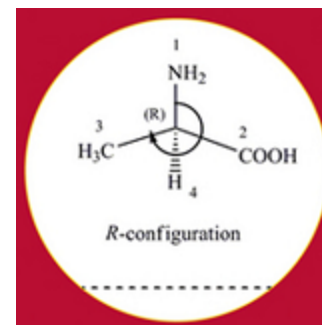
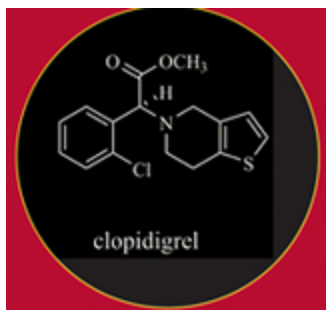


Fundamentals of Organic Chemistry and Hydrocarbons

(CHEM 226, Organic Chemistry I)



Contact information

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◆ Available time:

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◆ Office:

Room 201C – Building A3

Division of Organic Chemistry

Department of Chemistry, HNUE

Today's topic

- Main contents covered in this course
- How to study organic chemistry?
- Policy of the course
- Chapter 1: *General Notes of Organic Chemistry and Organic Compounds*

Syllabus*

1. Drawing 3D structures -
Stereochemistry

Chapter 3, 9

2. Structure and bonding -
An overview of organic reactions

Chapter 1, 5,
14

3. Saturated Hydrocarbons (Alkanes,
cycloalkanes)

Chapter 3, 4

4. Unsaturated hydrocarbon (Alkenes,
Alkynes)

Chapter 6, 7, 8

5. Aromatic hydrocarbons

Chapter 15, 16

6. IR, UV-Vis, NMR, MS

Chapter 12, 13,
14

* Organic Chemistry 7th Ed. by John Mc Murry

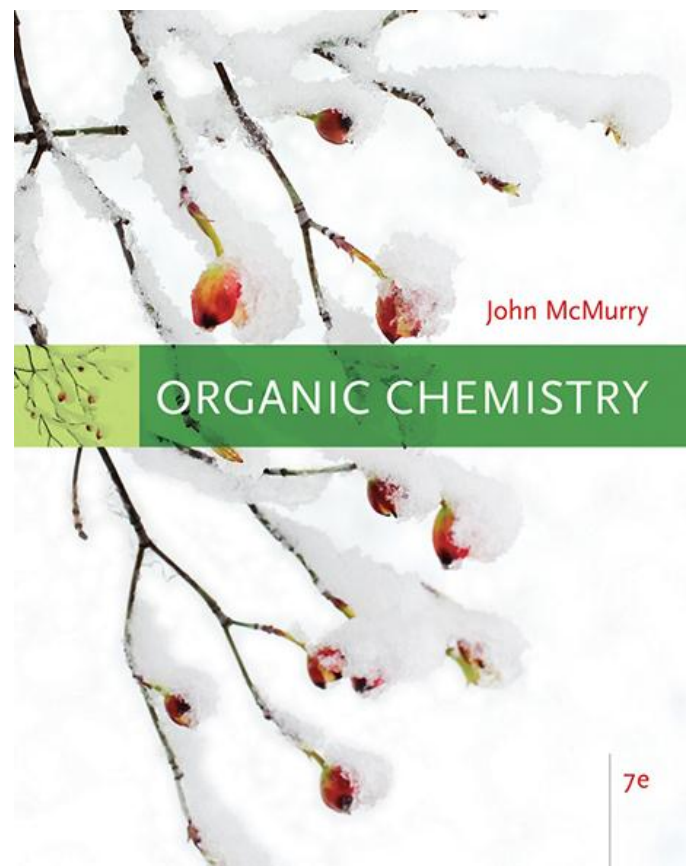
References

♦ Organic Chemistry, 7th Edition

John McMurry

♦ Websites:

Chemistry portal



How to study pass this course?

- 1. Go to lectures (Thursday, 8:00-11:50 am), ask questions, join the discussion during seminar (yourself, do not hesitate to criticize my points if they do not sound correctly).**
- 2. Use textbooks, handouts (will be sent through email) and learning materials from other sources.**
- 3. Prepare yourself for homework (before attending the seminars) or at least read them through if you do not have time to write them all down in details.**

Grading

- ◆ **Final exam (writing)** **60%**
 - ◆ **Midterm exam (× 1) (writing)** **30%**
 - ◆ **Attendance** **10%**
- (Being absence less than 20% of the total hours)**

Introduction

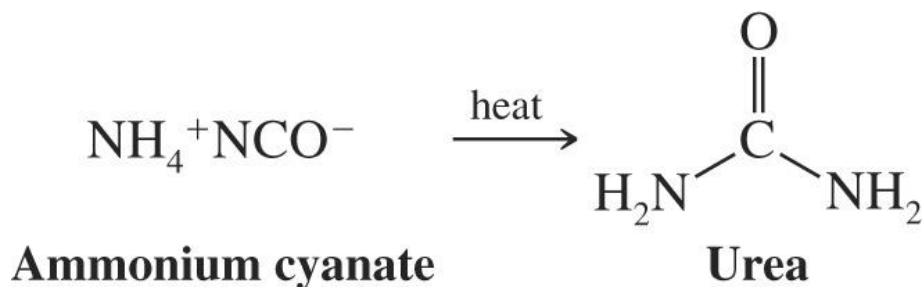
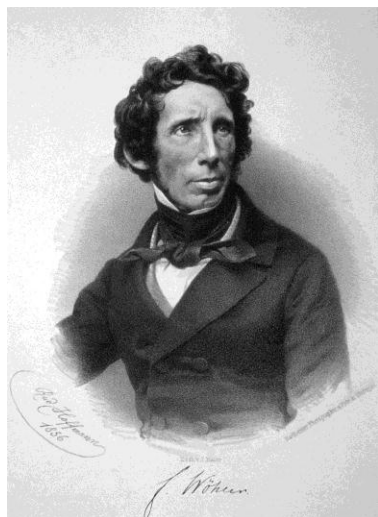
➤ Organic Chemistry

- The chemistry of the compounds of carbon. The term organic literally means “derived from living organisms”.

➤ Vitalism

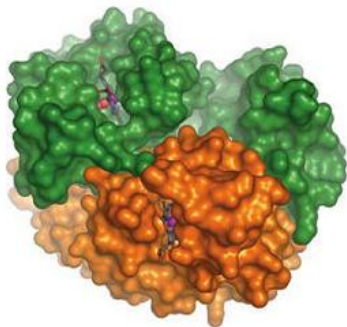
- It was originally thought organic compounds could be made only by living things by intervention of a “*vital force*”

- Fredrich Wöhler disproved vitalism in 1828 by making the organic compound urea from the inorganic salt ammonium cyanate by evaporation:

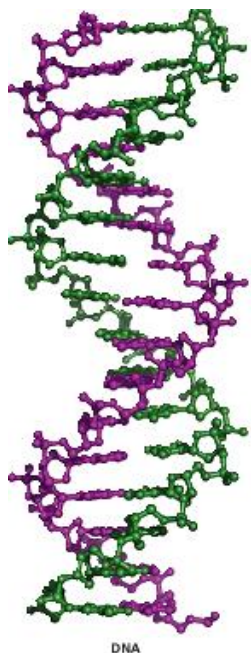


Role of organic compounds

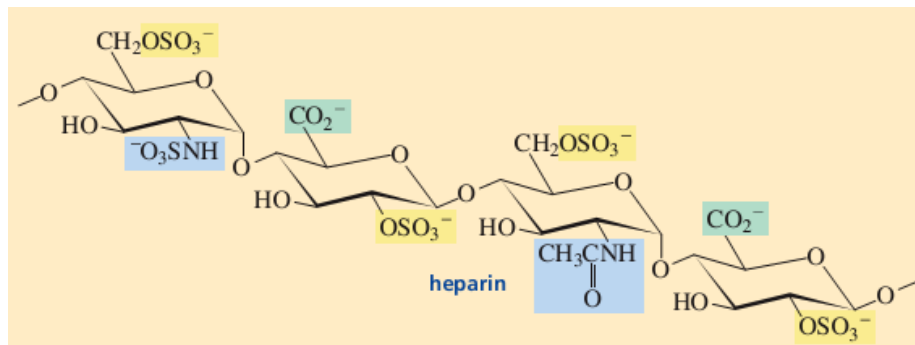
- The human body and animals is largely composed of organic compounds. Organic chemistry plays a central role in medicine, bioengineering etc.



Hemoglobin



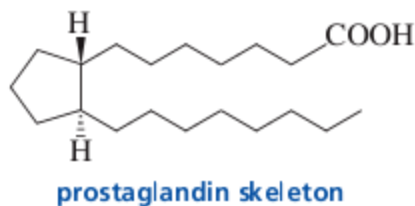
DNA



Heparin, a natural anticoagulant, is a polysaccharide found principally in cells that line arterial walls. Heparin is released when an injury occurs in order to prevent excessive blood clot formation.

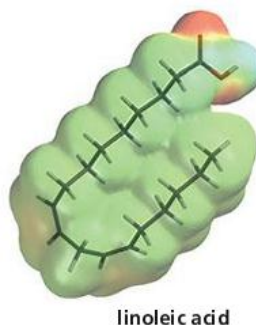
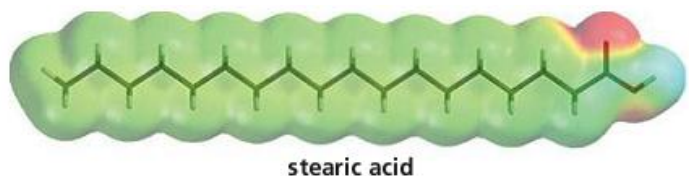
DNA encodes an organism's entire hereditary information and controls the growth and division of cells. In all organisms (except certain viruses), the genetic information stored in DNA is transcribed into RNA. This information can then be translated for the synthesis of all the proteins needed for cellular structure and function.

Role of organic compounds

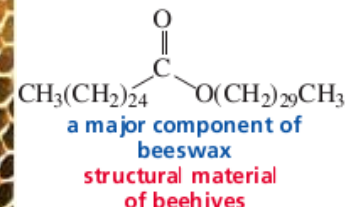


Prostaglandins are found in all body tissues and are responsible for regulating a variety of physiological responses, such as inflammation, blood pressure, blood clotting, fever, pain, the induction of labor, and the sleep wake cycle.

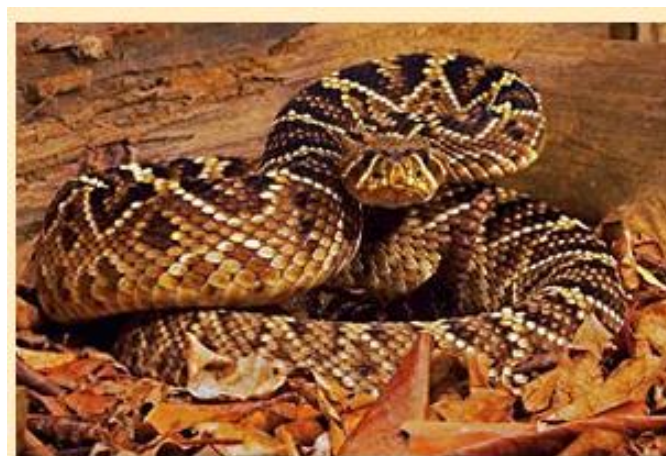
Fatty acids



Beeswax



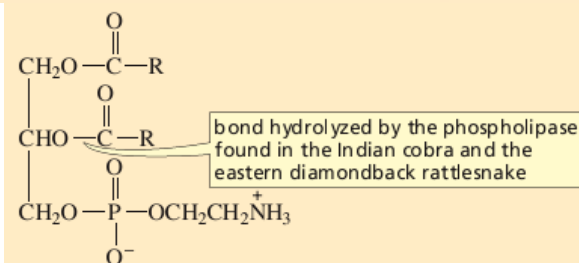
Layers of honeycomb in a
beehive.



An eastern diamondback rattlesnake.

Snake venom

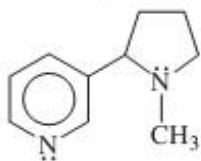
Chapter 1



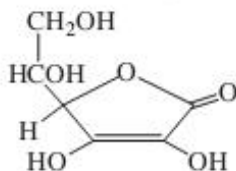
Other organic compounds in nature



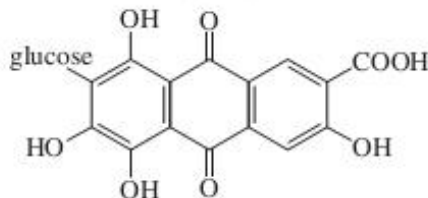
nicotine



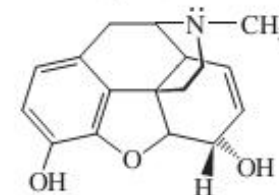
vitamin C



carmine



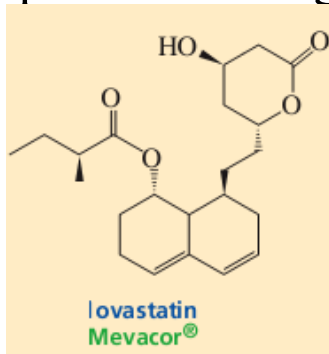
morphine



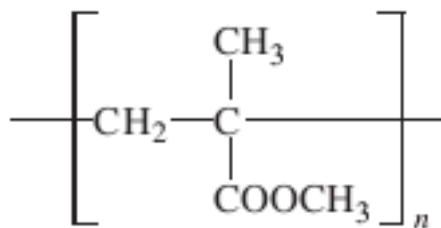
Four examples of organic compounds in living organisms: Tobacco contains **nicotine**, an addictive alkaloid. One of nicotine's effects is to increase the concentration of dopamine, a chemical in the brain's reward system. Release of this chemical makes smokers feel good and reinforces the need to smoke. Rose hips contain **vitamin C**, essential for preventing scurvy. The red dye **carmine** comes from cochineal insects, shown on a prickly pear cactus. Opium poppies contain **morphine**, a pain-relieving, addictive alkaloid.

“Artificial”-synthetic organic compounds

Chemists have learned to synthesize or simulate many of these complex molecules. The synthetic products serve as drugs, medicines, plastics, pesticides, paints, and fibers. New synthetic drugs are developed to combat disease, and new polymers are molded to replace failing organs. Organic chemistry has gone full circle. It began as the study of compounds derived from “organs,” and now it gives us the drugs and materials we need to save or replace those organs



Statins are the newest class of cholesterol-reducing drugs. Statins reduce serum cholesterol levels by inhibiting the enzyme that catalyzes the formation of a compound needed for the synthesis of cholesterol.



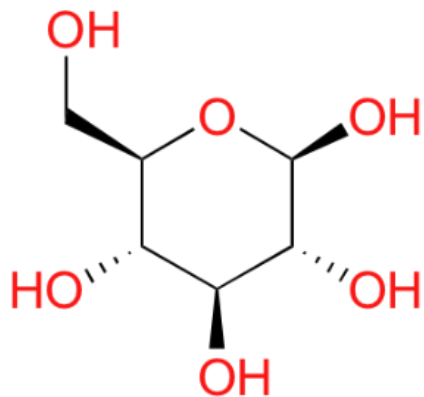
poly(methyl α-methacrylate)
Acrylic fibers
Plexiglas®
Lucite® paints



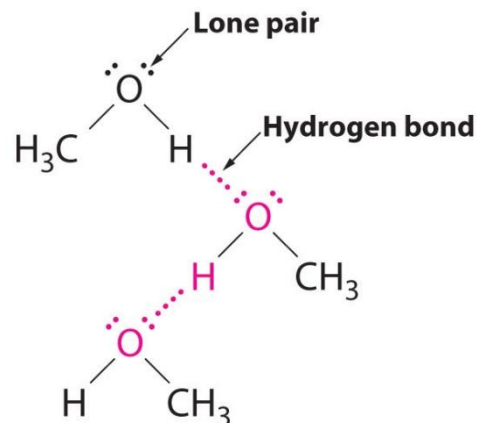
The AbioCor self-contained artificial heart, which was first implanted into a patient on July 3, 2001. The outer shell is polycarbonate, and the valves and inner bladder are polyurethane.

Physical properties of organic compounds

- General rule: '*like dissolves like*'. Non-polar organic compounds dissolve *limitedly* in polar solvents, especially those which can form hydrogen bonds, such as water.
- *Exceptions*: Dissolving glucose in the water is easy even though it has six carbons just like *n*-hexane and *n*-hexanol.



glucose



Hydrogen bonding in methanol

- + Methanol, ethanol, and propanol - dissolve easily in water. This is because the water is able to form hydrogen bonds with the hydroxyl group in these molecules.
- + From butanol, the solubility in water reduces significantly.

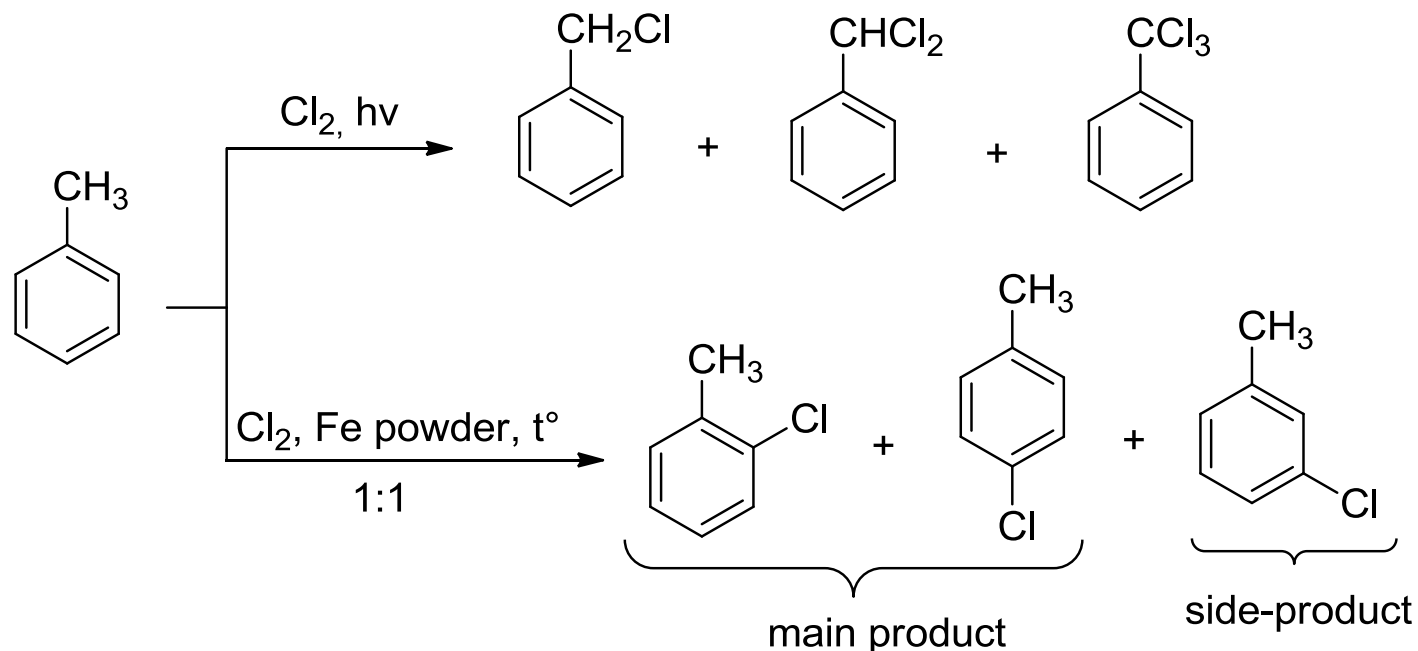
Physical properties

- Normally, organic compounds have rather **low** boiling points and melting points,
- *Exceptions*: polymers and other macromolecules, etc.
- The presence of polar and especially hydrogen-bonding groups generally leads to higher melting points.
- *Molecular shape*, and the ability of a molecule to pack tightly into a crystal lattice, has a very large effect on melting points. *For example*: The flat shape of aromatic compounds such as naphthalene allows them to stack together efficiently, and thus aromatics tend to have higher melting points compared to alkanes or alkenes with similar molecular weights.

Properties of organic compounds

Chemical properties

- General rule: their reactions are rather slow and occur in different directions
- Example:



Functional groups and classification of organic compounds

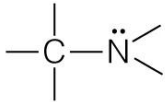
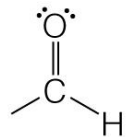
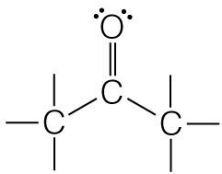
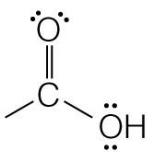
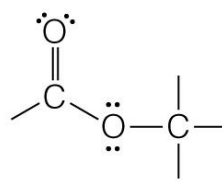
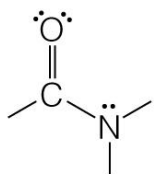
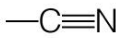




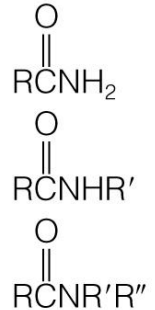

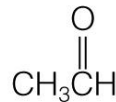
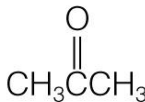
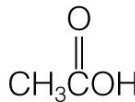
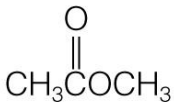
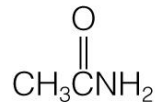
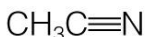
- Functional groups: characterized by the presence of a certain arrangement of atoms called a *functional group*. A functional group is the site of most chemical reactivity of a molecule. The functional group is responsible for many of the physical properties of a molecule.

- Important families of organic compounds and functional groups

	Family						
	Alkane	Alkene	Alkyne	Aromatic	Haloalkane	Alcohol	Ether
Functional group	C—H and C—C bonds		$\text{—C}\equiv\text{C—}$	Aromatic ring			
General formula	RH	RCH=CH ₂ RCH=CHR R ₂ C=CHR R ₂ C=CR ₂	RC≡CH RC≡CR	ArH	RX	ROH	ROR
Specific example	CH ₃ CH ₃	CH ₂ =CH ₂	HC≡CH		CH ₃ CH ₂ Cl	CH ₃ CH ₂ OH	CH ₃ OCH ₃
IUPAC name	Ethane	Ethene	Ethyne	Benzene	Chloroethane	Ethanol	Methoxymethane
Common name ^a	Ethane	Ethylene	Acetylene	Benzene	Ethyl chloride	Ethyl alcohol	Dimethyl ether

^aThese names are also accepted by the IUPAC.

- Important families of organic compounds and functional groups

Family						
Amine	Aldehyde	Ketone	Carboxylic Acid	Ester	Amide	Nitrile
						
RNH_2 R_2NH R_3N						
CH_3NH_2						
Methanamine	Ethanal	Propanone	Ethanoic acid	Methyl ethanoate	Ethanamide	Ethanenitrile
Methylamine	Acetaldehyde	Acetone	Acetic acid	Methyl acetate	Acetamide	Acetonitrile

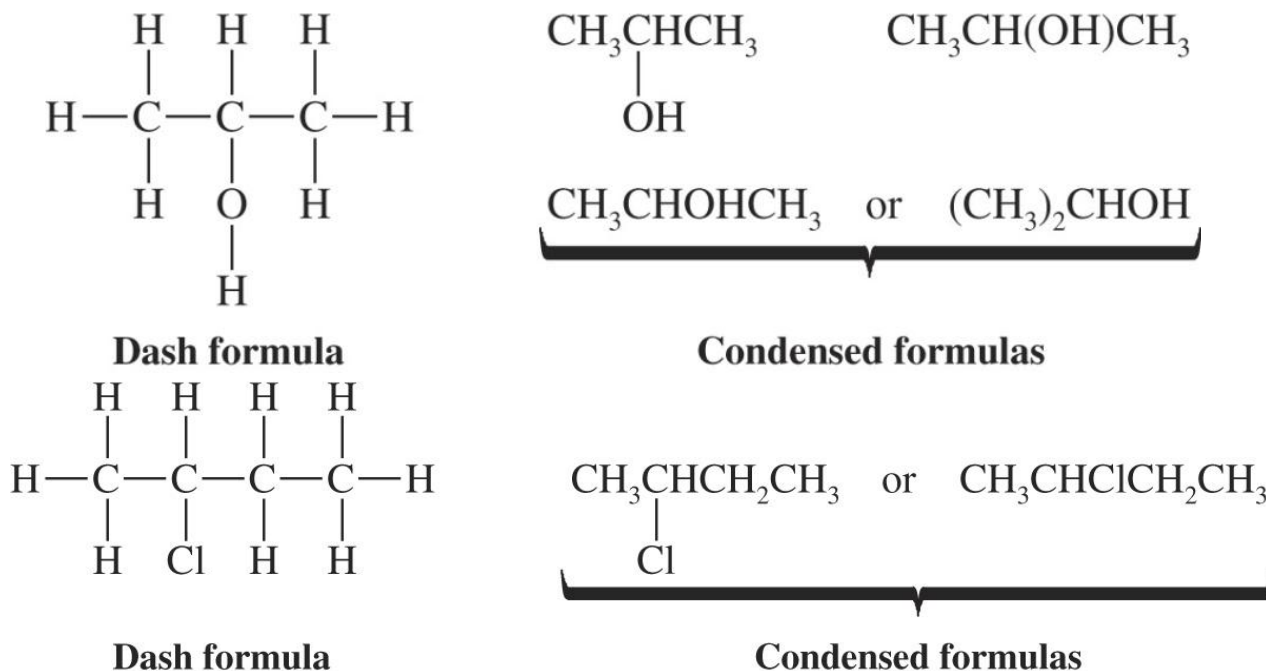
Chapter 1

How to present organic compounds?

How to present organic compounds

● Kekulé and condensed structural formulas

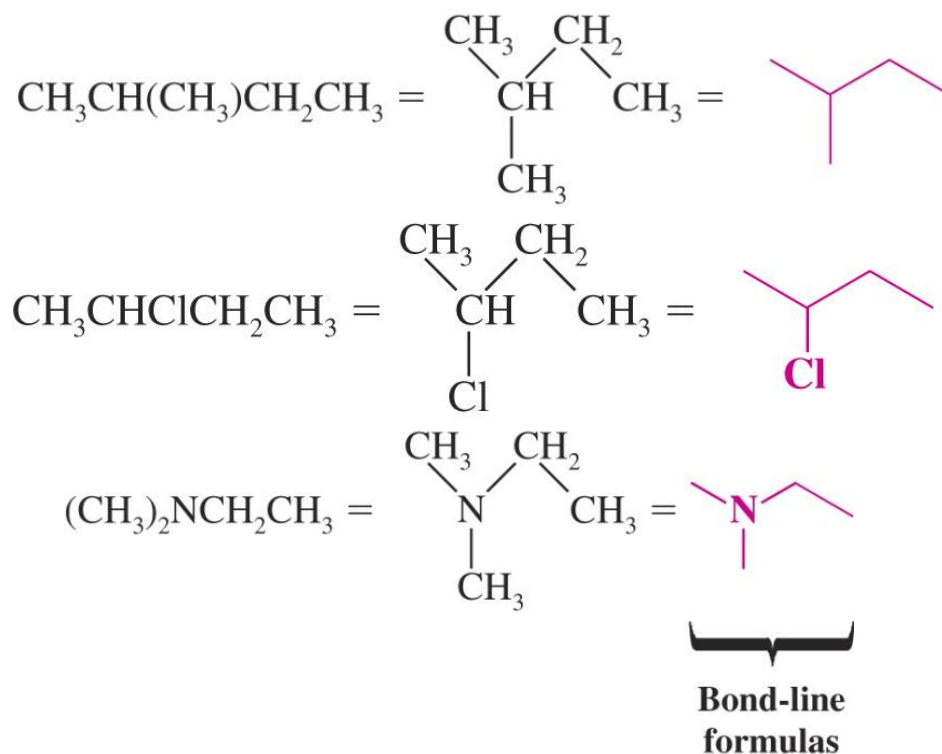
- In **Kekulé** structures (or dash formulas), the bonding electrons are drawn as lines and the lone-pair electrons are usually left out entirely, unless they are needed to draw attention to some chemical property of the molecule.
- Structures are simplified by omitting some (or all) of the covalent bonds and listing atoms bonded to a particular carbon (or nitrogen or oxygen) next to it with a subscript to indicate the number of such atoms. These kinds of structures are called **condensed** structures



How to present organic compounds

Bond-line formulas (skeleton formula)

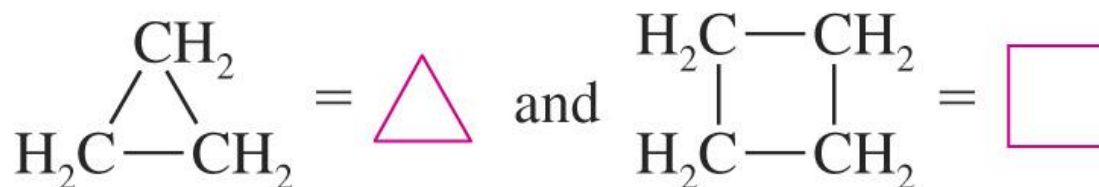
- A further simplification of drawing organic molecules is to completely omit all carbons and hydrogens and only show heteroatoms (*e.g.* O, Cl, N) explicitly. Each intersection or end of line in a zig-zag represents a carbon with the appropriate amount of hydrogens.
- Heteroatoms with attached hydrogens must be drawn in explicitly.



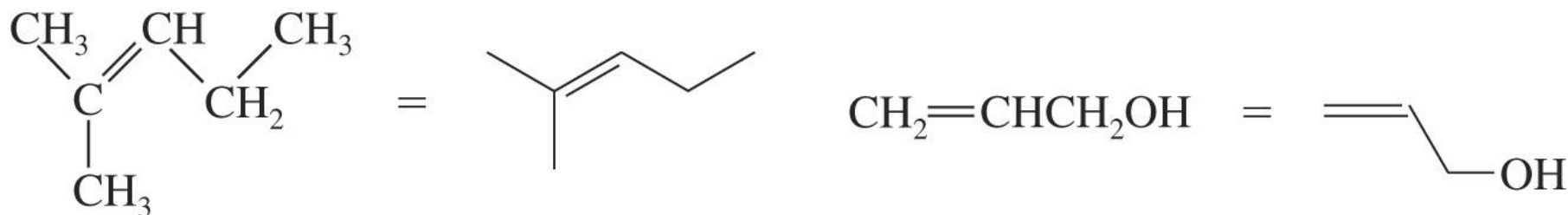
How to present organic compounds

Bond-line formulas (skeleton formula)

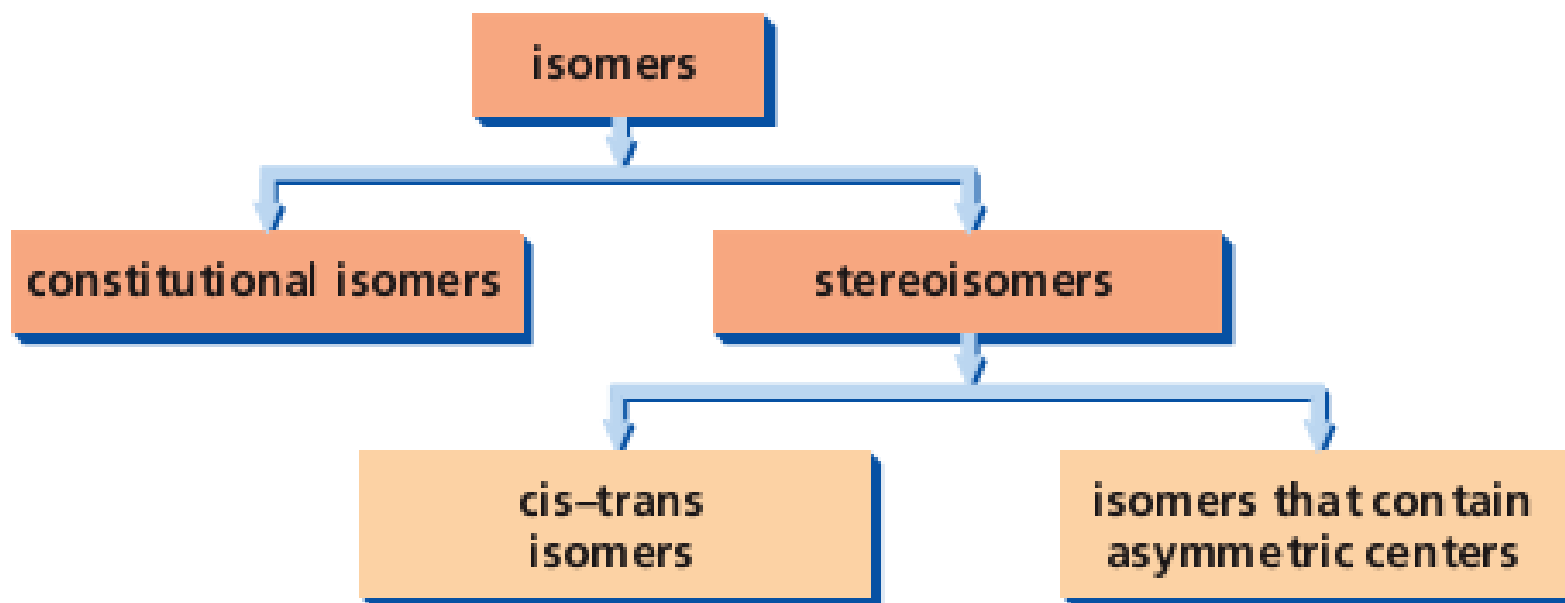
➔Cyclic compounds are condensed using a drawing of the corresponding polygon.



➔Multiple bonds are indicated by using the appropriate number of lines connecting the atoms.



Isomerism: Constitutional Isomers and Stereoisomers



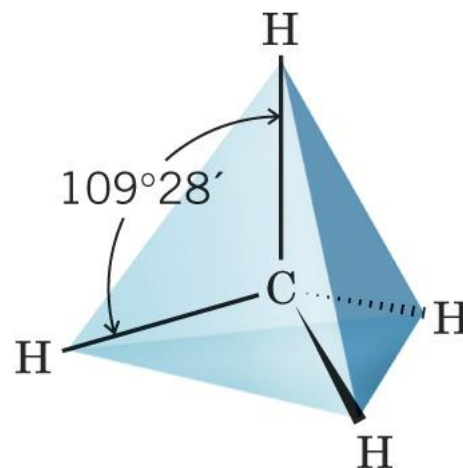
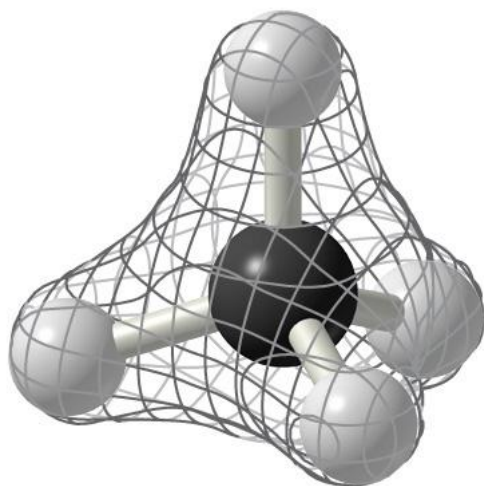
Constitutional isomers

- Constitutional isomers are different compounds that have the same molecular formula but different connectivity of atoms. They often differ in physical properties (e.g. boiling point, melting point, density) and chemical properties.
- Consider two compounds with molecular formula $\text{C}_2\text{H}_6\text{O}$. These compounds cannot be distinguished based on molecular formula; however they have different structures: The two compounds differ in the *connectivity* of their atom.

	Ethyl Alcohol $\text{C}_2\text{H}_6\text{O}$	Dimethyl Ether $\text{C}_2\text{H}_6\text{O}$
Boiling point ($^{\circ}\text{C}$)	78.5	-24.9
Melting point ($^{\circ}\text{C}$)	-117.3	-138

Three Dimensional shape of molecules

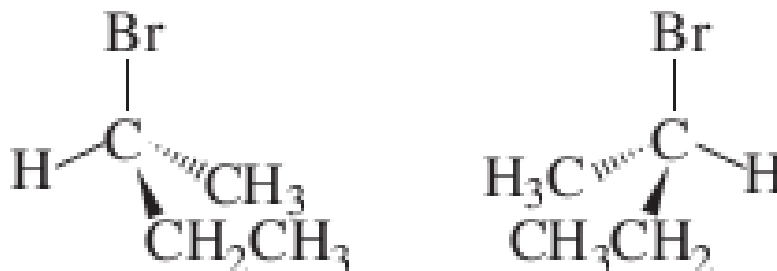
- It was proposed in 1874 by van't Hoff and le Bel that the four bonds around carbon were not all in a plane but rather in a tetrahedral arrangement *i.e.* the four C-H bonds point towards the corners of a regular tetrahedron.



- Virtually all molecules possess a 3-dimensional shape which is often not accurately represented by drawings.

In a perspective formula:

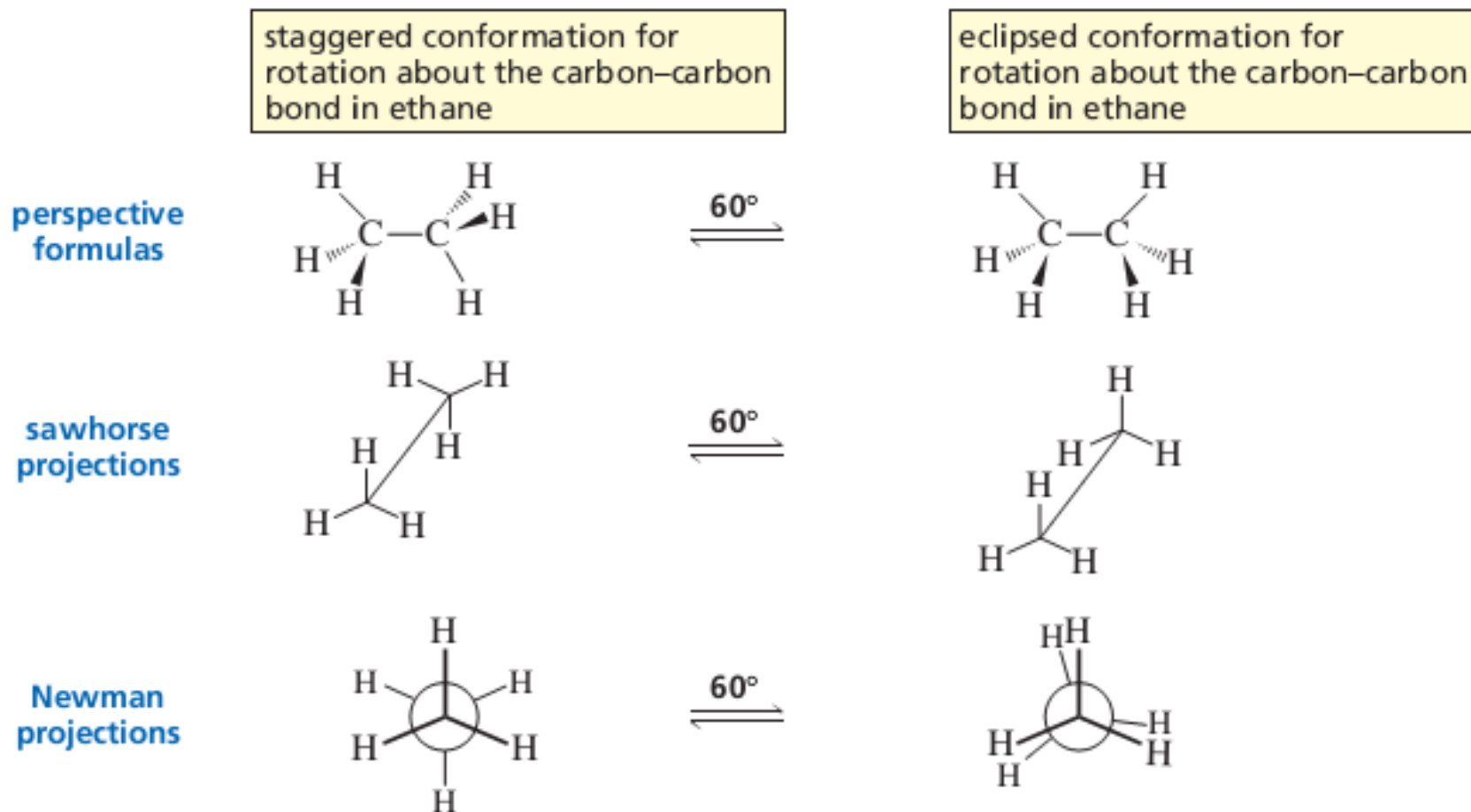
- + Solid lines (—) are used for bonds that lie in the plane of the paper
- + Solid wedges (▴) for bonds protruding out from the plane of the paper
- + Dashed wedges (▾) for bonds extending behind the paper.



perspective formulas of the enantiomers of 2-bromobutane

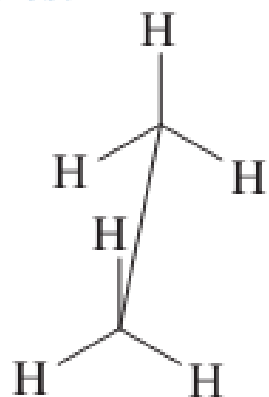
- + two of the bonds to the asymmetric carbon in the plane of the paper
- + one bond as a solid wedge protruding out of the paper
- + the fourth bond as a dashed wedge extending behind the paper.

Representation of two-carbon compounds

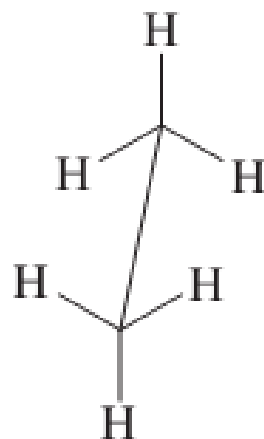


Newman projection

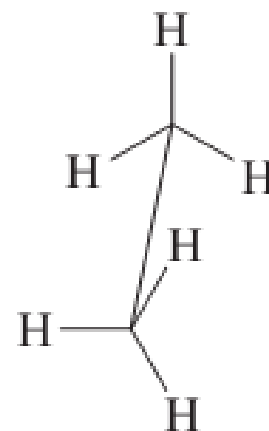
Sawhorse structures:



eclipsed, $\theta = 0^\circ$

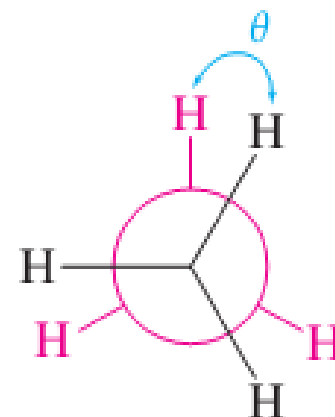
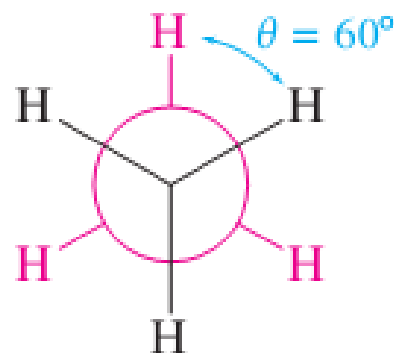
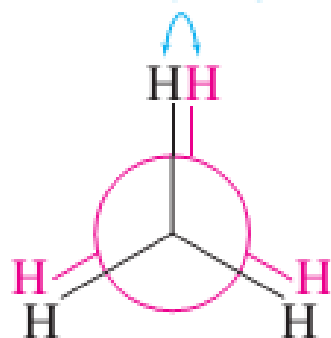


staggered, $\theta = 60^\circ$



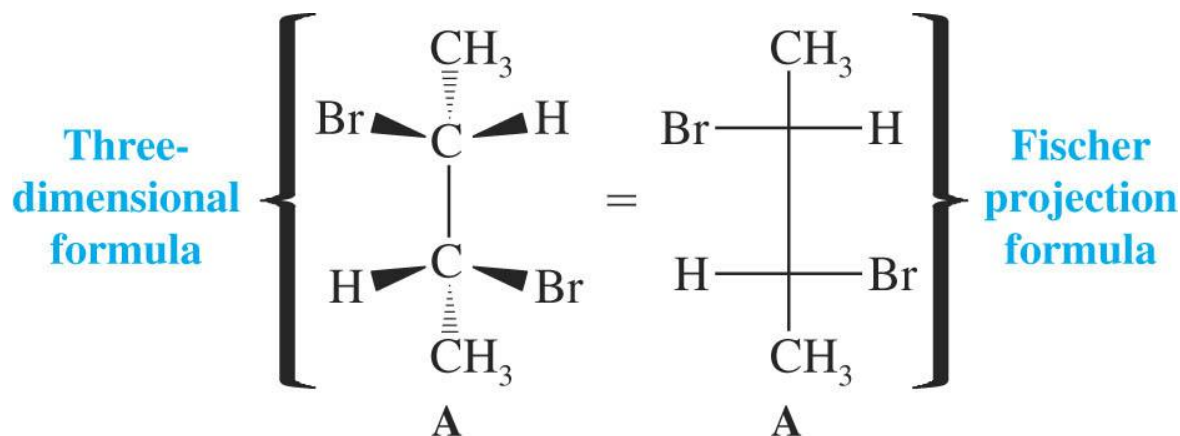
skew, $\theta = \text{anything else}$

Newman projections: $\theta = 0^\circ$



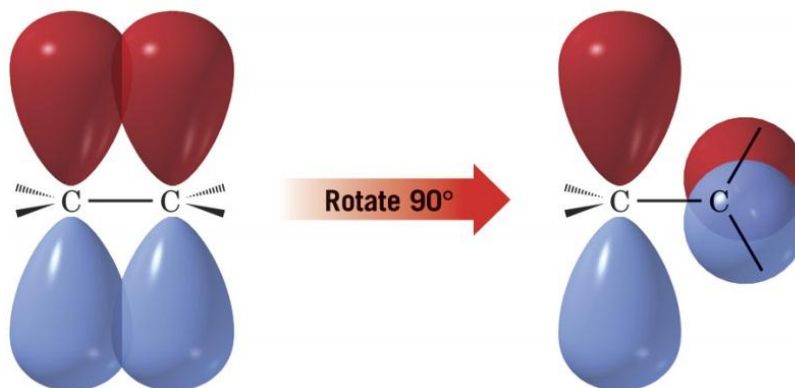
■ **Fischer Projection Formulas:** A 2-dimensional representation of chiral molecules.

- Vertical lines represent bonds that project behind the plane of the paper.
- Horizontal lines represent bonds that project out of the plane of the paper.



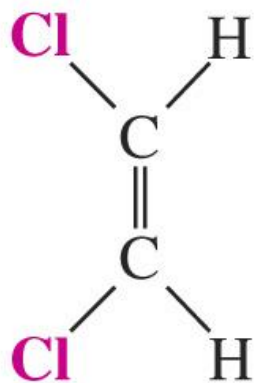
Restricted rotation about the double bond

- There is a large energy barrier to rotation (about **264** kJ/mol) around the double bond
 - ☞ This corresponds to the strength of a π bond
 - ☞ The rotational barrier of a carbon-carbon single bond is **13-26** kJ/mol
- This rotational barrier results because the p orbitals must be well aligned for maximum overlap and formation of the π bond.
- Rotation of the p orbitals 90° totally breaks the π bond.

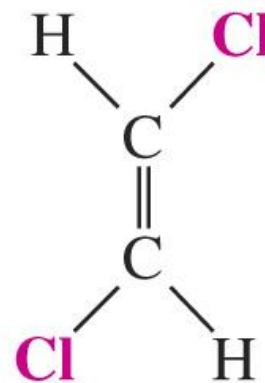


Geometrical isomers: *cis-trans* isomers

- *cis-trans* Isomers are the result of restricted rotation about double bonds.
- These isomers have the same connectivity of atoms and differ only in the arrangement of atoms in space.
- *cis* (in Greek “*on this side*”) is used to indicate groups on same side.
- *trans* (in Greek “*across*”) means groups on the opposite sides.



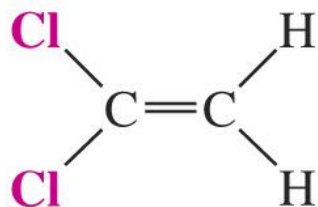
cis-1,2-Dichloroethene



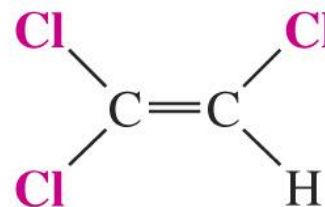
trans-1,2-Dichloroethene

- **Note:** The molecules do not superpose on each other are **diastereomers**.

- *cis-trans* isomerism is **NOT** possible if one carbon of the double bond has two identical groups.

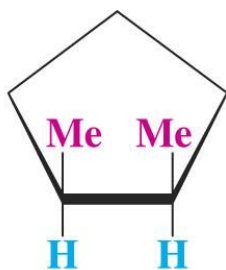


1,1-Dichloroethene
(no *cis-trans* isomerism)

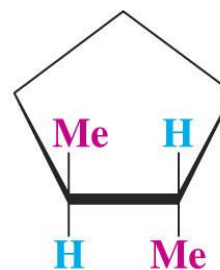


1,1,2-Trichloroethene
(no *cis-trans* isomerism)

- *cis* and *trans* cycloalkane isomers



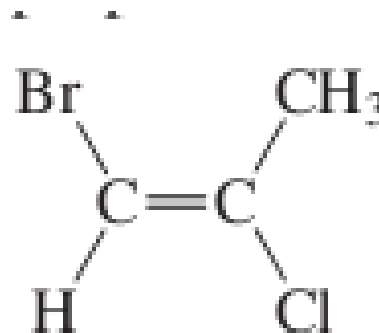
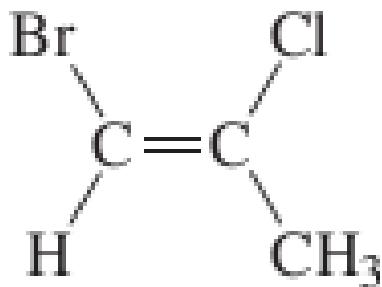
***cis*-1,2-Dimethylcyclopentane**
(C₇H₁₄)



***trans*-1,2-Dimethylcyclopentane**
(C₇H₁₄)

Limitation of the cis-trans system

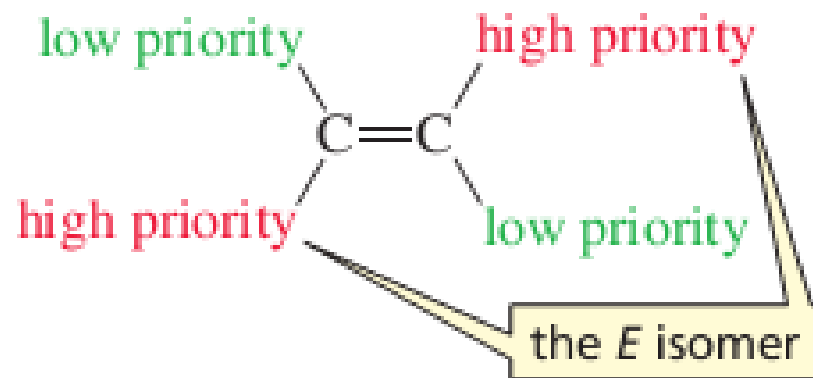
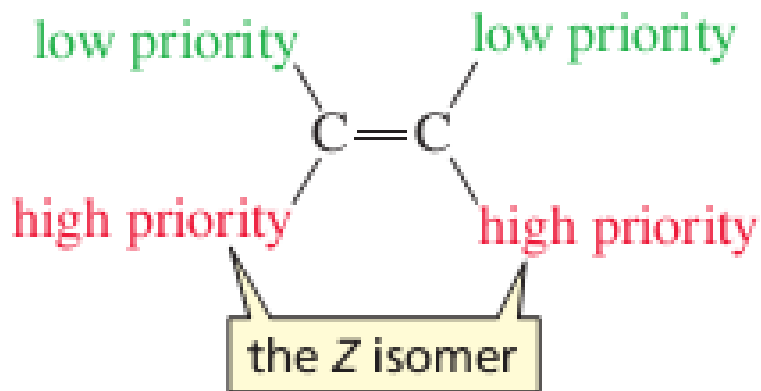
- As long as each of the carbons of an alkene is bonded to only one substituent, we can use the terms cis and trans to designate the structure of the alkene.
- But how would you designate the isomers of a compound such as 1-bromo-2-chloropropene?



Which isomer is cis and which is trans?

To name an isomer by the E,Z system

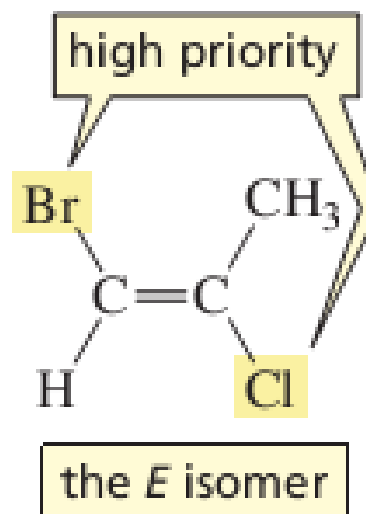
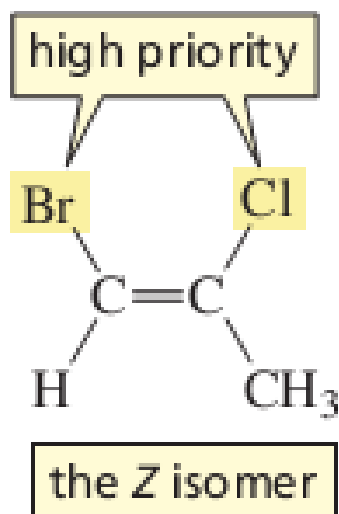
- + We first determine the relative priorities of the two groups bonded to one of the carbons and then the relative priorities of the two groups bonded to the other carbon (Cahn-Ingold-Prelog system).
- + High-priority groups *on the same side* of the double bond: the isomer has the *Z* configuration (Z is for *zusammen*, German for “together”).
- + High-priority groups *on opposite the sides* of the double bond: the isomer has the *E* configuration (E is for *entgegen*, German for “opposite”)



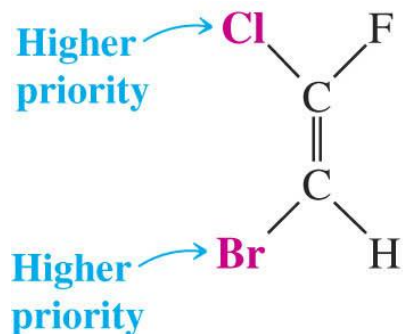
Note: IUPAC prefers the E and Z designations because they can be used for all alkene isomers. Many chemists, however, continue to use the cis and trans designations for simple molecules.

Determination of the relative priorities of the two groups bonded to an carbon

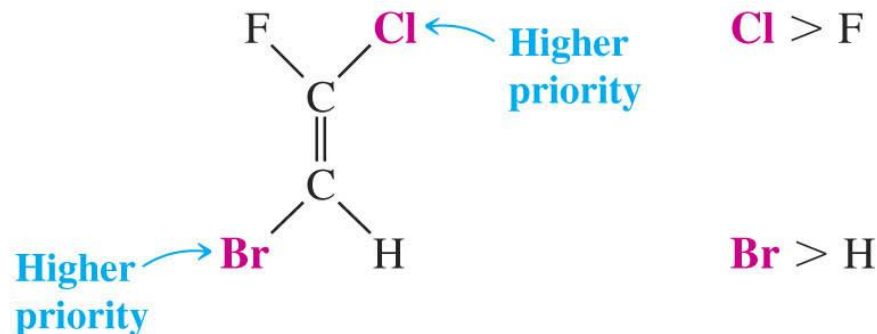
- Rule 1.** The relative priorities of the two groups depend on the atomic numbers of the atoms that are bonded directly to the carbon. The greater the atomic number, the higher is the priority.



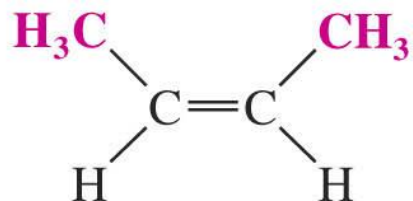
Notice that you use the atomic number of C, **NOT** the mass of the group, because the priorities are based on the atomic numbers of atoms, **NOT** on the masses of groups.



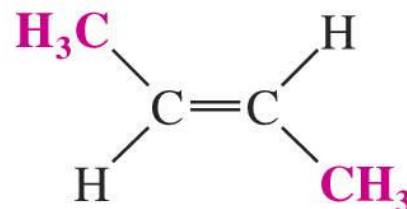
(Z)-2-Bromo-1-chloro-1-fluoroethene



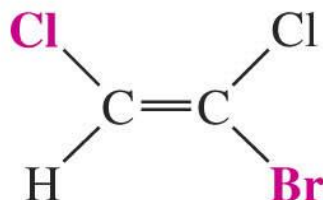
(E)-2-Bromo-1-chloro-1-fluoroethene



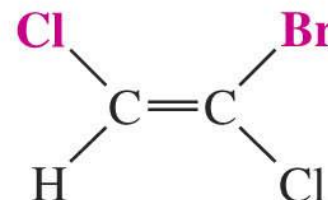
(Z)-2-Butene or (Z)-but-2-ene
(*cis*-2-butene)



(E)-2-Butene or (E)-but-2-ene
(*trans*-2-butene)



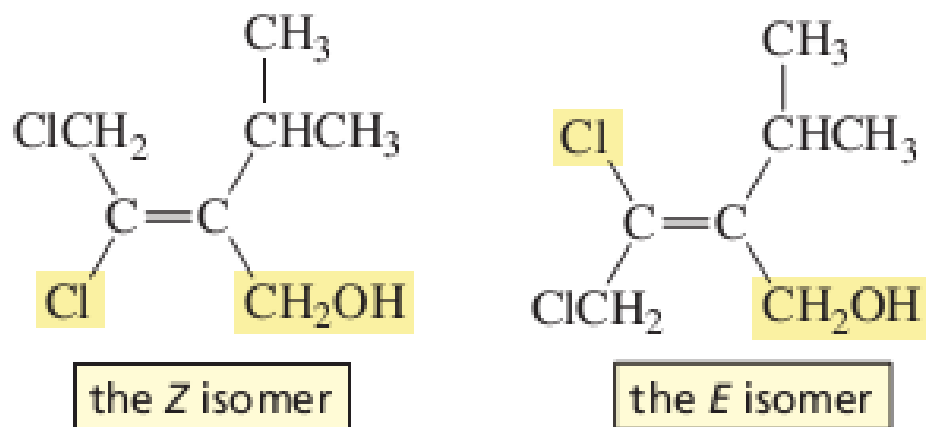
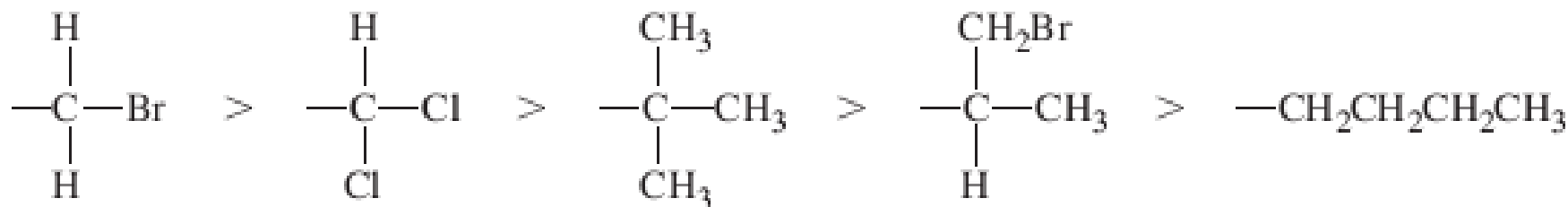
(E)-1-Bromo-1,2-dichloroethene



(Z)-1-Bromo-1,2-dichloroethene

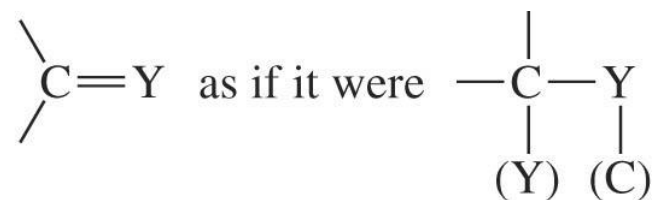
Rule 2. If the two substituents bonded to an carbon start with the same atom, you must move outward from the point of attachment and consider the atomic numbers of the atoms that are attached to the “tied” atoms. We look for the “**first point of different**”. We are not going to calculate the mass of the group.

Examples

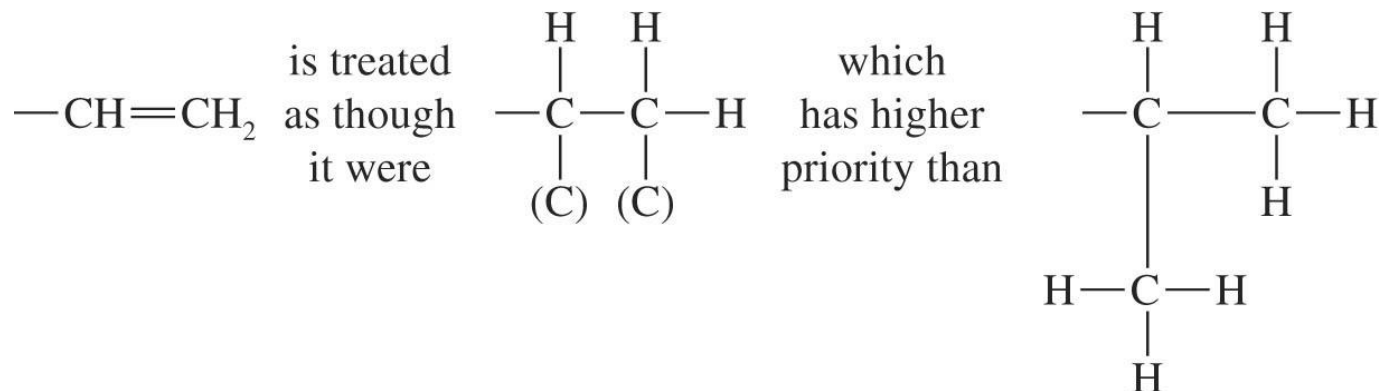
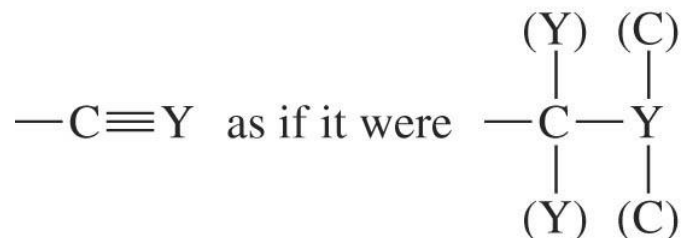


Note that you do not add the atomic numbers; you take the single atom with the greatest atomic number

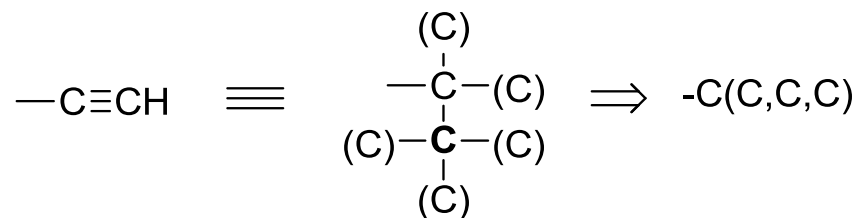
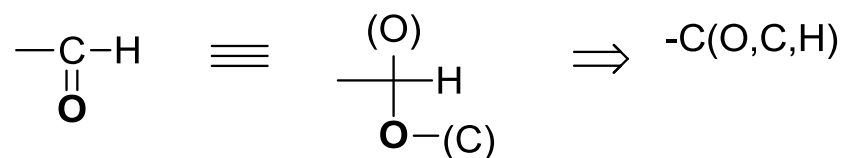
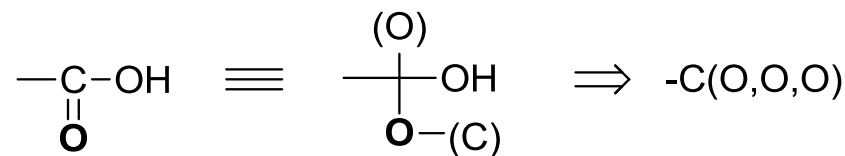
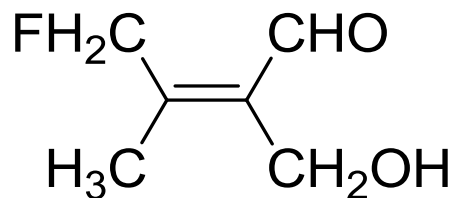
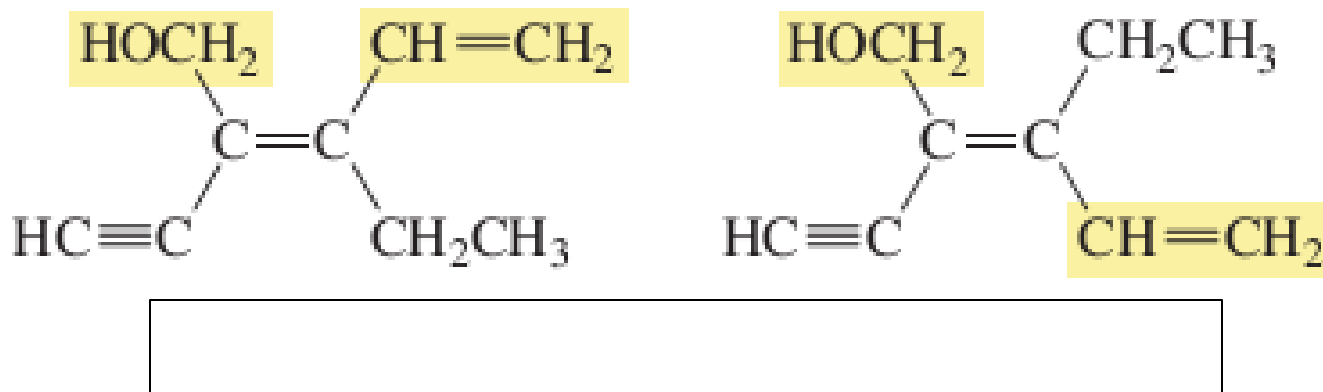
Rule 3. If an atom is doubly bonded to another atom, the priority system treats it as if it were singly bonded to two of those atoms. If an atom is triply bonded to another atom, the priority system treats it as if it were singly bonded to three of those atoms.



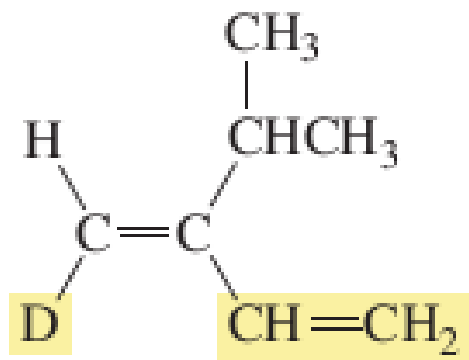
and



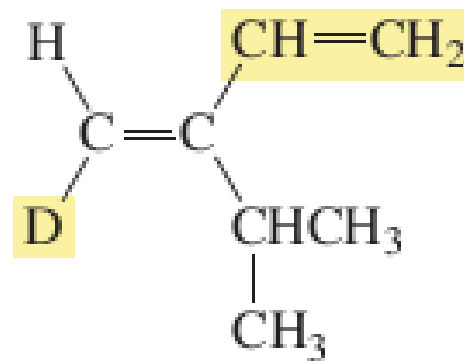
Example:



Rule 4. 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.



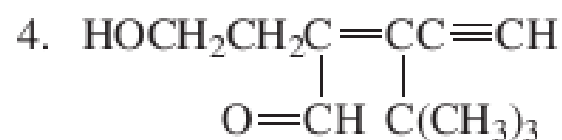
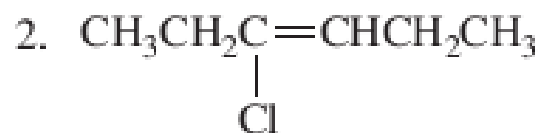
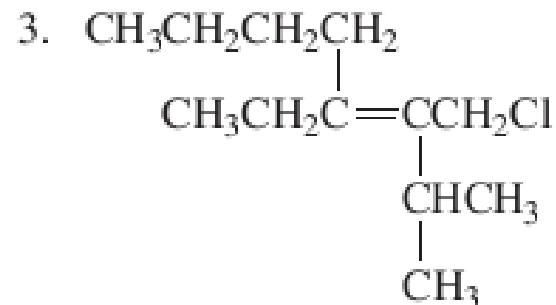
the Z isomer



the E isomer

PROBLEM 9

Draw and label the *E* and *Z* isomers for each of the following compounds:

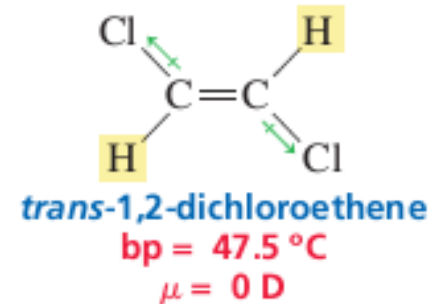
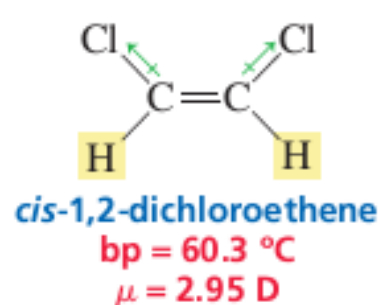
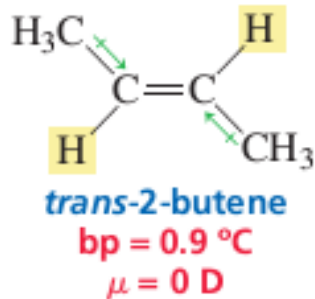
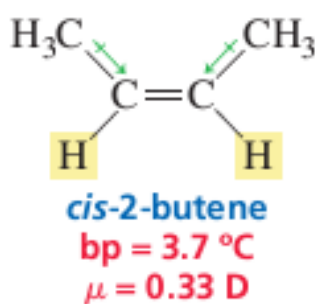


PROBLEM 10

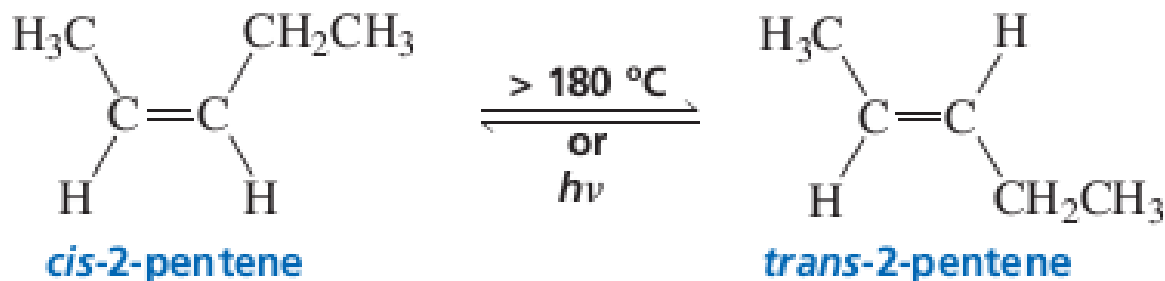
Draw the structure of (*Z*)-3-isopropyl-2-heptene.

Cis and trans isomers have different properties

- Because of the energy barrier to rotation about a double bond, cis and trans isomers cannot interconvert (except under conditions extreme enough to overcome the barrier and break the bond). This means that they can be separated from each other. In other words, the two isomers are different compounds with different physical properties.

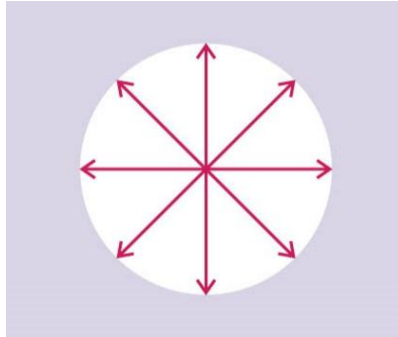


- Cis and trans isomers can be interconverted (in the absence of any added reagents) only when the molecule absorbs sufficient heat or light energy to cause the π bond to break

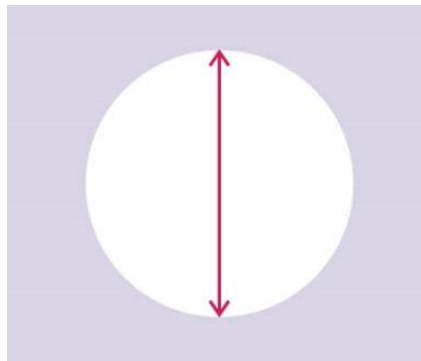


Plane polarized light

- The electric field of ordinary light oscillates/vibrating randomly in all possible planes perpendicular to the direction of propagation. It is unpolarized light.

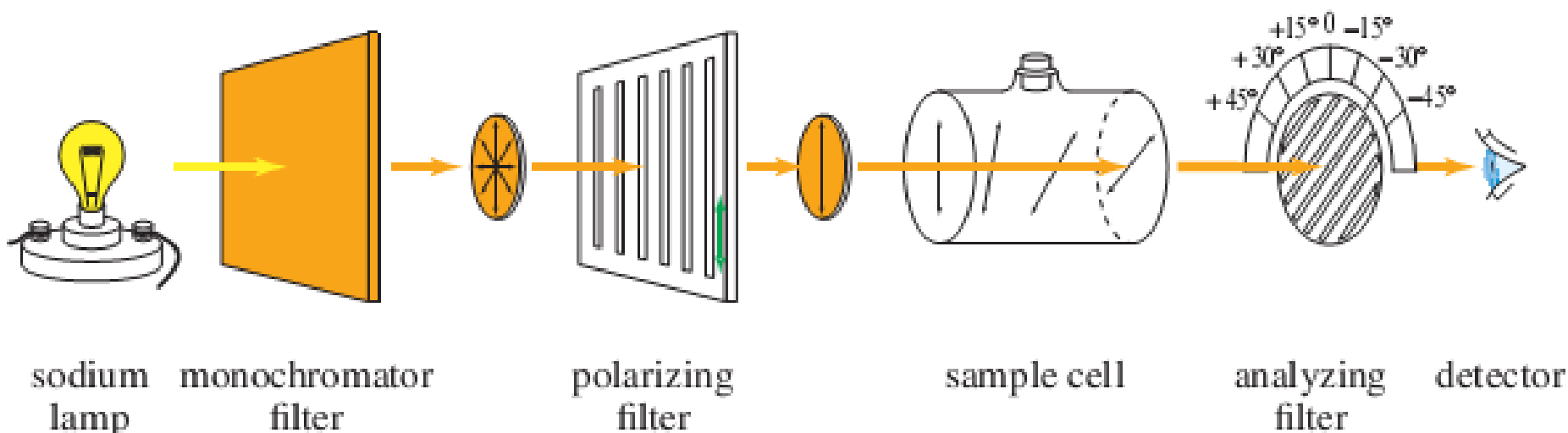


- When unpolarized light passes through a polarizing filter, the randomly vibrating light waves are filtered so that most of the light passing through is vibrating in one direction. It is then called “**plane polarized light**”.



- Plane-polarized light is composed of waves that vibrate in only one plane.

The polarimeter



- Schematic diagram of a polarimeter. The light originates at a source (usually a sodium lamp) and passes through a polarizing filter and the sample cell. An optically active solution rotates the plane of polarized light. The analyzing filter is another polarizing filter equipped with a protractor. It is turned until a maximum amount of light is observed, and the rotation is read from the protractor.

Dextrorotatory (clockwise) rotations are (+) or (*d*).
Levorotatory (counterclockwise) rotations are (−) or (*l*).

Optical activity

- Rotation of the plane of polarized light is called **optical activity**, and substances that rotate the plane of polarized light are said to be **optically active**.
- When polarized light passes through a solution containing a **chiral** compound, the chiral compound causes the plane of vibration to rotate.
 - Compounds that rotate the plane of polarized light toward the right (clockwise) are called *dextrorotatory*, from the Greek word *dexios*, meaning “*toward the right*”.
 - Compounds that rotate the plane toward the left (counterclockwise) are called *levorotatory*, from the Latin word *laevus*, meaning “*toward the left*”.

Dextrorotatory (clockwise) rotations are (+) or (*d*).

Levorotatory (counterclockwise) rotations are (−) or (*l*).

Specific rotation

- An optically active substance (*e.g.* one pure enantiomer) will rotate the plane-polarized light. The amount the analyzer needs to be turned to permit light through is called the observed rotation α . If the analyzer is rotated clockwise, the rotation is (+) and the molecule is *dextrorotatory*. If the analyzer is rotated *counterclockwise* the rotation is (-) and the molecule is *levorotatory*.
- The **standard value specific rotation** $[\alpha]$ (or **specific rotation**) can be calculated as in the following equation:

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

where

$\alpha(\text{observed})$ = rotation observed in the polarimeter

c = concentration in grams per mL

l = length of sample cell (path length) in decimeters (dm)

PROBLEM 5-8

A solution of 2.0 g of (+)-glyceraldehyde, $\text{HOCH}_2\text{—CHOH—CHO}$, in 10.0 mL of water was placed in a 100-mm cell. Using the sodium D line, a rotation of $+1.74^\circ$ was found at 25°C . Determine the specific rotation of (+)-glyceraldehyde.

PROBLEM 5-9

A solution of 0.50 g of (–)-epinephrine (see Figure 5-15) dissolved in 10.0 mL of dilute aqueous HCl was placed in a 20-cm polarimeter tube. Using the sodium D line, the rotation was found to be -5.1° at 25°C . Determine the specific rotation of epinephrine.

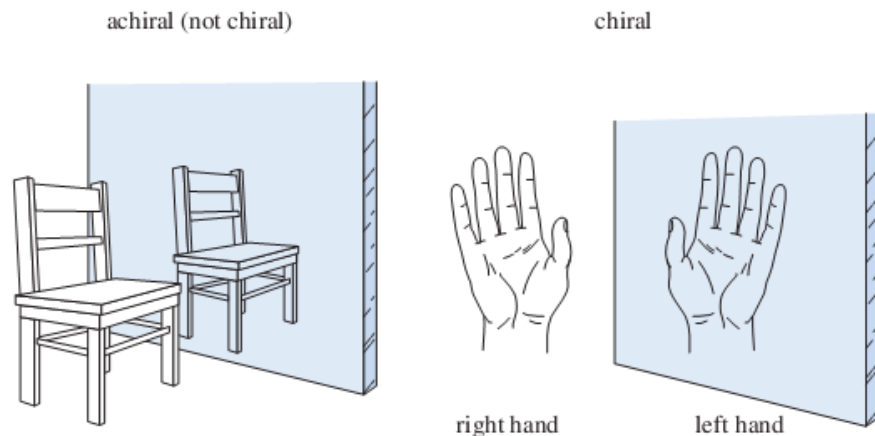
PROBLEM 5-10

A chiral sample gives a rotation that is close to 180° . How can one tell whether this rotation is $+180^\circ$ or -180° ?

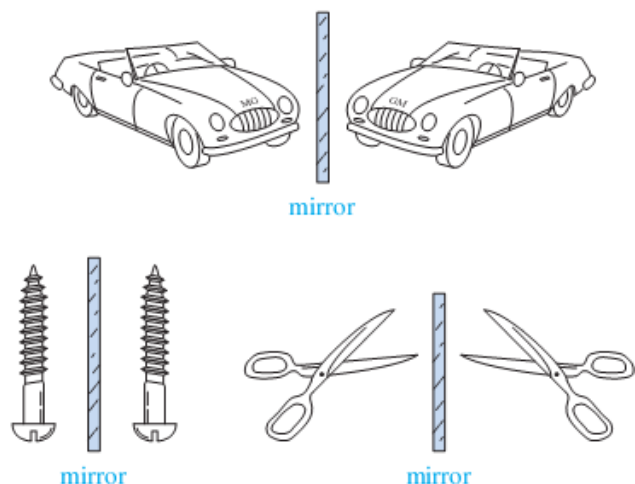
Chiral molecules

- + Chiral molecule: **not superposable (nonsuperimposable, nonidentical)** on its mirror image, can exist as a pair of enantiomers.
- + Pair of enantiomers: a chiral molecule and its mirror image.
- + *Nonsuperimposable* mirror-image molecules are called **enantiomers**.

Examples of chiral and achiral objects

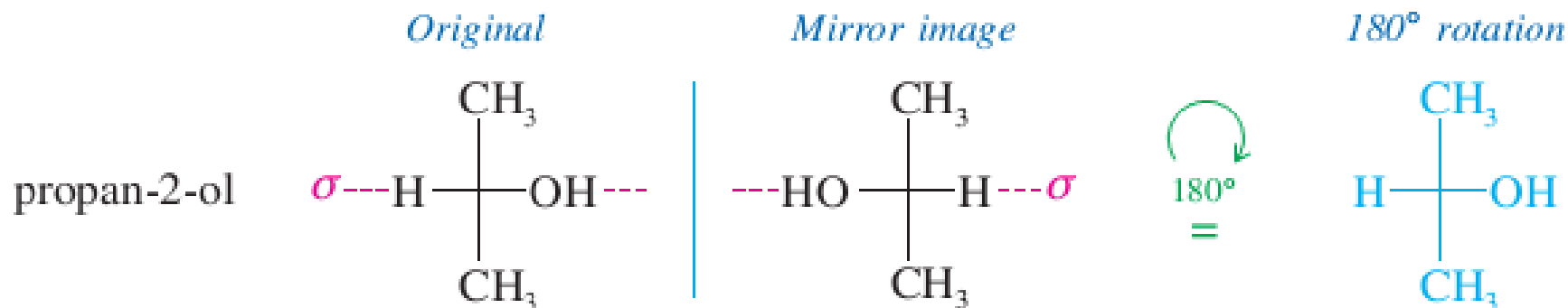


What is the difference between your **left hand** and your **right hand**? They look similar, yet a left-handed glove does not fit the right hand. The same principle applies to your feet. They look almost identical, yet the left shoe fits painfully on the right foot. The relationship between your two hands or your two feet is that they are **non-superimposable (non-identical)** mirror images of each other. Objects that have left-handed and right-handed forms are called **chiral**

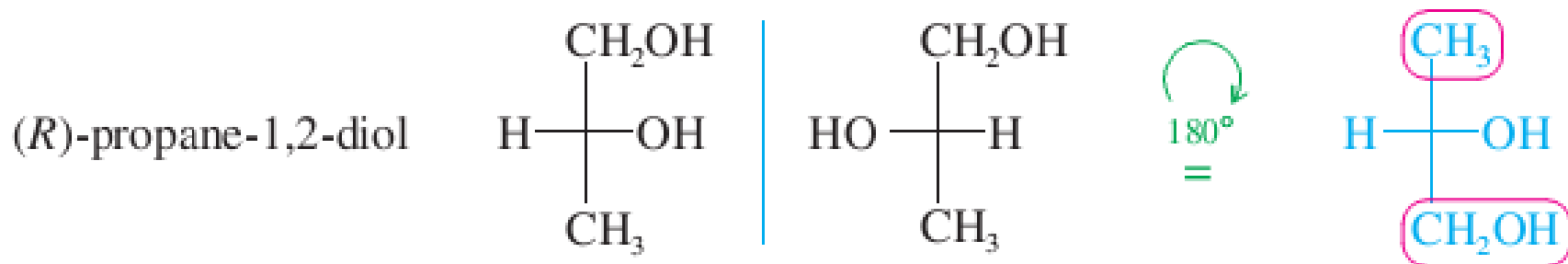


The **English car** has the steering wheel on the right-hand side, while the American car has it on the left. To a first approximation, the English and American cars are non superimposable mirror images. Most **screws** have right-hand threads and are turned clockwise to tighten. The mirror image of a right-handed screw is a left-handed screw, turned counterclockwise to tighten. Those of us who are left-handed realize that scissors are chiral. Most **scissors** are right-handed. If you use them in your left hand, they cut poorly.

How to decide if a molecule is chiral or achiral?



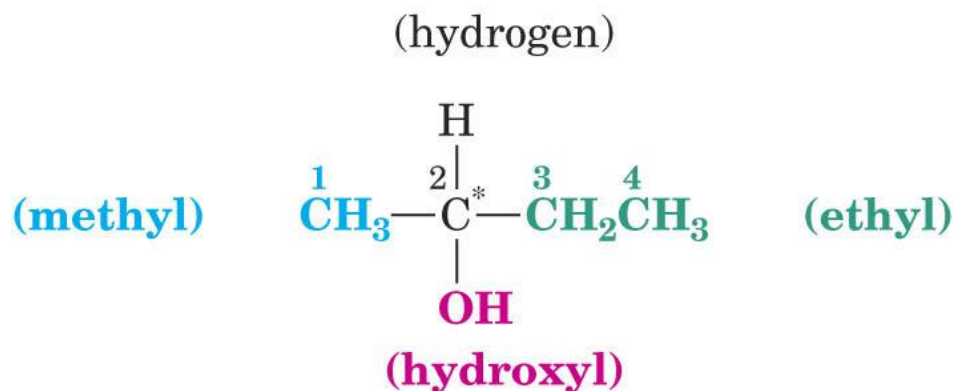
These mirror images are the same. Propan-2-ol is achiral.



Chiral molecule and stereogenic center

Chiral molecule

- The most common feature (*but not the only one*) that lends chirality is a carbon atom that is bonded to four different groups. Such a carbon atom is called an **asymmetric** carbon atom or a **chiral** carbon atom, and is often designated by an asterisk *).



- A molecule with a single **chiral** carbon atom will always be chiral.
- A molecule with more than one **chiral** carbon atoms is **NOT** always chiral.
- Switching two groups at the **chiral** carbon atom reverses its configuration.

Stereogenic center

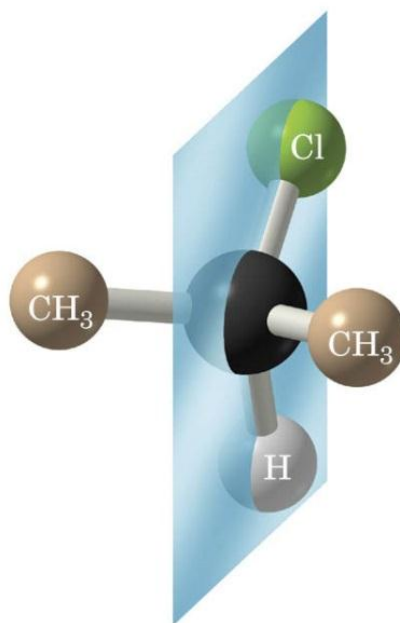
- An atom bearing groups of such nature that an interchange of any two groups will produce a stereoisomer.

Tests for chirality: Planes and centers of symmetry

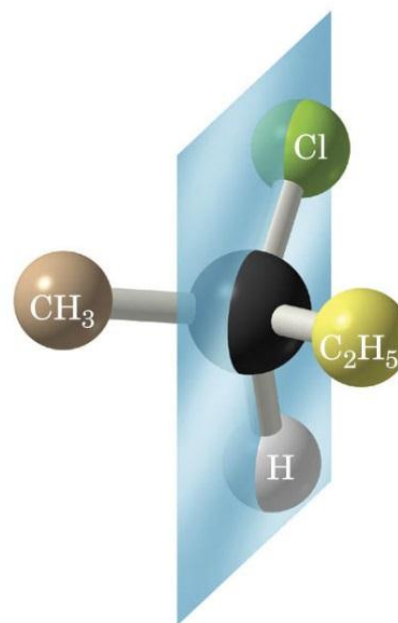
Plane of symmetry

- An imaginary plane that bisects a molecule in such a way that the two halves of the molecule are mirror images of each other
- A molecule with **a plane of symmetry cannot be chiral.**

Example: 2-Chloropropane (a) has a plane of symmetry but 2-chlorobutane (b) does not



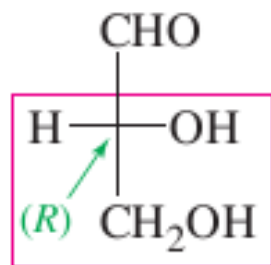
(a)



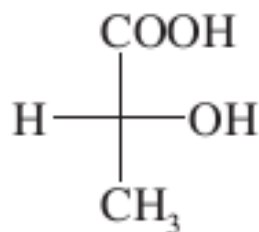
(b)

Nomenclature of optical active compounds: **The D,L system and its limitation**

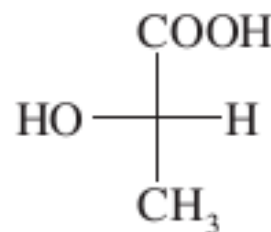
- (+)-Glyceraldehyde with –OH group on the right site was considered to have D configuration (D is for “Dextro” - rotates the plane to the right).
- (-)-Glyceraldehyde with –OH group on the left site was considered to have L configuration (L is for “Levulo” - rotates the plane to the left).



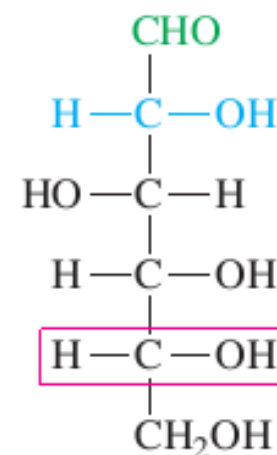
D-(+)-glyceraldehyde



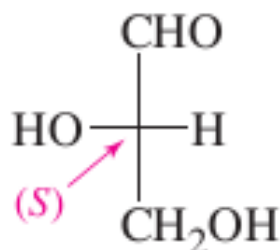
(R)-lactic acid



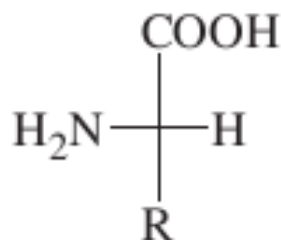
(S)-lactic acid



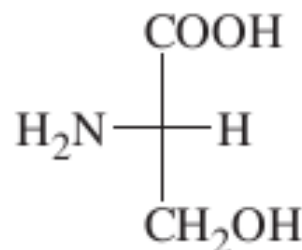
D-(+)-glucose



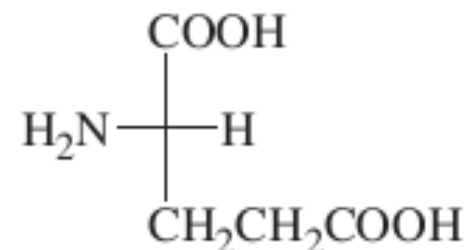
L-(-)-glyceraldehyde



an L-amino acid



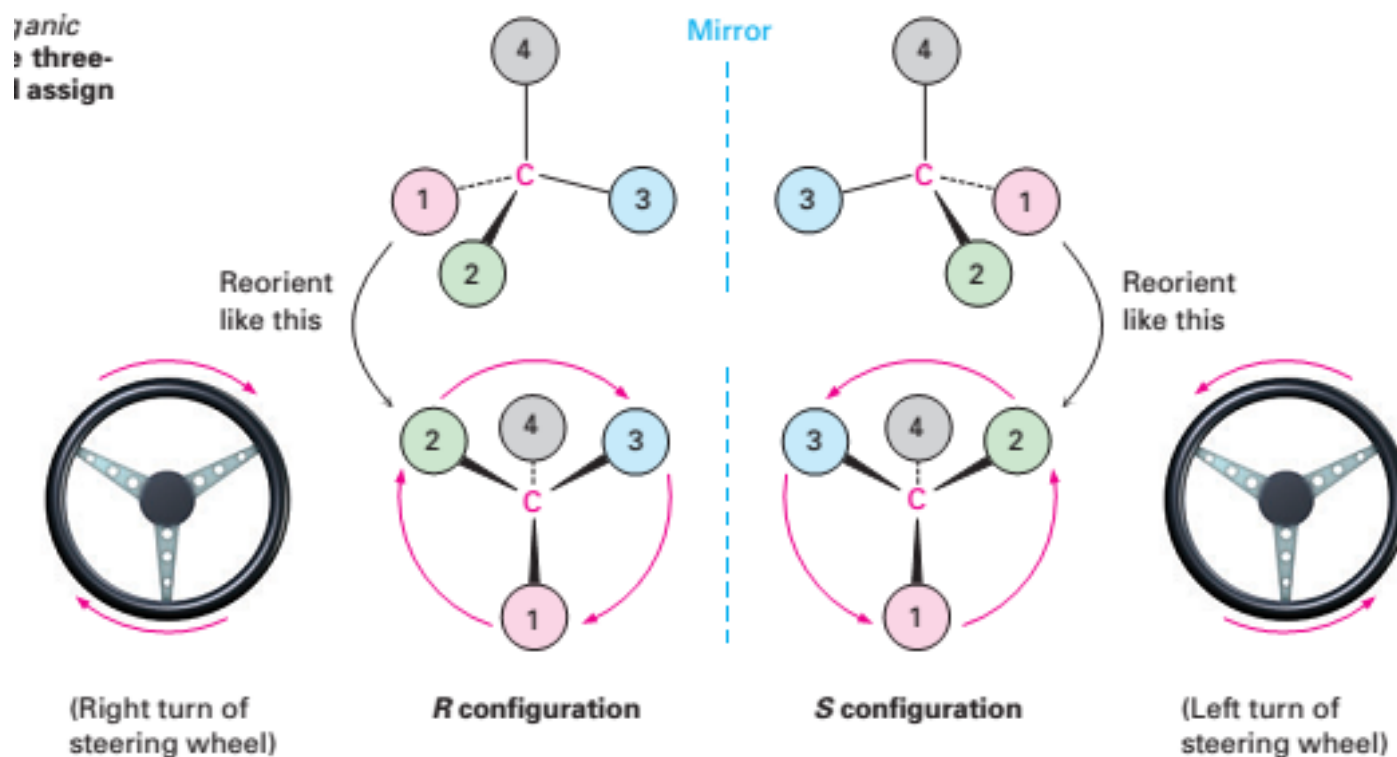
L-(-)-serine



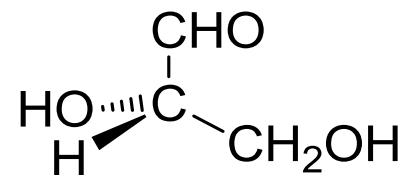
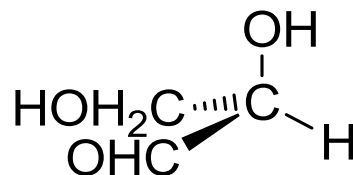
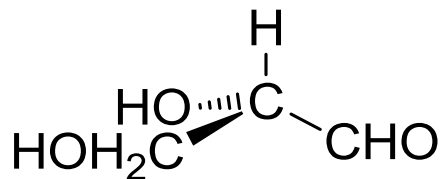
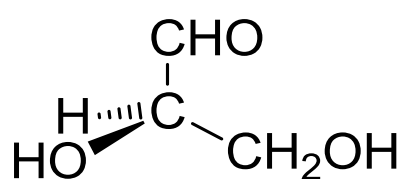
L-(+)-glutamic acid

Nomenclature of optical active compounds: The *R,S* System

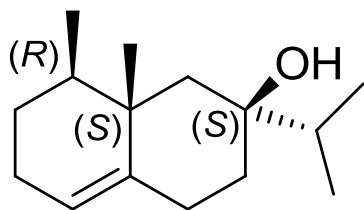
- Also called the Cahn-Ingold-Prelog (CIP) system.
- The four groups attached to the stereogenic carbon are assigned priorities from highest (1) to lowest (4)
- The molecule is rotated to put the lowest priority group (4) back.
- + If the groups descend in priority (1,2 then 3) in **clockwise** direction the enantiomer is *R*.
- + If the groups descend in priority in **counterclockwise** direction the enantiomer is *S*.



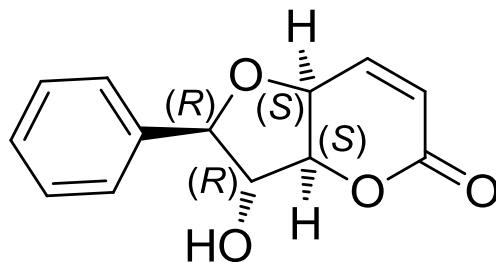
Exercise 1:



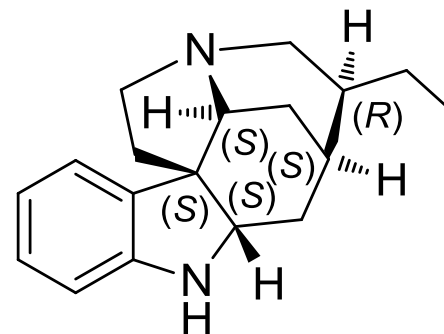
Exercise 2:



(+)-Valencenol



Altholacton



Tubifolidine

Relative and absolute configuration

- **Relative** configuration: the relationship between comparable stereogenic centers in two different molecules. **D** and **L** are **relative** configurations.

- ➔ D-Glucose and L-glucose have the same relative configuration.

- **Absolute** configuration: the actual 3-dimensional orientation of the atoms in a chiral molecule. **R** and **S** are **absolute** configurations.

- ➔ Can be determined by X-ray crystallography.

Related concepts

enantiomers: mirror-image isomers; pairs of compounds that are nonsuper-imposable mirror images

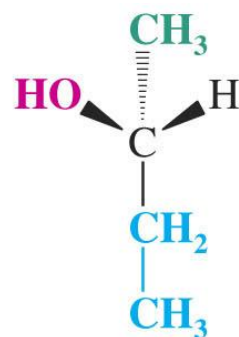
chiral: (“handed”) different from its mirror image; having an enantiomer

achiral: (“not handed”) identical with its mirror image; not chiral

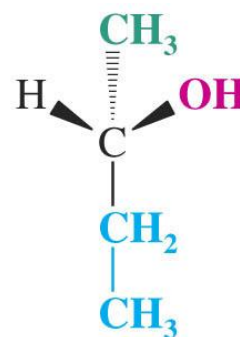
Properties of enantiomers

Enantiomeric compounds rotate the plane of polarized light by exactly the same amount but in opposite directions.

- Example: The specific rotation of the two pure enantiomers of 2-butanol are equal but opposite.



(*R*)-2-Butanol
 $[\alpha]_D^{25} = -13.52^\circ$



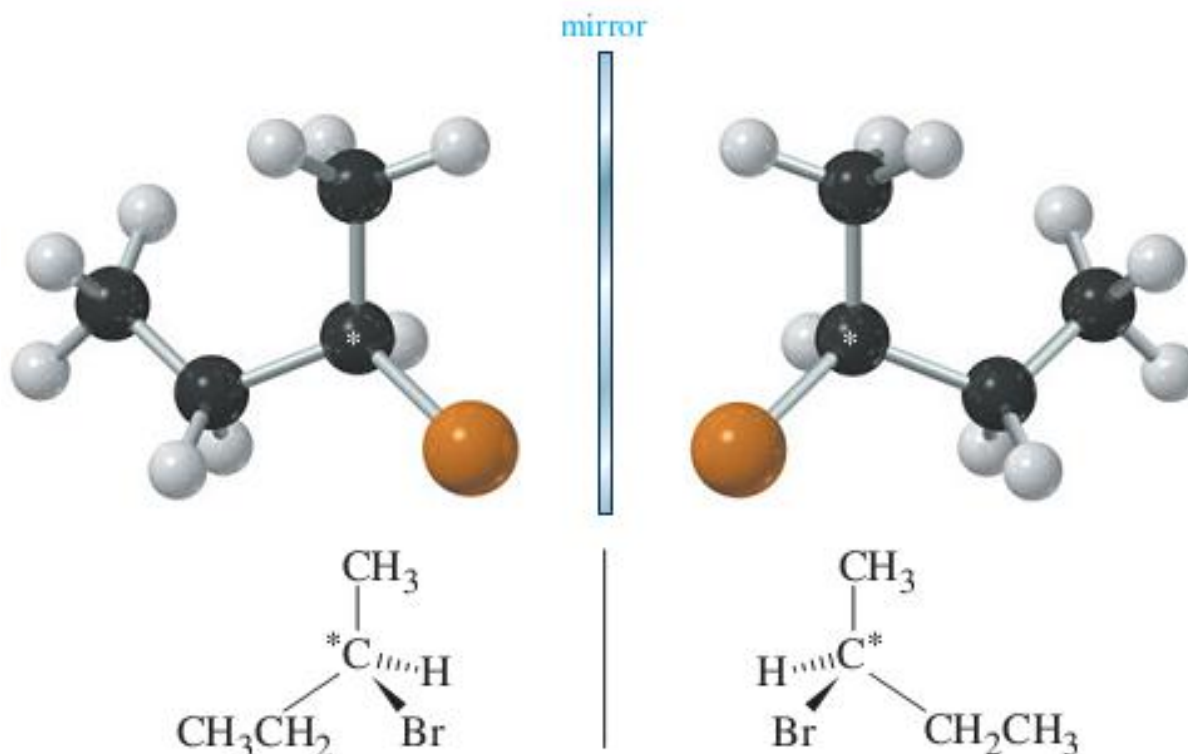
(*S*)-2-Butanol
 $[\alpha]_D^{25} = +13.52^\circ$

Mirror-image molecules have nearly identical physical properties. Compare the following properties of (*R*)-2-bromobutane and (*S*)-2-bromobutane.

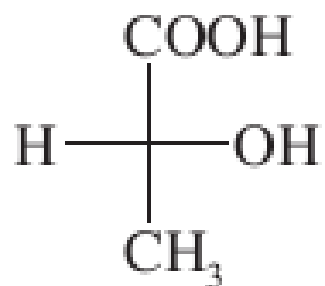
	(<i>R</i>)-2-Bromobutane	(<i>S</i>)-2-Bromobutane
boiling point (° C)	91.2	91.2
melting point (° C)	-112	-112
refractive index	1.436	1.436
density	1.253	1.253

Related concepts

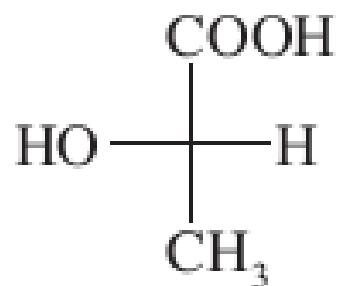
- To draw the mirror image of a molecule, simply draw the same structure with left and right reversed. The up-and-down and front-and-back directions are unchanged



Fischer projection formulas of enantiomers



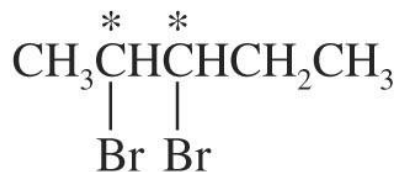
(R)-lactic acid



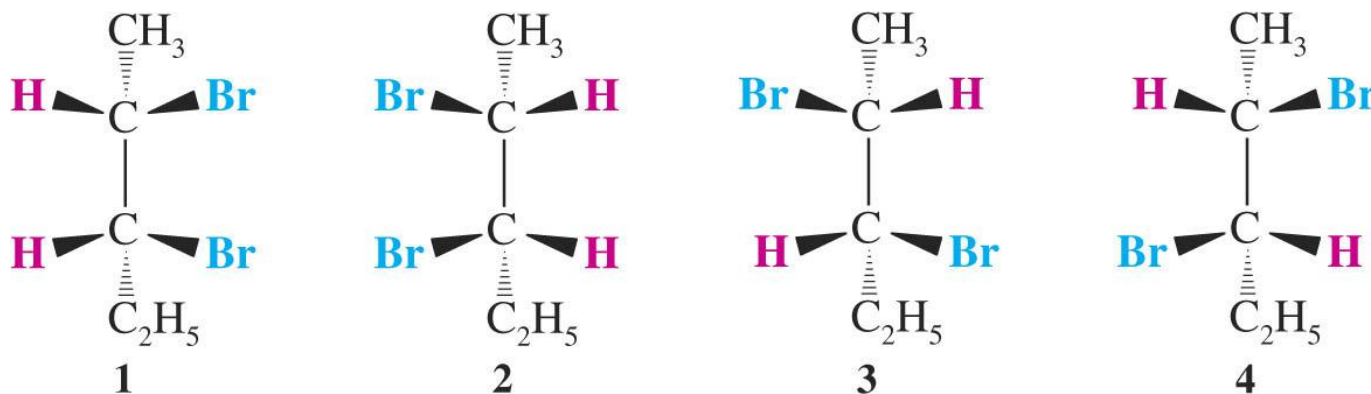
(S)-lactic acid

Molecules with more than one stereogenic center

- The maximum number of stereoisomers available will not exceed 2^n , where n is equal to the number of tetrahedral stereogenic centers (chiral carbons).



2,3-Dibromopentane

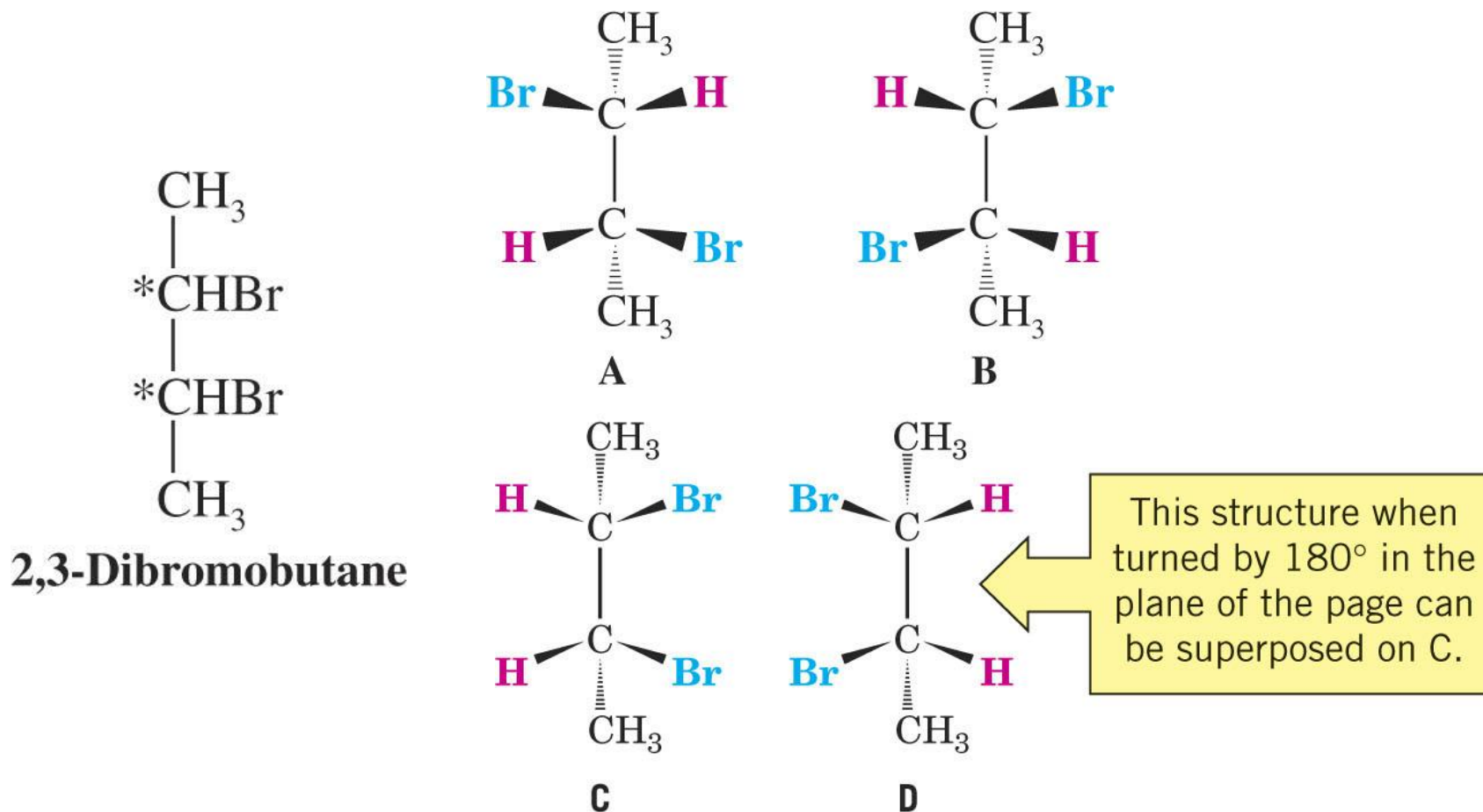


+ There are two pairs of **enantiomers**: (1, 2) and (3,4).

+ **Diastereomers**: stereoisomers which are not mirror images of each other. For instance 1 and 3 or 1 and 4. They have different physical properties and can be separated.

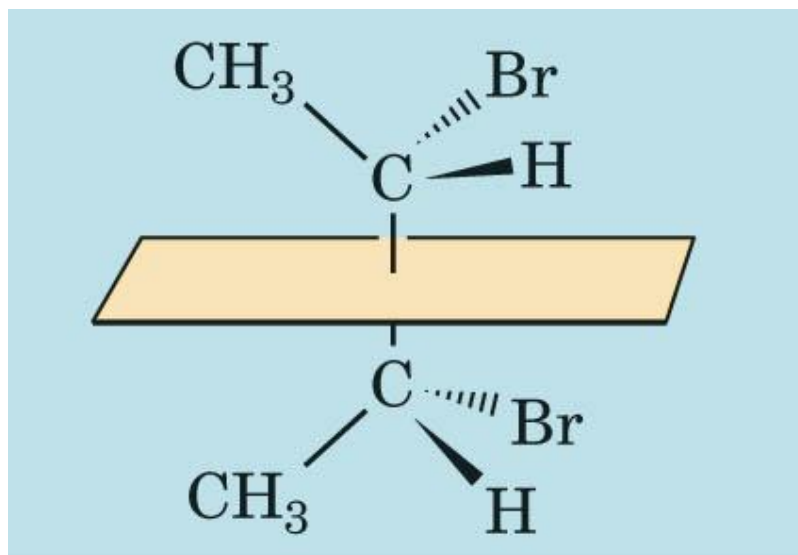
meso Compounds

- Sometimes molecules with two or more stereogenic centers will have less than the maximum amount of stereoisomers



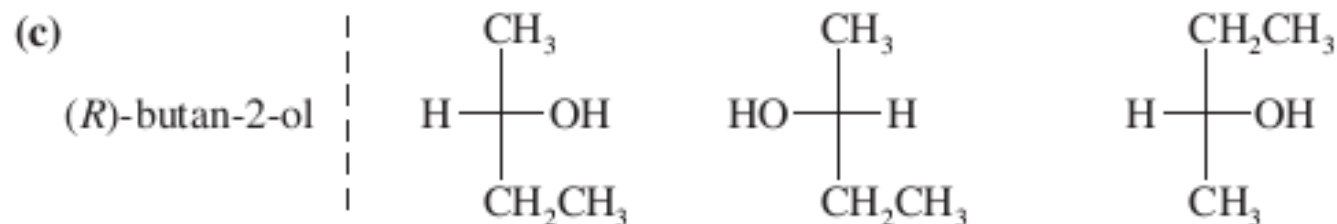
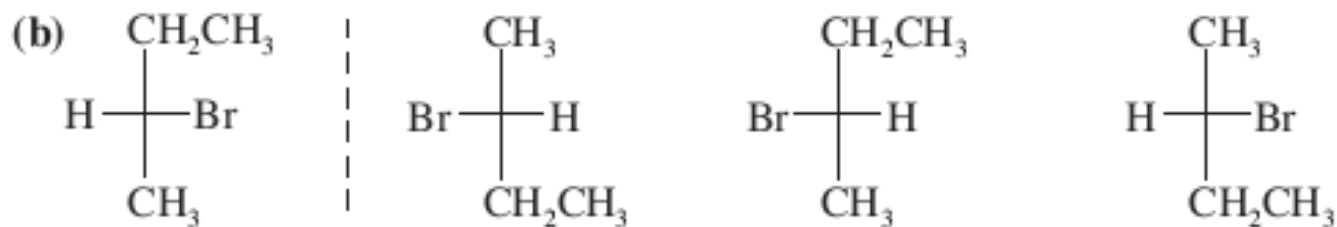
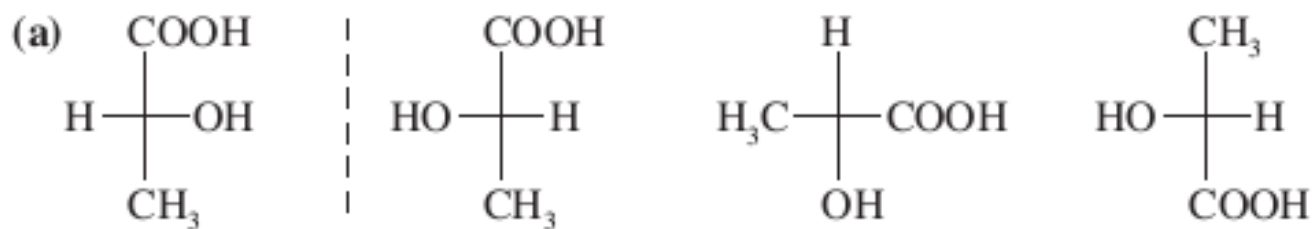
meso Compounds

- *meso* Compounds: achiral despite the presence of stereogenic centers.
 - + Not optically active
 - + Superposable on its mirror image
 - + Has a plane of symmetry



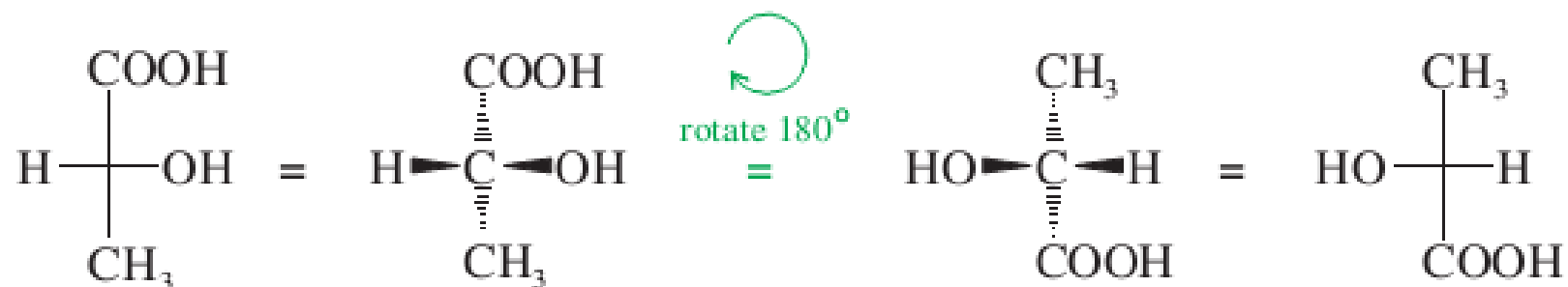
PROBLEM 5-16

For each set of examples, make a model of the first structure, and indicate the relationship of each of the other structures to the first structure. Examples of relationships: same compound, enantiomer, structural isomer.

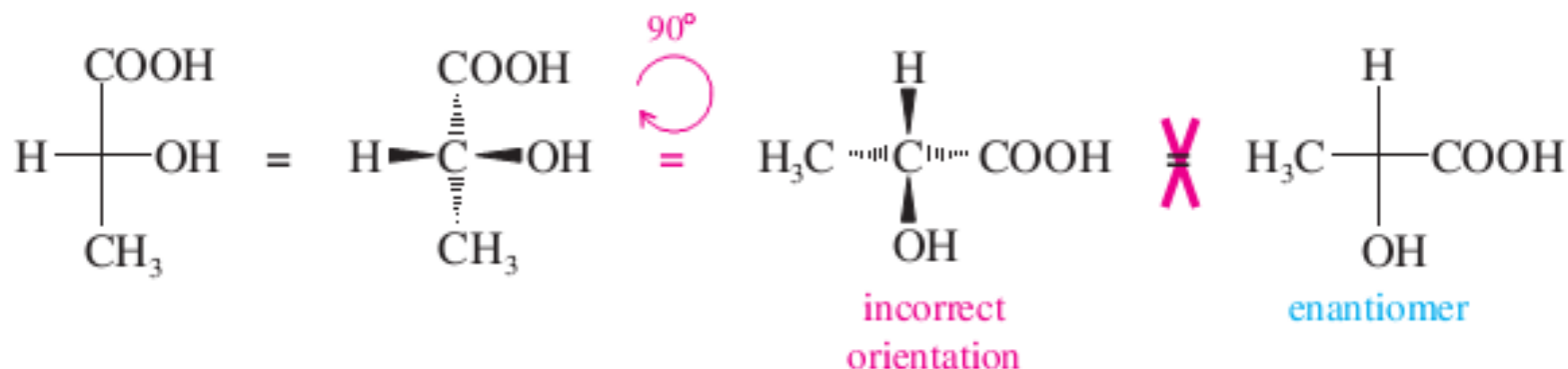


Can Fischer projection formula rotated randomly?

Rotation by 180° is allowed.



A 90° rotation is NOT allowed.



3.47 Draw the most stable conformation of pentane, using wedges and dashes to represent bonds coming out of the paper and going behind the paper, respectively.

3.51 ■ Increased substitution around a bond leads to increased strain. Take the four substituted butanes listed below, for example. For each compound, sight along the C2–C3 bond and draw Newman projections of the most stable and least stable conformations. Use the data in Table 3.5 to assign strain energy values to each conformation. Which of the eight conformations is most strained? Which is least strained?

- | | |
|------------------------|---------------------------|
| (a) 2-Methylbutane | (b) 2,2-Dimethylbutane |
| (c) 2,3-Dimethylbutane | (d) 2,2,3-Trimethylbutane |

4.26 ■ Draw two constitutional isomers of *cis*-1,2-dibromocyclopentane.

4.27 ■ Draw a stereoisomer of *trans*-1,3-dimethylcyclobutane.

- 6.27** ■ Ocimene is a triene found in the essential oils of many plants. What is its IUPAC name, including stereochemistry?



Ocimene

- 6.28** α -Farnesene is a constituent of the natural wax found on apples. What is its IUPAC name, including stereochemistry?



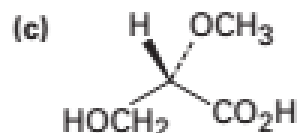
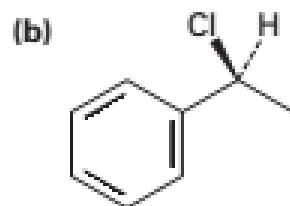
α -Farnesene

- 6.29** ■ Draw structures corresponding to the following systematic names:

- (a) (4*E*)-2,4-Dimethyl-1,4-hexadiene
- (b) *cis*-3,3-Dimethyl-4-propyl-1,5-octadiene
- (c) 4-Methyl-1,2-pentadiene
- (d) (3*E*,5*Z*)-2,6-Dimethyl-1,3,5,7-octatetraene
- (e) 3-Butyl-2-heptene
- (f) *trans*-2,2,5,5-Tetramethyl-3-hexene

-
- 9.39** What is the relationship between the specific rotations of (2*R*,3*R*)-dichloropentane and (2*S*,3*S*)-dichloropentane? Between (2*R*,3*S*)-dichloropentane and (2*R*,3*R*)-dichloropentane?
- 9.40** What is the stereochemical configuration of the enantiomer of (2*S*,4*R*)-2,4-octanediol?
- 9.41** What are the stereochemical configurations of the two diastereomers of (2*S*,4*R*)-2,4-octanediol?

9.44 ■ Assign *R* or *S* configurations to the chirality centers in the following molecules:



9.47 ■ Draw tetrahedral representations of the following molecules:

(a) (*S*)-2-Chlorobutane (b) (*R*)-3-Chloro-1-pentene

9.48 Draw tetrahedral representations of the two enantiomers of the amino acid cysteine, $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, and identify each as *R* or *S*.

9.52 ■ Draw tetrahedral representations of the following molecules:

(a) The $2S,3R$ enantiomer of 2,3-dibromopentane

(b) The meso form of 3,5-heptanediol

9.55 Assign R or S stereochemistry to the chirality centers in the following Newman projections:

