

CHEM 321 Organic Chemistry I - Professor Kathleen Kilway

"Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 3 - 3, 4, 5, 7, 11, 12, 13, 16, 22, 23, 26, 27, 30, 31, 32, 36, 38, 40, 41, 43, 44, 50.

CHAPTER 3: ALKENES AND ALKYNES

Section 3.1

I. Preview

Section 3.2

II. Alkenes: Structure and Bonding

A- Ethene

- 1- The simplest alkene, $\text{CH}_2=\text{CH}_2$.
- 2- It is universally called ethylene.
- 3- See Figure 3.2 on page 98 for ethylene framework.

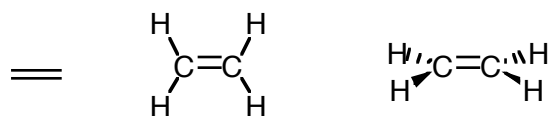


Figure 1

B- sp^2 hybrids

- 1- It is the combo of three atomic orbitals of carbon ($2s$, $2p_x$, $2p_y$).
- 2- $2p_z$ orbital on each carbon is occupied with one e^- .
- 3- See Figure 3.4 on page 100 for its orbital direction.

C- Double Bond

- 1- π orbital is the overlap of two p orbitals.
 - a- It is not a cylindrical bond.
 - b- It has a plane of symmetry.
 - c- There are both π and π^* molecular orbitals formed.
- 2- This is where two atoms are bonded with both a σ bond and a π bond.

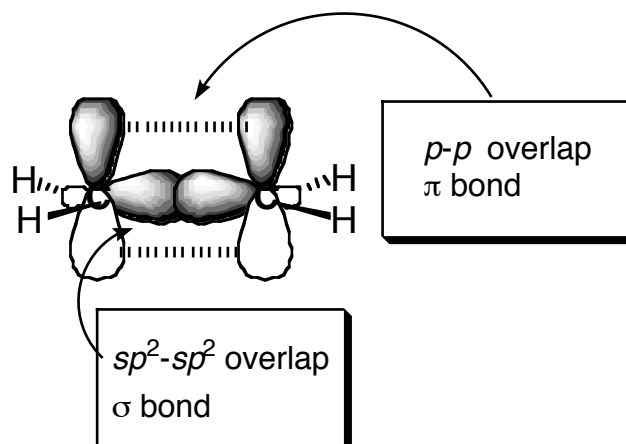


Figure 2

- 3- See Figure 3.13 on page 104 for examples of both types of bonds.
- 4- Rotation of a double bond from 0° through 90° to 180° costs 65.9 kcal/mol.
 - a- This rotation destroys the p - p overlap.
 - b- The resulting orbitals are orthogonal to one another.

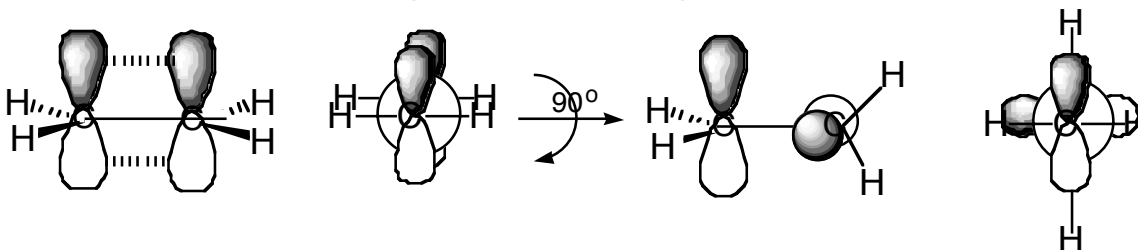


Figure 3

Section 3.3

III. Derivatives and Isomers of Alkenes

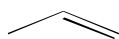
A- Vinyl Group

- 1- It is not named ethenyl or ethylenyl group.
- 2- E.g., Vinyl bromide ($\text{CH}_2=\text{CHBr}$).
- 3- See Figure 3.16 on page 107 for an example.

B- Propene

- 1- Structure is $\text{CH}_2=\text{CHCH}_3$.
- 2- Take the alkane, drop the -ane, and add -ene, leaving alkene.
- 3- Priority for naming starts with terminal C of double bond.
 - a- $\text{BrCH}=\text{CHCH}_3$, 1-Bromopropene.

C- Allyl Group



- 1- Structure is $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{X}$.
- 2- See Figure 3.19 on page 108 for some more allyl compounds.

D- There are two possible forms

- 1- Cisoid (*cis*) and Zusammen (*Z*)
 - a- *Cis* is where the hydrogens line up on the same side of the double bond.
 - b- *Z* is where two groups of highest priority are on the same side.
- 2- Transoid (*trans*) and Entgegen (*E*)
 - a- *Trans* is where the hydrogens line up on the opposite sides of the double bond.
 - b- *E* is where two groups of highest priority are on opposite sides.

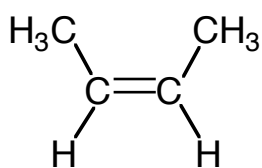
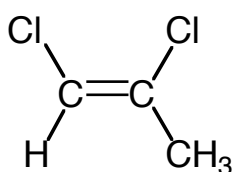
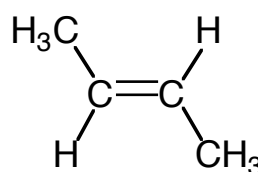
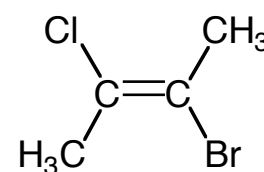
*cis**Z**trans**E*

Figure 4

- 3- See Figure 3.21 on page 109 for an example.
- 4- Problems 3.4 and 3.5 on page 110 are good examples of isomers!

Section 3.4

IV. Nomenclature

A- Most of the rules used for alkanes are also used for alkenes.

- 1- Chains are numbered so that the double bond has the smallest number.
- 2- When molecules contain more than one double bond they are called:
 - a- Dienes contain two double bonds.
 - b- Trienes contain three double bonds.

B- Cycloalkenes

- 1- Cycloalkenes are molecules that contain a ring.
- 2- See Figure 3.23 on page 111 for some examples of Nomenclature.

Section 3.5

V. The Cahn-Ingold-Prelog Priority System

A- Use of:

- 1- The first step is to assign the priority according to the atomic number.
- 2- For isotopes, look at the atomic weight to determine the priority (See Figure 3.28 on page 113).
- 3- For non-isotopes, look at the groups attached to the atoms, which are tied (See Figure 3.30 on page 113).
- 4- Multiple bonds are treated as multiplied single bonds (See Figure 3.32 on page 115).
- 5- Take a look at Figure 3.27 on page 113 for use of this system.

B- For E/Z Isomerism

- 1- Number (1 and 2) of each group attached to the sp^2 carbons.
- 2- If both 1 groups are on the same side of the double bond, then it is Z.
- 3- If 1 groups are on the opposite side of the double bond, then it is E.

Section 3.6

VI. Relative Stability of Alkenes: Heats of Formation

A- Heat of Formation, ΔH_f°

- 1- This is the heat required for the formation of a molecule/compound in a reaction of its constituent elements in their standard states (See Table 3.1 on page 116).
 - a- Exothermic Reactions
 - i- This is where heat is released.
 - b- Endothermic Reactions
 - i- This is where energy needs to be supplied.
 - c- Stability

- i- The more strong bonds present; the higher the stability.
- ii- For C-C bond strengths: $sp^2-sp^2 > sp^2-sp^3 > sp^3-sp^3$ (the more internal the double bond, the more stable the compound).
- iii- More negative ΔH_f° , more stable the molecule.
- iv- Stability goes as follows:

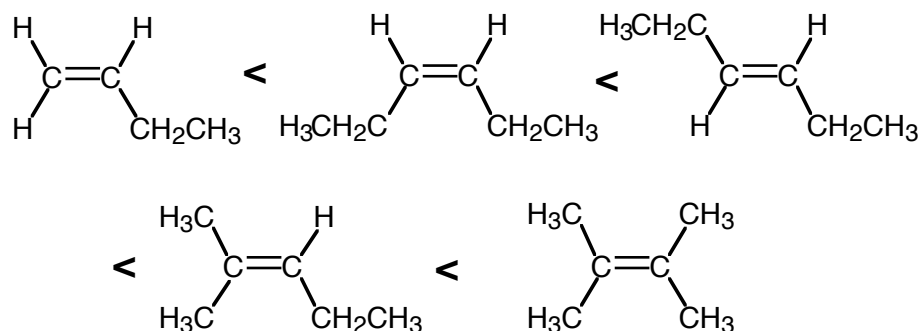


Figure 5

Section 3.7

VII. Double Bonds in Rings

A- Figure 3.39 on page 119 shows some cyclic polyenes.

B- It is difficult to add a *trans* double bond to small rings.

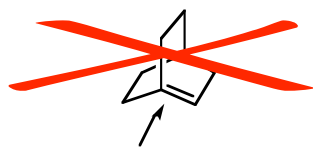
- 1- This is due to severe steric strain.
- 2- See Figure 3.41 on page 120 for the formation of *trans*-cyclopentene.
- 3- *Trans*-Cyclooctene does exist but is less stable than *cis*-cyclooctene.

C- Bridgehead Position

- 1- Atoms in this position are in a bicyclic position (i.e., bridgehead atom are contained in two rings).
- 2- See Figure 3.44 on page 122 for an example.

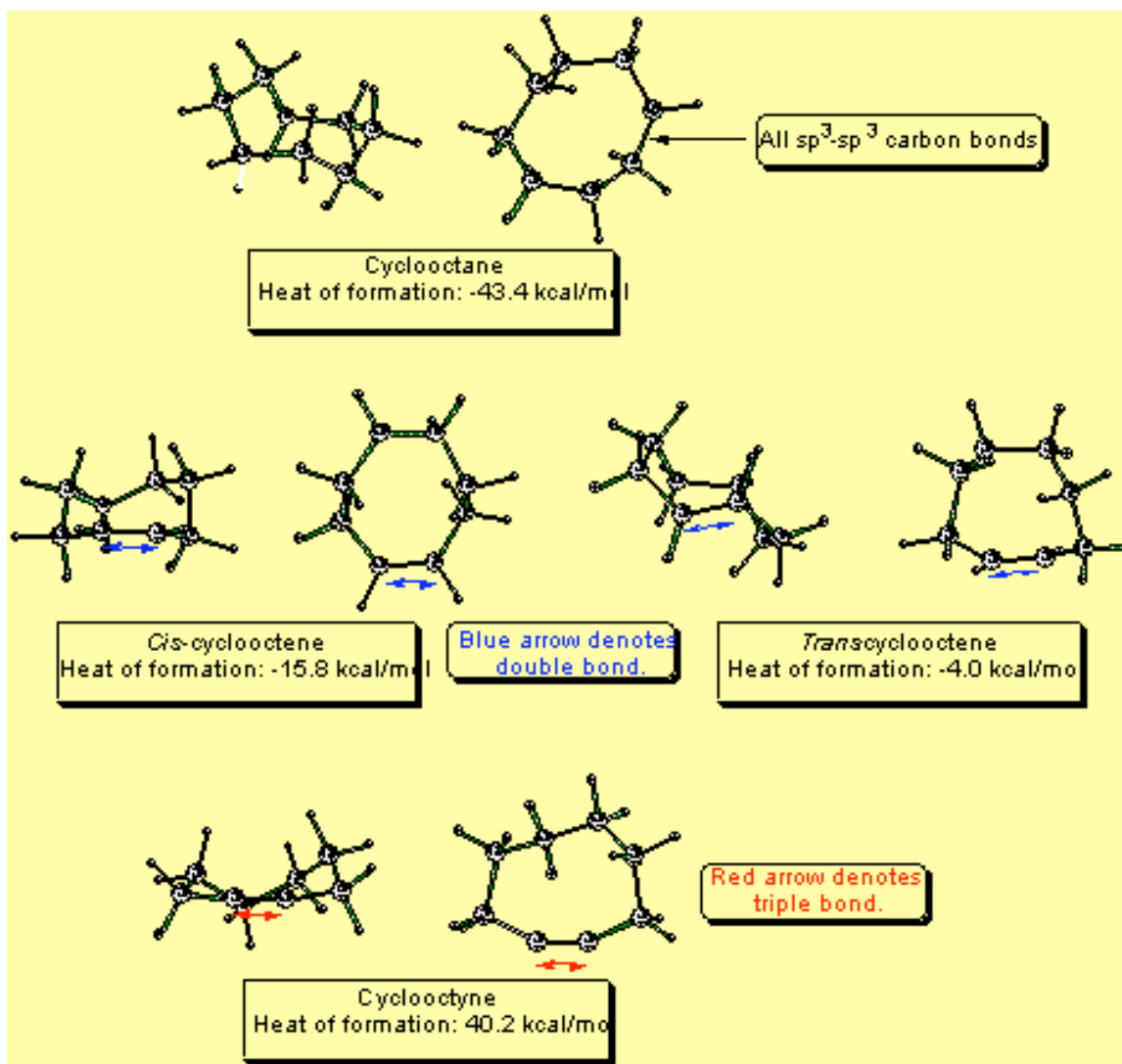
D- Bredt's Rule

- 1- No examples of double bonds are found in the bridgehead position.
- 2- This is due to poor *p* orbital overlap.



bridgehead position

- 3- See Figure 3.45 on page 122 for an illustration.



Section 3.8

VIII. Physical Properties of Alkenes

- 1- Olefins is the trivial name for alkenes.
- 2- Read section.

Section 3.9

IX. Alkynes: Structure and Bonding

A- Acetylene

- 1- This is the trivial name for the simplest alkyne.
- 2- Its structure is HCCH.

B- sp hybrids

- 1- sp bond yields a σ bond between the two carbon atoms.
- 2- $2p_y$ and $2p_z$ orbitals are occupied with one e^- each.
- 3- These $2p_y$ and $2p_z$ orbitals combine to give two π bonds, which are 90° to one another.

4- See Figure 3.53 on page 126 for the formation of acetylene.

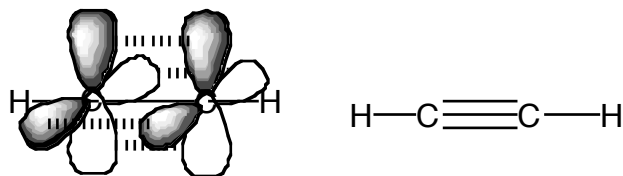


Figure 6

5- Carbon-carbon bond lengths are: single (1.54 Å) > double (1.33 Å) > triple (1.20 Å).

Section 3.10

X. Relative Stability of Alkynes: Heats of Formation

- 1- Read section.
- 2- In general, the more π bonds present, the less stable the molecule, and the more endothermic the reaction.

Section 3.11

XI. Derivatives and Isomers of Alkynes

A- For simple alkynes, take the -ane off the alkane, add -yne, gives alkyne.

B- Groups and Naming

- 1- Propynyl
 - a- 3-Propynyl is $\text{H}-\text{C}\equiv\text{C}-\text{CH}_2-\text{X}$.
 - b- Common name is propargyl.
 - c- See Figure 3.57 on page 128.
- 2- The ethynyl chloride may also be called 1-chloroacetylene.
- 3- Double bonds have higher priority than triple bonds.

Section 3.12

XII. Triple Bonds in Rings

- 1- Smallest ring to include a triple bond is cyclooctyne. It is reactive but stable at room temperature.

Section 3.13

XIII. Physical Properties of Alkynes

- 1- Refer to Table 3.5 on page 130.

Section 3.14

XIV. Acidity of Alkynes

A- Acetylide

- 1- This is where an anion is left behind from the removal of a terminal acetylenic hydrogen.
- 2- See Figure 3.64 on page 131 for an example.
- 3- Acetylene is a relatively strong acid for a hydrocarbon.

- 4- This acidity is a result of the lower energy *sp* orbital.

Section 3.15

XV. Molecular Formulas and Degrees of Unsaturation

A- Degree of Unsaturation, Ω

- 1- This is the total number of π bonds and rings in a hydrocarbon.
- 2- Formulas:
 - a- For normal compounds containing only C and H:

$$\Omega = (2C+2-H)/2 = \text{\# of rings} + \text{\# of multiple bonds.}$$
 - b- For molecules containing halogens (where X = # halogens):

$$\Omega = (2C+2-X-H)/2 = \text{\# of rings} + \text{\# of multiple bonds.}$$
 - c- For molecules containing nitrogen (where N = # nitrogens):

$$\Omega = (2C+N+2-H-X)/2 = \text{\# of rings} + \text{\# of multiple bonds.}$$
- 3- See Figure 3.66 on page 132 for some examples.

Section 3.16

XVI. An Introduction to Addition Reactions of Alkenes and Alkynes

A- Reactions

- 1- Alkenes and other molecules containing π systems such as alkynes undergo addition reactions with Brønsted acids (proton donors) of the general formula HX.
- 2- See Figure 3.67 on page 133 for an example reaction.

Section 3.17

XVII. Electronegativity

A- Definition

- 1- Ability of an atom to attract electrons.
- 2- The most electronegative atoms are in the upper right of the periodic table.

Section 3.18

XVIII. Mechanism of the Addition of Hydrogen Halides to Alkenes

A- Addition of Hydrogen Halide to Alkenes

- 1- The addition of hydrogen halides to alkenes is a two-step reaction.
 - a- HX donates a proton to one of the two equivalent carbons of the π bond.
 - i- HX molecule acts as a Brønsted acid.
 - ii- Alkene acts as Brønsted base.
 - b- Newly formed anion X^- captures the newly formed carbocation.
- 2- See Figure 3.71 on page 134 for the reaction with arrow formalism.

B- HOMO-LUMO Interactions

- 1- HOMO-Highest Occupied Molecular Orbital.
- 2- LUMO-Lowest Unoccupied Molecular Orbital.
- 3- When a filled occupied orbital overlaps an empty orbital, the two electrons are stabilized in the new, lower energy molecular orbital.

C- Reaction Energetics

- 1- Exothermic Reaction: products are more stable than the starting material.
- 2- Endothermic Reaction: products are less stable than the starting material.
- 3- See Figure 3.74 on page 137 for an example.

D- Energy versus Reaction Progress Diagram

- 1- Shows the overall change in energy as the reaction proceeds.
- 2- Energy is plotted on the vertical axis, and reaction progress on the horizontal axis.
- 3- See Figure 3.75 on page 138 for an example.
 - a- Activation energy: amount of energy that is required to pass over the highest transition state.

Section 3.19**XIX. The Regiochemistry of the Addition Reaction****A- Addition to Asymmetric Alkene**

- 1- Two possible additions of HCl to isobutene.
 - a- One possibility is the formation of a tertiary carbocation, the other the formation of a primary carbocation.
 - b- Tertiary carbocation is more stable than the primary carbocation, so only the tertiary carbocation leads to a product.
 - c- See Figure 3.76 on page 139 for an illustration.
- 2- Order of carbocation stability: tertiary > secondary > primary > methyl (See Figure 2.78 on page 140).

Section 3.20**XX. A Catalyzed Addition to Alkenes: Hydration****A- Some HX are not strong enough acids to protonate an alkene**

- 1- Water (H₂O) can't protonate an alkene.
- 2- Addition of a small amount of an acid as catalyst solves the problem.
 - a- A catalyst is a material that increases the rate of a reaction without being consumed.
- 3- See Figure 3.81 on page 143 for the mechanism.

Section 3.21**XXI. Synthesis: A Beginning****A- Synthesis**

- 1- The construction of target molecules from smaller pieces.
- 2- It's working a reaction backwards: from the product to the starting material.