

Faculty of Science

**Unit 5:
Stereochemistry**

CHEM 1503
Chemical Bonding and
Organic Chemistry

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Overview

In this unit, you will continue your study of organic chemistry with the family of compounds known as the *alkanes*. As you work through the material, remember that most of the concepts you will learn apply to other organic compounds. Virtually all of these compounds have carbon-carbon single bonds and carbon-hydrogen bonds; they also have tetrahedral carbon atoms, rotate freely around the carbon-carbon single bond, and exist in numerous isomeric forms. In studying the alkanes, you will meet other families of organic compounds, such as alcohols, alkyl halides, and alkenes. These can be considered as derivatives of alkanes, with an —OH group, a halide group, or a —C=C— group *substituted for one or more hydrogen atoms*.

You will cover several important aspects of alkane chemistry in this unit. One is the systematic drawing and naming of all the possible constitutional isomers of a compound. Structure and nomenclature are related topics. If you are unsure whether two structures are the same or different, you need only apply the rules of nomenclature to each. If they have the same name, you know they are the same compound.

Alkane molecules can twist and turn around single bonds, resulting in different **conformations**, or arrangements of the atoms in space. You will learn why some conformations are more stable than others, especially among the **cycloalkanes** (alkane chains with ends that join to form rings).

The phenomenon called **chirality**, or handedness, occurs commonly in nature. Your right hand is a mirror image of your left (ignore for a moment the ring you might be wearing on one hand, or the fact that one may be larger than the other!), and the hair on your head may grow in distinctive whorls. The shells of many snails and other molluscs show a right-hand spiral or a left-hand spiral, and vines can twine in one direction or the other.

Chirality occurs at the molecular level, too. The structure of some compounds makes it possible for them to have isomers that are mirror images of each other. Pairs of such isomers are known as **enantiomers**; each mirror image cannot be superimposed over the other. In nature, usually only one enantiomer is produced. In the laboratory, however, chemists have found it near impossible to produce just one member of a pair by completely synthetic means. Later in this unit, we shall see in cholesterol an example of nature's superiority as an organic chemist. Because this molecule has eight chiral centres, it can theoretically have 256 *different* isomers. Although nature produces just one, a chemist would produce a mixture of all 256.

Mixtures of enantiomers can be difficult to separate. Louis Pasteur, the famous French chemist and bacteriologist, was the first to accomplish this feat and the first to realize that handedness could be found in molecules. He observed that salts of tartaric acid derived from wine formed two distinct kinds of crystals that were non-superimposable mirror images of each other, as you can see in Figure 5.1 in this unit. Painstakingly, he examined each crystal under a microscope and with a pair of tweezers separated the crystals into two groups of enantiomers. Very few enantiomers crystallize in two distinct shapes, however, so this kind of mechanical sorting is not generally used. Chemists have had to devise other means of separation in pursuing the elusive goal of enantiomeric purity.

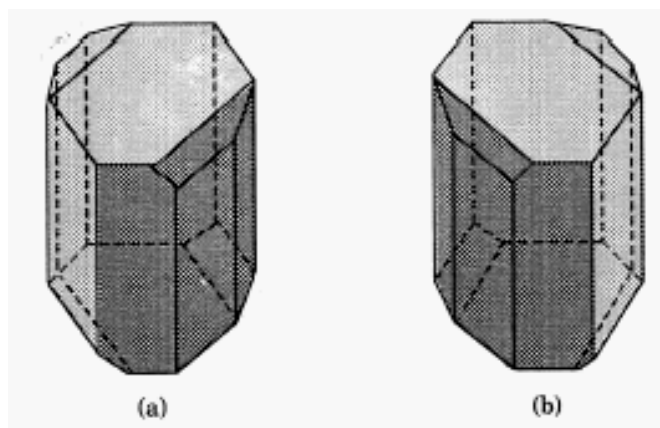


Figure 5.1: Sodium ammonium tartrate crystals

- The “right-handed” crystal of sodium ammonium tartrate
- The “left-handed” crystal of sodium ammonium tartrate

These illustrations are based on Pasteur’s original sketches. Note that the two are mirror images of each other and that one cannot be superimposed over the other.

Learning Objectives

By the time you complete Unit 5, you should be able to:

- Draw structural formulas for the constitutional isomers of alkanes.
- Using the IUPAC system, *name* alkane chains and monocyclic rings, including those with alkyl group, halide, and alcohol substituents.
- Explain trends in the physical properties of alkanes.
- Predict the stability of various substituted alkane and cyclohexane conformations.

- Determine the relative stability of conformers and isomers of substituted cyclohexanes.
- Identify enantiomers, diastereomers, chiral and achiral molecules, stereogenic carbon atoms, and molecular planes of symmetry.
- Name enantiomers and meso compounds using the (*R*)-(*S*) system.
- Explain plane-polarized light, optical activity, and racemic mixtures.
- Calculate specific rotation from data for an observed rotation.
- Distinguish between the designations (*R*) and (*S*), (+) and (–), D and L, and between absolute and relative configuration.
- Draw Fischer projection formulas.

Alkanes

In Unit 4, you learned that **alkanes** are a family of organic compounds that have no functional group. Unlike members of other families, they possess only carbon-carbon and carbon-hydrogen single bonds. The absence of any functional group gives alkanes their distinctive characteristics. In general, they are chemically unreactive and they used to be called **paraffins**, from the Greek words meaning “little affinity.” You may have heard of paraffin oil or paraffin wax. These substances consist of mixtures of liquid or solid alkanes.

Turn to Chapter 2 of your *Organic Chemistry* supplement and review Sections 2-4 and 2-6, on the structures and physical properties of alkanes.

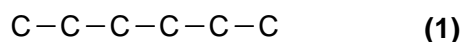
After you have finished going over these two sections, take out your model kit. In order to get a good idea of how isomeric alkanes differ in their shape, build models of the three isomeric pentanes shown on page 70 of your *Organic Chemistry* supplement. Then build a model of straight chain hexane and practise arranging the model in the zigzag pattern for hexane described on page 77, Fig. 2.3, of your supplement.

Do Exercise 2-16 on page 71 of your *Organic Chemistry* supplement. You were already instructed to do this question in Unit 4, but you should review it again now.

Drawing condensed structural formulas for a given molecular formula can be much more complicated than Exercise 2-16 suggests. Because of this, let's spend some time right now developing a system to help you tackle such exercises. This approach involves first determining the unbranched structure and then working out the branched structures in a logical manner.

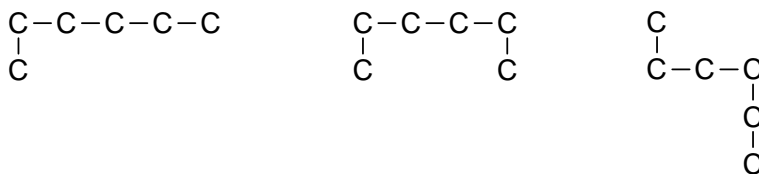
Let's use C_6H_{14} as an example. You can list the isomers of this molecule according to the following scheme:

Six in a row: First, draw the structures containing a chain of six carbon atoms joined one after another. Because there are only six carbon atoms in the molecule, there is only one way to arrange them so that they form an unbranched chain:



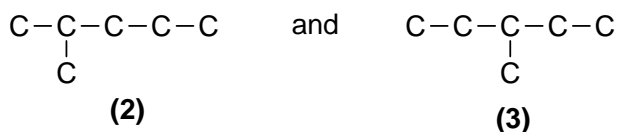
This structure does not show any of the hydrogen atoms. Leaving them out makes it easier to show the chain of carbon atoms. You may do this too, but remember that the proper condensed structure includes the hydrogen atoms and is written as $CH_3CH_2CH_2CH_2CH_2CH_3$.

Although the six carbon atoms in (1) are arranged in a straight line, the molecule is actually not linear. (Recall what you learned earlier when you made models of propane, butane, and pentane.) The following are equivalent structures for the same molecule:



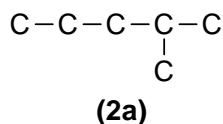
Make a model to convince yourself that these structures represent the same compound. You can convert one form into another by simply twisting and turning the model. You do not have to break old bonds and make new ones.

Five in a row: This time, draw only five carbon atoms so that one line passes through all of them. The sixth carbon atom therefore has to branch from this main chain. There are two possible five-in-a-row structures:

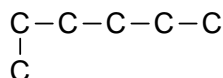


In (2), the sixth carbon atom is attached to the second carbon in the chain of five. In (3), the sixth carbon is attached to the third one in the chain. Again, make models of these structures and convince yourself that they indeed represent two different molecules. You cannot convert (2) into (3), and vice versa, by simply *twisting* the models. You would have to break one of the bonds and create another bond in a different place.

What about the following structure as another possible five-in-a-row isomer?



Structure (2a) is the same as (2). You can demonstrate this by taking your model of (2) and turning it around completely. There are no other possible five-in-a-row isomers. You have already seen that

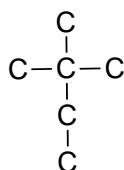


is actually a six-in-a-row structure.

Four in a row: What happens when you draw only four carbon atoms so that one line passes through all of them? The two structures that result are



Structures (1), (2), (3), (4), and (5) are the only constitutional isomers of C_6H_{14} . There is no three-in-a-row structure, as



is the same as (5). Again, you can demonstrate this clearly to yourself by making a model of (5) and turning it 90°.

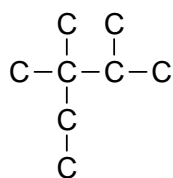
Before you leave this section, be sure you can use the approach just described. You will come across molecular formulas that have many more constitutional isomers than C_6H_{14} , and you will need to follow this systematic method for drawing and making models of all of them. The number of isomers increases very dramatically with the number of carbon atoms. CH_4 , C_2H_6 , and C_3H_8 each have only one structure, but C_4H_{10} has two constitutional isomers, C_5H_{12} has three, and C_6H_{14} has five. C_7H_{16} has nine such isomers, and C_8H_{18} has sixteen. You need not worry about being asked to draw all the isomers of an alkane such as $\text{C}_{20}\text{H}_{42}$ —in fact, there are too many!

You must, however, be able to work on such a problem in a systematic way, and you should be able to tell when two different drawings represent the same isomer.

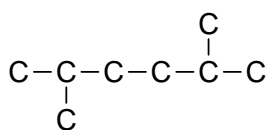
Practise with the following example to make sure you can distinguish identical structures:

Example

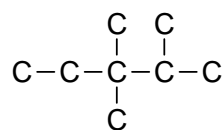
The structures below represent only four different constitutional isomers of C_8H_{18} . Identify which pairs represent the same isomers. Practise with your model set by making models of each of these structures.



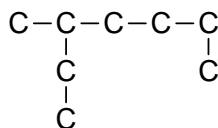
(a)



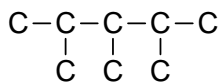
(b)



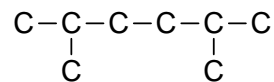
(c)



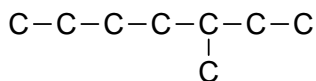
(d)



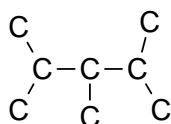
(e)



(f)



(g)



(h)

The bottom of page 78 in Section 2-6 of your *Organic Chemistry* supplement discusses how constitutional isomers have different physical properties. Recall the discussion of physical properties and molecular structure in Unit 4.

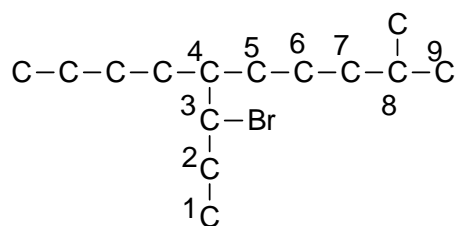
Nomenclature

Knowing what to call various organic compounds is a prerequisite for discussing them intelligibly. The IUPAC (pronounced I-u-pack; from International Union of Pure and Applied Chemistry) system of naming these compounds was established in the late nineteenth century and is the formal nomenclature used today. You will probably find it complicated and cumbersome at first, but the alternative, using “trivial” or “common” names, can often be confusing and imprecise. For example,

CH₃OH is known as methyl alcohol, methyl hydrate, and wood alcohol, and it has many other trivial names depending on what region or country one is in. IUPAC names, on the other hand, are unambiguous. Each compound has only one correct name, and only one compound has that name. (There are some exceptions: for example, although CH₃OH has the IUPAC name of methanol, methyl alcohol is also acceptable.) You will use the rules you learn now in many future situations. They are very logical. After some practice, you will be able to correctly name very large organic molecules.

Sections 2-5, 4-1, and 8-1 of your *Organic Chemistry* supplement describe how to name alkanes, haloalkanes (alkyl halides), cycloalkanes, and alcohols, respectively. Preview these sections by reading them, then study them. You should keep in mind a few things when you apply the rules for naming branched-chain alkanes, cycloalkanes, and alcohols. One is that *the functional group takes precedence over alkyl substituents in determining chain length*. This means that the longest chain used in naming the compound must include the carbon atom bearing the functional group, *and* this carbon atom must be given the lowest number possible.

For example, although the compound



has ten carbon atoms in its longest chain, its base name is nonane since it has only nine carbon atoms in the longest chain containing the bromine atom. Also, since the bromine atom takes precedence over the methyl group, the carbon bearing this atom is number 3 not number 7, as it would be if the chain were numbered starting from the other end. The IUPAC name of this compound is **3-bromo-4-butyl-8-methylnonane**.

Pay particular attention to the following points when you write a name like this:

- The name should be written as a single word.
- There should be no spaces between letters.
- There should be no capital letters in the middle of the name.
- Numbers should be separated from each other by commas.
- Numbers and letters should be separated from each other by hyphens.

Thus, the following versions of the above compound's name are wrong:

3-bromo-4-butyl-8-methyl nonane

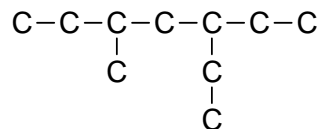
3-Bromo-4-Butyl-8-Methylnonane

3-bromo 4-butyl 8-methylnonane

Functional groups also take precedence over alkyl substituents in the naming of cycloalkanes. If both are present, the carbon bearing the functional group is considered number 1. You are not expected to name polycyclic compounds in this course, but you can read Section 4-6 of the *Organic Chemistry* supplement if you are interested in them.

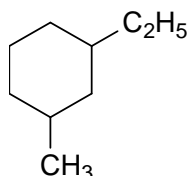
You should also take particular note of two other rules:

- If the rules you have already seen allow you to number a chain or ring in either direction, choose the direction where the smallest number is attached to the alkyl substituent that has a first letter that comes sooner in the alphabet (e.g., ethyl before methyl, e before m). For example,



is 3-ethyl-5-methylheptane, not 5-ethyl-3-methylheptane.

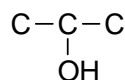
Similarly,



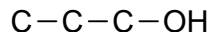
is correctly named **1-ethyl-3-methylcyclohexane**, not 3-ethyl-1-methylcyclohexane.

If the prefixes di- or tri- need to be added in front of the substituent name (e.g., diethyl), the prefix does not count in the alphabetical ordering (e.g., triethyl is still considered to be alphabetically before dimethyl).

- When a functional group is found on carbon number 1, you need not specify the number "1" in the name. For example,



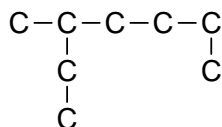
is 2-propanol, but



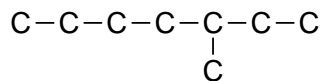
can be called simply *propanol* instead of 1-propanol. If the name of a compound does not specify a number for the functional group, the group is assumed to be found on carbon number 1.

Earlier in this unit, you spent some time learning how to tell whether two similar structures represent the same or different isomers. Naming the structures is a convenient way to do this. If two structures have the same name, they represent the same compound. For example, earlier in this unit, you were given eight structures representing only four different isomers of C_8H_{18} .

If you name structures (d) and (g)



(d)



(g)

according to the rules you have just learned, you will find that both have the IUPAC name of **3-methylheptane**. This confirms your earlier conclusion that the two are indeed identical as are (a) and (c), (b) and (f), and (e) and (h).

Before moving on to the next topic, do Exercises 2-18, 2-19, 4-2, 4-3, 8-1(c), 8-2(a) and (c), and Problem 36 at the end of Chapter 2 in your *Organic Chemistry* supplement.

Physical Properties

Sections 2-6 and 4-1 in your *Organic Chemistry* supplement are about the physical properties of alkanes and cycloalkanes. Study these sections now.

Conformations

In Unit 4 and earlier in this unit, you saw that atoms could rotate freely around single bonds. When this occurs around one of the carbon-carbon single bonds in an organic molecule, the result is a series of different spatial arrangements of the same molecule. These arrangements are known as **conformations**. A particular conformation is said to be exhibited by a **conformer** of the molecule. Note that conformers are not different compounds, nor are they constitutional isomers of each other. Remember that constitutional isomers have different connectivities, while conformers have the same connectivity.

Although some conformations are more stable than others, there is little difference between the most stable and the least stable at normal temperatures. Thus, a molecule has enough energy to rotate through the various possible conformations. The study of these conformations and the energy differences between them is called **conformational analysis**.

Sections 2-7 and 2-8 of your *Organic Chemistry* supplement discuss conformations and conformational analysis. Your model kit will help you to understand these concepts.

First, read through these two sections. Note the different kinds of conformations that they describe.

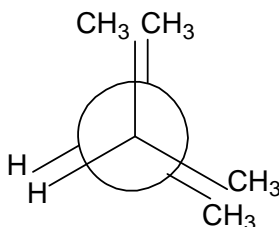
Next, build yourself models of an ethane and a butane molecule. Take the ethane molecule and hold it in front of you so that you are looking almost straight down the carbon-carbon bond (i.e., one CH_3 group will be toward you and one away from you). Slowly rotate the CH_3 group that is closest to you in a clockwise fashion and note the relative appearance of the hydrogens on the front and back carbons. You will notice that at times the hydrogens on the front carbon hide or “eclipse” the hydrogens on the back carbon (the carbon you are holding away from you) while at other times all six hydrogens are visible. This rotation is occurring at thousands of times per second at room temperature for carbon-carbon bonds in actual molecules. Your model of butane will have three carbon-carbon bonds, each of which, in turn, can be viewed the same way as you just viewed the rotation of the single carbon-carbon bond in ethane. Experiment with viewing the rotations about each carbon-carbon bond in your model of butane.

After viewing your models, study Sections 2-7 and 2-8 in your *Organic Chemistry* supplement, and then take a few moments to work on the following example:

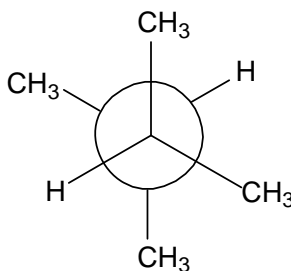
Example

Draw the Newman projection formula for the least stable and the most stable conformations of 2,3-dimethylbutane.

Answer



This is the *least stable conformation*. All four methyl groups are eclipsed.



This is the *most stable conformation*. The methyl groups are aligned in two pairs in the *anti* position.

Now try Exercises 2-22 and 2-23 in your *Organic Chemistry* supplement.

Ring Strain

Let's now look at cycloalkanes and the phenomenon of **ring strain**. Take out your model kit again and construct models of cyclopropane, cyclobutane, and cyclopentane. The difficulty in closing the bonds to make the rings in these models, particularly in the cases of cyclopropane and cyclobutane, is reflective of the ring strain in the actual molecules.

Study Section 4-2 in your *Organic Chemistry* supplement.

Conformations of Cycloalkanes

Earlier, we studied the conformational analysis of ethane and butane and saw how certain conformations were more stable than others. Cycloalkanes exhibit different

conformations, too. Because six-carbon molecules are the most common ringed organic compounds found in nature, let us now examine the conformers of cyclohexane.

Cyclohexane has two special non-planar conformations. They are known as the **chair** and **boat** forms, mainly because of their appearance in diagrams or models. You will see this for yourself when you make models of these conformations. Keep in mind that these are not two different molecules, but rather the same molecule twisted in different ways. The chair form is much more stable than the boat form because interactions between atoms are minimized, particularly when other groups are substituted for hydrogens.

When two such substituent groups are present, the cycloalkane exhibits cis-trans isomerism. Recall from Unit 4 that cis-trans isomers have the same connectivity but differ in the arrangement of their atoms in space. The two groups may be on the *same* side of the ring (cis) or on *opposite* sides (trans). This will become clearer shortly.

Now make a model of cyclohexane and study Sections 4-3 and 4-4 of your *Organic Chemistry* supplement. Read Section 4-5, but do not worry about the conformations of cycloheptane, and larger cycloalkanes. Use your model to help you visualize the concepts presented in these sections. Pay particular attention to Figure 4-10, as it gives you help in drawing the chair conformation.

After studying the three sections in the *Organic Chemistry* supplement, you should be able to explain how the chair and boat forms differ and what **axial** and **equatorial** substituents are. Prepare models of *cis*-1,4-dimethylcyclohexane and *trans*-1,4-dimethylcyclohexane, as illustrated on page 147 of the supplement. Practise with your models, flipping between the two chair conformations for each compound.

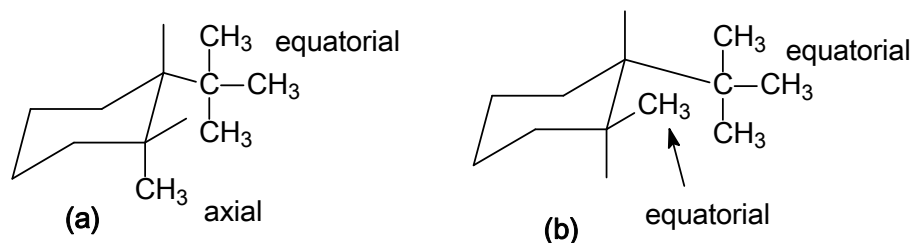
Take a few moments now to try the following example:

Example

Draw the most stable conformation of:

- cis*-1-(1,1-dimethylethyl)-2-methylcyclohexane
- trans*-1-(1,1-dimethylethyl)-2-methylcyclohexane

Answer



The 1,1-dimethylethyl (or *tert*-butyl) group is in the equatorial position in both molecules because it is so large compared to a methyl group. Note the H atoms have been omitted from these drawings only for clarity. You should normally place H atoms at the end of each line or else it signifies a methyl group.

Work on Exercises 4-11 and 4-16 in your *Organic Chemistry* supplement.

Chirality in Molecules

In the overview to this unit, we mentioned that molecules could exhibit the phenomenon of **chirality**, or handedness. A chiral molecule can be defined as one that cannot be superimposed on its mirror image.

As you work your way through the next few sections of the Organic Chemistry supplement, you will encounter several important terms: enantiomers, diastereomers, chiral, stereocentre, asymmetric carbon, and plane of symmetry. Make sure that you can define them, as you will see these terms again and again in this course as well as in subsequent organic chemistry courses.

The introduction to Chapter 5 and Section 5-1 in your *Organic Chemistry* supplement will introduce you to the topic of chirality in molecules. Chemical Highlight 5-1, mentions the importance of chirality in nature. The introductory section discusses something you have already seen in Unit 4 and earlier in this unit—the distinction between **constitutional isomers** and **stereoisomers**. The subdivision of isomers highlighted in Figure 5-1 should help you remember how the two differ from each other. Study these sections now.

There are two kinds of stereoisomers: **enantiomers** and **diastereomers**. Both kinds differ in the arrangement of their atoms in space. Note, however, that while enantiomers are nonsuperimposable mirror images of each other, diastereomers are not mirror images. Cis-trans isomers are diastereomers. The molecules *cis*-1,3-dimethylcyclopentane and *trans*-1,3-dimethylcyclopentane, at the bottom of page 170 in your *Organic Chemistry* supplement, are good examples. If you build models of

these compounds and look at them in a mirror, you will see that the trans form is not the mirror image of the cis form, or vice versa.

Section 5-1 of your *Organic Chemistry* supplement contains four terms that you should be able to define: **chiral**, **achiral**, **superimposable**, and **stereocentre (asymmetric atom)**. An asymmetric carbon atom is one that has four different groups attached to it. You will see that a pair of enantiomers results from the presence of such an atom in a molecule.

Section 5-1 of the supplement also discusses planes of symmetry. They divide achiral molecules into two halves that are mirror images of each other. Chiral molecules do not have a plane of symmetry. Try to build models of 2-bromopropane and 2-bromobutane; the latter compound is shown on page 171. Identify the plane of symmetry in the former and note its absence in the latter.

Now do Exercises 5-1 to 5-5 from your *Organic Chemistry* supplement. Use your model kit to help you work out the answers to these problems.

Enantiomers

The only structural difference between enantiomers is that one is a mirror image of the other. Since any compound can have only one mirror image, it is easy to see that enantiomers occur in pairs.

Each member of the pair is identical to the other in all physical properties (melting point, boiling point, density, solubility, colour) *except one*: the effect it has on the rotation of plane-polarized light. We'll come back to this a little later in this unit. Because of this similarity, separating a pair of enantiomers from each other poses a great challenge to an organic chemist. A number of ingenious physical methods, which you will see later, have been designed to accomplish this. Chemical separation, or resolution, is difficult because enantiomers undergo the same reactions at the same rate, although they do differ in the way they interact with other chiral molecules, such as enzymes.

Nomenclature

You have seen that enantiomers have their atoms connected in the same order and that they are not cis-trans isomers. How, then, can you name them so that they are distinguished from each other and so that the form of each enantiomer is clearly specified?

In order to address this problem, IUPAC adopted a method known as the **(R)-(S) system** or the **Cahn-Ingold-Prelog system**, after the three chemists who devised it. It may look quite complex at first glance, but it is really very logical and will be useful to you in other parts of this course.

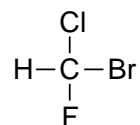
The (R)-(S) system is based on the assignment of a priority to each group attached to the asymmetric carbon atom of a chiral molecule. The priorities are then used to give a name to the molecule. Your *Organic Chemistry* supplement discusses the priority method and its application all at the same time, but you will probably find it helpful to learn how to assign priorities first. Once you know the rules for this, it will be easier to concentrate on actually naming enantiomers.

Let's summarize the priority rules here, and do some practice before referring to the *Organic Chemistry* supplement.

Each of the four atoms or groups attached to an asymmetric carbon atom is assigned a priority according to the following rules.

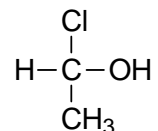
Rule 1: Assign the highest priority to the atom with the highest atomic number, the next highest priority to the atom with the next highest atomic number, and so on.

Consider the four atoms attached to this asymmetric carbon atom:



Br has the highest atomic number, followed by Cl, F, and then H. Therefore, the priority order is $\text{Br} > \text{Cl} > \text{F} > \text{H}$. This rule holds even if the atoms attached to the asymmetric carbon are themselves attached to other atoms.

Consider this example:

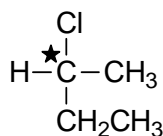


The atoms directly attached to the asymmetric carbon (the middle carbon) are H, Cl, O, and C. The priority order is $\text{Cl} > \text{O} > \text{C} > \text{H}$. It does not matter that the oxygen and the second carbon are also attached to other atoms (hydrogens in both cases).

Rule 2: If the four atoms directly attached to the asymmetric carbon are not all different from each other, continue examining the other atoms they are attached to

until you find a difference. Then assign a priority based on the difference. Do not use the sums of the atomic numbers but look for the single atom of highest priority.

Study the following example:

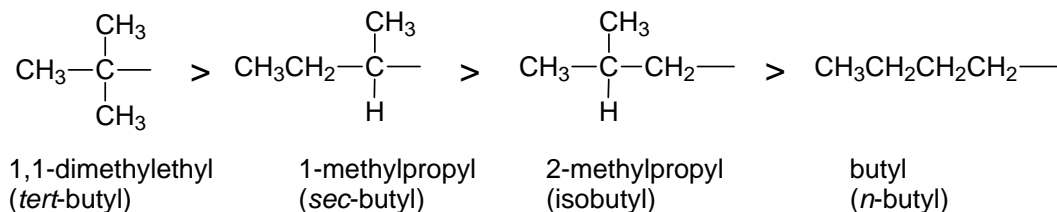


The asymmetric carbon atom is marked with a star. Clearly, the highest priority should be assigned to Cl and the lowest to H. But what about the remaining two atoms, both of which are carbons?

Look now at the *other* atoms that each of these carbons is attached to. In the $-\text{CH}_3$ group, C is also attached to three H's. In the $-\text{CH}_2\text{CH}_3$ group, the C attached to the asymmetric atom is also attached to two H's and another C. Thus at the first point of *difference*, we compare a C with an H. Because C has the higher atomic number, it takes precedence and $-\text{CH}_2\text{CH}_3$ is assigned a higher priority than $-\text{CH}_3$. The overall priority order, therefore, is $\text{Cl} > -\text{CH}_2\text{CH}_3 > -\text{CH}_3 > \text{H}$.

Now try to arrange the following groups from highest to lowest priority: butyl, 1-methylpropyl, 1,1-dimethylethyl, and 2-methylpropyl. The common names for these groups are included in parentheses under the structures.

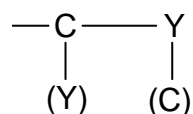
The answer is:



When a chiral molecule has a multiple bond, you will need the following rule for determining priority:

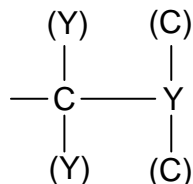
Rule 3: Treat groups that contain double or triple bonds as though the atoms involved in these bonds were duplicated or triplicated. Then apply Rule 2.

This does not mean that there are such duplicate or triplicate atoms in the compound. We just think of them as a means of assigning priority. Thus, if you have a $-\text{C}=\text{Y}$ group, treat it as though it were



(Y) and (C) are the “duplicates” or “phantoms” of the atoms involved in the double bond. *They do not exist* but are used to help assign priority.

Similarly, $\text{---C}\equiv\text{Y}$ is treated as



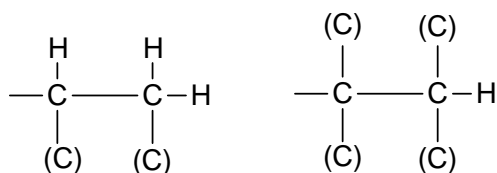
C and Y are considered in triplicate, again solely for the purpose of assigning priority using Rule 2.

Example

Which of the following groups has the higher priority: ---CH=CH_2 or $\text{---C}\equiv\text{CH}$?

Answer

First draw out the structures, showing atoms in duplicate or triplicate where necessary.



The first C of the $\text{---C}\equiv\text{CH}$ group is considered attached to three other C atoms. This group has a higher priority than ---CH=CH_2 , where the first C is considered attached to two C atoms and H.

Figure 5.2 in this unit shows the priority sequence for several common groups. Confirm this sequence for yourself by applying the three rules just discussed. Then work on the example that follows and compare your answer to the one given.

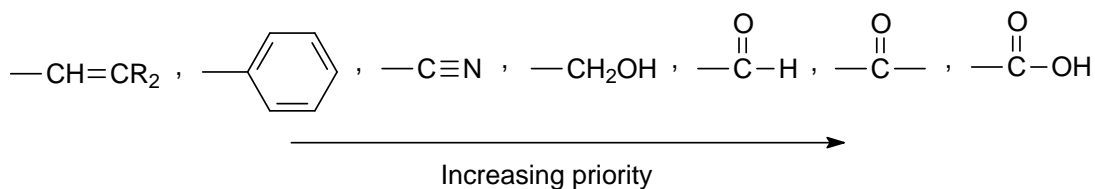
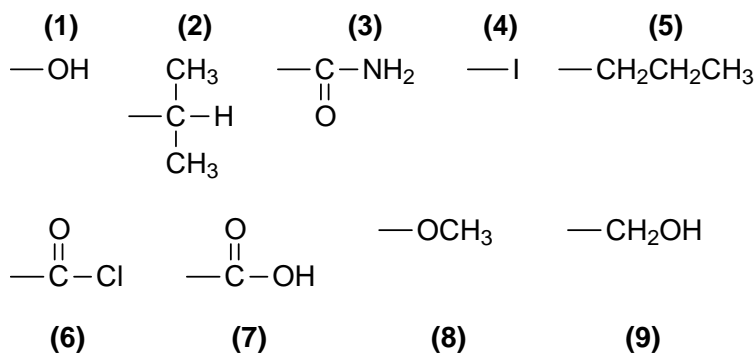


Figure 5.2: Priority sequence of some common groups

Example

List the following atoms or groups in order of decreasing priority.



Answer

The order of decreasing priority is: 4 > 8 > 1 > 6 > 7 > 3 > 9 > 2 > 5.

After learning these rules, you should find naming enantiomers fairly straightforward. Read Section 5-3 of your *Organic Chemistry* supplement. As you study this section, make models of the compounds it describes and use them to follow the explanation of the (*R*)-(*S*) system of naming enantiomers. Before proceeding further, be sure that you feel confident with the (*R*)-(*S*) sequence rules.

Now do Exercises 5-9, 5-11, and 5-12 from your *Organic Chemistry* supplement. Making models of the compounds discussed will help you understand the questions.

Nomenclature of Alkenes

The IUPAC rules of nomenclature for alkenes build on those you have already seen for alkanes and enantiomers. You will find that they follow a similar logical pattern.

In your *Organic Chemistry* supplement, read the introduction to Chapter 11 and Section 11-1. Alkenes used to be known as olefins and people still use the common names of many of these compounds, especially commercially, so we will occasionally refer to them.

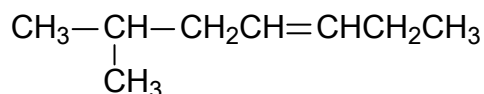
There are seven rules for naming alkenes in Section 11-1, which are really extensions of the rules used for naming alkanes. As before, you will be numbering the carbon atoms in a chain. Both carbons of the double bond must be included in the numbered chain, but only the lower number is specified in the name. Make sure you understand the ***E,Z* system** for designating the stereochemistry of a double bond as described on page 448 (Rule 5) in the *Organic Chemistry* supplement. It is similar to the (*R*)-(*S*) system we just covered for enantiomers. You will not need to be able to identify vinyl and allyl groups which are described in Rule 7.

Now try the following examples to make sure you can apply the rules for naming alkenes:

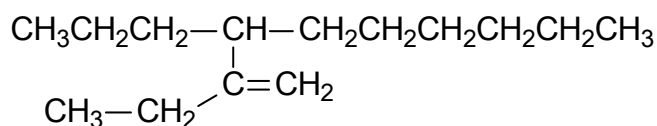
Examples

Give the IUPAC names for the following compounds:

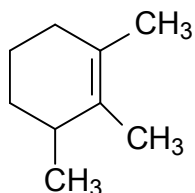
a.



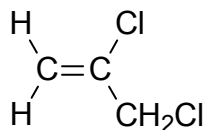
b.



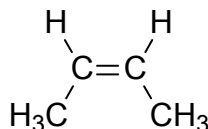
c.



d.

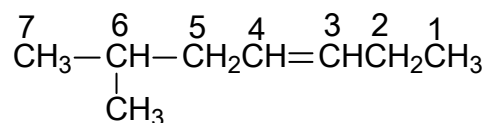


e.



Answers

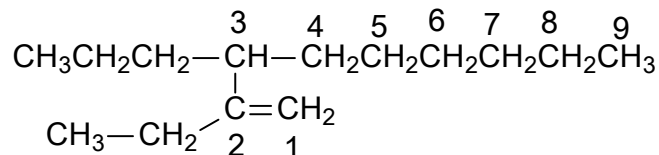
a.



6-methyl-3-heptene

Two rules conflict with each other here. Alkanes should be numbered so that the first point of branching has the lowest possible number. For alkenes, the first carbon of the double bond should have the lowest possible number. Because a *functional group takes precedence* over an alkyl branch, apply the alkene rule in a case like this. The correct name is then **6-methyl-3-heptene**, not 2-methyl-4-heptene.

b.

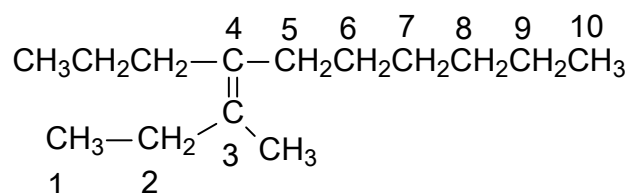


2-ethyl-3-propyl-1-nonene

A correct name for this compound is **2-ethyl-3-propyl-1-nonene**. The name 2-ethyl-3-propylnonene is also acceptable. Whenever a functional group (the *ene* in this case) is not numbered, it is assumed to be on carbon number 1.

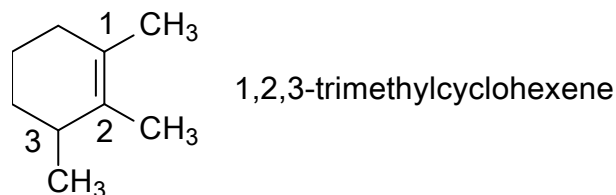
The longest chain in this compound actually consists of the ten carbons along the top. The numbered chain, however, should contain the double bond. Note that substituent groups are listed alphabetically, so that ethyl comes before propyl. This is consistent with the rules for naming alkanes, which you studied earlier in this unit. Remember to disregard prefixes such as “di-” or “tri-” and italicize prefixes such as “*sec-*” when deciding on the alphabetical order. Note also that numbers and letters are separated by hyphens.

If the double bond were instead between carbons 3 and 4,



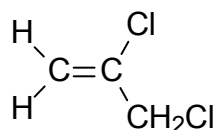
the compound would be a decene, as the longest chain through the double bond would have ten carbon atoms. The name would then be **(E)-3-methyl-4-propyl-3-decene**.

c.



Start numbering on one of the carbons of the double bond. Go through the other carbon in such a way that the substituent groups have the lowest possible numbers. The compound's name is thus **1,2,3-trimethylcyclohexene**.

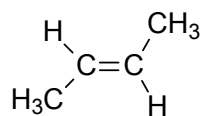
d. The correct name is 2,3-dichloropropene. Since



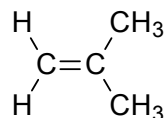
is not the allyl group, you cannot use the allyl notation to name the compound. But the compound $\text{CH}_2=\text{CHCH}_2\text{Cl}$ can be called **allyl chloride**.

- e. The correct name is (Z)-2-butene (or *cis*-2-butene). Both higher priority groups at each end of the double bond are on the same side of the double bond.

The compound



has methyl groups (both higher priority at each end of the double bond) on opposite sides of the double bond. It is (**E**)-2-butene (or **trans**-2-butene). Note that 2-methylpropene,



is a constitutional isomer of 2-butene rather than a stereoisomer. It does not have a Z or E designation.

Now try Exercises 11-1, 11-2, 11-3a, and 11-3c in your *Organic Chemistry* supplement.

Properties of Enantiomers

Let's turn now to the only physical characteristic in which enantiomers differ: their ability to rotate plane-polarized light.

When a beam of plane-polarized light passes through a solution containing one member of an enantiomeric pair, the plane of the beam rotates. The other member of the pair causes the plane to rotate to the same degree, but in the opposite direction.

A clockwise rotation is designated as positive (+) and the substance that causes such a rotation is said to be **dextrorotatory**. A counter-clockwise rotation is negative (–) and is caused by a **levorotatory** substance.

An enantiomer's name can include the designation (+), or (–), in addition to (R) or (S). Some older biology and organic chemistry textbooks use the symbols D and L to represent dextrorotatory and levorotatory compounds, respectively. Here, however, we will always use (+) and (–). Keep in mind two very important points about these designations:

- The designation (*R*) or (*S*) gives you the enantiomer's absolute configuration, that is, the direction that each group attached to the stereogenic carbon atom points to in space. It has *nothing* to do with measurements of optical rotation.
- The designation (+) or (–) tells you which way a solution of the enantiomer rotates the plane of plane-polarized light. It is *not* correlated with either the compound's structure or its (*R*)-(*S*) designation. Both the direction and the degree of rotation must be determined experimentally.

Turn now to your *Organic Chemistry* supplement and read Section 5-2. You should be able to describe what plane-polarized light is and how a polarimeter is used to measure optical rotation, but do not worry about drawing details such as those given in Figure 5-5 of the supplement. Study the information about specific rotation. Also note the example of (–)-lactic acid and (+)-sodium lactate in the margins of Section 5-3. Although both are (*R*) compounds, optical measurements show that one rotates a plane of light to the left and the other to the right.

You have just seen how an instrument called a polarimeter is used to measure a compound's rotation of plane-polarized light. Once the observed rotation is known, it can be used to calculate the specific rotation. Remember that the specific rotations of a compound and its enantiomer have the same value but opposite directions.

For example, (*S*)-2-iodobutane, shown in Figure 5.3 in this unit, has a specific rotation of +15.9°. (This value was originally determined by experiment.) Its enantiomer, (*R*)-2-iodobutane, has a specific rotation of –15.9°.

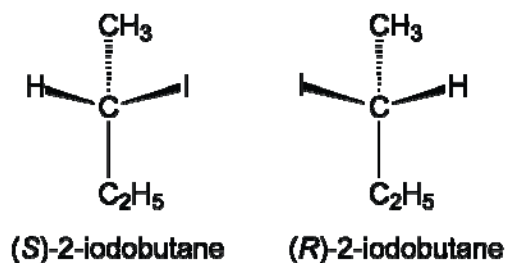


Figure 5.3: Enantiomers of 2-iodobutane

Now try the following example:

Example

A 3.0 g sample of coniine, the toxic material from poison hemlock, was dissolved in 20 mL of ethanol and placed in a polarimeter tube 5 cm long. The observed rotation at the sodium D line was +1.2°. Calculate the specific rotation for coniine.

Answer

Use the highlighted “Specific Rotation” equation in section 5.2 of your *Organic Chemistry* supplement:

$$[\alpha] = \frac{\alpha}{l \times c}$$

Substitute 1.2° for α , the observed rotation; $3.0 / 20 = 0.15$ for c , the concentration in grams per millilitre; and 0.50 for l , the length of the tube in decimetres. The specific rotation, $[\alpha]$, is

$$\frac{1.2^\circ}{0.50 \times 0.15} = +16^\circ$$

Although a solution of one enantiomer is optically active, an equal mixture of enantiomers is not. Such a mixture is called a **racemic mixture** or **racemate**. It is always produced during a laboratory synthesis of a chiral molecule from achiral reactants.

When a similar synthesis occurs in nature, it is usually **stereoselective**, producing just one of the enantiomers. Chemists have tried for many years to emulate this in the lab. However, the successful stereoselective reactions all require starting with a chiral compound, using chiral reagents obtained from naturally occurring products, or using an enzyme, which is also a naturally occurring molecule.

If you would like a Nobel Prize in Chemistry, devising a stereoselective synthesis with no help whatsoever from Mother Nature would probably make you a contender!

Fischer Projection Formulas

So far, your *Organic Chemistry* supplement has used three-dimensional formulas to represent most of the compounds it has discussed. **Fischer projection formulas** were introduced in the late 1800s by the German chemist Emil Fischer. They are easier to draw than three-dimensional formulas and, with some practice, you will be able to “see” quite well the molecules they represent.

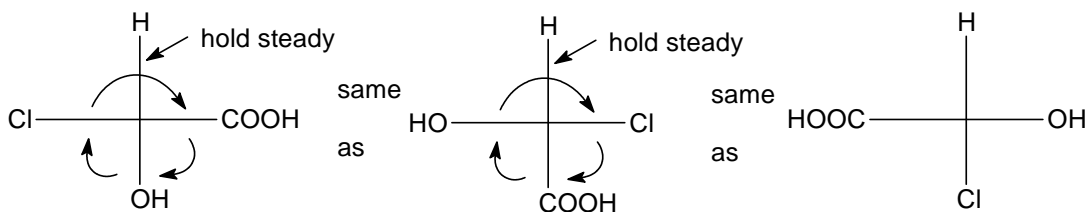
Because they are two-dimensional, however, you have to strictly follow the rules for drawing and working with them. At first, you may find it necessary to make models of the compounds you draw, in order to demonstrate to yourself the importance of

these rules and reinforce them in your mind. So use your model kit as much as you need to. In fact, it might be a good idea to report for your final exam with a few basic models, such as ethane or cyclohexane, already made.

Study Section 5-4 of your *Organic Chemistry* supplement carefully. Build models of (R)- and (S)-2-bromobutane, as shown in "Model Building" in Section 5-4. Work with these models in order to become familiar with the relationship between a Fischer projection and the equivalent dashed-wedged line structure.

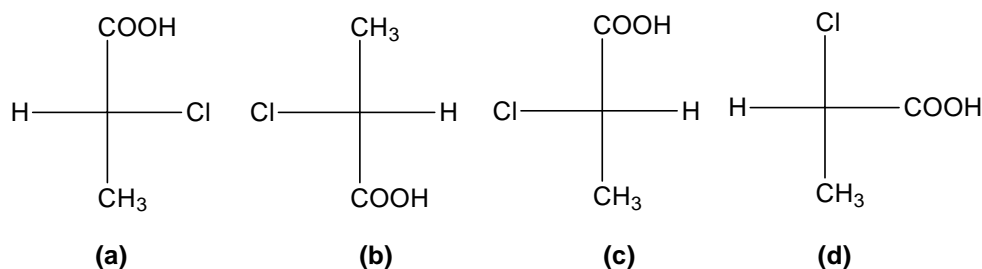
Now that you have seen drawings of what Fischer projection formulas are and how they relate to three-dimensional models, study the following rules for drawing and working with them:

- Represent a tetrahedral (sp^3 -hybridized) carbon atom by two crossed lines. Horizontal lines represent bonds projecting out of the page toward you, and vertical lines represent bonds projecting behind the page away from you.
- Rotate a Fischer projection formula *only* in the plane of the paper. You cannot flip it over and out of the plane of the paper.
- In testing whether two structures are superimposable, rotate a Fischer projection formula 180° *only*. When you do this, its configuration does not change. If you rotate it 90° or 270° , you invert its configuration. (This rule is easily overlooked!)
- Draw the main carbon chain of a Fischer projection formula vertically, with carbon atom number 1 at the top.
- Hold any one group steady and rotate the other three either clockwise or counter-clockwise to get other projection formulas of the same molecule, as shown below. Make a model of the compound and practise doing the indicated rotations and visualizations.

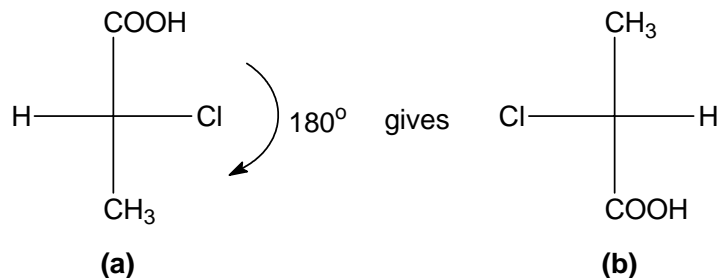


Example

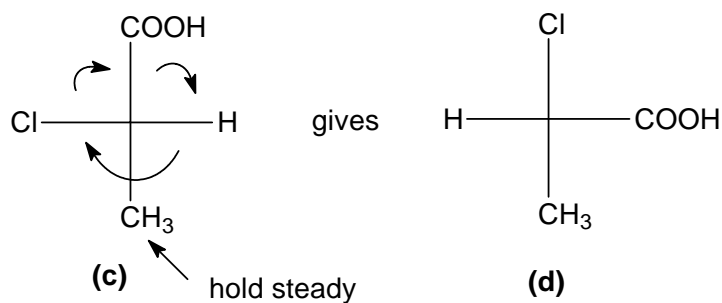
Which of the following Fischer projection formulas of 2-chloropropanoic acid represent the same enantiomers?

**Answer**

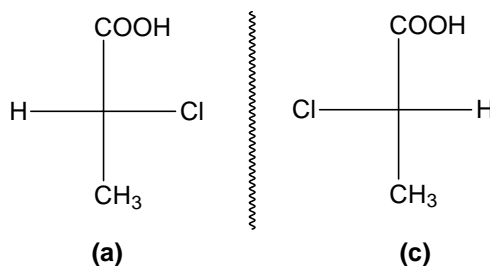
Compounds (a) and (b) are identical to each other. If you rotate (a) 180° in the plane of the paper, you get (b).



Compounds (c) and (d) are identical to each other. If you hold the CH_3 group steady and turn the remaining three groups one position in a clockwise direction, you get (d).

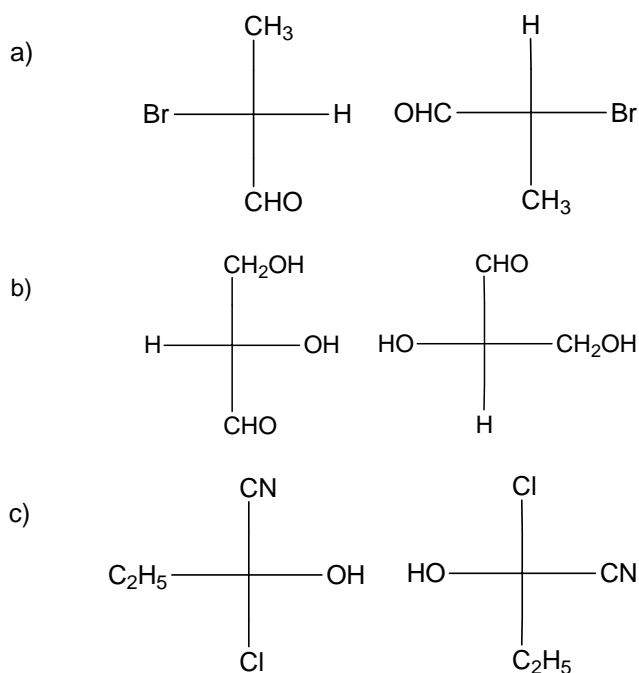


Note that (a) is the enantiomer of (c). The wavy line below represents a mirror plane, and you can see the mirror images clearly in the Fischer projections.



Example

State whether each of the following pairs of Fischer projection formulas consists of two identical compounds or two enantiomers:



Answer

Each pair consists of two enantiomers. Choose a structure from each pair. If you hold one group steady, you can rotate the other three groups so as to produce a mirror image of the other structure in the pair. Remember that if you rotate an entire projection formula, *you must rotate it 180° in order to maintain the same configuration*.

Do Exercises 5-13, 5-14, 5-15 and 5-16 in your *Organic Chemistry* supplement. Return to this unit when you have completed these exercises.

Molecules with More than One Asymmetric Carbon Atom

All the enantiomeric compounds we have talked about up to this point have had just one asymmetric carbon atom. Things are a little more complicated when a molecule has more than one such carbon. Many stereoisomers are possible because each asymmetric carbon can be either (*R*) or (*S*). Don't worry, though; the concepts you have learned so far in this unit can be applied to these more complex molecules.

Before you look at specific examples, let's use a few symbols to show you how to determine the number of isomers a molecule has.

First consider just one asymmetric carbon. It gives rise to a pair of enantiomers that we can call A and A*, respectively. If there is a second asymmetric carbon, it too gives rise to a pair of enantiomers, which we can call B and B*. Overall, then, there are four possible combinations:



In other words, the molecule could be right-handed at A and right-handed at B, or right-handed at A and left-handed at B, or left-handed at A and right-handed at B, or left-handed at A and left-handed at B.

Can you tell what the enantiomeric pairs are? A:B and A*:B* are mirror images of each other and therefore constitute one pair. A*:B and A:B* are also mirror images of each other and therefore constitute a second pair.

What about the relationship between A:B and A*:B? Although they are stereoisomers, they are not mirror images of each other and are therefore **diastereomers**.

What happens if there are three asymmetric carbon atoms? The possible structures are now:



If you work out the number of possible stereoisomers in a compound with four asymmetric carbons, you would find sixteen. We can make an important generalization: if there are n asymmetric carbon atoms, the maximum number of stereoisomers is 2^n .

You may remember this formula if you have taken a math course that covered combinations. Soon you will see that while the formula gives you the maximum number of stereoisomers possible, the actual number may be smaller.

Study Section 5-5 of your *Organic Chemistry* supplement and make models of the compounds discussed. Turn to the bottom of page 156 and see if you can locate all the asymmetric carbon atoms in cholesterol. These are marked for you in Figure 5.4 in this unit.

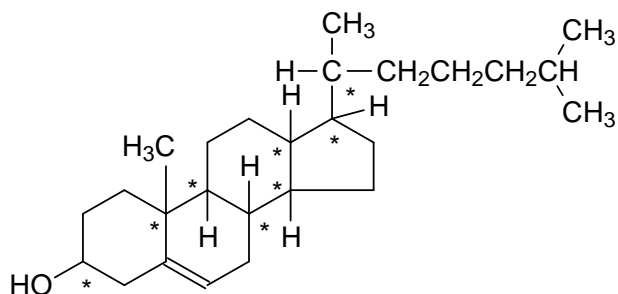


Figure 5.4: Cholesterol, showing stereogenic carbon atoms

Now study Section 5-6 in your *Organic Chemistry* supplement, which discusses **meso compounds**. In order to be considered a meso compound, a molecule must be achiral and contain two or more asymmetric carbon atoms. At this point, make models of 2,3-dibromobutane as drawn in Figure 5-10. Manipulate the models so that you can clearly see the relationships between them described in Figure 5-10.

Take some time now to work on Exercises 5-21, 5-22, and 5-23 in the supplement (build models of these compounds).

Nomenclature

The (*R*)-(*S*) system is easily extended to name compounds with more than one asymmetric carbon atom. Each such atom is considered independently to determine whether its absolute configuration is (*R*) or (*S*), and both designations are included in the name. Take careful note of the examples shown in Figure 5-7 in your *Organic Chemistry* supplement.

Work now on Exercise 5-19 in your *Organic Chemistry* supplement. Use your model kit to help you compare pairs of molecules.

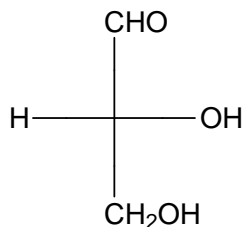
Relating Configurations of Enantiomers

In this unit, you have spent a good deal of time studying molecules with an asymmetric carbon atom, which are usually also optically active. What happens when these molecules undergo chemical reactions?

If no bonds to the asymmetric carbon are broken, the products will always show a retention of configuration around that carbon atom. However, a product's specific rotation, and even the direction of rotation, can differ from that of the original enantiomer.

Chemists have used retention of configuration to relate the configuration of one enantiomer to that of another. The D and L system mentioned earlier provides an example of this. In it various enantiomers are considered to have the same **relative configuration** as one or the other member of a standard pair, namely D-glyceraldehyde and L-glyceraldehyde.

The D and L system has now been superseded by the comprehensive and unambiguous (*R*)-(*S*) system. One of the reasons for this was that not every compound could be related to glyceraldehyde by reactions that proceeded with retention of configuration. Also, the assignment of the structure



to D-glyceraldehyde was entirely arbitrary. As it turned out, X-ray diffraction eventually showed that the above structure indeed correctly represented the absolute configuration of the enantiomer that rotated light to the right and that had been called D-glyceraldehyde. Review the "Chemical Highlight 5-2" section of your *Organic Chemistry* supplement for further details of this history.

Some organic chemistry textbooks remark that it was "fortunate" that the original guess turned out to be correct. Some often think it was unfortunate, however, because now students sometimes fail to realize that the assignment was an arbitrary one. This would have been quite clear if D-glyceraldehyde had turned out to be the mirror image of the previous structure!

We've spent some time talking about the D and L system because it is still used extensively in biology and biochemistry.

For example, D-glucose is the major fuel for most organisms as well as the basic building block of starch and cellulose. Most sugars found in nature are D sugars, although some L sugars are known. On the other hand, all amino acids that commonly occur in proteins belong to the L series. You may see the D and L system again in subsequent chemistry or biochemistry courses. In general, however, we will use the (*R*)-(*S*) system.

Review

We have covered a lot of material in Unit 5, which has included various sections from Chapters 2, 4, 5, and 11, and the section on naming alcohols in Chapter 8 in your *Organic Chemistry* supplement. Go over these sections and make sure you can explain the terms and concepts they mention.

And so we come to the end of Unit 5. Turn now to Practice Exercise 5 and follow the directions given there. There are also some suggested supplementary exercises for further review. After you are finished, go to your Assignments and complete Assignment 5. Good luck, and see you again in Unit 6!

Self-Assessment

Having reached the end of Unit 5, you should be able to:

- Draw structural formulas for the constitutional isomers of alkanes.
- Using the IUPAC system, name alkane chains and monocyclic rings, including those with alkyl group, halide, and alcohol substituents.
- Explain trends in the physical properties of alkanes.
- Predict the stability of various substituted alkane and cyclohexane conformations.
- Determine the relative stability of conformers and isomers of substituted cyclohexanes.
- Identify enantiomers, diastereomers, chiral and achiral molecules, stereogenic carbon atoms, and molecular planes of symmetry.
- Name enantiomers and meso compounds using the (*R*)-(*S*) system.
- Name alkenes using the IUPAC (*E*)-(*Z*) system.
- Explain plane-polarized light, optical activity, and racemic mixtures.
- Calculate specific rotation from data for an observed rotation.
- Distinguish between the designations (*R*) and (*S*), (+) and (–), D and L, and between absolute and relative configuration.
- Draw Fischer projection formulas.

Practice Exercise 5

Finish working through Unit 5 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in Unit 5 is integrated throughout the practice exercise. The solutions to these problems will be provided once you have completed this practice exercise.

You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can start the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 5. If you feel that you need more practice, go to the Suggested Supplementary Exercises that follow.

Suggested Supplementary Exercises

- At the end of each chapter in your *Organic Chemistry* supplement are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Some of the even-numbered exercises at the end of the chapter have their answers in the back of the textbook. If you decide to try the odd-numbered problems and need help, consult your Open Learning Faculty Member.
- From the Problems at the end of Chapter 2:
35–42, 45, 46, 52, 54, and 55.
- From the Problems at the end of Chapter 4:
21, 23, 25, 29–37, 43, 47, 55, and 56.
- From the Problems at the end of Chapter 5:
30–34, 36–46, 53, 54, 63, and 67–70.
- From the Problems at the end of Chapter 8:
26–28.
- From the Problems at the end of Chapter 11:
29 (a), (b), and (c), 30 (a), (b), (d), (f), (h), and 31.

Assignment 5

Now refer to your *Assignments* and complete Assignment 5. Consult your Course Guide for the week this assignment is due.

You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form.

Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.