Inter-Lecture A

Introduction to Resonance

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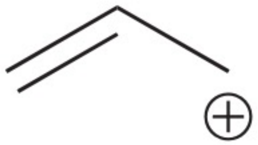
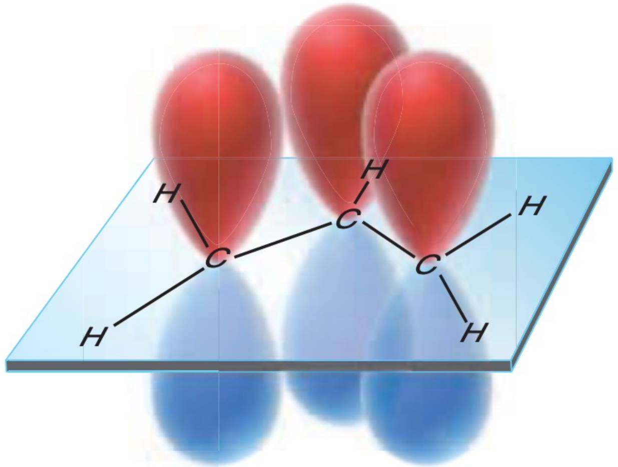
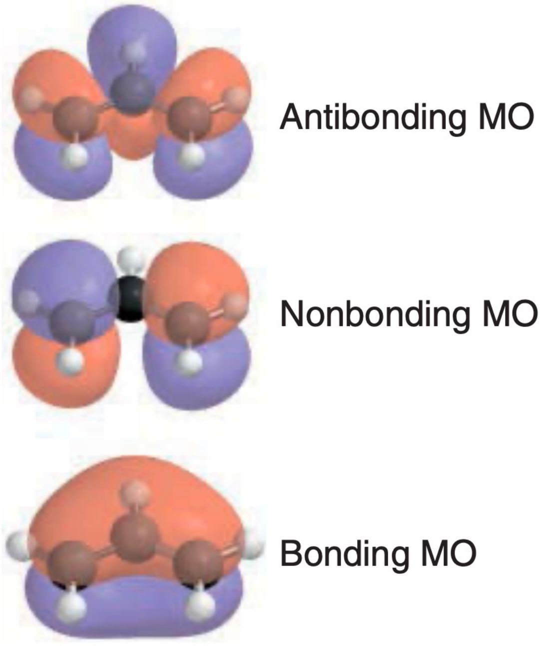
2022/2/12

- The birth of *Resonance*



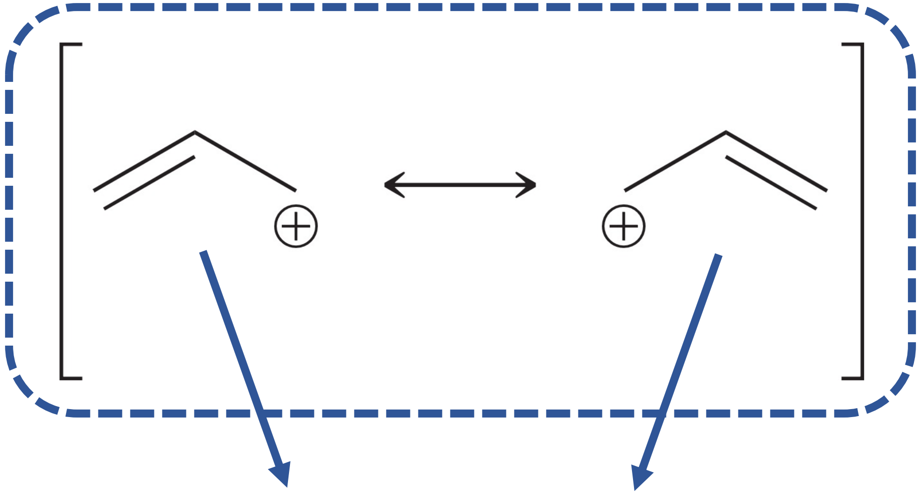
allyl carbocation





it is inadequate to represent this species just using one structure!

- Resonance



resonance hybrid

“one entity”

resonance structures

A resonance hybrid is not flipping back and forth between the different resonance structures!

- Imagine a nectarine if you have never seen it…

Picture a *peach* in your mind, and now picture a *plum* in your mind. Well, a *nectarine* has features of both fruits: the inside tastes like a peach, the outside is smooth like a plum, and the color is somewhere in between the color of a peach and the color of a plum. So take your image of a peach together with your image of a plum and *meld them together* in your mind into one image. That's a nectarine.

The nectarine does not vibrate back and forth
every second between being a peach and being a plum!

…similarly, with resonance structures, no single drawing adequately
describes the nature of the electron density spread out over the molecule!

Curved Arrows

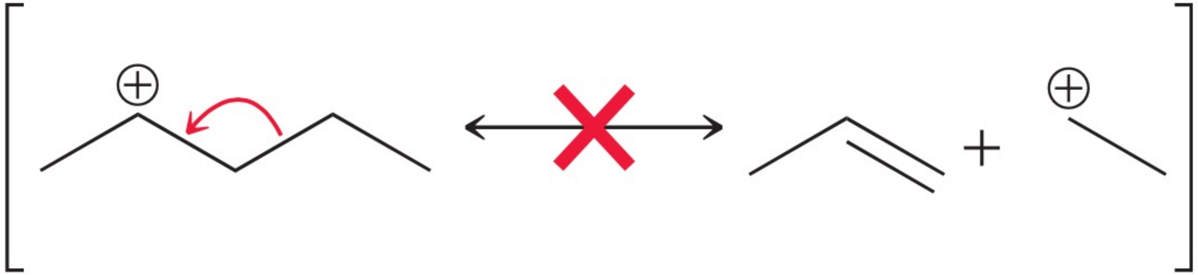
- Use curved arrows to represent resonance structures

a single arrow indicates the transfer of **a pair** of electrons

Rules

1. *Avoid breaking a single bond.*
2. *Never exceed an octet for second-row elements.*

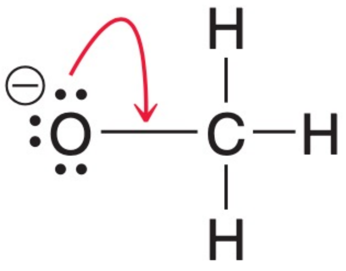
- Avoid breaking a single bond when drawing resonance structures



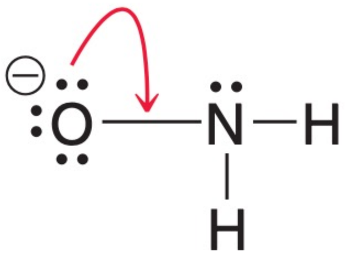
Don't break a single bond

Curved Arrows

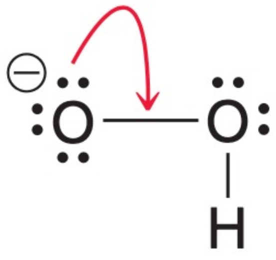
- Never exceed an octet for second-row elements



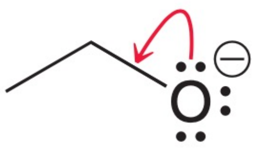
Bad arrow



Bad arrow

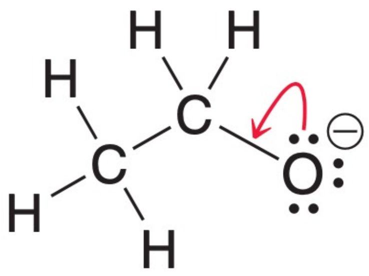


Bad arrow



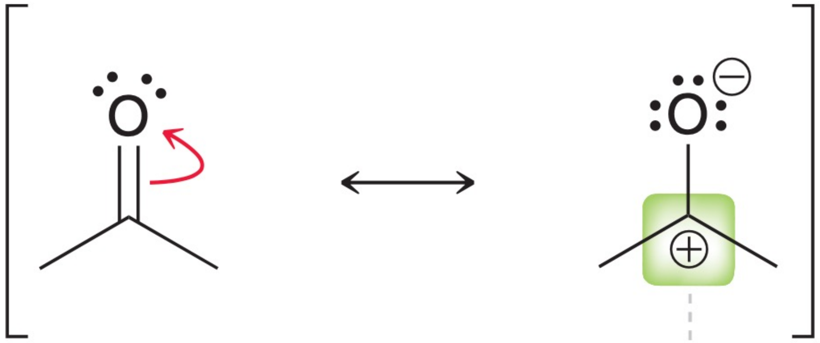
Bad arrow

is the same as



Bad arrow

- Never exceed an octet for second-row elements

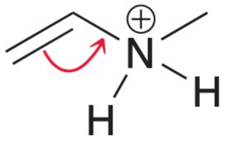


This carbon atom does not have an octet

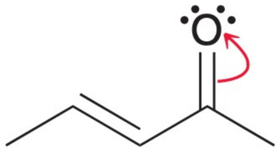
Curved Arrows

- Practice: in each of the following cases, determine whether the curved arrow violates either of the two rules and describe the violation, if any. (Don’t forget to count all hydrogen atoms and all lone pairs.)

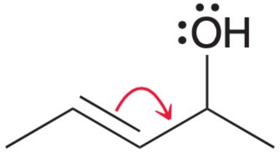
(a)



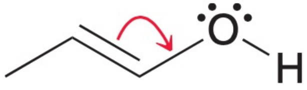
(b)



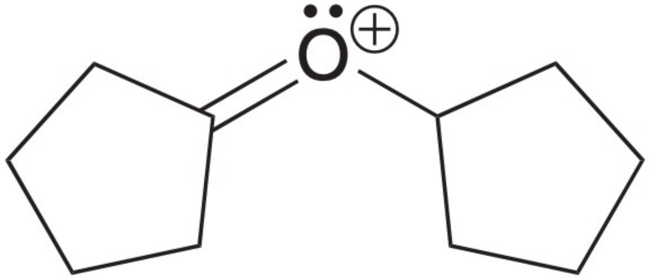
(c)



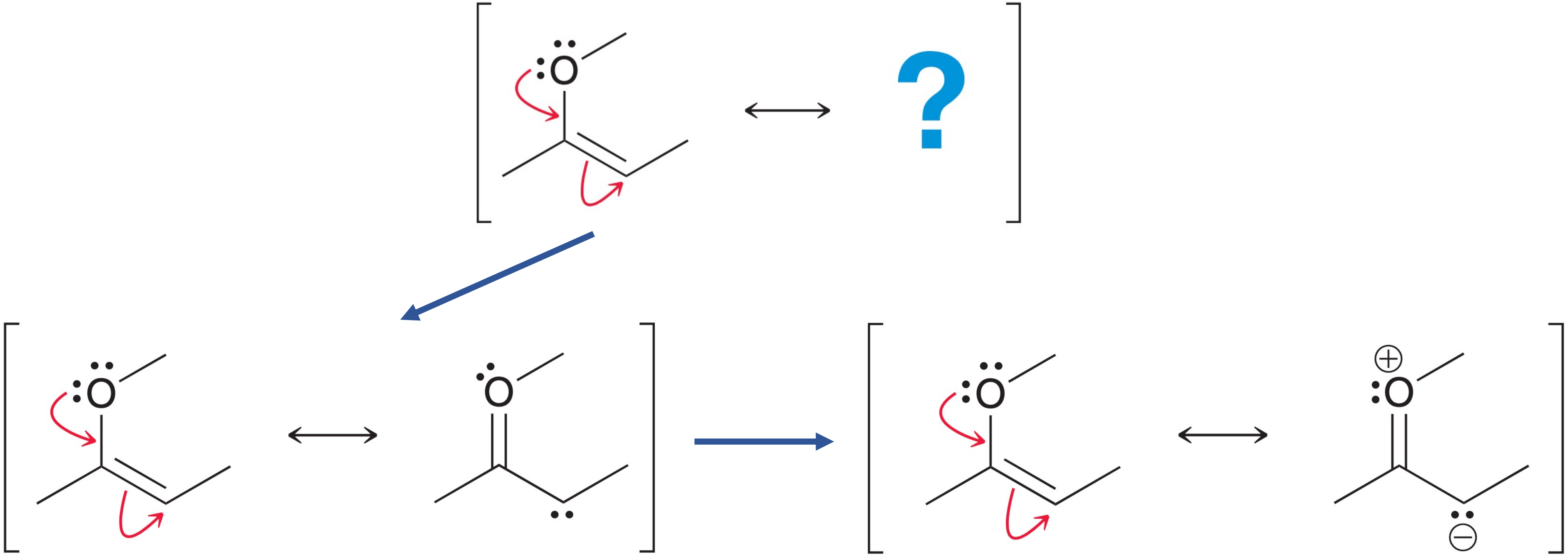
(d)



- Practice: drawing the resonance structure of the following compound requires one curved arrow.



- Formal Charges in Resonance Structures

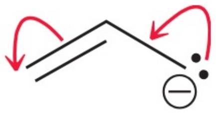


Formal Charges in Resonance Structures

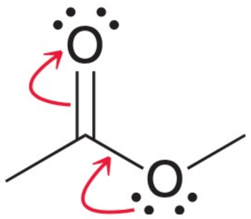
- Practice: for each of the structures below, draw the resonance structure that is indicated by the curved arrows. Be sure to include formal charges.

(a)

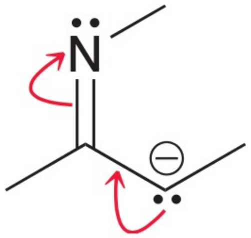
(b)



(c)



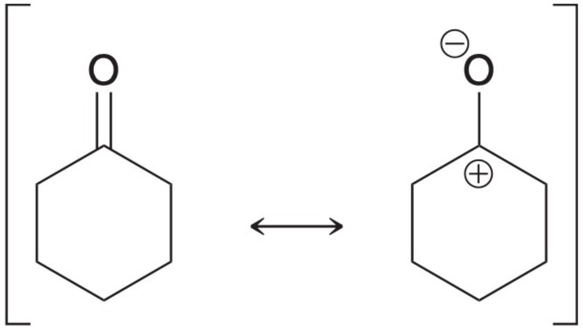
(d)



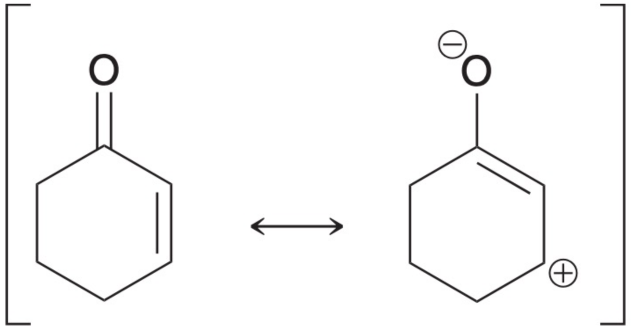
Formal Charges in Resonance Structures

- Practice: in each case below, draw the curved arrow(s) required in order to convert the first resonance structure into the second resonance structure. In each case, begin by drawing all lone pairs and then use the formal charges to guide you.

(a)



(b)



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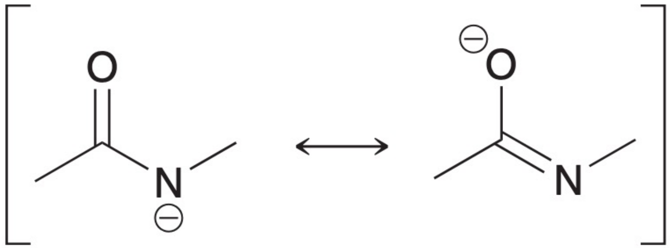

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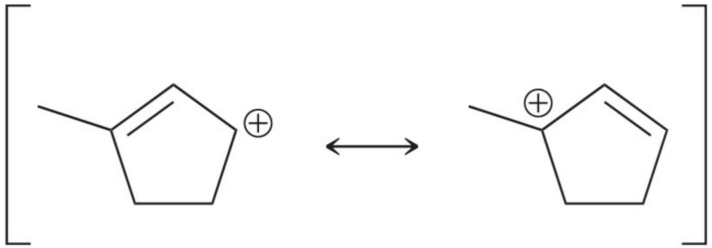
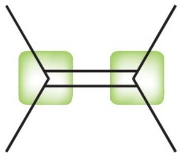
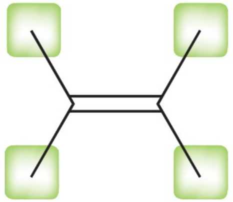


- Pattern recognition
  - Allylic lone pair
  - Allylic carbocation
  - Lone pair adjacent to C^+
  - π bond between two atoms of differing electronegativity
  - Conjugated π bonds enclosed in a ring

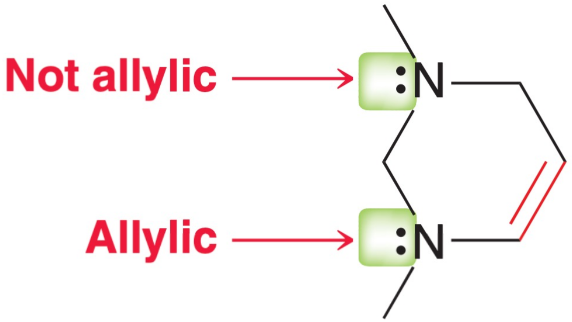
- Allylic lone pair

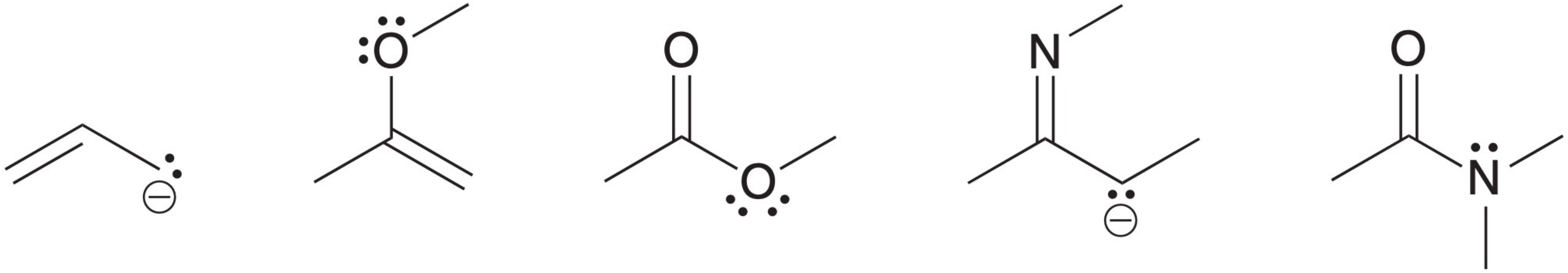


Vinylic positions

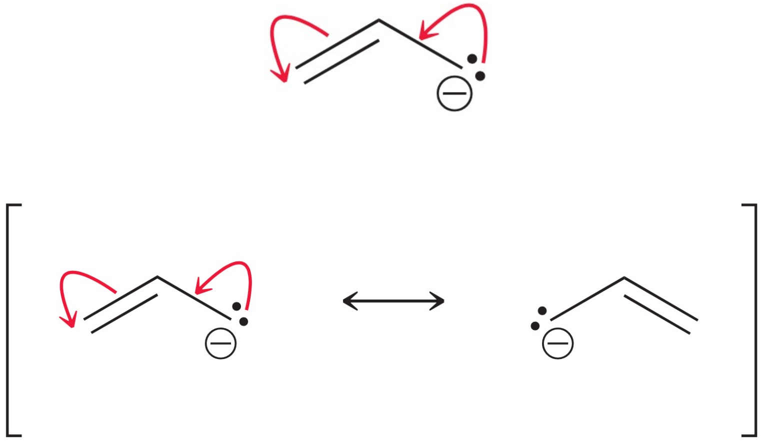


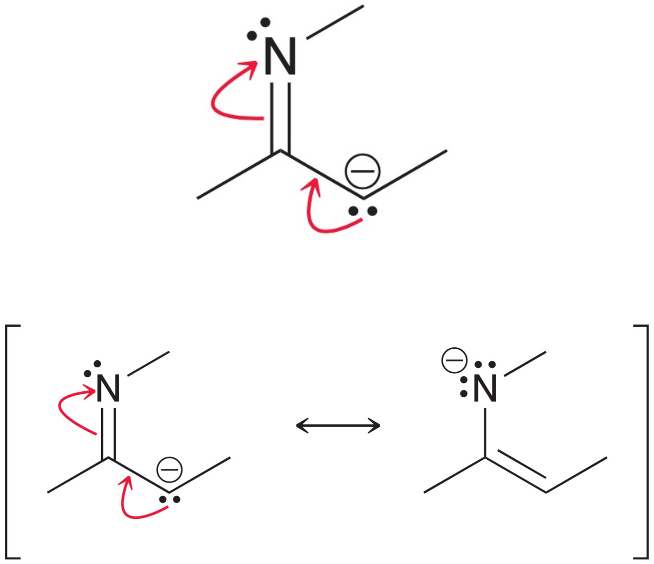
Allylic positions





- Allylic lone pair

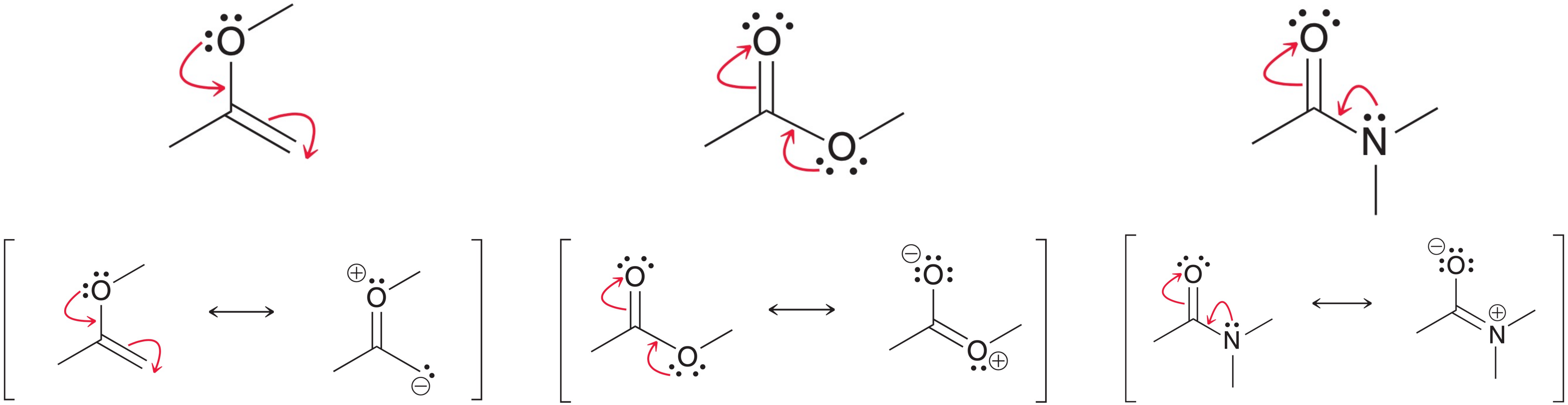




negative charge on lone pair-containing atom:

charge is transferred to the atom which receives the lone pair

- Allylic lone pair



neutral lone pair-containing atom:

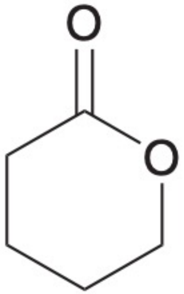
a positive charge is generated on this atom, and a negative charge

is generated on the atom which receives the lone pair

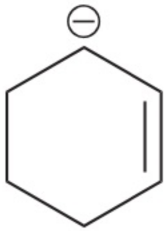
Drawing Resonance Structures

- Practice: for each of the compounds below, locate the pattern we just learned (lone pair next to a π bond) and draw the appropriate resonance structure:

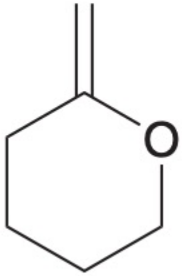
(a)



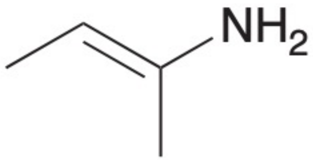
(b)



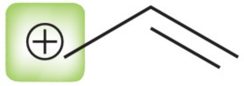
(c)



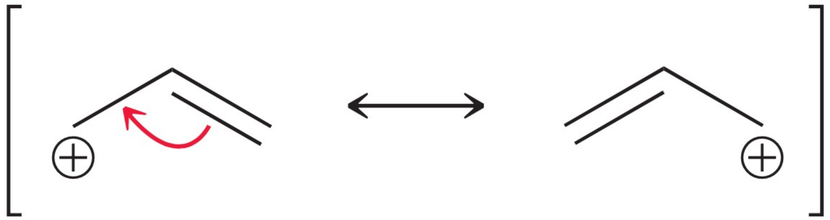
(d)



- Allylic carbocation



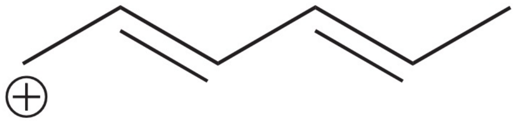
Allylic carbocation

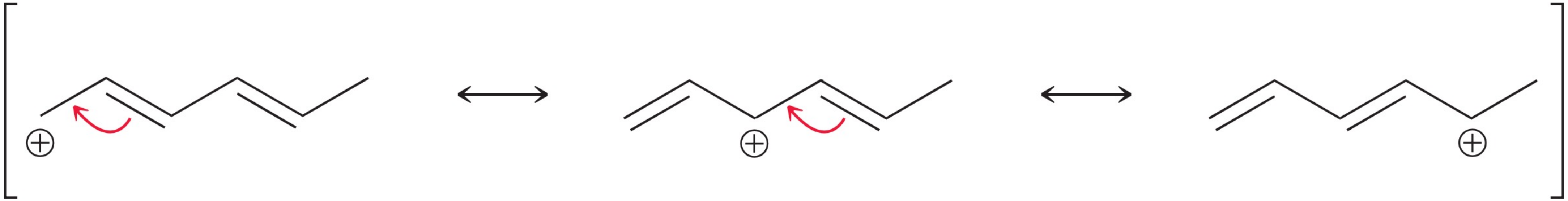


arrow start from the original π bond, pointing to the position of new π bond

Drawing Resonance Structures

- Allylic carbocation
  - Conjugate π system



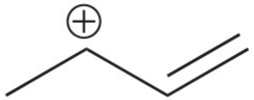


Attention! Never place the tail of a curved arrow on a positive charge!

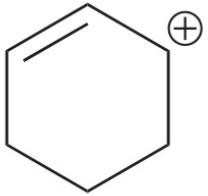
Drawing Resonance Structures

- Practice: draw the resonance structure(s) for each of the compounds below:

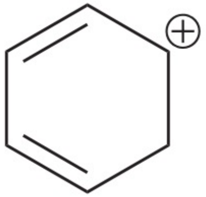
(a)



(b)



(c)



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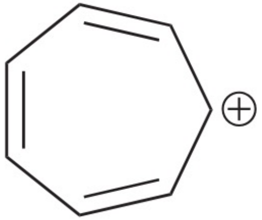
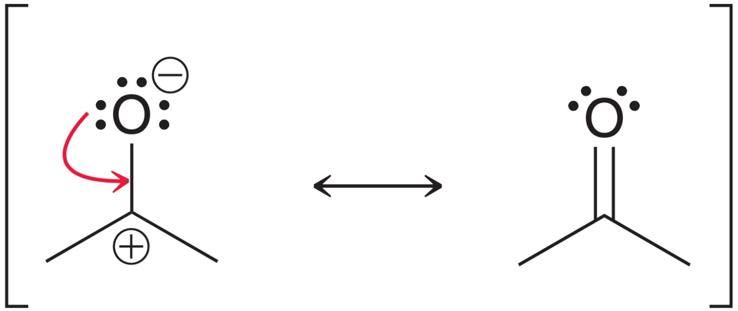
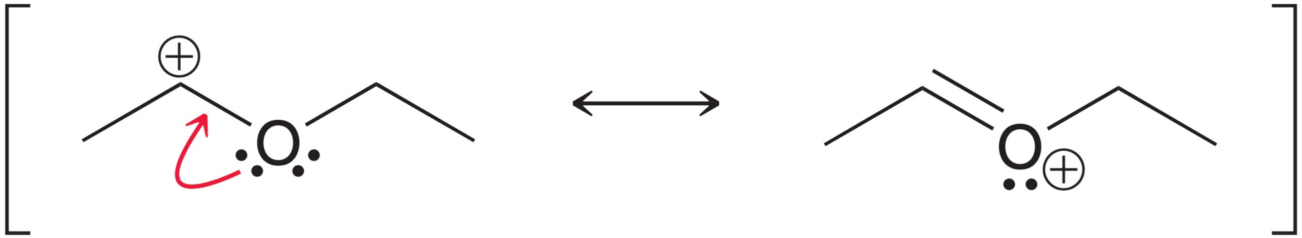


- Lone pair adjacent to C^+



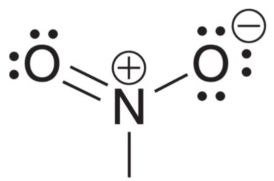
charges can be neutralized

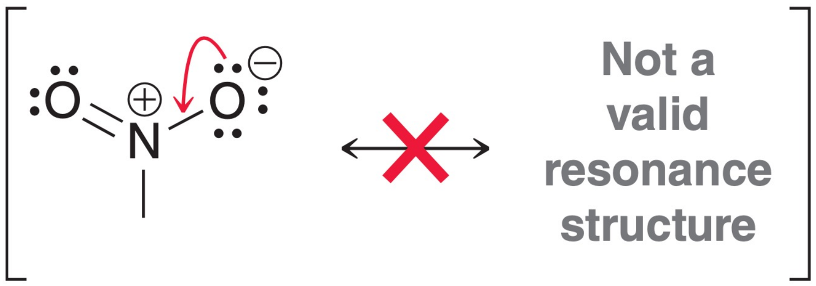


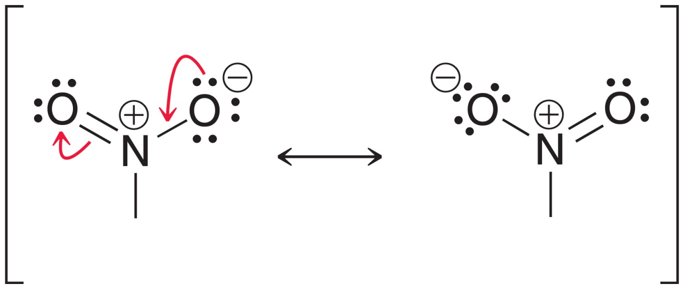
(no negative charge) cannot be neutralized

– conservation of charge

- Lone pair adjacent to C^+





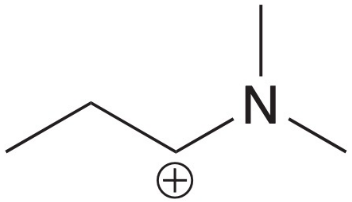


nitrogen is excess the octet

charge **CANNOT** be neutralized!

- Practice: for each of the compounds below, locate the lone pair adjacent to a positive charge and draw the resonance structure:

(a)



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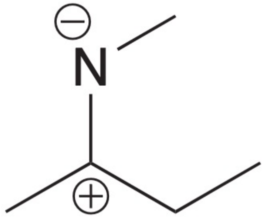

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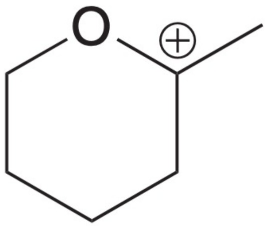
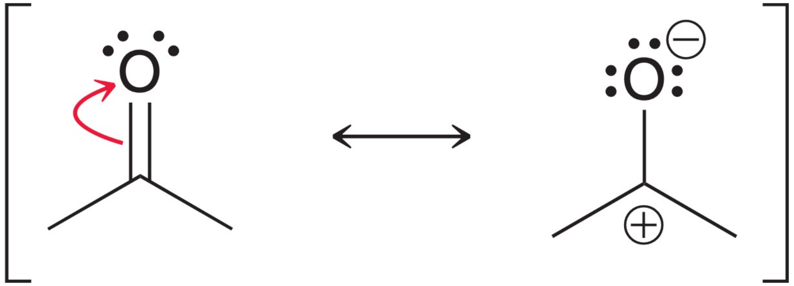


- π bond between two atoms of differing electronegativity



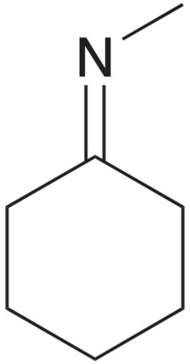
π electrons tend to transfer to the atom with relatively higher electronegativity

formal charges are generated

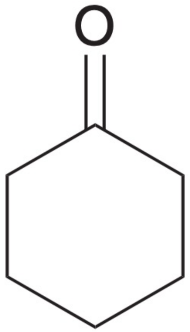
Drawing Resonance Structures

- Practice: draw a resonance structure for each of the compounds below.

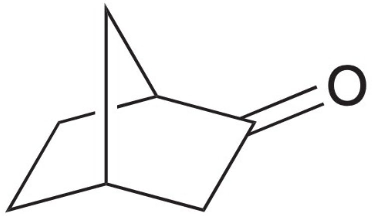
(a)



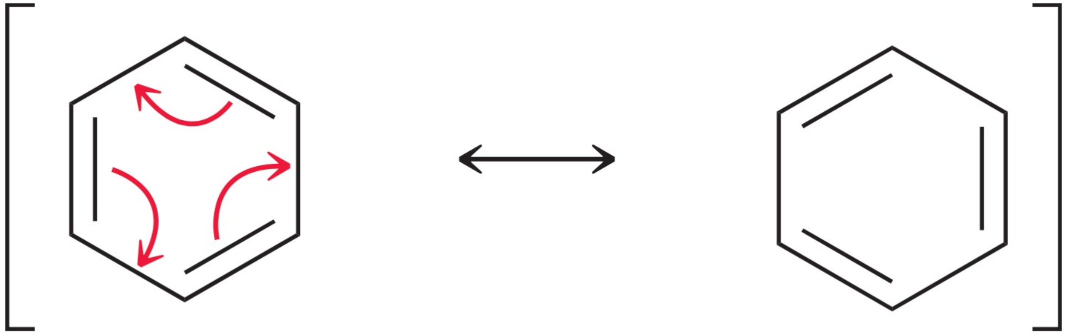
(b)



(c)



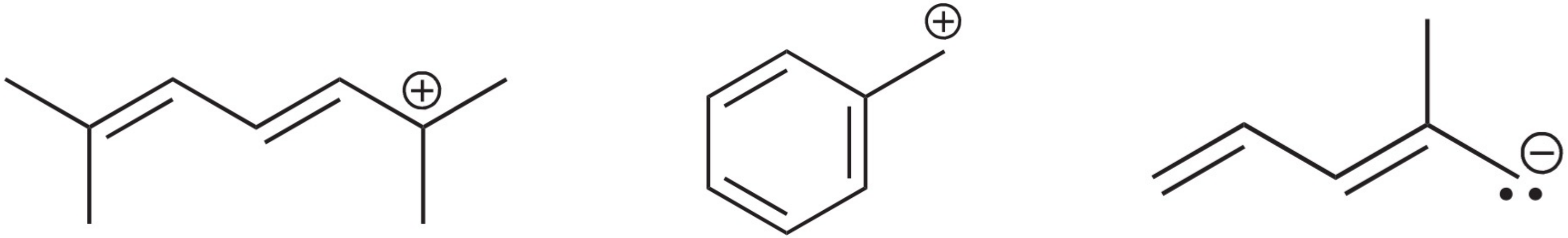
- Conjugated π bonds enclosed in a ring



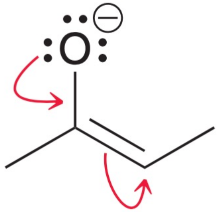
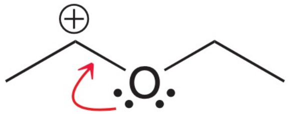
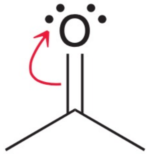
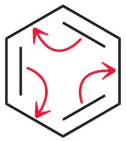
conjugated system: alternating single-double bond system

electrons are transferred clockwise or counterclockwise in the ring

- Practice: for each of the following compounds, draw the resonance structures.



- Summary of specific patterns

Allylic lone pair	Allylic carbocation	Lone pair adjacent to C+	π bond between two atoms of differing electronegativity	Conjugated π bonds enclosed in a ring
				
Two curved arrows	One curved arrow	One curved arrow	One curved arrow	Three curved arrows

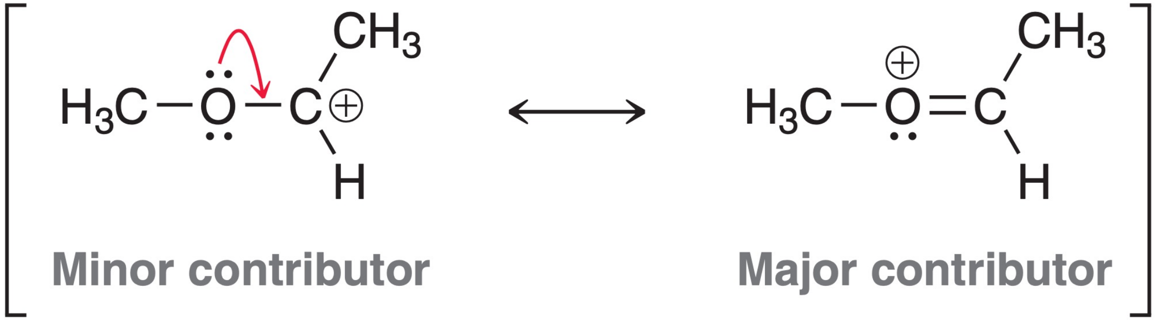
Relative Stabilities

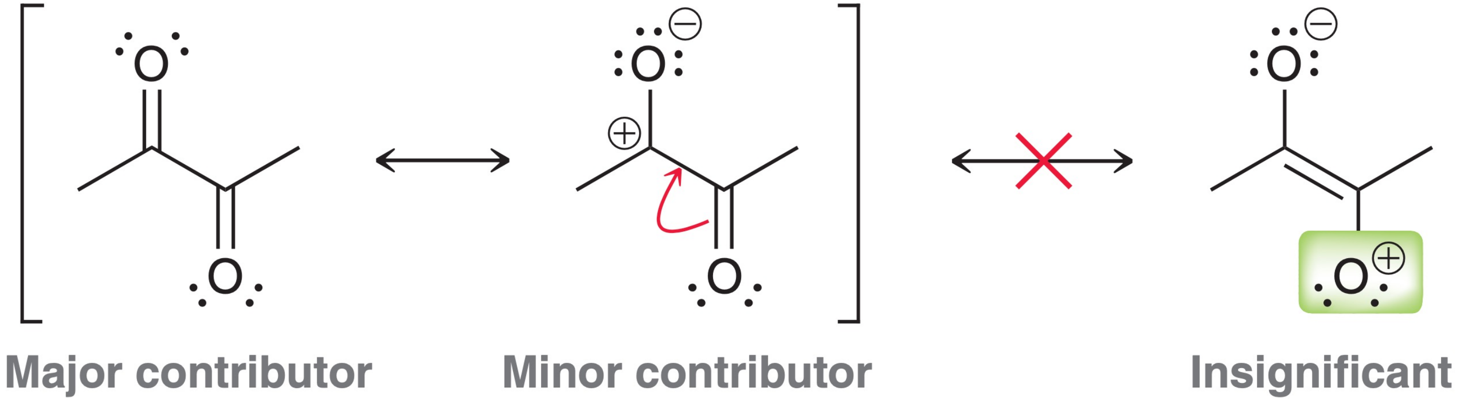
- Assessing relative stabilities of resonance structures
  - The most significant resonance forms have the greatest number of filled octets
  - The structure with fewer formal charges is more significant
  - A structure with a negative charge on the more electronegative element will be more significant
  - Resonance forms that have equally good Lewis structures are described as equivalent and contribute equally to the resonance hybrid

order

Relative Stabilities

- Greatest number of filled octet



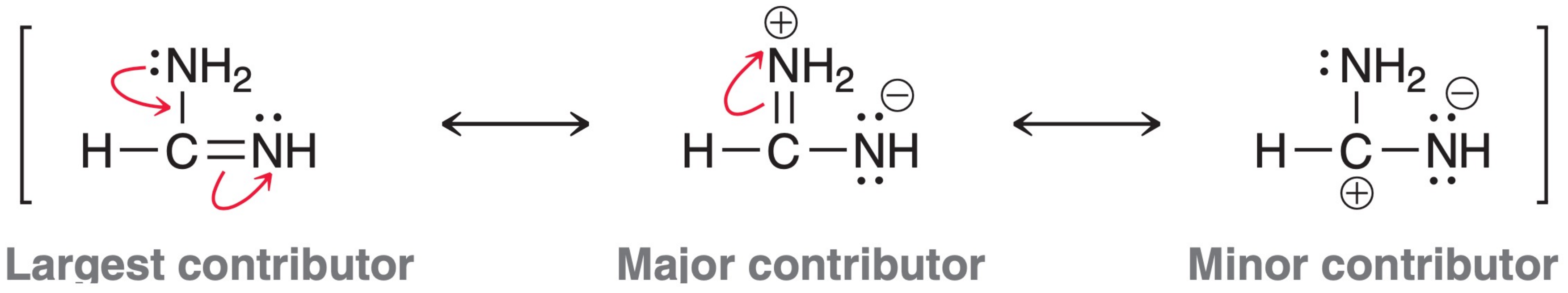


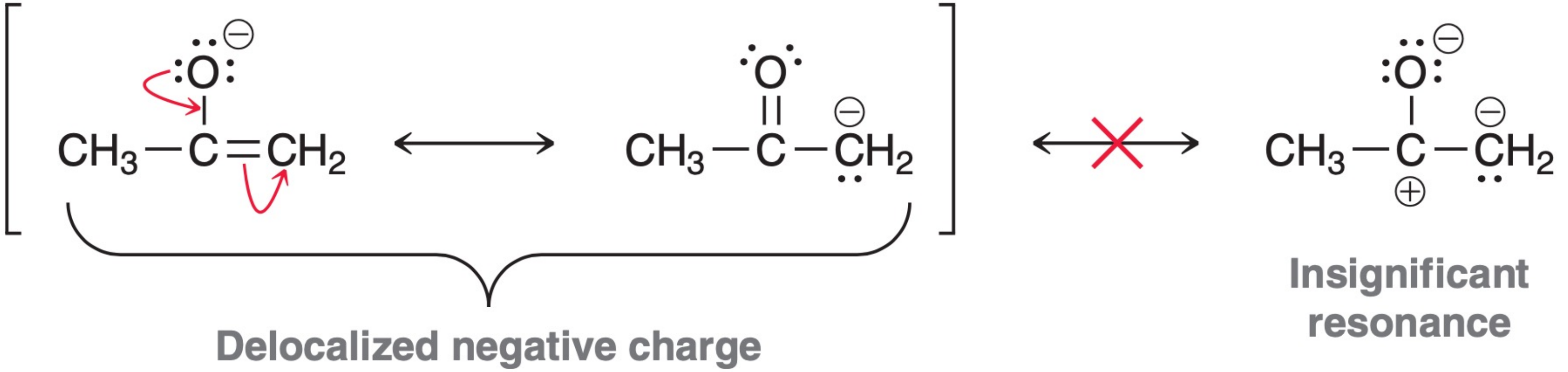
not filled octet

Relative Stabilities

- Fewer formal charges

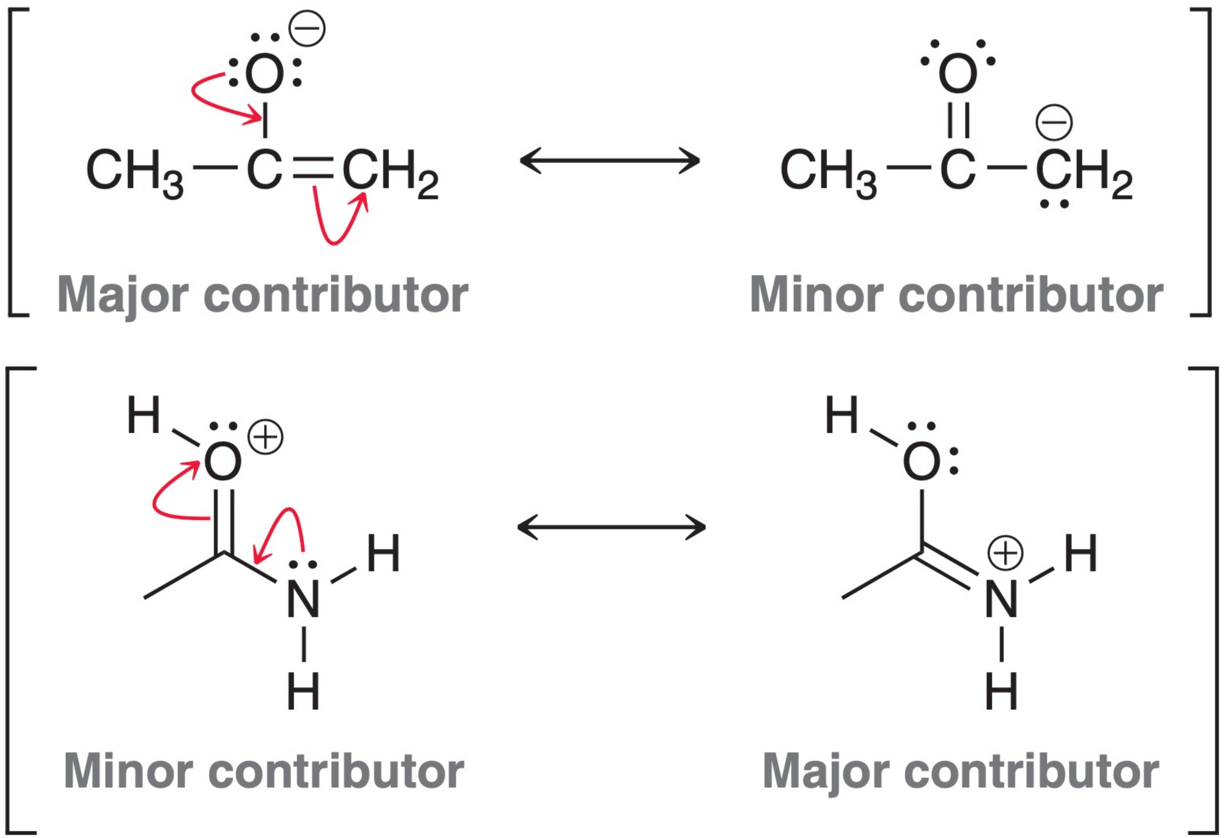
如某个<u>原子</u>携带有+2或-2的形式电荷
那么这个共振式将很不稳定
分子将极不易以这种形式存在





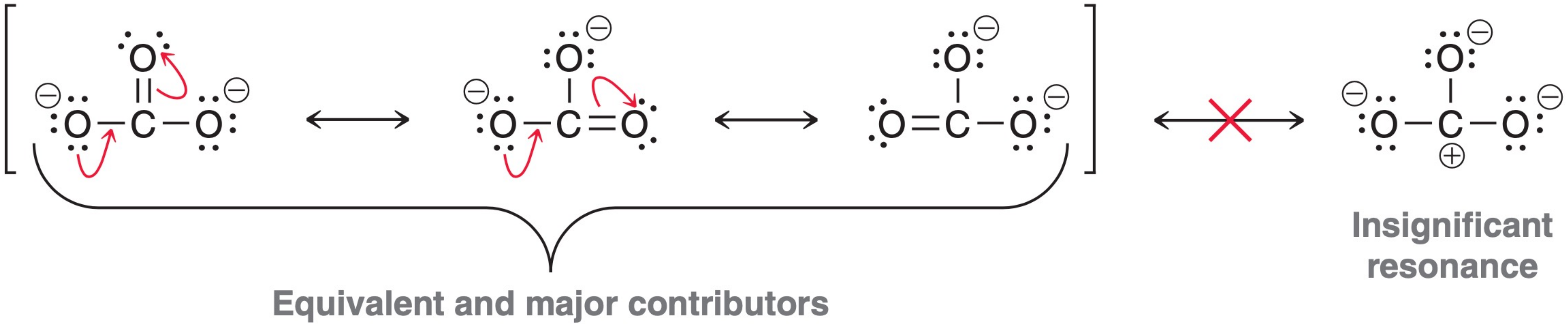
Relative Stabilities

- Negative charge on the more electronegative element

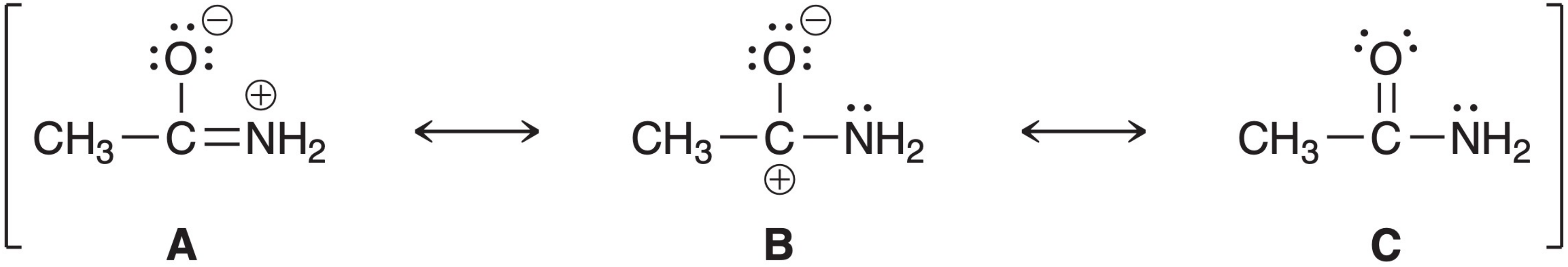


当然啦 正电荷在电负性相对较小的原子上
也会更稳定啦(´▽`)/

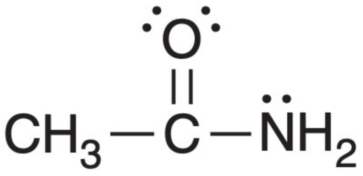
- Equally good Lewis structures – contribute equally



- Practice: rank the following resonance forms, from most significant to least significant, and briefly explain the rankings.



Relative Stabilities



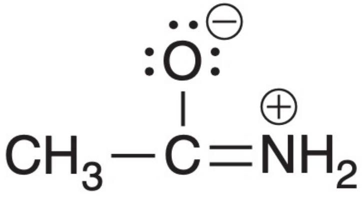
$$CH_3-\overset{\overset{\displaystyle :\ddot{O}:}{\|}}{C}-\ddot{N}H_2$$

Largest contributor (#1)

filled octet

no formal charges

>

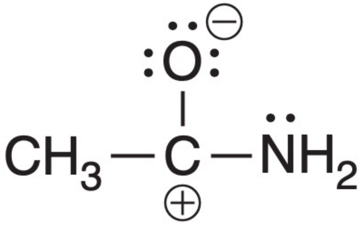


$$CH_3-\overset{\overset{\displaystyle :\ddot{O}:^{\ominus}}{|}}{C}=\overset{\oplus}{N}H_2$$

Major contributor (#2)

filled octet

>



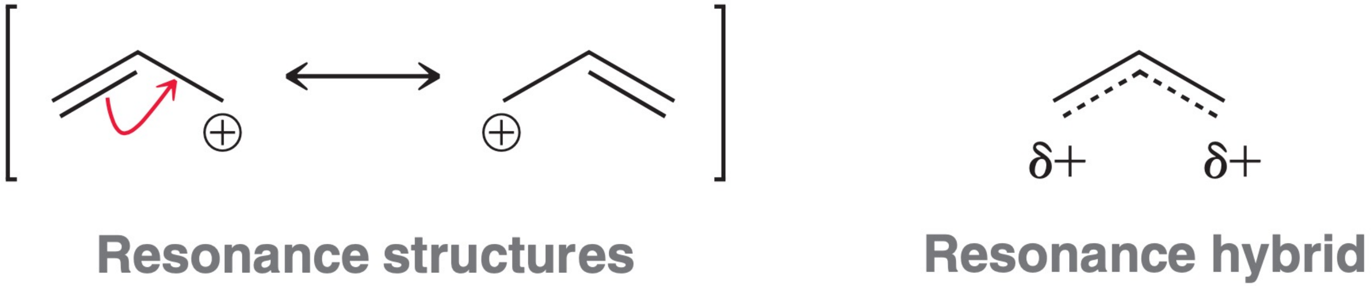
$$CH_3-\underset{\oplus}{\overset{\overset{\displaystyle :\ddot{O}:^{\ominus}}{|}}{C}}-\ddot{N}H_2$$

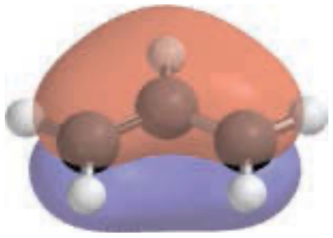
Minor contributor (#3)

carbocation – not filled octet

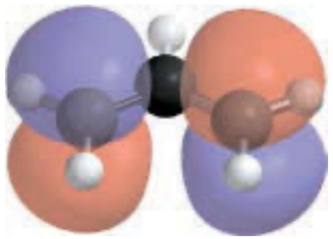
The Resonance Hybrid

- Rresonance hybrid





bonding π orbital



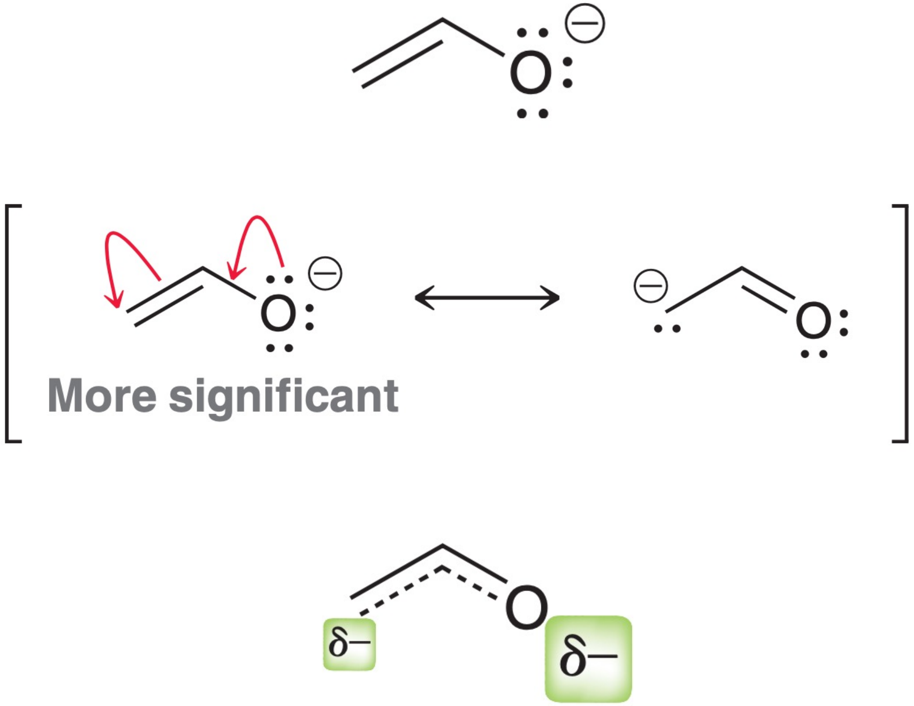
nonbonding π orbital

in electron deficiency

(positively charged)

The Resonance Hybrid

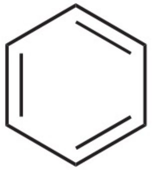
- Drawing a resonance hybrid



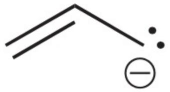
The Resonance Hybrid

- Practice: draw a resonance hybrid for each of the following.

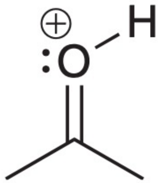
(a)



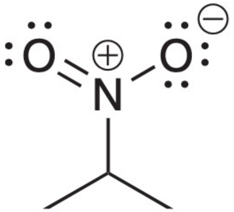
(b)



(c)

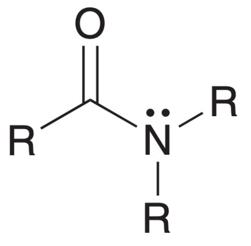


(d)

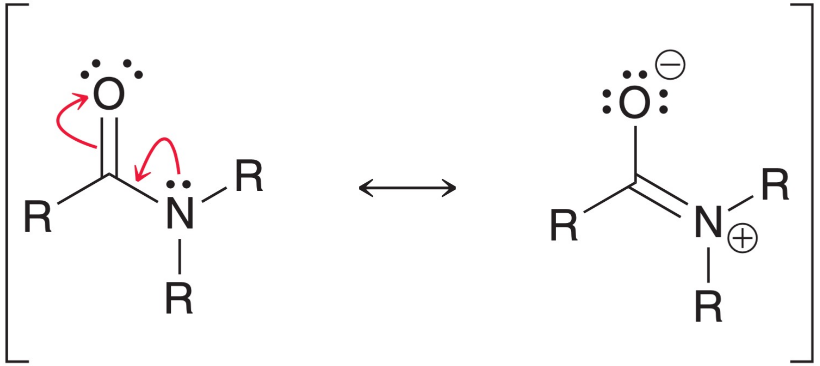


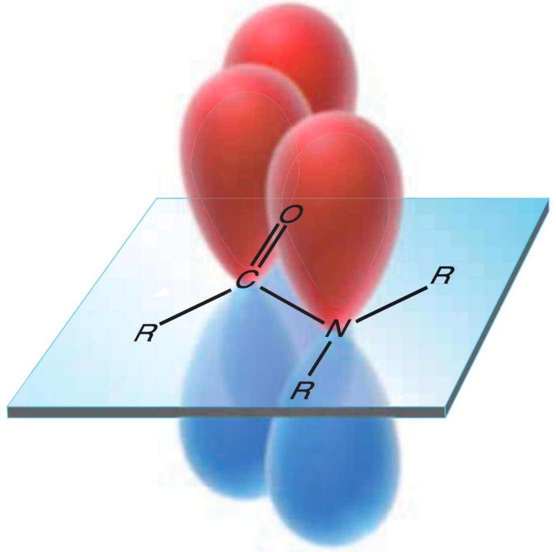
Delocalized & Localized Lone Pairs

- Delocalized lone pairs



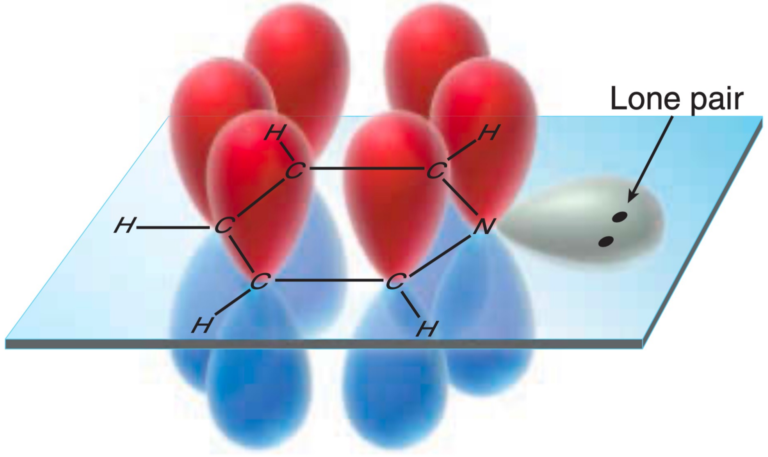
An amide





delocalized lone pairs
must located on *p* orbitals

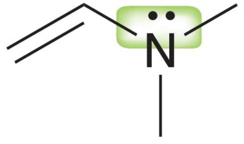
Delocalized & Localized Lone Pairs



- Localized lone pairs

not allylic lone pairs
must be localized

Localized

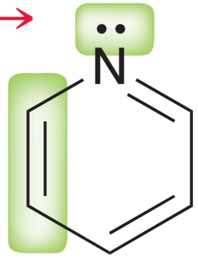


Delocalized

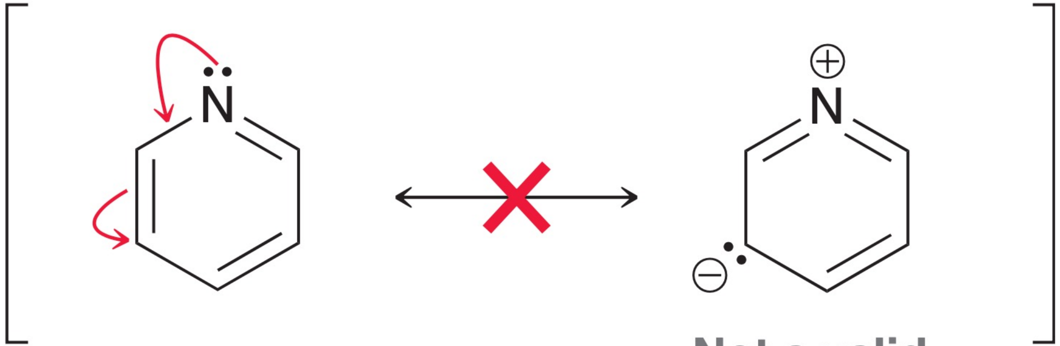
lone pairs on sp^2 orbitals
cannot delocalize

Lone pair ⟶

π bond ⟶



Pyridine



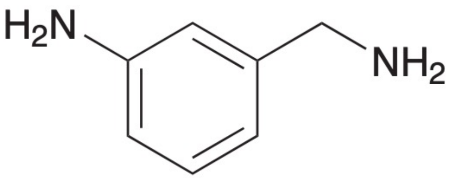
**Not a valid
resonance structure**

- Rules
  - When an atom has both π bonds and lone pair electrons, they will **not all participate** in resonance
  - **Lone pair electrons occupy** sp^2 or *sp* **hybrid orbitals** (parallel to the plane of atoms on the π bond)
  - The ***p* orbital** of an atom is used to **form a π bond**, and the **electrons on the *p* orbital participate in the resonance**

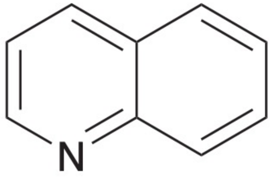
Delocalized & Localized Lone Pairs

- Practice: for each compound below, identify all lone pairs and indicate whether each lone pair is localized or delocalized. Then, use that information to predict the geometry for each atom that exhibits a lone pair.

(a)



(b)



(c)