5.12 Lecture 10

IX. Alkenes

Suggested Reading: Chapter 6 and 9.12

Suggested Problems: 6.23-6.29, 6.33, 6.36, 6.39-6.45, 6.47-6.54

A. Structure

B. Degrees of Unsaturation

C. Nomenclature

D. Double Bond Geometry

1. Configurational isomers (*cis-trans*)

2. *E-Z* Designation

E. Stability

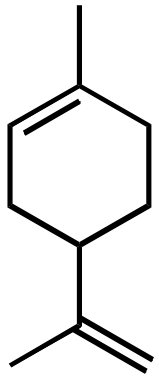
F. Cycloalkenes

G. Example: Addition of H-X to an Alkene

1. Regiospecificity
2. Carbocation Stability (Hyperconjugation, Inductive Effects)
3. Hammond Postulate
4. Stereochemistry
5. Carbocation Rearrangements

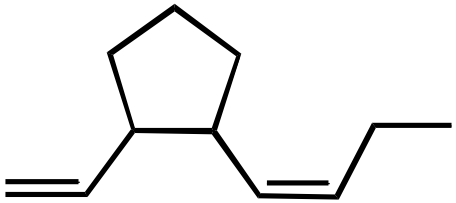
Alkenes!

limonene



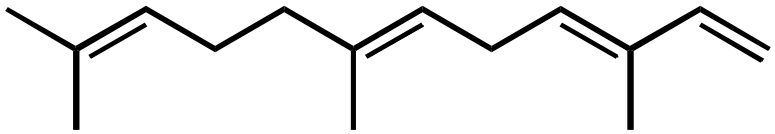
lemon and orange oils

multifidene



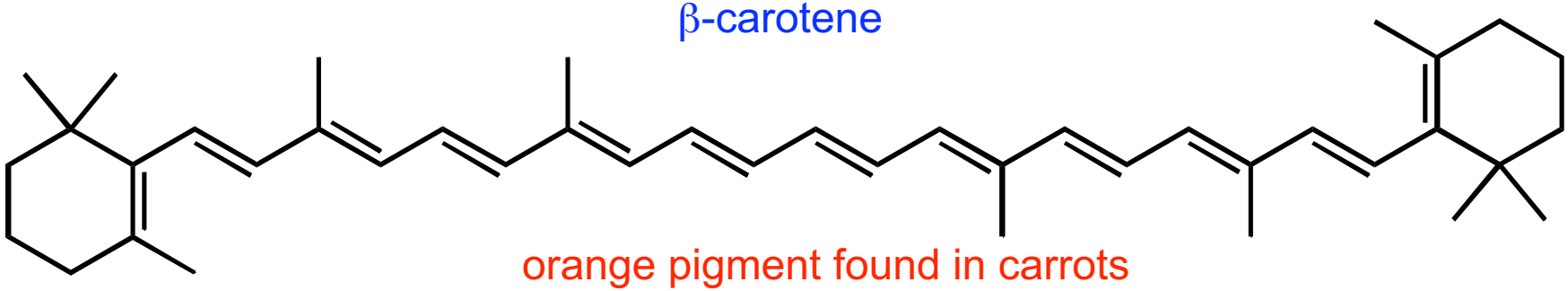
sex attractant of brown algae

α-farnesene



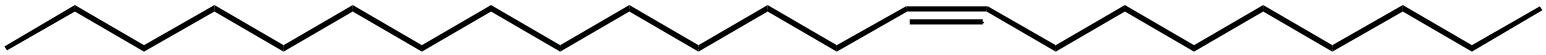
waxy coat on apples

β-carotene



orange pigment found in carrots

muscalure



pheromone of house fly

Calculating the Degrees of Unsaturation from a Molecular Formula

Alkane: C_nH_{2n+2}

Alkene: C_nH_{2n} (fewer hydrogen atoms)

Degrees of unsaturation = number of rings and/or multiple bonds

1 degree of unsaturation = 1 ring or 1 double bond

2 degrees of unsaturation = 2 double bonds, 2 rings, 1 ring + 1 double bond, or 1 triple bond

Example: **C_6H_{10}** (fully saturated would be C_6H_{14})

14 H - 10 H = 4 hydrogen atoms = **2 H_2** (pairs of hydrogen atoms) = **2 degrees of unsaturation**

If molecular formula contains:

1) Halogen (F, Cl, Br, I) - add number of halogens to number of hydrogen atoms

   $C_4H_6Br_2$ is equivalent to C_4H_8, degrees of unsaturation = 1

2) Oxygen - ignore it!

   C_5H_8O is equivalent to C_5H_8, degrees of unsaturation = 2

3) Nitrogen - subtract number of nitrogen atoms from number of hydrogen atoms

   C_5H_9N is equivalent to C_5H_8, degrees of unsaturation = 2

Naming Alkenes

Suffix is -ene instead of -ane

Straight-Chain Alkenes

1. Find parent (longest chain containing a double bond)
2. Number the chain

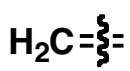
   Start at the end nearest the double bond

   If double bonds are equidistant from both ends, start at the end with the nearest branch point

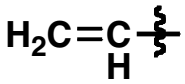
   (Want the double bond carbons to have the lowest number possible)
3. Write the full name. Place the number corresponding to the double bond before the parent name.
4. Use -diene, -triene, etc. if more than one double bond is present

Cycloalkenes - Number so that the double bond is between C1 and C2 and that the 1st substituent has the lowest number possible.

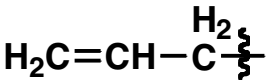
Special Groups:



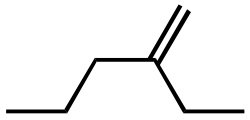
methylene



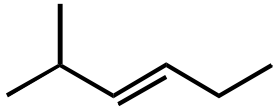
vinyl



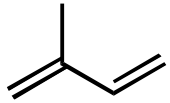
allyl



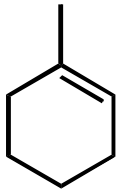
2-ethyl-1-pentene



2-methyl-3-hexene

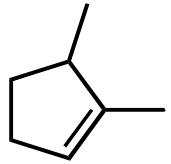


2-methyl-1,3-butadiene



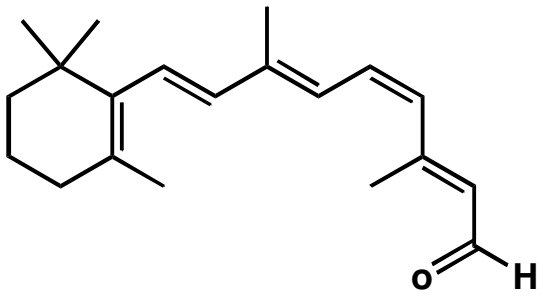
1-methylcyclohexene

1,4-cylcohexadiene

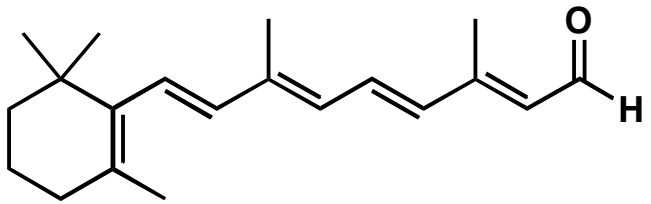


1,5-dimethylcyclopentene

Cis-Trans Isomerization in Life



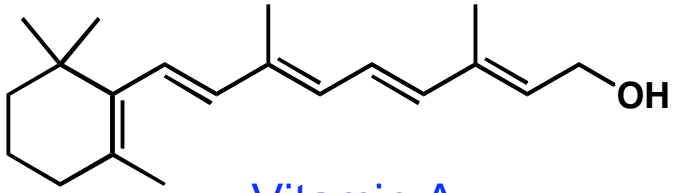
light



11-*cis*-retinal

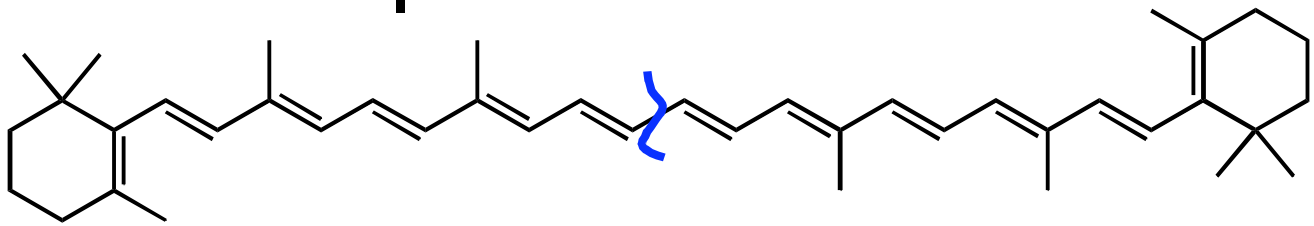
All-*trans*-retinal

(electrical signal to brain)



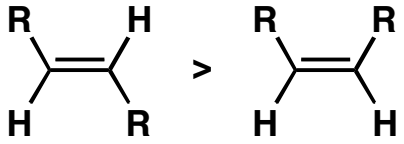
Vitamin A

This isomerization is the initial event in visual excitation!

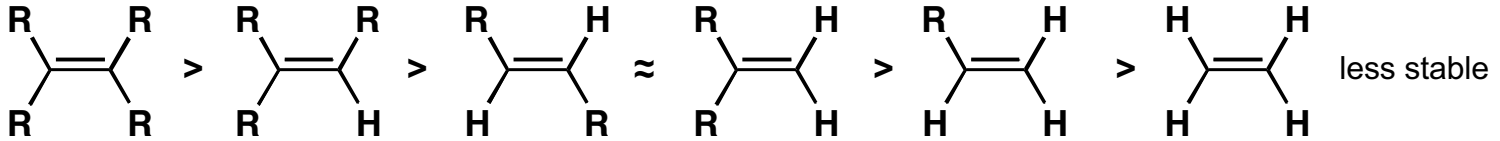


β-carotene

Alkene Stability

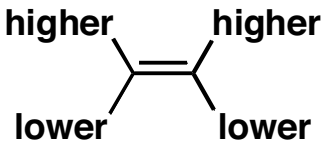
more stable  less stable

trans cis

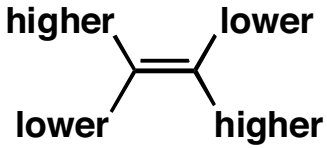
more stable  less stable

Substitution: tetra- tri- di- mono-

E-Z Nomenclature



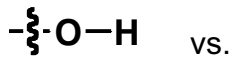
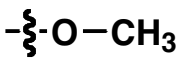
Z (zusammen)



E (entgegen)

Cahn-Ingold-Prelog Rules for Assigning Priority

1. Look at atoms directly attached to the double bond. Higher atomic number = higher priority
2. If no difference exists at the first attached atom, keep going down the line until the first difference is reached.
3. Multiple bonded atoms are equivalent to the same number of single-bonded atoms

 vs. 

lower higher