Learning Guide for Chapter 11 - Alkenes I

I. Introduction to alkenes - p 1 bond structure, classifying alkenes, reactivity, physical properties, occurrences and uses, spectroscopy, stabilty

- II. Unsaturation number p 6
- III. Nomenclature of alkenes p 7
- IV. Intro to C=C reactions p 11
- V. Addition of HX to alkenes p 11

VI. Hydration of alkenes - p 14 acid-catalyzed hydration oxymercuration-reduction hydroboration-oxidation

I. Introduction to alkenes

Bond structure

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

hybridization:

geometry:

molecular orbitals:

What is wrong with the following line structures?





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

Classifying compounds with C=C's

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

alkene:

aromatic compound:

unsaturated compound:

Label each of the following.



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?



Physical properties

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

polarity:

water solubility:

density:

flammability:

What can you conclude from the following boiling points?









 $bp = 0^{\circ}C$

 $bp = -6^{\circ}C$

 $bp = 30^{\circ}C$

 $bp = 25^{\circ}C$

How does the reactivity of alkenes compare to alkanes?

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

nucleophile electrophile acid base	radical
------------------------------------	---------

How strong of a reagent is an alkene? Why?

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







Occurence and uses of alkenes

Are alkenes common in nature?

Where are the following two compounds found?



Where do alkenes come from?

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



<u>Spectroscopy</u>

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



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





Stability of alkenes

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



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





Which of these two rules takes precedence?

Why are small cyclic alkenes less stable?



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

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

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?



If you have a formula, how can you figure out how many pi bonds or rings are present?

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

Oxygen:



Halogens:





,ci:

Nitrogen:





Generate a formula for figuring out how many H's a saturated compound would need if you have the number of C's, O's, X's, and N's:

Generate a formula for figuring out how many double bonds or rings you have:

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

$$C_{6}H_{8}$$
 $C_{6}H_{12}Cl_{2}$
 $C_{6}H_{12}O$ $C_{6}H_{10}O$

C₆H₁₀NBr C₆H₁₃N

III. Nomenclature of Alkenes

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



With alkenes, there is an addition, higher priority.



What are the priorities for numbering an alkane?



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.



What about cyclic alkenes?







What if there are two or more C=C?



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

How would you specify the location of the C=C?



 \bigcirc

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

If the C=C cannot be included in the principle chain, it must be named as a substitutent. What are the two smallest ones called?



For all other substitutents, the name comes from the alkyl name. How is it numbered?





Stereochemistry in nomenclature

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

When may cis and trans be used?

When are \underline{E} and \underline{Z} appropriate?

What are the priorities for E and Z?

When is a number needed in the name with the E or Z?





Practice:











IV. Introduction to C=C reactions

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



Addition reactions of C=C are NOT effective on benzene rings. These pi bonds are pread 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?

What if two carbocations of equal energy could be formed?

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?



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?

Will rearranged products form?

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



VI. Hydration of alkenes

Acid-catalyzed hydration

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

$$\xrightarrow{H_2SO_4}$$

Why is this reaction different from the reaction with HX?

If H₂SO₄ in water solution is used, what is the acid that actually reacts with the alkene?

How much acid is needed to make the reaction work?

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

Would phosphoric acid (H₃PO₄) work?

If one side of the C=C is more substituted than the other, which side gets the OH? Why?

If both sides are equally substituted, what will happen?

Will rearrangements occur?

Predict the products of the following reactions:



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



What limitations does acid-catalyzed hydration have when using it for synthesis?

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?



What is does OAc stand for?

What happens in the first step?

What happens in the second step?

How can both steps be shown with one arrow?

What is the regioselectivity of this reaction?

Will we learn the mechanism for this reaction?

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

ÖН

Examples:



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

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

Hydroboration-oxidation

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



What happens in the first step?



What happens in the second step?

How can both steps be shown with one arrow?

 \bigcirc \longrightarrow

The regioselectivity of this reaction is controlled by sterics. Which side do you think is most likely to attach to the B? How does this affect the product?

Why is BH₃ difficult to work with?

How else can BH_3 be represented?

Why is it often dissolved in THF?



Do rearrangements occur in this reaction?

Predict the products of the following reactions.



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.







Summary of reactions:

