3 Alkenes and Alkynes

CHAPTER 3
Alkenes & Alkynes

3.1 Definition & Classification

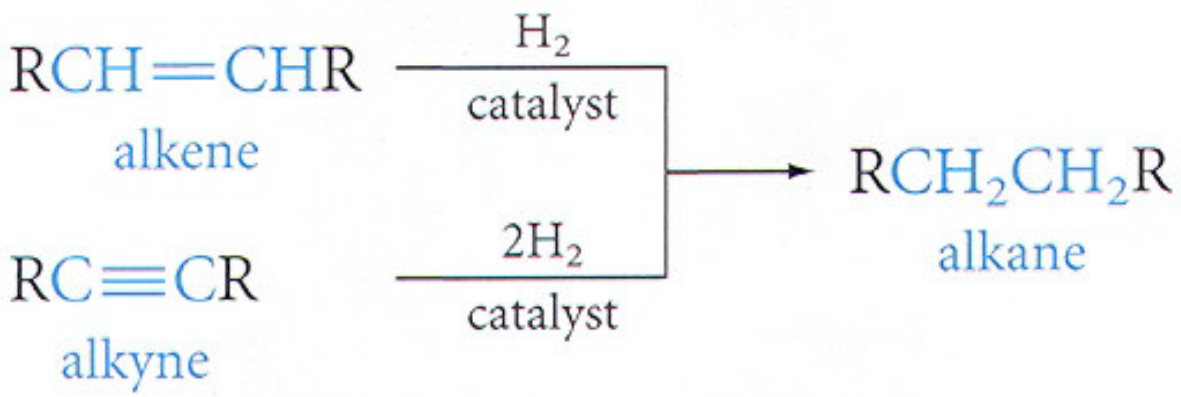
- Alkenes:
  - Hydrocarbons that contain C=C
  - Their general formula is

$$C_nH_{2n}$$

- Alkynes:
  - Contains C≡C
  - Have the general formula

$$C_nH_{2n-2}$$

- Both of these classes of hydrocarbons are ***unsaturated*** (contain fewer hydrogens per carbon than alkanes)
- Can be converted to alkenes:

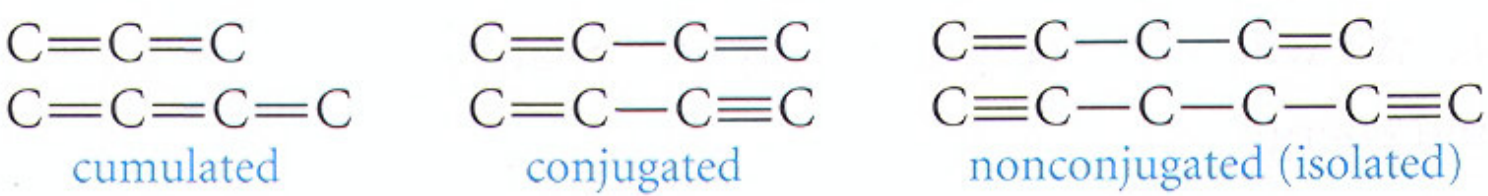


In Addition

- Compounds with more than one C=C or C≡C bond exist.
  - If 2C=C, the compounds are called ***Alkadienes*** or, more commonly, ***dienes***.
  - There are also ***trienes, tetraenes,*** and even ***polyenes.***
  - Compounds with more than one C≡C, or with C=C and C≡C, are also known.

Further Classification

- When 2 or more multiple bonds are present in a molecule, *depending on the relative position of the multiple bonds*, the following classification is used.

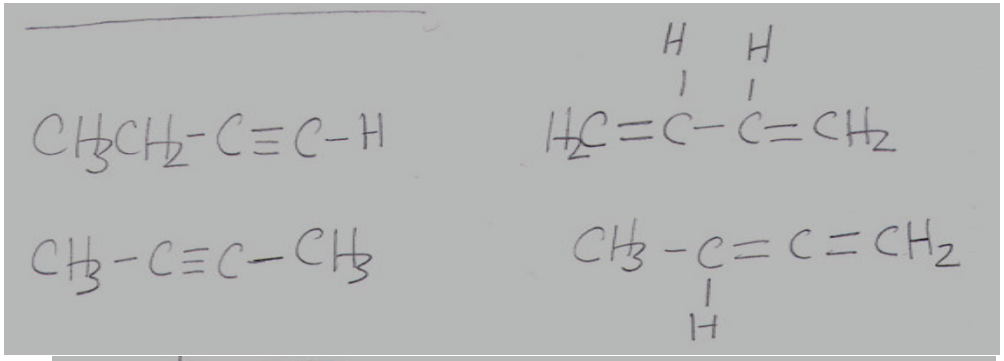


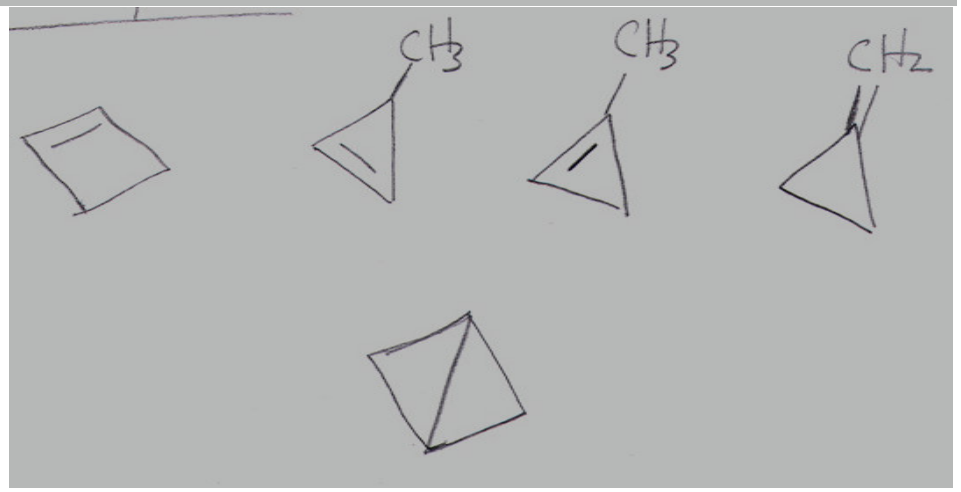
Sample Questions

PROBLEM 3.1 What are all the structural possibilities for C_4H_6? (Nine compounds, four acyclic and five cyclic, are known.)

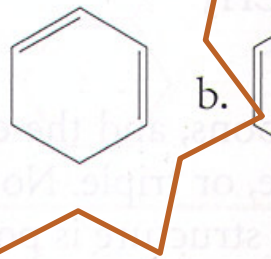
4 acyclic

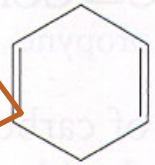
5 cyclic

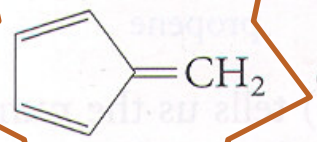


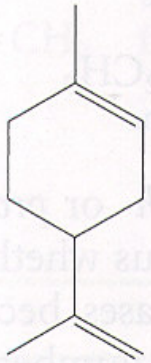


PROBLEM 3.2 Which of the following compounds have conjugated multiple bonds?

a. 

b. 

c. 

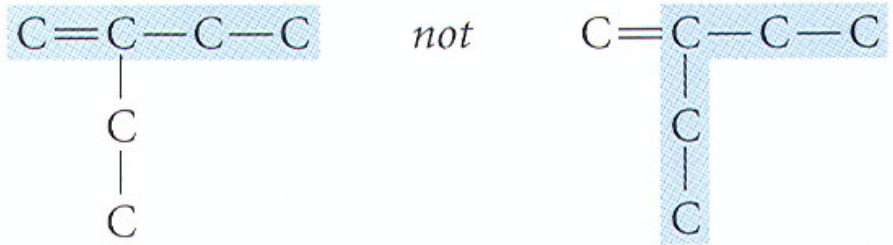
d. 

3.2 NOMENCLATURE

IUPAC Rules

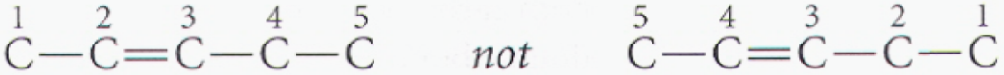
1. The ending *-ene* is used to designate a carbon–carbon double bond. When more than one double bond is present, the ending is *-diene, -triene,* and so on. The ending *-yne* (rhymes with wine) is used for a triple bond (*-diyne* for two triple bonds, and so on). Compounds with a double *and* a triple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

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



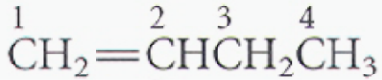
named as a butene, not as a pentene

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



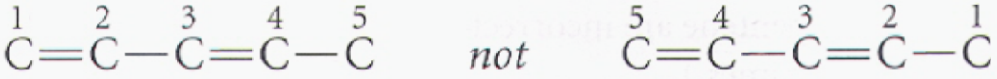
If the multiple bond is equidistant from both ends of the chain, number from the end nearest the first branch point.

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



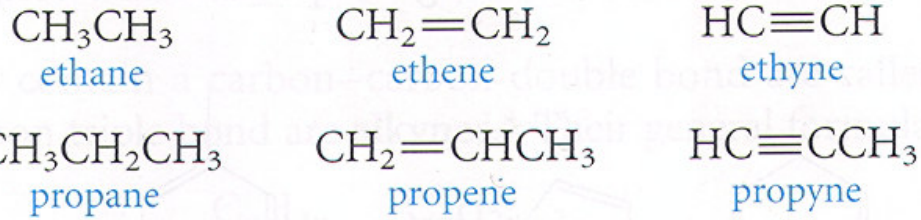
1-butene, *not* 2-butene

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



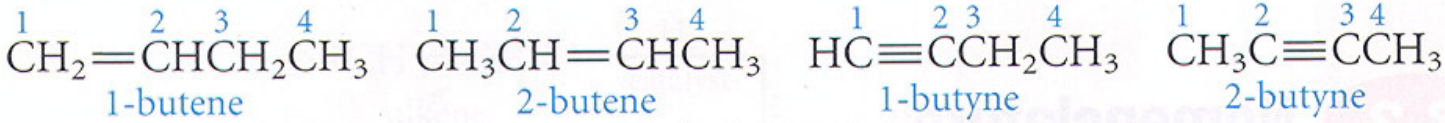
If a double and a triple bond are equidistant from the end of the chain, the *double* bond receives the lowest numbers. For example,

Let us see how these rules are applied. The first two members of each series are

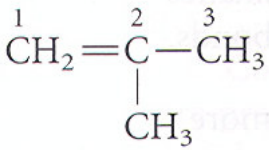


The root of the name (*eth-* or *prop-*) tells us the number of carbons, and the ending (*-ane, -ene,* or *-yne*) tells us whether the bonds are single, double, or triple. No number is necessary in these cases, because in each instance, only one structure is possible.

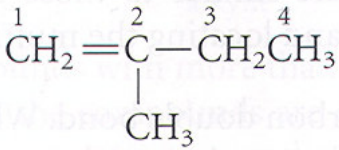
With four carbons, a number is necessary to locate the double or triple bond.



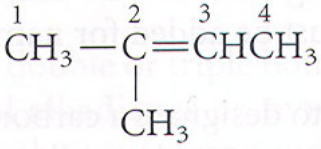
Branches are named in the usual way.



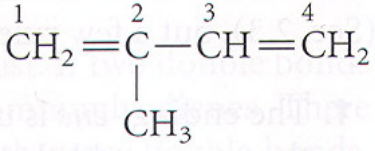
methylpropene
(isobutylene)



2-methyl-1-butene

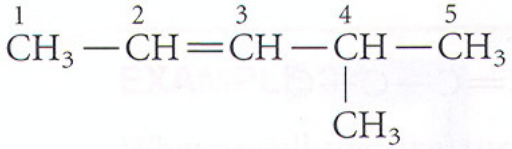


2-methyl-2-butene

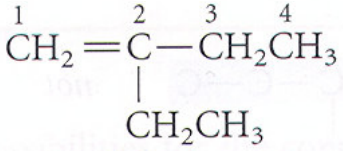


2-methyl-1,3-butadiene
(isoprene)

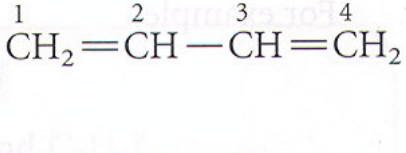
Note how the rules are applied in the following examples:



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



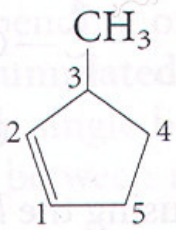
2-ethyl-1-butene
(Named this way, even though there is a five-carbon chain present, because that chain does not include both carbons of the double bond.)



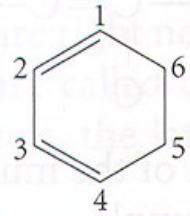
1,3-butadiene
(Note the *a* inserted in the name, to help in pronunciation.)

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

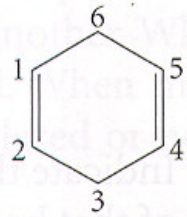
cyclopentene
(No number is necessary, because there is only one possible structure.)



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

In addition to the IUPAC rules, it is important to learn a few common names. For example, the simplest members of the alkene and alkyne series are frequently referred to by their older common names, **ethylene, acetylene,** and **propylene.**

$CH_2=CH_2$	$HC\equiv CH$	$CH_3CH=CH_2$
ethylene	acetylene	propylene
(ethene)	(ethyne)	(propene)

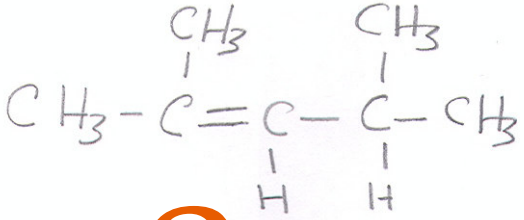
Two important groups also have common names. They are the **vinyl** and **allyl** groups (their IUPAC names are in parentheses below), shown on the left. These groups are used in common names, illustrated in the examples on the right.

$CH_2=CH-$	$CH_2=CHCl$
vinyl	vinyl chloride
(ethenyl)	(chloroethene)
$CH_2=CH-CH_2-$	$CH_2=CH-CH_2Cl$
allyl	allyl chloride
(2-propenyl)	(3-chloropropene)

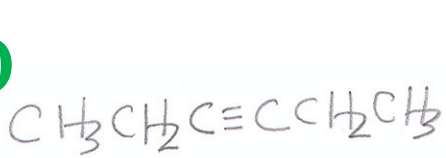
Sample Questions

PROBLEM 3.4 Write structural formulas for the following:

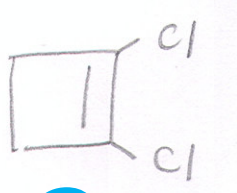
a. 2,4-dimethyl-2-pentene
b. 3-hexyne
c. 1,2-dichlorocyclobutene
d. 2-chloro-1,3-butadiene



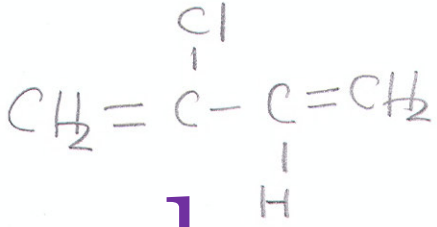
a



b



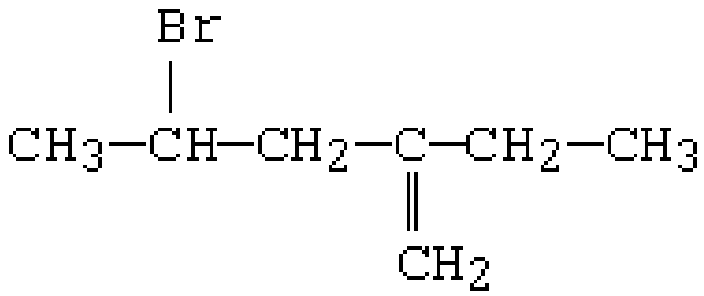
c



d

More Sample Problems

The correct IUPAC name for the following compound is:



A) 2-Bromo-4-methylenehexane

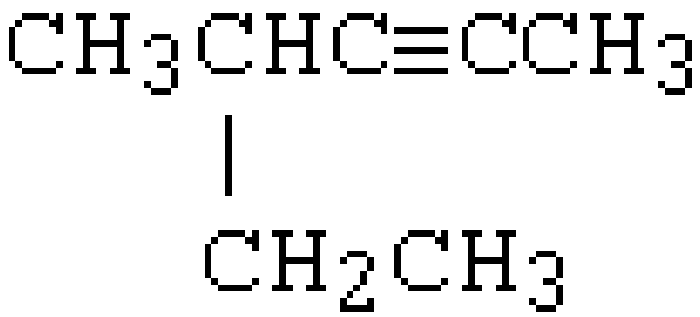
B) 2-(2-Bromopropyl)-1-butene

C) 4-Bromo-2-ethyl-1-pentene

D) 2-Bromo-4-ethyl-1-pentene

E) 2-Bromo-4-ethyl-4-pentene

Give the IUPAC name for



3-Methyl-4-hexyne

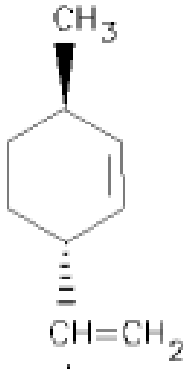
4-Methyl-2-hexyne

2-Ethyl-3-pentyne

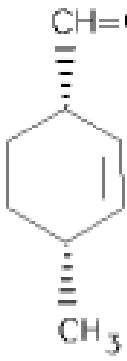
4-Ethyl-2-pentyne

3-Methyl-2-hexyne

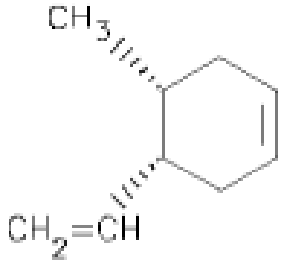
Select the structure for cis-3-methyl-6-vinylcyclohexene.



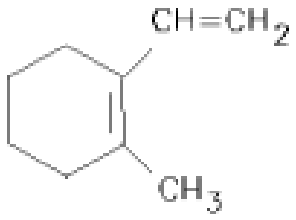
I



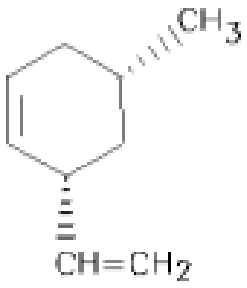
II



III



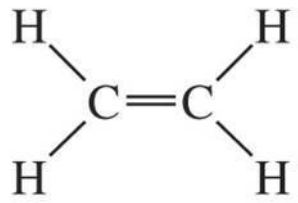
IV



V

3.3 Some Facts About Double Bonds

- The Structure of Ethene (Ethylene):



Ethene

- The geometry around each carbon is called ***trigonal planar***
  - All atoms directly connected to each carbon are in a plane
  - The bonds point towards the corners of a regular triangle
  - The bond angle are approximately 120°

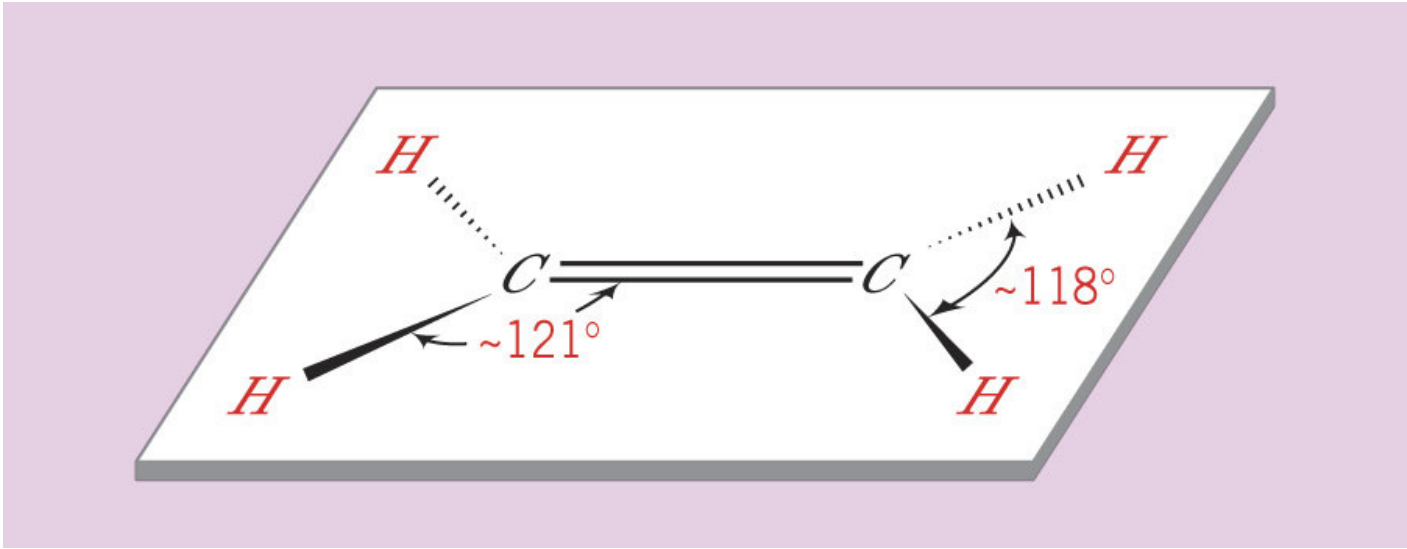


TABLE 3.1 COMPARISON OF C-C AND C=C BONDS

Table 3.1 Comparison of C—C and C═C bonds

Property	C—C	C═C
1. 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 Double Bond; the Pi Bond

sp^2 hybridized orbitals

- There are three σ bonds around each carbon of ethene and these are formed by using sp^2 hybridized orbitals
- The three sp^2 hybridized orbitals come from mixing one *s* and two *p* orbitals
  - One *p* orbital is left unhybridized
- The sp^2 orbitals are arranged in a trigonal planar arrangement
  - The *p* orbital is perpendicular (orthoganol) to the plane

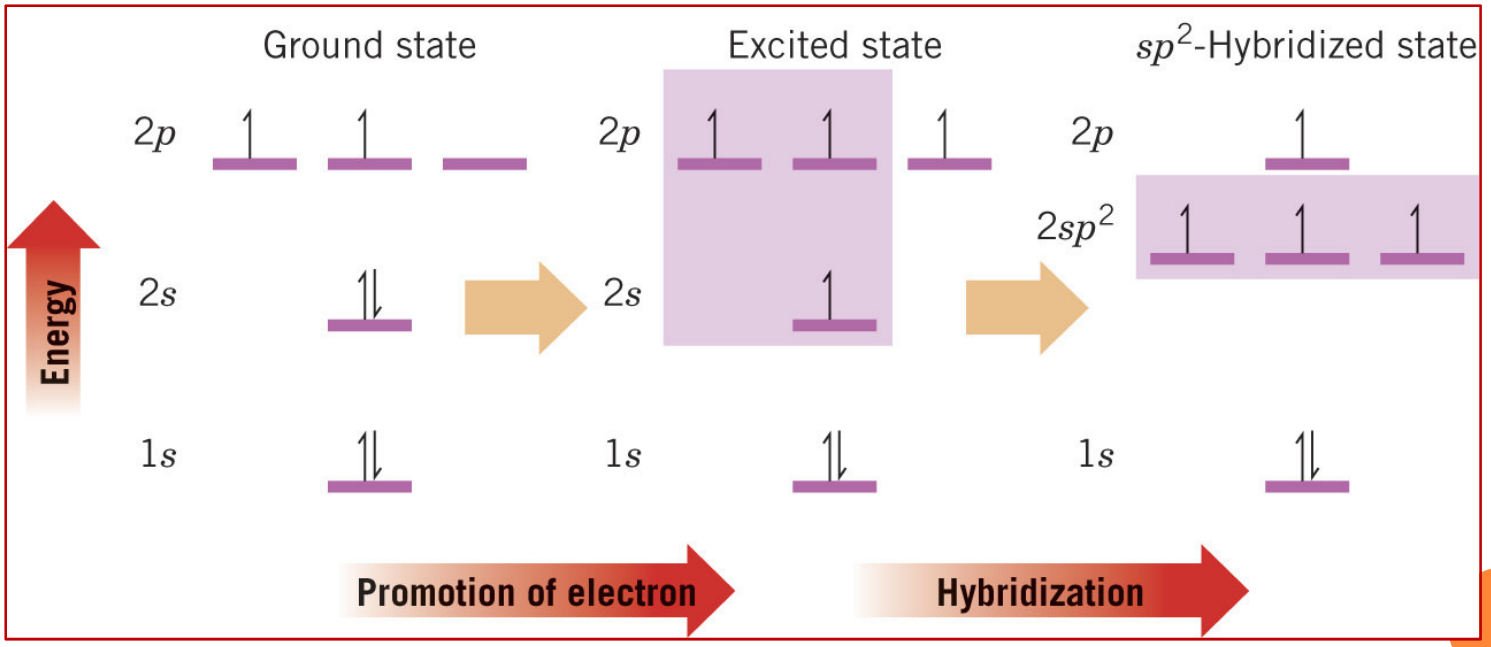
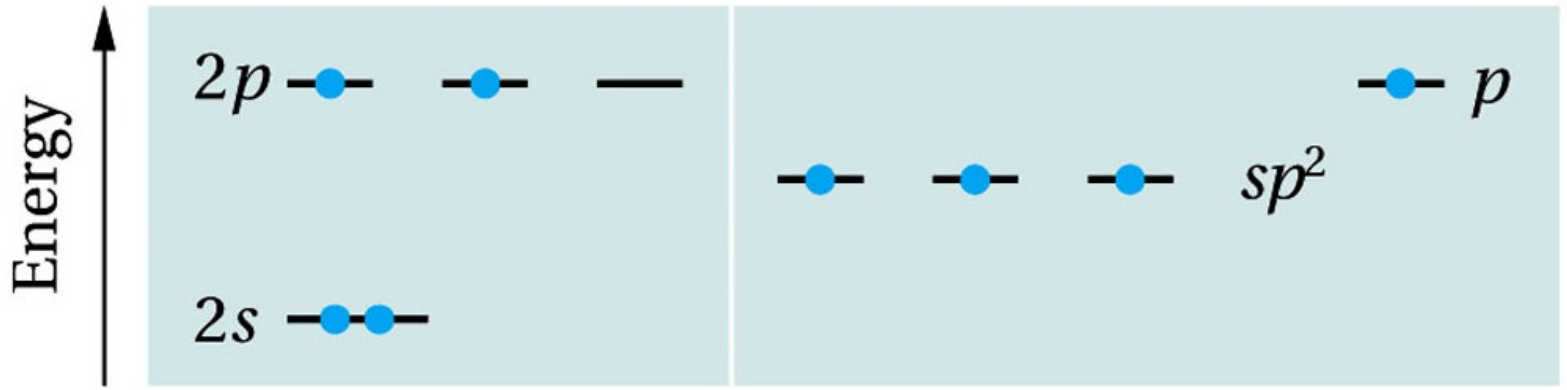


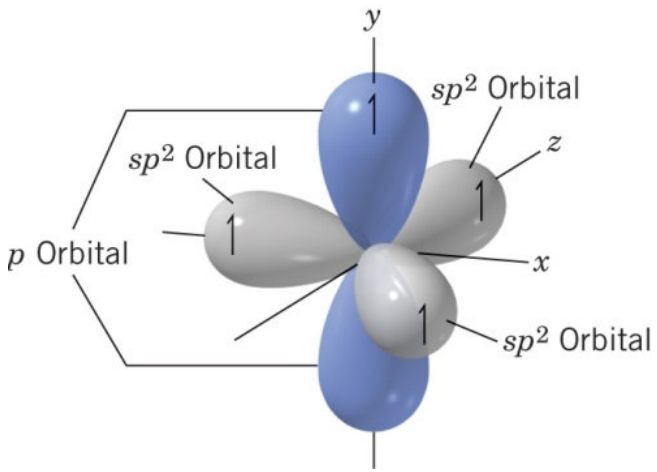
FIGURE 3.2

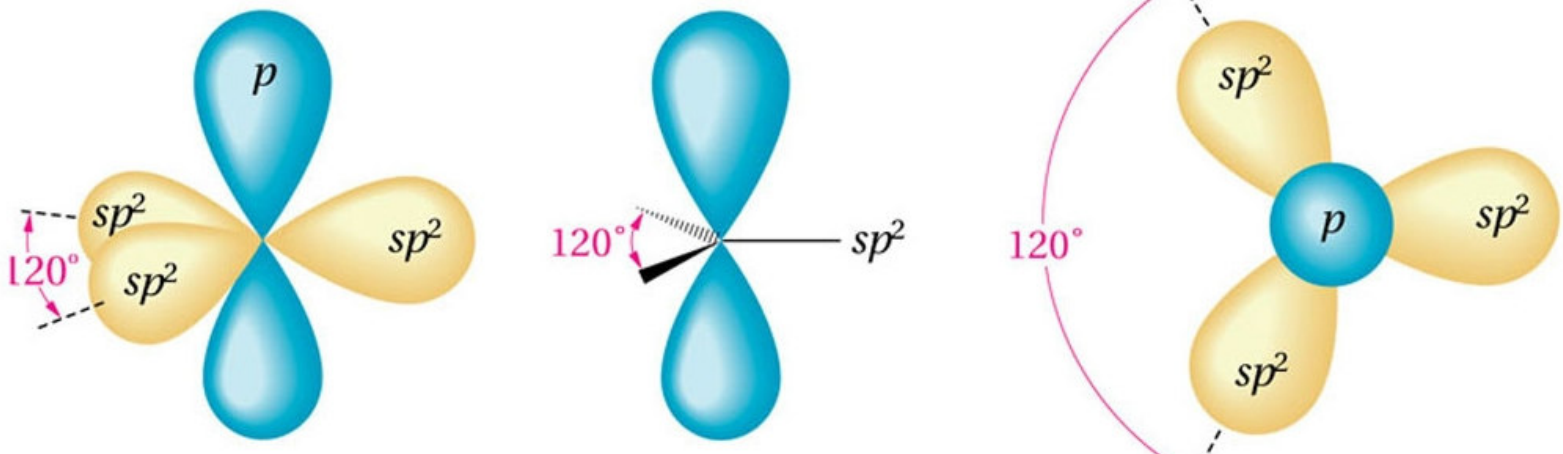
UNHYBRIDIZED VS SP^2-HYBRIDIZED ORBITALS ON CARBON



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.





side view

side view with the sp^2 orbitals represented by lines

top view

- Overlap of sp^2 orbitals in ethylene results in formation of a σ framework
  - One sp^2 orbital on each carbon overlaps to form a carbon-carbon σ bond; the remaining sp^2 orbitals form bonds to hydrogen
- The leftover *p* orbitals on each carbon overlap to form a bonding π bond between the two carbons
- A π bond results from overlap of *p* orbitals above and below the plane of the σ bond
  - It has a nodal plane passing through the two bonded nuclei and between the two lobes of the π molecular orbital

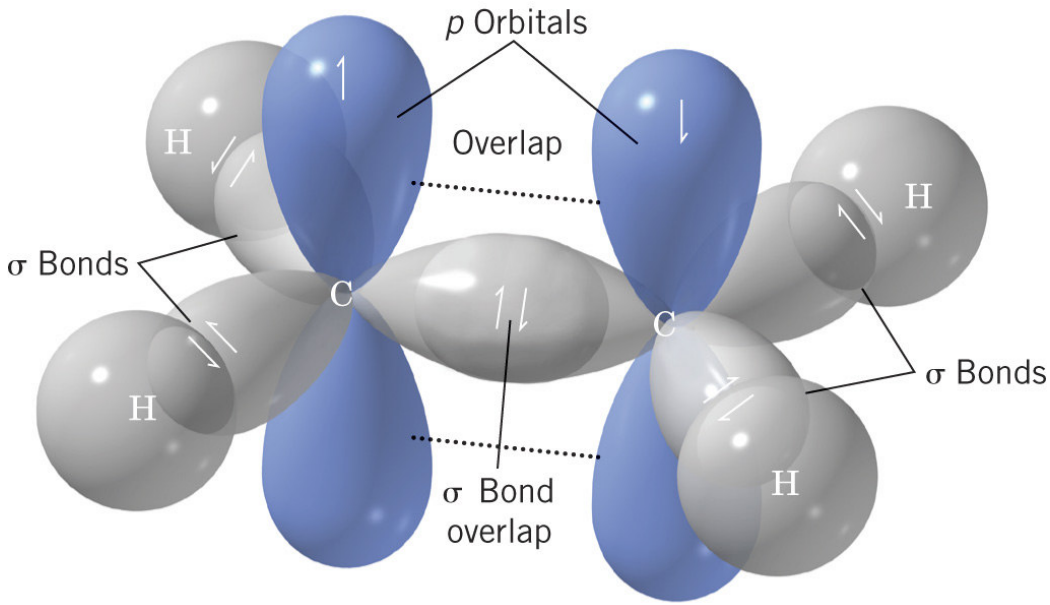


FIGURE 3.4

SCHEMATIC FORMATION OF A CARBON-CARBON DOUBLE BOND

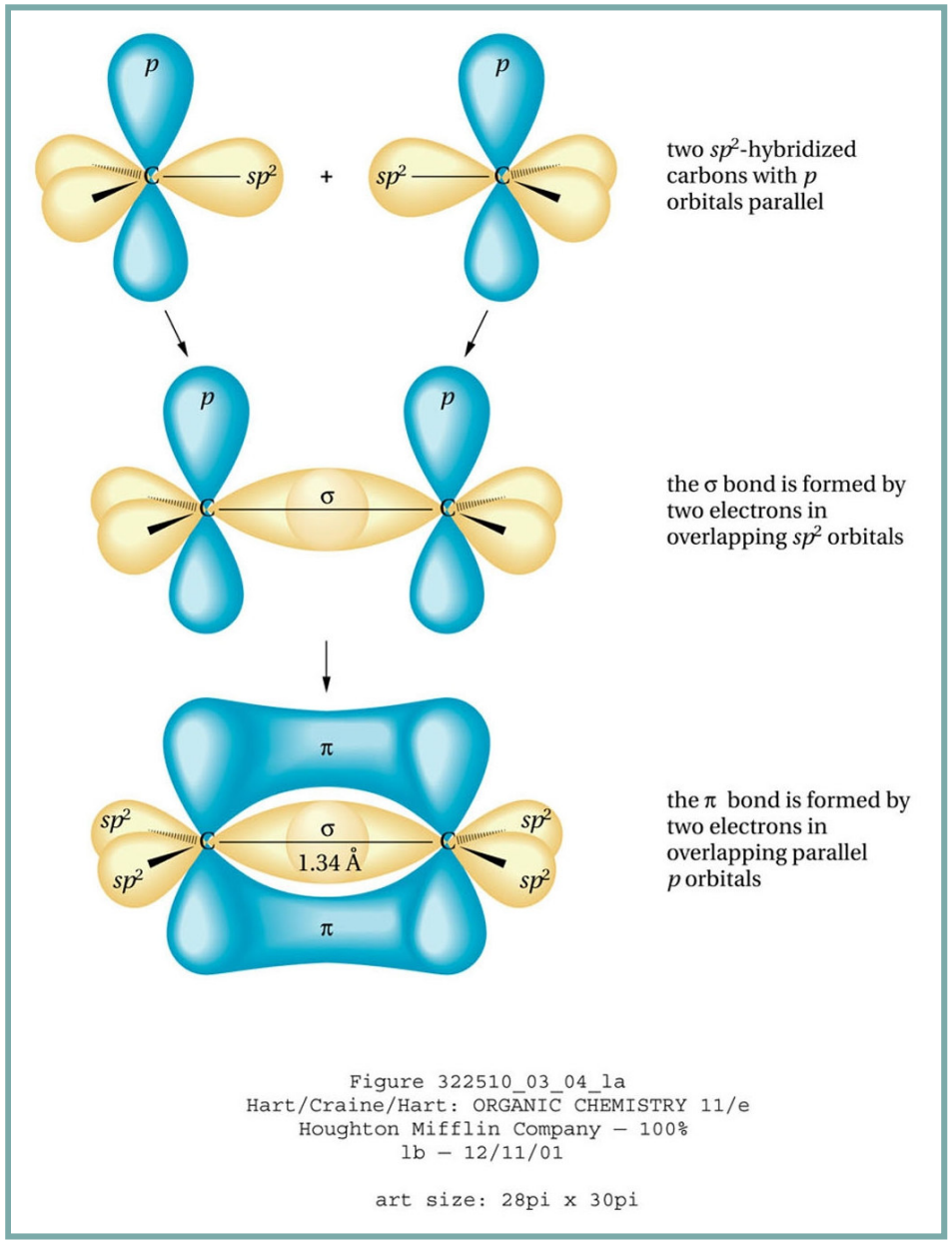


Figure 322510_03_04_1a
Hart/Craine/Hart: ORGANIC CHEMISTRY 11/e
Houghton Mifflin Company — 100%
1b — 12/11/01

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FIGURE 3.5 THE BONDING IN ETHYLENE

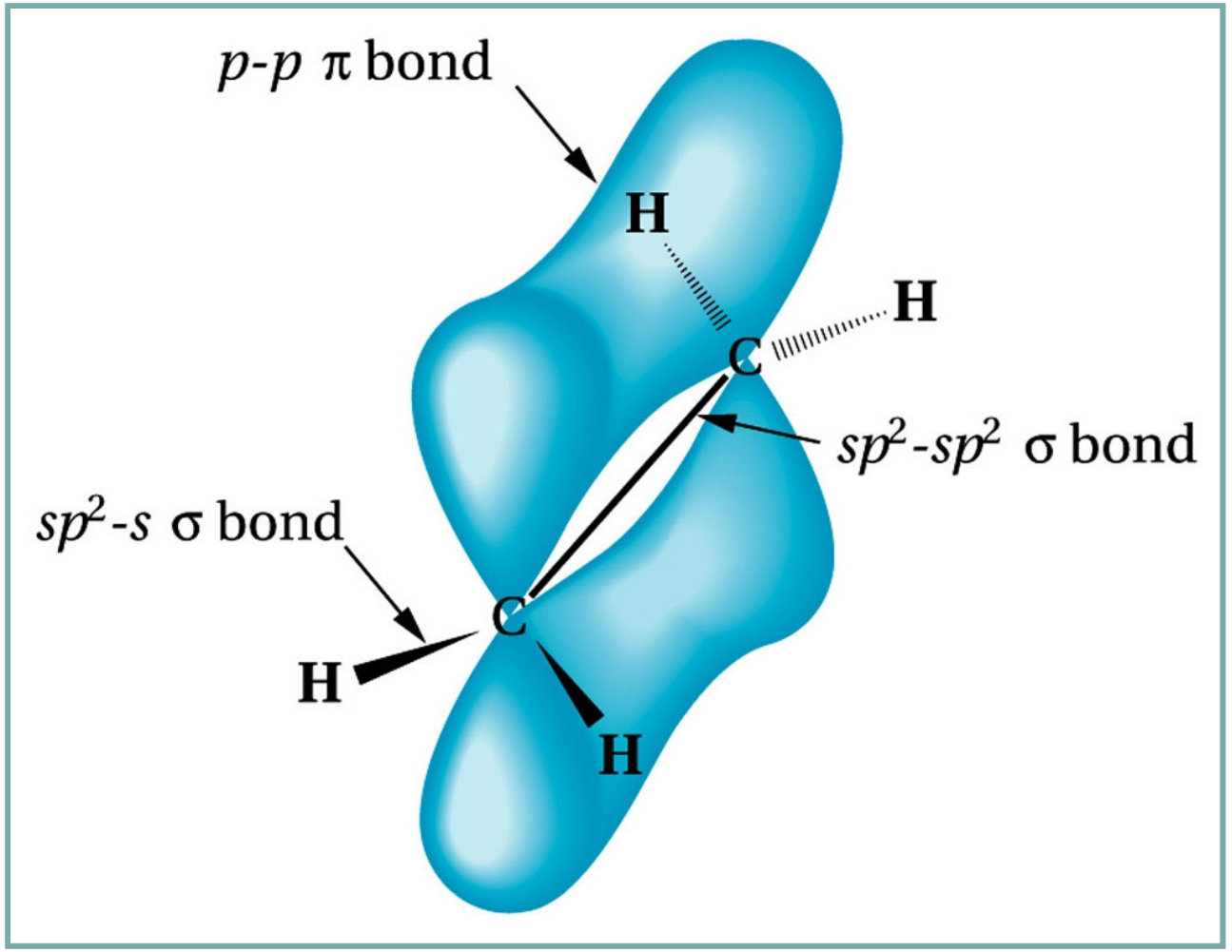
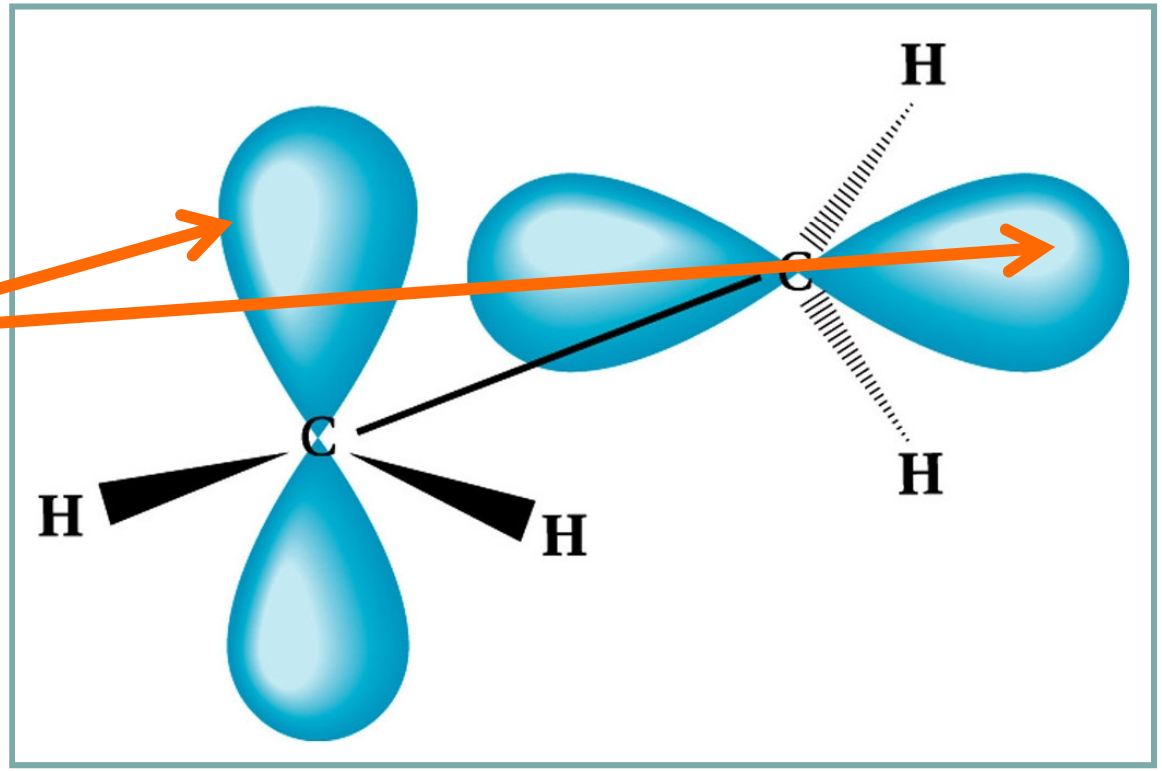


FIGURE 3.6 ROTATION OF ONE SP^2 CARBON

THE ORBITAL MODEL (SP^2) EXPLAIN THE FACTS ABOUT DOUBLE BOND. ROTATION AROUND DOUBLE BOND IS RESTRICTED.

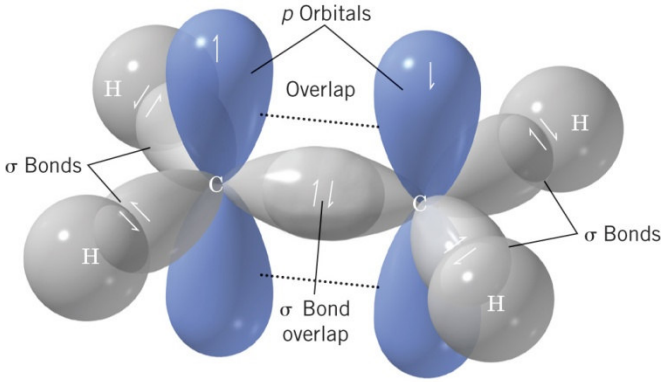
No Orbitla overlap

No π bond

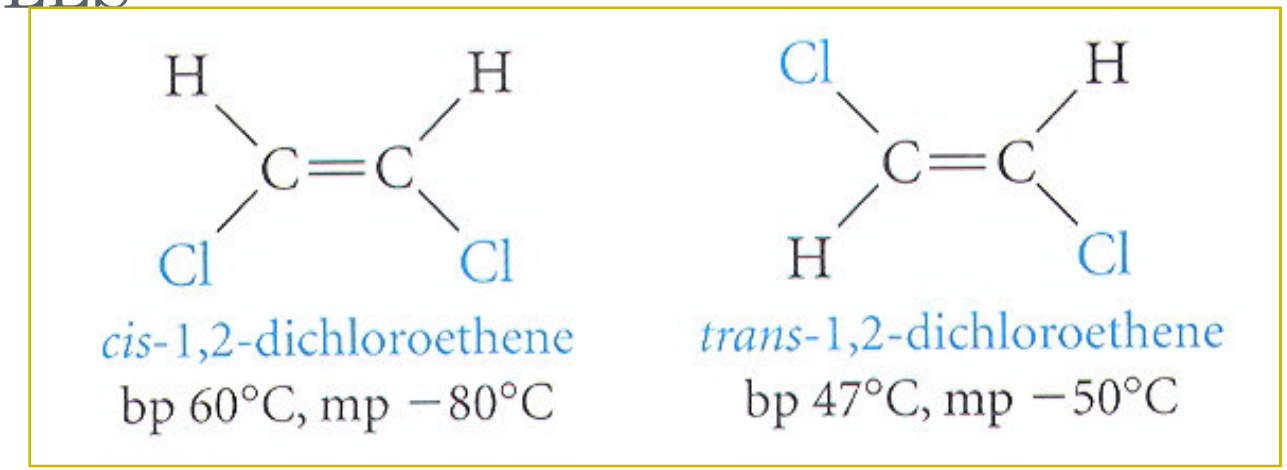


3.5 Cis-Trans Isomerism in Alkenes

- The double bond is formed by end-on overlap of sp^2 orbitals to form a **σ** bond and lateral overlap of aligned *p* orbitals to form a **π bond** (Figure).
- Since rotation around the double bond is restricted, ***cis–trans* isomerism** is possible if each carbon atom of the double bond has two different groups attached to it.

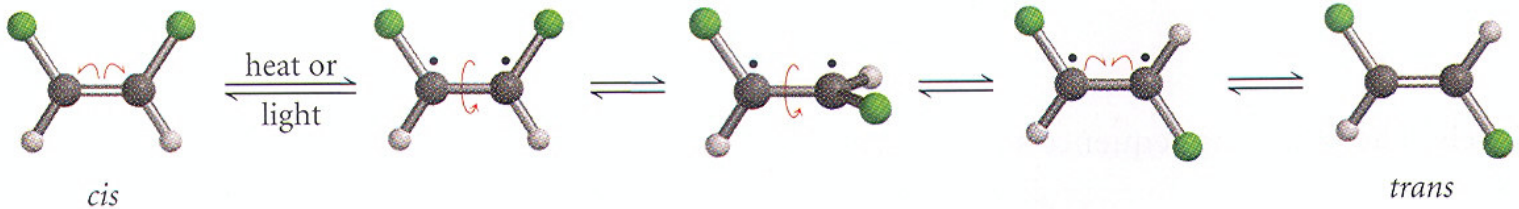


EXAMPLES



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

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



cis *trans*

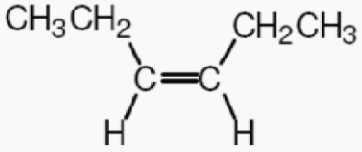
This conversion does not occur under normal laboratory conditions.

PROBLEM 3.6 Which of the following compounds can exist as *cis–trans* isomers? Draw their structures.

a. propene b. 3-hexene c. 2-methyl-2-butene d. 2-hexene

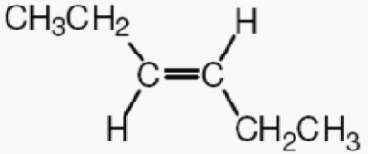
Compounds a and c have only one possible structure because in each case one of the carbons of the double bond has two identical substituents:

a. $H_2C{=}CHCH_3$

b. 

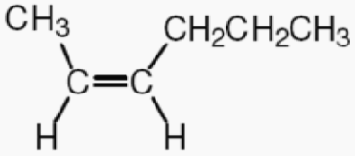
cis-3-hexene

and



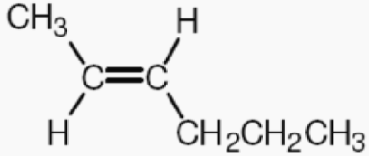
trans-3-hexene

c. $(CH_3)_2C{=}CHCH_3$

d. 

cis-2-hexene

and



trans-2-hexene