Ch 4: Alkenes

- Naming
- Structure
- Reactivity

Some alkenes in nature: http://www.youtube.com/watch?v=H2atn8YD9UE

1.) **Ethylene -** hormone in plants responsible for seed germination and fruit ripening

A) How do stores get fruit to ripen on arrival?

B) Why do your bananas ripen faster when placed next to spotty bananas?

2.) **Pheromones -** produced by plants and animals - used to communicate

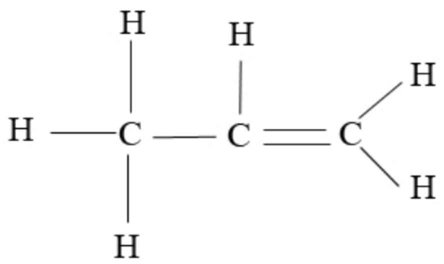
- Sex (attraction)
- Alarm
- Trail

A) Detection of pheromones is done through smell (bugs use antennae)

http://www.youtube.com/watch?v=gcHt5n3NGK0

B) Use of artificial (man made) pheromones - to attract and trap insects

Alkenes (Structure):



Formula - C_nH_{2n} (straight chain)

C_nH_{2n-2} (cyclic)

Saturation vs Unsaturation:

Saturated - has max amount of H possible (alkanes)

Unsaturated - fewer than the max amount of H (alkenes, cyclic alkanes, and alkynes)

Formula for unsaturation level ID:

Compare the hydrogen count to an alkane formula for the C # (C_nH_{2n+2})

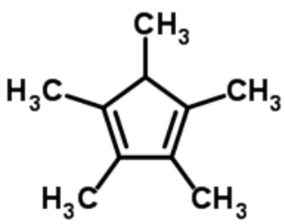
- For every 2 H less than for the alkane, it has 1 Pi bond

REMEMBER: A) = bond (1 pi bond)

B) ≡ bond (2 pi bonds)

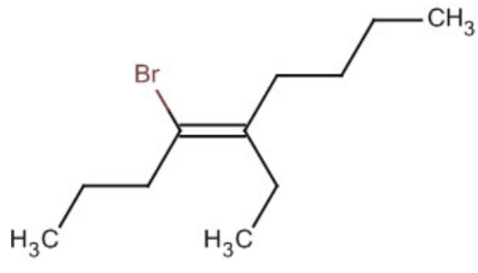
C) a cyclic structure reduces by -2 H

EX: $C_{10}H_{16}$



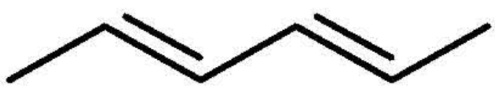
<u>Naming alkenes:</u> ** ALWAYS replace -ane with -ene

1) Find the longest chain containing the functional group (C=C)
   - it may not be the longest carbon chain

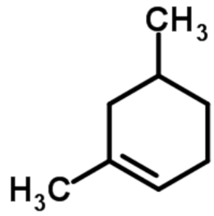


2) You must number through the double bond (# so the = is lowest number possible)

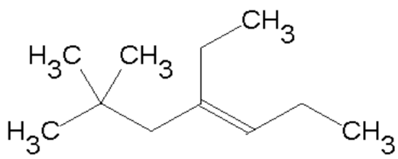
3) If there are two double bonds the ending is *-diene*



4) The functional (=) group gets the lowest number, not the substituent

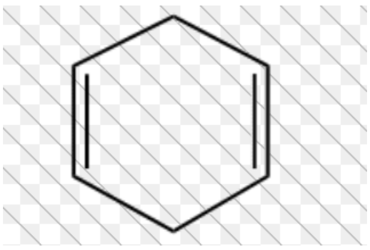


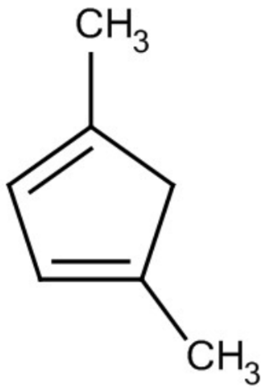
5) The substituents are listed in alphabetical order like alkanes



6) ***If there is only one double bond in a cyclic structure***, a number is not needed (the = bond will always b ... ıe 1=2 carbon)

7) ***If there are 2 or more (=) in a cyclic structure***, count and number the C=C bonds





Summary for naming any functional group:

- substituents in alphabetical order
- functional group gets lowest #
- parent hydrocarbon chain = base word

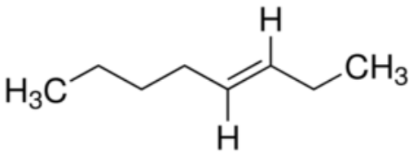
substituent - parent hydrocarbon - functional group suffix

Number if needed

Types of carbons in an alkene:

vinylic carbons: sp^2 carbons of the alkene

allylic carbons: sp^3 carbons attached adjacent to the vinylic carbon



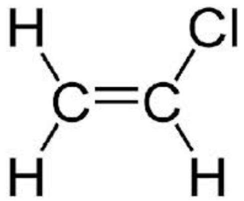
Vinyl group: smallest possible group containing C=C

$H_2C=CH-R$

Allyl group: smallest possible group adjacent to allylic carbon

$H_2C=CHCH_2-R$

EXAMPLE: Name these by systematic name and common name



$Br-CH_2-CH=CH_2$

Structure:

cyclohexene

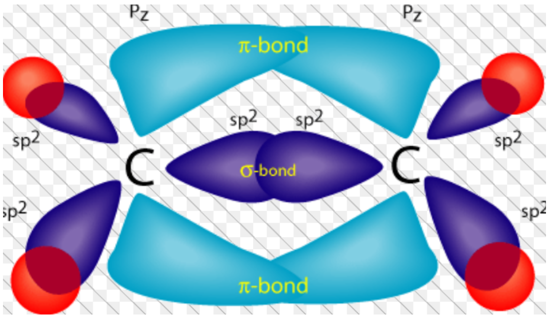
2,3-dimethyl-2-butene

1) Write the structural or skeletal formula for:

a) vinylcyclopentane

b) allylcyclopropane

Geomtry of alkenes:



**All orbitals in the same plane
** C=C bond prevents rotation (try it)

Degree of Unsaturation:

1) **Organohalogen compounds (C,H,X where X = F,Cl,Br, or I)**

- a halogen acts simply as a replacement for hydrogen in an organic compound, so we add the number of halogens and hydrogens to arrive at the equivalent hydrocarbon formula

$C_4H_6Br_2 = C_4H_8$

Organooxygen compounds (C,H,O)

- oxygen forms 2 bonds, so it does not affect the formula of the equivalent hydrocarbon and can be ignored when calculating the degree of unsaturation.

$C_5H_8O = C_5H_8$

Organonitrogen Compounds:

- nitrogen forms 3 bonds, so an organonitrogen compound has one more hydrogen than a relate hydrocarbon; therefore we subtract the number of nitrogens from the number of hydrogens to arrive at the equivalent hydrocarbon formula.

$C_5H_9N = C_5H_8$

To summarize saturation of O, N, Halogen compounds:

- add the number of halogens to the number of hydrogens
- ignore the number of oxygens
- subtract the number of nitrogens from the number of hydrogens

Calculate the degree of unsaturation for each:

1) C_4H_8

2) C_4H_6

3) C_3H_4

4) C_6H_5N

5) $C_6H_5NO_2$

6) $C_8H_9Cl_3$

7) $C_9H_{16}Br_2$

8) $C_{10}H_{12}N_2O_3$

9) $C_{20}H_{32}ClN$

Geometric Isomers (Cis and Trans):

cis - main branches/substituents on same side
trans - main branches/substituents on opposite sides

ex. 2-pentene (draw the cis and trans)

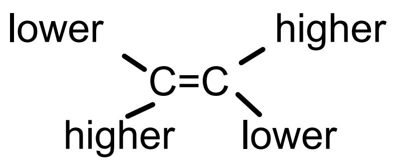
ex. cis-2-butene vs trans-2-butene

The E, Z Designation:

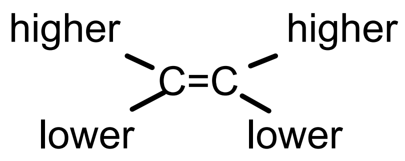
cis/trans : works only with disubstituted alkenes
(If substituents are different, it doesn't work)

E: entgegen - opposite

Z: zuzammen - together ("ze zame zide")



E double bond



Z double bond

Cahn-Ingold-Prelog Rules:

1) Considering the double bond carbons separately, look at the atoms directly attached to each carbon and rank them according to atomic number.

ex. 2-chloro-2-butene

2) If a decision can't be reached by ranking the first atoms in the substituents, look at the second, third, or fourth atoms away from the double-bond carbons until the first difference is found.

ex. 2-chloro -3-methylpent-2-en-1-ol

3) Multiple-bonded atoms are equivalent to the same number of single-bonded atoms. For example, an aldehyde substitute (-CH=O), which has a carbon atom ***doubly*** bonded to ***one*** oxygen, is equivalent to a substitute having a carbon **singly** bonded to ***two*** oxygens.

A) Draw the structure of (E)-3-methyl-1,3-pentadiene

B) Draw the structure of (E)-1-bromo-2-methyl-2-butene

C) Draw the structure of (Z)-1,2-dibromo-3-isopropyl-2-hexene

Stability of Alkenes:

1) Stabilizing interaction between the C=C pi bond and adjacent C-H sigma bonds on substituents. The interaction is called ***hyperconjugation***.

What this means: alkyl substituents on alkene C=C causes stability and THE MORE SUBSTITUENTS = MORE STABILITY

2) A bond between an ***sp***^{2} carbon and an ***sp***^{3} carbon is somewhat stronger than a bond between two ***sp***^{3} carbons

Ex: Cis-2-butene vs trans-2-butene (Draw and then ID who is more stable)

Why do you think increased substitution = more stability?

Reacting alkenes and use of curved arrows:

functional groups - centers of reactivity in organic chemistry

Alkenes = functional group

Forces that make organic reactions occur:

A) Electron rich atoms/molecules

B) Electron deficient atoms/molecules

"Electron rich atoms/molecules are attracted to electron deficient atoms/molecules"

Electrophile - Electron deficient atom/molecule

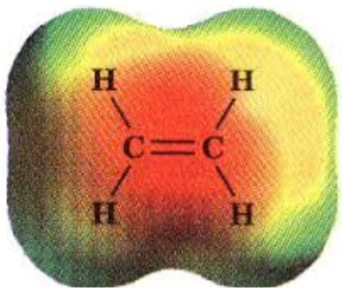
phile = "loving"

Ex: H^+ $CH_3C^+H_2$

Nucleophile - Electron rich atom/molecule

Ex: $H\text{-}\ddot{O}:^-$ $:\ddot{Cl}^-$ $CH_3\ddot{N}H_2$ $H_2\ddot{O}$

So... Is an alkene rich or poor for electrons?

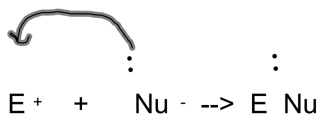


4.7: How Alkenes React:

- bond breaking:
  - a) homolytic - symmetrical cleavage
    - 1 electron remains with each product (free radical)
  - b) heterolytic - unsymmetrical cleavage
    - both electrons remain with 1 product
    - reactions that involve unsymmetrical bond breaking and making are called ***Polar Reactions***

- Bond formation:
  bonds are made when an electron-rich atom shares a pair of electrons with an electron-poor atom

- electron-rich atoms or molecules are attracted to electron-deficient atoms or molecules



-Nucleophiles: - has a negatively polarized, electron-rich atom
- can either be neutral or negatively charged

- OH^- , Cl^- , NH_3

- Electrophiles: - positively polarized, electron-poor atom
- can be either neutral or positively charged

- CH_3 - Br , - C - (with =O) , $^+CH_3$

* Electrons move from a nucleophilic source to an electrophile

Which of the following species is likely to behave as a nucleophile and which as an electrophile?

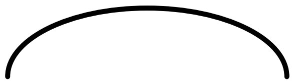
a) NO_2^+ b) CH_3O^- c) CH_3OH

Mechanism of a reaction:

-step by step description of product to reactant change

- use of curved arrows to show what happens

    - Curved arrows = **:** movement (2e-) from e-rich to e- deficient



e- rich area e- deficient area

Example of how arrows work in a reaction: (2-butene + HBr)

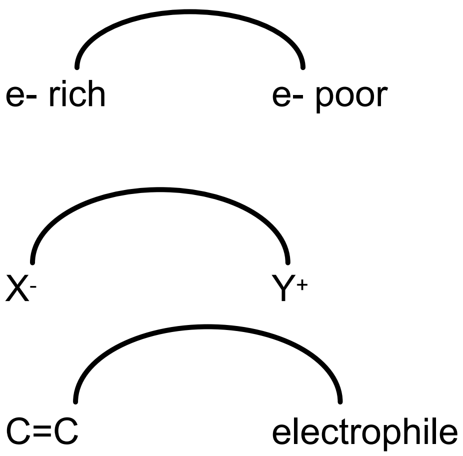
What type of reaction is this

<u>**Some more notes about alkene reactions:**</u>

A) Alkenes typically undergo electrophilic addition reactions

More notes about Curved arrows: (see blue box pt 98-99)

A) Always move curved arrow from



B) Never show atom movements with a curved arrow

C) Curved arrow always points to an atom or new bond, never empty space

D) Start arrow at electron source

Reaction coordinate diagrams:

Transition states - in between state of 2 rxn steps

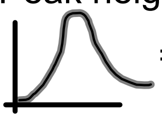
- always shown in [ ] brackets
- shows partially broken/formed bonds
- shows partial +/- charges

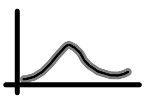
Example: 2-butene + HBr

Reaction Coordinate diagram - graphically shows the energy change that takes place through reaction

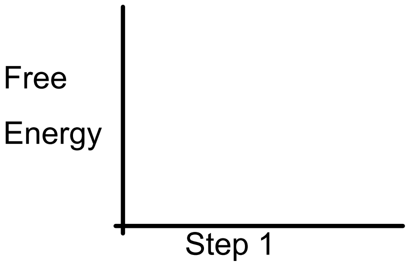
reactants ---> transition states ---> products

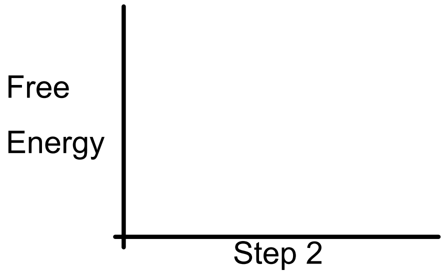
Peak height = energy value

 = high energy = less stable

 = low energy = more stable

Ex: Drawing the reaction coordinate diagram for 2-butenene + HBr





Graph of whole reaction:

Transition vs intermediate states

Transition - partially - - - - - bonds

Intermediate - fully formed bonds

Concentration of reactant vs product

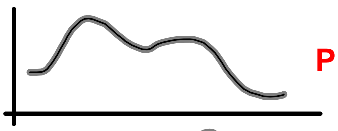
- Reaction is done when equilibrium is reached
- Relative concentration of reactant to product depends on energy

a.) Product energy < reactant energy = products favored

b.) Product energy > reactant energy = reactants favored

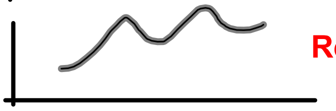
c.) To see the energy comparison, look at graph

Product E < reactant E



Products favored

Product E> reactant E



Reactants favored

Why? Less energy = more stable

Favorable reaction - reaction where Product E < Reactant E and products are formed

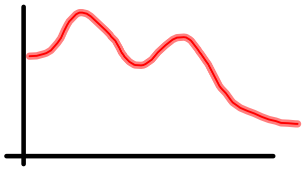
Speed of a reaction:

- Speed is determined by the energy barrier (hill) it needs to climb

Free Activation Energy- the energy barrier (hill), indicated by ΔG

$\Delta G^{\ddagger}$ - (Free energy of the transtion state) - (free energy of the reactants)

Rate determining step - in a reaction with 2 or more steps, the step with the highest ΔG



What determines how fast a reaction will go?

1) # of collisions that take place in a certain time period
2) The fraction of collisions occurring with sufficient energy to overcome energy barrier
3) Fraction of collisions with proper orientation (ex: H needs to approach pi bond, not the methyl group)

Rate of reaction = (# of collisions per unit of time) * (fraction with sufficient energy) * (fraction with proper orientation)

How to increase rate of reaction:

1) ***Increase concentration*** of reactants (it increases # of collisions)
2) ***Increase temp*** of reaction (it increases # of collisions and the fraction of collsions with enough energy)
3) ***Catalyst*** (catalyst gives reactants a new pathway to follow, with a lower activation energy)

Catalyst is:

A) Not consumed or changed
B) Only a small amount is needed (1-10% of reactants used)
C) Only effects rate of reaction, amount of product produced is still the same