

Chapter 3 Alkenes and Alkynes

Excluded sections 3.15&3.16

3.1 Definition and Classification

- Alkene: a hydrocarbon that contains one or more carboncarbon double bonds.
 - ethylene is the simplest alkene.
- Alkyne: a hydrocarbon that contains one or more carboncarbon triple bonds.
 - acetylene is the simplest alkyne.

Their general formulas are

Both of these classes of hydrocarbons are unsaturated, because they contain fewer hydrogens per carbon than alkanes (C_nH_{2n+2}) .

- If two double bonds are present, the compounds are called alkadienes or, more commonly, dienes. There are also trienes, tetraenes, and even polyenes (compounds with many double bonds, from the Greek poly, many). Polyenes are responsible for the color of carrots (β-carotene) and tomatoes (lycopene). Compounds with more than one triple bond, or with double and triple bonds, are also known.
- PROBLEM 3.1 What are all of the structural possibilities for C₄H₆? (Nine compounds, four acyclic and five cyclic, are known.)

The formula C_4H_6 corresponds to C_nH_{2n-2} . The possibilities are one triple bond, two double bonds, one double bond and one ring, or two rings.

acyclic
$$HC \equiv C - CH_2CH_3 \qquad H_3C - C \equiv C - CH_3$$
$$H_2C = CH - CH = CH_2 \qquad H_2C = C = CHCH_3$$
$$H_3C \qquad \qquad H_3C \qquad H$$

 When two or more multiple bonds are present in a molecule, it is useful to classify the structure further, depending on the relative positions of the multiple bonds.

$$\begin{array}{cccc} C=C=C & C=C-C=C & C=C-C-C=C \\ C=C=C=C & C=C-C\equiv C & C\equiv C-C-C-C\equiv C \\ cumulated & conjugated & nonconjugated (isolated) \end{array}$$

PROBLEM 3.2 Which of the following compounds have conjugated multiple bonds?



3.2 Nomeclature

• The IUPAC rules for naming alkenes and alkynes are similar to those for alkanes ,but a few rules must be added for naming and locating the multiple bonds.

 The ending -*ene* is used to designate a carbon–carbon double bond. When more than one double bond is present, the ending is -*diene*, -*triene*, and so on. The ending -*yne* is used for a triple bond (-*diyne* for two triple bonds and so on). Compounds with a double *and* a triple bond are -*enynes*.

2. Select the longest chain that includes *both* carbons of the double or triple bond.

For example,



named as a butene, not as a pentene

3. Number the chain from the end nearest the multiple bond so that the carbon atoms in that bond have the lowest possible numbers.

If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.

4. Indicate the position of the multiple bond using the lower numbered carbon atom of that bond. For example,

1
 2 3 4 3 4 1 1 1 1 1 1 2 1 2 1 2 1 2 1

5. If more than one multiple bond is present, number the chain from the end nearest

$$C = C - C = C - C$$
 not $C = C - C - C$

If a double and a triple bond are equidistant from the end of the chain, the double bond *receives the lowest numbers*. For example,

$$C = C - C = C$$
 not $C = C - C = C$

$$\overset{1}{\text{CH}_2} = \overset{2}{\text{CHCH}_2} \overset{3}{\text{CH}_3} \overset{4}{\text{CH}_3} \overset{1}{\text{CH}_3} \overset{2}{\text{CH}_3} \overset{3}{\text{CH}_3} \overset{4}{\text{HC}_3} \overset{1}{\text{HC}_2} \overset{2}{=} \overset{3}{\text{CH}_3} \overset{4}{\text{CH}_3} \overset{1}{\text{CH}_3} \overset{2}{\text{CH}_3} \overset$$

methylpropene (isobutylene)







 $\overset{1}{\overset{2}{\text{CH}_{3}}} - \overset{2}{\overset{C}{\text{CH}}} = \overset{3}{\overset{C}{\text{CH}}} - \overset{4}{\overset{C}{\text{CH}}} - \overset{5}{\overset{C}{\text{CH}_{3}}} \qquad \overset{1}{\overset{1}{\text{CH}_{2}}} = \overset{2}{\overset{3}{\text{C}}} - \overset{3}{\overset{4}{\text{CH}_{3}}} \qquad \overset{1}{\overset{1}{\text{CH}_{2}}} = \overset{2}{\overset{C}{\text{CH}}} - \overset{3}{\overset{C}{\text{CH}_{2}}} = \overset{4}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{3}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{4}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{4}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{3}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{4}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{4}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{4}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} = \overset{4}{\overset{C}{\text{CH}_{2}}} + \overset{4}{\overset{C}{\text{CH}_{2}}} +$

4-methyl-2-pentene (Not 2-methyl-3-pentene; the chain is numbered so that the double bond gets the lower number.)

2-ethyl-1-butene (Named this way, even though there is a five-carbon chain present, because that chain does not include both carbons of the double bond.)

1,3-butadiene (Note the *a* inserted in the name, to help in pronunciation.)

With cyclic hydrocarbons, we start numbering the ring with the carbons of the multiple bond.









cyclopentene (No number is necessary, because there is only one possible structure.)

.

3-methylcyclopentene (Start numbering at, and number through the double bond; 5-methylcyclopentene and 1-methyl-2-cyclopentene are incorrect names.)

1,3-cyclohexadiene

1,4-cyclohexadiene

Two important groups also have common names.

$CH_2 = CH -$	$CH_2 = CHCl$
vinyl	vinyl chloride
(ethenyl)	(chloroethene)
$CH_2 = CH - CH_2 - allyl$	CH ₂ =CH-CH ₂ Cl allyl chloride
(2-propenyl)	(3-chloropropene)

PROBLEM 3.4

Write structural formulas for the following:

- a. 1,4-dichloro-2-pentene
- b. 3-hexyne
- c. 1,2-diethylcyclobutene
- d. 2-bromo-1,3-pentadiene



3.3 Some Facts About Double Bond

Carbon–carbon double bonds have some special features that are different from those of single bonds.



TABLE 3.1 – Comparison of C—C and C=C Bonds			
Property	С—С	C==C	
 Number of atoms attached to a carbon 	4 (tetrahedral)	3 (trigonal)	
2. Rotation	relatively free	restricted	
3. Geometry	many conformations are possible; staggered is preferred	planar	
4. Bond angle	109.5°	120°	
5. Bond length	1.54 Å	1.34 Å	

3.4 The Orbital Model of a Double Bond; the Pi Bond



Atomic orbitals of carbon

The 2*s* and two 2*p* orbitals are combined to form three hybrid sp^2 orbitals, leaving one electron still in a *p* orbital.















Rotation of one sp^2 carbon 90° with respect to another orients the *p* orbitals perpendicular to one another so that no overlap (and therefore no p bond) is possible.

3.5 Cis-Trans Isomerism in Alkenes

Because rotation at carbon–carbon double bonds is restricted, *cis–trans* isomerism (geometric isomerism) is possible in substituted alkenes.



cis-1,2-dichloroethene bp 60°C, mp -80°C



trans-1,2-dichloroethene bp 47°C, mp -50°C

Are cis-trans isomers possible for 1-butene and 2-butene?





Geometric isomers of alkenes can be interconverted if sufficient energy is supplied to break the pi bond and allow rotation about the remaining sigma bond.



3.6 Addition and Substitution Reaction Compared

The most common reaction of *alkanes* is substitution.

 $\mathbf{R} - \mathbf{H} + \mathbf{A} - \mathbf{B} \longrightarrow \mathbf{R} - \mathbf{A} + \mathbf{H} - \mathbf{B}$

While, the most common reaction of alkenes is **addition** of a reagent to the carbons of the double bond to give a product with a C-C single bond.



pi and sigma bond were broken, and two sigma bonds were formed. Because sigma bonds are usually stronger than pi bonds, the net reaction is favorable.



3.7 Polar Addition Reaction

Several reagents add to double bonds by a two-step polar process.

3.7a Addition of Halogens

 $CH_{3}CH = CHCH_{3} + Cl_{2} \longrightarrow CH_{3}CH - CHCH_{3}$ | | | Cl Cl 2-butene $bp 1-4^{\circ}C$ 2,3-dichlorobutane $bp 117-119^{\circ}C$

 The addition of bromine can be used as a chemical test for the presence of unsaturation in an organic compound. Bromine solutions in tetrachloromethane are dark reddish-brown, and both the unsaturated compound and its bromine adduct are usually colorless.



• PROBLEM 3.8

Write an equation for the reaction of bromine at room temperature with

a. propene

b.

b. 4-methylcyclohexene

3.8 a. One bromine atom adds to each doubly bonded carbon, and the double bond in the starting material becomes a single bond in the product:

$$H_{2}C = CHCH_{2}CH_{3} + Br_{2} \longrightarrow H_{2}C - CHCH_{2}CH_{3}$$

$$Br Br$$

$$Br Br$$

$$H_{2}C = CHCH_{2}CH_{3} + Br_{2} \longrightarrow H_{2}C - CHCH_{2}CH_{3}$$

$$Br Br$$

3.7b Addition of Water (Hydration)

If an acid catalyst is present, water adds to alkenes to form alcohol.



3.7c Addition of Acids



Acids are the hydrogen halides (H-F, H-Cl, H-Br, H-I) and sulfuric acid (H-OSO₃H)



3.8 Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule

Table 3.2 — Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	Br + Br	H + Br
		н—он
	н-н	H – OSO ₃ H
Alkenes	$CH_2 = CH_2$	$CH_3CH = CH_2$
		CH ₃
	mirror plane	not a mirror plane

3.8 Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule



• The products of equation are sometimes called regioisomers. If a reaction of this type gives only one of the two possible regioisomers, it is said to be regiospecific. If it gives mainly one product, it is said to be regioselective.





not observed

• When an unsymmetric reagent adds to an unsymmetric alkene, the electropositive part of the reagent bonds to the carbon of the double bond that has the greater number of hydrogen atoms attached to it.

• **PROBLEM 3.11**

Use Markovnikov's Rule to predict which regioisomer predominates in each of the following reactions:

- a. 1-pentene 1 HBr
- b. 2-methyl-2-hexene + H_2O (H⁺ catalyst)

a.
$$H_2C = CHCH_2CH_3 + H - CI \longrightarrow CH_3 - CHCH_2CH_3$$

b. $CH_3 - C = CHCH_3 + H - OH \longrightarrow CH_3 - C - CH_2CH_3$
 $CH_3 - C = CHCH_3 + H - OH \longrightarrow CH_3 - C - CH_2CH_3$
 $CH_3 - C = CHCH_3 + H - OH \longrightarrow CH_3 - C - CH_2CH_3$

3.9 Mechanism of Electrophilic Addition to Alkenes

- The *pi* electrons of a double bond are more exposed to an attacking reagent than are the sigma electrons.
- The *pi* bond is also weaker than the σ bond.
- It is the *pi* electrons, then, that are involved in additions to alkenes.
- The double bond can act as a supplier of *pi* electrons to an electron-seeking reagent.
- Polar reactants can be classified as either electrophiles or nucleophiles
- Electrophiles are electron-poor reactants; they seek electrons.
- Nucleophiles are electron-rich reactants; they form bonds by donating electrons to electrophiles.



A carbocation is a positively charged carbon atom bonded to three other atoms.





Since the first step in these additions is attack by the electrophile, the whole process is called an **electrophilic addition reaction**.

3.10 Markovnikov's Rule Explained



The stability of carbocations decreases in the following order:



Markovnikov's Rule can now be restated :

The electrophilic addition of an unsymmetric reagent to an unsymmetric double bond proceeds in such a way as to involve the most stable carbocation.

PROBLEM 3.13 Classify each of the following carbocations as primary, secondary, or tertiary:



3.11 Reaction Equilibrium: What Makes a Reaction Go?

• A chemical reaction can proceed in two directions.

$$aA + bB \rightleftharpoons cC + dD$$

• we describe the chemical equilibrium for the forward and backward reactions by the following equation:

$$K_{eq} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

- If K_{eq} is greater than 1, the formation of products C and D will be favored over the formation of reactants A and B.
- if K_{eq} is less than 1, the preferred direction for the reaction is from right to left.

• What determines whether a reaction will proceed to the right, toward products?

- A reaction will occur when the products are lower in energy (more stable) than the reactants. A reaction in which products are higher in energy than reactants will proceed to the left, toward reactants.
- When products are lower in energy than reactants, heat is given off in the course of the reaction. Such a reaction is *exothermic*.
- On the other hand, heat must be added to ethane to produce two methyl radicals .This reaction is *endothermic* (takes in heat).



(a)

3.11 Reaction Rate: How Fast a Does Reaction Go?

- A reaction energy diagram shows the changes in energy that occur in the course of a reaction.
- A transition state is a structure with maximum energy for a particular reaction step.
- Activation energy, *Ea*, is the difference in energy between reactants and the transition state, and the activation energy determines the reaction rate.



Reaction coordinate





3.13 Hydroboration of Alkenes

• Hydroboration involves addition of a hydrogen—boron bond to an alkene.

$$R-CH=CH_{2}+H-B \longrightarrow R-CH-CH_{2}-B \bigvee$$

• A two-step alcohol synthesis which involves the addition of a hydrogen—boron bond to an alkene.



$(CH_3CH_2CH_2)_3B + 3 H_2O_2 + 3 NaOH \longrightarrow$ tri-*n*-propylborane

3 CH₃CH₂CH₂OH + Na₃BO₃ + 3 H₂O *n*-propyl alcohol sodium borate

One great advantage of this hydroboration—oxidation sequence is that it provides a route to alcohols that *cannot* be obtained by the acid-catalyzed hydration of alkenes



PROBLEM 3.20 What alkene is needed to obtain

-CH₂CH₂OH

via the hydroboration-oxidation sequence? What product would this alkene give with acid-catalyzed hydration?

3.14 Addition of Hydrogen

• Hydrogen adds to alkenes in the presence of an appropriate catalyst. The process is called **hydrogenation**.



- The catalyst is usually a finely divided metal, such as nickel, platinum, or palladium.
- Both hydrogen atoms usually add from the catalyst surface to the same face of the double bond.

• For example, 1,2-dimethylcyclopentene gives mainly *cis*-1,2-dimethylcyclopentane.



PROBLEM 3.21 Write an equation for the catalytic hydrogenation of

- a. 2-methyl-2-pentene
- b. 4-methylcyclopentene
- c. 3-methylcyclohexene
- d. vinylcyclobutane

3.17 The Oxidation of Alkenes

Alkenes are more easily oxidized than alkanes by chemical oxidizing agents. These reagents attack the pi electrons of the double bond. The reactions may be useful as chemical tests for the presence of a double bond or for synthesis.

3.17 a Oxidation with permanganate; a Chemical Test



3.17b Ozonolysis of Alkenes

Alkenes react rapidly and quantitatively with ozone, O_3 .



The net result of this reaction is to break the double bond of the alkene and to form two carbon–oxygen double bonds (carbonyl groups), one at each carbon of the original double bond. The overall process is called **ozonolysis**.



PROBLEM 3.28

Which alkene will give only acetone, $(CH_3)_2C=O$, as the ozonolysis product?

$(CH_3)_2C = C(CH_3)_2$

3.17 c Other Alkene Oxidations



$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$

3.18 Some Facts About Triple Bond

A carbon atom that is part of a triple bond is directly attached to only two other atoms, and the bond angle is 180°. The carbon–carbon triple bond distance is about 1.21 Å, appreciably shorter than that of most double (1.34 Å) or single (1.54 Å) bonds. Apparently, three electron pairs between two carbons draw them even closer together than do two pairs. Because of the linear geometry, no cis–trans isomerism is possible for alkynes.



3.19 The Orbital Model of a Triple Bond



Atomic orbitals of carbon

The 2*s* and one 2*p* orbital are combined to form two hybrid *sp* orbitals, leaving one electron in each of two *p* orbitals.



The resulting carbon–carbon triple bond, with a hydrogen atom attached to each remaining *sp* bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

3.20 Addition Reaction of Alkenes

As in alkenes, the pi electrons of alkynes are exposed to electrophilic attack. Therefore, many addition reactions described for alkenes also occur, though usually more slowly, with alkynes.

For example, bromine adds as follows:



In the first step, the addition occurs mainly trans

With an ordinary nickel or platinum catalyst, alkynes are hydrogenated all the way to alkanes.

However, a special palladium catalyst (called Lindlar's catalyst) can control hydrogen addition so that only 1 mole of hydrogen adds. In this case, the product is a *cis* alkene, because both hydrogens add to the same face of the triple bond from the catalyst surface.



To get *trans* product, Na in NH_3 is used for hydrogenation.

With unsymmetric triple bonds and unsymmetric reagents, Markovnikov's Rule is followed in each step, as shown in the following example:





Addition of water to alkynes requires not only an acid catalyst but mercuric ion as well. The product is a methyl ketone or, in the case of acetylene itself (R"H), acetaldehyde.

$$R-C \equiv CH + H - OH \xrightarrow{H^{+}}_{HgSO_{4}} \begin{bmatrix} HO & H \\ R - C = C - H \end{bmatrix} \longrightarrow R - C - CH_{3}$$

a vinyl alcohol, a methyl ketone
or enol

PROBLEM 3.29 Write equations for the following reactions:

a. $CH_3CH_2C \equiv CH + Br_2 (1 \text{ mole})$ c. 1-hexyne + HBr (1 and 2 moles) b. $CH_3CH_2C \equiv CCH_3 + Cl_2 (2 \text{ moles})$ d. 1-butyne + $H_2O (Hg^{2+}, H^+)$

3.21 The Acidity of Alkynes

A hydrogen atom on a triply bonded carbon is weakly acidic and can be removed by a very strong base. Sodium amide, for example, converts acetylenes to acetylides.





As the hybridization at carbon becomes more *s*-like and less *p*-like, the acidity of the attached hydrogen increases.

Homework

35 37 38 41 42 45 53 56 58