Learning Guide for Chapter 11 - Alkenes I

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   hydroboration-oxidation

I. Introduction to alkenes

Bond structure

What is the hybridization, geometry, and molecular orbitals of an alkene?

\[
\begin{align*}
\sigma & \quad \text{hybridization: } sp^2 \\
\pi & \quad \text{geometry: trigonal planar} \\
sp^2 & \quad \text{molecular orbitals: } sp^2 + sp^2 \rightarrow \sigma \\
& \quad p + p \rightarrow \pi
\end{align*}
\]

What is wrong with the following line structures?

- C=C atoms are trigonal planar can't go up and down
- angle should be 120° not tetrahedral
- usually this problem occurs when making C=C from 3° C

Which is higher in energy, the sigma or the pi bond? Why?

\begin{align*}
\text{pi bond} & \quad \text{farther from C nuclei}
\end{align*}

Classifying compounds with C=C's

What is the difference between alkenes, aromatic compounds, and unsaturated compounds?

alkene: hydrocarbon with a C=C

aromatic compound: any compound containing a benzene ring

unsaturated compound: any compound containing a C=C or C---C, can have O, N, X
Label each of the following.

- alkene unsaturated
- aromatic ring (not an alkene)
- aromatic alkene unsaturated
- unsaturated alcohol (not an alkene)

Compounds with more than one C=C are classified by how far apart they are. Which of the following structures is isolated, conjugated, and cumulated?

- cumulated: 2 C=C's sharing a C
  - less stable than isolated, more reactive
- isolated: at least one sp³ C between the C=C
  - behave like normal alkenes
- conjugated: 2 or more C=C's next to each other
  - more stable than isolated
  - can absorb UV and visible light

Physical properties

How do the physical properties of alkenes compare to those of alkanes? very similar

- polarity: nonpolar
- water solubility: very low
- density: less than water
- flammability: high

What can you conclude from the following boiling points?

- bp = 0°C
- bp = -6°C
- bp = 30°C
- bp = 25°C

- alkenes and alkane have similar bp's
- alkene bp's increase as MW increases
- branching causes a slight drop in bp (less surface area)
Reactivity

How does the reactivity of alkenes compare to alkanes?  alkenes are more reactive!

Which of the following would you predict that an alkene could react with? Why?

nucleophile  electrophile  acid  base  radical

electrons in pi bond can attach a C or H or split apart

How strong of a reagent is an alkene? Why?  not very strong
no charge, no lone pairs

Predict the three types of mechanistic steps that an alkene can undergo.

\[
\begin{align*}
\text{Nu} & \quad \begin{array}{c}
\text{E}^+ \\
\uparrow \\
\end{array} & \quad \begin{array}{c}
\text{carbocation} \\
\text{will continue the reaction by} \\
\text{reaction as an electrophile} \\
\end{array} \\
\text{base} & \quad \begin{array}{c}
\text{H-base} \\
\uparrow \\
\end{array} & \quad \begin{array}{c}
\text{carbocation} \\
\text{ditto} \\
\end{array} \\
\text{radical} & \quad \begin{array}{c}
\text{attackee} \\
\cdot \text{X} \\
\uparrow \\
\end{array} & \quad \begin{array}{c}
\text{radical} \\
\text{will now act as a radical attacker} \\
\end{array}
\end{align*}
\]

Occurrence and uses of alkenes

Are alkenes common in nature?  no

Where are the following two compounds found?

\[
\begin{align*}
\alpha\text{-pinene} & \quad \text{extract of evergreen trees (terpentine)} \\
\text{muscalure} & \quad \text{sex attractant of the common housefly}
\end{align*}
\]

Where do alkenes come from?  petroleum

What is the most abundantly used organic compound, and what can you make with it?

\[
\begin{align*}
\text{polyethylene (HDPE, LDPE)} \\
\text{ethanol} & \quad \text{milk jugs, plastic bags} \\
\text{acetic acid (vinegar)} & \quad \text{also used to make fruit} \\
\text{ethylene glycol (antifreeze)} & \quad \text{and tomatoes ripen after} \\
\text{picking}
\end{align*}
\]
Spectroscopy

IR: What bands does an alkene have that an alkane does not?

* C=O 1680-1620 cm\(^{-1}\) sharper, smaller than a C=O band (not very polar)
* C-H on C=C 3100-3000 cm\(^{-1}\) spike on the left side of the C-H (fewer of them)
C=C bending 960-730 cm\(^{-1}\) sometimes useful for stereochemistry
* memorize these

NMR: What chemical shift do H's on C=C's have? 4.5-6.5 ppm
What happens to the splitting in an alkene?

- coupling constants are different - neighbor rule doesn't work

\[
\begin{align*}
\text{a} & \quad \text{b} \\
\text{O} & \quad \text{a - singlet 2.2-2.5 ppm} \\
\text{\textbullet} & \quad \text{b - doublet of doublets 7.3 ppm (next to O and on C=C)} \\
\text{\textbullet} & \quad \text{c, d - doublet of doublets 4.6 and 4.9 ppm (on C=C and near O)}
\end{align*}
\]
Stability of alkenes

Put the following alkenes in order from most to least stable.

least stable
4

most stable
1

4 C > 3 C > 2 C > 1 C

Now consider the alkenes below. Which is the most and least stable?

trans > geminal > cis

least crowded = most stable

E > Z

Which of these two rules takes precedence?

amount of substitution is more important than stereochemistry

Why are small cyclic alkenes less stable? ring strain

more reactive than other alkenes

What stereochemistry do most cyclic alkenes have? cis (or Z)

cis stable

How big does a ring have to be before it is stable with a trans C=C?

at least 8 carbons stable

less than 8 carbons is too strained doesn't exist
II. Unsaturation Number

In chapter 2 we discussed molecular formulas for alkanes, cycloalkanes, and unsaturated hydrocarbons. What was the formula for a straight chain or branched alkane?

\[ \text{2C + 2} \quad \text{C}_6\text{H}_{14} \quad \text{C}_6\text{H}_{14} \]

What happens when a pi bond or ring is present? lose 2 H's for every pi bond or ring

rings: \[
\begin{array}{c}
\text{1} \quad \text{C}_6\text{H}_{12} \\
\text{2} \quad \text{C}_6\text{H}_{10}
\end{array}
\]

pi bonds: \[
\begin{array}{c}
\text{1} \quad \text{C}_6\text{H}_{12} \\
\text{2} \quad \text{C}_6\text{H}_{10} \\
\text{2} \quad \text{C}_6\text{H}_{10}
\end{array}
\]

both: \[
\begin{array}{c}
\text{2} \quad \text{C}_6\text{H}_{10} \\
\text{3} \quad \text{C}_6\text{H}_{8} \\
\text{4} \quad \text{H}_2\text{S}
\end{array}
\]

How can you write a formula to show the number of pi bonds and/or rings are present?

\[
\frac{\text{maximum # - actual #}}{2} = \frac{(\text{2C + 2}) - \text{H}}{2} = \text{unsaturation number}
\]

Now let's see what happens when we add other elements to the compounds.

Oxygen: no change - same number of H's required

\[
\begin{array}{c}
\text{C}_6\text{H}_{14}\text{O} \\
\text{C}_6\text{H}_{12}\text{O}
\end{array}
\]

Halogens: need one less H for every X (X takes the place of an H)

\[
\begin{array}{c}
\text{C}_6\text{H}_{13}\text{Cl} \\
\text{C}_6\text{H}_{11}\text{Cl}
\end{array}
\]

Nitrogen: need one more H for every N

\[
\begin{array}{c}
\text{C}_6\text{H}_{15}\text{N} \\
\text{C}_6\text{H}_{13}\text{NO}
\end{array}
\]

C - 4 bonds, add a carbon, add 2 H's; N - 3 bonds, add a N, add 1 more H)
Generate a formula for figuring out how many double bonds or rings you have:

\[
\text{unsaturation #} = \frac{(2C + 2 - X + N) - H}{2}
\]

Practice - calculate the unsaturation number for each molecular formula. Then draw a possible structure.

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Structure</th>
<th>Unsaturation #</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₈</td>
<td><img src="image1" alt="Structure" /></td>
<td>3</td>
</tr>
<tr>
<td>C₆H₁₂Cl₂</td>
<td><img src="image2" alt="Structure" /></td>
<td>0</td>
</tr>
<tr>
<td>C₆H₁₂O</td>
<td><img src="image3" alt="Structure" /></td>
<td>1</td>
</tr>
<tr>
<td>C₆H₁₀O</td>
<td><img src="image4" alt="Structure" /></td>
<td>2</td>
</tr>
<tr>
<td>C₆H₁₀NBr</td>
<td><img src="image5" alt="Structure" /></td>
<td>2</td>
</tr>
<tr>
<td>C₆H₁₃N</td>
<td><img src="image6" alt="Structure" /></td>
<td>1</td>
</tr>
</tbody>
</table>

**III. Nomenclature of Alkenes**

What are the priorities in choosing the principle chain for an alkane?

1. longest chain/ring
2. most substituents

With alkenes, there is an addition, higher priority.

1. must contain the C=C
2. longest chain/ring
3. most substituents
**LG Ch 11 p 8**

What are the priorities for numbering an alkane?

1. lowest # to first substituent (then second, etc)
2. alphabetize

With alkenes, the C=C takes priority. The numbers must go across the C=C, and the number of the first carbon is the number of the alkene.

1. lowest # to C=C
2. lowest # to first substituent (then second, etc)
3. alphabet

What about cyclic alkenes? start on C=C, go across it

What if there are two or more C=C?

If alkanes end in "ane," what do you think alkenes end in? ene

How would you specify the location of the C=C? give the number before the name

trans-2-hexene
cyclopentene

How will the name change where there is more than one C=C?

1,3-pentadiene 1,3,5-heptatriene

add "adi", "atri" before ending
If the C=C cannot be included in the principle chain, it must be named as a substituent. What are the two smallest ones called?

4-vinyl-1-cyclohexene 4-allyl-1-cyclohexene

For all other substituents, the name comes from the alkyl name. insert "en" before "yl"
How is it numbered? from the point of attachment

4-(3-butenyl)-1-cyclohexene 4-(1-cyclobutenyl)-1-pentene

**Stereochemistry in nomenclature**

When is it necessary to specify the stereochemistry of an alkene?

*when there are two possible stereoisomers*

When may *cis* and *trans* be used?

*when there are only 2 substituents*

[cis] [E]  [trans] [Z]

When are *E* and *Z* appropriate?

*can be used anytime*
*must be used when there are 3 or 4 substituents*
*or when there is more than one C=C*

[E]  [Z]

What are the priorities for *E* and *Z*?

1. mass of atom attached to C=C
2. mass of 3 atoms attached to that atom, etc
When is a number needed in the name with the E or Z? when there is more than one both are stereoisomers

\[
\text{trans-2-pentene} \quad \text{could be either - 2 substituents no number}
\]

\[
\text{(E)-3-methyl-2-pentene} \quad \text{has to be E/Z - 3 substituents no number}
\]

\[
\text{(E)-1,3-pentadiene} \quad \text{could be either - only one C=C has stereochemistry no number}
\]

\[
\text{(2E, 4Z)-2,4-hexadiene} \quad \text{has to be E/Z - 2 double bonds give numbers!}
\]

Practice:

\[
\text{(E)-2-cyclopropyl-3-methyl-3-hexene}
\]

\[
\text{3-isobutyl-1-cyclopentene or 3-(2-methylpropyl)-1-cyclopentene}
\]

\[
\text{4-isopropyl-1,6-heptadiene or 4-(1-methylethyl)-1,6-heptadiene}
\]

\[
\text{1-methyl-1,4-cyclohexadiene}
\]

\[
\text{trans-1-(2-butyl)-1-cyclopentene}
\]

\[
\text{1-vinyl-1,3-cyclohexadiene}
\]
IV. Introduction to C=C reactions

The following are three basic types of reactions - substitution, elimination, and addition.

**substitution**

\[
\text{C} - \text{L.G.} \xrightarrow{\text{Nu}} \text{C} - \text{Nu} + \text{L.G}^{-}
\]

**elimination**

\[
\text{C} - \text{C} \xrightarrow{\text{base}} \text{C} = \text{CH}_2 + \text{H} - \text{base} + \text{L.G}^{-}
\]

**addition**

\[
\text{C} = \text{C} \xrightarrow{\text{Y-Z}} \text{C} - \text{C}
\]

Addition reactions of C=C are NOT effective on benzene rings. These pi bonds are spread across the whole ring, and therefore don't behave the same as isolated C=C.

V. Addition of HX to alkenes

**Carbocation mechanism**

Alkyl halides can be formed by the reaction of alkenes with hydrogen halide acids like HI, HBr, and HCl. How could this happen?

Which side will the halogen end up on, and why?

on the side where the more stable C+ was formed - more substituted side

What if two carbocations of equal energy could be formed? a mixture of products will be formed

bad for synthesis
What will happen if the carbocation can rearrange?

Show the carbocation(s) and product(s) of the following reactions.

Which of these alkyl halides could be synthesized using this reaction?

same

2 products

2 products

2 products

wrong side

wrong side + rearrangements
Radical mechanism

When chemists were first investigating this reaction, they noticed that once in a while with HBr, the products were opposite of what they expected. The halogen was on the spot where the less stable C+ would have been. Therefore, a C+ must not be involved in the reaction.

Eventually they discovered that this only occurred when trace amounts of organic peroxides were present. These caused a radical reaction to occur instead.

Why is only a small amount of peroxides necessary to change the products? it is catalytic - once Br is produced, it keeps being regenerated

Will rearranged products form? no - radicals don't rearrange

Give the reactive intermediate, then the products of the following reactions.

- no organic peroxide more subst. side
- radical mechanism less subst. side
- no effect on HCl or HI - more subst. side
- no rearrangements
VI. Hydration of alkenes

Acid-catalyzed hydration

If sulfuric acid is used instead of HBr or HCl, a different product is formed.

\[
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+ \\
\text{resonance not a Nu!}
\]

1. protonate
2. attack

Why is this reaction different from the reaction with HX?

\[X^- \text{ is a Nu, } \text{HSO}_4^- \text{ is not}\]

If \(\text{H}_2\text{SO}_4\) in water solution is used, what is the acid that actually reacts with the alkene?

\[\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+ \]

this reaction may be written with just \(\text{H}_3\text{O}^+\) as the reagent

How much acid is needed to make the reaction work?

only a drop - is it regenerated (catalytic)

Why do you think this reaction is called "hydration of an alkene"?

water is added - an H to one side, an OH to the other

Would phosphoric acid (\(\text{H}_3\text{PO}_4\)) work?

\[
\begin{array}{c}
\text{HO} - \text{P} - \text{OH} \\
\text{yes} \\
\text{H} - \text{O} \\
\end{array}
\]

If one side of the \(\text{C} = \text{C}\) is more substituted than the other, which side gets the OH? Why?

\(\text{OH}\) goes to the more subst side - that's where the more stable \(\text{C}^+\) forms

If both sides are equally substituted, what will happen?

mixture of two products will form - OH on either side :(?

Will rearrangements occur? yes - if the \(\text{C}^+\) could become more stable
Predict the products of the following reactions:

\[
\begin{align*}
\text{H}_3\text{O}^+ & &\rightarrow & \text{benzyl} & 2^\circ \text{C}^+ \text{ is more stable than } 1^\circ \\
\text{H}_2\text{SO}_4 & &\rightarrow & \text{2 products} & \text{both C}^+ \text{ are } 2^\circ \\
\text{H}_3\text{PO}_4 & &\rightarrow & \text{2 products} & \text{2}^\circ \text{C}^+ \text{ forms, then rearranges} \\
\text{H}_2\text{SO}_4 & &\rightarrow & \text{2 products} & \text{two } 2^\circ \text{C}^+ \text{ form, then both can rearrange}
\end{align*}
\]

Which of the following alcohols could be formed as the only products of a hydration reaction?

- \[\text{no - wrong side}\]
- \[\text{no - rearrangements}\]
- \[\text{no - wrong side}\]
- \[\text{no - both sides plus rearrangements}\]
What limitations does acid-catalyzed hydration have when using it for synthesis?

forms C+, rearrangements
OH always goes to the more substituted side
equally substituted C=C give two products

Two other hydration reactions have been developed which solve some of these problems; however, they have more complex mechanisms.

**Oxymercuration-reduction**

What are the reagents necessary for the two steps of oxymercuration-reduction?

\[ \text{Hg(OAc)}_2, \text{H}_2\text{O} \rightarrow \text{Hg(OAc)} \rightarrow \text{NaBH}_4 \rightarrow \text{H} \]

What does OAc stand for?

What happens in the first step?

OH is added to one side, Hg to the other

What happens in the second step?

C-Hg bond is broken, C-H bond is formed

How can both steps be shown with one arrow?

\[ \text{1. Hg(OAc), H}_2\text{O} \rightarrow \text{2. NaBH}_4 \rightarrow \text{OH} \]

What is the regioselectivity of this reaction?

OH goes to the more substituted carbon

Will we learn the mechanism for this reaction?

Nope - too complex, not necessary to understand results

No rearrangements occur in this reaction - what does this imply?

no carbocation is formed
Examples:

\[
\begin{align*}
\text{benzene} & \quad \xrightarrow{\text{Hg(OAc)}_2, \text{H}_2\text{O}} & \quad \text{phenylmercury acetate} & \quad \xrightarrow{\text{NaBH}_4} & \quad \text{phenol} \\
\text{alkene} & \quad \xrightarrow{1. \text{Hg(OAc)}, \text{H}_2\text{O}} & \quad \text{alkene} & \quad \xrightarrow{2. \text{NaBH}_4} & \quad \text{no rearrangements} \\
\text{cycloalkene} & \quad \xrightarrow{1. \text{Hg(OAc)}, \text{H}_2\text{O}} & \quad \text{cycloalkene} & \quad \xrightarrow{2. \text{NaBH}_4} & \quad \text{equally substituted}
\end{align*}
\]

Which of the problems with acid-catalyzed hydration does this solve?

no C+, no rearrangements

Which of the products above couldn't be synthesized with acid-catalyzed hydration, but could be with oxymercuration-reduction.

both would undergo rearrangements

Hydroboration-oxidation

What are the reagents necessary for the two steps of hydroboration-oxidation?

\[
\begin{align*}
\text{cycloalkene} & \quad \xrightarrow{\text{BH}_3} & \quad \text{boron alkyl compound} & \quad \xrightarrow{\text{H}_2\text{O}_2, \text{NaOH}} & \quad \text{cycloalkene}
\end{align*}
\]

What happens in the first step?

Write in the actual stoichiometry of the reaction.
What happens in the second step?
the C-B bond is broken, C-OH bond is formed
don't worry about the mechanism of this step

How can both steps be shown with one arrow?

The regioselectivity of this reaction is controlled by steric effects. Which side do you think is most likely to attach to the B? How does this affect the product?
less substituted side attached to B, so the OH ends up there

Why is BH₃ difficult to work with? its a gas

How else can BH₃ be represented? B₂H₆ - forms a dimer in the gas phase

Why is it often dissolved in THF? it forms a more stable complex

Do rearrangements occur in this reaction? no - no C⁺ is formed

Predict the products of the following reactions.

1. BH₃
2. H₂O₂, OH⁻
OH goes to less subst. side

ditto
equally substituted
no hydride shift
Draw all alkenes from which the following alcohols could be synthesized. Then decide if oxymercuration-reduction or hydroboration-oxidation could be used to give only the desired product.

\[
\begin{array}{c}
\text{HB-Ox :) } \\
\end{array}
\]

\[
\begin{array}{c}
\text{OM-red :) } \\
\end{array}
\]

\[
\begin{array}{c}
\text{OM-red :) } \\
\end{array}
\]

\[
\begin{array}{c}
\text{OM-red or HB-ox :) } \\
\end{array}
\]

Summary of reactions:

\[
\begin{array}{c}
\text{HX } & \rightarrow & \text{X goes to more subst. side rearrangements} \\
\end{array}
\]

\[
\begin{array}{c}
\text{HBr } & \rightarrow & \text{Br goes to less subst. side no rearrangements} \\
\text{ROOR } & & \\
\end{array}
\]

\[
\begin{array}{c}
\text{H}_2\text{SO}_4 & \rightarrow & \text{OH goes to more subst side rearrangements} \\
\text{H}_2\text{O } & & \\
\end{array}
\]

\[
\begin{array}{c}
\text{OH goes to more subst. side no rearrangements} \\
1. \text{Hg(OAc), H}_2\text{O} \\
2. \text{NaBH}_4 \\
\end{array}
\]

\[
\begin{array}{c}
\text{OH goes to less subst. side no rearrangements} \\
1. \text{BH}_3 \\
2. \text{H}_2\text{O}_2, \text{NaOH} \\
\end{array}
\]