Semester-I (Hons)

Organic chemistry Notes

STEREOCHEMISTRY

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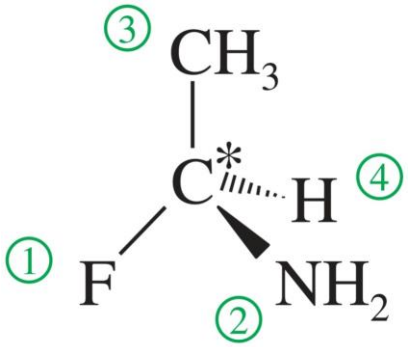
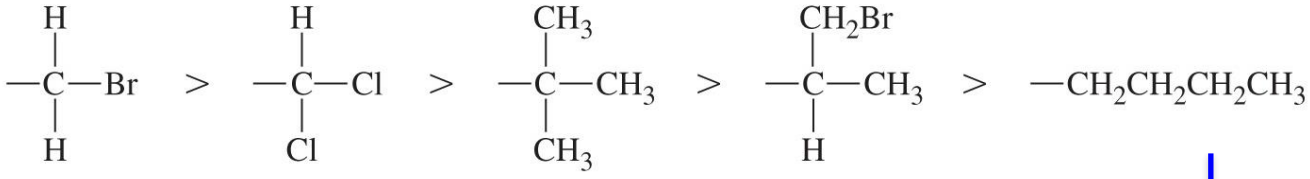
(*R*) and (*S*) Configuration: Assign Priority

- Atoms with higher atomic numbers receive higher priorities

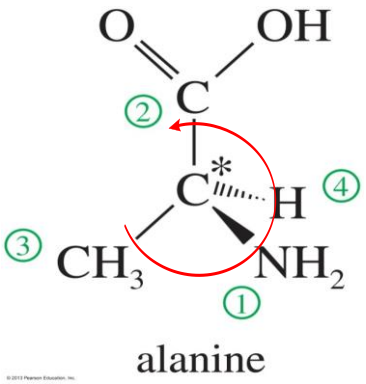
$$I > Br > Cl > S > F > O > N > {}^{13}C > {}^{12}C > {}^{2}H > {}^{1}H$$



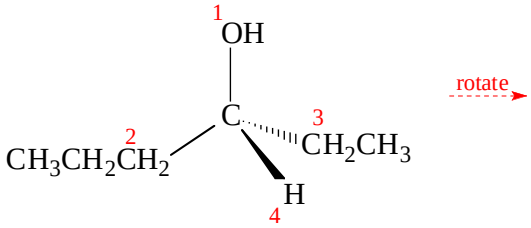
- In case of ties, use the next atoms along the chain of each group



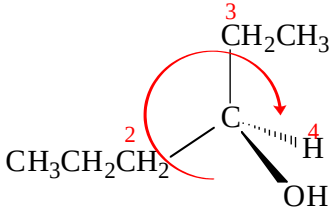
Examples



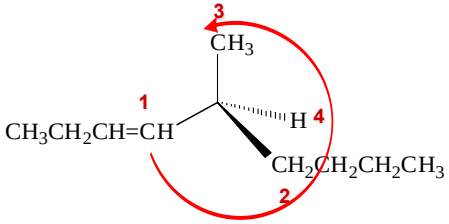
Counterclockwise (*S*)



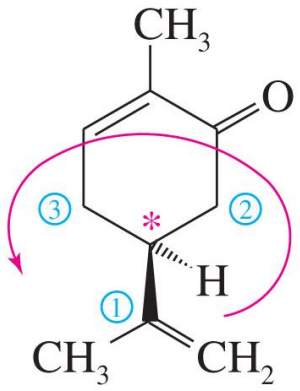
rotate



Clockwise (*R*)



Counterclockwise (*S*)

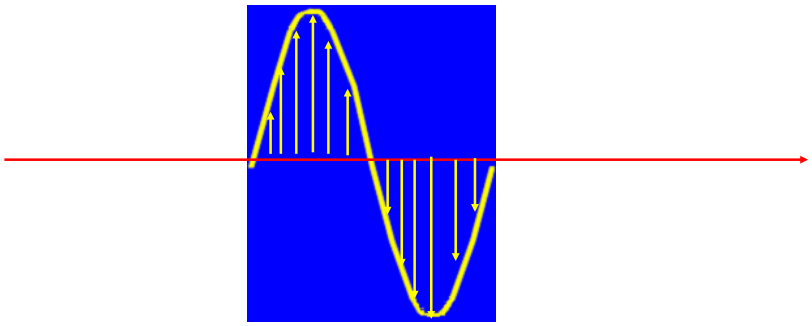


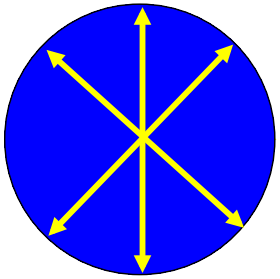
(*S*)-carvone

Optical Activity

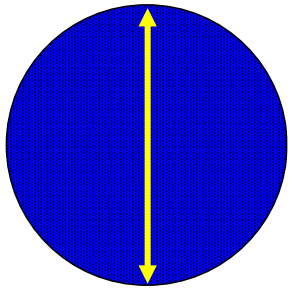
- **A substance is optically active if it rotates the plane of polarized light.**
- In order for a substance to exhibit optical activity, it must be chiral and one enantiomer must be present in excess of the other.

optical activity is usually measured using light having a wavelength of 589 nm this is the wavelength of the yellow light from a sodium lamp and is called the D line of sodium



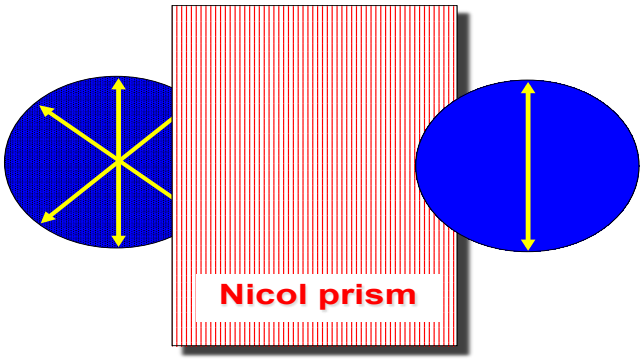


Ordinary (nonpolarized) light consists of many beams vibrating in different planes

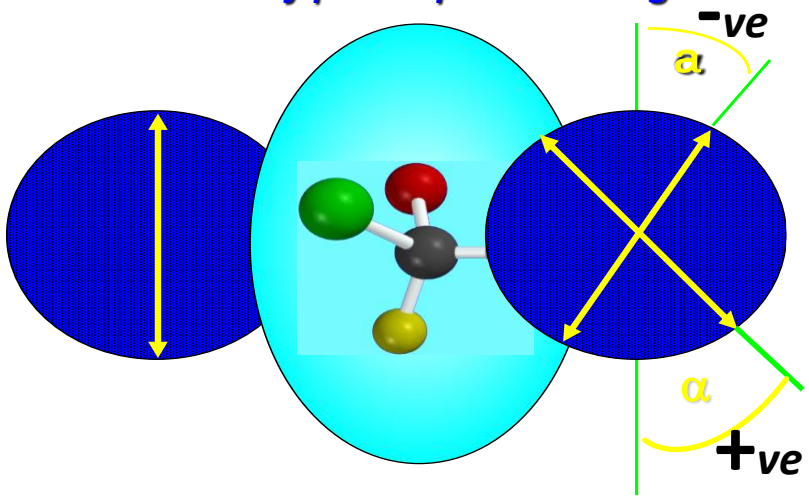


plane-polarized light consists of only those Beams that vibrate in the same plane

Polarization of light



Rotation of plane-polarized light



Specific rotation

Observed rotation depends on the length of the cell and concentration, as well as the strength of optical activity, temperature, and wavelength of light.

$$[\alpha] = \frac{\alpha \text{ (observed)}}{c \bullet l}$$

Where α (observed) is the rotation observed in the polarimeter, c is concentration in g/mL, and l is length of sample cell in decimeters.

Problem

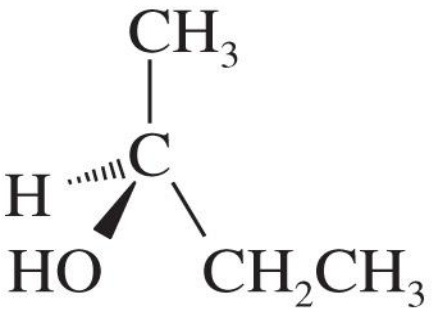
When one of the enantiomers of 2-butanol is placed in a polarimeter, the observed rotation is 4.05° counterclockwise. The solution was made by diluting 6 g of 2-butanol to a total of 40 mL, and the solution was placed into a 200-mm polarimeter tube for the measurement. Determine the specific rotation for this enantiomer of 2-butanol.

Solution

Since it is levorotatory, this must be (–)-2-butanol The concentration is 6 g per 40 mL = 0.15 g/mL, and the path length is 200 mm = 2 dm. The specific rotation is

$$[\alpha]_D^{25} = \frac{-4.05^\circ}{(0.15)(2)} = -13.5^\circ$$

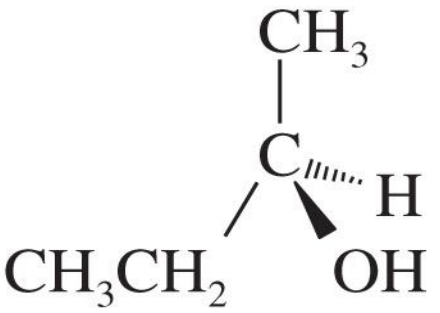
Racemic Mixtures



(*S*)-(+)-butan-2-ol

+13.5° rotation

and



(*R*)-(−)-butan-2-ol

−13.5° rotation

A racemic mixture contains equal amounts of the two enantiomers.

- ✓ Equal quantities of *d*- and *l*-enantiomers.
- ✓ Notation: (*d*,*l*) or (±)
- ✓ No optical activity.
- ✓ The mixture may have different boiling point (b. p.) and melting point (m. p.) from the enantiomers!

Optical Purity

- Optical purity is sometimes called enantiomeric excess (e.e.)
- One enantiomer is present in greater amounts.

$$\text{o.p.} = \frac{\text{observed rotation}}{\text{rotation of pure enantiomer}} \times 100$$

The specific rotation of (*S*)-2-iodobutane is +15.90°. Determine the % composition of a mixture of (*R*)- and (*S*)-2-iodobutane if the specific rotation of the mixture is -3.18°.

Sign is from the enantiomer in excess: levorotatory.

$$\text{o.p.} = \frac{3.18}{15.90} \times 100 = 20\%$$

$2l = 120\%$ $\quad l = 60\%$ $\quad d = 40\%$