COURSE : SC202 (CHEMISTRY)

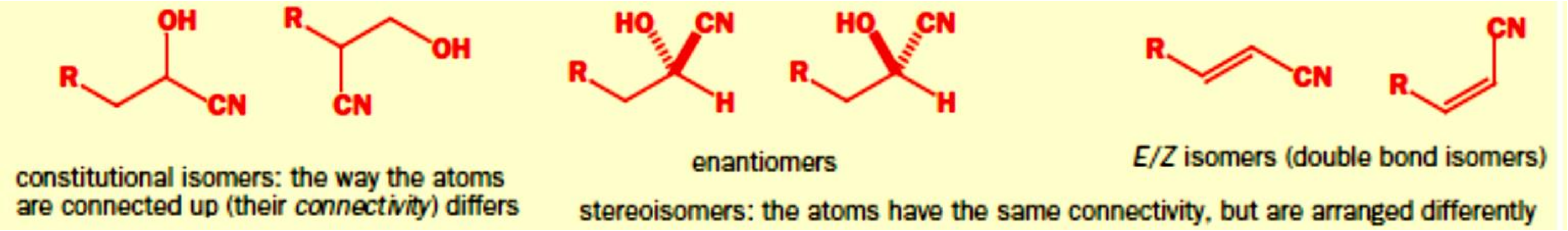
DR. SANGITA TALUKDAR

LECTURE-4

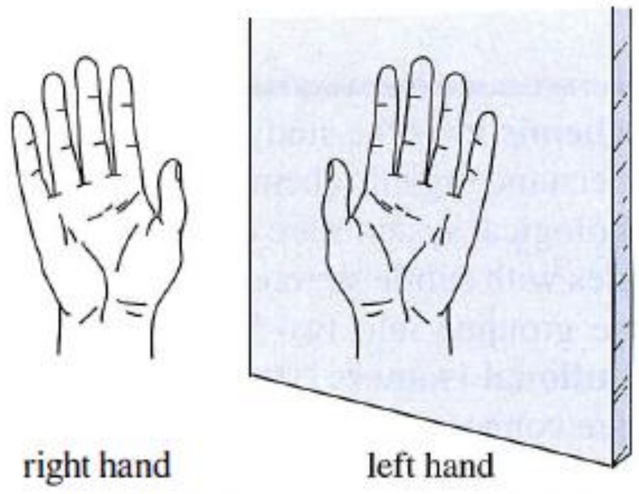
DATE: 12.1.2021

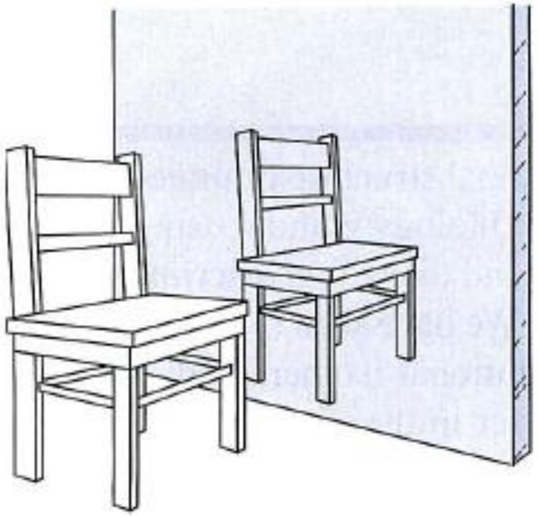
Stereochemistry

- **Isomers:** Isomers are compounds that contain the same atoms bonded together in different ways i.e. different compounds with the same molecular formula.
- **Constitutional isomers:** isomers with a different connectivity.
- **Stereoisomers:** isomers with the same connectivity but a different orientation of their atoms in space.

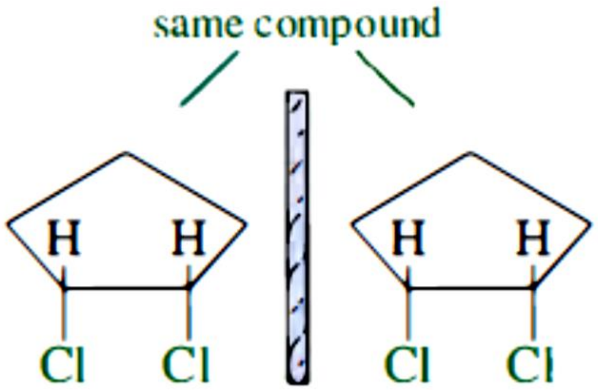


- **Enantiomers** are stereoisomers that are non-superimposable *mirror images* of each other

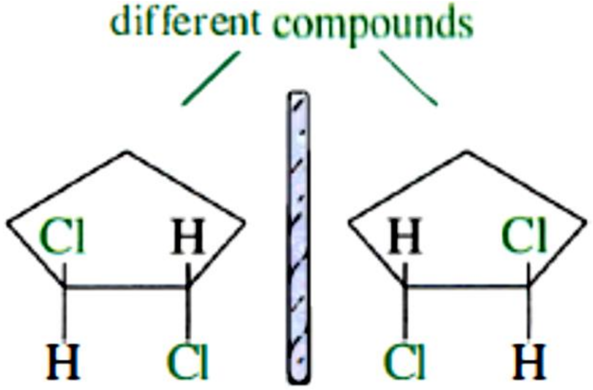




- enantiomers: mirror-image isomers; pairs of compounds that are nonsuperimposable minor images.
- chiral: ("handed") different from its mirror image; having an enantiomer.
- achiral: ("not handed") identical with its mirror image; not chiral.

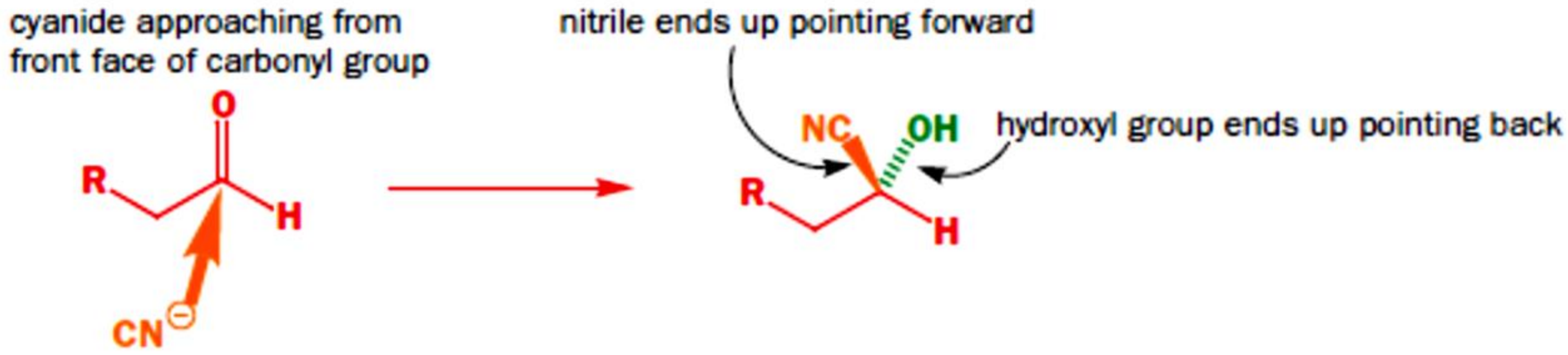


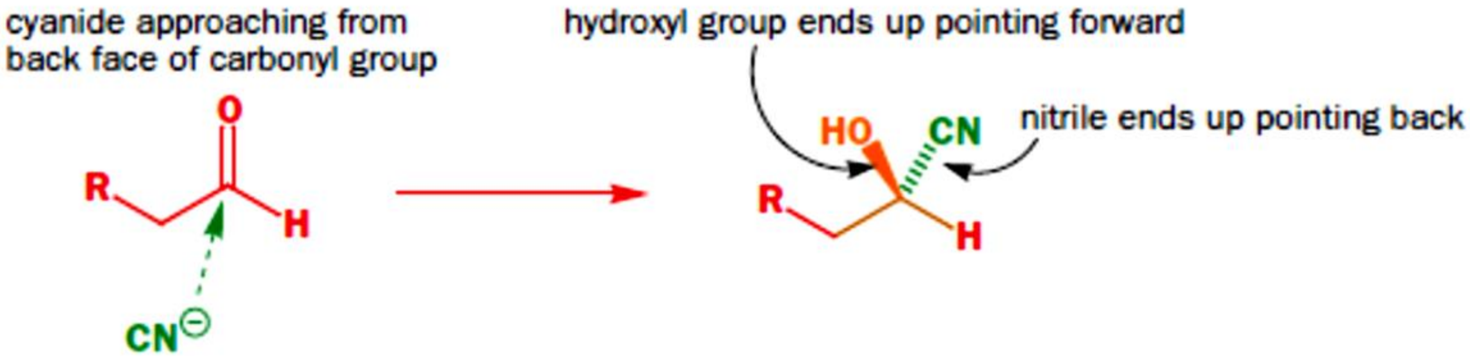
cis-1, 2-dichlorocyclopentane
(achiral)

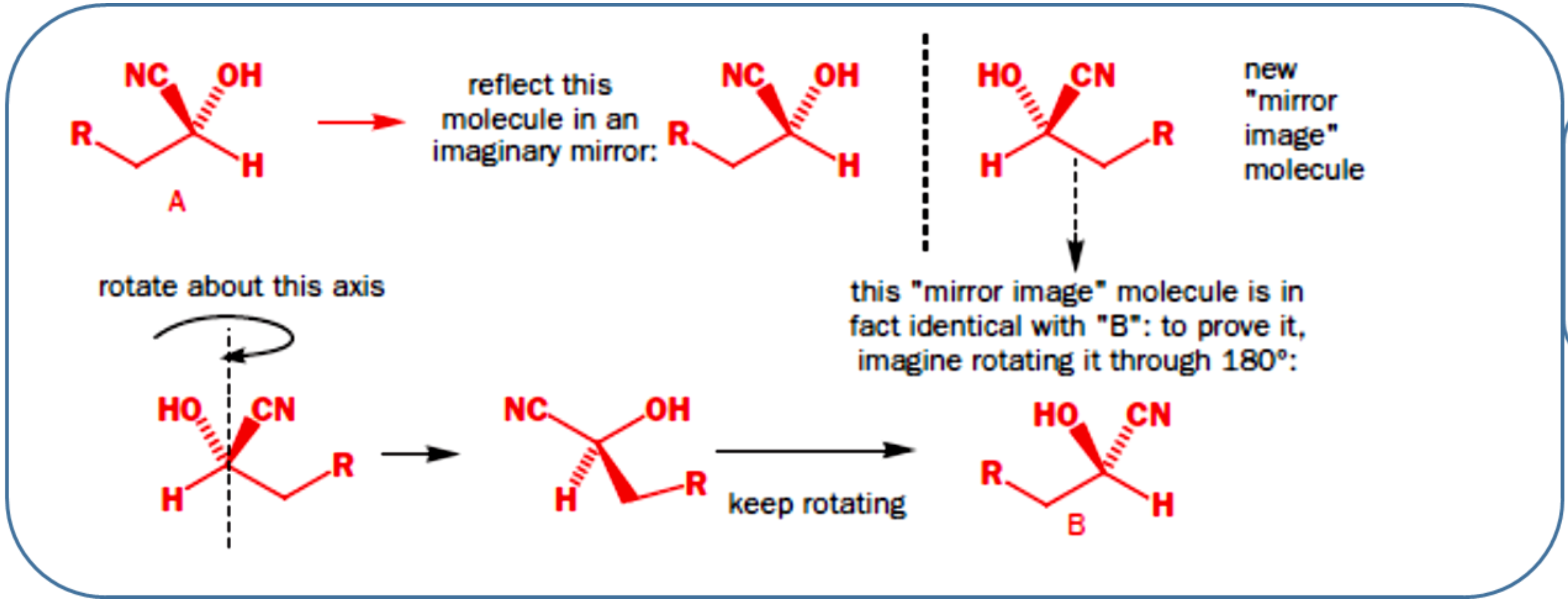


trans-1, 2-dichlorocyclopentane
(chiral)

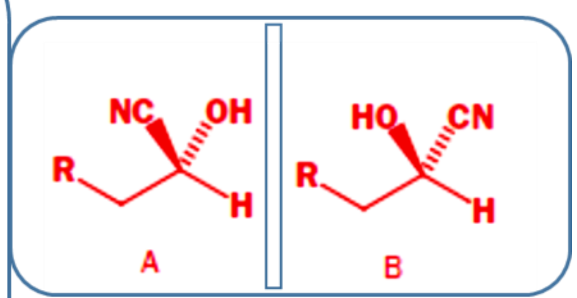
Stereoisomers of 1,2-dichlorocyclopentane. The cis isomer has no enantiomers; it is achiral. The trans isomer is chiral; it can exist in either of two nonsuperimposable enantiomeric forms.

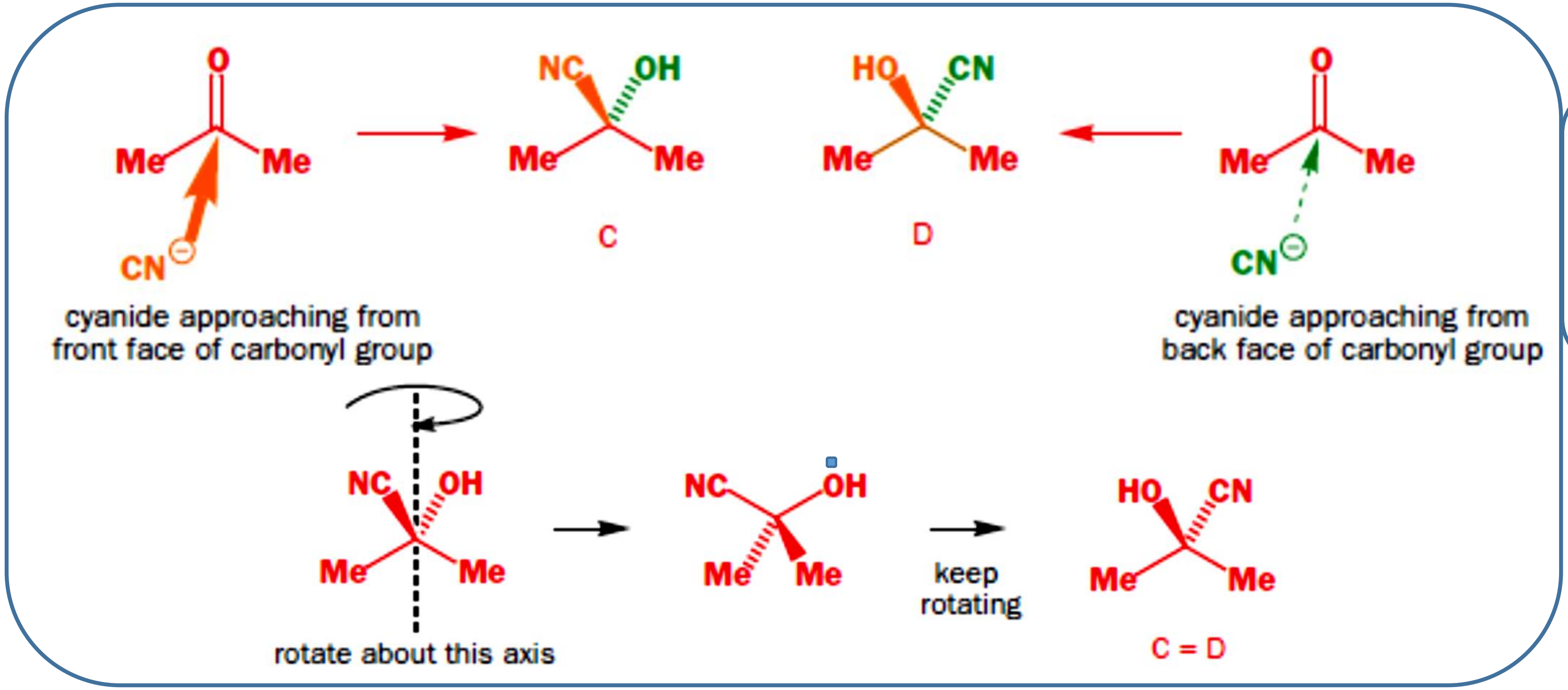




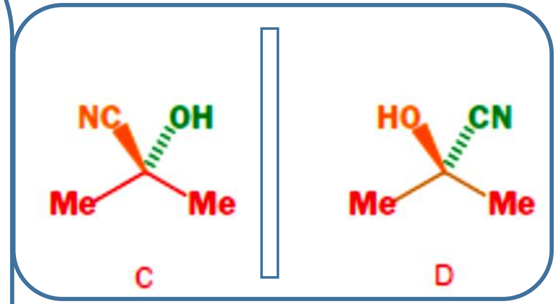


Chiral molecule





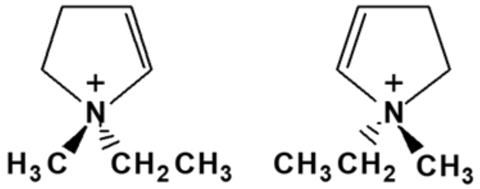
Achiral molecule



Chiral: a structure is chiral if it is not superimposable on its mirror image.

A carbon with four different groups bonded to it is called a **chiral center.**

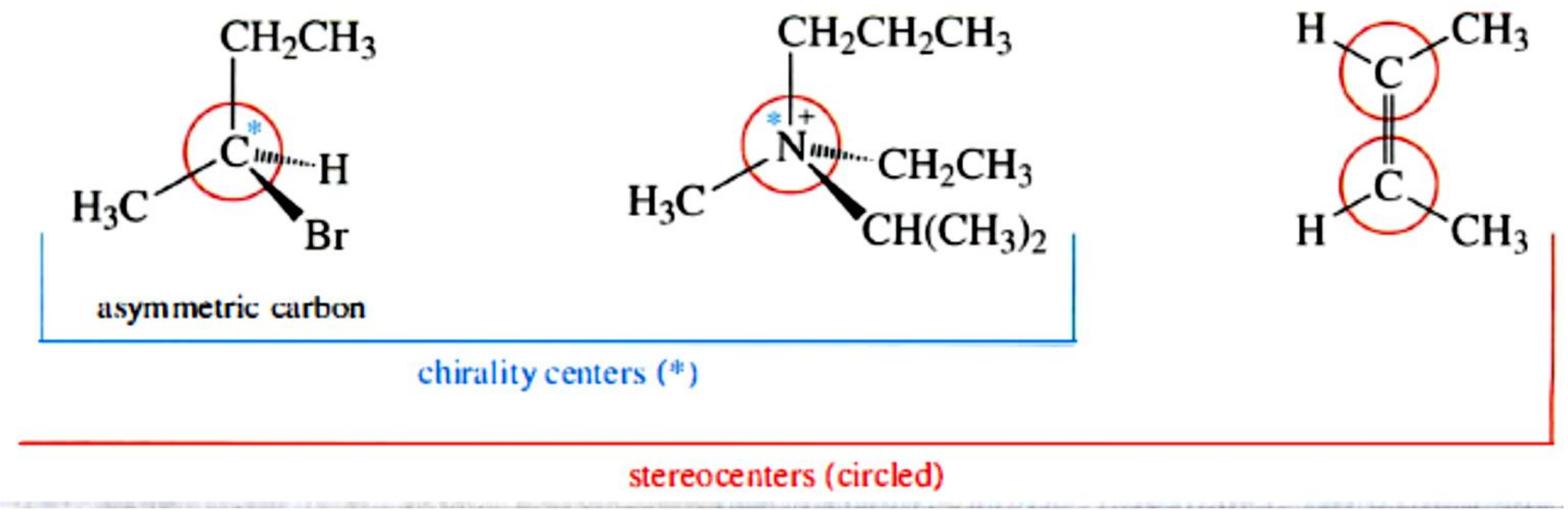
- all chiral centers are stereocenters, but not all stereocenters are chiral centers

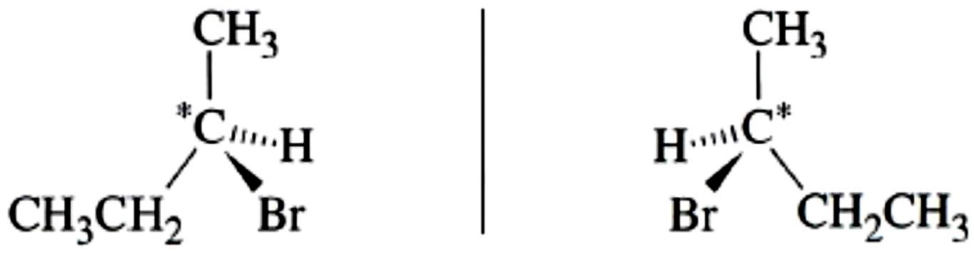


A pair of enantiomers

- **Chiral molecules have no plane of symmetry**

A **stereocenter** (or stereogenic atom) is any atom at which the interchange of two groups gives a stereoisomer. Asymmetric carbons and the double-bonded carbon atoms in cis-trans isomers are the most common types of stereocenters.

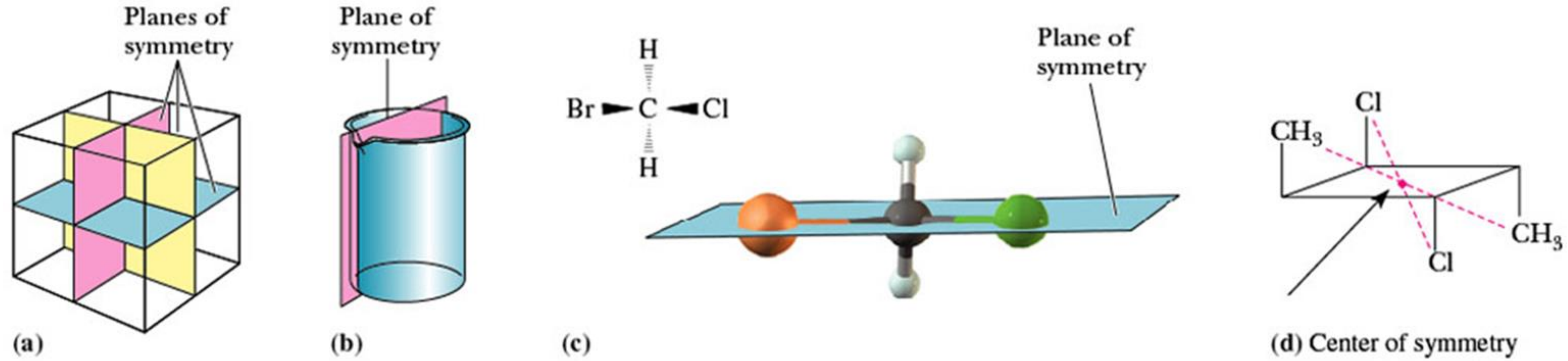




2-Bromobutane is chiral by virtue of an asymmetric carbon atom (chiral carbon atom), marked by an *

Achiral: structures that are superimposable on their mirror images.

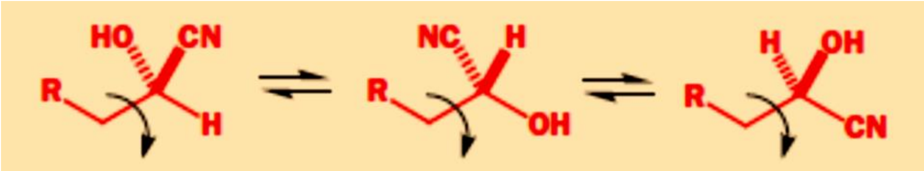
- **an achiral object has at least one element of symmetry**
- **plane of symmetry**: an imaginary plane passing through an object dividing it so that one half is the mirror image of the other half.
- **center of symmetry**: a point so situated that identical components are located on opposite sides and equidistant from that point along the axis passing through it.



Configuration and conformation

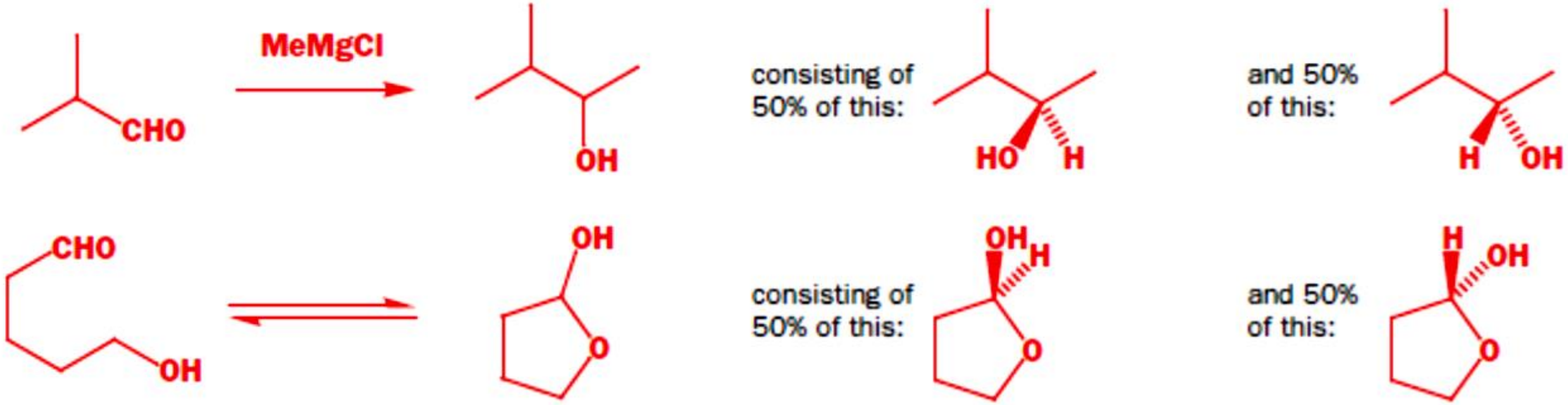
- Changing the *configuration* of a molecule always means that bonds are broken
- A different configuration is a different molecule
- Changing the *conformation* of a molecule means rotating about bonds, but not breaking them
- Conformations of a molecule are readily interconvertible, and are all the same molecule

two configurations: going from one enantiomer to the other requires a bond to be broken



three conformations of the same enantiomer: getting from one to the other just requires rotation about a bond: all three are the same molecule

- A racemic mixture is a mixture of two enantiomers in equal proportions.
- If the starting materials of a reaction are achiral, and the products are chiral, they will be formed as a racemic mixture of two enantiomers.



R,S Convention (Cahn-Ingold-Prelog convention)

Priority rules

1. Each atom bonded to the chiral center is assigned a priority based on atomic number; the higher the atomic number, the higher the priority

(1)	(6)	(7)	(8)	(16)	(17)	(35)	(53)
-H	$-CH_3$	$-NH_2$	-OH	-SH	-Cl	-Br	-I

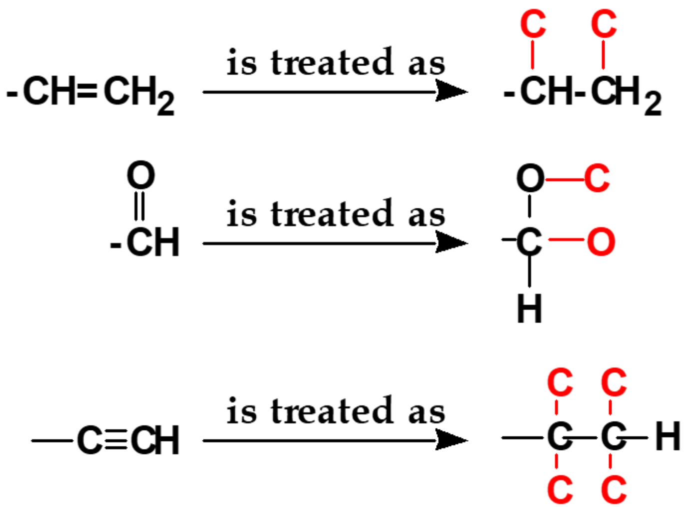
Increasing priority →

2. If priority cannot be assigned per the atoms bonded to the chiral center, look to the next set of atoms; priority is assigned at the first point of difference

(1)	(6)	(7)	(8)
$-CH_2-H$	$-CH_2-CH_3$	$-CH_2-NH_2$	$-CH_2-OH$

Increasing priority →

3. Atoms participating in a double or triple bond are considered to be bonded to an equivalent number of similar atoms by single bonds



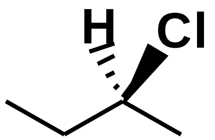
Naming Chiral Centers

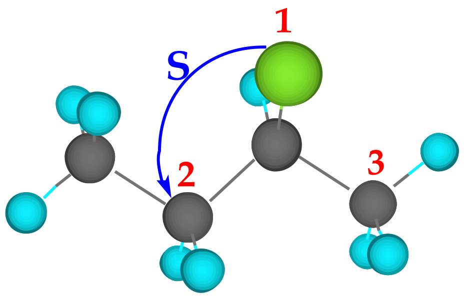
1. Locate the chiral center, identify its four substituents, and assign priority from 1 (highest) to 4 (lowest) to each substituent

2. Orient the molecule so that the group of lowest priority (4) is directed away from you

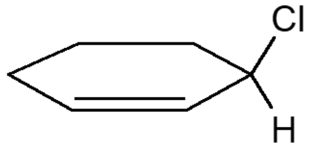
3. Read the three groups projecting toward you in order from highest (1) to lowest priority (3)

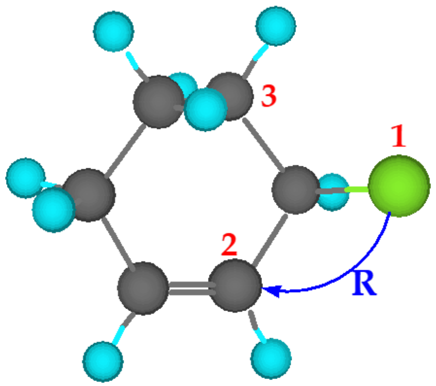
4. If the groups are read clockwise, the configuration is *R*; if they are read counterclockwise, the configuration is *S*



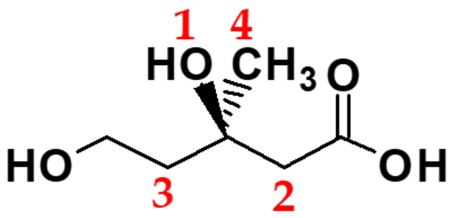


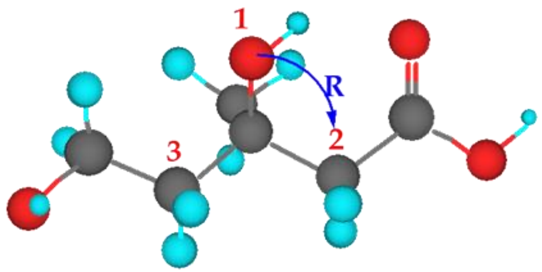
(*S*)-2-Chlorobutane



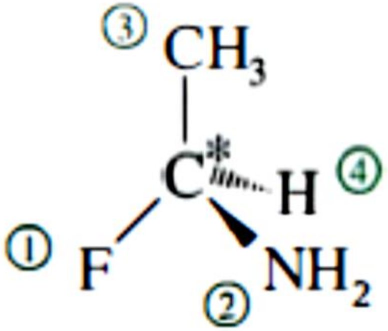


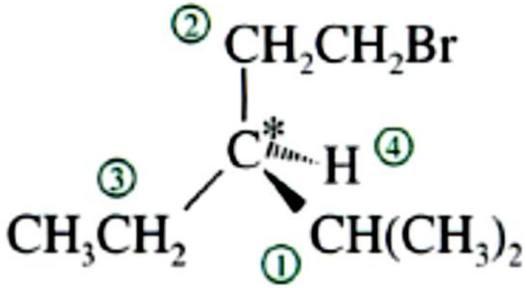
(*R*)-3-Chlorocyclohexene

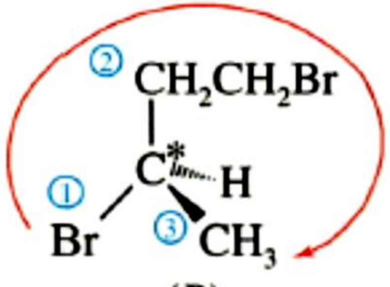




(*R*)-Mevalonic acid

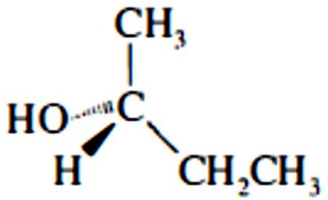


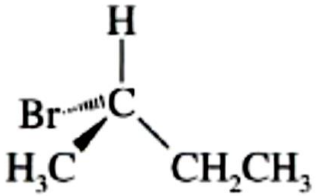


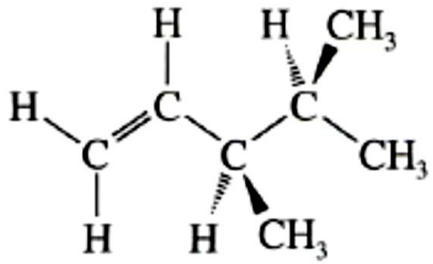


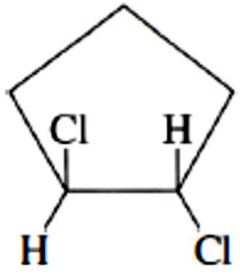
(*R*)

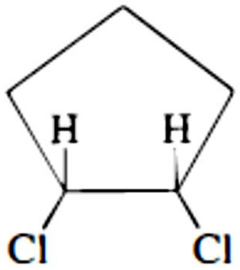
Problem : Star (*) each asymmetric carbon atom in the following examples, and determine whether it has the (R) or (S) configuration.

(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

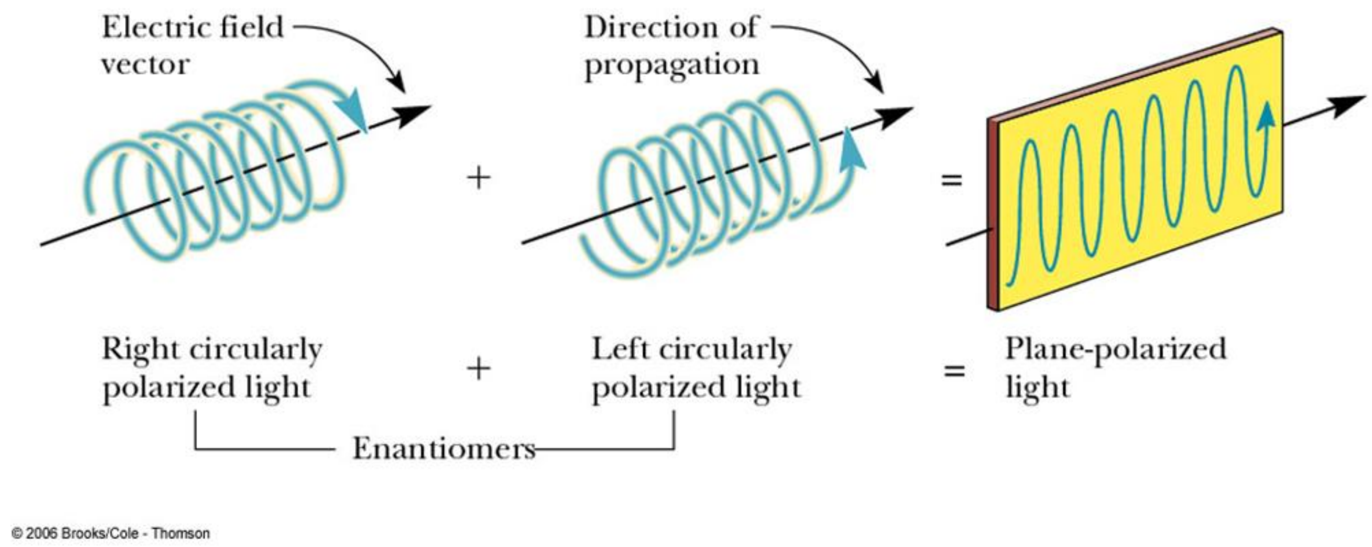
Properties of Enantiomers

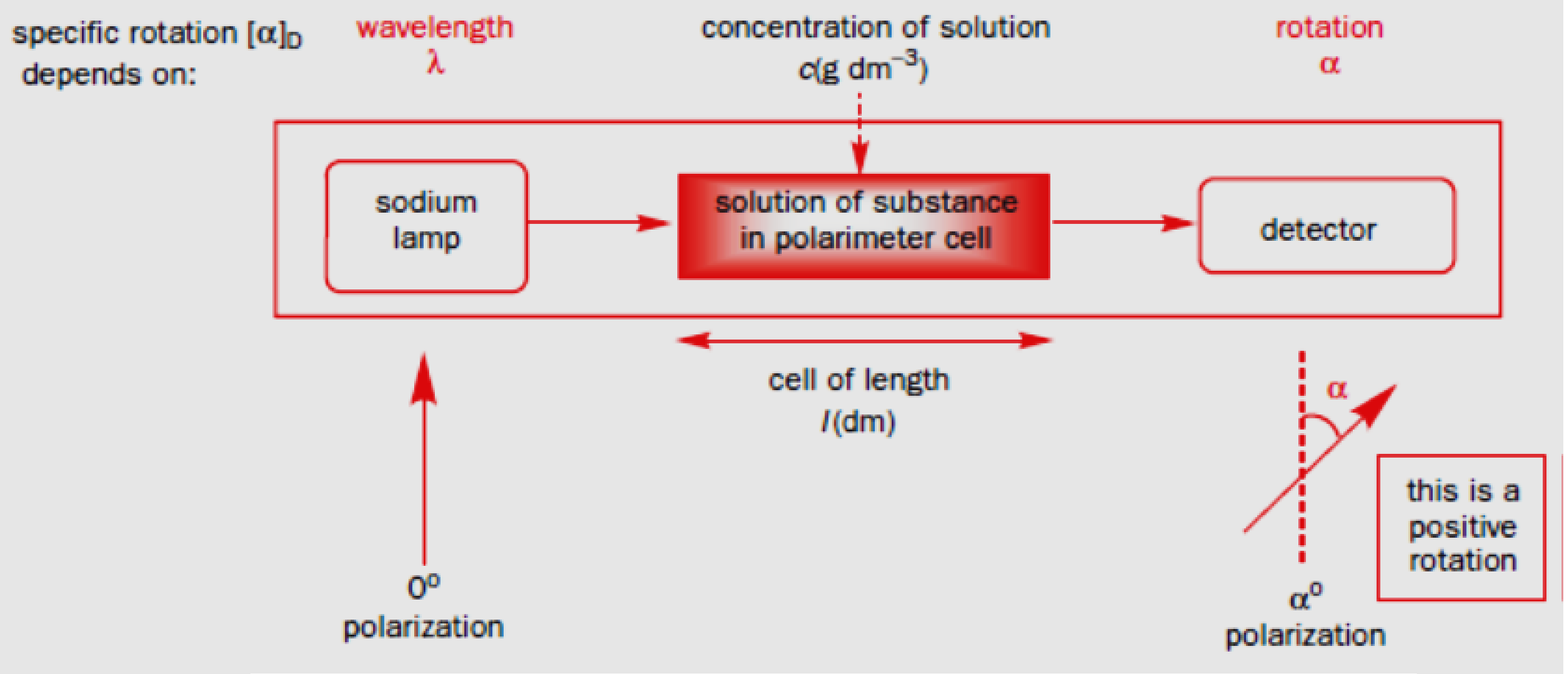
- Enantiomers have identical physical and chemical properties in achiral environments.
- They both have identical NMR and IR spectra.
- The enantiomers rotate the plane polarized light in opposite direction.

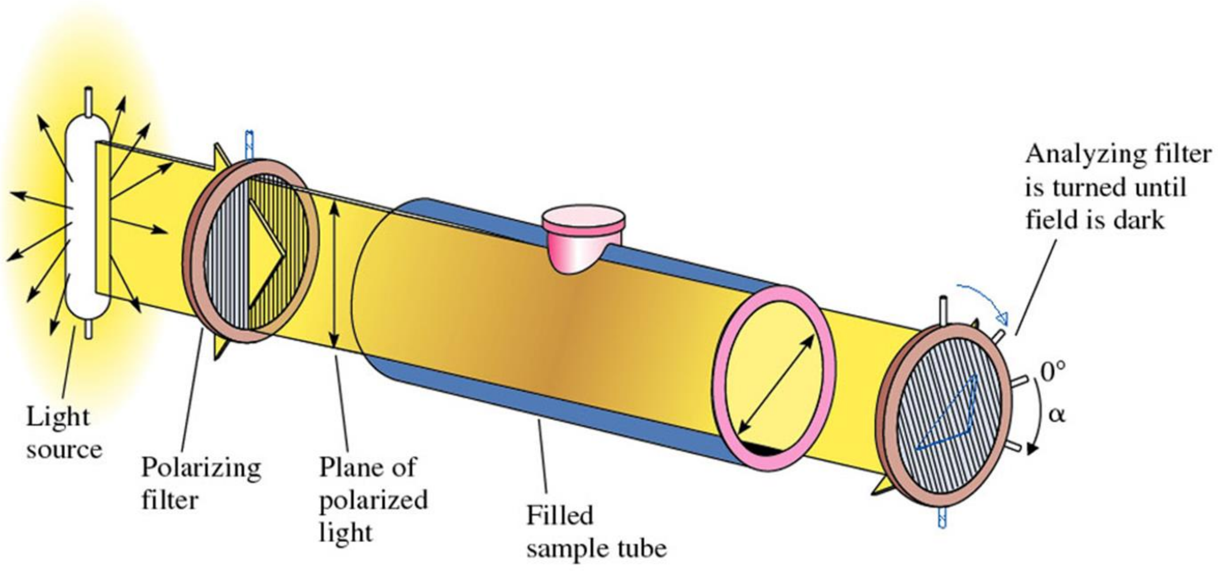
Ordinary light: light vibrating in all planes perpendicular to its direction of propagation.
Plane-polarized light: light vibrating only in parallel planes. Plane-polarized light is the vector sum of left and right circularly polarized light.

The rotation of plane-polarized light is known as optical activity
Observation of the rotation of plane-polarized light is known as **polarimetry**

circularly polarized light reacts one way with an *R* chiral center, and the opposite way with its enantiomer
the result of interaction of plane-polarized light with a chiral compound is rotation of the plane of polarization




specific rotation [α]D depends on:
wavelength λ
concentration of solution c(g dm−3)
rotation α
sodium lamp
solution of substance in polarimeter cell
detector
cell of length l(dm)
α
this is a positive rotation
0° polarization
α° polarization

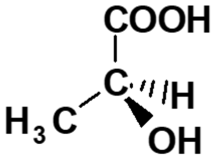

Analyzing filter is turned until field is dark
0°
α
Light source
Polarizing filter
Plane of polarized light
Filled sample tube

observed rotation: the number of degrees, , through which a compound rotates the plane of polarized light

dextrorotatory (+): refers to a compound that rotates the plane of polarized light to the right

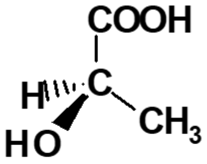
levorotatory (-): refers to a compound that rotates of the plane of polarized light to the left

specific rotation: observed rotation when a pure sample is placed in a tube 1.0 dm in length and concentration in g/mL (density); for a solution, concentration is expressed in g/ 100 mL



(*S*)-(+)-Lactic acid

$[\alpha]^{21}_{D} = +2.6°$



(*R*)-(-)-Lactatic acid

$[\alpha]^{21}_{D} = -2.6°$

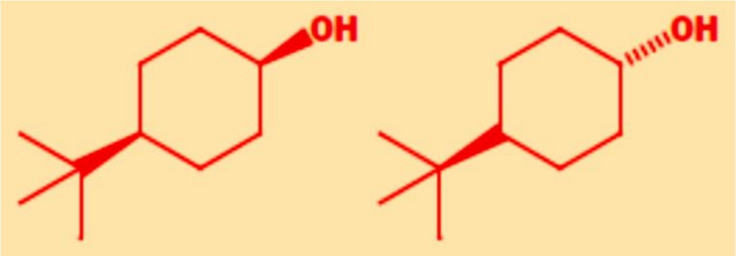
Optical purity: a way of describing the composition of a mixture of enantiomers

$$\text{Percent optical purity} = \frac{[\alpha]_{\text{sample}}}{[\alpha]_{\text{pure enantiomer}}} \times 100$$

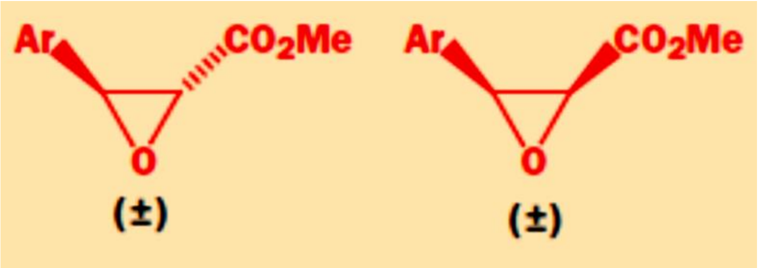
Diastereoisomers

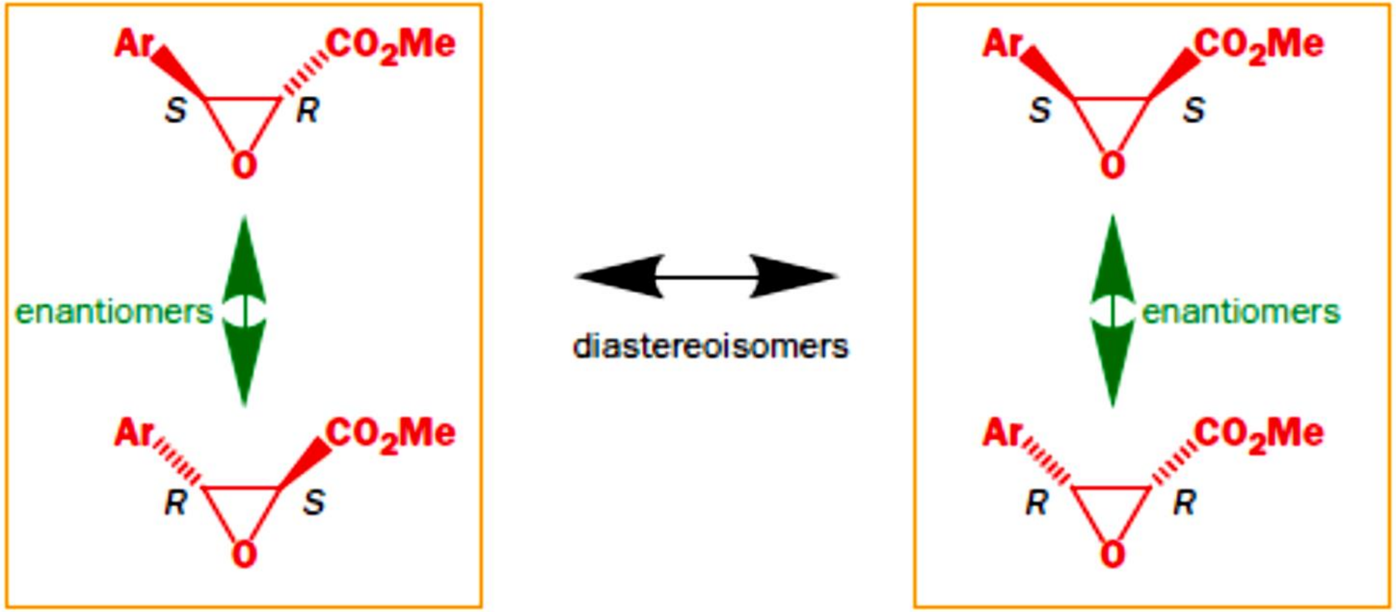
Diastereoisomers are stereoisomers that are not mirror images. Two diastereoisomers are different compounds, and have different relative stereochemistry

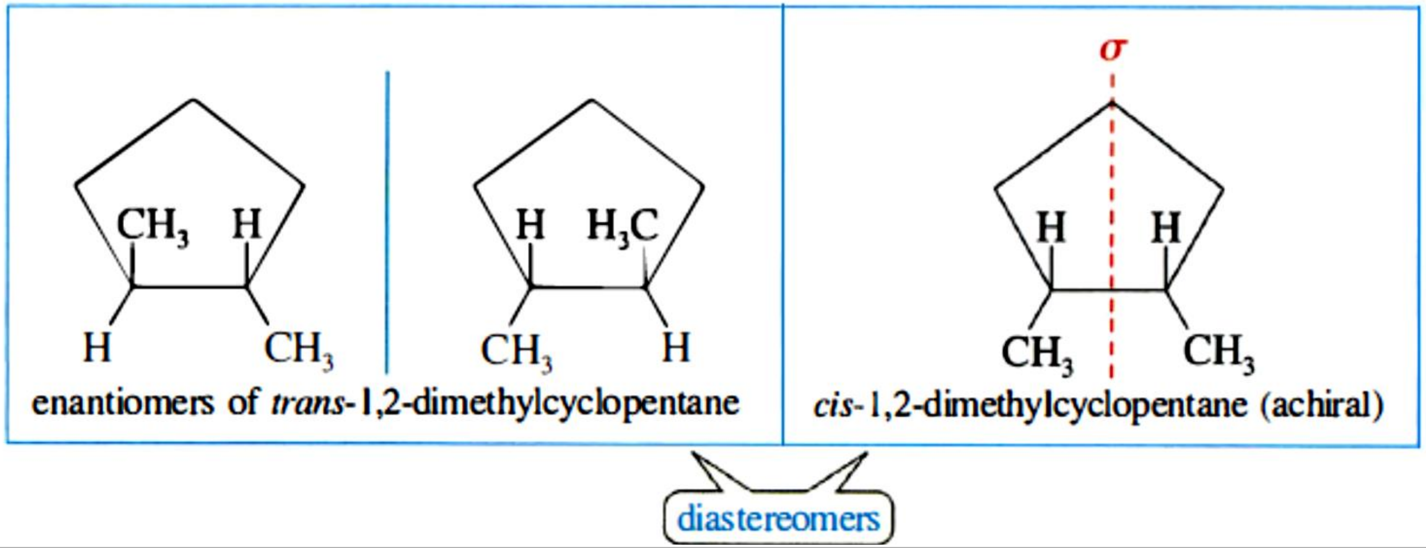
Diastereoisomers may be achiral (have a plane of symmetry); for example,



Or they may be chiral (have no plane of symmetry); for example,

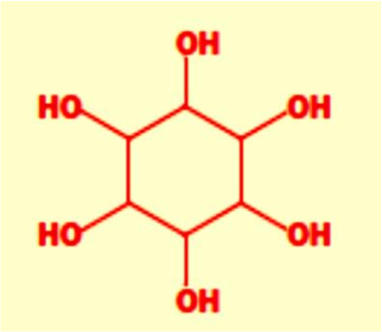


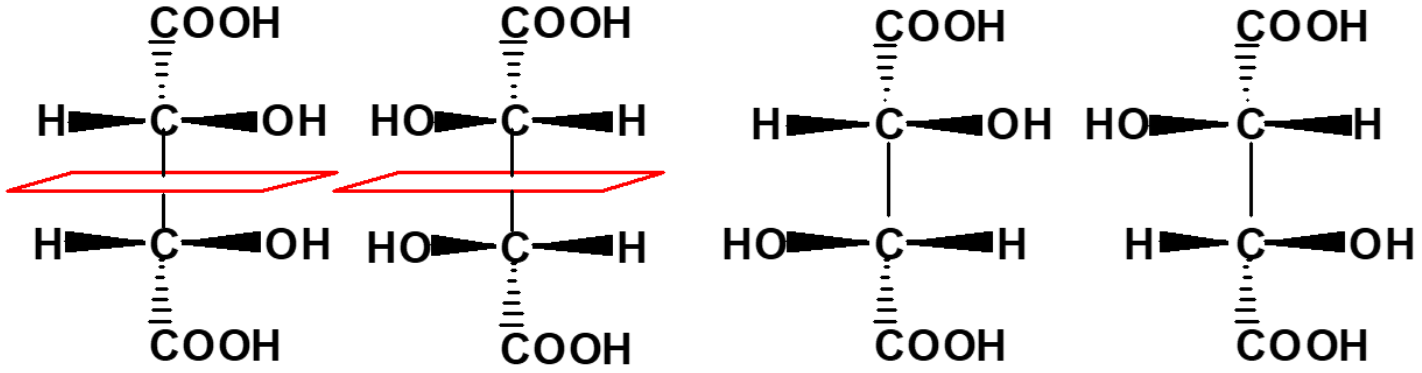




- **the diastereoisomers are different compounds with different names and different properties, while the pair of enantiomers are the same compound and differ only in the direction in which they rotate polarized light.**

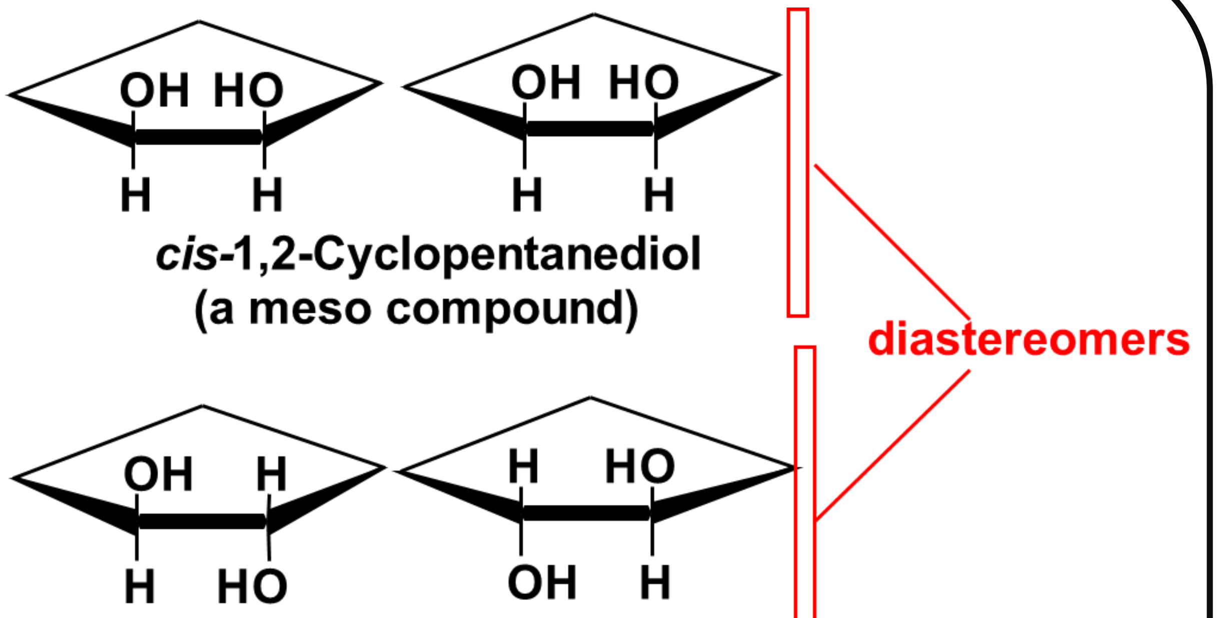
Meso Compounds : Compounds that contain stereogenic centres but are themselves achiral are called ***meso* compounds.** This means that there is a plane of symmetry with *R* stereochemistry on one side and *S* stereochemistry on the other.





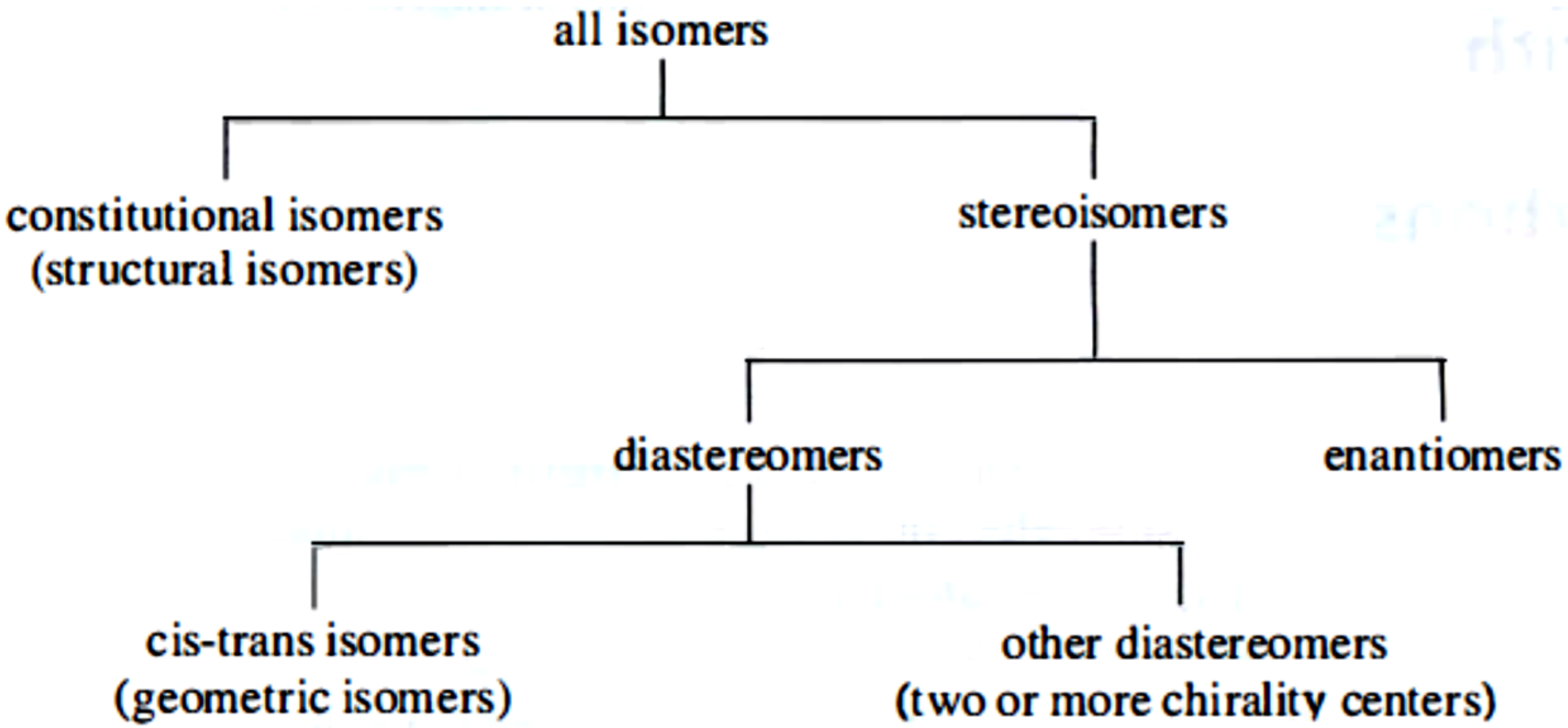
A meso compound
(plane of symmetry)

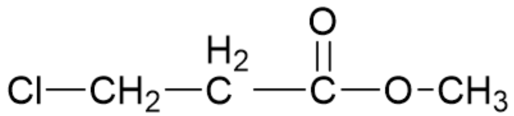
A pair of enantiomers

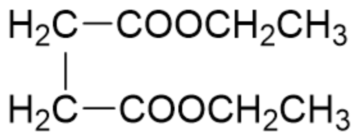


trans-1,2-Cyclopentanediol
(a pair of enantiomers)

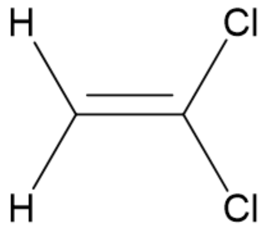
Summary


all isomers
constitutional isomers
(structural isomers)
stereoisomers
diastereomers
enantiomers
cis-trans isomers
(geometric isomers)
other diastereomers
(two or more chirality centers)

(a) 

(b) 

(c) $(CH_3)_2CH-CH_2-CHO$

(d) 

(e)