Al-Rasheed University College
Department of Dentistry
1st Stage

MEDICAL CHEMISTRY

lecture 7
Unsaturated and Aromatic Hydrocarbons

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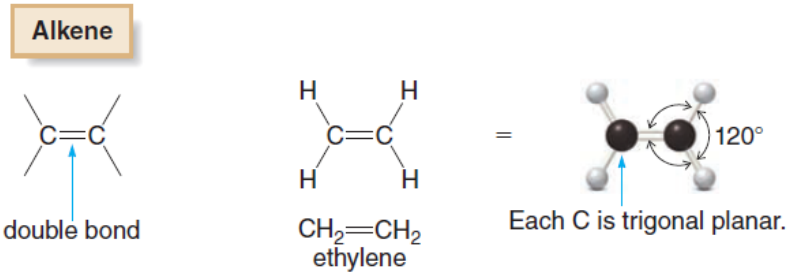
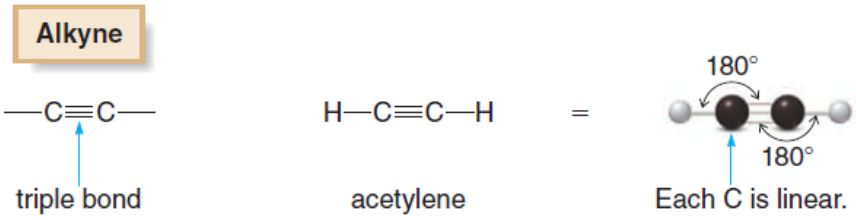
Introduction

we continue our study of hydrocarbons by examining three families of compounds that contain carbon–carbon multiple bonds. ***Alkenes*** contain a double bond and ***alkynes*** contain a triple bond. ***Aromatic hydrocarbons*** contain a benzene ring, a six- membered ring with three double bonds. These compounds differ from the ***alkanes*** because they each have a functional group, making them much more reactive. Thousands of biologically active molecules contain these functional groups, and many useful synthetic products result from their reactions.

- **Alkanes** are called saturated hydrocarbons, because they contain the maximum number of hydrogen atoms per carbon. In contrast, **alkenes and alkynes** are called unsaturated hydrocarbons.
- **Unsaturated hydrocarbons** are compounds that contain fewer than the maximum number of hydrogen atoms per carbon (or contain double or triple bond).
- **Alkenes and alkynes** are two families of organic molecules that contain multiple bonds.
- **Alkenes** are compounds that contain a carbon–carbon double bond.
- The general molecular formula of an alkene is C_nH_{2n}, so an alkene has **two fewer** hydrogens than an alkane.

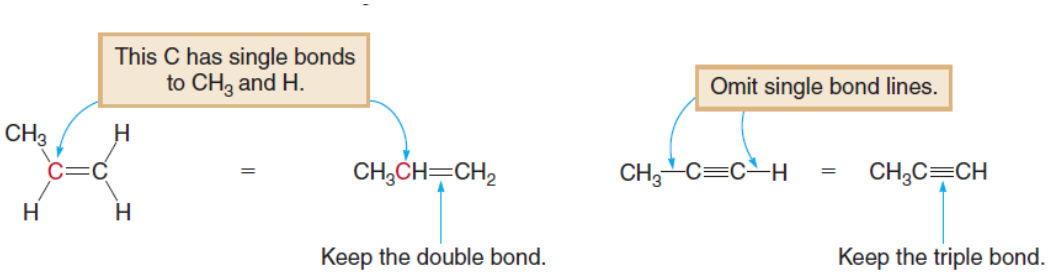


- **Alkynes** are compounds that contain a carbon–carbon triple bond.
- The general molecular formula for an alkyne is C_nH_{2n-2}, so an alkyne has **four fewer** hydrogens than an acyclic alkane.



- Because alkenes and alkynes are composed of nonpolar carbon–carbon and carbon–hydrogen bonds, their physical properties are similar to other hydrocarbons. Like alkanes.
- ***Alkenes and alkynes*** *have low melting points and boiling points and are insoluble in water.*

The multiple bonds of an alkene or alkyne is always drawn in a condensed structure. To translate a condensed structure to a complete structure with all bond lines drawn in, make sure that each carbon of a double bond has three atoms around it, and each carbon of a triple bond has two atoms around it.



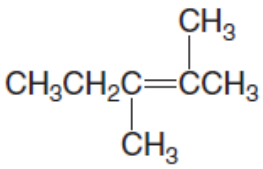
Nomenclature of Alkenes and Alkynes

Whenever we encounter a new functional group, we must learn how to use the IUPAC system to name it. In the IUPAC system:

- ☒ *An alkene is identified by the suffix -ene.*
- ☒ *An alkyne is identified by the suffix -yne.*

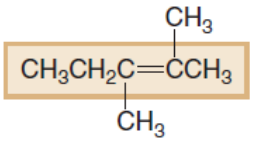
- A few simple alkenes and alkynes have names that do not follow the IUPAC system. The simplest alkene, $CH_2=CH_2$, is called ethene in the IUPAC system, but it is commonly called ethylene.
- The simplest alkyne, HC≡CH, is called ethyne in the IUPAC system, but it is commonly named acetylene. We will use these common names since they are more widely used than their systematic IUPAC names.

Problem: Give the IUPAC name for the following compound.



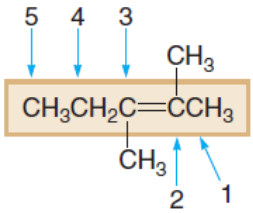
Analysis and Solution

[1] Find the longest chain containing both carbon atoms of the multiple bond.



5 C's in the longest chain ⟶ **pentene**

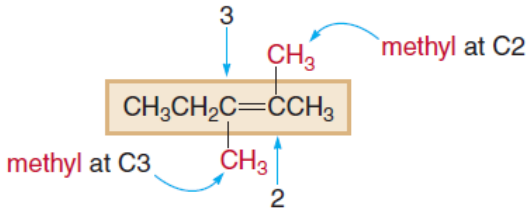
[2] Number the chain to give the double bond the lower number.



- Numbering from right to left is preferred since the double bond begins at C2 (not C3). The molecule is named as a **2-pentene.**

[3] Name and number the substituents and write the complete name.

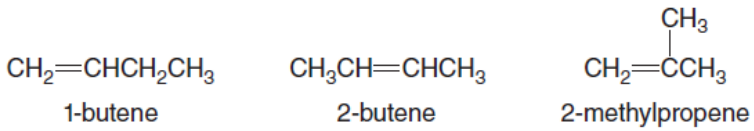
- The alkene has two methyl groups located at C2 and C3. Use the prefix di- before methyl → 2,3-**dimethyl**.



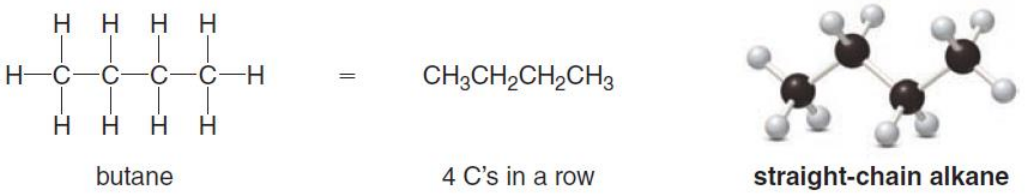
Answer: 2,3-dimethyl-2-pentene

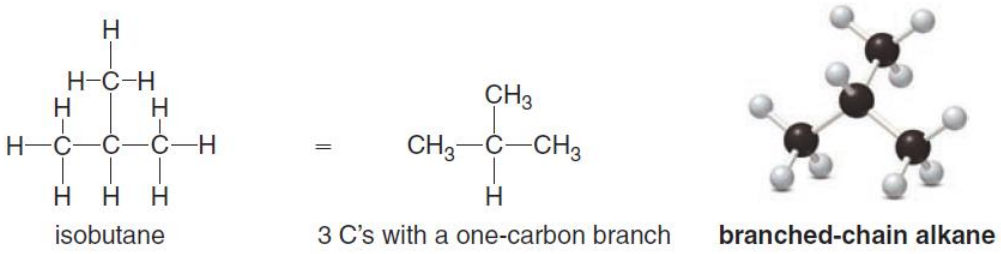
Isomerism and Stereoisomers

As we learned in previous lecture on alkanes, constitutional isomers are possible for alkenes of a given molecular formula. For example, there are three constitutional isomers for an alkene of molecular formula C_4H_8….1-butene, 2-butene, and 2-methylpropene.



- **Isomers** are two different compounds with the same molecular formula.



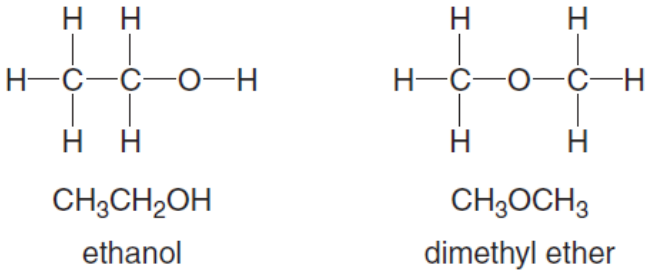


- *They are two major classes of isomers:*

- ✓ **Constitutional isomers**: differ in the way the atoms are connected to each other.
- ✓ **Stereoisomer**: are isomers that differ only in the 3D arrangement of atoms.

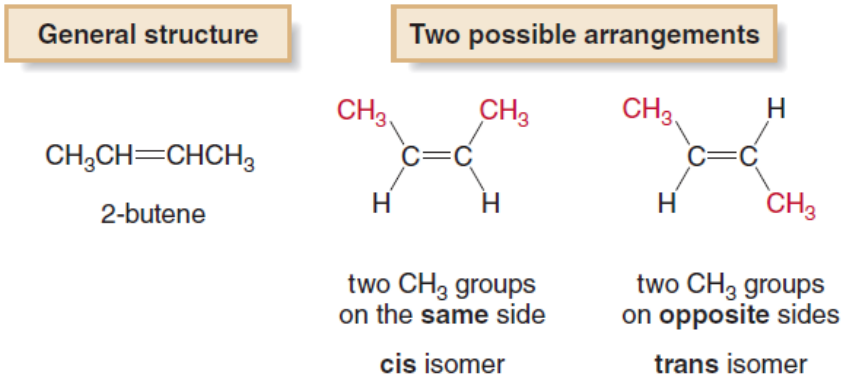
1. **Constitutional isomers** like butane and isobutane belong to the same family of compounds: they are both alkanes.

✓ Ethanol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3) are constitutional isomers with different functional groups: CH_3CH_2OH is an alcohol and CH_3OCH_3 is an ether.



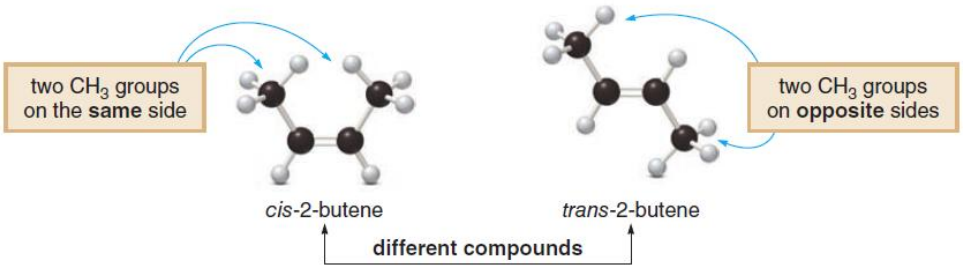
2. **Stereoisomers:**

- 2-Butene illustrates another important aspect about alkenes. There is restricted rotation around the carbon atoms of a double bond. As a result, the groups on one side of the double bond cannot rotate to the other side.
- With 2-butene, there are two ways to arrange the atoms on the double bond. The two CH_3 groups can be on the same side of the double bond or they can be on opposite sides of the double bond. These molecules are different compounds with the same molecular formula; that is, they are isomers.



- When the two CH_3 groups are on the same side of the double bond, the compound is called the ***cis isomer***.
- When the two CH_3 groups are on opposite sides of the double bond, the compound is called the ***trans isomer***.

☒ Thus, one isomer of 2-butene is called cis-2-butene, and the other isomer is called trans-2-butene.

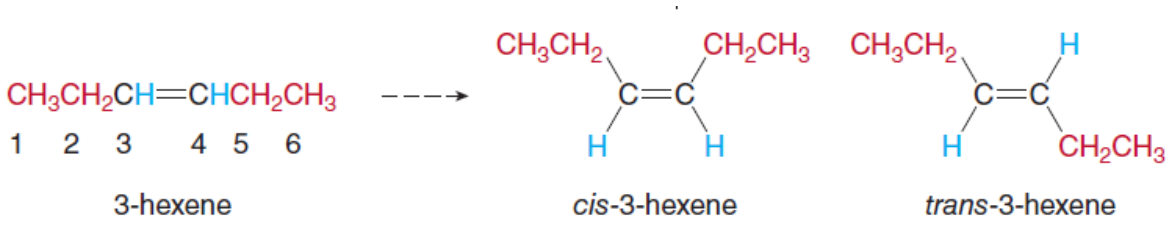


☒ The cis and trans isomers of 2-butene are a specific example of a general class of isomer that occurs at carbon–carbon double bonds. Whenever the two groups on each end of a C=C are different from each other, two isomers are possible.

☒ Cis and trans compounds are isomers, but they are not constitutional isomers. Each carbon atom of cis- and trans-2-butene is bonded to the same atoms. The only difference is the three-dimensional arrangement of the groups around the double bond. Isomers of this sort are called ***stereoisomers***.

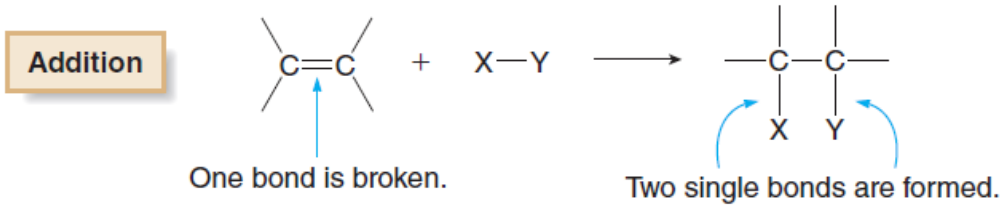
Problem: Draw cis- and trans-3-hexene.

Each C of the double bond is bonded to a CH_3CH_2 group and a hydrogen. A cis isomer has the CH_3CH_2 groups bonded to the same side of the double bond. A trans isomer has the two CH_3CH_2 groups bonded to the opposite sides of the double bond.



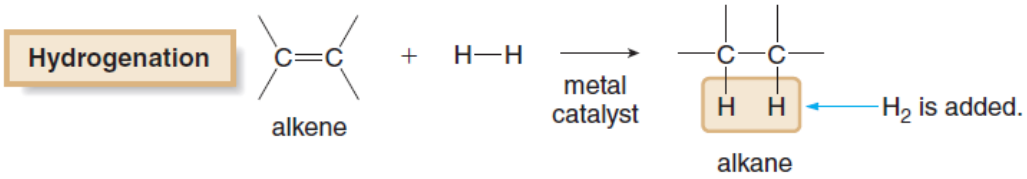
Reactions of Alkenes

- Most families of organic compounds undergo a characteristic type of reaction. Alkenes undergo addition reactions. In an **addition reaction**, new groups X and Y are added to a starting material. One bond of the double bond is broken and two new single bonds are formed.
- Addition reaction is a reaction in which elements are added to a compound.
- **Why does addition occur?**
  - A double bond is composed of one strong bond and one weak bond. In an addition reaction, the weak bond is broken and two new strong single bonds are formed.

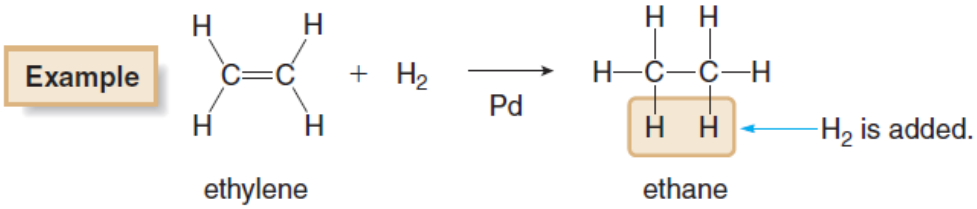


1. Addition of Hydrogen—Hydrogenation

Hydrogenation is the addition of hydrogen (H_2) to an alkene. Two bonds are broken: one bond of the carbon–carbon double bond and the H-H bond—and two new C-H bonds are formed.

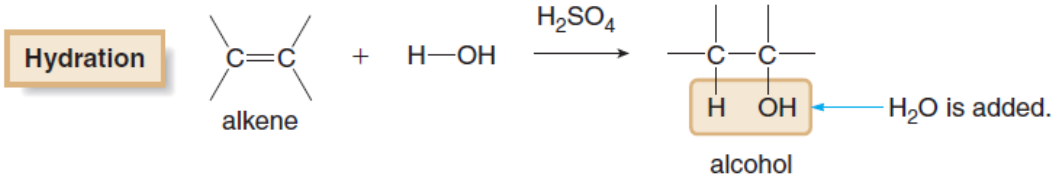


The addition of H_2 occurs only in the presence of a metal catalyst such as palladium (Pd). The metal provides a surface that binds both the alkene and H_2, and this speed up the rate of reaction. Hydrogenation of an alkene forms an ***alkane*** since the product has only C-C single bonds.

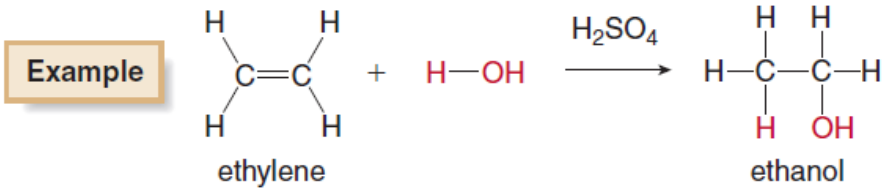


2. Addition of Water—Hydration

Hydration is the addition of water to an alkene. Two bonds are broken—one bond of the carbon–carbon double bond and the H-OH bond—and new C-H and C-OH bonds are formed.

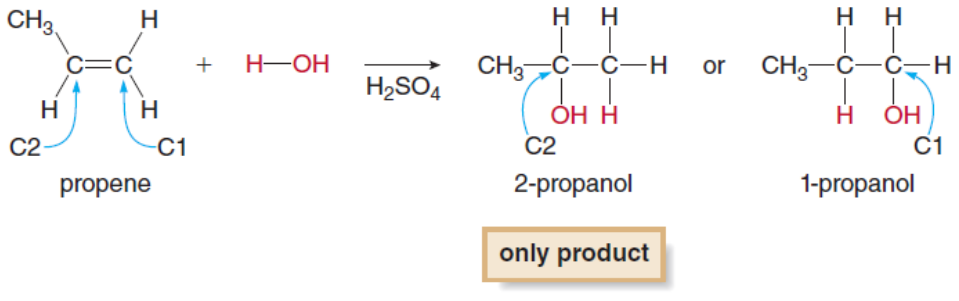


- **Hydration** occurs only if a **strong acid** such as **H_2SO_4** is added to the reaction mixture. The product of hydration is an ***alcohol***.



Ethanol is used as a solvent in many reactions in the laboratory. Ethanol is also used as a gasoline additive because, like ***alkanes***, it burns in the presence of oxygen to form CO_2 and H_2O with the release of a great deal of energy. Although ethanol can also be formed by the fermentation of carbohydrates in grains and potatoes, much of the ethanol currently used in gasoline and solvent comes from the hydration of ethylene.

- There is one important difference in this addition reaction compared to the addition of H_2. In this case, addition puts different groups-H and OH-on the two carbons of the double bond. As a result, *H_2O can add to the double bond to give two **constitutional isomers** when an **unsymmetrical alkene** is used as starting material.*

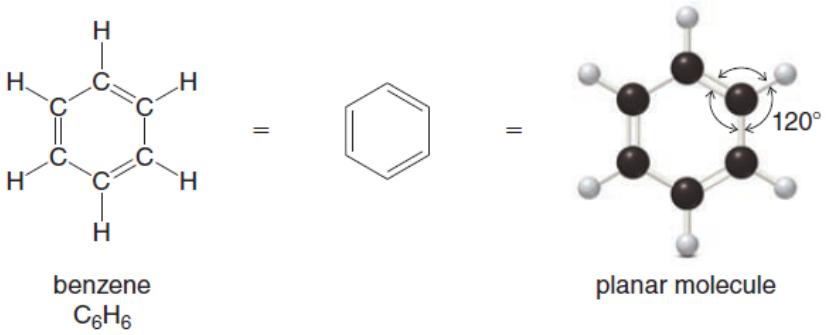


For example, the addition of H_2O to propene could in theory form two products. If H adds to the end carbon (labeled C1) and OH adds to the middle carbon (C2), ***2-propanol*** is formed. If OH adds to the end carbon (C1) and H adds to the middle carbon (C2), ***1-propanol*** is formed. In fact, addition forms only 2-propanol. This is a specific example of a general trend.

- This is specific example of a general trend called **Markovnikov's rule**
- In the addition of H_2O to an unsymmetrical alkene, the H atom bonds to the less substituted carbon atom—that is, the carbon that has more H's to begin with.

Aromatic Compounds

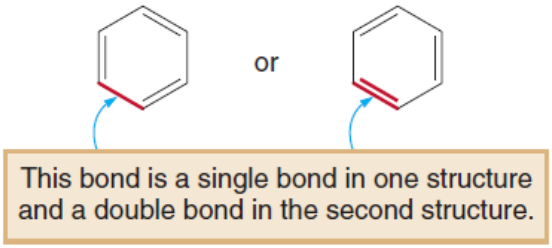
- **Aromatic compounds** represent another example of unsaturated hydrocarbons. Aromatic compounds were originally named because many simple compounds in this family have characteristic odors. Today, the word **aromatic refers to compounds that contain a benzene ring**, or **rings that react in a similar fashion to benzene**.
- **Benzene**, the simplest and most widely known aromatic compound, contains a six-membered ring and three double bonds. Since each carbon of the ring is also bonded to a hydrogen atom, the molecular formula for benzene is C_6H_6.



benzene
C_6H_6

planar molecule

Although benzene is drawn with a six-membered ring and three double bonds, there are two different ways to arrange the double bonds so that they alternate with single bonds around the ring. Each of these representations is equivalent.

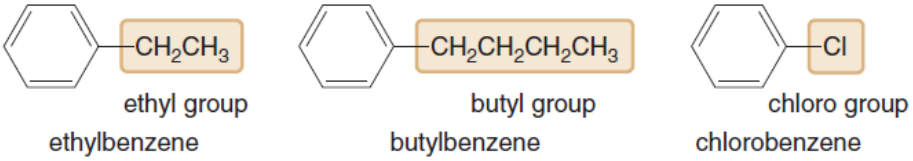


The physical properties of aromatic hydrocarbons are similar to other hydrocarbons—they have low melting points and boiling points and are water insoluble.

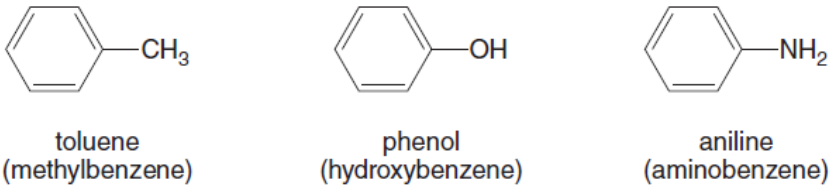
Nomenclature of Benzene Derivatives

Many organic molecules contain a benzene ring with one or more substituents, so we must learn how to name them.

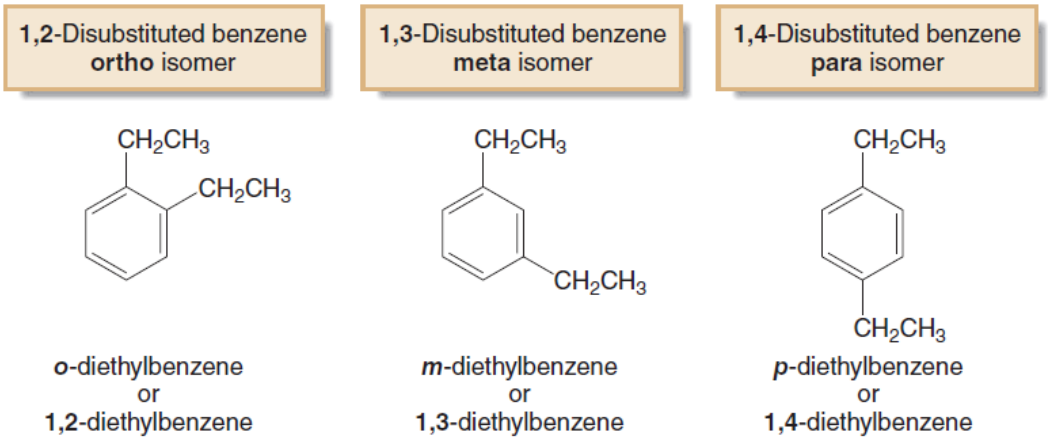
To name a benzene ring with one substituent, name the substituent and add the word benzene. Carbon substituents are named as alkyl groups. When a halogen is a substituent, name the halogen by changing the -ine ending of the name of the halogen to the suffix -o; for example, chlorine → chloro.



Many monosubstituted benzenes, such as those with methyl (CH_3–), hydroxyl (–OH), and amino ($–NH_2$) groups, have common names that you must learn, too.



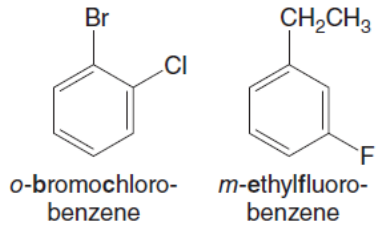
To name a benzene ring with two substituent, there are three different ways that two groups can be attached to a benzene ring, so a prefix— ***ortho***, ***meta***, or ***para***—is used to designate the relative position of the two substituents. Ortho, meta, and para are generally abbreviated as ***o***, ***m***, and ***p***, respectively.



If the two groups on the benzene ring are different, ***alphabetize the name of the substituents*** preceding the word benzene. If one of the substituents is part of

a ***common root***, name the ***molecule as a derivative of that monosubstituted benzene***.

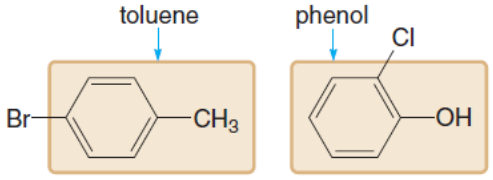
Alphabetize two different substituent names:



o-bromochloro-benzene

m-ethylfluoro-benzene

Use a common root name:

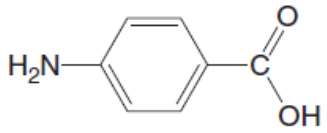


p-bromo**toluene**

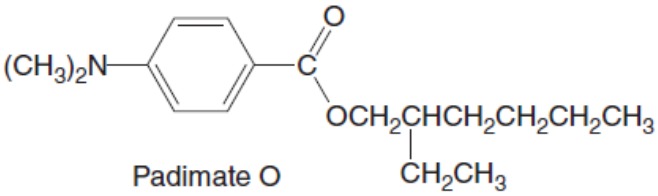
o-chloro**phenol**

Sunscreens
(FOCUS ON HEALTH & MEDICINE)

- All commercially available sunscreens contain a benzene ring. A sunscreen absorbs ultraviolet radiation and thus shields the skin for a time from its harmful effects. Two sunscreens that have been used for this purpose are **p-aminobenzoic acid (PABA)** and **Padimate O**.



p-aminobenzoic acid (PABA)



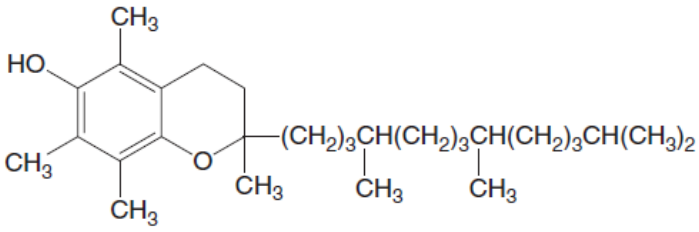
Padimate O

Phenols as Antioxidants
(FOCUS ON HEALTH & MEDICINE)

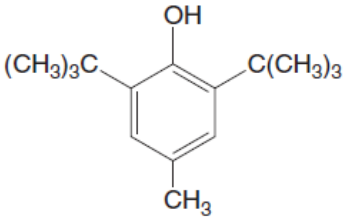
- A wide variety of **phenols**, compounds that contain a **hydroxyl group** bonded to a **benzene ring**, occur in nature. **Vanillin** from the vanilla bean is a phenol, as is **curcumin**, a yellow pigment isolated from turmeric.
- Many **phenols are antioxidants**, compounds that prevent unwanted oxidation reactions from occurring. Two examples are naturally occurring **vitamin E** and **synthetic BHT**. The OH group on the benzene ring is the key functional group that prevents oxidation reactions from taking place.
- Vitamin E is a natural antioxidant found in fish oil, peanut oil, wheat germ, and leafy greens. Although the molecular details of its function remain obscure, it is thought that vitamin E prevents the unwanted oxidation of

unsaturated fatty acid residues in cell membranes. In this way, vitamin E helps retard the aging process.

- Synthetic antioxidants such as BHT—butylated hydroxy toluene—are added to packaged and prepared foods to prevent oxidation and spoilage. BHT is a common additive in breakfast cereals.

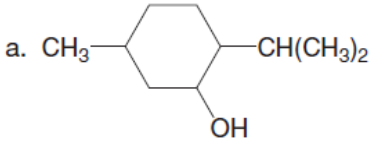


vitamin E



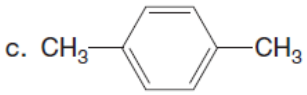
BHT
(butylated hydroxy toluene)

Problem: Which of the following compounds might be antioxidants?



menthol

b. curcumin



p-xylene
(gasoline additive)