1.2 Alkenes and Alkynes

As you learned in Section 1.1, all of the carbon–carbon bonds in an alkane are single bonds. In other organic compounds, however, double or triple covalent bonds connect some of the pairs of carbon atoms. A hydrocarbon containing carbon–carbon double or triple bonds is called an **unsaturated hydrocarbon** because each molecule contains fewer than the maximum number of hydrogen atoms. Unsaturated hydrocarbons have a variety of uses in industry and everyday life. For example, ethyne (commonly known as acetylene) is the fuel used in welding and cutting torches. This molecule contains a triple bond between its 2 carbon atoms (**Figure 1**).

unsaturated hydrocarbon an organic compound, consisting of carbon and hydrogen, with one or more double or triple bonds joining pairs of carbon atoms within the molecules

(b) H—C≡C—H

Figure 1 (a) An oxyacetylene torch burns ethyne (acetylene) in oxygen. (b) Ethyne contains a triple bond.

Ethene, another unsaturated hydrocarbon, is used in agriculture to help ripen fruit more quickly. Ethene contains a carbon–carbon double bond (**Figure 2**). Note that each carbon atom always has four bonds. In an ethene molecule each carbon bonds to 3 atoms (1 carbon and 2 hydrogen atoms), but the carbon–carbon bond is a double bond. In ethyne (Figure 1), each carbon atom is bonded to only 1 hydrogen atom; the remaining three bonds connect to the other carbon atom. In this section, you will learn about hydrocarbons that contain multiple bonds.

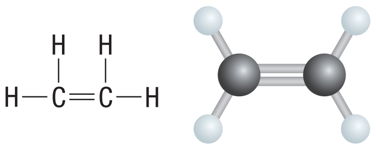


Figure 2 The 2 carbon atoms in ethene are joined by a double bond.

Alkenes and Alkynes: Unsaturated Hydrocarbons

A hydrocarbon that contains at least one carbon–carbon double bond is called an **alkene**. Alkenes with one double bond have the general formula C_nH_{2n}. The simplest alkene is ethene, C_2H_4 (Figure 2).

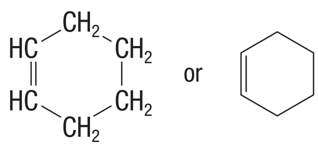
An unsaturated hydrocarbon that contains at least one triple bond between 2 carbon atoms is called an **alkyne**. Alkynes with one triple bond have the formula C_nH_{2n-2}. The simplest alkyne is ethyne (Figure 1).

Longer unsaturated compounds can include both single and multiple bonds. Like alkanes, alkenes and alkynes can form ring structures (**Figure 3**).

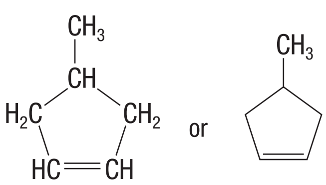
Scientists use the general term **aliphatic hydrocarbon** to refer to a compound that has a structure based on straight or branched chains or rings of carbon atoms. Alkanes, alkenes, and alkynes are all aliphatic hydrocarbons.

alkene a hydrocarbon that contains at least one carbon–carbon double bond

alkyne a hydrocarbon that contains at least one carbon–carbon triple bond



cyclohexane



4-methyl cyclopentene

Figure 3 Structural formulas for two cyclic alkenes

aliphatic hydrocarbon a compound that has a structure based on straight or branched chains or rings of carbon atoms

Naming Alkenes and Alkynes

Like alkanes, unsaturated hydrocarbon names are based on the longest hydrocarbon chain. The name of an alkene ends in *-ene* and the name of an alkyne ends in *-yne*. For example, the alkane C_3H_8 is propane, the alkene C_3H_6 is propene, and the alkyne C_3H_4 is propyne. Tutorial 1 describes in detail the process for naming and drawing unsaturated hydrocarbons using the IUPAC convention. WEB LINK

Tutorial 1 Naming and Drawing Alkenes and Alkynes

The rules for naming alkenes and alkynes are similar to those for alkanes.

1. Identify the parent chain or ring that contains the multiple bond.
2. Identify whether the chain or ring contains a double bond (in which case it is an alkene) or a triple bond (in which case it is an alkyne). If the hydrocarbon chain has more than one double or triple bond, add a suffix to show the number of multiple bonds (such as *-diene* or *-triene*).
3. Number the parent chain or ring so that the first carbon atom involved in a multiple bond has the lowest possible number. Write this number before the suffix. (This is only necessary if there are more than 3 carbon atoms.)
4. Number and name any substituents using the same rules as were used for alkanes. If the double or triple bond is in the middle of a chain, start the numbering from the end nearer the substituent group.

Following these rules, $CH_2{=}CHCH_2CH_3$ is called but-1-ene and $CH_3CH{=}CHCH_3$ is called but-2-ene. You may encounter an older naming method in which the number of the first carbon to include the multiple bond is written at the beginning of the name. For example, but-2-ene would be called 2-butene.

As another example, a chain of 8 carbon atoms with double bonds at the second, fourth, and sixth carbon atoms is named octa-2,4,6-triene. An 8-carbon chain with triple bonds at the second, fourth, and sixth carbon atoms is octa-2,4,6-triyne.

$CH_3CH{=}CHCH{=}CHCH{=}CHCH_3$

octa-2,4,6-triene

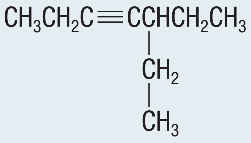
$CH_3C{\equiv}CC{\equiv}CC{\equiv}CCH_3$

octa-2,4,6-triyne

In the following sample problem, you will learn how to name unsaturated hydrocarbons by examining their structural formulas. Next, you will learn how to draw their structural formulas from their names.

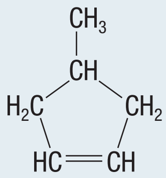
Sample Problem 1: Naming Alkenes and Alkynes

Determine the correct name for each of the following compounds:

(a) 

(b) $CH_3CH{=}CHCH{=}CH_2$

(c) $CH_2{=}CHCHClCH_2CH_3$

(d) 

Solution (a)

Step 1. Identify the parent chain or ring that contains the multiple bond.

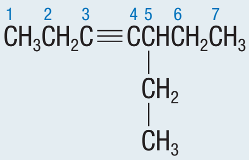
In this compound, the longest chain is 7 carbon atoms with one triple bond, so the root name contains *hept*-.

Step 2. Identify whether the chain contains a double bond (in which case it is an alkene) or a triple bond (in which case it is an alkyne).

The molecule contains a triple bond, so it is an alkyne. Its name contains -*yne*. The root name is therefore heptyne.

Step 3. Number the parent chain so that the first carbon atom involved in a multiple bond has the lowest possible number. Write this number before the suffix.

The triple bond is attached to the third carbon atom: hept-3-yne.



Step 4. Number and name any substituents using the same rules as were used for alkanes. If the double or triple bond is in the middle of a chain, start the numbering from the end nearer the substituent.

The ethyl group is bonded to the fifth carbon atom in the chain: 5-ethyl.

This compound is 5-ethylhept-3-yne.

Solution (b)

Step 1. Identify the parent chain or ring that contains the multiple bond.

The unbranched chain has 5 carbon atoms: *pent*-.

Step 2. Identify whether the chain contains a double bond or a triple bond.

There are two double bonds, so it is a pentadiene.

Step 3. Number the parent chain so that the first carbon atom involved in a multiple bond has the lowest possible number.

The double bonds are on the first and third carbon atoms so this compound is penta-1,3-diene.

Solution (c)

Step 1. Identify the parent chain or ring that contains the multiple bond.

There are 5 carbon atoms in the chain: *pent*-.

Step 2. Identify whether the chain contains a double bond or a triple bond.

There is one double bond, so the compound is a pentene.

Step 3. Number the parent chain so that the first carbon atom involved in a multiple bond has the lowest possible number.

The double bond is between the first and second carbon atoms: pent-1-ene.

Step 4. Number and name any substituents using the same rules as were used for alkanes. If the double or triple bond is in the middle of a chain, start the numbering from the end nearer the substituent.

This compound contains a chlorine atom bonded to atom 3.

Therefore, this compound is 3-chloropent-1-ene.

Solution (d)

Step 1. Identify the parent chain or ring that contains the multiple bond.

The ring contains 5 carbon atoms: *cyclopent*-.

Step 2. Identify whether the ring contains a double bond or a triple bond.

There is one double bond, so it is a cyclopentene.

Step 3. Number the parent ring so that the first carbon atom involved in a multiple bond has the lowest possible number.

In a ring, the carbon atoms are always numbered so that the multiple bond is between carbon atoms 1 and 2: cyclopent-1-ene.

Step 4. Number and name any substituents using the same rules as were used for alkanes.

Whichever way you count around the ring, the methyl group is attached to carbon atom 4.

This compound is therefore 4-methylcyclopent-1-ene.

When you are given the name of an alkene or alkyne and asked to draw its structure, the steps are similar to those for drawing an alkane:

1. Draw the parent chain or carbon ring from the last part of the compound name.
2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.
3. Draw the multiple bonds (and substituents) at the appropriate locations.

Sample Problem 2: Drawing Structures of Alkenes and Alkynes

Draw the structural formula of each of the following compounds:

(a) 2-methylpenta-1,4-diene

(b) 4,5-dimethylhept-2-yne

Solution (a)

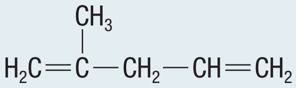
Step 1. Draw the parent chain or carbon ring from the last part of the compound name.

The name *penta-1,4-diene* tells us that the longest carbon chain is 5 carbon atoms.

Step 2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.

The name *diene* indicates that the compound contains two double bonds. The number 1,4 tells us that these double bonds are between the first and second and fourth and fifth carbon atoms. The *2-methyl* part of the name indicates that the molecule also contains a methyl group bonded to the second carbon atom.

Step 3. Draw the multiple bonds (and substituents) at the appropriate locations.



Solution (b)

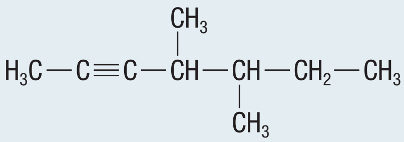
Step 1. Draw the parent chain or carbon ring from the last part of the compound name.

The longest carbon chain is 7 carbon atoms.

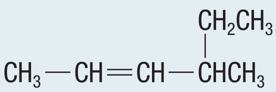
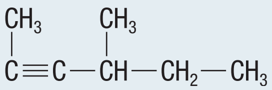
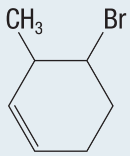
Step 2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.

It contains one triple bond between the second and third carbon atoms. It also contains two methyl groups, bonded to the fourth and fifth carbon atoms.

Step 3. Draw the multiple bonds and substituents at the appropriate locations.



Practice

1. Name each of the following compounds: K/U
   (a) $CH_2{=}CH-CH_2-CH_3$
   (b)
   
   (c)
   
   (d)
   

2. Draw the structural formula for each of the following compounds: K/U C
   (a) hex-3-ene
   (b) 6-methylhepta-2,4-diene
   (c) 7-bromooct-3-yne
   (d) 3-ethylcyclopent-1-ene

Mini **Investigation**

Isomers of Pentene

Skills: Performing, Observing, Communicating — SKILLS HANDBOOK A2.4

Equipment and Materials: molecular modelling kit

1. Use the molecular modelling kit to build all the possible isomers of pentene.
2. After building each isomer, draw its structural formula and write its molecular formula.

A. How many isomers of pentene are there? K/U

B. Are there more isomers of pentene than pentane? Explain your answer. T/I

C. Look for a predictive pattern based on the number of multiple bonds in a hydrocarbon and the number of possible isomers. Explain your conclusion. T/I

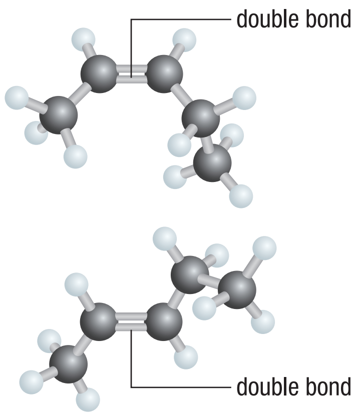
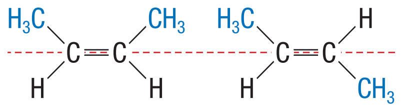


Figure 4 These two pentene structures represent two different compounds because the molecule cannot rotate around the double bond.

stereoisomers molecules that have the same chemical formula and structural backbone, but with a different arrangement of atoms in space

***cis* isomer** a stereoisomer in which the groups of interest are located on the same side of a double bond

***trans* isomer** a stereoisomer in which the groups of interest are located on opposite sides of a double bond



(a) *cis*-but-2-ene **(b)** *trans*-but-2-ene

Figure 5 Two stereoisomers of but-2-ene. In *cis*-but-2-ene, the methyl groups are on the same side of the double bond. In *trans*-but-2-ene, the methyl groups are on opposite sides of the double bond.

Cis–Trans Isomerism

If you used a molecular modelling kit in Section 1.1 to build isomers of pentane, you probably noticed that you can rotate the carbon "atoms" around the single bonds connecting each atom. As a result, you could create many three-dimensional models that look different but are actually identical, having 5 carbon atoms in a chain. However, when you made the models of pentene, you may have noticed that you cannot rotate the carbon atoms around the double bond. Therefore, the groups on different sides of a double bond are in a fixed position relative to each other (**Figure 4**).

The two pentene structures in Figure 4 are stereoisomers. **Stereoisomers** have the same kind and number of atoms bonded in the same order but have different arrangements in space. Stereoisomers cannot be changed from one to another by simple rotation. Bonds would have to be broken and re-formed. Stereoisomers are distinct compounds with different properties, such as different melting points.

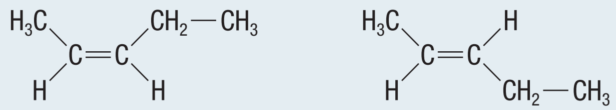
In this textbook we use the terms *cis* and *trans* to describe the positions of the parts of a molecule around a double bond. A ***cis* isomer** has matching alkyl groups located on the same side of the double bond. The ***trans* isomer** has the groups located on opposite sides of the double bond (**Figure 5**). When we refer to the "sides" of the double bond, we mean the two sides of the molecule divided by a line running along the double bond. We use the *cis/trans* naming system only when two of the substituents are the same (methyl groups in this case), and only for alkenes. IUPAC conventions use a different system, incorporating the letters E and Z, which you may see in other contexts.

Tutorial 2 Naming and Drawing *Cis–Trans* Isomers

In this tutorial, you will practise naming and drawing *cis* and *trans* isomers of alkenes.

Sample Problem 1: Naming Stereoisomers

Figure 6 shows two stereoisomers of pent-2-ene. Name each stereoisomer.



(a) **(b)**

Figure 6

Solution

In Figure 6(a), the substituent groups are bonded to the same sides of the pair of double-bonded carbon atoms. Therefore, Figure 6(a) shows *cis*-pent-2-ene. In Figure 6(b), the two substituent groups are on opposite sides of the double bond, so Figure 6(b) shows *trans*-pent-2-ene.

When drawing structural formulas for compounds that are stereoisomers, follow the same steps that you have already practised for drawing structural formulas. The only difference is the position of the parts of the molecule on either side of the double bond.

1. Draw the parent chain or carbon ring from the last part of the compound name. Leave the bonds on either side of the double bond empty for now.
2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.
3. Draw the substituent groups on either side of the double bond according to whether the name includes *cis* or *trans*.
4. Add any substituents at the appropriate locations.

Sample Problem 2: Drawing Stereoisomers

Draw structural formulas for *cis*-1,2-dichloroethene and *trans*-1,2,-dichloroethene.

Solution

Step 1. Draw the parent chain or carbon ring from the last part of the compound name. Leave the bonds on either side of the double bond empty for now.

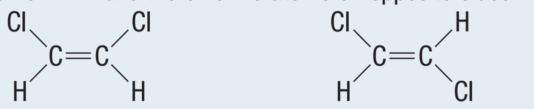
Ethene contains 2 carbon atoms with a double bond between them: C═C

Step 2. Identify the carbon atom where each of the multiple bonds (and substituents) is attached.

For ethene, the double bond can only be in one place: between the 2 carbon atoms.

Step 3. Draw the substituent groups on either side of the double bond according to whether the name includes *cis* or *trans*.

From the name of the compound, you know that it contains 2 chlorine atoms. You also know that each chlorine atom is bonded to a different carbon atom. Therefore, add 2 chlorine atoms: 1 on each of the carbon atoms. The *cis* isomer will have the chlorine atoms on the same side of the double bond; the *trans* isomer will have the chlorine atoms on opposite sides:

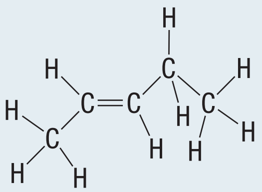
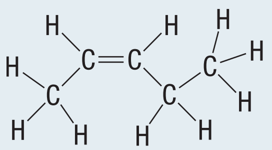


cis-1,2-dichloroethene   *trans*-1,2-dichloroethene

Step 4. Add any substituents at the appropriate locations.

In this case, there are no other substituents to add.

Practice

1. Draw the *cis* and *trans* isomers of the following compounds: K/U C
   (a) hex-3-ene
   (b) 1-bromoprop-1-ene
2. Name each of the following compounds: K/U
   (a)
   
   (b)
   
3. Draw the structural formulas and write the names of the two stereoisomers of 2,4-dimethylhex-3-ene. K/U C

LEARNING TIP

Remembering *Cis* and *Trans*

To use *cis* and *trans* correctly, you could think of *cis* as being like sisters: side by side. And *trans* means "across," as in transatlantic.

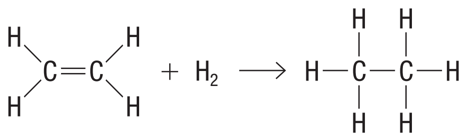
Reactions of Alkenes and Alkynes

A **functional group** is a specific group of atoms within a molecule that affects the properties of the compound, such as solubility, melting point, boiling point, and chemical reactivity with other elements or compounds. Multiple bonds are considered to be functional groups because they affect the properties of the molecules that contain them. For example, alkenes and alkynes are more reactive than alkanes. The double-bonded and triple-bonded carbon atoms are more likely to take part in reactions because the multiple bonds are less stable than single bonds between carbon atoms.

functional group a group of atoms within a molecule that determines the properties of the molecule

One common type of reaction that alkenes and alkynes undergo is an addition reaction. In an **addition reaction** two molecules react to form one. The multiple bonds in alkenes and alkynes enable the organic molecules to react with hydrogen. The addition of hydrogen is a type of addition reaction known as hydrogenation, and results in the hydrocarbon becoming saturated (**Figure 7**).

addition reaction a reaction in which the atoms from one molecule are added to another molecule to form a single molecule



ethene (unsaturated)   ethane (saturated)

Figure 7 An unsaturated molecule of ethene becomes saturated by the addition of a hydrogen atom on either side of the double bond. A molecule of ethane is formed.

Hydrogenation reactions, in which hydrogen atoms are added on either side of a multiple bond, can occur with alkenes, alkynes, or cyclic alkenes (**Figure 8**).

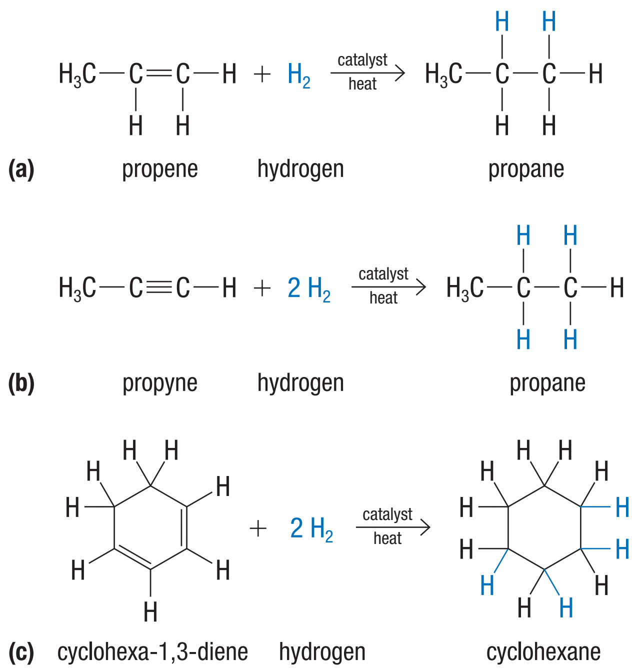


Figure 8 Hydrogenation reactions for alkenes and alkynes in the presence of heat and a catalyst. (a) Propene reacts with hydrogen to form propane. (b) Propyne reacts with two moles of hydrogen per mole of propyne to form propane. (c) Cyclohexa-1,3-diene reacts with hydrogen to form cyclohexane.

The alkene (or alkyne) gains atoms from the reacting molecule but does not lose any atoms. Addition reactions may also occur with halogens, hydrogen halides such as hydrogen chloride, and water.

In a halogenation reaction, a halogen such as bromine or chlorine reacts with an alkene or alkyne (**Figure 9**). The halogenation of an alkene produces an alkyl halide. The halogenation of an alkyne produces a halogenated alkene or, if excess halogen is present, an alkyl halide. A hydrogen halide such as hydrogen chloride or hydrogen bromide may also react with an alkene or alkyne. This reaction is called a hydro-halogenation reaction. The resulting compound includes both the halogen and the hydrogen atoms and may be a halogenated alkene or an alkyl halide.

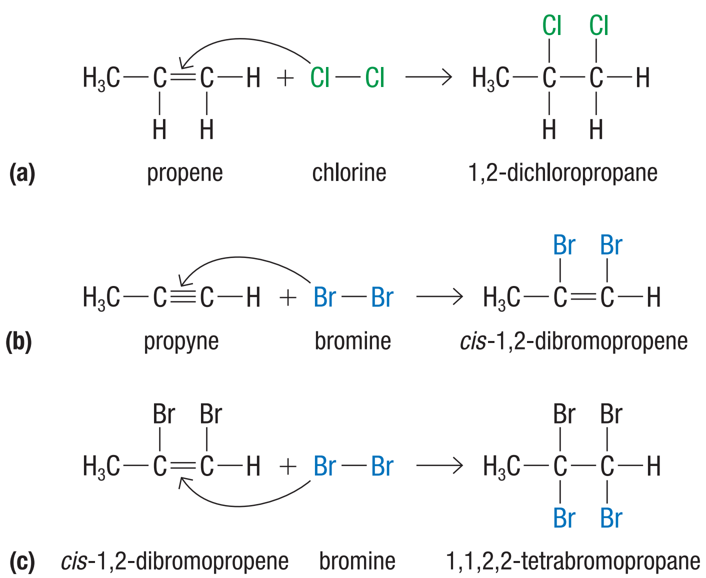


Figure 9 Halogenation reactions for alkenes and alkynes.

In a hydration reaction (**Figure 10**), water reacts with an unsaturated hydrocarbon. This reaction produces a type of organic compound that contains a hydroxyl group (−OH). This compound is called an alcohol.

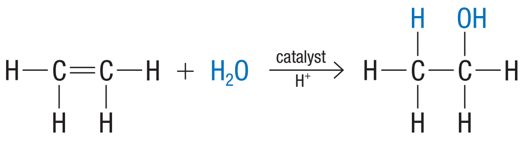


Figure 10 In this hydration reaction, ethene reacts with water in the presence of a catalyst and acid to form ethanol.

Look again at Figures 8 and 9. In all of these reactions, the substance that is added to the hydrocarbon (H_2, Cl_2, or Br_2) is made up of 2 identical atoms. Therefore, only one possible product can form in each case. For example, you could switch the positions of the 2 chlorine atoms in 1,2-dichloropropane (Figure 9(a)), but the product would be the same substance. In contrast, hydration reactions (Figure 10) and hydrohalogenation reactions add 2 non-identical atoms to the multiple bond. Therefore, more than one product is possible (**Figure 11**).

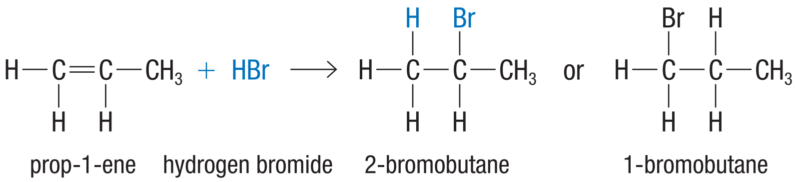


Figure 11 When a hydrogen halide reacts with an alkene, two different products are possible.

How can we predict which product will be formed? **Markovnikov's rule** provides guidance on how the atoms will be added to the double bond. Markovnikov's rule is as follows:

Markovnikov's rule the rule for predicting the products of addition reactions: when a hydrogen halide or water is added to an alkene, the hydrogen atom generally bonds to the carbon atom within the double bond that already has more hydrogen atoms bonded to it

> When a hydrogen halide or water molecule reacts with an alkene, the hydrogen atom will generally bond to the carbon atom in the multiple bond that has the most hydrogen atoms already bonded to it.

Markovnikov's rule applies to hydrohalogenation of both straight-chain and cyclic hydrocarbons (**Figure 12**). It also applies to hydration reactions.

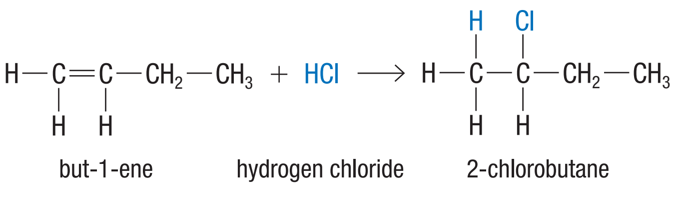


Figure 12 According to Markovnikov's rule, the hydrogen atom from the hydrogen chloride molecule bonds to the carbon atom that has the most hydrogen atoms already attached to it.

Despite Markovnikov's rule, small quantities of the other product will be produced. If both of the carbon atoms have the same number of hydrogen atoms, an equal mixture of products will result.

Sometimes a chemist may need to perform a hydrohalogenation or hydration reaction in which the hydrogen atom is added to the carbon atom that has the fewest hydrogen atoms already bonded to it. Therefore, chemists have developed strategies to overcome Markovnikov's rule. They can use catalysts or other reaction conditions to change the expected outcome of a reaction. CAREER LINK

Tutorial 3 Predicting Products of Addition Reactions

You can use the familiar skills of writing and balancing chemical equations, along with strategies for naming organic compounds, to predict the main products of addition reactions. Remember to look carefully at the multiple bonds in the organic reactant, and consider Markovnikov's rule to establish where each atom will be placed in the product molecule.

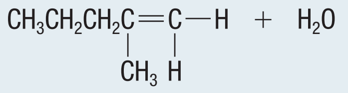
Sample Problem 1: Applying Markovnikov's Rule

Predict the major product of a hydration reaction of 2-methylpent-1-ene.

Solution

Step 1. Draw the substances involved in the reaction.

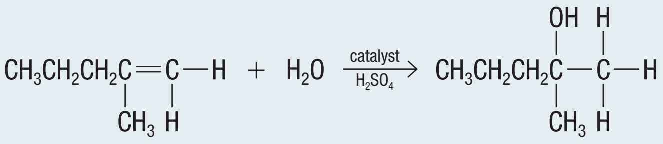
You will likely find it helpful to draw the structural formula for the organic reactant. Recall that a hydration reaction involves the addition of water to an unsaturated hydrocarbon.



2-methylpent-1-ene water

Step 2. Determine where the added entities will attach.

During the reaction, the water molecule splits into a hydrogen atom and a hydroxyl group (—OH). These two entities will be added to the carbon atoms on either side of the double bond in the organic molecule. According to Markovnikov's rule, the hydrogen atom will be added to the carbon atom that already has the most hydrogen atoms bonded to it. ("The rich get richer!") Therefore, the hydrogen atom will bond to carbon 1, and the hydroxyl group will bond to carbon 2.



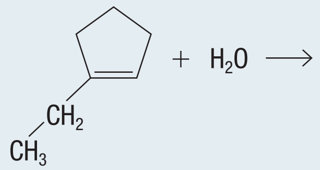
2-methylpent-1-ene water 2-hydroxy-2-methylpentane

Step 3. Name the product.

The major product of the reaction is 2-hydroxy-2-methylpentane.

Practice

1. Draw the structural formula and write the name of the major product in the reaction of 3-methylbut-1-ene and hydrogen chloride. T/I C
2. Predict the major product of the reaction involving the following reactants. (You can ignore the fact that a catalyst is required for this reaction.) T/I C

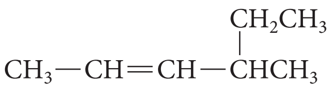
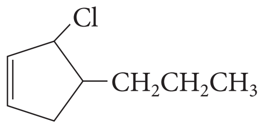
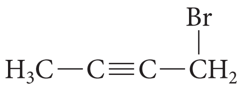
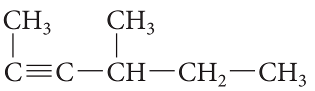
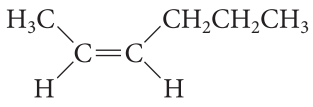
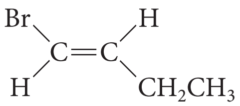


1.2 Review

Summary

- An alkene is a hydrocarbon that has at least one double bond between 2 carbon atoms. The carbon chain is numbered using the lowest number for the double bond. The root name ends in *-ene*.
- An alkyne is a hydrocarbon that has at least one triple bond between 2 carbon atoms. Naming alkynes is similar to naming alkenes. The root name ends in *-yne*.
- *Cis* and *trans* isomers are compounds that are identical except for the position of groups on either side of a double bond. In *cis* isomers, the groups are located on the same side of the double bond. In *trans* isomers, the groups are located on opposite sides of the double bond.
- Hydrocarbons with multiple bonds are more reactive than alkanes and participate in addition reactions in which atoms from one molecule are added to another molecule. Addition reactions include hydrogenation, halogenation, hydrohalogenation, and hydration.
- Markovnikov's rule states that, when two non-identical entities are added at a double bond, the major product will be formed by the hydrogen atom bonding to the carbon atom with more hydrogen atoms attached.

Questions

1. Create a flow chart to summarize the naming of alkenes and alkynes. K/U C
2. Classify each of the following compounds as an alkane, an alkene, or an alkyne. Explain your reasoning. K/U
   (a) $CH_3CH_2CHCHCH_3$
   (b) $CH_2CHCH_2CH_3$
   (c) $CHCCH_2CCH$
3. Name each of the following alkenes. (Ignore *cis–trans* isomerism for now.) K/U T/I
   (a) $CH_2{=}CH{-}CH_2{-}CH_3$
   (b) 
   (c) 
4. Draw the structure of each of the following compounds: T/I C
   (a) 2,5-dimethylhept-3-ene
   (b) 3-bromopropyne
5. Name each of the following alkynes: K/U T/I
   (a) 
   (b) 
6. Describe how you would identify whether a compound is a *cis* isomer or a *trans* isomer. K/U T/I
7. Name each of the following compounds. Use *cis–trans* conventions. K/U T/I
   (a) 
   (b) 
8. There is only one compound that is named 1,2-dichloroethane, but there are two distinct compounds that can be named 1,2-dichloroethene. Why? K/U
9. Write chemical equations, using condensed structural formulas, to represent the addition reactions that produce the following compounds. Include the names of the reactants. T/I A
   (a) 2,3-dichlorobutane
   (b) 3-bromohexane
10. Predict the product(s) of the reaction that occurs when the following reactants are combined: T/I A
   (a) pent-1-ene reacts with water and a catalyst.
   (b) Chlorine gas is bubbled through 3-methylcyclohexene.