Chapter Outline

6. Organic Chemistry 2.

6.1 Alkenes and Alkynes

6.1.1 Introduction

6.1.2 Nomenclature of Alkenes and Alkynes

6.1.3 Cis and trans isomers

6.1.4 Reactions of Alkene and Alkynes

6.2Aromatic Compounds

Chapter 6 Instructional Goals

In this chapter you will learn how to:

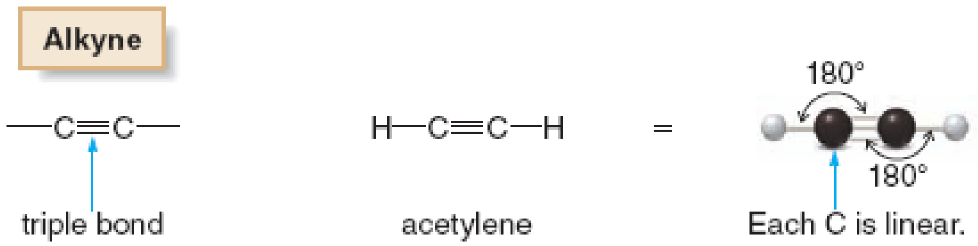
❶ Identify the three major types of unsaturated hydrocarbons- alkenes, alkynes, and aromatic compounds

❷ Name alkenes, alkynes, and substituted benzenes

❸ Recognize the difference between constitutional isomers and stereoisomers, as well as identify cis and trans isomers

❹ Draw the products of addition reactions of alkenes

❺ Explain the structure of benzene



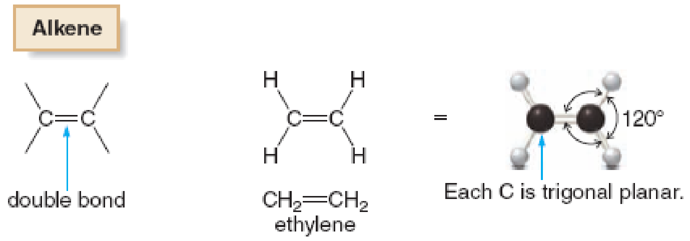
6- Unsaturated Hydrocarbons

6.1 Alkenes and Alkynes

6.1.1 Introduction

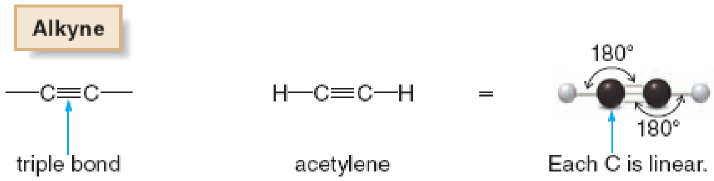
Alkenes and alkynes are two families of organic molecules that contain multiple bonds.

☝ **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 acyclic alkane, which has a general molecular formula of C_nH_{2n+2}. Ethylene (C_2H_4) is the simplest alkene. Since each carbon of ethylene is surrounded by three atoms, each carbon is **trigonal planar.** All six atoms of ethylene lie in the same plane, and all bond angles are **120°.**

☝ **Alkynes are compounds that contain a carbon–carbon triple bond.**



The general molecular formula for an alkyne is **$CnH2n - 2$,** so an alkyne has **four** fewer hydrogens than an acyclic alkane. Acetylene ($C2H2$) is the simplest alkyne. Each carbon of acetylene is surrounded by two atoms, making each carbon **linear** with bond angles of **180°.** 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.**

Those acyclic 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.**

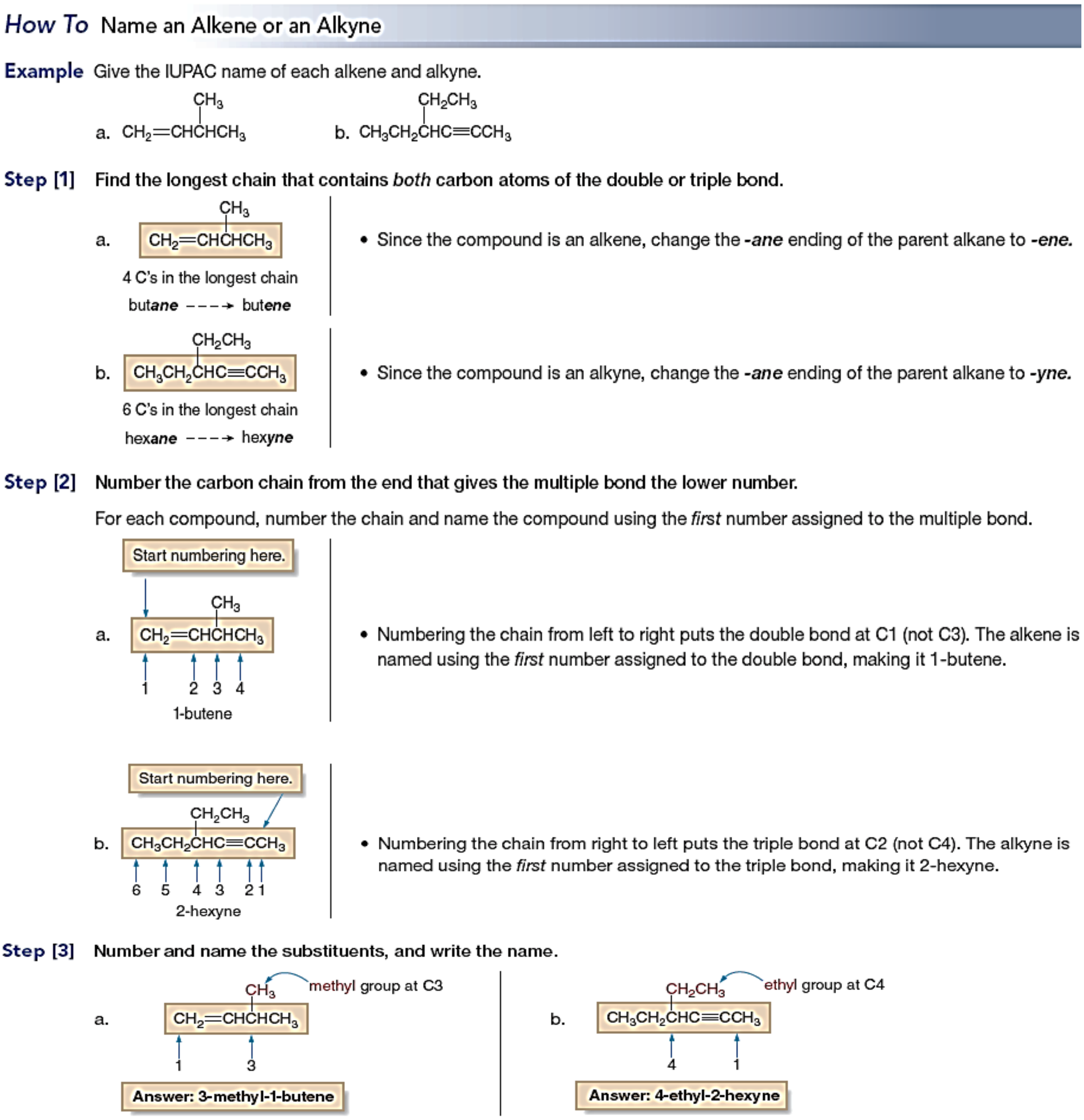
- **Unsaturated hydrocarbons are compounds that contain fewer than the maximum number of hydrogen atoms per carbon.**

6. 1.2 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.***



How To Name an Alkene or an Alkyne

Example Give the IUPAC name of each alkene and alkyne.

a. $CH_2{=}CH\overset{CH_3}{C}HCH_3$ b. $CH_3CH_2\overset{CH_2CH_3}{C}HC{\equiv}CCH_3$

Step [1] **Find the longest chain that contains *both* carbon atoms of the double or triple bond.**

a. $CH_2{=}CH\overset{CH_3}{C}HCH_3$

4 C's in the longest chain

but*ane* ---→ but*ene*

- Since the compound is an alkene, change the ***-ane*** ending of the parent alkane to ***-ene.***

b. $CH_3CH_2\overset{CH_2CH_3}{C}HC{\equiv}CCH_3$

6 C's in the longest chain

hex*ane* ---→ hex*yne*

- Since the compound is an alkyne, change the ***-ane*** ending of the parent alkane to ***-yne.***

Step [2] **Number the carbon chain from the end that gives the multiple bond the lower number.**

For each compound, number the chain and name the compound using the *first* number assigned to the multiple bond.

Start numbering here.

a. $CH_2{=}CH\overset{CH_3}{C}HCH_3$

1 2 3 4

1-butene

- Numbering the chain from left to right puts the double bond at C1 (not C3). The alkene is named using the *first* number assigned to the double bond, making it 1-butene.

Start numbering here.

b. $CH_3CH_2\overset{CH_2CH_3}{C}HC{\equiv}CCH_3$

6 5 4 3 2 1

2-hexyne

- Numbering the chain from right to left puts the triple bond at C2 (not C4). The alkyne is named using the *first* number assigned to the triple bond, making it 2-hexyne.

Step [3] **Number and name the substituents, and write the name.**

a. $CH_2{=}CH\overset{CH_3}{C}HCH_3$ methyl group at C3

1 3

Answer: 3-methyl-1-butene

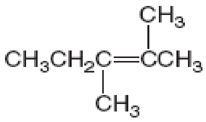
b. $CH_3CH_2\overset{CH_2CH_3}{C}HC{\equiv}CCH_3$ ethyl group at C4

4 1

Answer: 4-ethyl-2-hexyne

Example

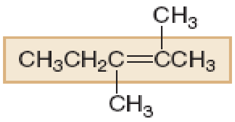
Give the IUPAC name for the following compound.



$$CH_3CH_2\underset{\displaystyle CH_3}{C}{=}\overset{\displaystyle CH_3}{C}CH_3$$

Analysis and Solution

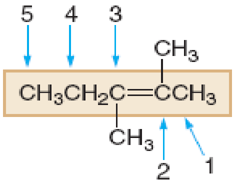
[1] Find the longest chain containing both carbon atoms of the multiple bond.



$$\boxed{CH_3CH_2\underset{\displaystyle CH_3}{C}{=}\overset{\displaystyle CH_3}{C}CH_3}$$

5 C's in the longest chain ---→ **pentene**

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

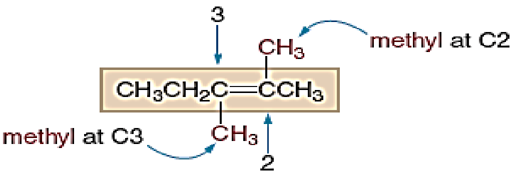


$$\boxed{CH_3CH_2\underset{\displaystyle CH_3}{C}{=}\overset{\displaystyle CH_3}{C}CH_3}$$

- 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-**di**methyl.

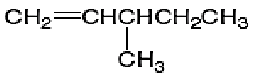


$$\boxed{CH_3CH_2\underset{\displaystyle CH_3}{C}{=}\overset{\displaystyle CH_3}{C}CH_3}$$

Answer: 2,3-dimethyl-2-pentene

PROBLEM

Give the IUPAC name for each alkene.

a. 

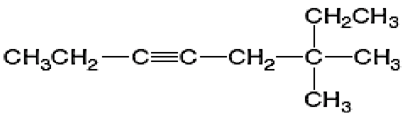
$CH_2{=}CH\underset{\displaystyle CH_3}{C}HCH_2CH_3$

b. $(CH_3CH_2)_2C{=}CHCH_2CH_2CH_3$

PROBLEM

Give the IUPAC name for each alkyne.

a. $CH_3CH_2CH_2CH_2CH_2C{\equiv}CCH(CH_3)_2$

b. 

$CH_3CH_2{-}C{\equiv}C{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_3}{C}}{-}CH_3$

PROBLEM

Give the structure corresponding to each name.

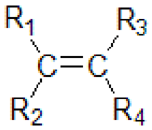
a. 4-methyl-1-hexene
b. 5-ethyl-2-methyl-2-heptene
c. 2,5-dimethyl-3-hexyne
d. 4-ethyl-1-decyne

6.1.3 Cis- and trans- isomers

If alkenes have **two different substituents** at each end of the C=C then they can exist as **stereoisomers** (as **geometric isomers**). This is because there is restricted rotation of the double bond due to the pi bond which means they don't readily interconvert. **Examples**:

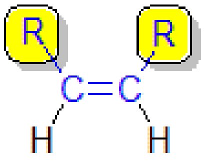
- All terminal alkenes *i.e*. those with a $C=CH_2$ unit **cannot** exist as *cis*- and *trans*- isomers.
- Similarly, all 1,1-symmetrically di-substituted alkenes *i.e*. those with a $C=CR_2$ unit **cannot** exist as *cis*- and *trans*- isomers.
- Alkenes with the R_1-CH=CH-R_2 unit **can** exist as *cis*- and *trans*- isomers.

If we consider the general alkene unit shown below, then the alkene **can exist as *cis* and *trans* isomers *only*** if R_1 is not equal to R_2 **and** R_3 is not equal to R_4.

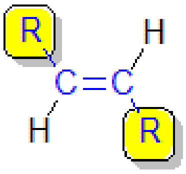


1,2-disubstituted alkenes are described as*:*

- *cis*- if the two alkyl groups, R-, are on the same side of the C=C
- *Trans*- if the two alkyl groups, R-, are on opposite sides of the C=C.
- These terms are inserted into the name as prefixes.



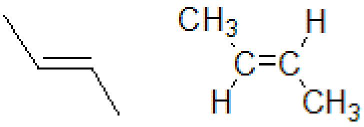
cis-



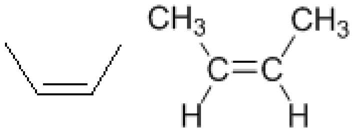
trans-

For example, but-2-ene, where both R = methyl :

***trans*-but-2-ene**



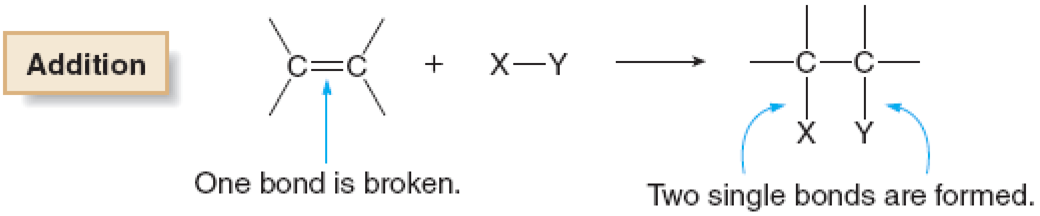
***cis*-but-2-ene**



6.1.4 Reactions of Alkenes and Alkynes

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 is a reaction in which elements are added to a compound.**



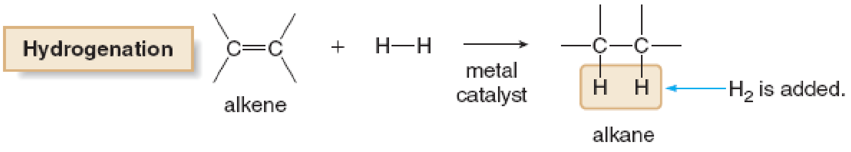
Why does addition occur?

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. For example, alkenes react with hydrogen (H_2, Section A) and water (H_2O,

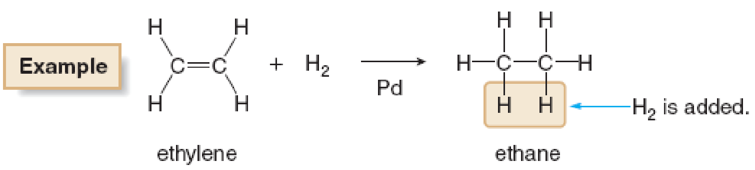
Section B). and Hydro-halide (HX, Section C)

A- 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.

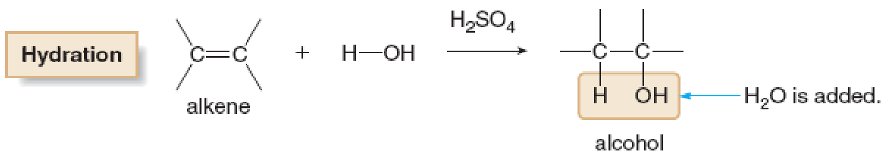


The addition of H_2 occurs only in the presence of a **metal catalyst** such as palladium (Pd). The metal provides a surface that binds both the alkene and H_2, and this speed up the rate of reaction. Hydrogenation of an alkene forms an **alkane** since the product has only C-C single bonds.

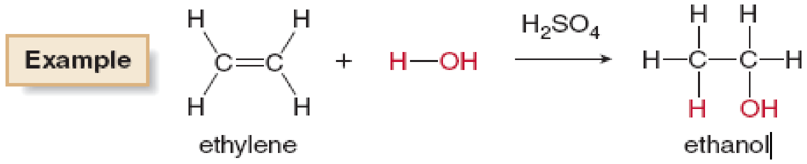


B- Addition of Water—Hydration

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.

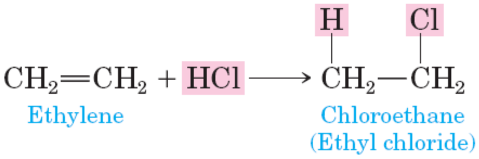


Hydration occurs only if a strong acid such as H_2SO_4 is added to the reaction mixture. The product of hydration is an **alcohol.** For example, hydration of ethylene forms ethanol.



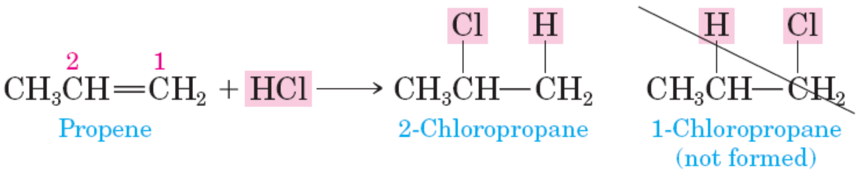
C- Addition of Hydrogen Halides (Hydro-halogenation)

Haloalkanes (alkyl halides) are formed when a hydrogen halide (HCl, HBr, and HI) is added to an alkene. Addition of HCl to ethylene, for example, gives chloromethane (ethyl chloride):



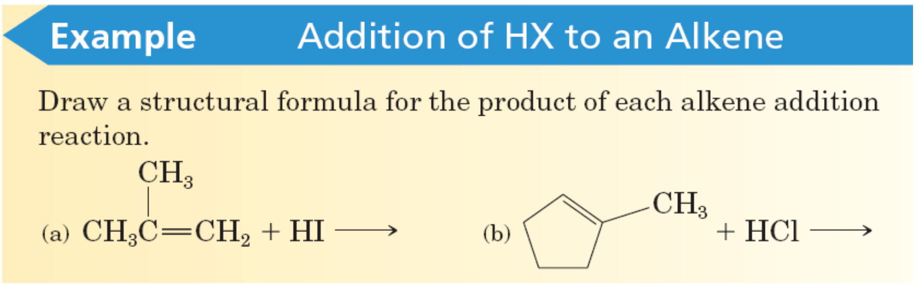
$$CH_2{=}CH_2 + HCl \longrightarrow \overset{H}{CH_2}{-}\overset{Cl}{CH_2}$$

Addition of HCl to propene gives 2-chloropropane (isopropyl chloride); hydrogen adds to carbon 1 of propene and chlorine adds to carbon 2. If the orientation of addition were reversed, 1-chloropropane (propyl chloride) would form. The observed result is that almost no 1-chloropropane forms. Because 2-chloropropane is the observed product, we say that addition of HCl to propene is **regio-selective**.



$$CH_3\overset{2}{C}H{=}\overset{1}{C}H_2 + HCl \longrightarrow CH_3\overset{Cl}{C}H{-}\overset{H}{CH_2} \quad \cancel{CH_3\overset{H}{C}H{-}\overset{Cl}{CH_2}}$$

This regio-selectivity was noted by Vladimir Markovnikov (1838–1904), who made the following generalization, known as **Markovnikov's rule**: In the addition of HX (where X =halogen) to an alkene, hydrogen adds to the double bonded carbon that already has the greater number of hydrogens bonded to it; halogen adds to the other carbon.

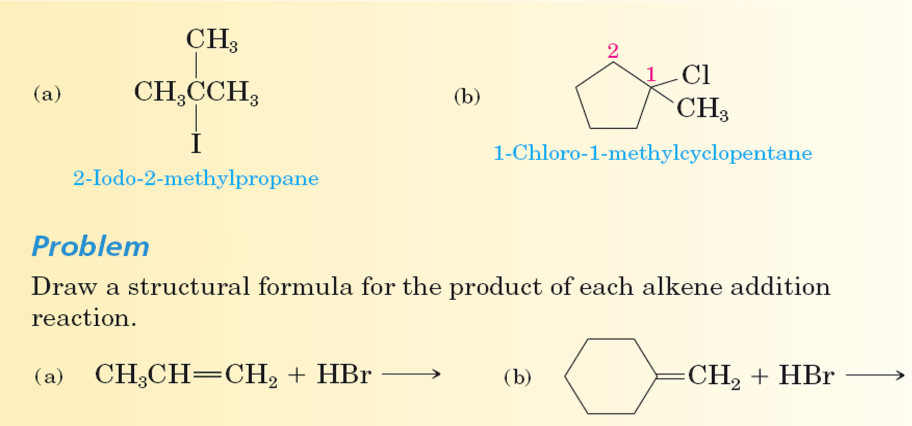


Example Addition of HX to an Alkene

Draw a structural formula for the product of each alkene addition reaction.

(a) $CH_3C(CH_3){=}CH_2 + HI \longrightarrow$

(b) + HCl ⟶



(a) $CH_3C(CH_3)(I)CH_3$

2-Iodo-2-methylpropane

(b) 1-Chloro-1-methylcyclopentane

Problem

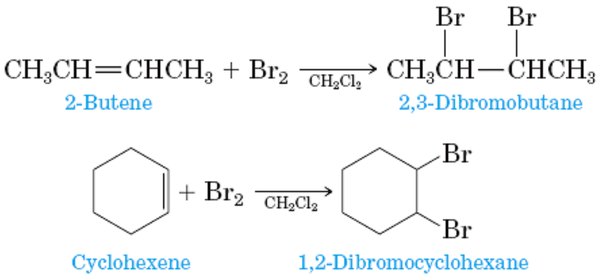
Draw a structural formula for the product of each alkene addition reaction.

(a) $CH_3CH{=}CH_2 + HBr \longrightarrow$

(b) $=CH_2 + HBr \longrightarrow$

D- Addition of Bromine and Chlorine (Halogenation)

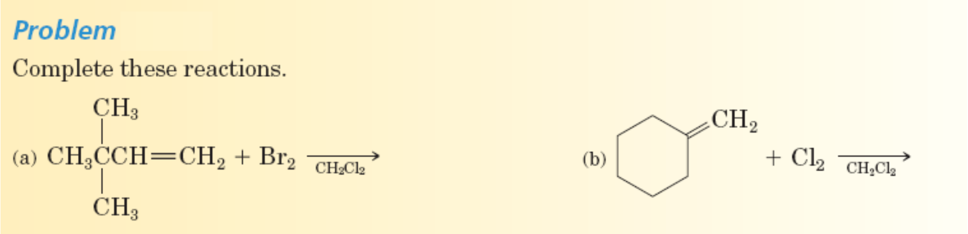
Chlorine, Cl_2, and bromine, Br_2, react with alkenes at room temperature by addition of halogen atoms to the carbon atoms of the double bond. This reaction is generally carried out by mixing the pure reagents together or by mixing them in an inert solvent such as dichloromethane, CH_2Cl_2.



$CH_3CH{=}CHCH_3 + Br_2 \xrightarrow{CH_2Cl_2} CH_3CH(Br)CH(Br)CH_3$

2-Butene 2,3-Dibromobutane

Cyclohexene 1,2-Dibromocyclohexane



Problem

Complete these reactions.

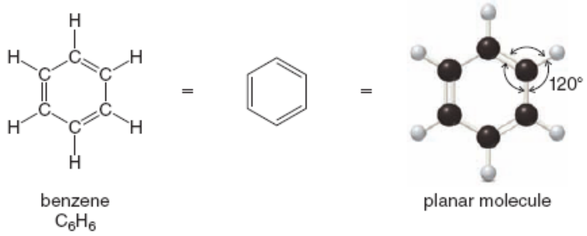
(a) $CH_3C(CH_3)_2CH{=}CH_2 + Br_2 \xrightarrow{CH_2Cl_2}$

(b) $+ Cl_2 \xrightarrow{CH_2Cl_2}$

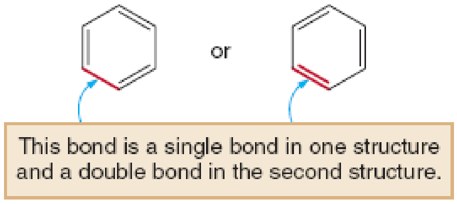
6.2 Aromatic Compounds

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. Each carbon is surrounded by three groups, making it trigonal planar. Thus, **benzene is a planar molecule,** and all bond angles are **120°.**



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.



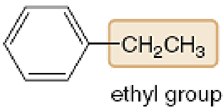
The physical properties of aromatic hydrocarbons are similar to other hydrocarbons they have low melting points and boiling points and are water insoluble.

☞ *Nomenclature of Benzene Derivatives*

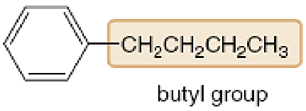
Many organic molecules contain a benzene ring with one or more substituents, so we must learn how to name them.

❖ Mono-substituted Benzenes

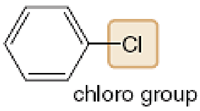
To name a benzene ring with one substituent, **name the substituent and add the word *benzene.*** Carbon substituents are named as alkyl groups. When a halogen is a substituent, name the halogen by changing the *-ine* ending of the name of the halogen to the suffix *-o*; for example, chlor***ine*** →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



ethylbenzene

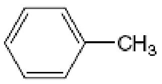


butylbenzene

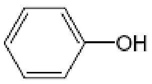


chlorobenzene

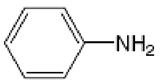
Many monosubstituted benzenes, such as those with methyl (CH_3–), hydroxyl (–OH), and amino (–NH_2) groups, have common names that you must learn, too.



toluene
(methylbenzene)



phenol
(hydroxybenzene)

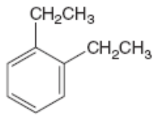


aniline
(aminobenzene)

❖ Disubstituted Benzenes

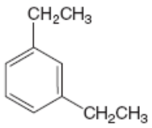
There are three different ways that two groups can be attached to a benzene ring, so a prefix-**ortho, meta,** or **para** is used to designate the relative position of the two substituents. ortho, meta, and para are generally abbreviated as ***o*, *m*,** and ***p*,** respectively.

1,2-Disubstituted benzene
ortho isomer



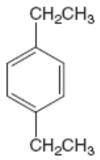
***o*-diethylbenzene**
or
1,2-diethylbenzene

1,3-Disubstituted benzene
meta isomer



***m*-diethylbenzene**
or
1,3-diethylbenzene

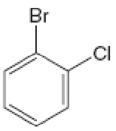
1,4-Disubstituted benzene
para isomer



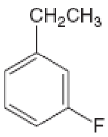
***p*-diethylbenzene**
or
1,4-diethylbenzene

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 mono-substituted benzene.**

Alphabetize two different substituent names



o-bromochloro-
benzene



m-ethylfluoro-
benzene