Announcements:

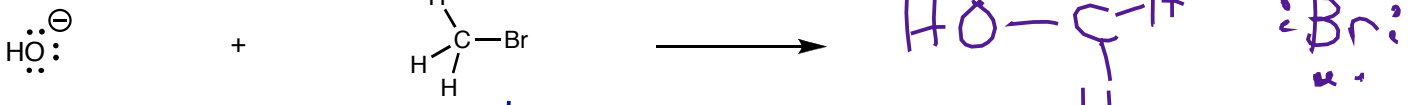
- Lab starts today

- Check website for useful things.

Arrows: Non-Bonding HOMO + Antibonding LUMO

- For the following species:

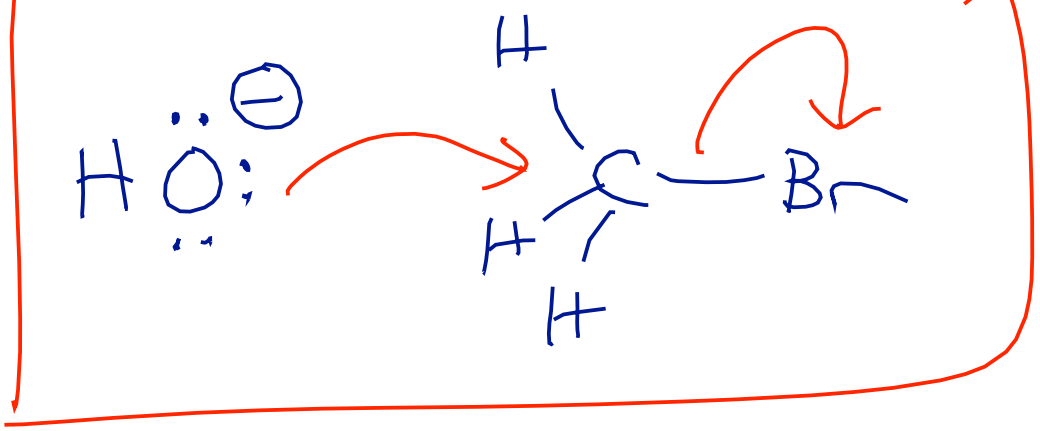
1) Identify the possible HOMO's and LUMO's
2) Select the likely **nucleophile** and **electrophile** from these two species
3) Show how these species will react using **curved arrows**
4) Predict the immediate product of that reaction



hydroxide methyl bromide

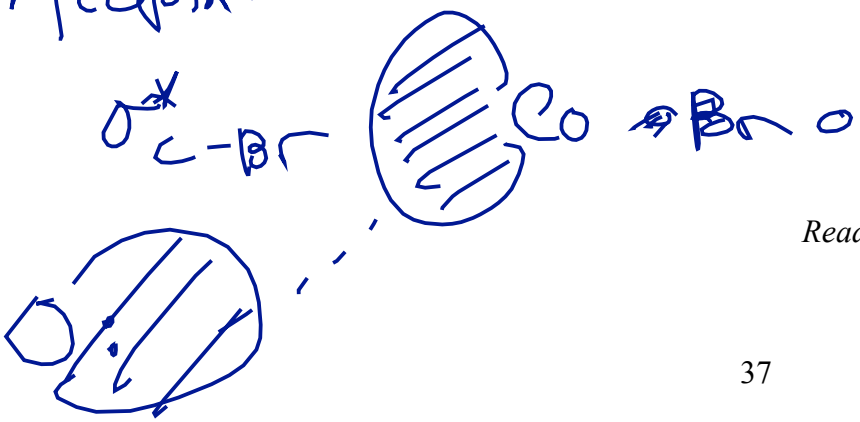
Donor: O lp → Acceptor: σ^*_{C-Br}

nucleophile electrophile



Put e⁻ in antibonding orbital → break corresponding bond.

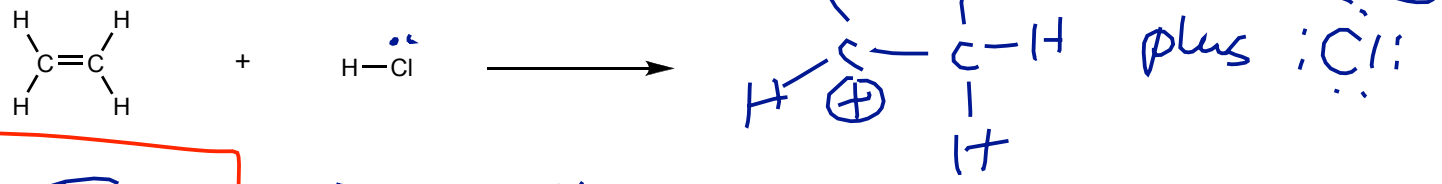
Acceptor: σ^*_{C-Br}



Reading: Supplemental Handout, Section 2.5

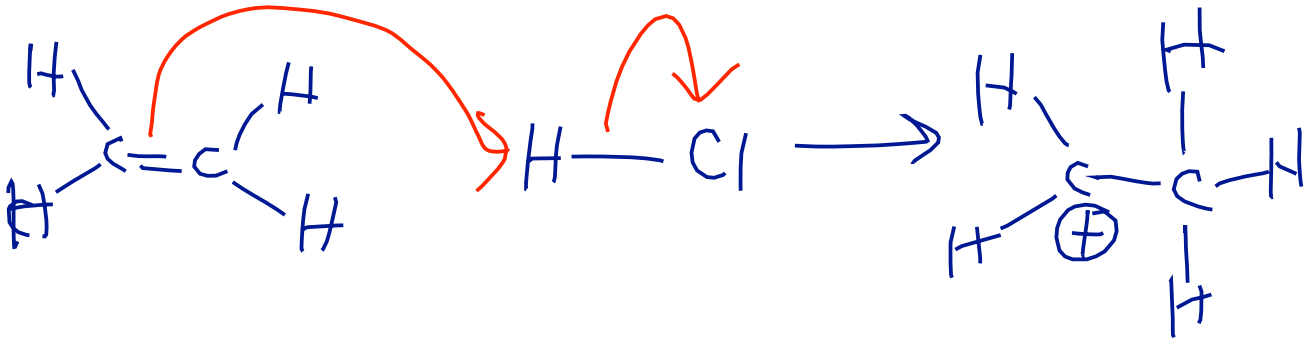
Predicting Reactions Using Frontier Orbitals

- Here are two species you have **never seen before**. Using Frontier Molecular Orbital Theory (FMO Theory), *predict* the first step of the reaction between these two species. Draw the curved-arrow mechanism that shows how they react, and predict the immediate product of that reaction.



Donor: $\pi_{C=C}$ Donor: Cl lp

Acceptor ~~$\pi^*_{C=C}$~~ Acceptor: σ^*_{H-Cl}



$\pi_{C=C} \rightarrow \sigma^*_{H-Cl}$

Reading: Supplemental Handout, Section 2.5

$HA \rightleftharpoons H^+ + A^-$

conj. acid conj. base

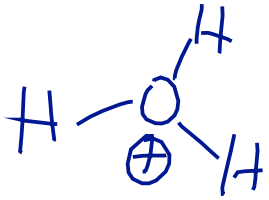
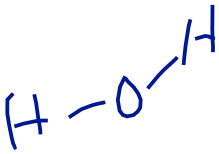
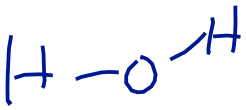
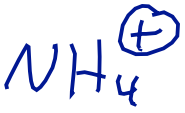
Brønsted-Lowry Acids and Bases

- One of the most useful theories of acidity and basicity is the **Brønsted-Lowry Theory**. In this theory, acids and bases are defined as follows:

  A **Brønsted Acid** is a species that can **donate** a proton (H^+).

  A **Brønsted Base** is a species that can **accept** a proton.

- Every Brønsted acid, therefore, must have a **conjugate base**. What are some examples of Brønsted acids? For each one, identify its conjugate base.

	Brønsted Acid	*Conjugate Base*	plus
hydrochloric acid			H^+
hydronium			H^+
water			H^+
ammonium		NH_3	H^+

- When a Brønsted acid reacts with a Brønsted base, a proton is transferred from the acid to the base. These reactions are called **proton-transfer reactions**. Give some examples of proton-transfer reactions using the above list of acids and bases.

acid — base

$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

base — acid

Proton transfer

Reading: Section 3.4

Strengths of Acids and Bases: K_a and pK_a

- All proton-transfer reactions are **reversible** (at least in principle). In general, though, one direction of the reaction will predominate over the other (that is, the proton transfer will tend to be unequal). For instance, consider the reaction between the ammonium ion and the hydroxide ion. Do you have a sense of whether this reaction proceeds mainly to the right or mainly to the left?

$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

(favors products)

- Because so much chemistry takes place in water, we typically use water as a "standard reference" for the strengths of acids and bases. For any Brønsted acid HA, the reaction with water will reach some equilibrium:

$HA + H_2O \rightleftharpoons \underbrace{H_3O^+}_{H^+(aq)} + A^-$

The equilibrium constant of this reaction is $K_a =$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

(don't include $[H_2O]$ because it's solvent)

* Just as "pH" means "the negative log of the H^+ concentration," we use the term "pKa" to refer to "the negative log of the K_a" How can we express that fact mathematically?

$pH = -\log[H^+]$ so $pK_a = -\log K_a$ or $K_a = 10^{-pK_a}$

- Fill in the blanks: "A **strong** acid will have a negative (small) pKa"

large K_a

"A **strong** base will have a *conjugate acid* with a large (positive) pKa"

Reading: Section 3.4

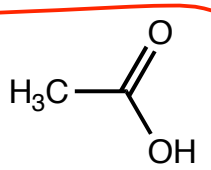
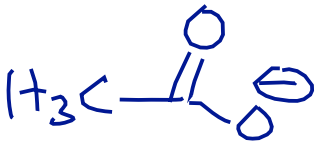
Larger K_a → stronger acid → better proton donor

Memorize these

pKa Values for Common Acids

(also functional groups)

- Here are some important pKa values. You should **memorize these values**, at least to the nearest 5 pKa units:

Conjugate Acid		pKa	Conjugate Base	
methane	CH_4	48	$:CH_3^-$	strong base
ammonia	NH_3	35	$:NH_2^-$	amide
acetylene	$HC\equiv CH$	24	$HC\equiv C:^-$	acetylide
methanol (R-OH)	H_3C-OH	16	$H_3C-O:^-$	methoxide
water	H_2O	16	HO^-	hydroxide
ammonium	NH_4^+	9	NH_3	ammonia
hydrogen cyanide	HCN	9	^-CN	cyanide
acetic acid (R-COOH)		5		acetate
hydronium	H_3O^+	−2	H_2O	water
hydrochloric acid	HCl	−7	Cl^-	chloride

strong bases

strong acids

weak base

weak acid

strong acid

- For each of the above acids, fill in the **conjugate base**.
- We typically define a **strong acid** as an acid that is at least as strong as H_3O^+, and a **strong base** as a base that is at least as strong as OH^-. Identify the strong acids and strong bases in the above list.

Reading: Section 3.4

Using pKa Values to Predict Acid-Base Equilibria

- Consider, again, the reaction between the ammonium ion and the hydroxide ion. What will be the **predominant species** present in this system at equilibrium?

$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

ammonium — hydroxide — ammonia — water

acid — acid

$pK_a = 9$ — $pK_a = 16$

- Can you calculate the **equilibrium constant** for this reaction? How?

$K_{eq} = 10^{(pK_a \text{ acid product} - pK_a \text{ acid reactant})}$

$K_{eq} = 10^{\Delta pK_a}$

In this case

$K_{eq} = 10^{(16-9)} = 10^7 \gg 1$

So products favored at equilibrium.

- What does the value of the equilibrium constant tell you about the concentrations of reactants and products at equilibrium?

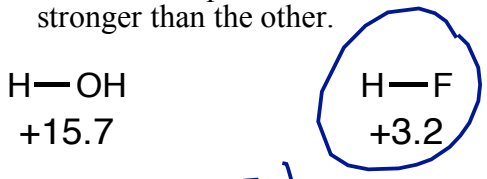
$K_{eq} > 1$ products favored

$K_{eq} < 1$ reactants favored

Reading: Section 3.4

Factors That Influence Acidity: The Main Atom

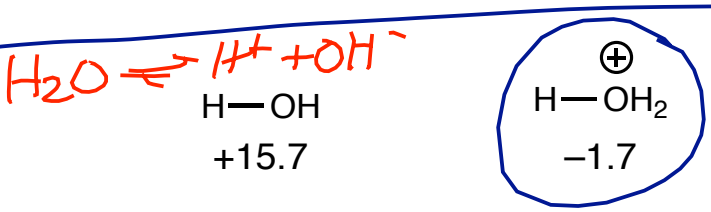
- Examine the pKa's for each of the following pairs of acids, and explain why one acid is stronger than the other.



Stronger acid

$HF \rightleftharpoons H^+ + F^-$

more electroneg. gives more stable anion

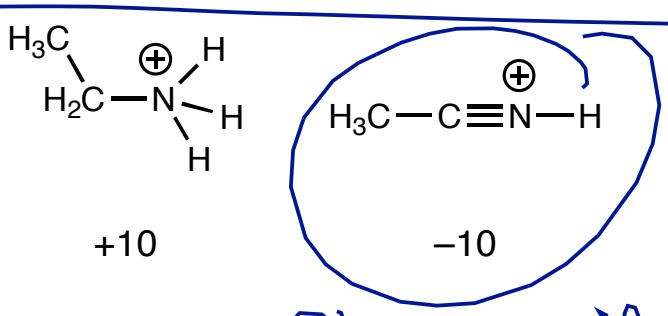


$H_2O \rightleftharpoons H^+ + OH^-$

positive formal charge

Stronger acid

more acidic



Stronger acid

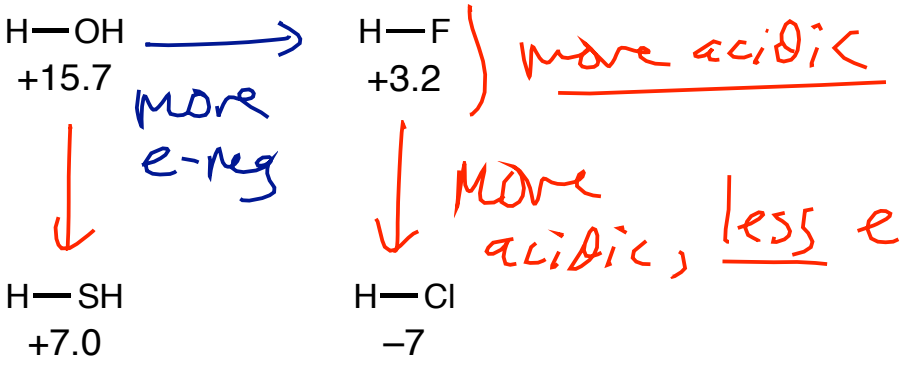
hybridization!

Sp hybrid more acidic

- Compare these trends with the "*low-energy trifecta*" you saw earlier.... any similarities?

Same! ⟹ Stabilizes lone pair orbital on conj. base

- Now examine the four acids from the upper-right corner of the perioidic table. Do the strengths of these acids follow the trend you would expect? Why or why not?



more acidic

more e-neg

more acidic, less e-neg.

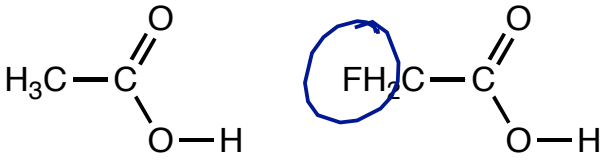
more acidic, less e-neg.

Reading: Section 3.6

Larger atoms → longer H—X bonds → weaker H—X bonds.

Factors That Influence Acidity: Adjacent Groups

- The acidity of a particular proton can be influenced by adjacent or nearby groups in the molecule. Can you explain the difference in the following pKa's?

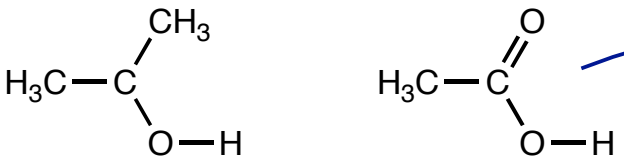


4.76 2.66

Replace H with F: more eneg; F is "electron withdrawing" group

→ more acidic. Inductive effect

- Whenever a molecule exhibits resonance, **and** the resonance allows **charge to be delocalized**, then the charged structure will be more stable than a comparable structure that does not have the delocalized charge. Thus, resonance can stabilize *either* the conjugate acid *or* the conjugate base, whichever is charged. Let's look at some examples:



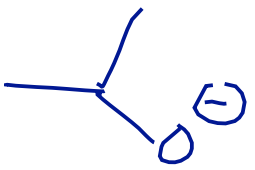
Delocalized charge in conj. base → more stable

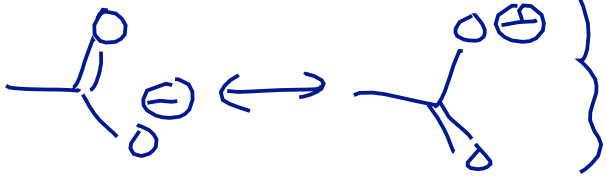
∴ More acidic

conj. acid

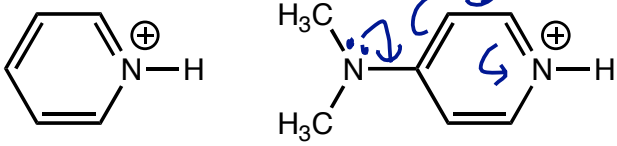
16.5 4.76

conj. base





delocalized neg. charge



5.25 9.2

delocalized ⊕ charge in conj. acid → more stable

∴ less acidic

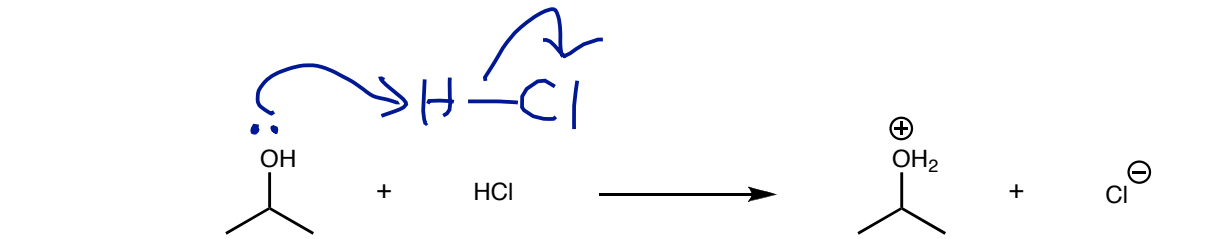
Reading: Section 3.6

Conj. acid ⟹ acceptor is σ^*_{H-X}

Frontier Orbitals of Proton-Transfer Reactions

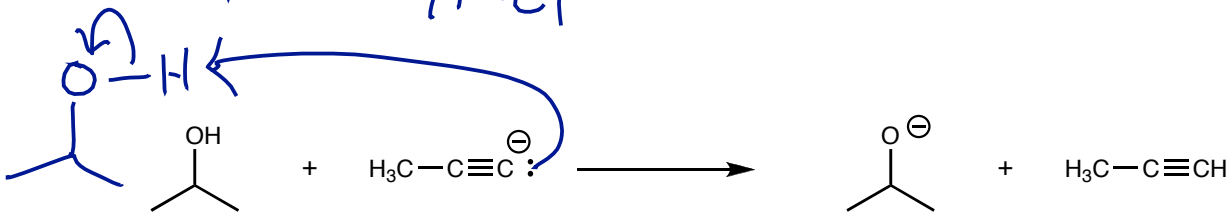
some atom.

- We can, of course, look at proton-transfer reactions in terms of the HOMO and LUMO involved in the reaction. Can you find the HOMO and LUMO of the following proton-transfer reactions?



Donor: O lp

Acceptor: σ^*_{H-Cl}



Acceptor: σ^*_{H-O}

Donor: C lp

- What generalization can we make about the LUMO in **any** proton-transfer reacton?

Acceptor in proton transfer rxn.

σ^*_{H-X}

any atom.

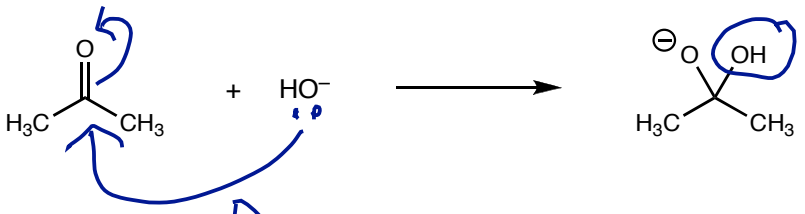
Reading: Supplemental Handout, Section 2.6

Roles Electrophile Nucleophile
Acid Base
if H+ transfer

What's Your Role: Acid or Electrophile?

- In one of the following reactions, acetone ($(CH_3)_2C=O$) plays the role of an acid; in the other it plays the role of an electrophile. Which is which, and why? Can you draw the curved arrows and identify the HOMO and LUMO of each reaction?

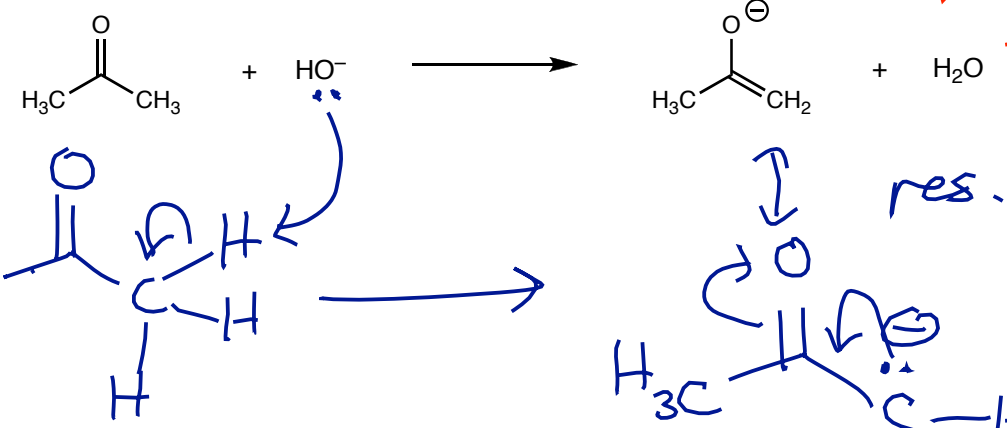
ketone



Acceptor Donor
$\pi^*_{C=O}$ O lp
Electrophile Nucleophile

Both happen!

Generally try to draw best res. str. for any species.



res. struct.

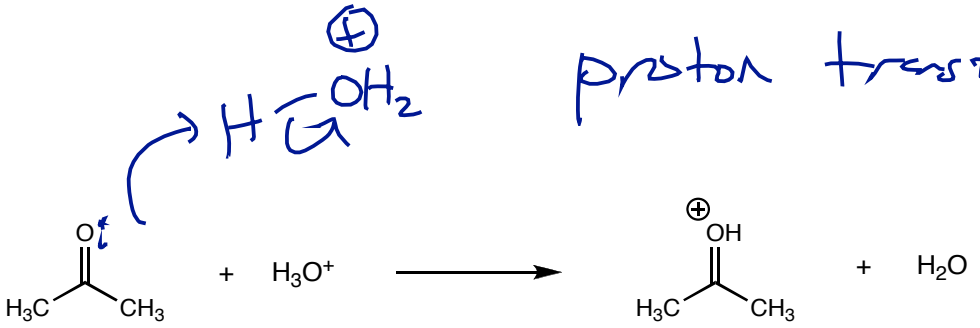
Acceptor Donor
σ^*_{H-C} O lp
Acid Base

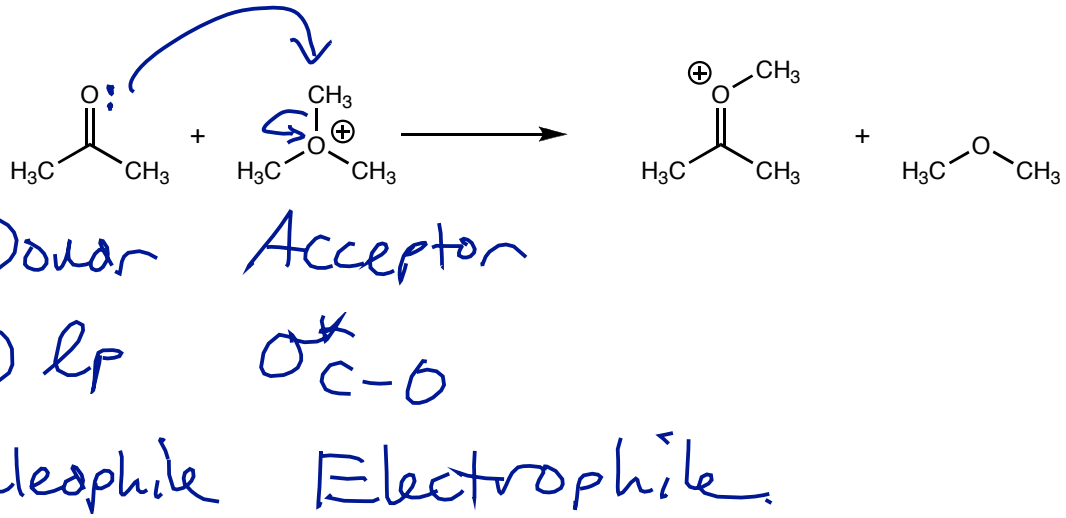
(proton donor)

Reading: Supplemental Handout, Section 2.7

What's Your Role: Base or Nucleophile?

- In one of the following reactions, acetone ($(CH_3)_2C{=}O$) plays the role of a base; in the other it plays the role of a nucleophile. Which is which, and why? Can you draw the curved arrows and identify the HOMO and LUMO of each reaction?





Reading: Supplemental Handout, Section 2.7

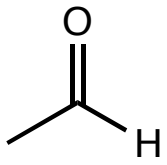
Try this at home...

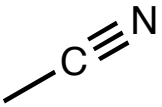
answers ~~tomorrow~~ online.

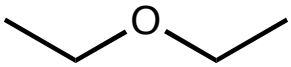
Pop Quiz

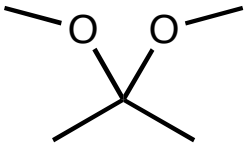
(don't worry, this will not be graded!)

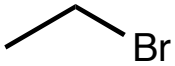
- For each of the following molecules:
  - Identify the HOMO (donor)
  - Identify the LUMO (acceptor)
  - Name the functional group

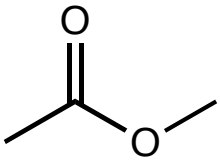


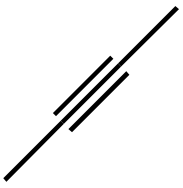








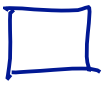




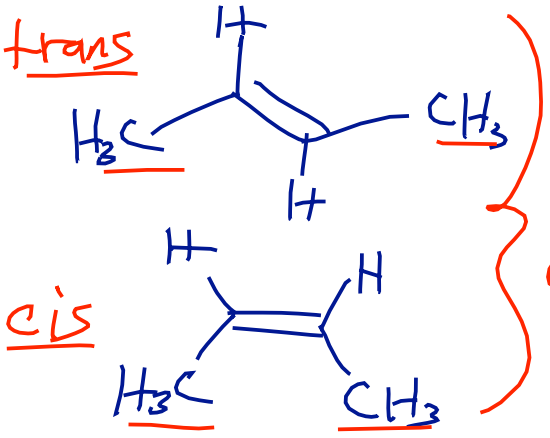
Hydrocarbons with Double bonds

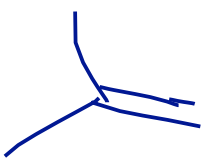
An Introduction to Alkenes

- Draw the skeletal structures of all hydrocarbons with the formula C_4H_8. What can we note about these structures?

Alkanes:  cyclobutane  methylcyclopropane

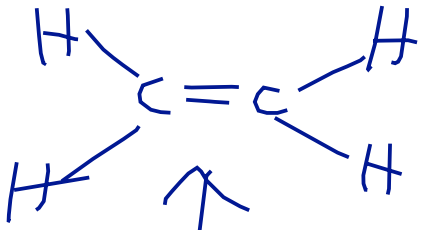
Alkenes: 





distinct molecules with same constitution.

- Some of the above structures contain a C=C double bond. What orbitals are involved in a C=C double bond?



orbitals

σ^*_{C-C} —

$\pi^*_{C=C}$ —

$\pi_{C=C}$ 4t

σ_{C-C} 4t

- What do we call different molecules that have the same molecular formula?

isomers

Reading: Section 4.1

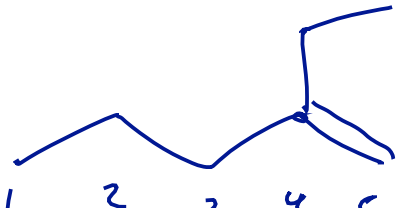
Naming Alkenes

- Each of the following names describes an alkene. However, these names are not the correct names for these molecules. Draw the skeletal structure of the molecule and provide a correct systematic name.

location of C=C

4-ethyl-4-pentene

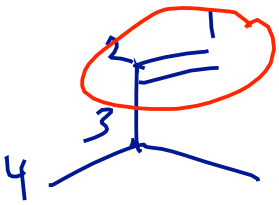
(1) Find longest Chain of C's - Must contain double bond. Number so the double bond has lowest #.



2-ethyl-1-pentene

2-vinylpropane

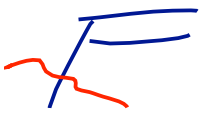
(2) Deal with Substituents.



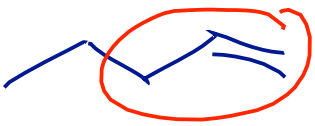
3-methyl-1-butene

Examples:

Vinyl

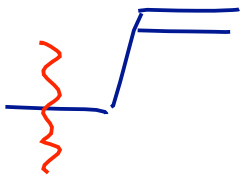


allylethane



allyl

Allyl

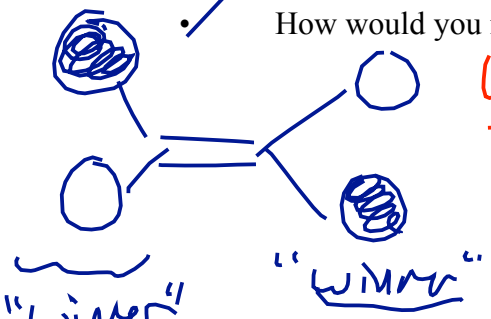


1-pentene → (pent-1-ene)

Reading: Section 4.2

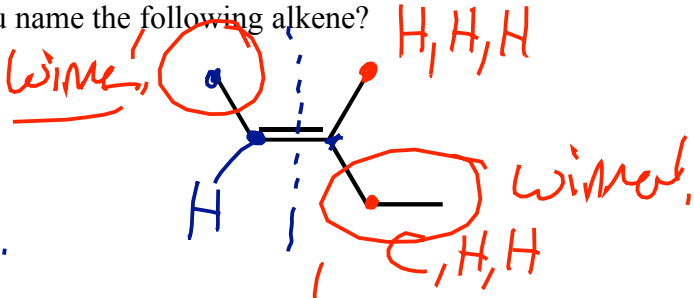
The Problem with Cis and Trans

- How would you name the following alkene?



"winner"

"winner"



- We need better rules: The *E*/*Z* rules for naming alkanes require that we determine the *priority* of the four groups attached to the alkene, as follows:

Step 1. Greater atomic number = higher priority.
If atomic number is the same, heavier isotope = higher priority.
If there is a **tie**, go on to Step 2.

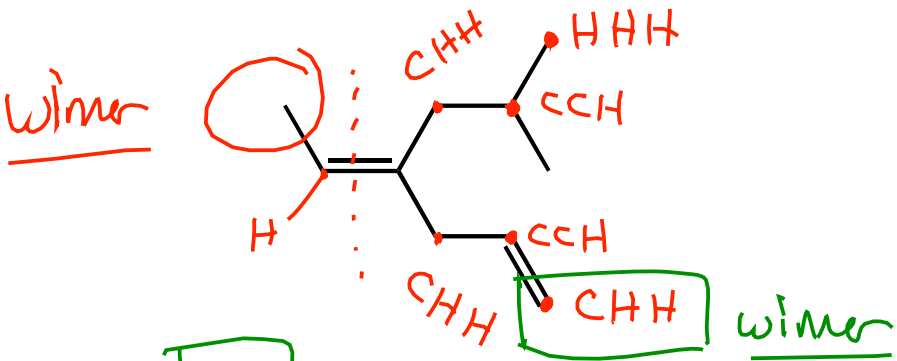
Step 2. If the atoms are the same, consider the atoms that are attached. (For carbon, there will be 3 other atoms). List those atoms in descending order of priority, and make a pairwise comparison between the two sets. One "wins" at the first point of difference. If there is a **tie**, go on to Step 3.

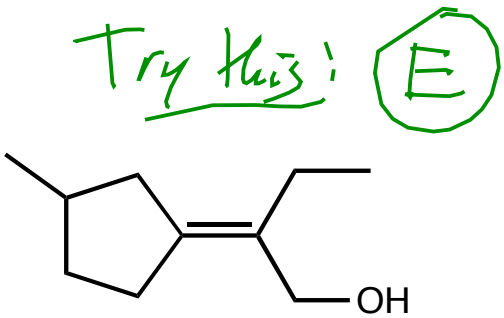
Step 3. If the two sets of atoms are the same, follow the path of highest priority and move one atom away along each path. Then go back to Step 2, but with the *new* atoms. Continue in this fashion until one of the branches ultimately "wins" over the other.

Step 4. If the *high-priority* groups are on the same side of the double bond, then the configuration is *Z* (German "zusammen" = together). Otherwise, the configuration is *E* (German "entgegen" = opposite).

This is not any more difficult that figuring out NFL playoff schedules! They key concept is the application of specific rules as "tiebreakers." Let's look at some examples:

- Determine whether the double bonds in the following alkenes has the *E* or *Z* configuration:





Reading: Section 4.2

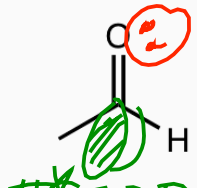
Answers to Pop Quiz

- For each of the following molecules:
  - Identify the HOMO → Donors in red
  - Identify the LUMO → Acceptors in green
  - Name the functional group

HOMO's (circled) are either lone pairs or $\pi_{C=C}$
LUMO's (antibonding orbitals) are indicated on each molecule

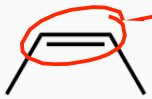
Focus on biggest lobes

aldehyde



$\pi^*_{C=O}$

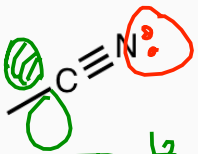
alkene



$\pi_{C=C}$

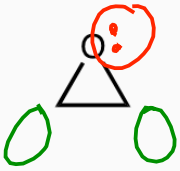
$\pi^*_{C=C}$ not great

nitrile



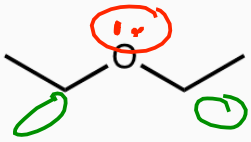
$\pi^*_{C=N}$

epoxide



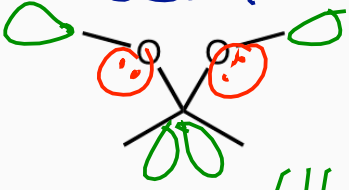
σ^*_{C-O} (two of them)

ether



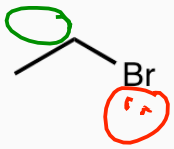
σ^*_{C-O} (×2)

acetal



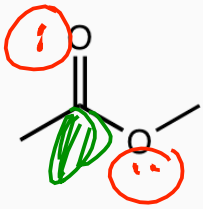
σ^*_{C-O} (4 of them!)

alkyl halide



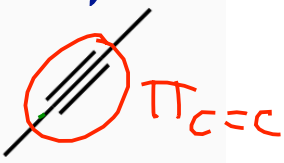
σ^*_{C-Br}

ester



$\pi^*_{C=O}$

alkyne



$\pi_{C=C}$

$\pi^*_{C=C}$ not great acceptor