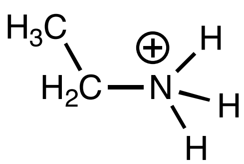
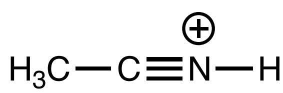
Factors That Influence Acidity: The Main Atom

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

H—OH H—F
+15.7 +3.2

H—OH $H—OH_2^{\oplus}$
+15.7 –1.7

+10 –10

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

- 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?

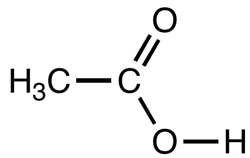
H—OH H—F
+15.7 +3.2

H—SH H—Cl
+7.0 –7

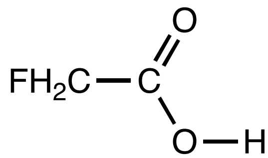
Reading: Section 3.6

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?

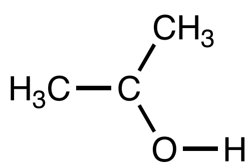


4.76

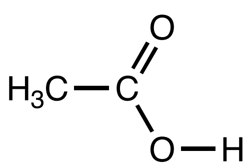


2.66

- 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:



16.5



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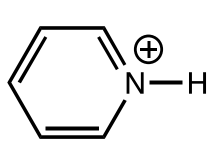

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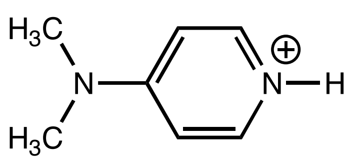
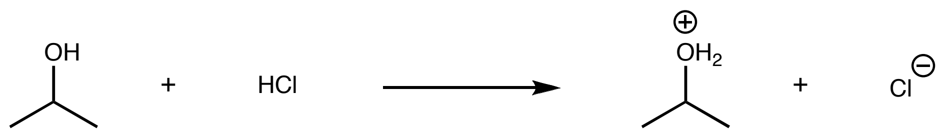


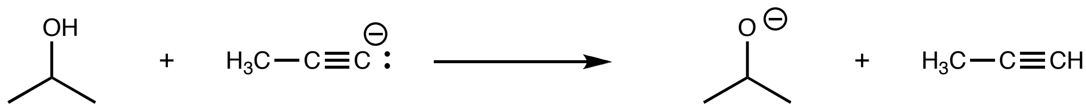
9.2

Reading: Section 3.6

Frontier Orbitals of Proton-Transfer Reactions

- 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?



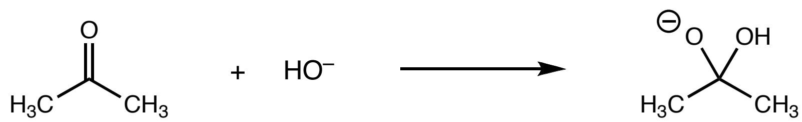


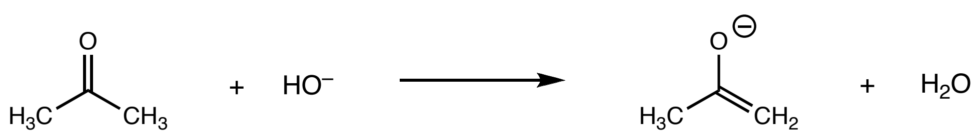
- What generalization can we make about the LUMO in **any** proton-transfer reacton?

Reading: Supplemental Handout, Section 2.6

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?

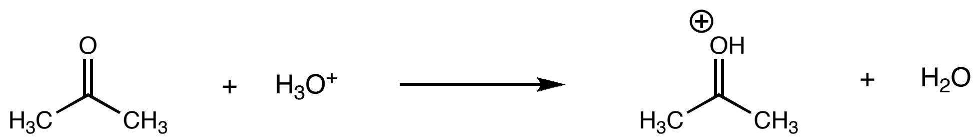


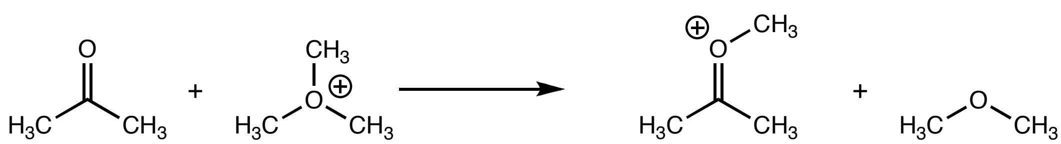


Reading: Supplemental Handout, Section 2.7

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?



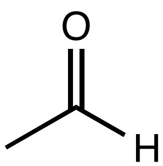
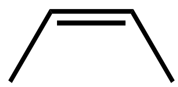
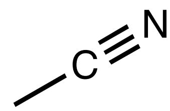


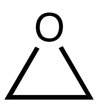
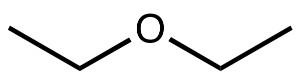
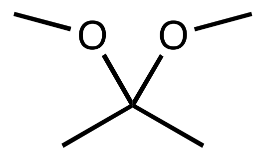
Reading: Supplemental Handout, Section 2.7

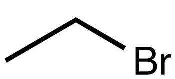
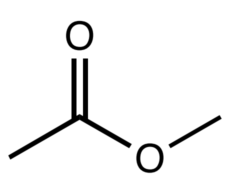
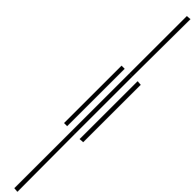
Pop Quiz

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

- For each of the following molecules:
  - Identify the HOMO
  - Identify the LUMO
  - Name the functional group

An Introduction to Alkenes

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

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

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

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.

4-ethyl-4-pentene

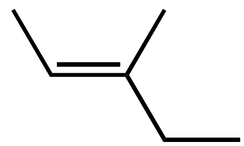
2-vinylpropane

allylethane

Reading: Section 4.2

The Problem with Cis and Trans

- How would you name the following alkene?



- 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.

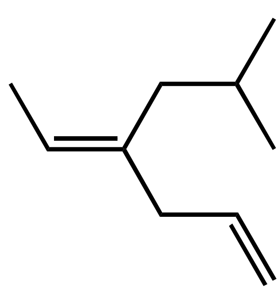
Step 2. If the atoms are the same, consider the atoms that are attached. (For carbon, there will be 3 other atoms). List those atoms in descending order of priority, and make a pairwise comparison between the two sets. One "wins" at the first point of difference.
If there is a **tie**, go on to Step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

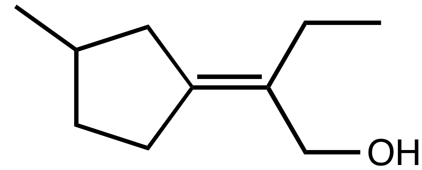
Step 3. If the two sets of atoms are the same, follow the path of highest priority and move one atom away along each path. Then go back to Step 2, but with the *new* atoms. Continue in this fashion until one of the branches ultimately "wins" over the other.

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:



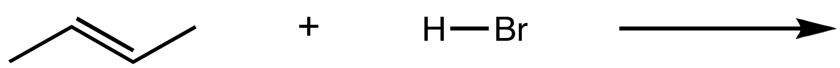


Reading: Section 4.2

An Introduction to Reactions of Alkenes

- A review: What are the important orbitals in an alkene?

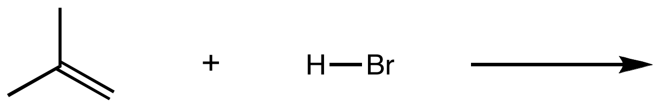
- Let's see if we can *predict* what will happen in the following reaction:



Reading: Section 4.7

Regioselectivity: "Markovnikov's Rule"

- Now consider the following reaction. Can you *predict* what will happen?



- What is the *observed* product of this reaction? What does this observation tell you about the *mechanism* of this reaction?

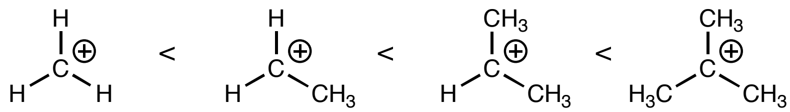
- Is there a general *rule* that we can formulate about alkene additions?

- The central lesson: First, **predict** what will happen. Then, **compare** that prediction with the experimental result. Finally, **refine** your understanding of the reaction. **PCR**!

Reading: Section 4.7

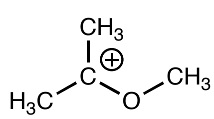
The Stability of Carbocations

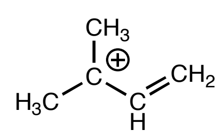
- The relative stability of carbocations exhibits the following trend:



- How can we explain this trend?

- Here are two other examples of "carbocations." Can you make any statement about their stability, relative to the carbocations above (and relative to each other)?

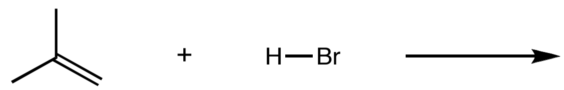




Reading: Section 4.7

Reactive Intermediates and Hammond's Postulate

- For the following reaction, draw out the **reaction coordinate** for the reaction that leads to the observed ("Markovnikov") product. Then, draw the reaction coordinate for the reaction that leads to the other ("anti-Markovnikov") product.



Markovnikov:

Anti-Markovnikov:

- How can we analyze these reaction coordinate diagrams?

- Does this help to explain why the Markovnikov product is the one that is observed?

Reading: Section 4.8

Answers to Pop Quiz

- For each of the following molecules:
  - Identify the HOMO
  - Identify the LUMO
  - Name the functional group

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