

WILLIAM H. BROWN
THOMAS POON

www.wiley.com/college/brown

CHAPTER FOUR

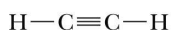
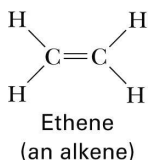
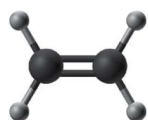
Alkenes and Alkynes

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

1

Unsaturated Hydrocarbons

- **Unsaturated Hydrocarbon:** Contains one or more carbon-carbon double or triple bonds or benzene-like rings.
 - **Alkene:** contains a carbon-carbon double bond and has the general formula C_nH_{2n} .
 - **Alkyne:** contains a carbon-carbon triple bond and has the general formula C_nH_{2n-2} .



Ethyne
(an alkyne)



WILEY

Copyright © John Wiley & Sons, Inc. All rights reserved.

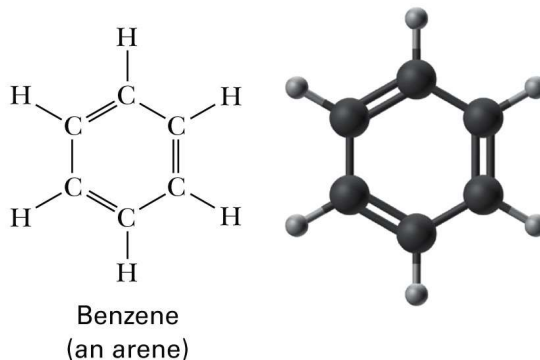
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-2

2

Unsaturated Hydrocarbons

- **Arene**: benzene and its derivatives (Ch 9)



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

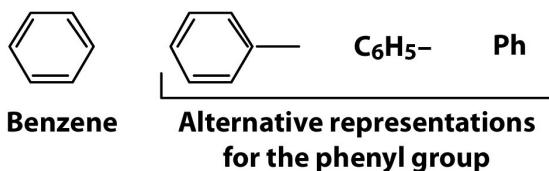
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-3

3

Benzene and Phenyl Groups

- We do not study benzene and its derivatives until Chapter 9.
 - However, we show structural formulas of compounds containing a phenyl group before that time.
 - The phenyl group is not reactive under any of the conditions we describe in chapters 5-8.



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

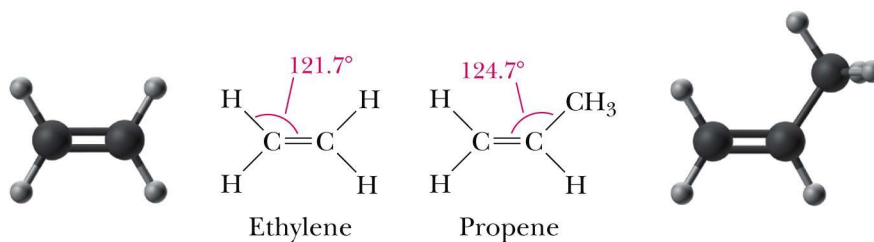
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-4

4

Structure of Alkenes

- The two carbon atoms of a double bond and the four atoms bonded to them lie in a plane, with bond angles of approximately 120° .



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

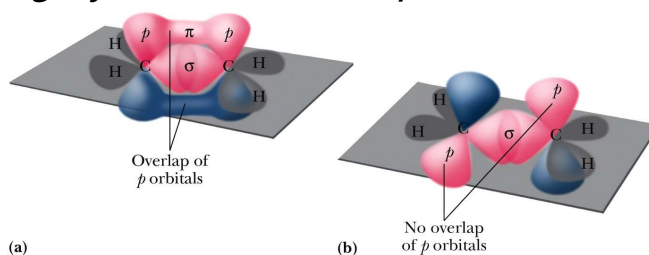
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-5

5

Structure of Alkenes

- According to the orbital overlap model, a double bond consists of one σ bond formed by overlap of sp^2 hybrid orbitals and one π bond formed by overlap of parallel $2p$ orbitals.
- Rotating by 90° breaks the π bond.*



WILEY

(a)
Copyright © John Wiley & Sons, Inc. All rights reserved.

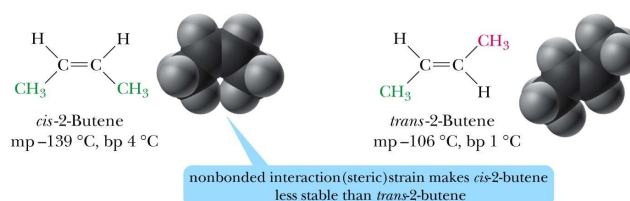
(b)

4-6

6

Cis-Trans Isomerism

- Because of restricted rotation about a C–C double bond, groups on adjacent carbons are either *cis* or *trans* to each other.
 - Because of nonbonded interaction strain between alkyl substituents of the same side of the double bond, a *trans* alkene is more stable than an isomeric *cis* alkene.



WILEY

Copyright © John Wiley & Sons, Inc. All rights reserved.

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-7

7

Structure of Alkynes

- The functional group of an alkyne is a carbon-carbon triple bond.
- A triple bond consists of:
 - One σ bond formed by the overlap of *sp* hybrid orbitals.
 - Two π bonds formed by the overlap of sets of parallel *2p* orbitals.



© John Wiley & Sons, Inc. All rights reserved.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-8

8

Nomenclature of Alkenes

- IUPAC Nomenclature of alkenes
 - Use the infix **-en-** to show the presence of a carbon-carbon double bond.
 - Number the parent chain to give the 1st carbon of the double bond the lower number.
 - Follow IUPAC rules for numbering and naming substituents.
 - For a cycloalkene, the numbering of the atoms of the ring must begin with the two carbons of the double bond.

WILEY

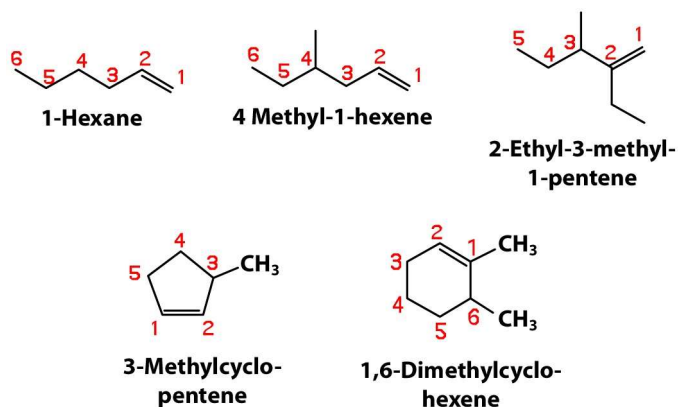
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-9

9

Nomenclature of Alkenes

- IUPAC nomenclature of alkenes



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-10

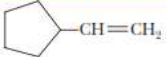
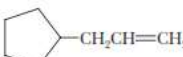
10

Nomenclature of Alkenes

- Some alkenes, particularly low-molecular-weight ones, are known almost exclusively by their common names.

	$\text{CH}_2=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CH}_2$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$
IUPAC name:	Ethene	Propene	2-Methylpropene
Common name:	Ethylene	Propylene	Isobutylene

Copyright © John Wiley & Sons, Inc. All rights reserved.

Alkenyl Group	Common Name	Example	Common Name
$\text{CH}_2=\text{CH}-$	Vinyl		Vinylcyclopentane
$\text{CH}_2=\text{CHCH}_2-$	Allyl		Allylcyclopentane

WILEY

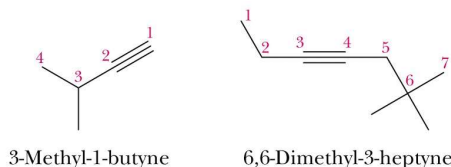
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-11

11

Nomenclature of Alkynes

- IUPAC nomenclature of alkynes
 - Use the infix **-yne** to show the presence of a carbon-carbon triple bond.
 - Number the parent chain to give the 1st carbon of the triple bond the lower number.
 - Follow IUPAC rules for numbering and naming substituents.



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

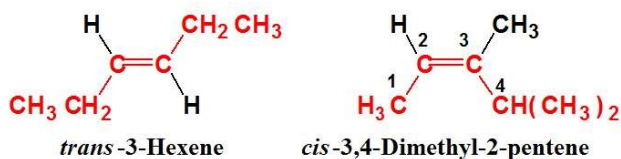
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-12

12

Configuration: *Cis-Trans*

- **The *cis-trans* system:** Configuration is determined by the orientation of atoms of the main chain.



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

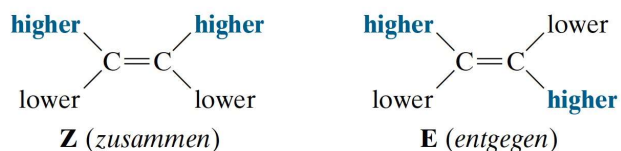
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-13

13

Configuration: *E,Z*

- To Assign an *E,Z* configuration, first assign a priority to the substituents on each carbon of the double bond.
 - If the groups of higher priority are on the same side of the double bond, the configuration is **Z** (German: *zusammen*, together).
 - If the groups of higher priority are on opposite sides of the double bond, the configuration is **E** (German: *entgegen*, opposite).



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

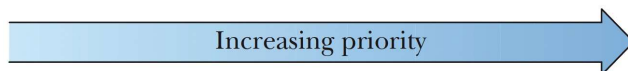
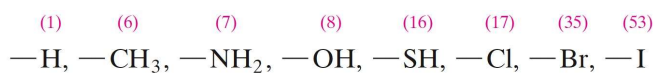
4-14

14

Configuration: E,Z

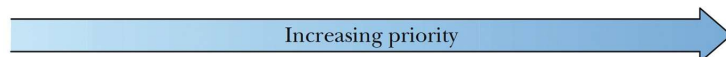
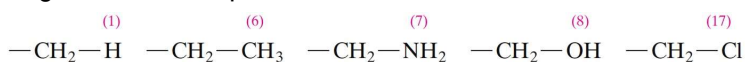
- Priority rules

1. Priority is based on atomic number; the higher the atomic number, the higher the priority.



Copyright © John Wiley & Sons, Inc. All rights reserved.

2. If priority cannot be assigned on the basis of the atoms bonded directly to the double bond, look to the next set of atoms; priority is assigned at the first point of difference.



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

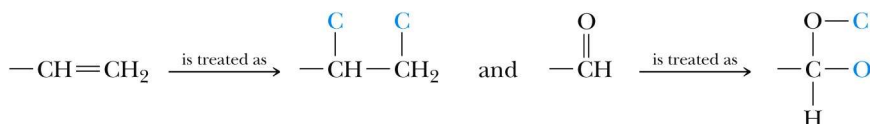
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-15

15

Configuration - E,Z

3. Atoms participating in a double or triple bond are considered to be bonded to an equivalent number of similar atoms by single bonds.



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

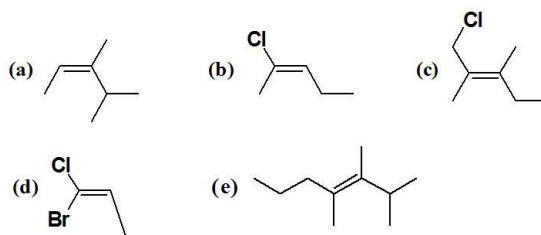
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-16

16

Configuration - E,Z

- **Example:** Name each alkene by the E,Z system and specify its configuration.



Copyright © John Wiley & Sons, Inc. All rights reserved.

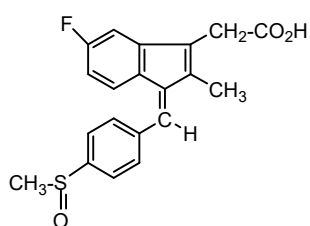
WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

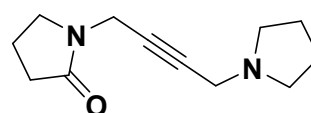
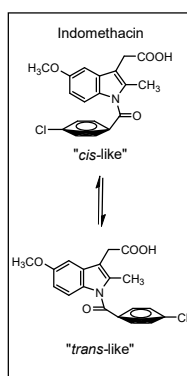
4-17

17

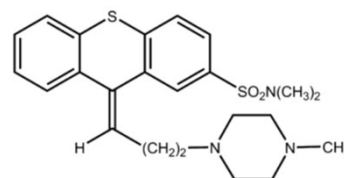
MC Drugs example of Cis/Trans “like” & Alkynes



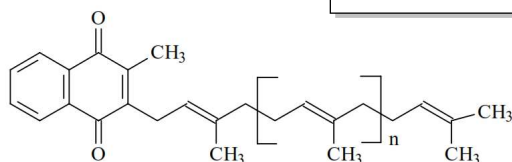
Z-Sulindac



***trans*-**
Oxotremorine



Thiothixene



Vitamin K.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

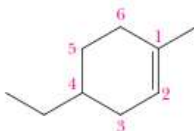
4-18

18

Naming Cycloalkenes

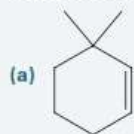


3-Methylcyclopentene
(not 5-methylcyclopentene)

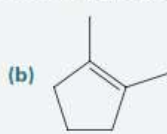


4-Ethyl-1-methylcyclohexene
(not 5-ethyl-2-methylcyclohexene)

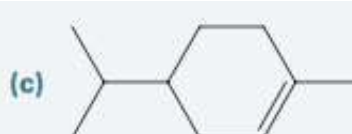
Write the IUPAC name for each cycloalkene:



(a) 3,3-Dimethylcyclohexene



(b) 1,2-Dimethylcyclopentene



(c) 4-Isopropyl-1-methylcyclohexene

WILEY

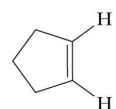
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-19

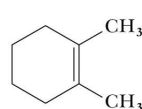
19

Cis-Trans Isomerism

- The configuration of the double bond in cyclopropene through cycloheptene must be *cis*. These rings are not large enough to accommodate a *trans* double bond.
- Cyclooctene is the smallest cycloalkene that can accommodate a *trans* double bond.



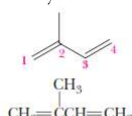
Cyclopentene



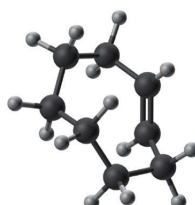
Cyclohexene



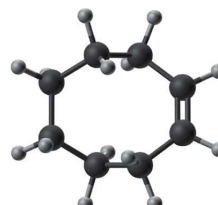
1,3-Cyclopentadiene



2-Methyl-1,3-butadiene
(Isoprene)



trans-Cyclooctene



cis-Cyclooctene

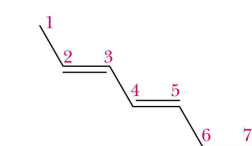
4-20

20

Cis-Trans Isomerism

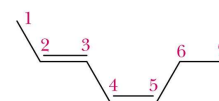
- Dienes, trienes, and polyenes
 - For an alkene with n carbon-carbon double bonds, each of which can show *cis-trans* isomerism, 2^n *cis-trans* isomers are possible.
 - Consider 2,4-heptadiene; it has four *cis-trans* isomers, two of which are drawn here.

Double bond	
C ₂ —C ₃	C ₄ —C ₅
<i>trans</i>	<i>trans</i>
<i>trans</i>	<i>cis</i>
<i>cis</i>	<i>trans</i>
<i>cis</i>	<i>cis</i>



trans,trans-2,4-Heptadiene

Copyright © John Wiley & Sons, Inc. All rights reserved.



trans,cis-2,4-Heptadiene

WILEY

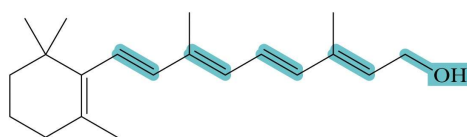
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-21

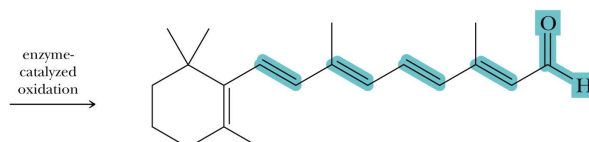
21

Cis-Trans Isomerism

- Vitamin A has five C-C double bonds.
- Four of the five can show *cis-trans* isomerism.
- Vitamin A is the all-*trans* isomer.



Vitamin A (retinol)



Vitamin A aldehyde (retinal)

Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-22

22

Physical Properties

- Alkenes and alkynes are nonpolar compounds.
 - The only attractive forces between their molecules are **dispersion forces**.
- The physical properties of alkenes and alkynes are similar to those of alkanes of similar carbon skeletons.
 - Those that are liquid at room temperature are less dense than water (1.0 g/mL).
 - They dissolve in each other and in nonpolar organic solvents.
 - They are insoluble in water.

WILEY

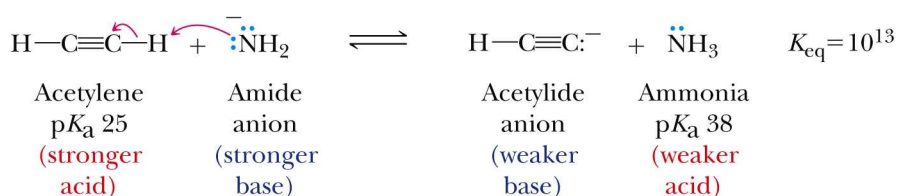
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-23

23

The Acidity of Terminal Alkynes

- One of the major differences between the chemistry of alkynes, and alkanes and alkenes is that the hydrogen atom of a terminal alkyne is sufficiently acidic (pK_a 25) that it can be removed by a strong base such as sodium amide, NaNH_2 , to give an alkyne anion.



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

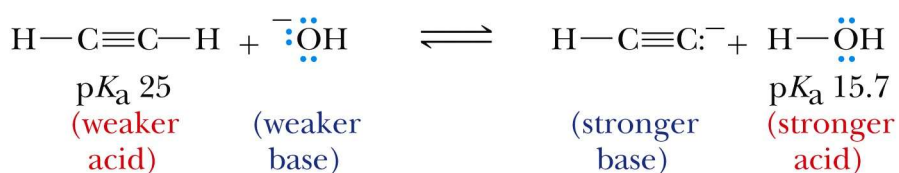
Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-24

24

The Acidity of Terminal Alkynes

- Because water (pK_a 15.7) is a stronger acid than acetylene or a terminal alkyne, hydroxide ion is not a strong enough base for an acid-base reaction with a terminal alkyne.



Copyright © John Wiley & Sons, Inc. All rights reserved.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-25

25

The Acidity of Terminal Alkynes

- The pK_a values for alkane and alkene hydrogens are so large that no base is strong enough to remove a hydrogen from either of these classes of compounds.

TABLE 4.1 Acidity of Alkanes, Alkenes, and Alkynes

Weak Acid		Conjugate Base	pK_a
Water	HO—H	HO [−]	15.7
Alkyne	HC≡C—H	HC≡C [−]	25
Alkene	CH ₂ =CH—H	CH ₂ =CH [−]	44
Alkane	CH ₃ CH ₂ —H	CH ₃ CH ₂ [−]	51



WILEY

Copyright © John Wiley & Sons, Inc. All rights reserved.

4-26

26

The Acidity of Terminal Alkynes

- How do we account for the acidity of a terminal alkyne compared to an alkane or alkene?
- To answer this question, we must focus on the stability of the anion derived from each class of hydrocarbon.
- The lone pair of electrons of an alkane anion lies in an sp^3 hybrid orbital, which has 25% s character.
- For an alkene anion, the lone pair lies in an sp^2 hybrid orbital, which has 33% s character.
- For a terminal alkyne anion, the lone pair lies in an sp hybrid orbital, which has 50% s character.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-27

27

The Acidity of Terminal Alkynes

- The greater the s character of the orbital bearing the negative charge, the greater the stability of the anion, and thus the greater acidic the hydrogen removed.
- Of the series of compounds alkane, alkene, and alkyne, the carbon of a terminal alkyne is the most electronegative (50% s character). Therefore, a terminal alkyne anion is the most stable of the series, and a terminal alkyne is the most acidic.

WILEY

Copyright © 2014 John Wiley & Sons, Inc. All rights reserved.

4-28

28