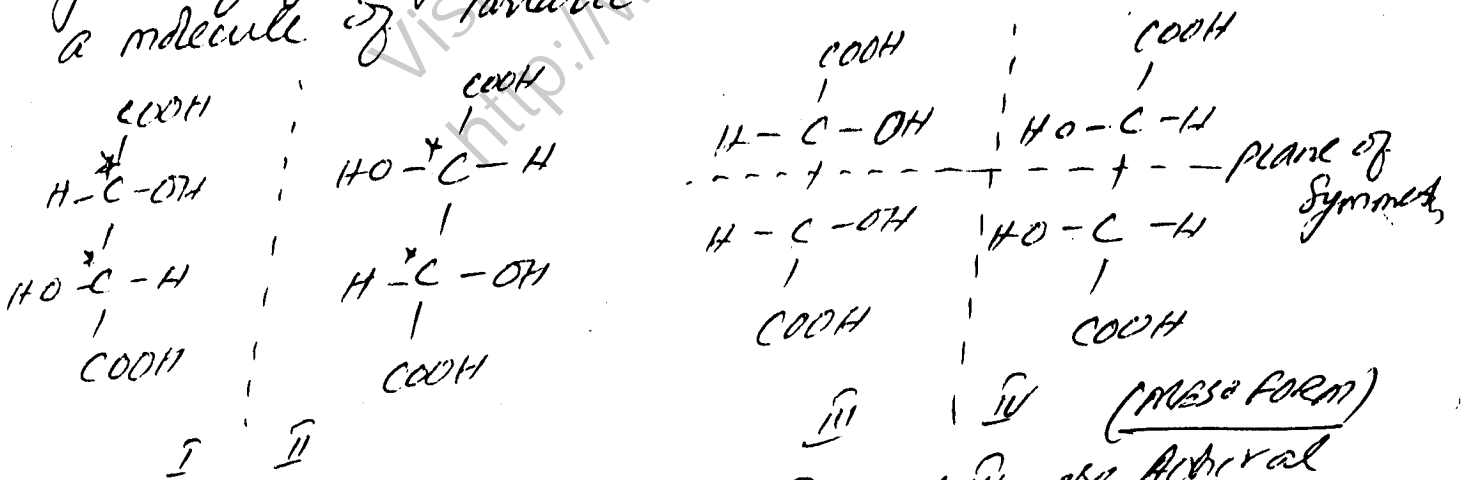
WRITE A NOTE ON EPIMERS & MESO ISOMERS

EPIMERS / The diastereoisomers which differ in configuration at one asymmetric centre are called epimers. The epimers differ in physical properties and optical rotation and chemical reactivities. All epimers are diastereoisomers but all diastereoisomers are not epimers. Consider following diastereoisomers



(A) and (B) are diastereoisomers which differ in configuration at 'C₄' only.

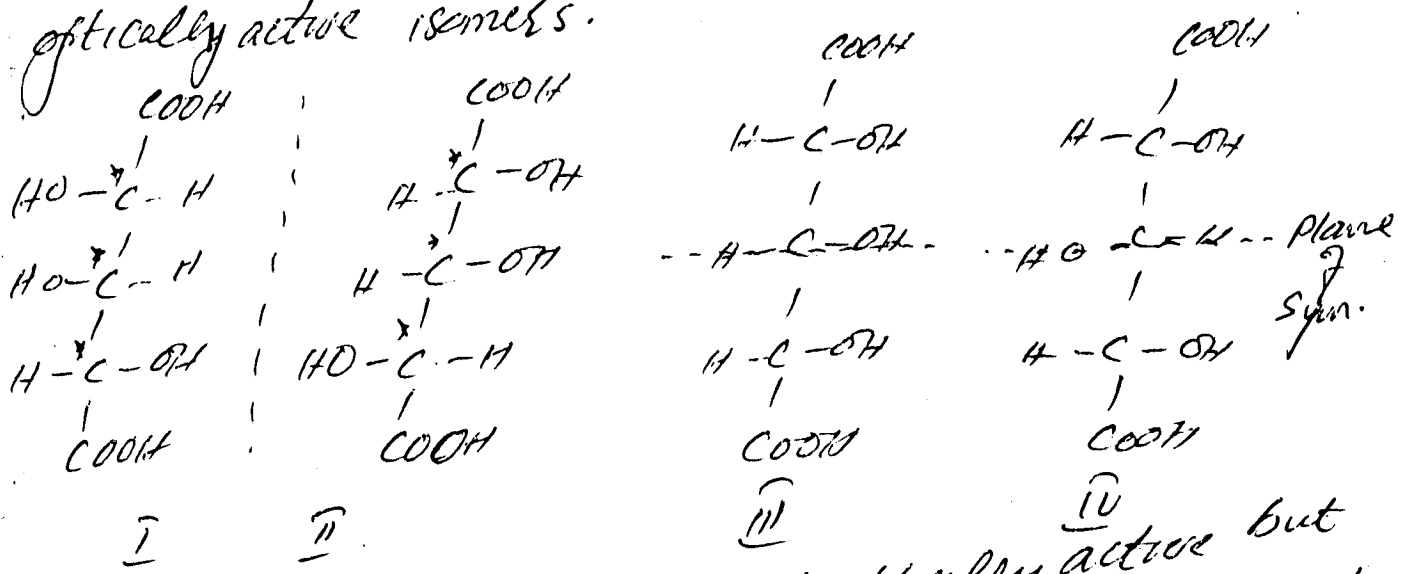
MESO ISOMERS / The stereoisomers which have more than one chiral centres but still achiral due to plane of symmetry are called meso isomers. For example consider a molecule of tartaric acid.



I & II are enantiomers but III and IV are Achiral due to plane of symmetry and they are optically inactive.

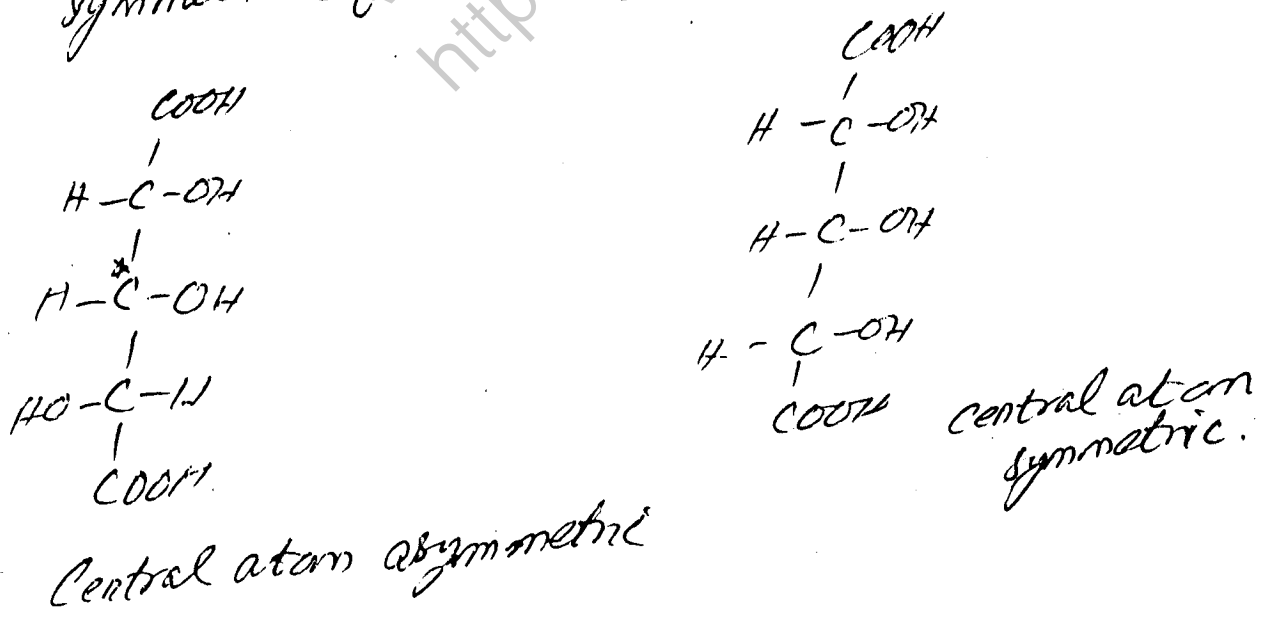
The actual number of optical isomers for a compound having more than one similar chiral carbons is some

times less than 2^n . For example trihydroxyglutaric acid has three chiral atoms but it has only two optically active isomers.



I, II are enantiomers and optically active but III and IV are MESO-ISOMERS and optically inactive they are ACHIRAL.

PSEUDOASYMMETRIC ATOM | The central carbon atom may be symmetric or asymmetric depending upon ~~config~~ configuration of other two asymmetric atoms. If two is same then the central atom will be called symmetric. If it is different it becomes asymmetric.



HOW TO DRAW FISCHER PROJECTION.

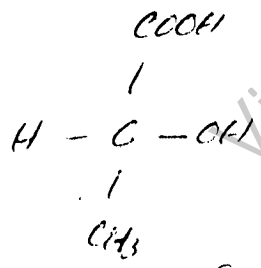
Fischer projection is a method of representing arrangement of different groups attached to tetrahedral carbon.

The steps involved in writing Fischer projection are

- (i) Hold the molecule in such a way that longest carbon chain is vertical.
- (ii) Its preferable to have most oxidized group is at the top.
- (iii) The molecule is held in such a way that tetrahedral carbon is within the plane and vertical groups are below the plane and horizontal groups are projecting above the plane.
- (iv) The vertical groups are ~~and~~ shown by dotted line and horizontal groups shown by wedge shaped lines.

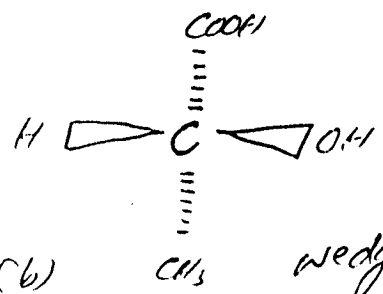
Let us consider an example of Lactic acid.

Planar Model.



(a)

FISCHER PROJECTION.



(b)

wedge and dotted line structure

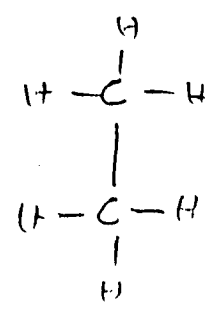
However for simplicity it is usually written as 'α'

The configurations of optically active compounds are generally represented by Fischer projection.

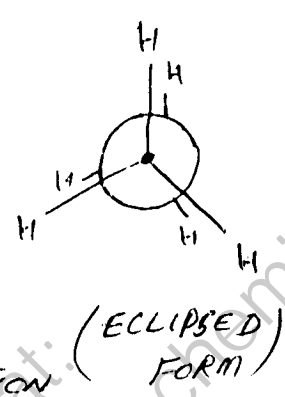
NEWMAN PROJECTION:- It's also a method of representing molecules on plane of paper. In this method molecule is held in such a way that one carbon is in front of observer and other carbon is behind that carbon. The front carbon is represented by a dot and groups attached to it are accordingly arranged from this dot.

The carbon on the far side is represented by a circle around the dot of front carbon. The groups attached to far side carbon are shown from outer circle. Consider ~~Fischer~~ Newman projection of

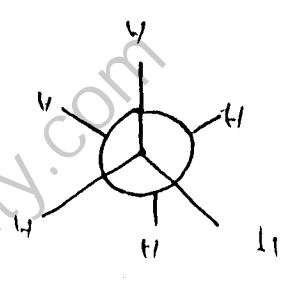
of Ethane



FISCHER PROJECTION



(ECLIPSED FORM)



STAGGARD (FORM)

R,S-NOMENCLATURE:-

WHAT ARE RULES OF ASSIGNING R,S-NOMENCLATURE TO ASYMMETRIC COMPOUNDS.

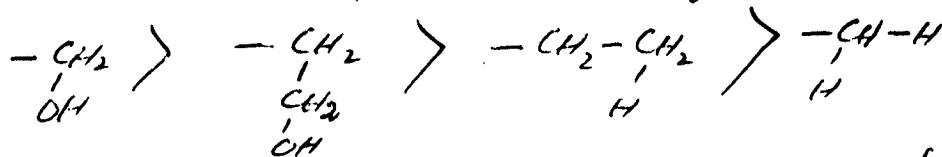
The D,L-System of naming chiral compounds has been replaced by Cahn-Ingold-Prelog system of Nomenclature. In this system, letter "R" or "S" is written to express configuration at chiral centre.

In order to determine R,S configuration, the four groups attached to ^{CHIRAL} central atom are assigned priority order. The following rules are observed while assigning priority order.

MISCELLANEOUS
DATE: / /
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CLASS: /

SEQUENCE RULES

- 1) The substituents are written in order of decreasing atomic number of atom directly attached to chiral atom.
For example $(-Cl) > (-OH) > (-CH_3) > H$
- 2) If two atoms directly bonded to chiral atom have same atomic number, then second atom attached to directly bonded atom will determine priority.



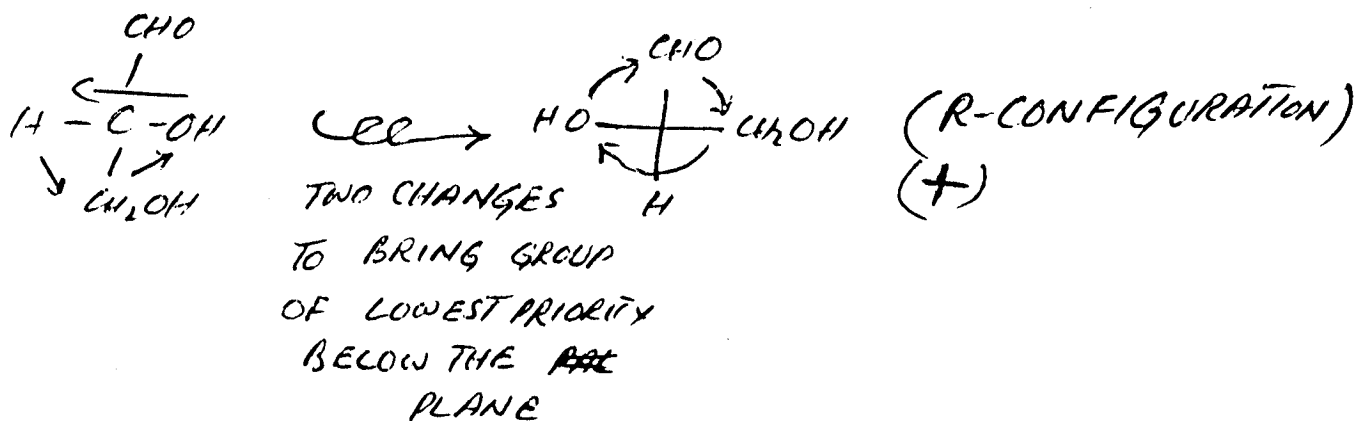
- 3) In case of isotopes, heavy isotope takes precedence over lighter isotope e.g. $-T > -D > -H$

- 4) The double or triple bond is considered as two bonds or three bonds respectively. For $-C \equiv N$ is considered as three nitrogens attached to carbon. $(-C \equiv CH) > (-CH=CH_2)$

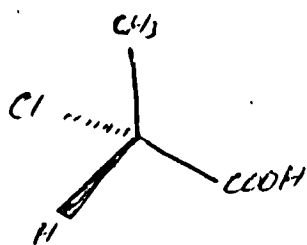
- 5) If choice is to be made between two groups, the more branched chain is preferred. $(-CH(CH_3)(CH_2CH_3)) > (-CH_2-CH_3)$

Once priority order has been assigned molecule is held such that group of lowest priority is below the plane (away from observer). If sequence of substituents of decreasing priority order is clockwise it is called "R" configuration and if it is counter clockwise it is called S configuration.

For example consider following molecule. (PRIORITY ORDER $-OH > CHO > CH_2OH > H$)

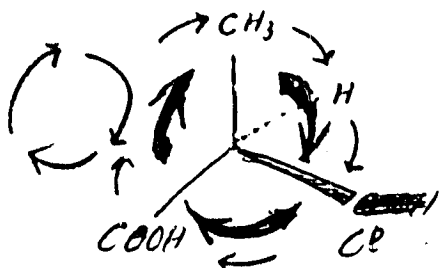


Q NO: 3 (EXERCISE) LABEL FOLLOWING AS R- or S-



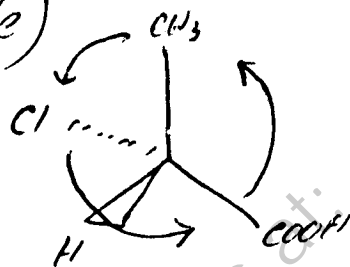
PRIORITY ORDER = $-Cl > COOH > CH_3 > H$

(SINCE group of lowest priority is projecting below the plane so the molecule is rotated such that group of lowest priority goes below the plane) Now assigning sequence "R" configuration is obtained.



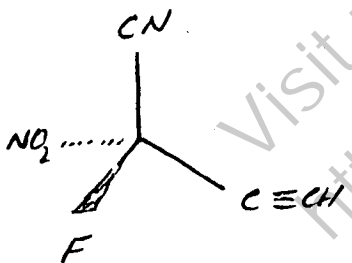
(R-CONFIGURATION)

METHOD :- 2 :- It is better to assign priority order and determine sequence of substituents as such and inverting the observed rotation to get correct rotation. (because molecule is being observed from back side)



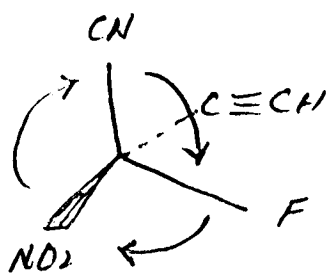
OBSERVED CONFIG. = S
ACTUAL CONFIG = "R"

(b)

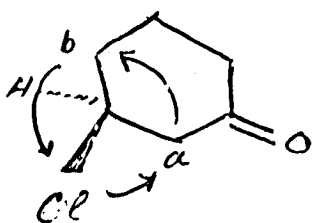


PRIORITY ORDER = $-F > NO_2 > -CN > -C\equiv CH$

(ROTATING THE MOLECULE SUCH THAT $(-C\equiv CH)$ GOES BELOW THE PLANE)
(R-CONFIGURATION)

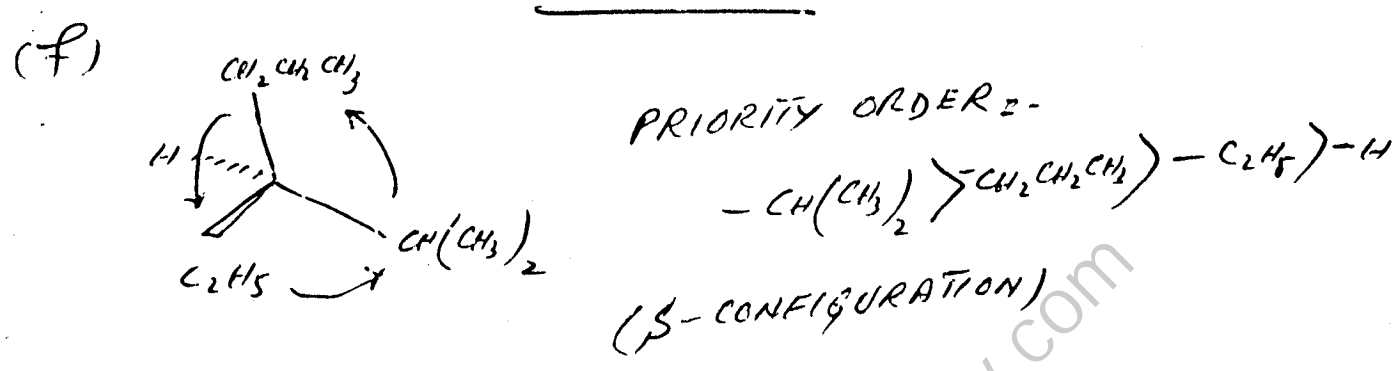
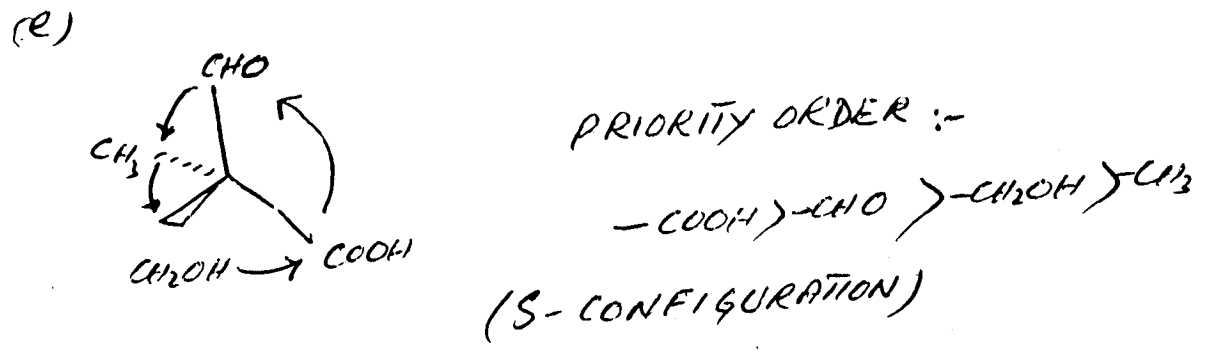
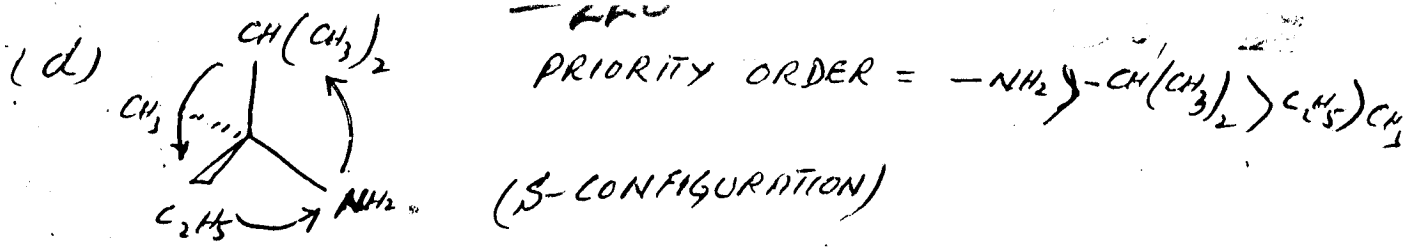


(c)

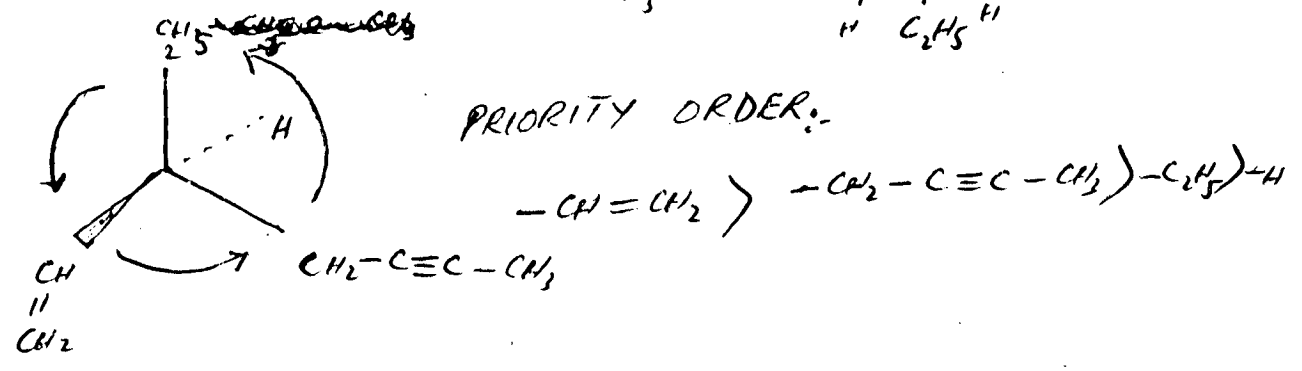
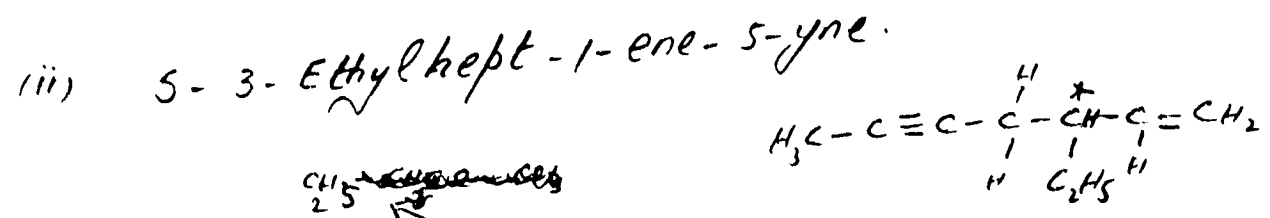
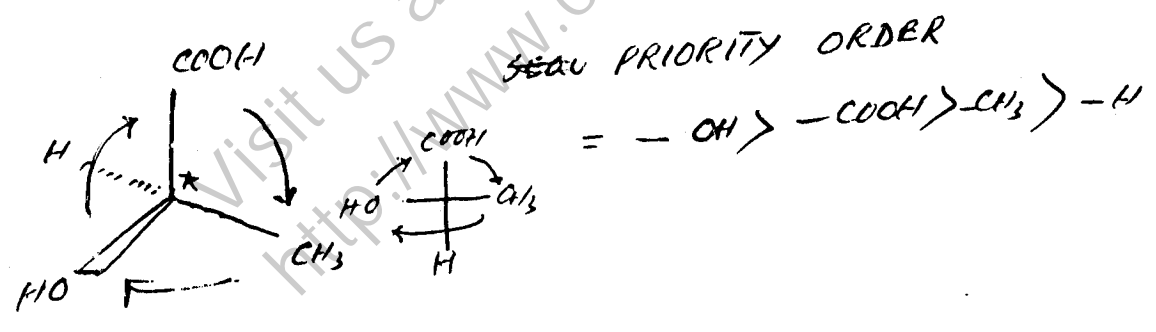
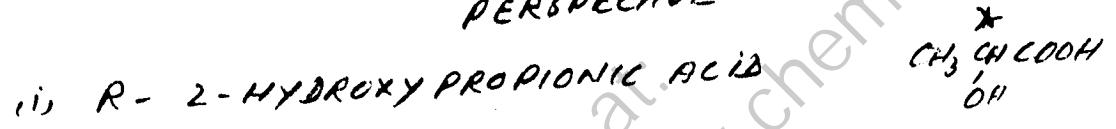


PRIORITY ORDER $-Cl > a > b > H$

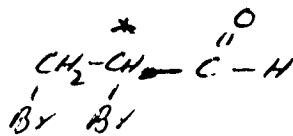
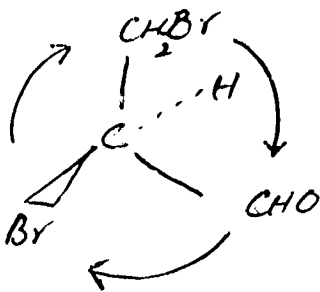
(S-CONFIGURATION)



DRAW FOLLOWING IN CORRECT ASYMMETRIC PERSPECTIVE.

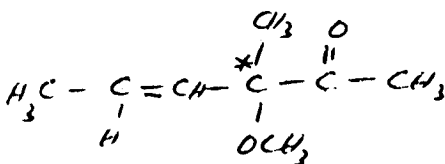
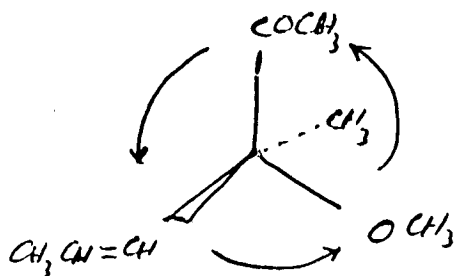


(iii) R- 2,3-Dibromopropanal.



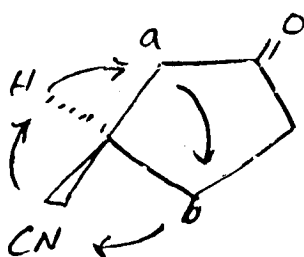
PRIORITY ORDER: -Br > -CH₂-CHO > H

(iv) S- 3-Methyl-3-methoxy-4-hexene-2-one.



PRIORITY ORDER
-OCH₃ > -COCH₃ > -CH=CHCH₃ > CH₃

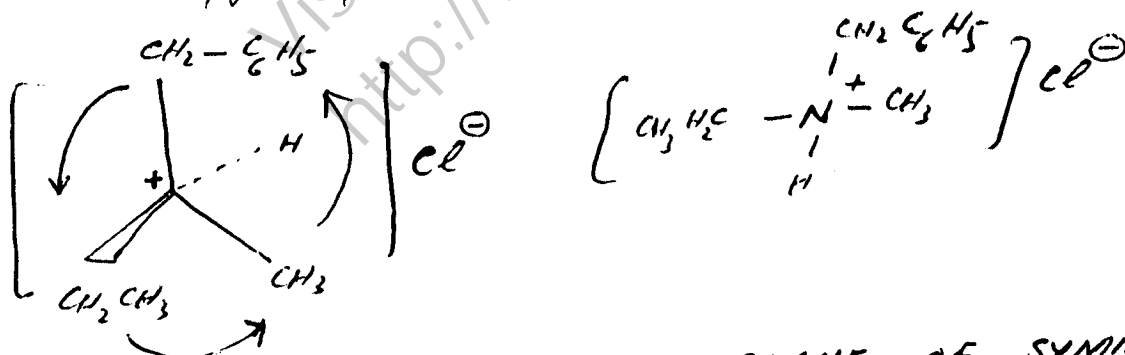
(v) R- 3-Cyanocyclopentanone.



PRIORITY ORDER
-CN > a > b > H

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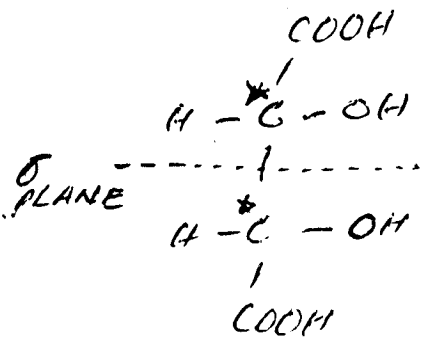
(vi) S- Methyl ethyl-benzyl ammonium chloride.



Q:- WHY A MOLECULE HAVING PLANE OF SYMMETRY DOES NOT SHOW OPTICAL ACTIVITY?
It is due to two factors which support each other.
(i) A molecule having plane of symmetry (σ-plane) is superimposable on its mirror image so it is "ACHIRAL" and achiral molecules are optically inactive.

(ii) A molecule having plane of symmetry has two halves which are nonsuperimposable mirror images of each other, thus they have equal but opposite rotation. Thus they cancel each other's effect. Thus molecule is optically inactive (NO NET ROTATION)

CONSIDER FOLLOWING EXAMPLE. OF TARTARIC ACID.

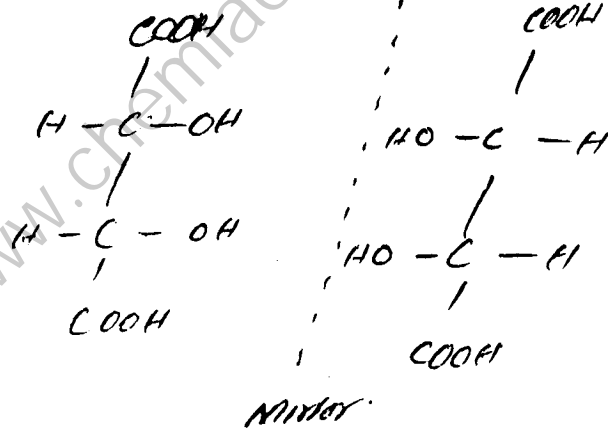


The isomer has two carbons attached & with four different substituents but still molecule is optically inactive because of two reasons.

(i) It has a sigma plane and two halves have equal but opposite rotation.

(ii) It is achiral because it is superimposable on its mirror image (After rotation through 180° along its length.)

So it is MESO FORM. (OPTICALLY INACTIVE)



Q.: WHAT IS OPTICAL ISOMERISM? WHAT TYPE OF OPTICAL ISOMERISM IS PRESENT IN TARTARIC ACID?

Ans:- ISOMERS:- The chemical compounds having same chemical formula but different structural formulae are called isomers, and phenomenon is called ISOMERISM.

(The isomers are basically divided into two categories. (1) CONSTITUTIONAL ISOMERS (DIFFER IN CONNECTIVITY)

(2) STEREOISOMERS (Having same connectivity but differ in three dimensional arrangement of atoms in space).

The stereoisomers are further divided into two categories

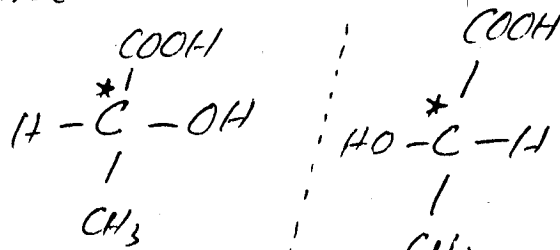
(1) CONFIGURATIONAL ISOMERS: These are isomers which can be interconverted by breaking and remaking of bonds.

(2) CONFORMATIONAL ISOMERS:- which can be interconverted just by rotation around single bond.

OPTICAL ISOMERS:- These are geo configurational isomers. The compounds which rotate plane polarized light are called OPTICALLY ACTIVE COMPOUNDS. The first and foremost condition for optical activity is ~~also~~ CHIRALITY.

The compounds which are not superimposable on its mirror images are called CHIRAL COMPOUNDS. The atom responsible for optical rotation (chirality) is called CHIRAL CENTRE.

The carbon which is attached with four different substituents is chiral carbon. The compounds which contain chiral atom are non superimposable on their mirror image.



(d,l) Lactic Acid

(A)

(B)

These two (A & B) have no element of symmetry
 So these are called Asymmetric compound.

The compound "A" and "B" are nonsuperimposable mirror images of each other are called ENANTIOMERS.
 They have same physical and chemical properties but differ in sign of rotation.

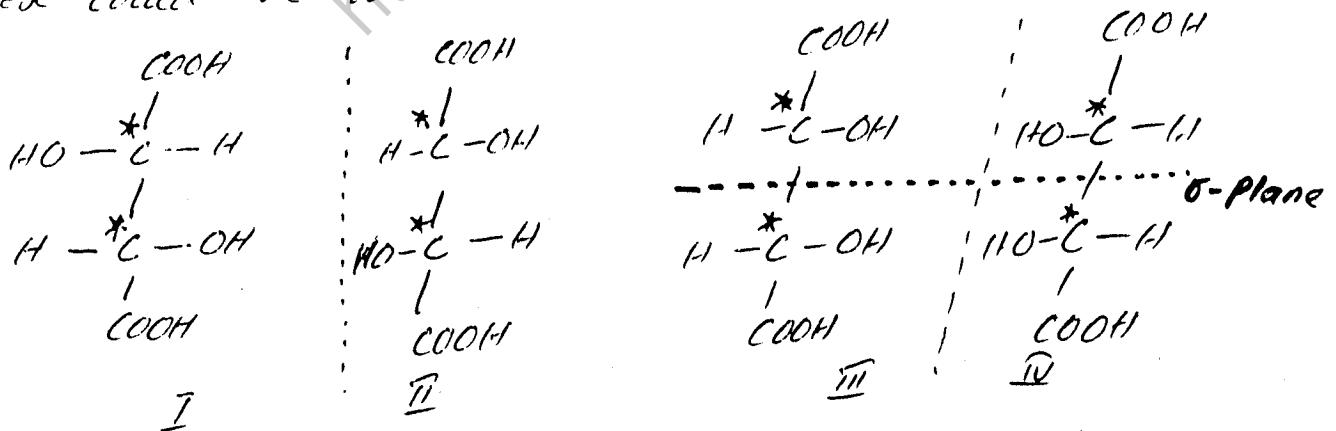
The enantiomer which rotates plane polarized light in right side ~~are~~ is called dextro rotatory (d) or (+).
 The enantiomer which rotates plane polarized light in ~~right~~ left side is called levo rotatory or (l) or (-). These are called OPTICAL ISOMERS.

This phenomenon is called OPTICAL ISOMERISM.
 The maximum number of optical isomers possible for a compound are 2^n where "n" is number of chiral atoms. But this number may be sometimes smaller than expected ones.

OPTICAL ISOMERISM IN TARTARIC ACID:-

Tartaric acid is very compound in study of optical isomerism.

The formula of tartaric acid $\text{COOH}-\text{CH}^*(\text{OH})-\text{CH}^*(\text{OH})-\text{COOH}$
 There are two carbons attached with four different substituents so maximum number of isomers = 4.
 These could be written as



The compound I and II are non superimposable mirror images so these are ENANTIOMERS. An equimolar mixture of these two will produce racemic mixture.

The structure III and IV are the same compound. These are not ENANTIOMERS (These are superimposable on each other (by rotation of 180° along its length). These are ACIRAL hence optically inactive.

The III and IV (have a sigma plane (MIRROR PLANE) hence it is not asymmetric.

The compounds having two or more atoms attached with four different substituents but still optically inactive due to sigma plane are called MESO-ISOMERS. The two halves of the same compound are mirror images of each other so they cancel each others effect internally. It is called INTERNAL RACEMIZATION.

However compound I and III are not related to each other as mirror images nor they are same compounds. These are called DIASTEREOMERS. Similarly II, III and II, IV are also diastereoisomers.

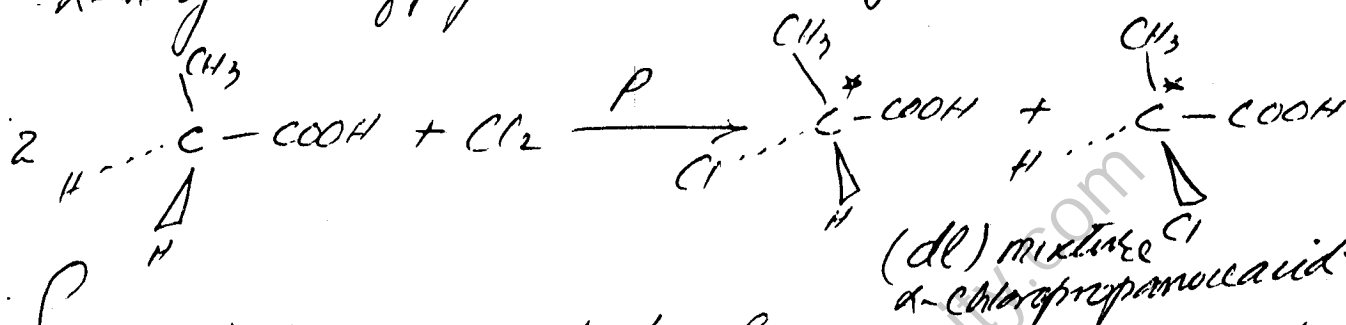
It also shows that diastereoisomers (I & III) differ in extent of rotation (I is optically active but III is not).

Thus compounds having more than one chiral centres may have lesser number of optical isomers (due to sigma plane).

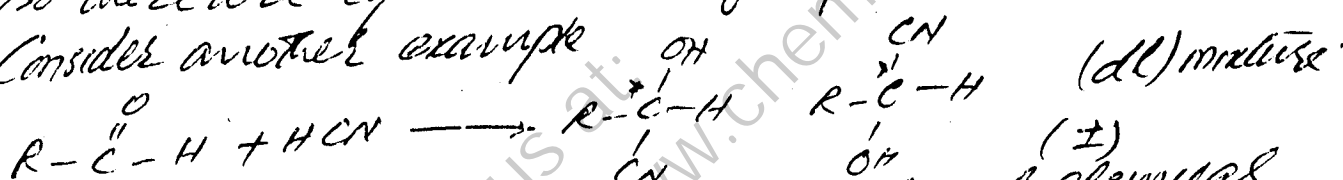
WRITE A NOTE ON RACEMIC MIXTURE & RACEMIZATION.

An equimolar mixture of a pair of enantiomers is called RACEMIC MIXTURE. A racemic mixture does not rotate plane polarized light despite of the fact that it contains chiral compounds. Actually two enantiomers are present in equal concentration and they rotate plane polarized light in equal but opposite directions. Thus the mixture becomes optically inactive.

Whenever a chiral centre is produced from an achiral compound a pair of enantiomers is obtained in equal concentration. Thus it is Racemic mixture. Consider α -halogenation of propanoic acid which produces Racemic mixture

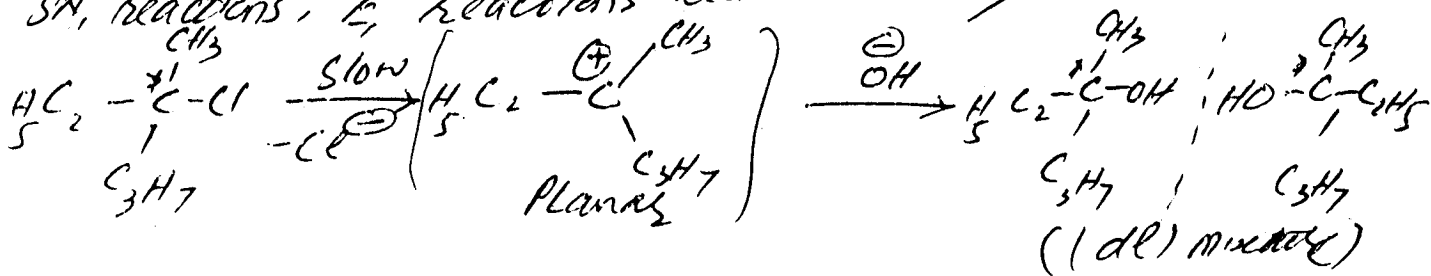


Since two hydrogens are identical so there are equal chances of replacement of any hydrogen. Consider another example



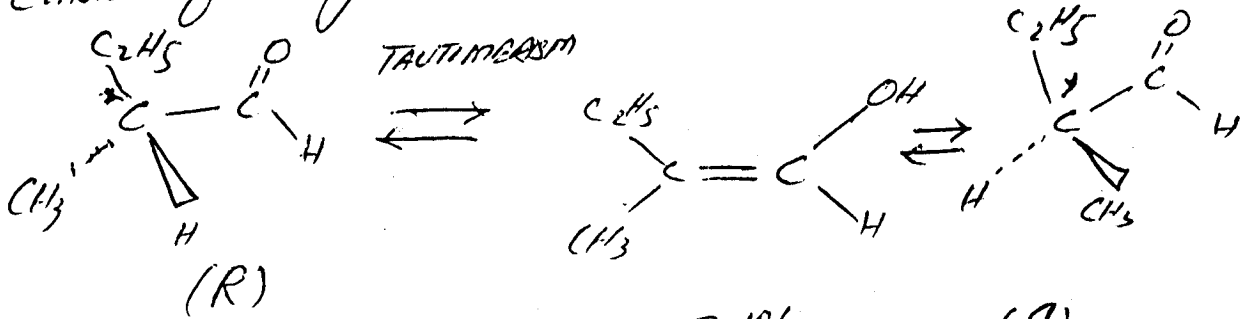
Since enantiomers have same physical and chemical prop. so a racemic mixture behaves like a single compound. Racemic mixture has sharp m.p., b.p., like pure comp.

RACEMIZATION | The production of racemic mixture from an optically active compound is called RACEMIZATION. During Racemization 50% inversion of configuration at every asymmetric atom takes place. All those reactions which proceed through planar intermediates like $\text{S}_\text{N}1$ reactions, E_1 reactions lead to Racemization.



Racemization is common in those compounds which have carbonyl group adjacent to chiral atom so that hydrogen of chiral atom may show tautomerism with carbonyl group.

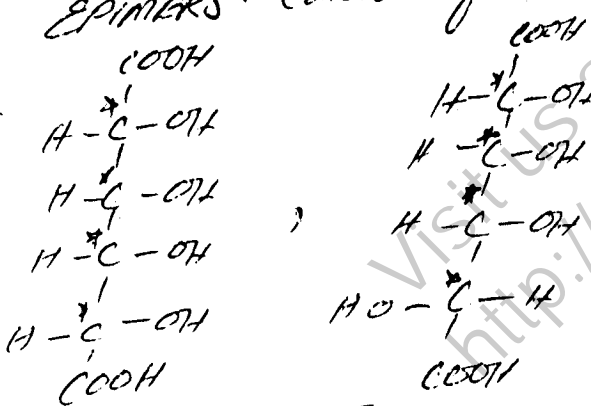
Consider following example



Thus there is an equilibrium between two enantiomers through an enol intermediate. Therefore whenever α -methyl butyraldehyde is heated its optical activity is lost due to racemization through enol form.

EPIMERIZATION | The compounds which differ in configuration at one chiral atom out of

two or more chiral atoms in a compound are called epimers. Consider following example



I and II are epimers because they differ in configuration at last chiral carbon (C₅). While configuration at all other carbons is retained.

I \neq II

The process of inversion at one asymmetric centre out of two or many is called epimerization. Epimerization may not lead to racemization (with few exceptions). The resulting mixture is optically active however the angle of rotation and physical properties of the mixture may change because epimers are actually diastereoisomers which have different physical and chem properties.

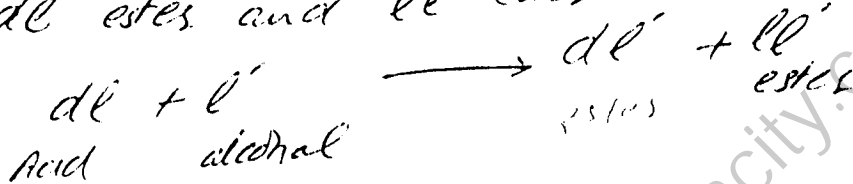
(11)

WHAT IS RESOLUTION OF RACEMIC MIXTURE? WRITE VARIOUS METHODS OF RESOLUTION.

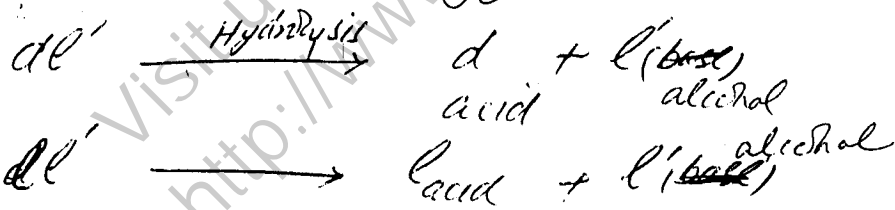
The process by which a racemic mixture is separated into even two individual enantiomers is called Resolution of racemic mixture. A racemic modification can be resolved by following methods.

CHEMICAL METHOD:- In this method racemic mixture is treated with a pure enantiomer. The reaction produces two diastereoisomeric products. These diastereoisomeric products can easily be separated.

In order to separate d' acid it is treated with an optically active base like l'-brucine or l'-morphine. The two diastereoisomers produced are d' ester and l' ester.



These diastereoisomers have different physical properties. These can be separated by fractional crystallization. Then these are hydrolyzed to get pure acids.



The racemic alcohols are generally converted into acid ester by reaction with phthalic anhydride. These acid esters are now treated with optically pure alcohol to get diastereoisomers.

BIOCHEMICAL METHODS:- A biological method makes use of special type of bacteria which attack one enantiomer, dextro and consume it leaving behind other type unaffected. In this method one enanti-

12 is isolated at the cost of other.

For example *Penicillium glaucum* destroy 'd' tartaric acid and leaves 'l' form unaffected.

CHROMATOGRAPHIC METHOD: - In this method racemic mixture is passed through a chromatographic column which contains optically active absorbance substance. Different enantiomers will separate due to different extent of absorption powers. Both paper chromatography and column chromatographic techniques can be used in this respect.

For example 'd' mandelic acid has been ^{almost} completely resolved by paper chromatography on starch.

MECHANICAL METHOD: - This method has very limited application. This method can be used if two enantiomers have different crystalline forms (crystals are mirror images of each other). Pasteur used this method to resolve a racemic mixture of tartaric acid. He mechanically picked up the crystals of one type from mixture.

KINETIC METHOD OF RESOLUTION: - This method is applicable if one enantiomer reacts at a faster rate than other enantiomer. Thus one enantiomer is converted into products at faster rate and other is left behind.

For example (-) menthol reacts with (+) mandelic acid at a faster rate than its reaction with (-) mandelic acid (The ~~two~~ transition states are diastereoisomeric \pm (-,+) and (-,-)).

Thus when racemic mixture of mandelic acid (\pm) is treated with insufficient amount of (-) menthol, more (+) mandelic acid will react with (-) menthol.

to form (-) methyl (+) mandelate than (-) menthyl (-) mandelate. The resulting mixture will be richer in (-) mandelic acid. Thus partial resolution can be effected by this method.

DIFFERENTIAL REACTIVITY:- The enantiomers react with optically active reagents at different rates, it is possible to effect partial resolution by stopping reaction before completion.

PREFERENTIAL CRYSTALLIZATION:- A super saturated solution of racemic mixture is prepared. A small crystal of one pure enantiomer is added to it. The enantiomer whose crystal has been added will preferentially crystallize out. The \pm glutamic acid has been resolved by this method.

RESOLUTION OF MOLECULAR COMPLEXES:-

When a racemic mixture is treated with an optically active reagent, such that resulting compound is a crystalline complex, the diastereoisomeric crystalline products are obtained. These have different solubilities. These are separated by physical method. The pure enantiomers can be obtained by decomposition of complex by heating or chemical treatment.

$\#$ 2-Chlorooctane has been resolved by using urea. It crystallizes in spiral shaped asymmetric crystals.

WRITE A COMPREHENSIVE NOTE ON GEOMETRICAL ISOMERISM

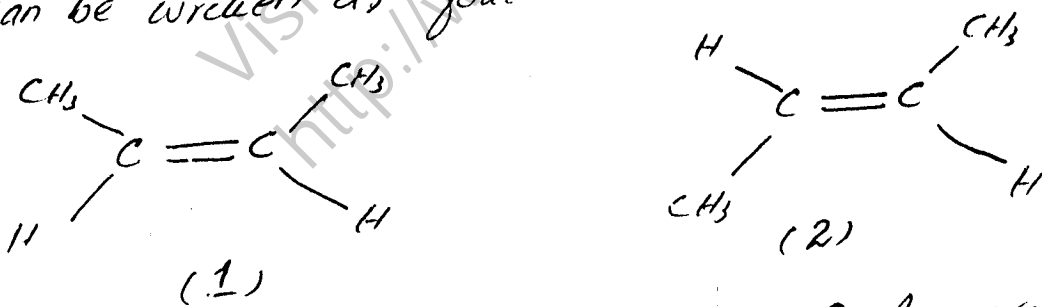
Ans:- The isomers formed due to restricted rotation between two carbons are called **GEOMETRICAL ISOMERS** and phenomenon is known as **GEOMETRICAL ISOMERISM**.

OR

The **cis, trans** isomerism exhibited by compounds having restricted rotation between two carbon atoms is called **GEOMETRICAL ISOMERISM**.

EXPLANATION In a double bond there is always a sigma bond and a π -bond. The π -bond is formed by parallel overlap of p-orbitals. The p-orbitals forming π -bond must be co-planar. When rotation is to be carried out in carbon to carbon double bonded compound, the π -bond will have to be broken. The energy required to break this bond is 263 KJ/mole. This energy is not available at room temperature. So, one isomer cannot be converted into other isomer without breaking and remaking a bond.

EXAMPLE Let us consider an example of 2-Butene. It can be written as follows.



The isomers '1' and '2' are Geometrical Isomers.

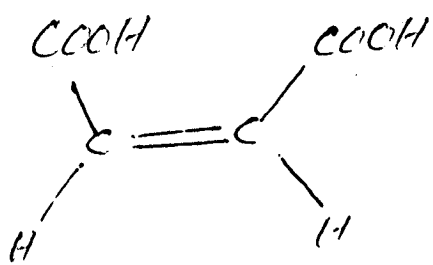
Cis Isomer In structure 1 two similar groups are present on same side. It is called **Cis isomer** (Cis = ON THIS SIDE)

Trans Isomer In isomer '2' the similar groups are on opposite side it is called **trans isomer (ACROSS)**.

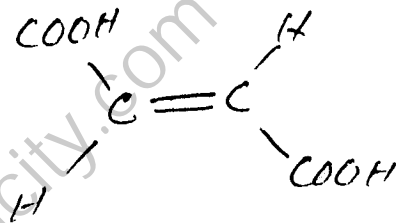
This type of isomerism is called **"cis-trans" ISOMERISM**.

Since there is a double bond between two carbons so "cis" and "trans" isomers cannot be interconverted by rotation. They can be interconverted by breaking and remaking of bonds.

Isomer '1' and '2' (cis-trans isomers) are 'NOT' related to each other as non superimposable mirror images. Thus they are called DIASTEREOMERS. They differ in chemical and physical properties. For example cis isomer of Butenedioic acid is called MALEIC ACID while trans-isomer is called FUMARIC ACID due to entirely different physical and chemical properties.



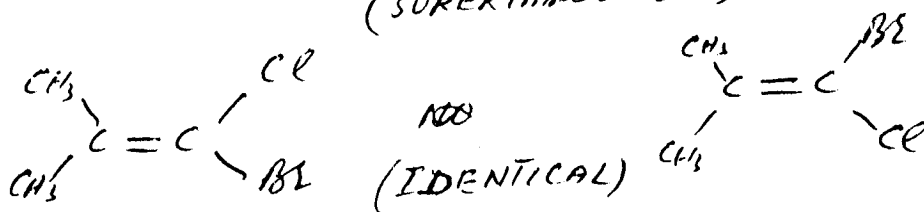
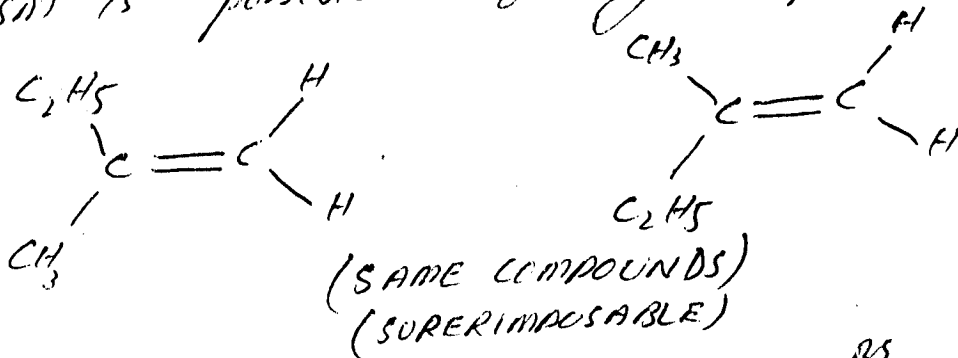
(cis) Butenedioic acid
(MALEIC ACID)



Trans-Butenedioic acid
(FUMARIC ACID)

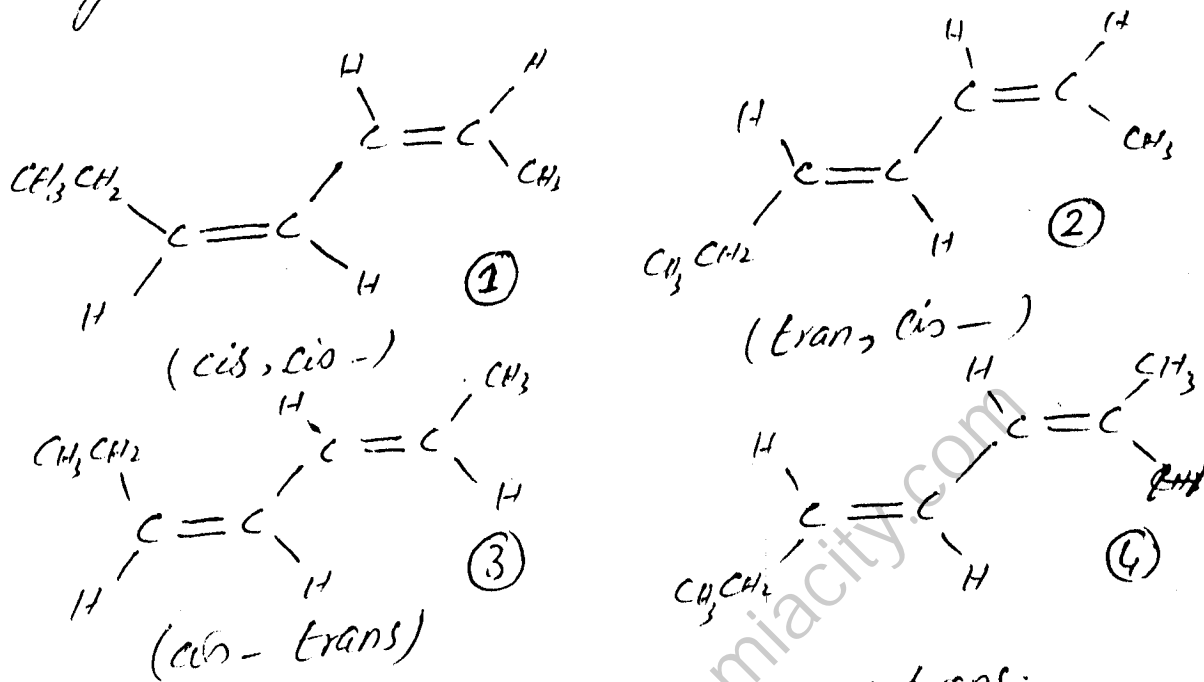
CONDITION FOR GEOMETRICAL ISOMERISM

Geometrical isomerism is possible in those alkenes which have two different substituents attached to each carbon atom. For example NO GEOMETRICAL ISOMERISM is possible in following compounds



GEOMETRICAL ISOMERISM IN COMPOUNDS HAVING TWO OR MORE DOUBLE BONDS

If a compound having two or more double bonds, have 2^n geometrical isomers (n = Number of double bonds). Each double leads to cis-trans isomerism individually. For example consider an example of 2,4-Heptadiene. Four geometrical isomers are possible in this alkene.



However number of ^{isomers} double bonds is reduced if a double bonded ~~two~~ carbon ~~have~~ has identical substituents.

GEOMETRICAL ISOMERISM IN CYCLIC COMPOUNDS

Some times double bond may be present in cyclic compound. The isomers depend upon size of ring.

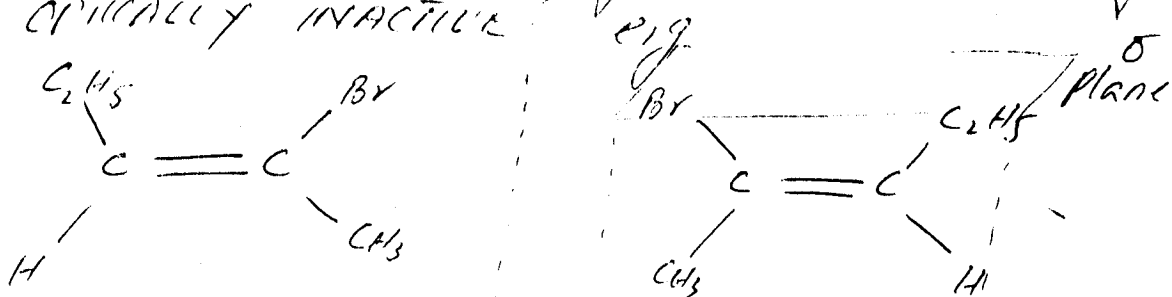
CYCLOPROPENE TO CYCLOPENTENE In small sized rings such as cyclopropene to cycloheptene the double bond is so ~~not~~ constrained that it must be "cis".

CYCLOOCTANE RING In a cyclooctane the double bond ~~may be~~ could exist in trans. form.

LARGER THAN 10-CARBONS In ^{d.b.} compounds having more than 10-carbons trans-isomer is more stable.

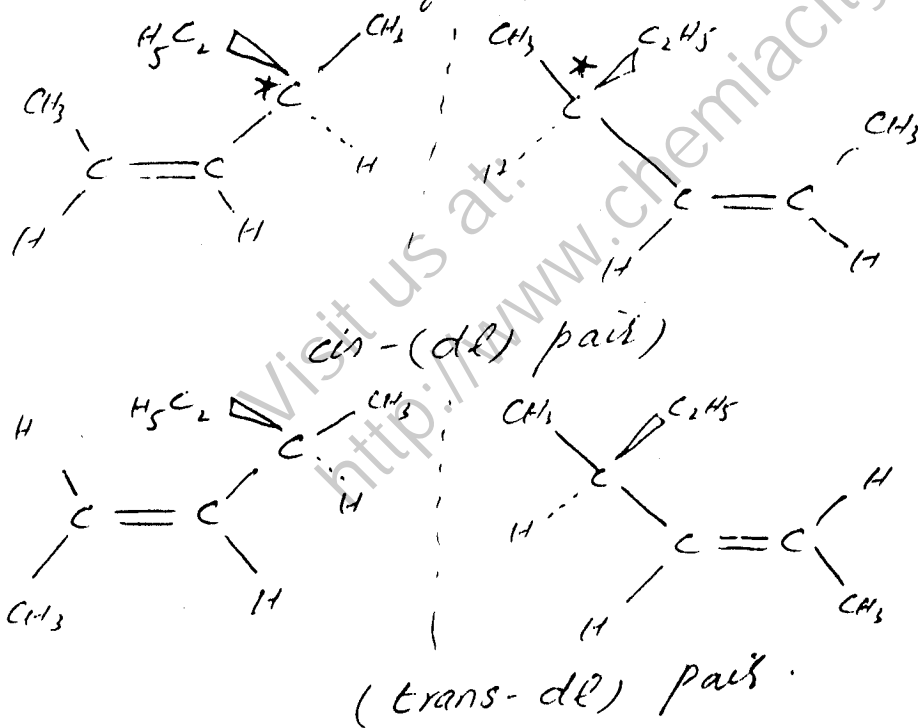
GEOMETRICAL ISOMERISM AND OPTICAL ISOMERISM COMBINED TOGETHER.

The double bonded carbons and substituents attached to them are planar so each isomer is superimposable on its mirror image (has a PLANE OF SYMMETRY). So GEOMETRICAL ISOMERS are normally ACHIRAL. Hence they are OPTICALLY INACTIVE.



(SUPERIMPOSABLE HENCE IDENTICAL COMPOUNDS)

However if a double bonded carbon has substituents having chiral carbon atom, it can show geometrical as well as OPTICAL ISOMERISM. There are four isomers possible i.e. cis-(dl) pair and trans-(dl) pair.

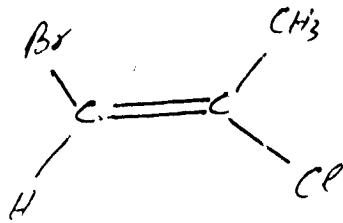
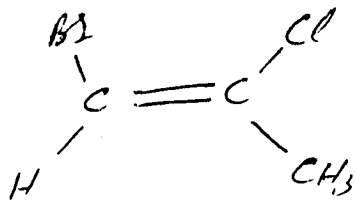
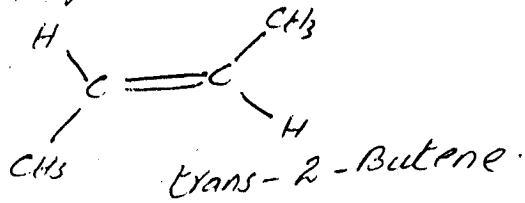
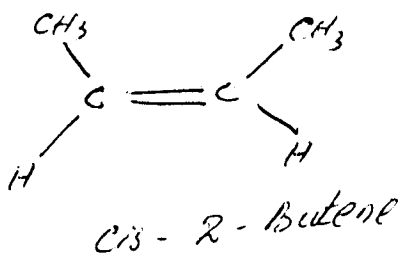


NOMENCLATURE OF GEOMETRICAL ISOMERS:-

Cis, trans Nomenclature:- According to this nomenclature if two similar groups are present on same side they are said to be "cis".

If two similar groups are on opposite side they are said to be trans.

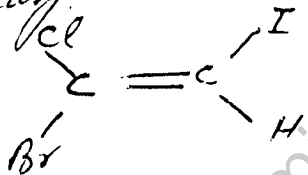
Let us consider following example.



cis- (Two halogens on same side). (Two halogens on opposite sides)

LIMITATIONS OF Cis-trans- NOMENCLATURE.

The cis trans nomenclature becomes complicated and a bit confusing in larger molecules. For example



This compound cannot be assigned cis- or trans configuration. To this type of compound E/Z nomenclature is applied.

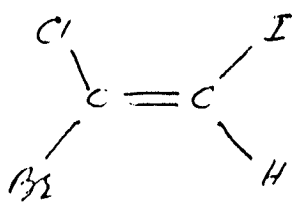
E/Z NOMENCLATURE

In this type of nomenclature substituents attached to each double bonded carbon are assigned priority order according to Cahn-Prelog rules.

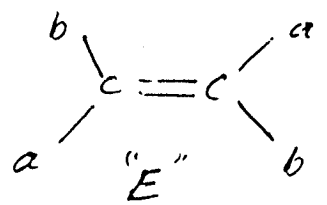
If both groups of higher priority are on same side of double bond, the geometrical isomer is said to be "Z" (Zusammen) mean together.

If groups of higher priority are on opposite side it is said to be "E" (entgegen mean opposite)

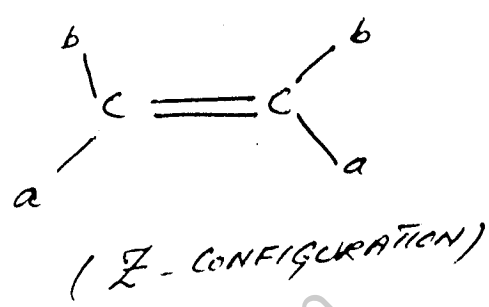
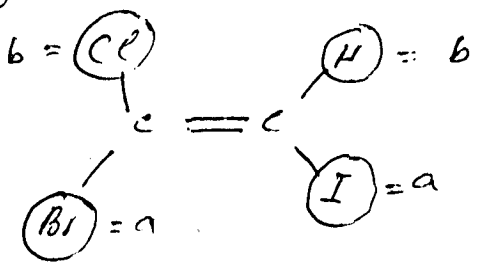
Let us apply this system to above compound on which cis-trans system is not applicable



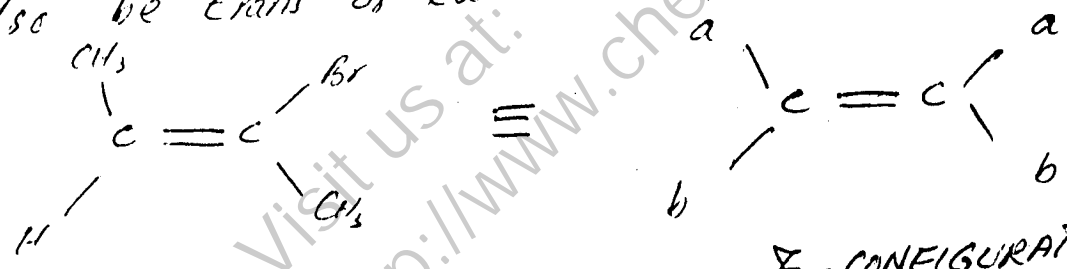
The groups with higher atomic number are preferred over groups with smaller atomic number. The groups with higher priority are designated as "a" and lower priority as "b" on each carbon.



If two "a" are on same side then it is "Z" and if two "a" are on opposite side it is "E" config.



One thing must be kept in mind that "E" and "Z" are not necessarily equivalent to trans and cis respectively. (The "E" may be cis or trans and "Z" may also be trans or cis. For example



(trans-CONFIGURATION)

Z-CONFIGURATION.

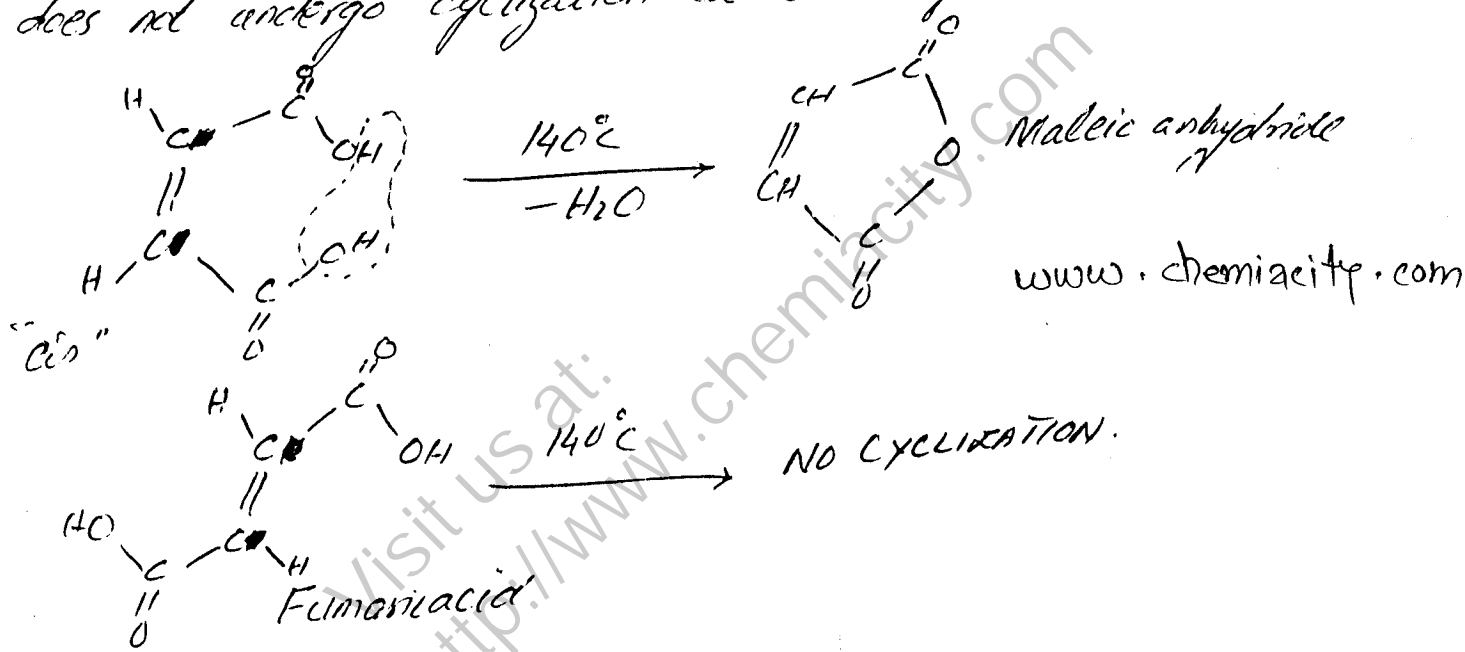
Thus above compound is "trans" according to cis-trans nomenclature but "Z" according to E/Z nomenclature.

HOW TO DETERMINE CONFIGURATION OF GEOMETRICAL ISOMERS.

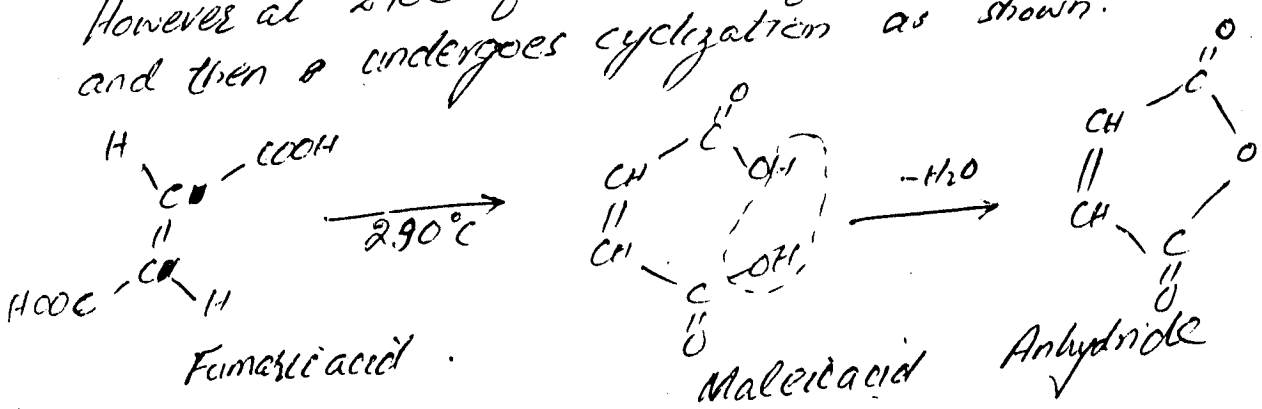
A number of methods are used to determine configuration of geometrical isomers. Some more applicable methods are given below.

Cyclization Reaction:- In general intramolecular reactions leading to formation of rings take place easily if the reacting groups are closer together in molecule. Thus geometrical isomer with reacting groups on same side (cis isomer) will undergo cyclization at lower temperature than trans isomer. ("MALEIC ACID")

EXAMPLE:- cis-isomer of 2-Butenedioic acid undergoes cyclization at 140° while trans isomer (FUMARIC ACID) does not undergo cyclization at this temperature.



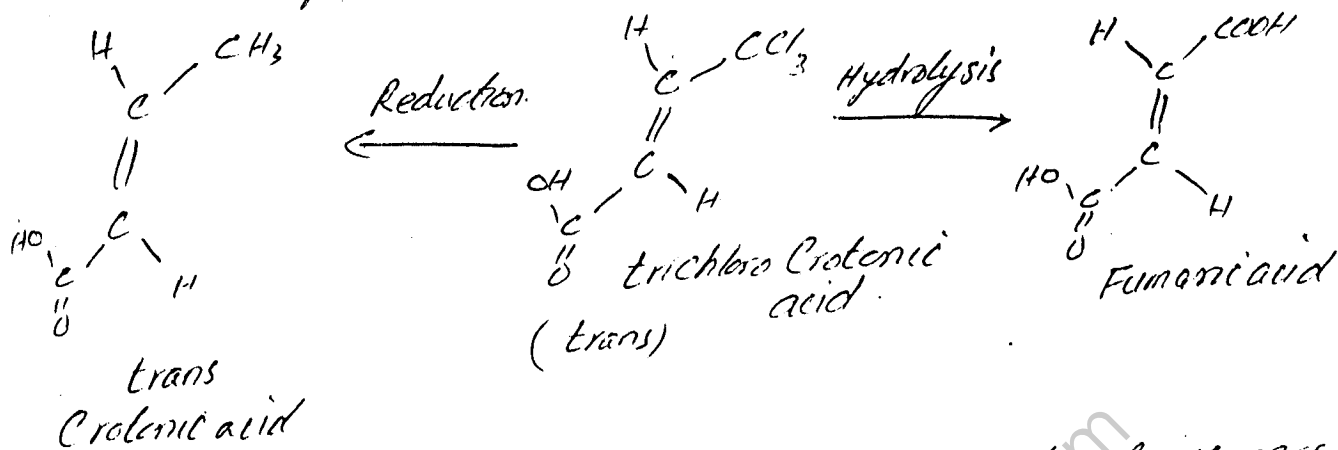
However at 290°C fumaric acid first converted into maleic acid and then undergoes cyclization as shown.



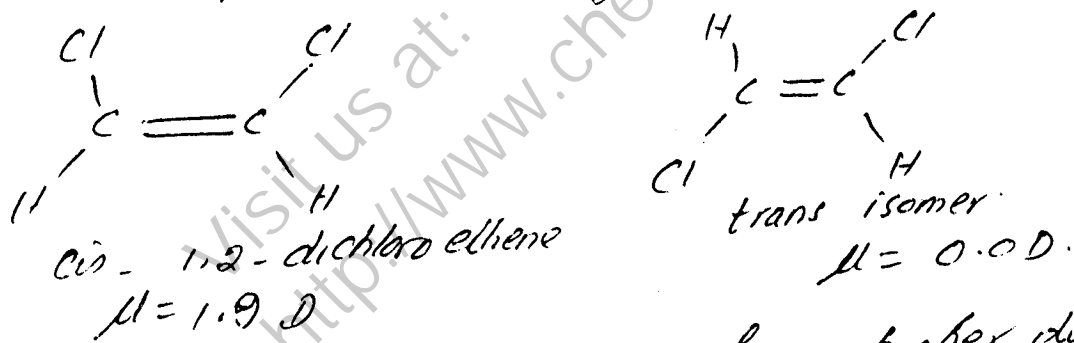
The anhydride on acid hydrolysis produces cis isomer under mild conditions.

Correlation with compounds of known Configuration.

In this method compound whose configuration is to be determined is converted into compound of known configuration. For example "trichloro crotonic acid" which on hydrolysis produce Fumonic acid and on reduction produce Crotonic acid, must be trans-~~is~~ trichloro crotonic acid. Thus acid produced will also be trans-Crotonic acid.



MEASUREMENT OF DIPOLE MOMENT:- Geometrical isomers differ in magnitude of dipole moment. For example cis-1,2-dichloro ethene has dipole moment 1.9 D while trans isomer has dipole moment has zero dipole moment.



Either cis or trans isomer have higher dipole moment, depending upon nature of compound. For example trans isomer of crotonic acid has higher dipole moment.

SOME OTHER METHODS: There are some other methods which can be used to determine geometry of molecule. A few of them are given below.

SPECTROSCOPIC METHODS: The cis- and trans isomers can be distinguished by spectroscopic techniques. For

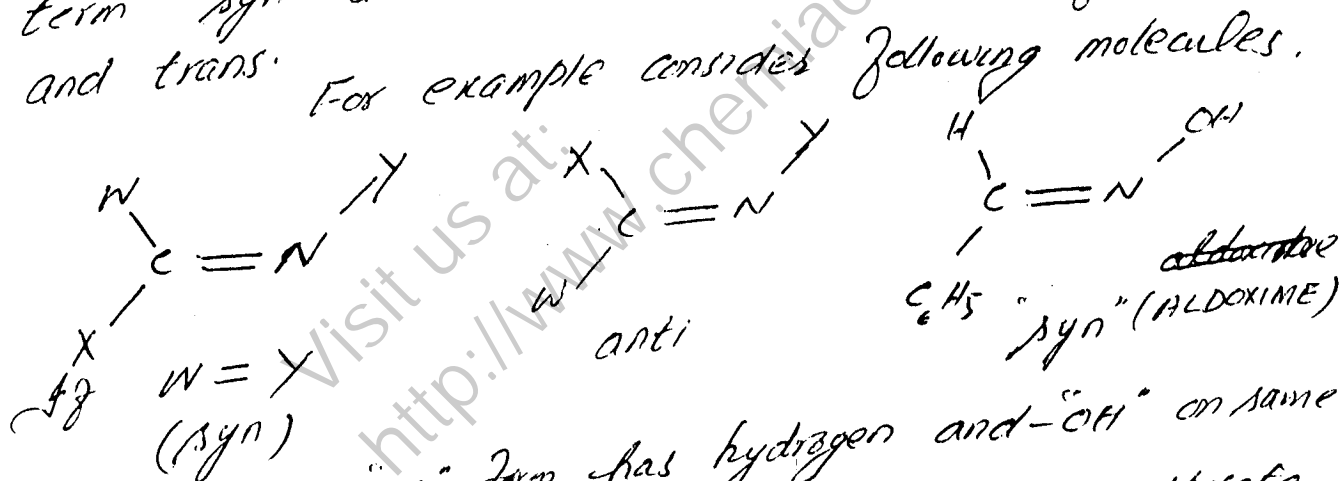
example N.M.R. (nuclear magnetic spectrum) of cis isomer is different from trans-isomer.

PHYSICAL PROPERTIES:- The geometrical isomers are actually diastereoisomers hence they differ in physical constants e.g. M.P., B.P., heat of combustion, chemical reactivity. It has been observed that trans-isomer have higher M.P., B.P. than cis-isomer. The cis isomer have high heat of combustion indicating that it is less stable than trans-isomer. The B.P., density dissociation constant of cis are larger than trans isomer.

GEOMETRICAL ISOMERISM WITH OTHER DOUBLE BONDS.

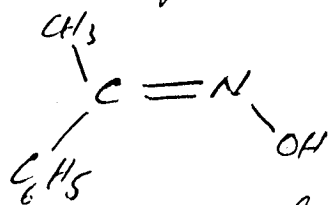
(syn/anti NOMENCLATURE)

Geometrical isomerism is also possible with double bonds other than C=C double bonds. For example in imines oximes geometrical isomerism is possible. In such a case term "syn" and "anti" is used instead of "cis" and "trans". For example consider following molecules.



In aldoxime "syn" form has hydrogen and -OH on same side and "anti" has hydrogen and -OH on opposite side.

In ketoxime special relationship between first group named and hydroxyl group. For example

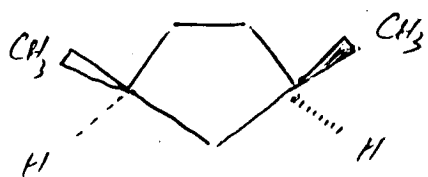


syn-Phenyl methyl ketoxime OR anti-methylphenyl ketoxime.

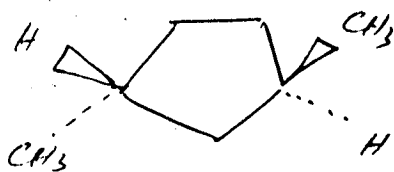
[Thus same compound may be written syn or anti depending upon order of substituents named]

GEOMETRICAL ISOMERISM IN CYCLIC COMPOUNDS.

Geometrical isomerism is also possible in cyclic compounds. Although cyclobutane and larger rings are not planar but yet they are considered as planar. If substituents are in same ^{side of} plane (above or below) it is called "cis" isomer. If one group is above the plane and other is below the plane they are said to be trans. For example consider following molecules.



cis-1,3-dimethylcyclopentane

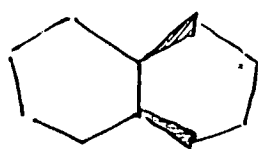


(trans-isomer)

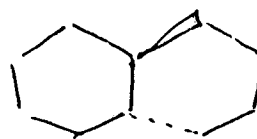
The E/Z system is not used for cyclic compounds. (The ring behaves like a double bond and prevents free rotation about C-C bond)

The cyclic geometrical isomers may also show optical isomerism. In such a case the number of stereoisomers are more than expected.

The fused rings may have 'cis' ring junction or trans ring junction as shown below



cis junction



trans-junction

However trans configuration is not possible when rings are small sized. In such a case junction must be cis.

WHAT ARE CONFORMATIONAL ISOMERS DISCUSS ENERGY CHANGES IN CONFORMATIONAL ISOMERS OF ETHANE, PROPANE AND BUTANE.

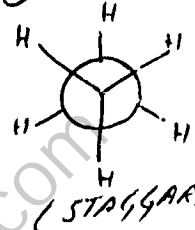
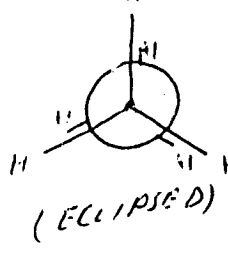
CONFORMATIONAL ANALYSIS OF ETHANE: CH_3-CH_3

The stereoisomers which are readily interconvertible by rotation around a single bond are called conformational isomers. These conformational isomers differ in energy. The study of energy changes in different conformations of same compound is called conformational analysis.

In ethane there is C-C single bond and infinite number of conformational isomers can be written for ethane, by rotation of one methyl group w.r. to other. The two conformations one with maximum energy and other with minimum energy are shown below with Newman projection.

ECLIPSED CONFORMATION

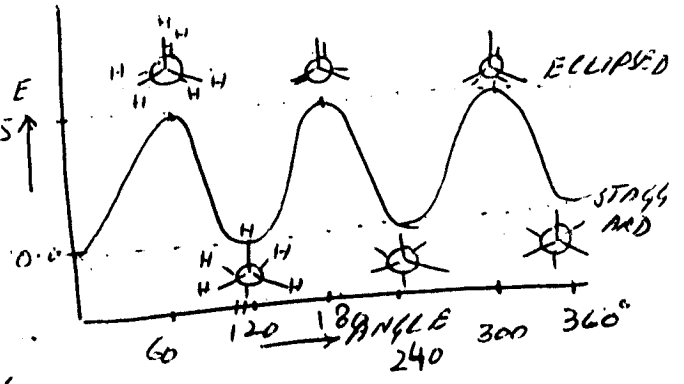
It is maximum energy conformation. In this conformation hydrogens attached to each carbon are directly opposite to each other i.e. one behind the other.



The high energy of eclipsed conformation is due to repulsion between bonding electron pairs of adjacent carbons. The lateral distance between these bonds is minimum.

STAGGERED CONFORMATION

It is minimum energy conformation in which hydrogen atoms are at maximum distance from each other. The distance between electron pair of C-H bond is maximum and repulsion is minimum.

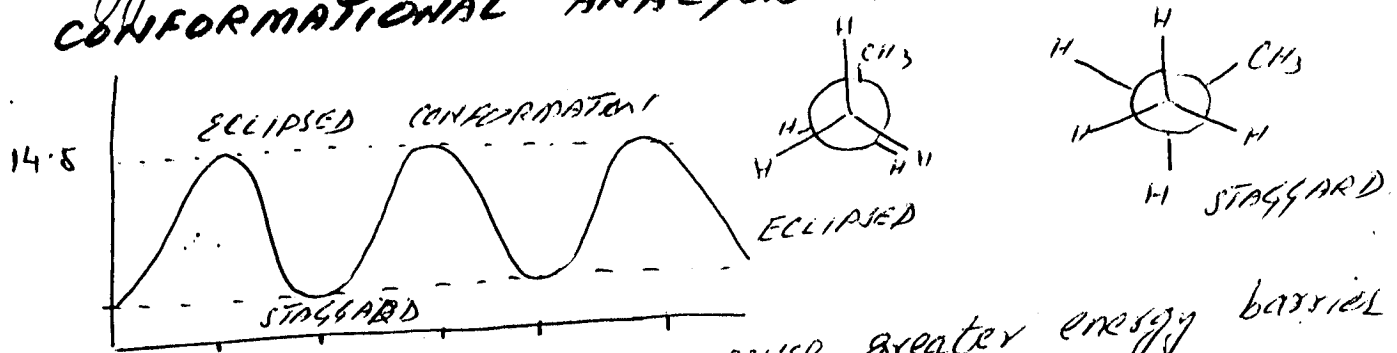


DIHEDRAL ANGLE

The angle of rotation in different conformation of an alkane is called dihedral angle. The energy of conformation increases with angle of rotation and becomes maximum with eclipsed conformation. Then it begins to decrease and becomes minimum for staggered conformation.

conformation has energy difference of 12.5 kJ. At room temperature thermal energy of molecule is sufficient to interchange these conformations. These conformations are not separate. These two remain in equilibrium with staggered conformation in high concentration.

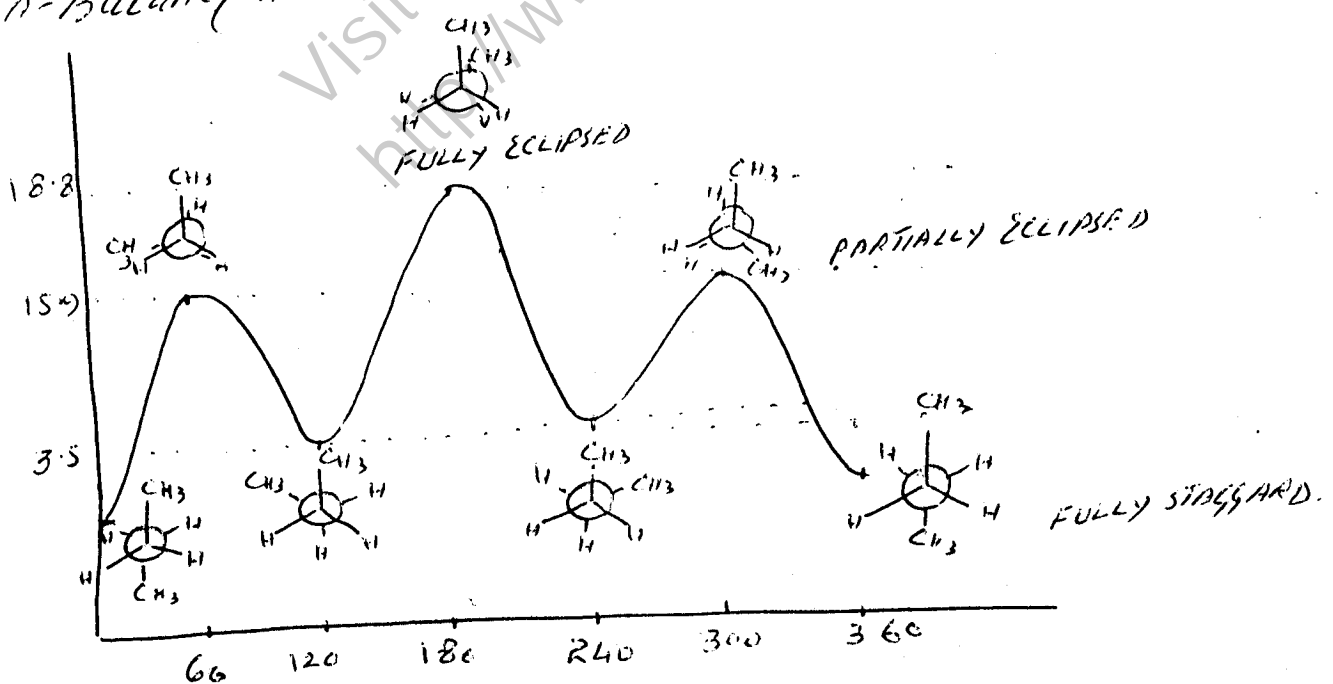
CONFORMATIONAL ANALYSIS OF PROPANE:-



The groups larger than Hydrogen cause greater energy barrier. In eclipsed conformation methyl hydrogen interaction cause torsional strain and also Van der Waals non-bonding repulsive interactions. Thus energy difference between eclipsed and staggered conformation is greater than that in ethane. This barrier to rotation is 14.2 kJ/mole. The conformational energy diagram for propane is similar to that of ethane.

CONFORMATIONAL ANALYSIS OF n-BUTANE:-

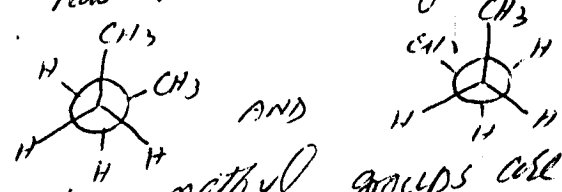
The following eclipsed and staggered conformations are possible for n-butane. Their relative energies are shown below.



FULLY STAGGARD OR ANTI STAGGARD

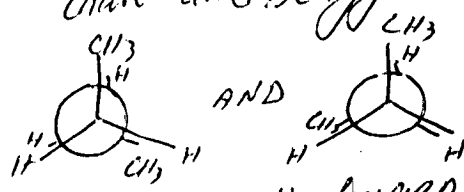
This is the lowest energy conformation with no-Vander Waals repulsive interactions. n-Butane at room temperature has 70% this conformation. It is free of torsional strain.

GAUCH STAGGARD



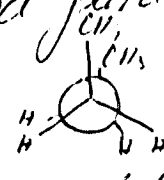
In this conformation two methyl groups are adjacent to each other. The two gauche staggered conformations are equal in energy and they are mirror images of each other. They are less stable than anti-staggered conformation by 3.5 kJ/mole.

PARTIALLY ECLIPSED



These two have eclipsing of Hydrogen and methyl groups. These two are equal in energy but higher than that of Gauch and anti-staggered. The difference of energy between anti-staggered and partially eclipsed is 15.9 kJ.

FULLY ECLIPSED



It is the highest energy conformation in which two methyl groups are eclipsed. Its energy is 18.8 kJ relative to anti-staggered. The Vander Waals repulsive interactions are max. in this conformation.

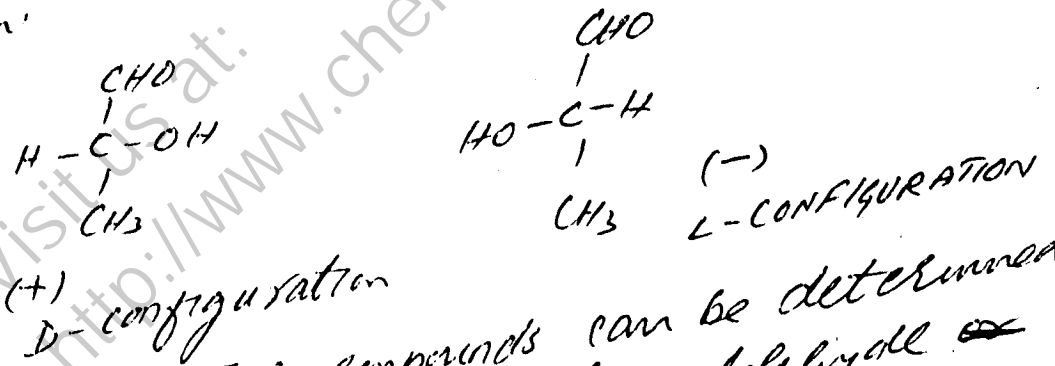
torsional strain due to bending electron pairs is the same the basic difference is the repulsive interactions between substituents (Vander Waals interactions). Similarly in all staggered conformations there is no torsional strain but repulsive interactions between different groups is different.

The energy difference in difference between different conformations is higher than ethane and propane but it these conformations cannot be isolated. The total energy of molecule is sufficient enough to bring about these interconversions. At room temp. n-Butane can be considered to be a mixture of 70% anti-staggered and 30% gauche conformation. At -230°C or below these conformations can be separated.

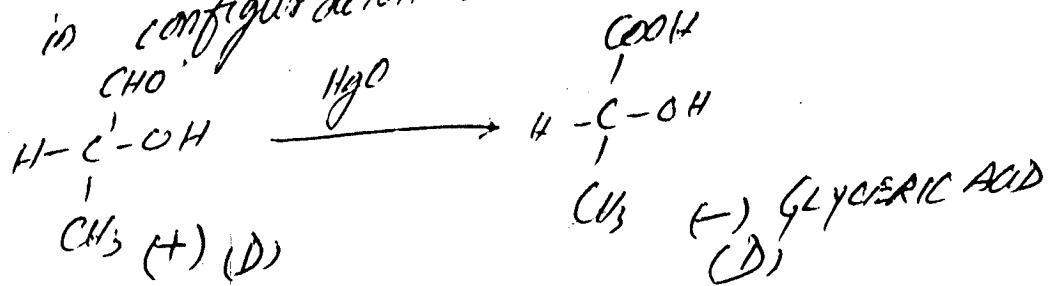
ABSOLUTE AND RELATIVE CONFIGURATION

D.L. CONVENTION The enantiomers differ in their behaviours towards plane polarized light. However from simple Fischer projection it is not possible to determine which isomer is dextro rotatory and which one is levorotatory. There is no simple relationship between sign of rotation and configuration of molecule. In many compounds, by changing nature of substituents without changing configuration at chiral centre results in change in sign of rotation. Some times even the same compound can rotate the plane polarized light in opposite directions in different conditions.

In 1906 M.A. RASANOFF proposed that some compound may be chosen as standard reference and a configuration may be assigned to it. Configuration could then be assigned to other compounds by correlations with reference compounds. The compound chosen for this purpose was glyceraldehyde. The (+) isomer was assigned D-configuration.



The configuration of other compounds can be determined by ~~either~~ correlation with D or L glyceraldehyde or by preparing these compounds from glyceraldehyde or converting these compounds to glyceraldehyde. For example when (+) glyceraldehyde is oxidized with H₂O it is changed into (-) glyceric acid without any change in configuration at central carbon atom.



It means (-) glyceric acid has same configuration as (+) glyceraldehyde (both have D-configuration). The other enantiomer was L-configuration. Once configuration of (+) and (-) glyceric acid was known the other compounds can be correlated with it and configuration of other compounds can be determined. In this way numerous compounds can be correlated directly or indirectly to glyceraldehyde.

Any substance configurationally correlated to D (+) glyceraldehyde is said to belong to D-Series even though it may be levo rotatory and its enantiomer will be L-Series. Even compounds without chiral atom have been assigned D or L configuration. When a compound has been placed in D or L series its ^{absolute} configuration is then said to be known.

SHORT-COMINGS / The letters "D" or "L" are sometimes confused with "d" or "l" which are actually dextro or levo rotatory nature of compound. The designation of particular enantiomer as "D" or "L" can depend on the compound to which it is correlated. A structure can be related to a ^{known} D-compound by one route and same structure can be related to L-compound by some other route. Because of its flaws this nomenclature is rarely used except for carbohydrates and amino acids. This system of nomenclature has been replaced by R, S nomenclature.

ELECTROMAGNETIC RADIATION:-

radiations may be considered as energy that is propagated by means of electric and magnetic fields, that oscillate in a direction perpendicular to the direction of travel of energy.

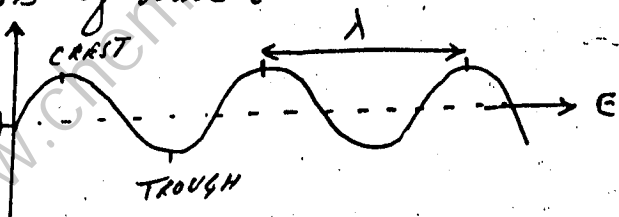
Waves similar to electromagnetic waves are produced when a stone is thrown in a pond of water. The stone makes the water molecules vibrate up and down and transmit its energy as wave on the surface of water. These waves travel to the bank of the pond.

Electromagnetic radiations are named so because they have an electrical and magnetic component. These are produced by periodic motion of charged particles. The vibratory motion of electrons produces electromagnetic radiations with electric oscillating electric and magnetic fields.

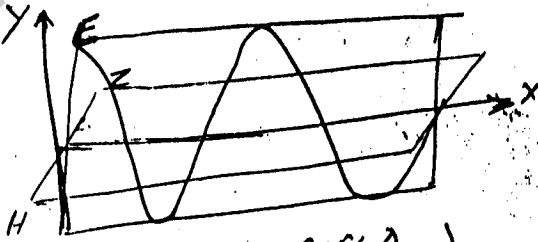
Radiant energy travels with velocity of light in vacuum i.e. 3×10^8 m/sec.

The waves are characterized by following terms.

WAVE LENGTH :- λ It is defined as distance between two successive crests or troughs of wave train. It is expressed in metres or Angstroms or nanometers.



FREQUENCY ν
The number of crests or trough which pass a given point per second is called frequency. Its unit is sec^{-1} or Hertz (Hz).



The frequency is related to wavelength and speed by following relationship
(E = ELECTRIC FIELD)
(H = MAGNETIC FIELD)

$$c = \nu \times \lambda$$

The speed of all electromagnetic radiation is same in vacuum which is 3×10^8 m/sec