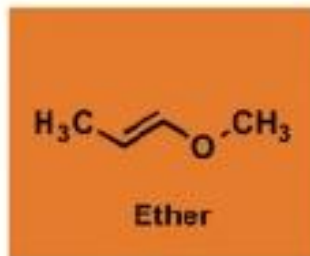
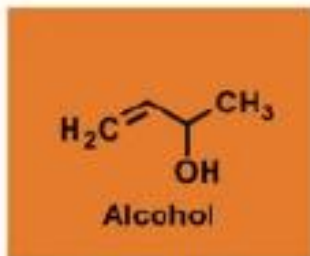


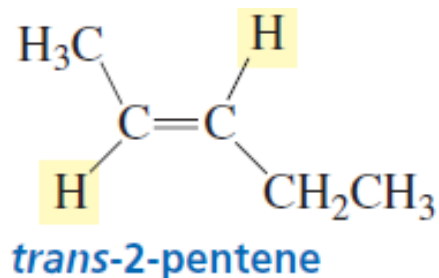
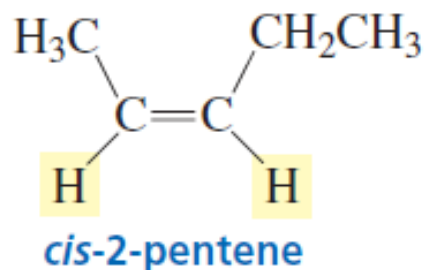
Optical Isomerism

Isomerism of Organic Molecules: Optical Isomerism



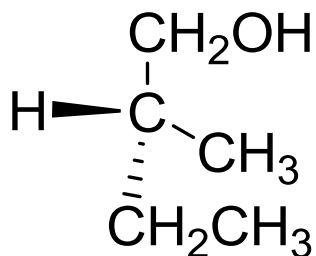
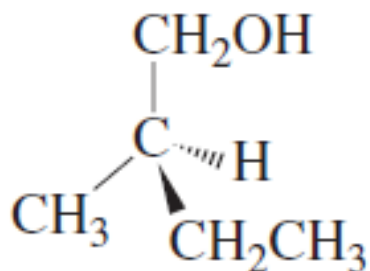
Structural isomers:

Different compounds; all properties like boiling points, melting points, and solubilities are different



Geometrical isomers:

Different compounds; all properties like boiling points, melting points, and solubilities are different



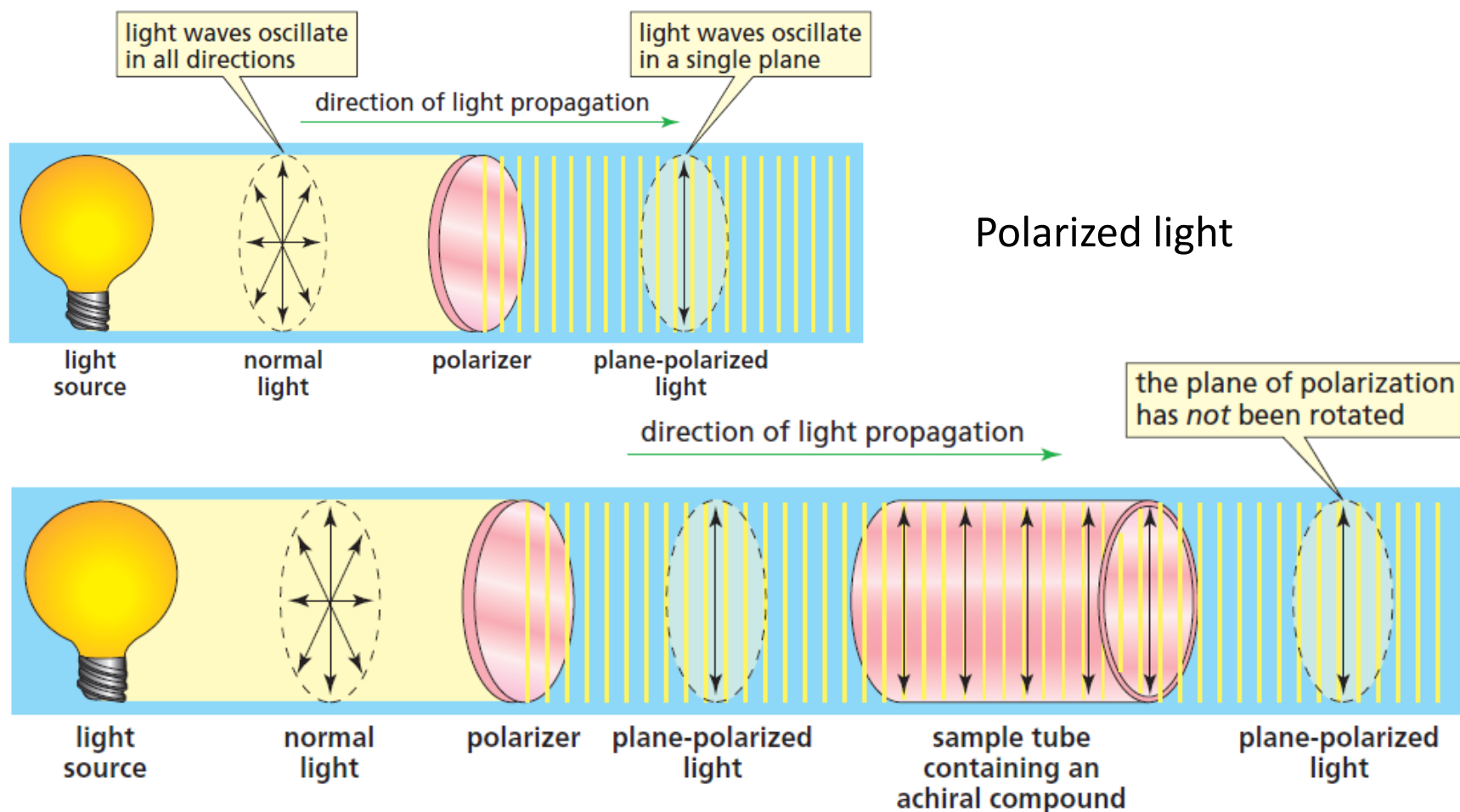
all properties like boiling points, melting points, and solubilities are same

Are they different compound?

What is the distinguishable property?

They interact differently with polarized light. These are called optical isomer

Isomerism of Organic Molecules: Optical activity

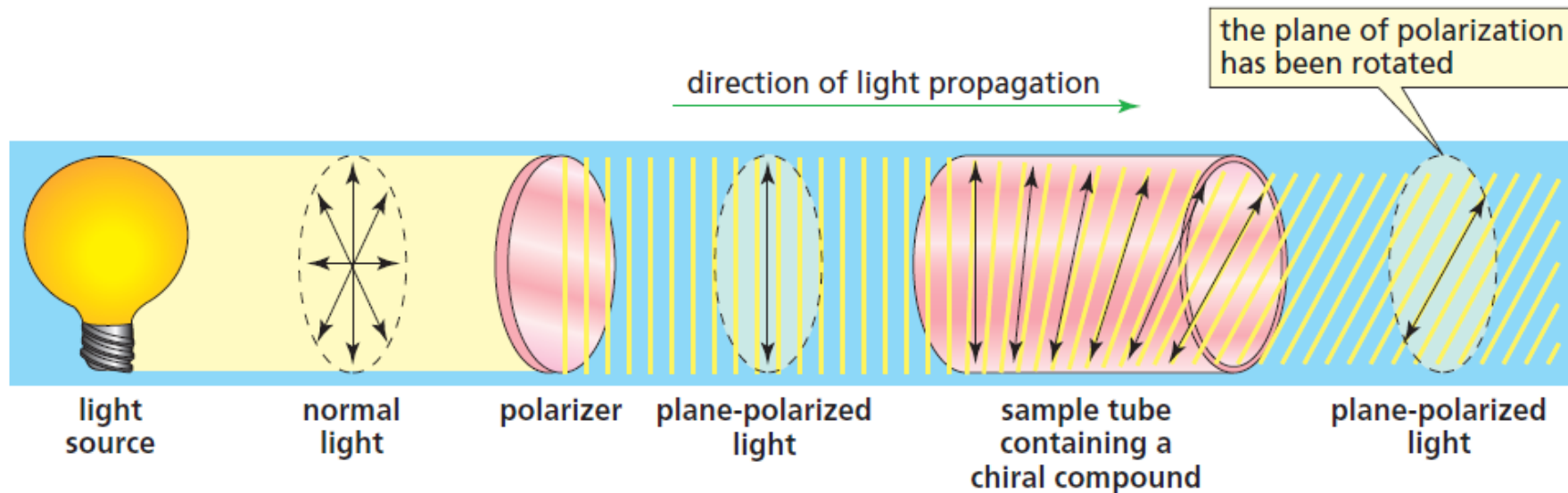


Achiral Molecule: does not rotate the plane of the polarized light

A compound that does not rotate the plane of polarization is said to be **optically inactive**.

THIS MOLECULE WILL NOT SHOW OPTICAL ISOMERISM

Isomerism of Organic Molecules: Optical activity



Chiral Molecule: rotate the plane of the polarized light

A compound that rotates the plane of polarization is said to be **optically active**.

THIS MOLECULE Will SHOW OPTICAL ISOMERISM

If an optically active compound rotates the plane of polarization clockwise, it is called **dextrorotatory**, indicated by **(+)** or **Dextro** or **d**

If an **optically active compound** rotates the plane of polarization counterclockwise, it is called **levorotatory**, indicated by **(-)** or **Levo** or **l**

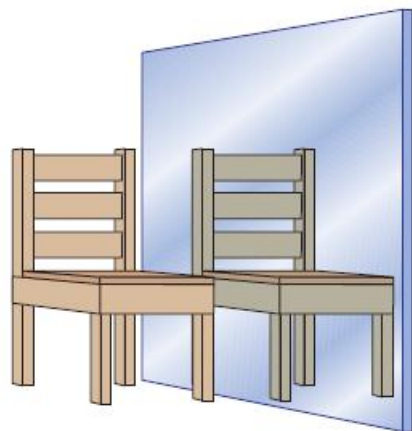
In other words, chiral compounds are optically active and achiral compounds are **optically inactive**.

Isomerism of Organic Molecules: Enantiomer

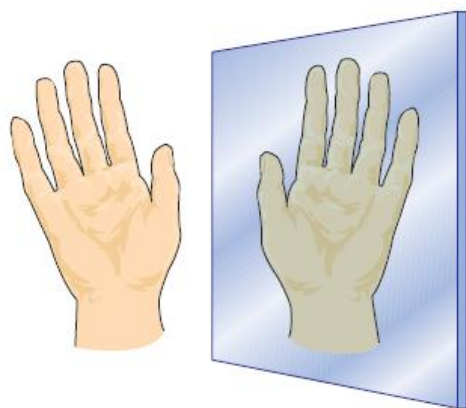
How do we find that a given molecule will rotate the plane of a polarized light or Not?

Or

how do we know that which molecule is chiral and which is achiral?



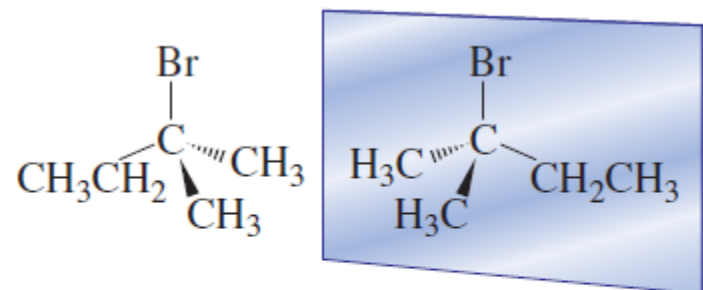
superimposable



right hand

left hand

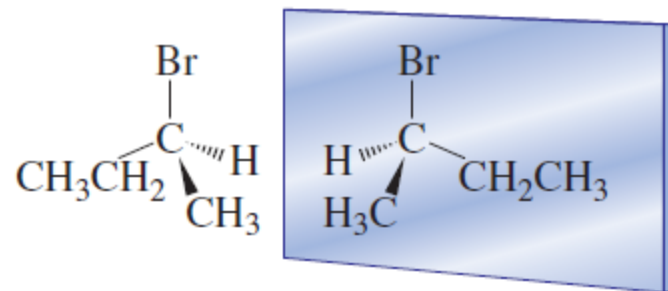
nonsuperimposable



an achiral molecule

superimposable mirror image

identical molecules



a chiral molecule

nonsuperimposable mirror image

enantiomers

A chiral molecule/ object has a *nonsuperimposable mirror image*.

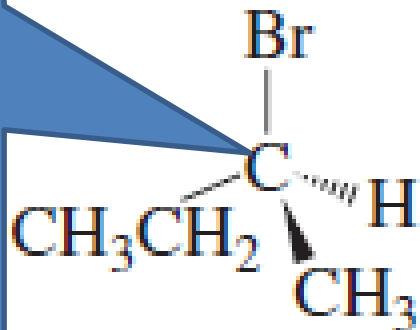
An achiral molecule/ object has a *superimposable mirror image*.

Isomerism of Organic Molecules: Chirality

What is the key difference between a chiral molecule and an achiral molecule ?

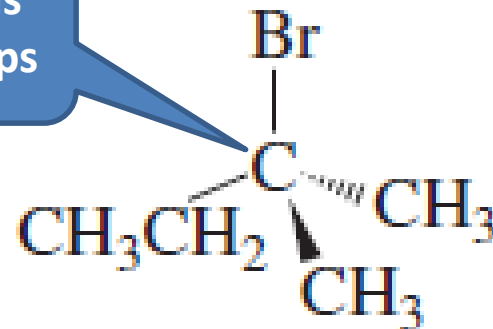
This carbon has all different groups

Carbon is called asymmetric carbon or chiral center



Chiral Molecule

This carbon has two same groups

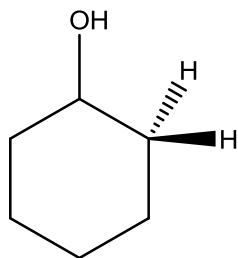


Achiral Molecule

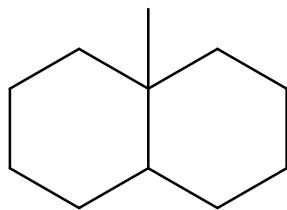
Optically active Molecule or Chiral Molecule should have

1. one asymmetric center or chiral center (there are exception)
2. *nonsuperimposable mirror image*

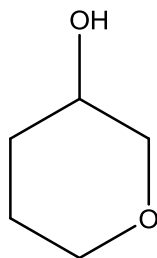
Mark the following molecule as chiral or achiral



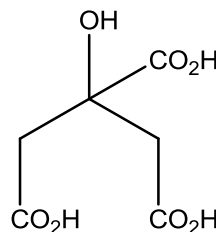
A



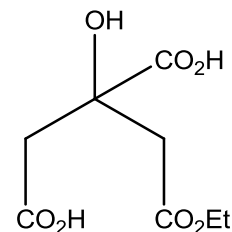
B



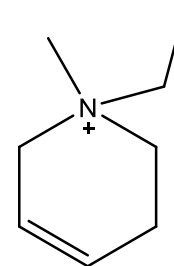
C



D



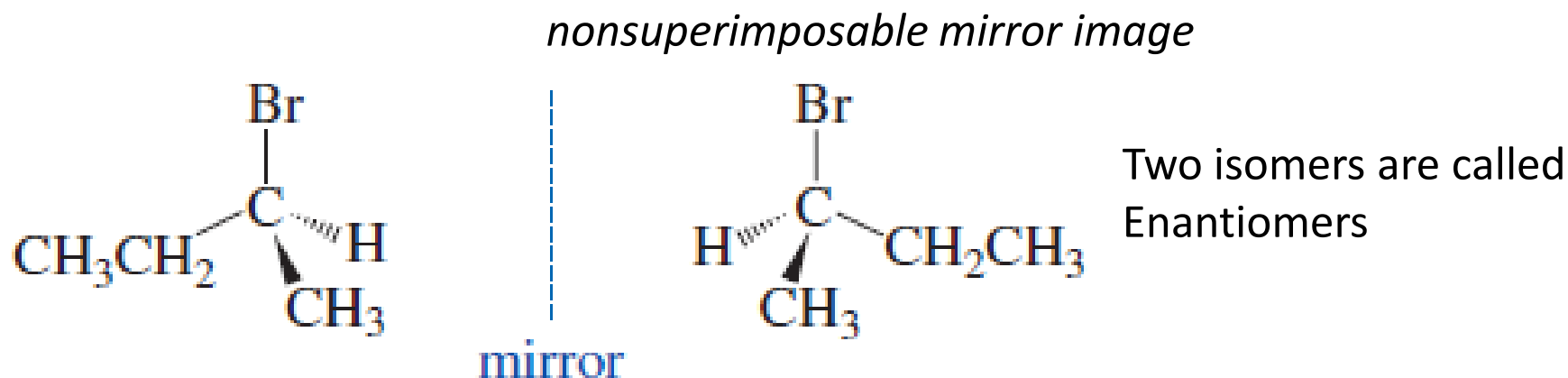
E



G

Isomerism of Organic Molecules: Enantiomer

As chiral or optically active molecule with only one chiral center will have two isomers. One isomer rotates the plane of a polarized light to the right and the other will rotate to the left.



Need a way to name the individual stereoisomer

Cahn, Ingold, and Prelog devised ***R,S System of Nomenclature*** to indicate the **configuration (arrangement)** of the atoms or groups about the asymmetric carbon.

pair of enantiomers with one asymmetric carbon, one will have the ***R configuration*** and the other will have the ***S configuration***.

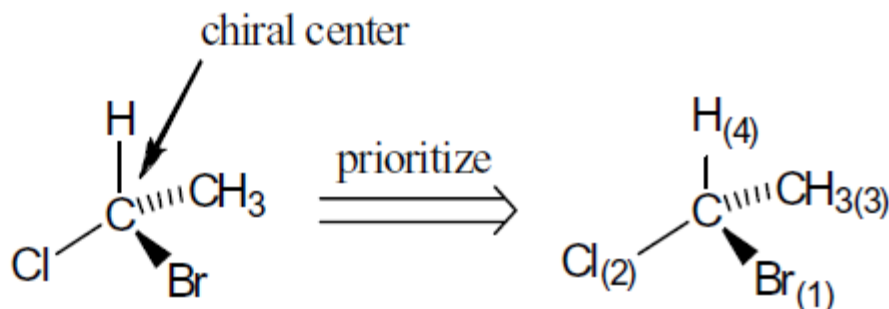
Isomerism of Organic Molecules: *R,S* Nomenclature

1. Rank the groups (or atoms) bonded to the asymmetric carbon in order of *priority*. The atomic numbers of the directly attached to the asymmetric carbon determine the relative priorities.

The higher the atomic number, the higher the priority.

atomic numbers

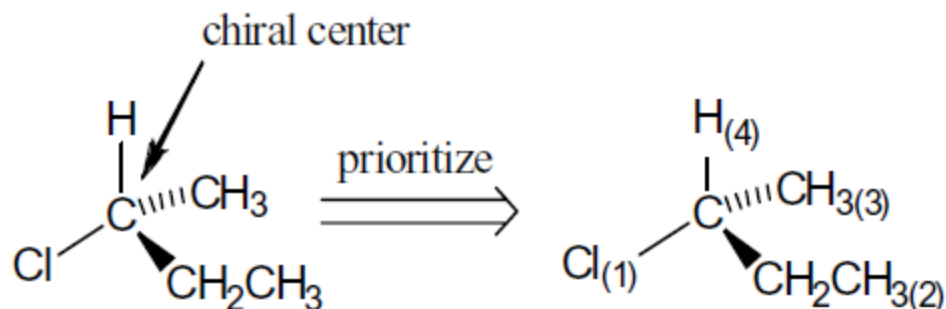
H	1
C	6
Cl	17
Br	35



2. If the two substituents bonded to *the asymmetric* carbon start with the same atom (there is a tie), you must move outward from the point of attachment and consider the atomic numbers of the atoms that are attached to the “tied” atoms.

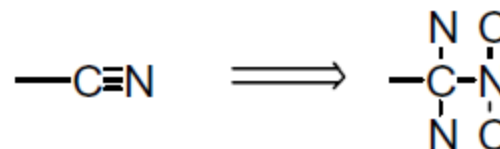
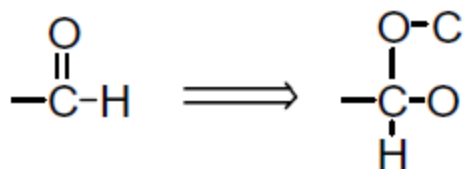
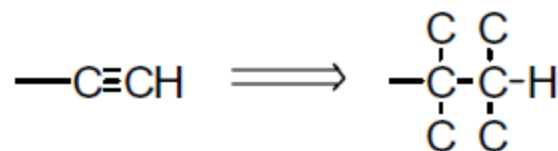
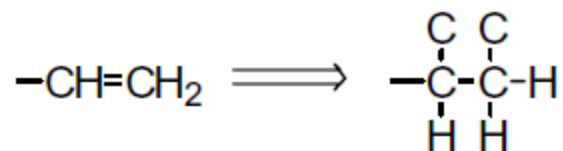
atomic numbers

H	1
C	6
Cl	17

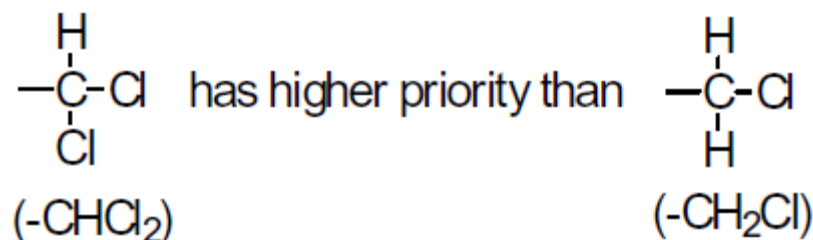


Isomerism of Organic Molecules: *R,S* Nomenclature

3. If an atom is doubly bonded to another atom, the priority system treats it as if it were singly bonded to two of those atoms. If an atom is triply bonded to another atom, the priority system treats it as if it were singly bonded to three of those atoms.



4. If two atoms have substituents of the same priority, higher priority is assigned to the atom with *more of these substituents*.



Isomerism of Organic Molecules: *R,S* Nomenclature

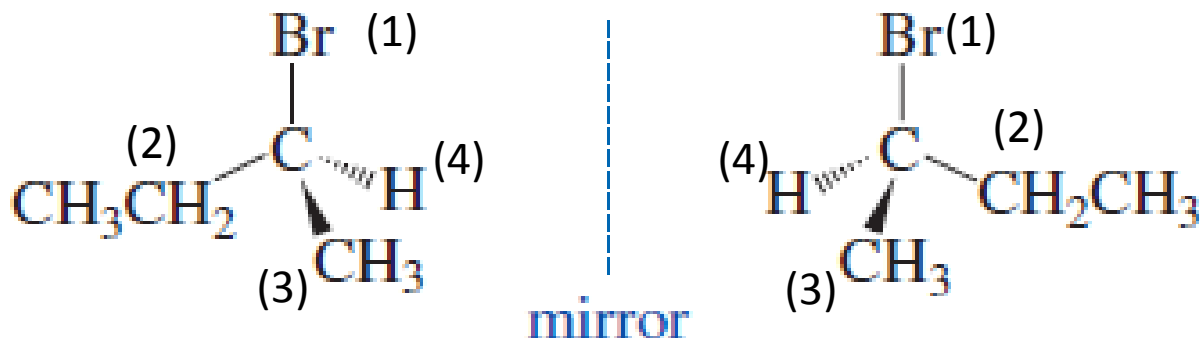
A larger group (i.e., more atoms) may not necessarily have a higher priority over another (smaller) group.

$-\text{CH}_2\text{Cl}$ has higher priority than $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

5. In the case of isotopes (atoms with the same atomic number, but different mass numbers), the mass number is used to determine the relative priorities.

$-\text{CHD}$ has higher priority than $-\text{CH}_2$

Example:

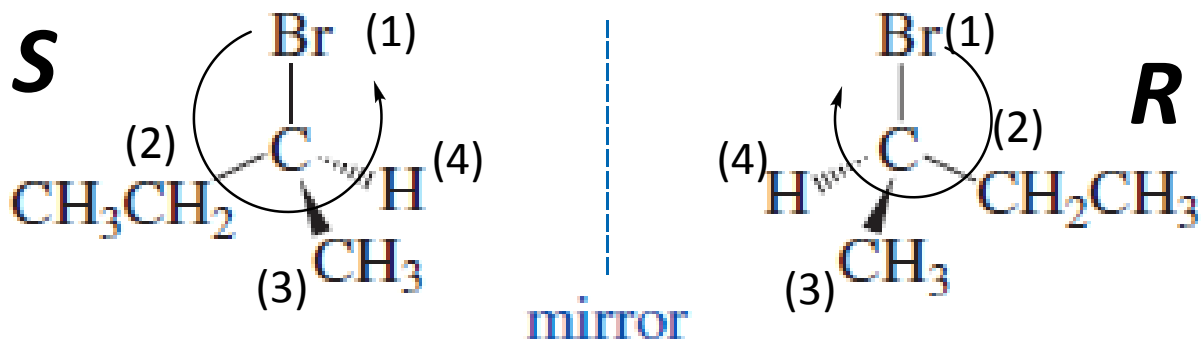


Isomerism of Organic Molecules: *R,S* Nomenclature

Draw a curved arrow from 1 **to** 2 **to** 3 and **back to** 1 and note which direction this arrow goes, clockwise (cw) or counterclockwise (ccw)

If the lowest priority group is ***behind*** the plane of the molecule, ***clockwise is R*** and ***counter-clockwise is S***

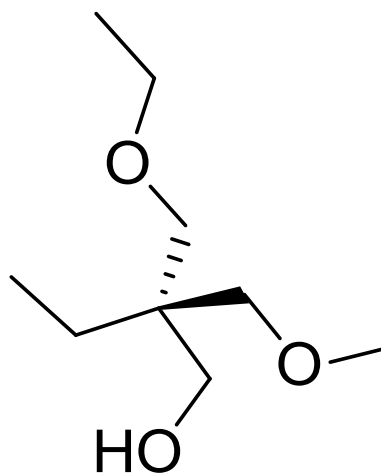
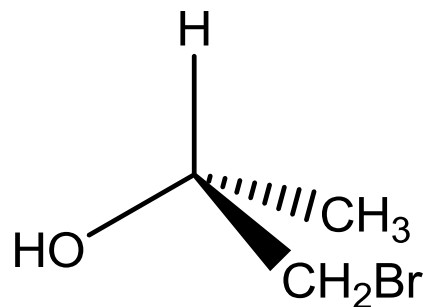
If the lowest priority group is ***in front*** of the plane of molecule, then the assignment is reversed: ***clockwise is S*** and ***counterclockwise is R***



Counterclockwise
lowest priority group is ***behind of the plane***

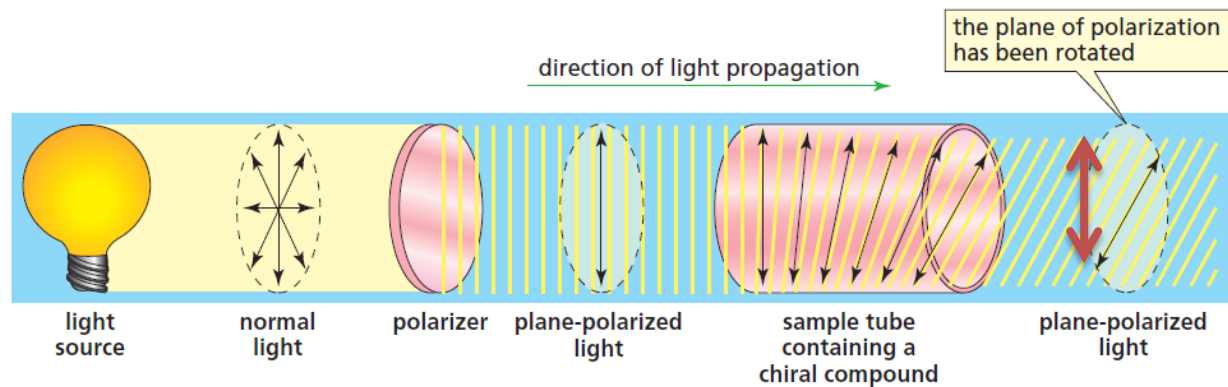
clockwise
lowest priority group is ***behind of the plane***

Isomerism of Organic Molecules: *R,S* Nomenclature



Isomerism of Organic Molecules: **Specific rotation**

optically active compound will rotate the plane of polarization



Observed rotation (α) is measured in degrees.

The observed rotation depends on the concentration of the sample and the length of the sample tube. The observed rotation also depends on the temperature, the wavelength of the light source and solvent.

For a given temperature T and given wavelength λ
Observed rotation α is related with specific rotation $[\alpha]_{\lambda}^T$ as

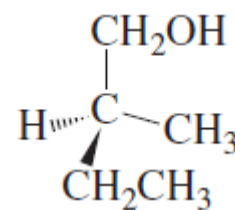
$$[\alpha]_{\lambda}^T = \frac{\alpha}{l \times c}$$

l = length (dm) of sample tube

c = concentration (g mL^{-1}) of molecule

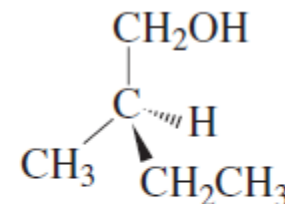
The **specific rotation is the number of degrees of rotation caused by a solution of 1.0 g of the compound per mL of solution in a sample tube 1.0 dm long at a specified temperature and wavelength.**

Specific rotation is specific to the molecule.



(S)-2-methyl-1-butanol

$$[\alpha]_{\text{D}}^{20^{\circ}\text{C}} = -5.75^{\circ}$$



(R)-2-methyl-1-butanol

$$[\alpha]_{\text{D}}^{20^{\circ}\text{C}} = +5.75^{\circ}$$

Isomerism of Organic Molecules: **Specific rotation**

A solution of 2.0 g of (+)-glyceraldehyde in 10.0 mL of water was placed in a 10 cm polarimeter tube. Using the sodium D line, a rotation of $+1.74^\circ$ was observed at 25°C . **Calculate the specific rotation of (+)-glyceraldehyde.**

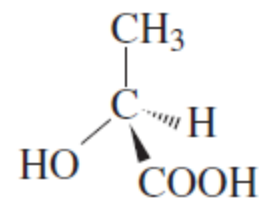
$$[\alpha]_{\lambda}^T = +1.74 / (0.2 \times 1) = +8.7$$

***R** or the **S** configuration **does not** tell us the direction the compound rotates the plane of polarization*

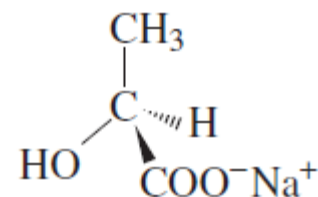
For some compounds with the ***R** configuration rotate the plane to the **right*** and some rotate the plane to the **left**

We can tell by looking at the structure of a compound whether it has the ***R** or the **S** configuration*

One can tell whether a compound is dextrorotatory or levorotatory only after measurement of optical rotation in a polarimeter



(S)-(+)-lactic acid



(S)-(-)-sodium lactate

Isomerism of Organic Molecules: **Optical Purity**

a 1:1 mixture of opposite *enantiomers* is called a *racemic mixture*

a racemic mixture is optically inactive ($\alpha = 0$)

a optically inactive sample can be either an achiral substance or a racemic mixture

If the mixture contain one of the enantiomer in excess to other, the mixture will show optical activity

Excess in the enantiomers is quantified by **enantiomeric excess (ee)**

$$\text{enantiomeric excess} = \frac{\text{excess of a single enantiomer}}{\text{entire mixture}} \times 100\%$$

If a substance contain exclusively one enantiomers, the substance is called optically pure substance

$$\text{optical purity} = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}}$$

$$\text{enantiomeric excess} = \% \text{ optical purity} = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}} \times 100$$

Isomerism of Organic Molecules

(-)-2-butanol has a specific rotation of -13.5° while the specific rotation of (+)-2-butanol is $+13.5^\circ$. Calculate the optical purity of a mixture containing (+) and (-)-2-butanol if the mixture has an observed specific rotation of -8.10° .

Does the mixture contain more (+) or more (-)-2-butanol?

What is the enantiomeric excess (ee) of the mixture?

What is the ratio of two enantiomers in the mixture?

Looking forward

Optical Isomerism:

compounds with more than one chiral center

compounds having chiral center and alkene

importance of chirality

conformation vs configuration

Course material will be uploaded **after 17:00 h** on **every Friday@**

<http://www.iitg.ac.in/ckjana/ckjana/Teaching.html>