Structure and Properties of Alkenes

Reading: Wade chapter 7, sections 7-1- 7-8
Study Problems: 7-32, 7-33, 7-35, 7-50

Key Concepts and Skills:
- Draw and name all alkenes with a given molecular formula.
- Use the E-Z and cis-trans systems to name geometric isomers.
- Predict the relative stabilities of alkenes based on structure and stereochemistry.

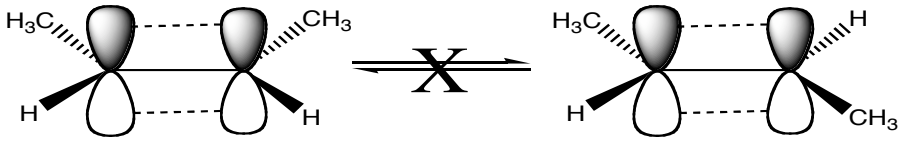
Lecture Topics:

I. Structure of Alkenes

Aspects of the C=C: Bond strength 146 kcal/mol
Sigma bond: 83 kcal/mol
Pi bond: 63 kcal/mol
Pi bonds are more reactive than sigma bonds.

The greater the s character of overlapping orbitals leads to shorter bonds

Restricted rotation about C=C of alkenes



cis trans

II. Elements of Unsaturation

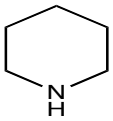
The presence of a pi bond or a ring in a compound decreases the number of H atoms in its molecular formula. Each ring or pi bond decreases 2 H atoms, corresponding to a single **element of unsaturation**. Remember, a fully saturated compound has molecular formula: C_nH_{2n+2}
Thus, C_4H_8 has one element of unsaturation, which may indicate the presence of either one double bond or one ring. See the possibilities below:

C_4H_8 C_4H_8 C_4H_8 C_4H_8 C_4H_8

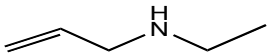
Rules for determining possibilities for molecular structure from molecular formula.
To calculate degrees of unsaturation:

1. Halogens can be counted as H atoms since they are also monovalent
2. Oxygen, which is divalent, is usually ignored in calculating degrees of unsaturation
3. Nitrogen can be counted as 1/2 C, or simply remove an NH from the molecular formula and determine the degrees of unsaturation as you would normally.

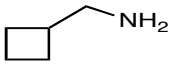
Example: consider $C_5H_{11}N$
Removing NH gives C_5H_{10}, which has one degree of unsaturation (relative to C_5H_{12}, the fully saturated formula)
Possibilities:



$C_5H_{11}N$

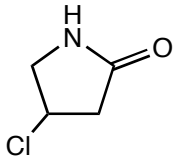


$C_5H_{11}N$

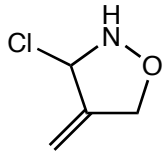


$C_5H_{11}N$

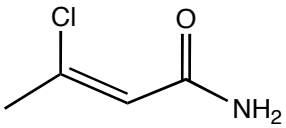
Consider C_4H_6NOCl
Removing NH and counting Cl as H, removing O, gives: C_4H_6, which is missing 4H's relative to the saturated case (C_4H_{10}), thus we have two elements of unsaturation, which could be present as two rings, two double bonds, or a ring and a double bond:
Possibilities:



C_4H_6NOCl



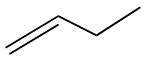
C_4H_6NOCl



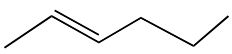
C_4H_6NOCl

III. Nomenclature

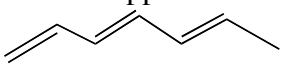
Alkenes are named like alkanes, with the longest chain containing a double bond as the parent. A number is usually given for the location of the double bond. A compound with two double bonds is a diene, three double bonds, a triene, and four double bonds, a tetraene. Otherwise, a logical extension of normal IUPAC rules applies:



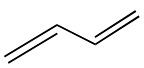
1-butene
but-2-ene



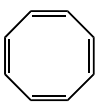
2-hexene
hex-2-ene



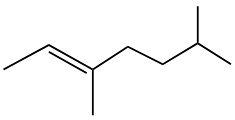
1,3,5-heptatriene
hepta-1,3,5-triene



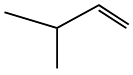
butadiene
buta-1,3-diene



cyclooctatetraene

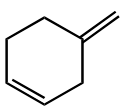


3,6-dimethyl-2-heptene
3,6-dimethylhept-2-ene

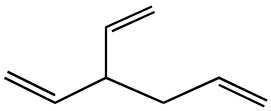


3-methyl-1-butene
3-methylbut-1-ene

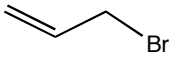
Groups: $=CH_2$ (methylene); $-CH=CH_2$ (vinyl); $-CH_2CH=CH_2$ (allyl)



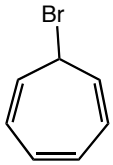
4-methylenecyclohexene



3-vinyl-1,5-hexadiene
3-vinylhexa-1,5-diene



allyl bromide



7-bromocyclohepta-
1,3,5-triene

Cis-trans nomenclature is straightforward for disubstituted alkenes; what about trisubstituted and tetrasubstituted alkenes?

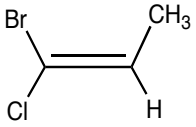
IV. E/Z nomenclature

Rules for unambiguous naming of di-, tri-, and tetrasubstituted alkenes

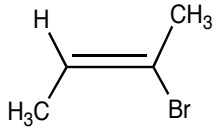
1.Give priorities to the two substitutents on each carbon. Follow the normal Cahn-Ingold-Prelog rules

2. If the highest priority substituents are cis, then the alkene is termed a Z alkene

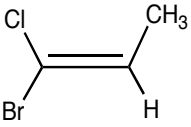
3. If the highest priority substitutents are trans, then the alkene is termed an E alkene



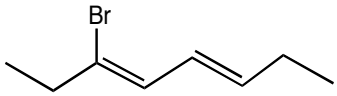
Z-1-bromo-1-chloropropene



Z-3-bromo-2-butene
Z-3-bromobut-2-ene



E-1-bromo-1-chloropropene

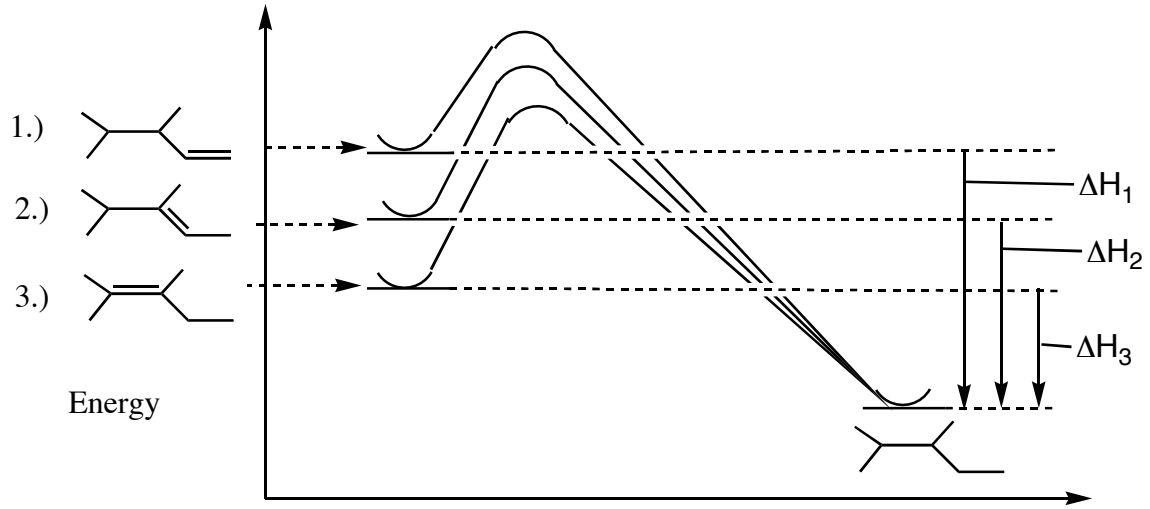


3-bromo-(3Z, 5E)-octadiene
3-bromo-(3Z, 5E)oct-3,5-diene

V. Stability of alkenes

Heats of hydrogenation of various alkenes show that more substituted alkenes (ones with more alkyl groups) are more stable. Alkyl groups stabilize double bonds by electron donation.

Hydrogenation is an exothermic process



A cis double bond is 1 kcal/mol higher in energy than a trans double bond. This difference is attributable to steric repulsion of the cis alkyl groups on the double bond.

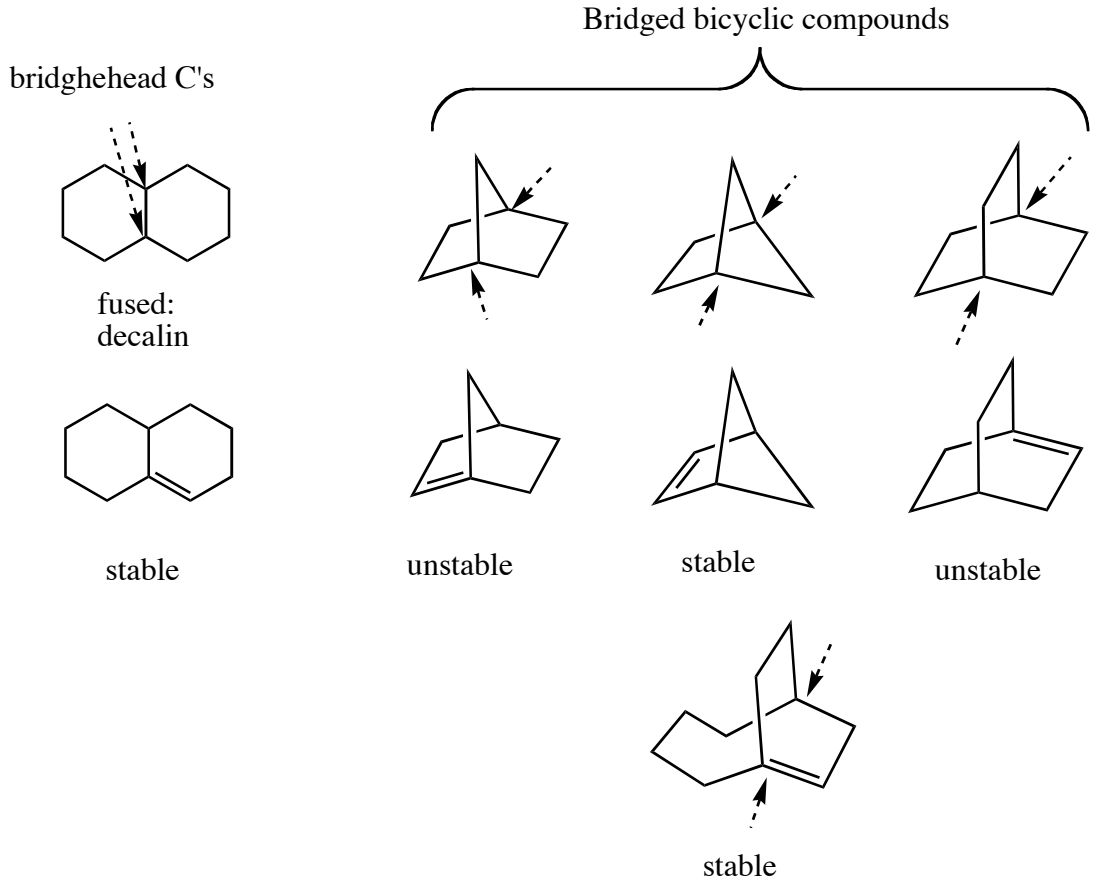
VI. Cycloalkenes

•**Cycloalkenes** from 3-7 membered rings exist in cis form; the trans form is geometrically impossible in small rings without breaking the ring open. In very small rings like cyclobutene and cyclopropene, ring strain is quite large because of angle strain: the ideal alkene bond angle of 120° is compressed to 90° (in the case of cyclobutene) or 60° (in the case of cyclopropene). Thus cyclopentene is 4 kcal/mol more stable than cyclobutene.

•Trans cycloalkenes are possible for ring sizes 8 and above. See cis and trans cyclodecene:

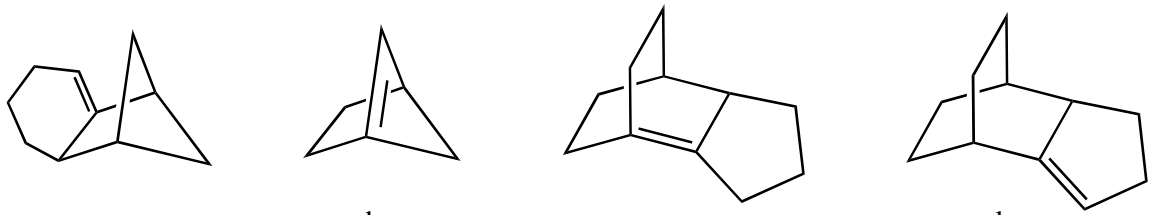
cis-cyclodecene trans-cyclodecene

•Bredt's rule states that in a **bridged bicyclic compound**, the bridgehead carbons cannot have a double bond unless one of the rings contains 8 carbons or more. *Note*: distinguish between fused ring systems and bridged bicyclic ring systems. Bredt's rule does not apply to fused ring systems.



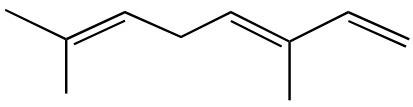
Additional Problems for practice:

1. Identify any Bredt's rule violators from the following:

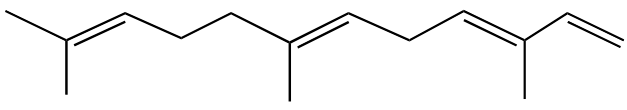


2. Give correct IUPAC names for the following compounds:

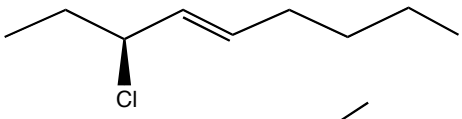
a



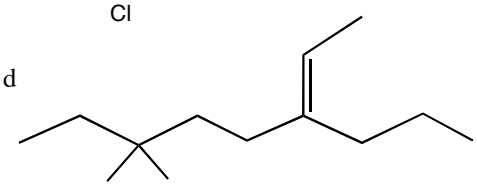
b



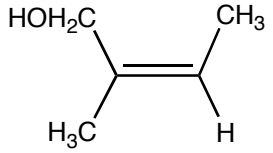
c

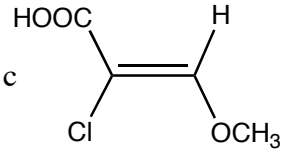


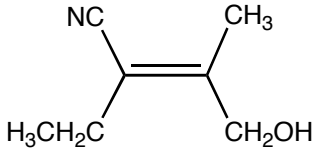
d

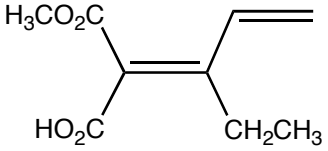


3. Assign E or Z configuration to the following alkenes:

a 

c 

b 

d 

4. Calculate the degrees of unsaturation in these formulas and suggest structures:
   a. $C_8H_{10}N_4O_2$
   b. $C_{14}H_9Cl_5$
   c. $C_{17}H_{23}NO_3$