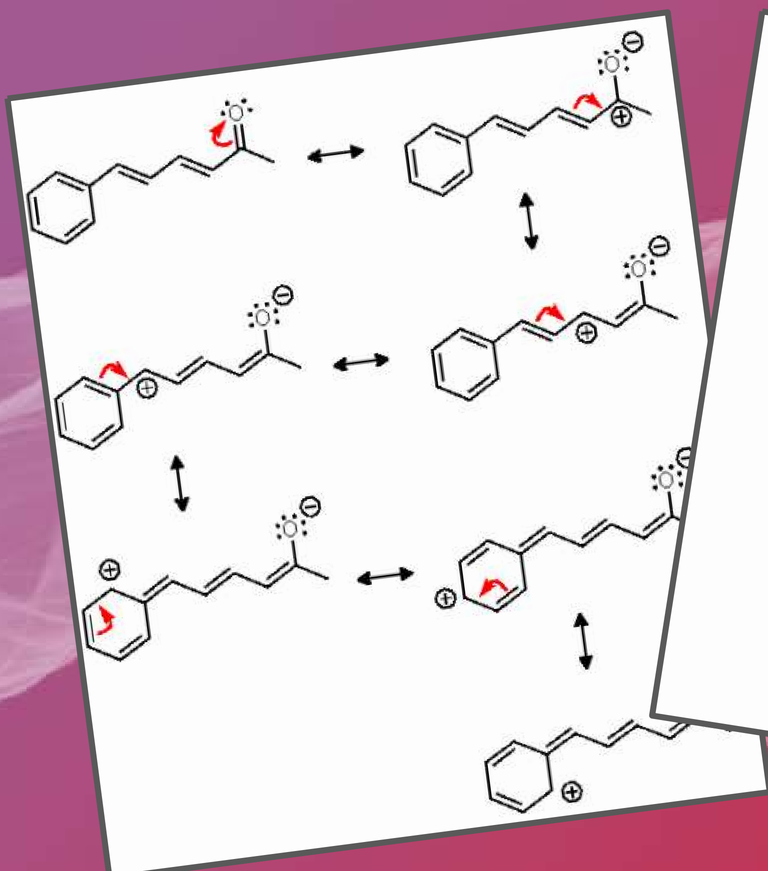
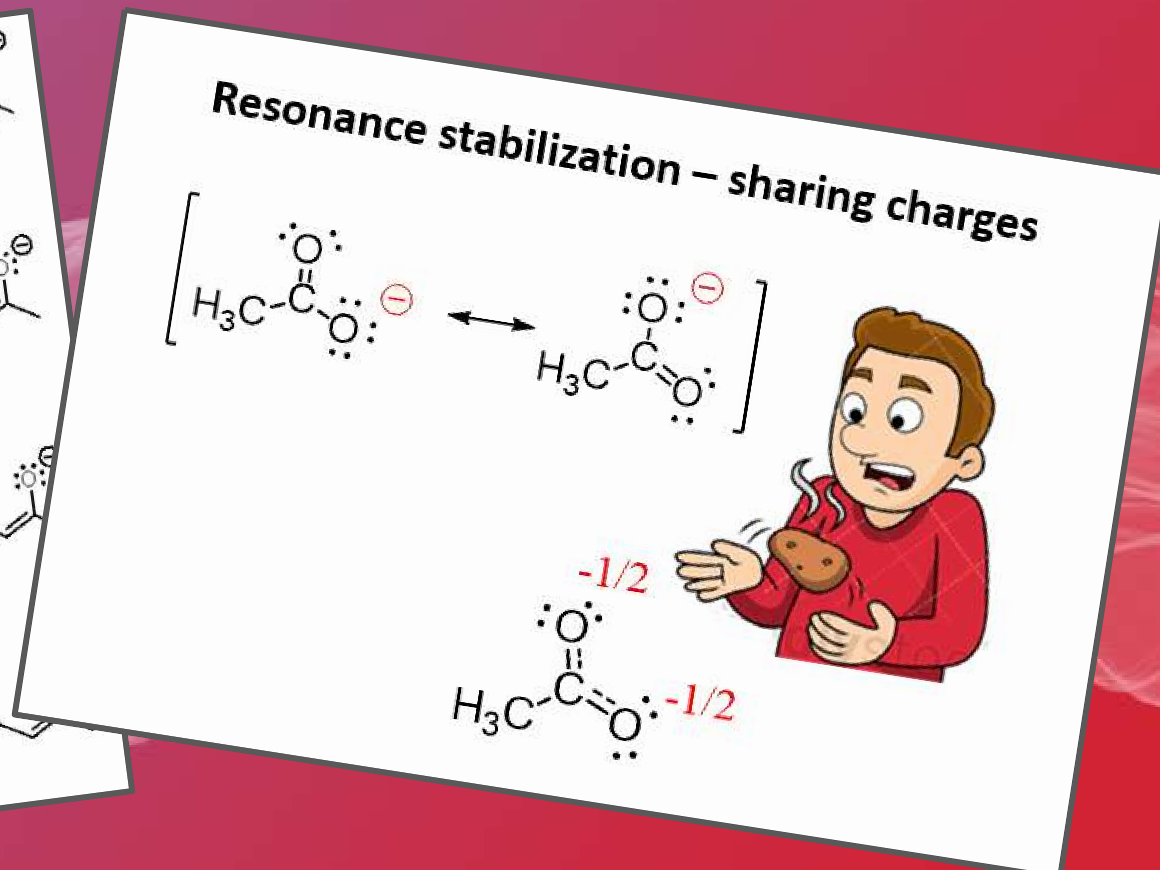
Organic Chemistry

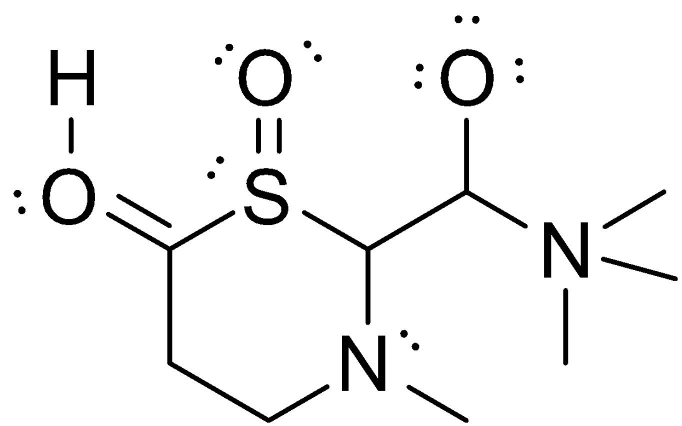
Chapter 2 Notes: Resonance





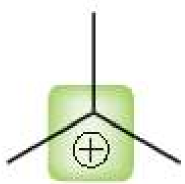
First: A Quick Recap/Rational!

- **Formal charge** affects the **stability** and **reactivity** of molecules, so you must be able to identify formal charges in bond-line representations
- Formal charges must always be shown in the bond-line drawing!
- Label all of the formal charges in the following molecule

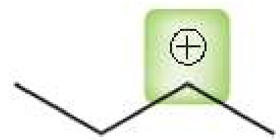


A Special Note on Carbon!

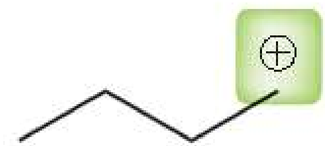
- Most carbon atoms will have 4 covalent bonds and no lone pairs to avoid carrying a formal charge
- Sometimes carbon will have a +1 charge. In such cases, the carbon will only have **3 bonds**. These are called CARBOCATIONS



No hydrogen atoms on this C^+

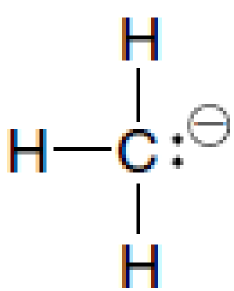


One hydrogen atom on this C^+



Two hydrogen atoms on this C^+

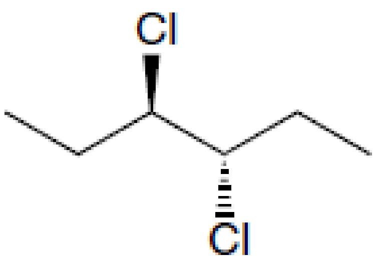
- Sometimes carbon will have a -1 charge. It will still only make 3 bonds!

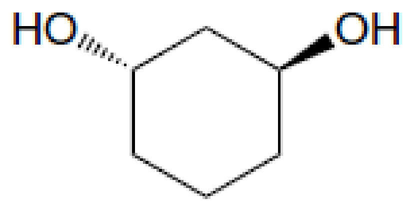


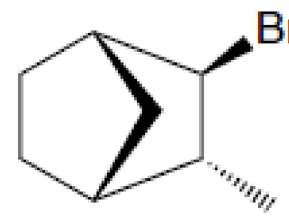
<u>REMEMBER:</u> If carbon has a charge it must be shown and that means it will only make 3 bonds!!! Count H's appropriately!

Ways We Visualize Molecules

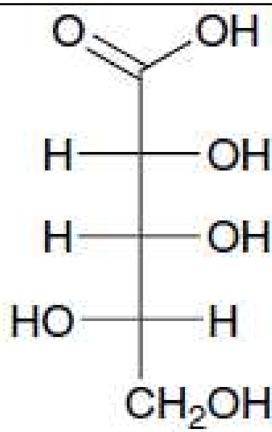
- The vast majority of molecules are 3-dimensional, but it is difficult to represent a 3D molecule on a 2D piece of paper.
- We will use **dashed** and **solid** wedges to show groups that point **back into the paper** or **out of the paper**



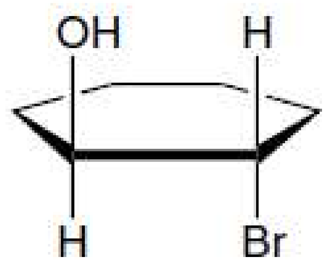




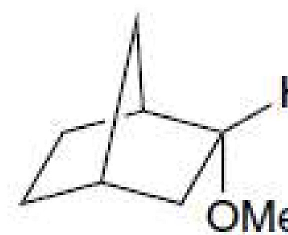
These are other ways you may encounter drawings of molecules. We will spend part of a chapter on Fischer projections later on!



Fischer projection
(Used only for acyclic compounds)



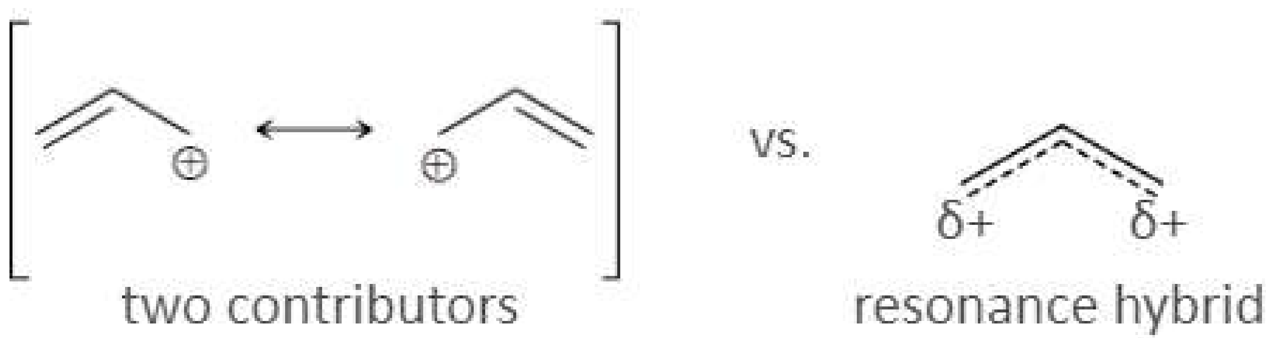
Haworth projection
(Used only for cyclic compounds)



(Used only for bicyclic compounds)

2.1 What is Resonance?

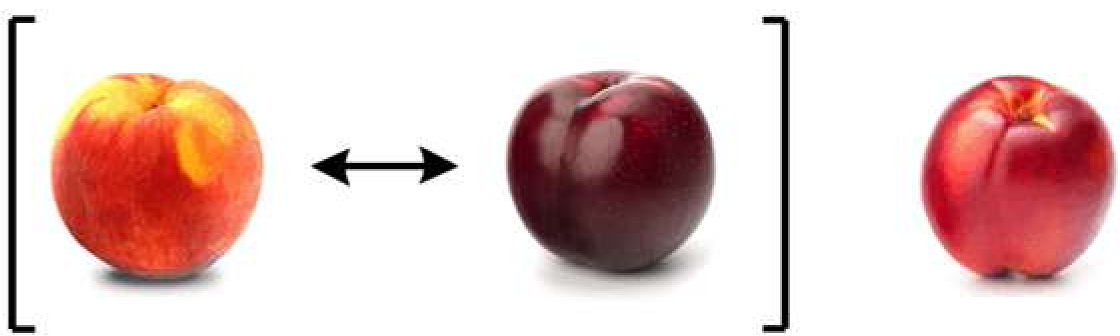
- In Chapter 1 we learned about bond-line drawings, lone pairs, formal charges, etc. However, *electrons really exist in* ***clouds of electron density***.
- We can't actually draw the exact location of where the electrons are. So our solution is **Resonance**.
  - We will need more than one drawing to represent the overall hybrid of where the electrons are. We call these **resonance structures**.



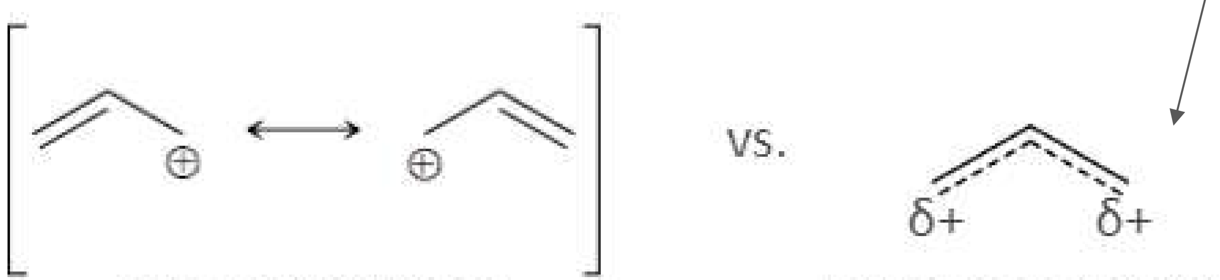
- *The brackets indicate that both resonance contributors exist simultaneously*

- How is a resonance arrow different from equilibrium?
- **Analogy:** a nectarine is a hybrid formed by mixing a peach and a plum. A nectarine is NOT sometimes a peach and sometimes a plum.

It is always a nectarine.



Resonance forms **Hybrid**



two contributors resonance hybrid

We are alway really representing the hybrid, but we are limited by our ability to draw in charges & electrons in the bond-line models.
So use your imagination!

What is the purpose of Resonance?

- **Resonance makes a molecule <u>MORE</u> stable**

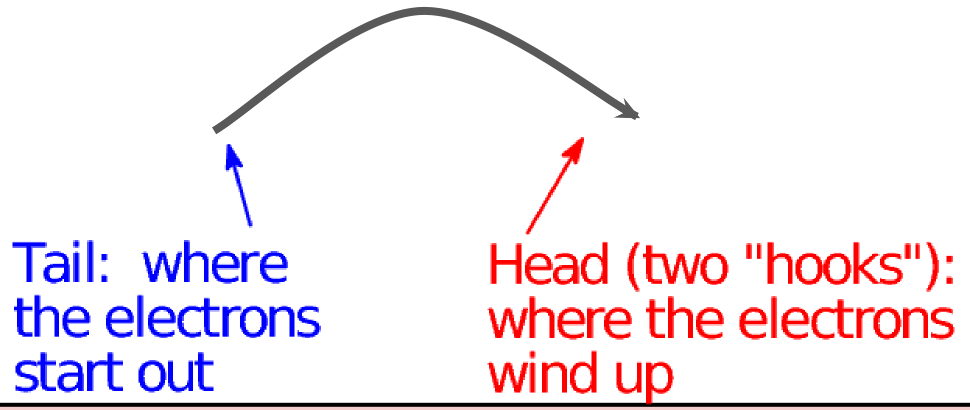
  - **Delocalization of electrons**
    - Electrons exist in orbitals that span a greater distance giving the electrons more freedom minimizing repulsions
    - Electrons spend time close to multiple nuclei all at once maximizing attractions

  - **Delocalization of charge**
    - The charge is spread out over more than one atom. The resulting partial charges are more stable than a full +1 charge.

resonance hybrid

2.2 Curved Arrows: The Tools for Resonance

- Throughout Organic Chemistry, we will be using **curved arrows** to **show electron movement**
  - The sooner you master this skill, the easier the course will be!
- Curved arrows generally show electron movement for **pairs** of electrons (2 at a time!) *You will see arrows for 1 e- in college.*



<u>CAUTION:</u> We are NOT actually "moving" electrons!!! We are always thinking of the overall hybrid - but we have to have a method of drawing each of the contributing structures. This will cause us to say thing like "The electrons are coming from here and going over there" but we are NOT actually moving them!!!

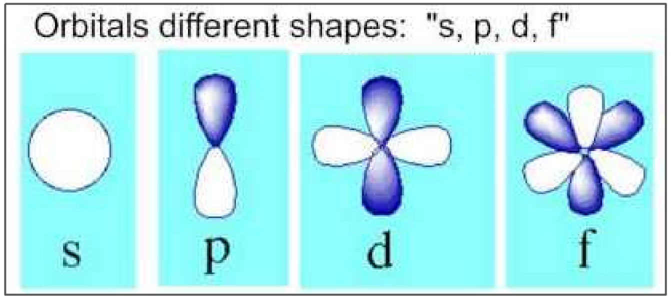
You have two things you must get correct!

1. Where the electrons are “coming from” (Tail)
2. Where the electrons are “going” (head)

Let’s start with where we “get” electrons from. Electrons exist in **orbitals**. Each orbital can hold a maximum of 2 electrons. *Orbitals holding a single electron generally overlap from separate atoms to create a bond which totals 2 electrons.*

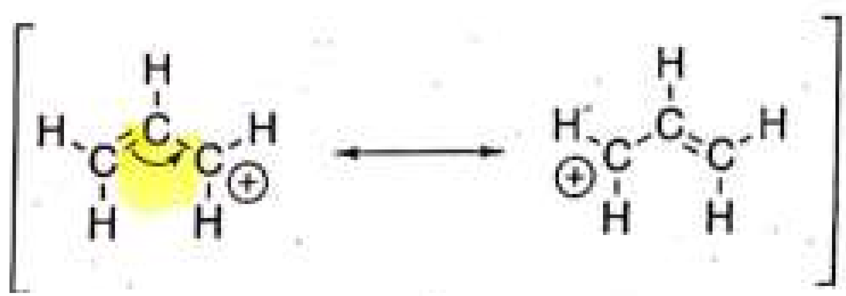
There are 3 possibilities for an orbital:

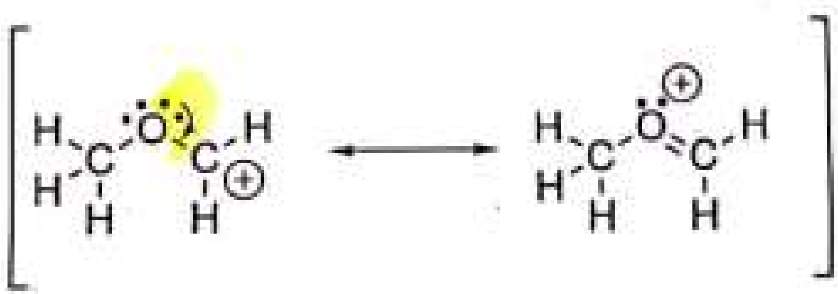
a. it has 0 electrons
b. it has 1 electron (forms bond)



Keep an eye on those arrows!

1. The **“tail”** of the arrow must come from a source of electrons
   a. it can NEVER come from a positive charge!
2. The **“head”** of the arrow must point to a place where we can add more electrons *(watch that you do NOT violate an octet for any second-row atoms - they can not have more than 4 orbitals being used.)*





2.3 The Two Commandments

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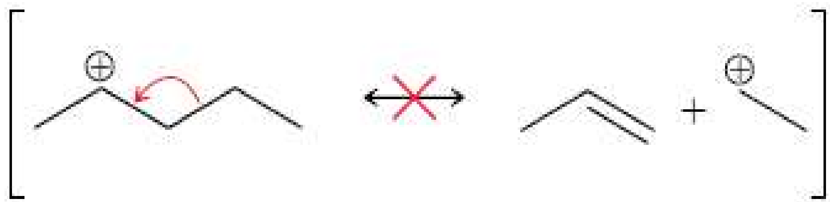
Rules for using curved arrows to show RESONANCE

1. **NEVER break a single bond**

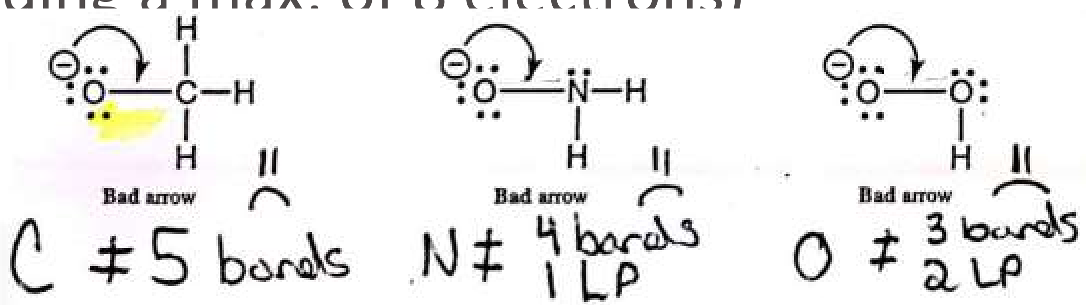


Don't break a single bond

- Single bonds can "break", but NOT in RESONANCE
- You'll avoid doing this by never drawing the tail of an arrow can never come from a single bond

1. **Never exceed an octet for 2nd row elements**

- Atoms in the 2nd row can only have four orbitals (holding a max. of 8 electrons)

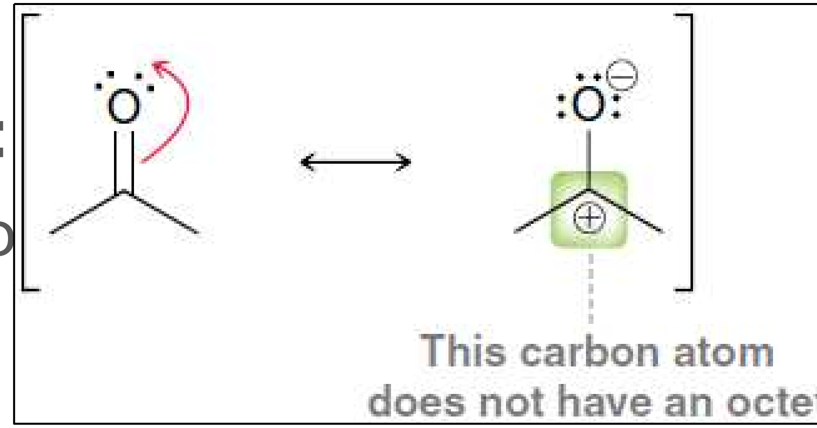


Special note: We just cannot EXCEED an octet (using 4 orbitals) for second row elements, but we CAN have less than 4 orbitals being used…

Look at this example:

The positive carbo

is only using 3 orbitals

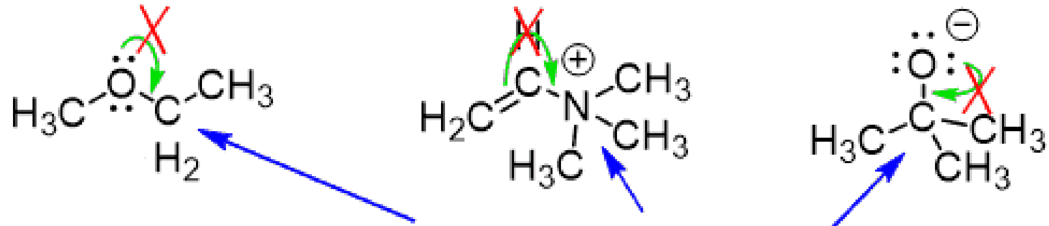


Steps to Checking if an Arrow is Violating an Octet:

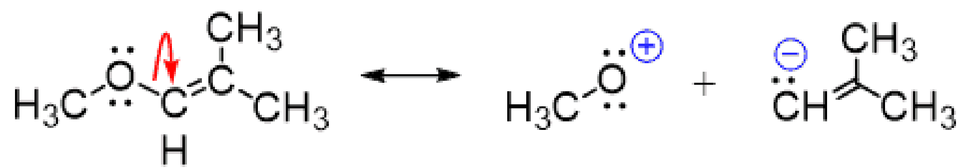
1. Look at the atom (or atoms) where the head of the arrow is pointing. Determine how many orbitals that atom is currently using (for bonds or lone pairs).
    - Watch out for “hidden” hydrogens!
2. If the atom has space, it should be able to accept the bond or lone pairs.
    - always double check the amount of orbitals.
    - the overall charge should be maintained for the molecule

2.3 The Two Commandments: **Practice #1**

Completed Examples

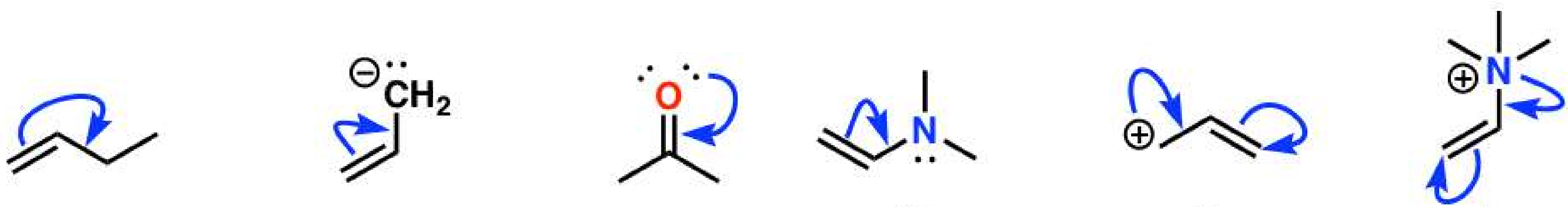


Wrong - exceeds the octet for the atom



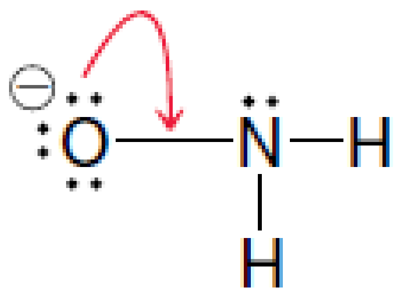
Wrong - breaking a single bond is not allowed in resonance structures

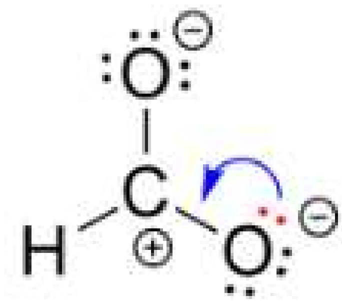
Practice: Why are each of the arrows "illegal"?

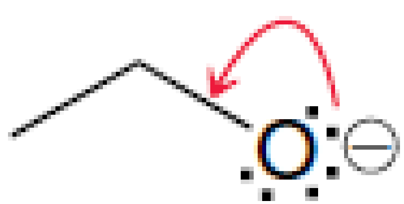


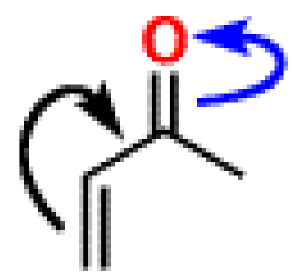
A **B** **C** **D** **E** **F**

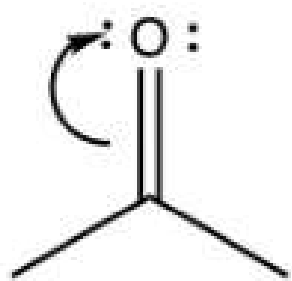
Practice: Determine if the arrows violate either of the 2 commandments or if they are correct

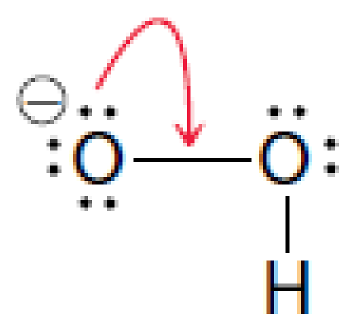












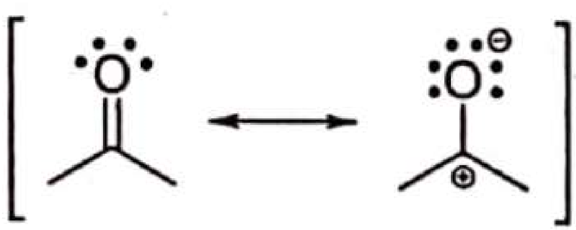
2.4 Drawing Good Arrows

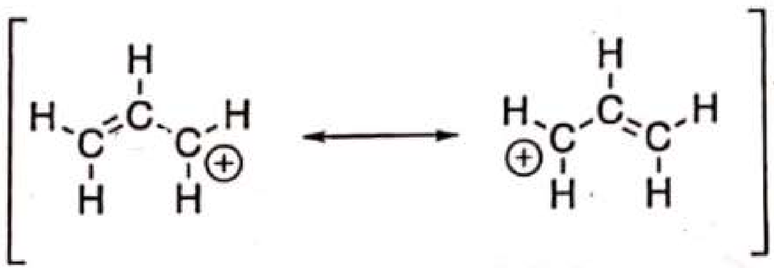
We will begin by learning to draw in arrows to get us from one structure to the next. It is very important to draw correct arrows!

<u>Things to look for:</u>

- double bonds or lone pairs that are disappearing (this is where the tail of the arrow will originate)
- double bonds or lone pairs that are appearing (this is where the head of the arrow will point)
- *NOTE: sometimes we will need more than one arrow to get us from one structure to another. Electrons cannot "jump" across atoms!*

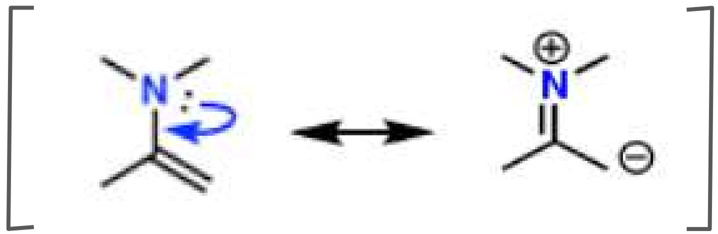
Draw arrows on the first structure to get to the second one.



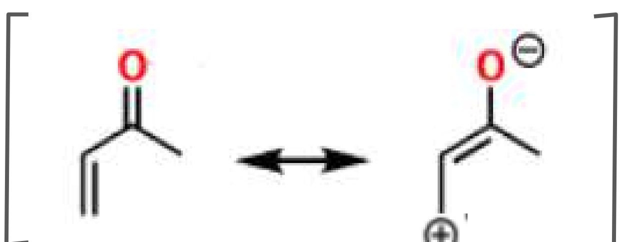


<u>Sometimes you need more than one arrow!</u> Keep looking to see if you can continue to “push” electrons farther away. Don’t forget to draw in lone pairs! This example needs one more arrow to be correct.

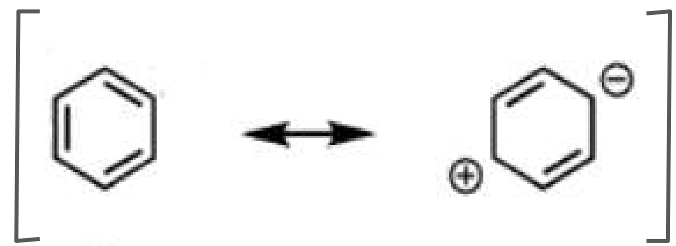
Example:



Practice #1 The resonance structures will need TWO arrows to get you to the second image.



A



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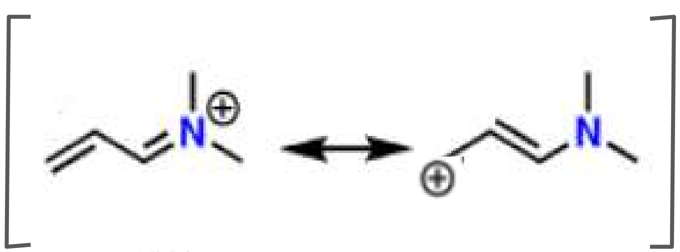
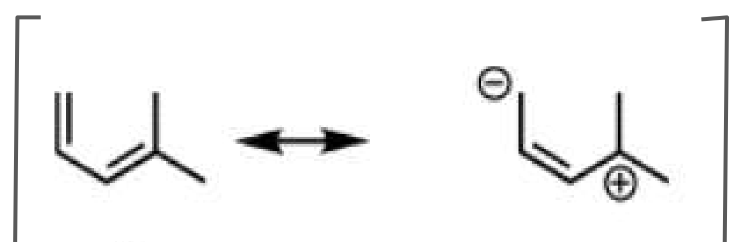
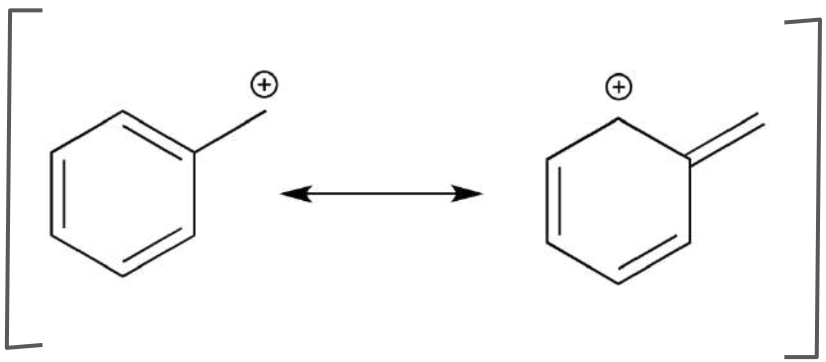


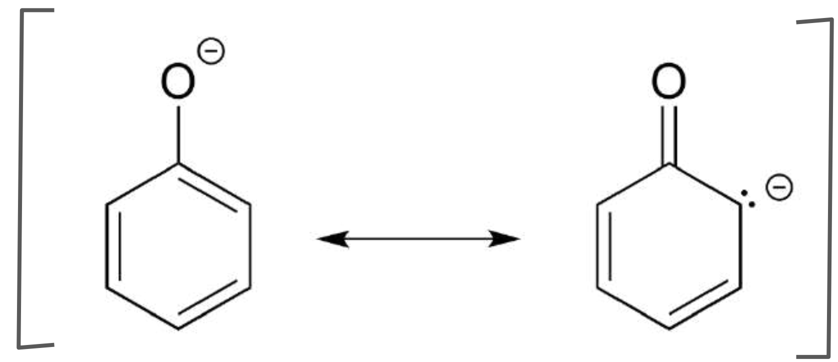
C

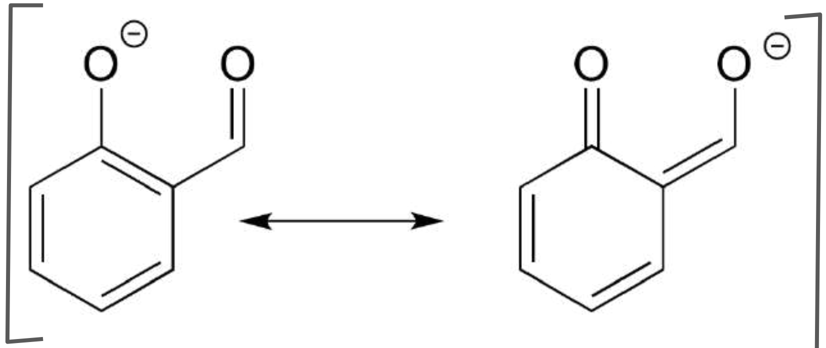


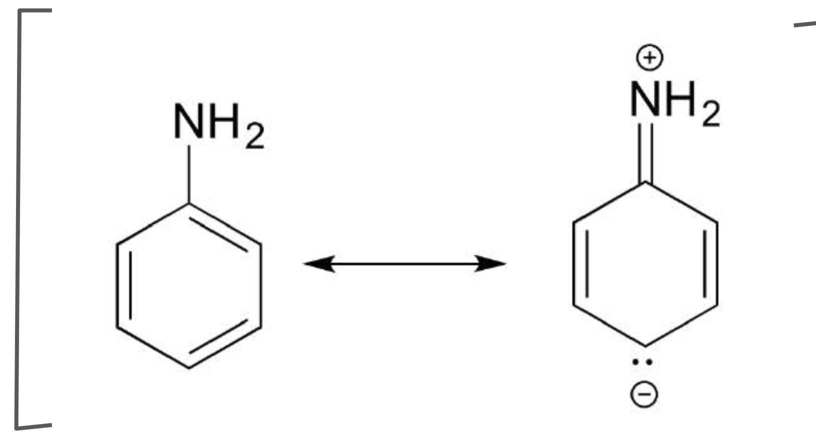
D

Practice #2: Draw the arrow(s) needed to get from one resonance structure to the next. You may need to draw in lone pairs that are not shown.







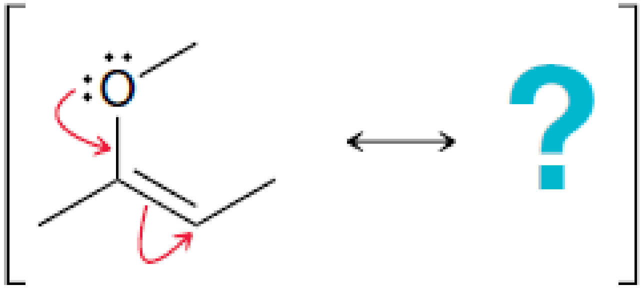


2.5 Formal Charges in Resonance

Now that we can draw in the arrows, we need to work on “following arrows” that are provided so we can draw the second structure.

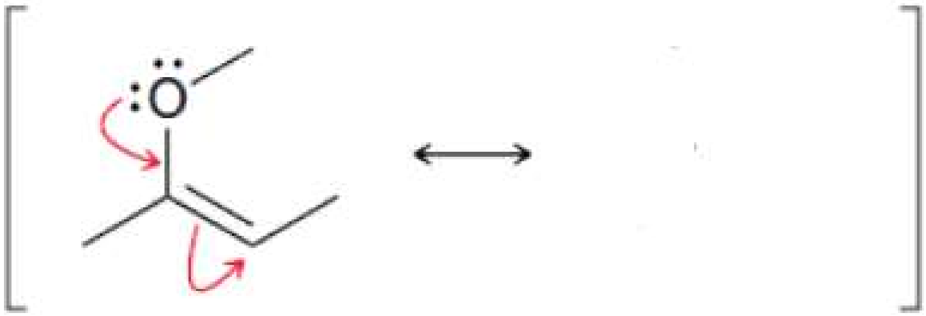
To do this - we have to make sure we **account for any formal charges that will be created.**

- **The overall charge from the original structure must be maintained throughout each of the resonance structures!**



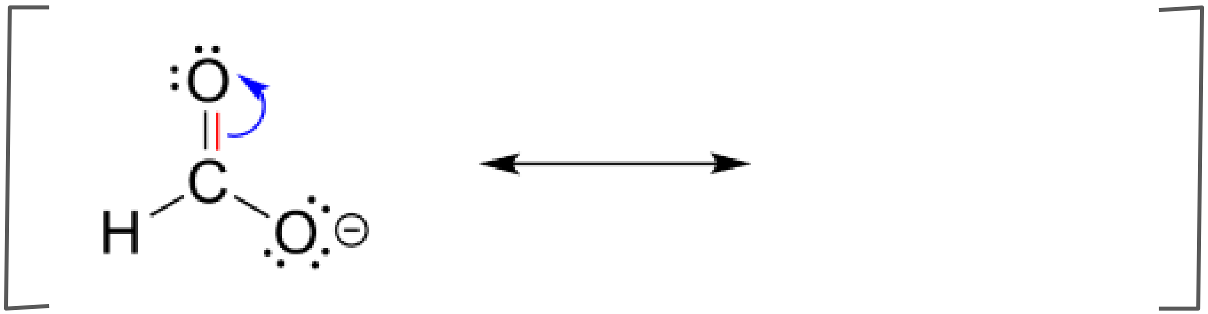
Step 1: Draw the resulting structure, I recommend drawing in lone-pairs that would exist.

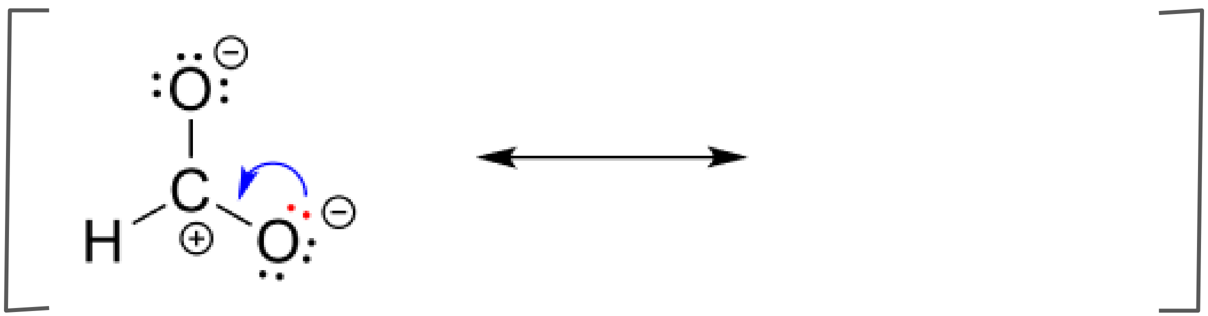
Step 2: Place in formal charges for the structure you drew. *Typically negative charges appear where you “pushed” the electrons to and positive charges tend to appear where you “took” electrons from.*

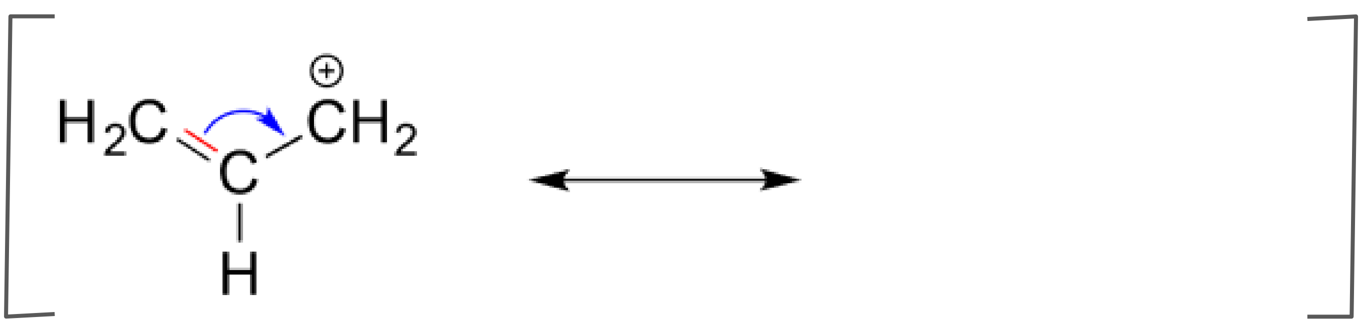


Step 3: Add up all of the formal charges to make sure the overall charge matches the original structure. If not - you better double check!

Practice #1: "Follow the arrows" and draw the second resonance structure that would be created. Make sure to include formal charges and check the overall charge.

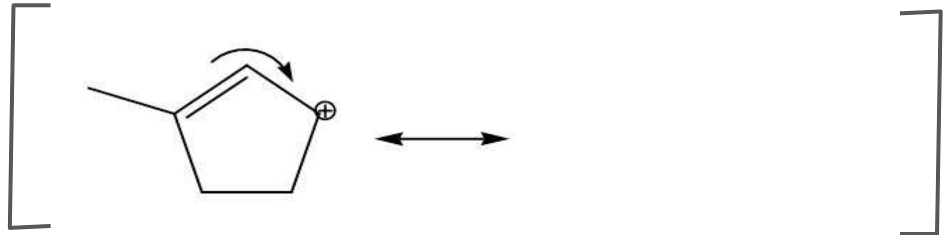


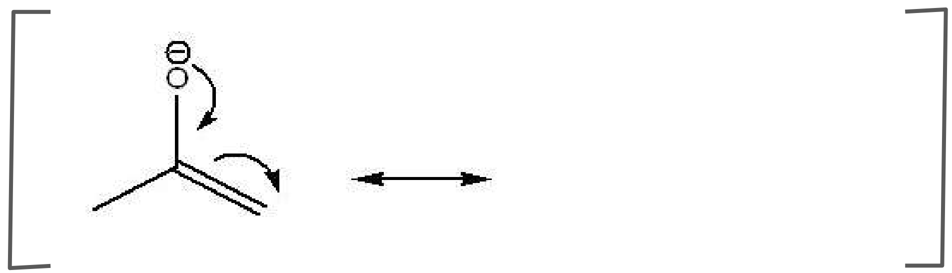


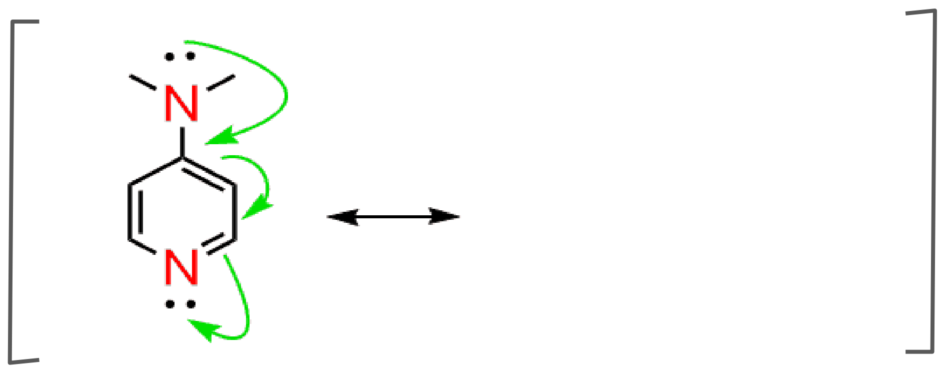


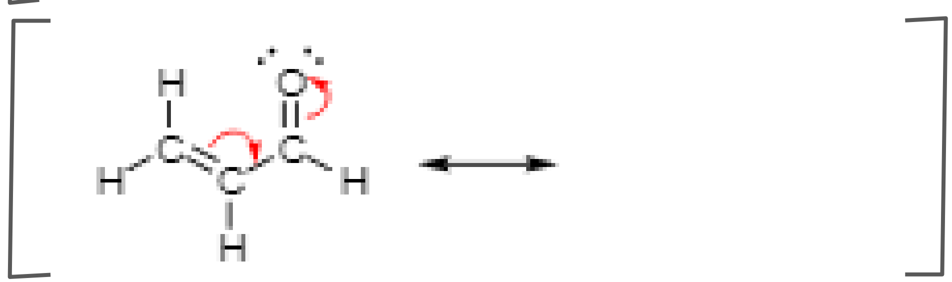
2.5 Formal Charges in Resonance: **Practice #2**

Practice #2: “Follow the arrows” and draw the second resonance structure that would be created. Make sure to include formal charges and check the overall charge.









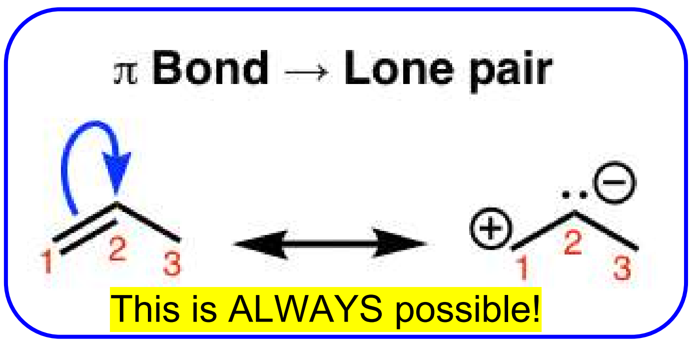
2.6 Drawing Resonance Structures - Step by Step

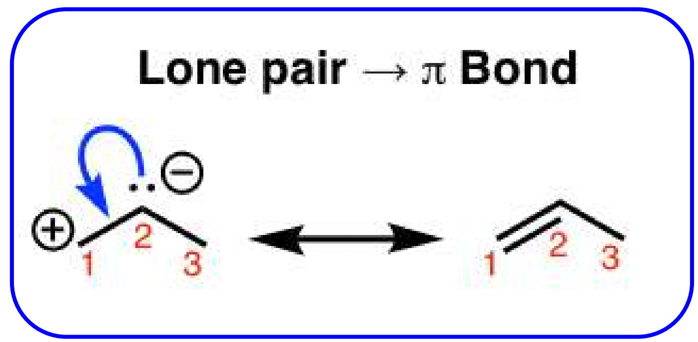
Sigma Bond - (bond) refers to a single bond

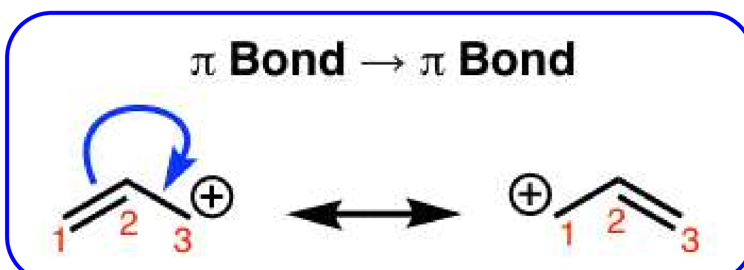
Pi Bond - (π bond) refers to a double or triple bond. Each "additional" bond counts as 1 pi bond. *(more on this later!)*

- single bonds = 1 sigma bond an 0 pi bonds
- double bonds = 1 sigma bond and 1 pi bond
- triple bonds = 1 sigma bond and 2 pi bonds

We really only have THREE "Dance moves" that we can make during Resonance







You must have "space" available for the incoming electrons or you will violate the octet of the "receiving" atom

5 Main Bonding Patterns in Resonance

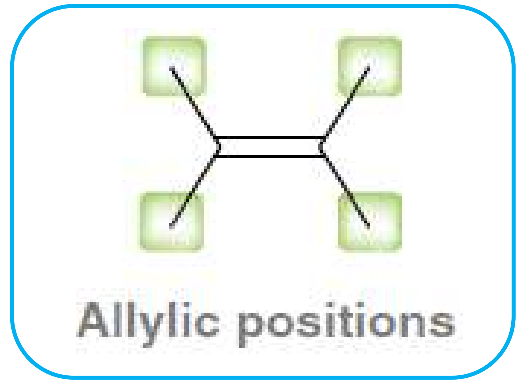
Recognize these patterns to predict when resonance will occur:

1. Allylic lone pairs
2. Allylic positive charge
3. Lone pair of electrons adjacent to a positive charge
4. A pi bond between two atoms with different electronegativities
5. Conjugated pi bonds in a ring

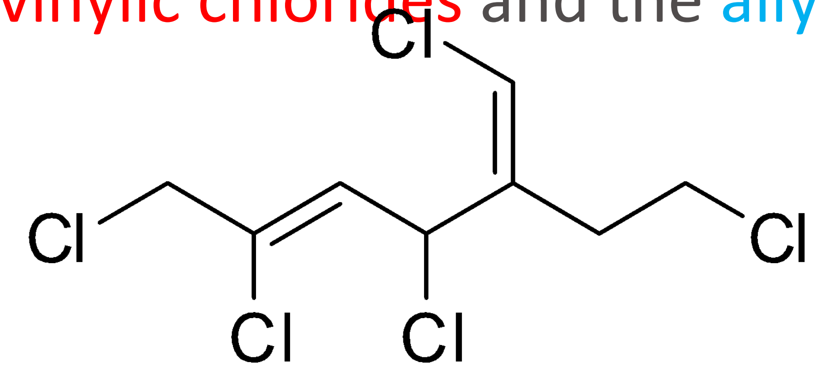
2.7 Recognizing Patterns in Resonance

A Quick Side Note on “Fancy Names” for atom positions

- Vinyl positions are directly bonded to a C=C double bond
- Allyl positions are one atom away from a C=C double bond

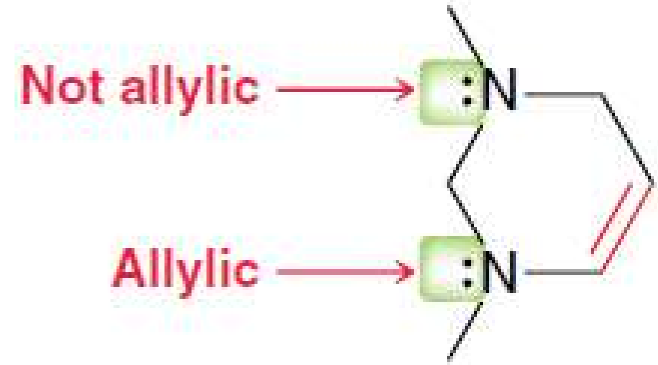


- Label the vinylic chlorides and the allylic chlorides

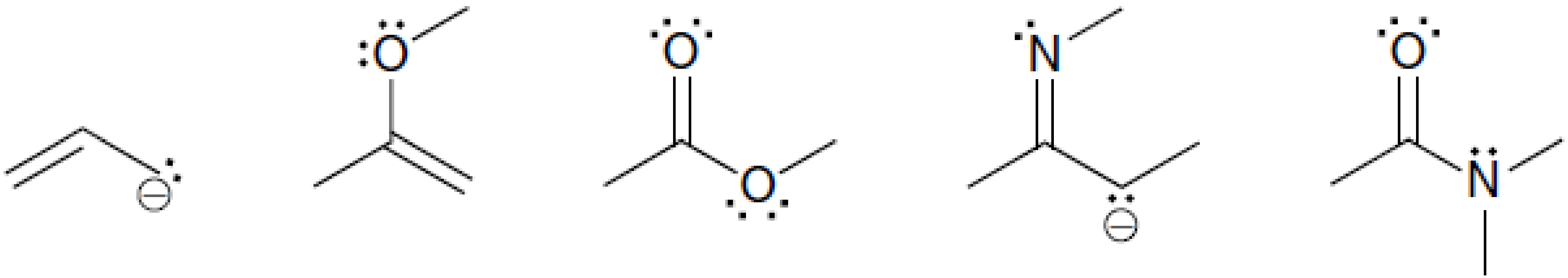


2.10 Patterns in Resonance

1. Identifying allylic lone pairs



- Circle all of the allylic lone pairs

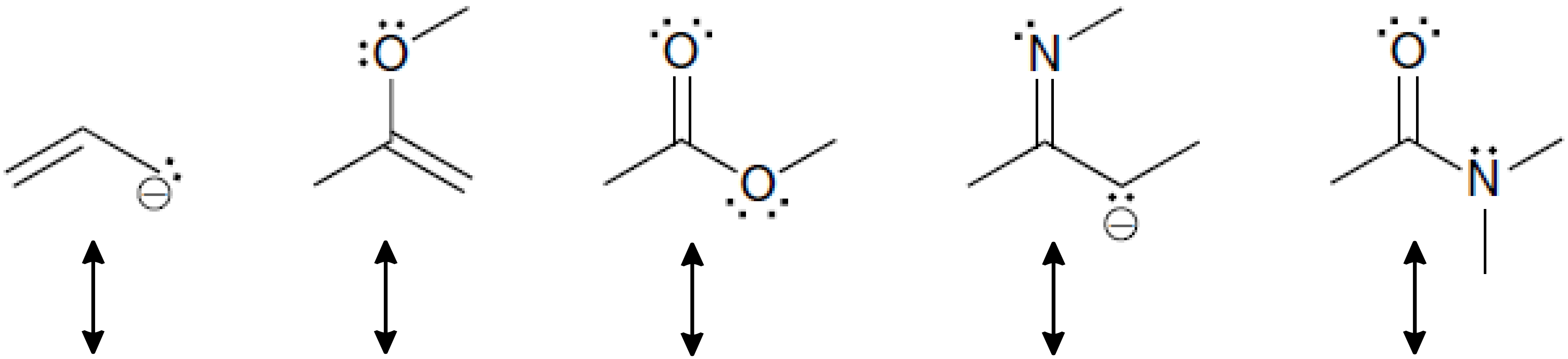


- Draw arrows on each structure to show resonance

2.10 Patterns in Resonance

1. Identifying allylic lone pairs

- For each, show the resulting resonance contributor and all formal charges

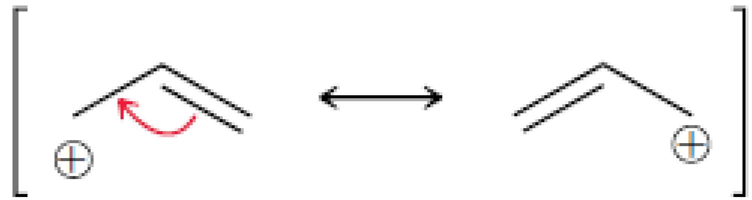


- Practice with conceptual check point 2.25

2.10 Patterns in Resonance

2. Dealing with allylic positive charge

- Only one curved arrow is needed

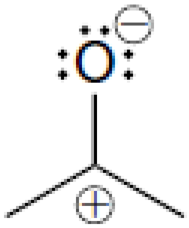


- If there are multiple double bonds (conjugated), then multiple contributors are possible. Show the resonance contributors and curved arrows below

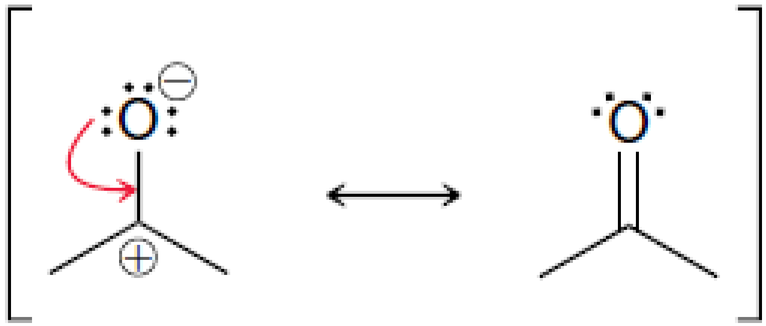
- Draw a resonance hybrid
- Practice with conceptual checkpoint 2.26

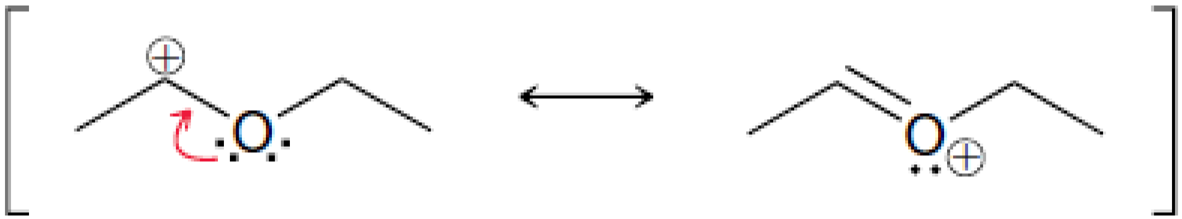
2.10 Patterns in Resonance

3. A lone pair adjacent to a positive charge



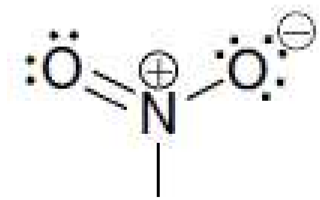
- Only one arrow is needed
- Explain how the formal charges are affected by the electron movement in the following examples





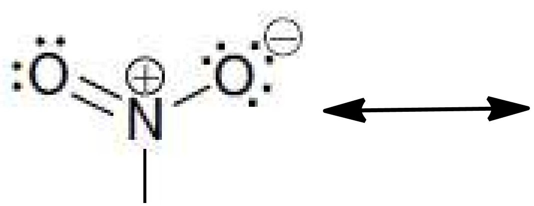
2.10 Patterns in Resonance

3. A lone pair adjacent to a positive charge



- Consider the resonance in the NITRO group
- Why can't ONE arrow be used to cancel out the formal charge and create a resonance contributor?

- Draw all possible resonance contributors

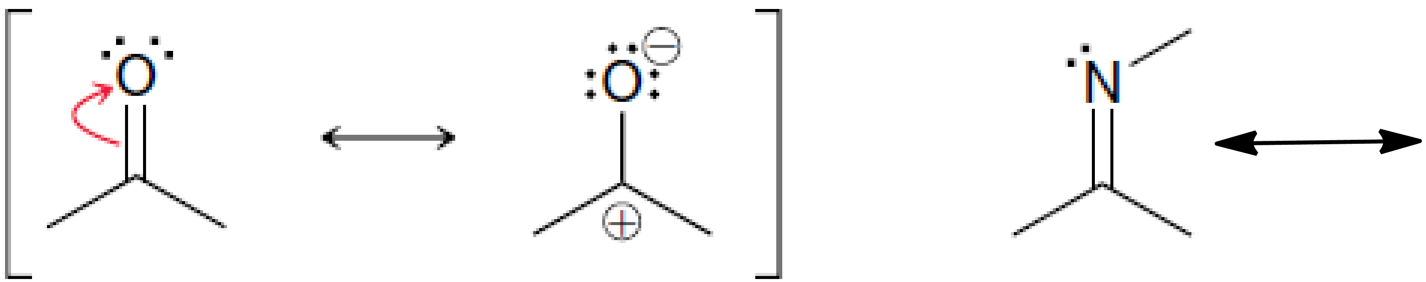


- Practice with conceptual checkpoint 2.27

2.10 Patterns in Resonance

4. A pi bond between atoms of different electronegativity

- The pi electrons will be more attracted to the more electronegative atom
- Explain how the formal charges are created by the electron movement in the following examples

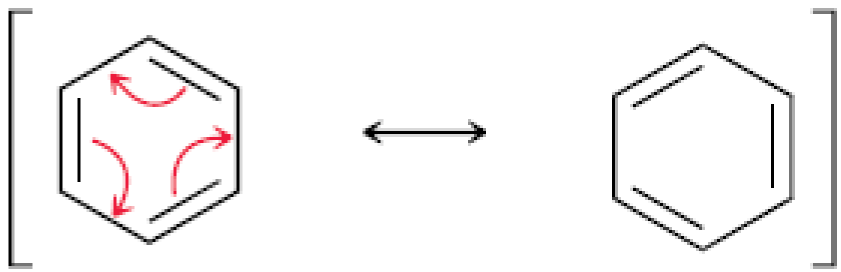


- Practice with conceptual checkpoint 2.28

2.10 Patterns in Resonance

5. Conjugated pi bonds in a ring

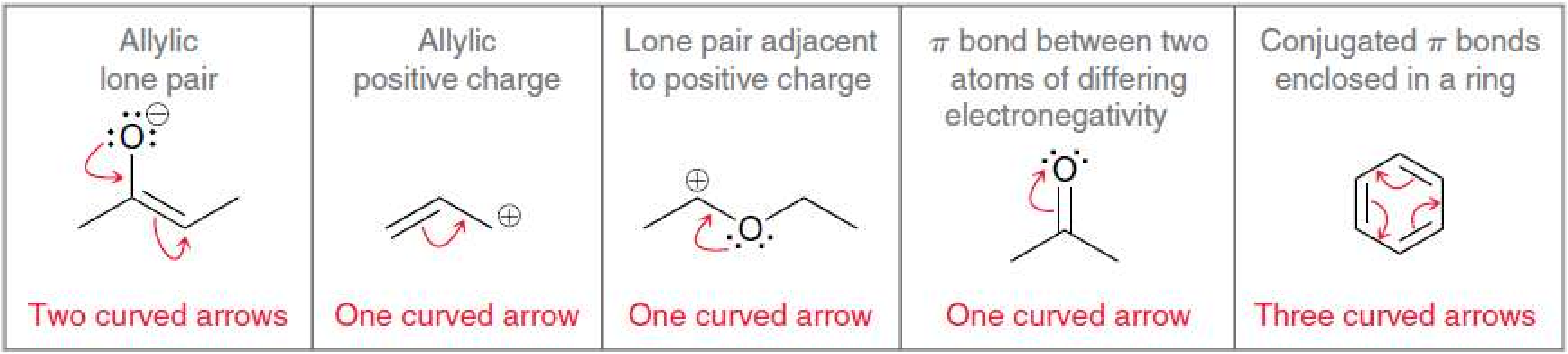
- Each atom in the ring MUST have an unhybridized p orbital that can overlap with its neighbors



- Electrons can be shown to move clockwise or counterclockwise
- What type of motion do the electrons actually have?
- Practice with conceptual checkpoint 2.31

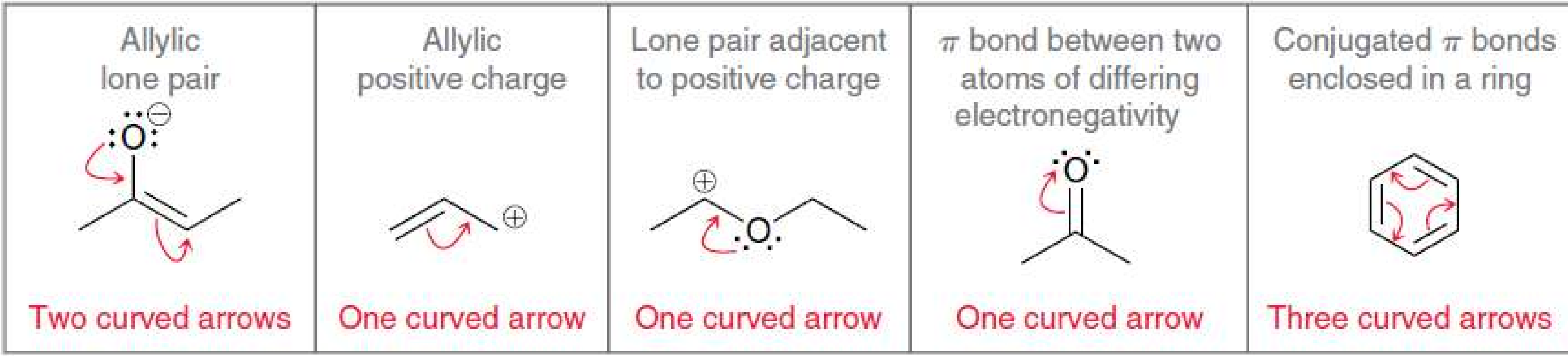
2.10 Patterns in Resonance

- Summary figure 2.5

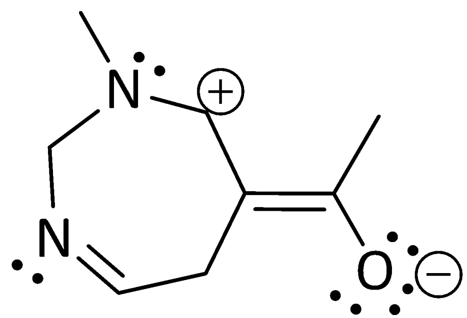


- Practice with conceptual checkpoint 2.32

2.10 Patterns in Resonance



- Show all of the resonance contributors for the following molecule



- Notice that carbons with 4 bonds (sp^3) isolate areas of resonance from one another

Study Guide for sections 2.3-2.10

DAY 4, Terms to know:
<u>Sections 2.3-2.10</u> functional groups, Fischer projection, Haworth projection, resonance
DAY 4, Specific outcomes and skills that may be tested on exam 1:
<u>Sections 2.3-2.10</u>

- Be able to identify functional groups in bond-line structures and Lewis structures.
- Given an atom with bonds and lone pairs shown, be able to determine its formal charge.
- Given an atom with bonds and formal charge shown, be able to determine how many lone pairs it has.
- Be able to use solid and dashed wedges to represent the three dimensionality of molecules.
- Be able to use Haworth projections to show the three dimensionality of molecules.
- Be able to recognize that resonance requires the overlapping of consecutive unhybridized p-orbitals on adjacent atoms and that molecular orbitals are created extending across all of the atoms involved in the resonance allowing the electrons to be anywhere in the MO.
- Be able to explain where and why formal charge is spread out in a structure that involves resonance.
- Be able to draw bond-line representations for resonance contributors and a resonance hybrid.
- Be able to explain how resonance makes molecules more stable with respect to the location of the electrons being delocalized and also with respect to the formal charge if there is formal charge.
- Be able to explain the rules for drawing curved arrows showing electron movement, and be able to use such arrows to show electron movement between resonance contributors.
- Be able to describe the 5 main bonding patterns in which resonance exists and use curved arrows to show all reasonable contributors for such structures as well as a resonance hybrid.
- Be able to accurately describe the type of motion that electrons undergo when resonance occurs.

Prep for day 5

Must Watch videos:

https://www.youtube.com/watch?v=zm1-gUxKr3g (drawing a resonance hybrid)
https://www.youtube.com/watch?v=-t-UkKdvBk0 (major versus minor resonance contributors)
https://www.youtube.com/watch?v=kQCS1AhAnMI (localized versus delocalized)
https://www.youtube.com/watch?v=jIL333CKE9A (curved arrows in acid base reactions)
https://www.youtube.com/watch?v=vfHnnASd3RM (using pK_a to quantify strength)

Other helpful videos:

https://www.youtube.com/watch?v=qpP8D7yQV50 (common mistakes drawing resonance structures)
https://www.youtube.com/watch?v=m8mmMiNGILo (acid base basics)
https://www.youtube.com/watch?v=0JEyMYTKqCY (acid base practice)
http://ps.uci.edu/content/chem-51a-organic-chemistry (UC-Irvine lecture 5)

Read sections 2.11-2.12, 3.1-3.3