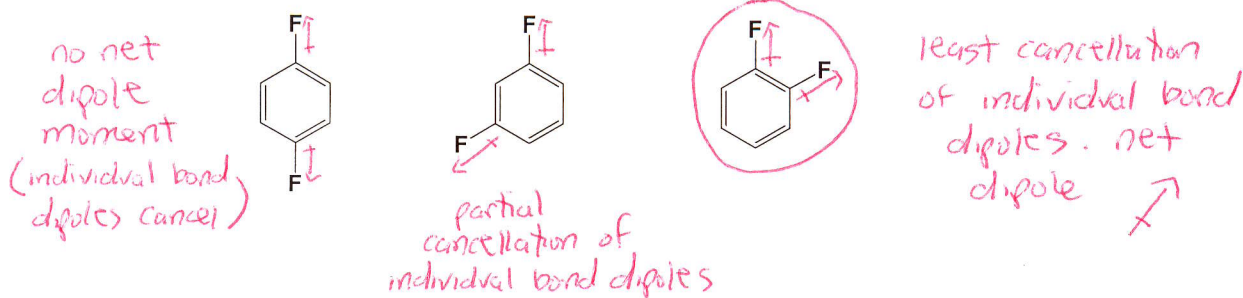
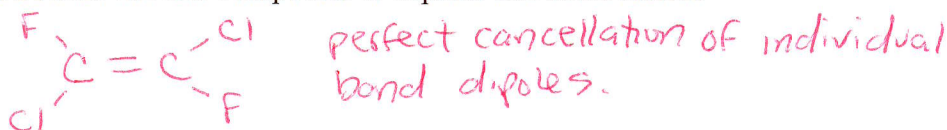


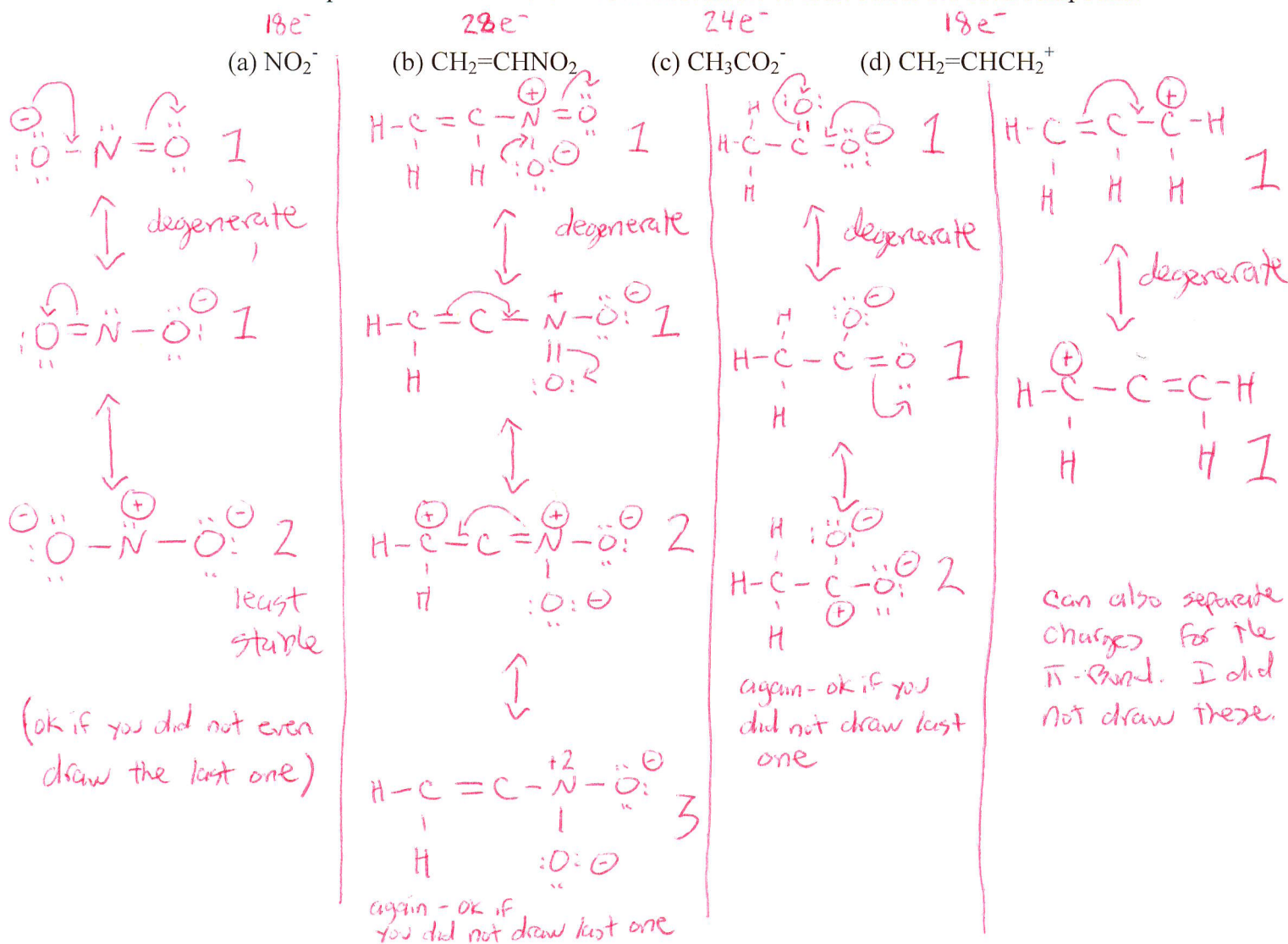
1. Which of the following molecules is the most polar?



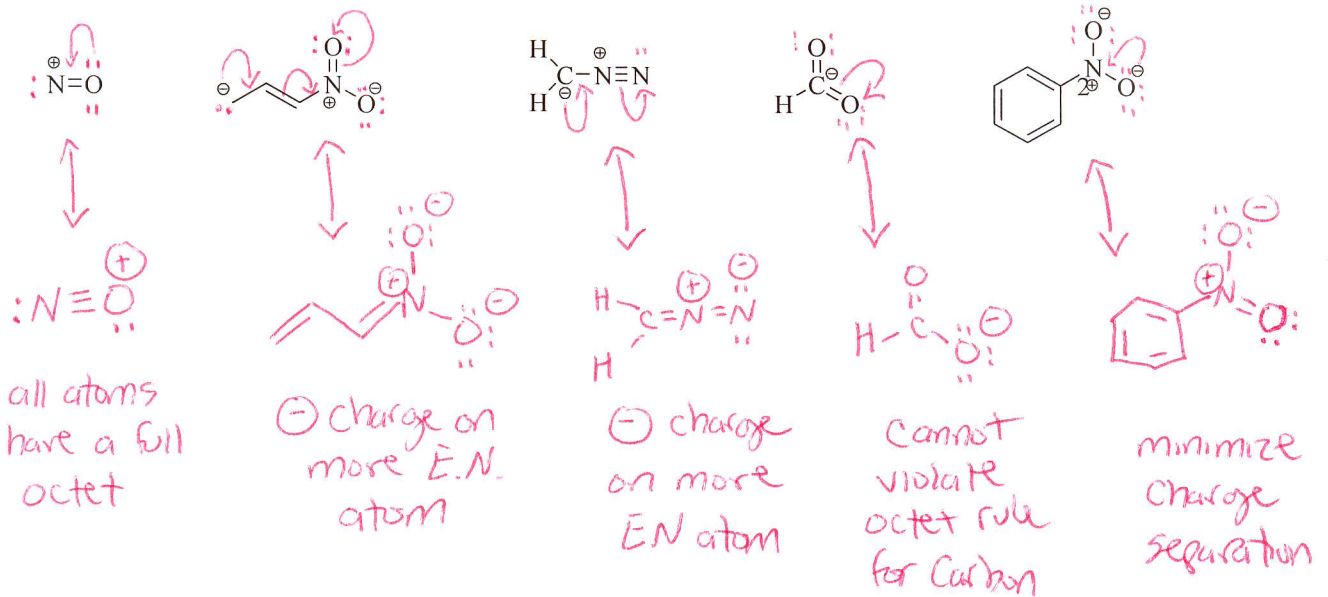
2. Trans-dichlorodifluoroethylene, $C_2Cl_2F_2$, has a number of polar bonds but no net dipole moment. Draw skeletal structure for this compound to explain this observation.



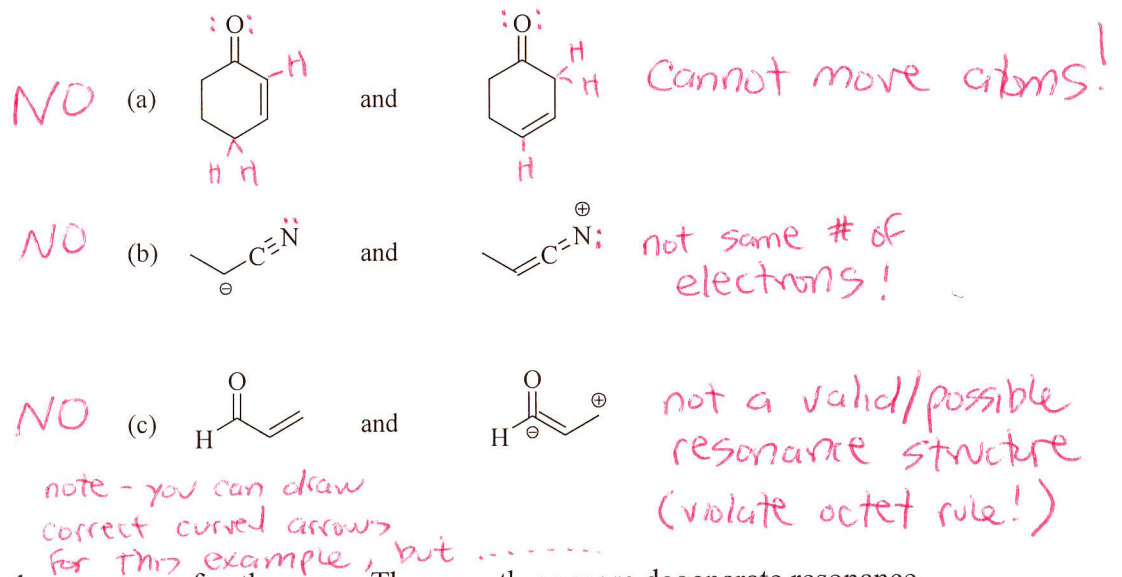
3. Draw the Kekule structures and all the possible resonance structures for the following compounds. Be sure to use curved arrows to show how these resonance structures are interconvertible for each individual compound. Indicate whether or not any of these resonance structures are equivalent and rank them from most stable to least stable for each compound.



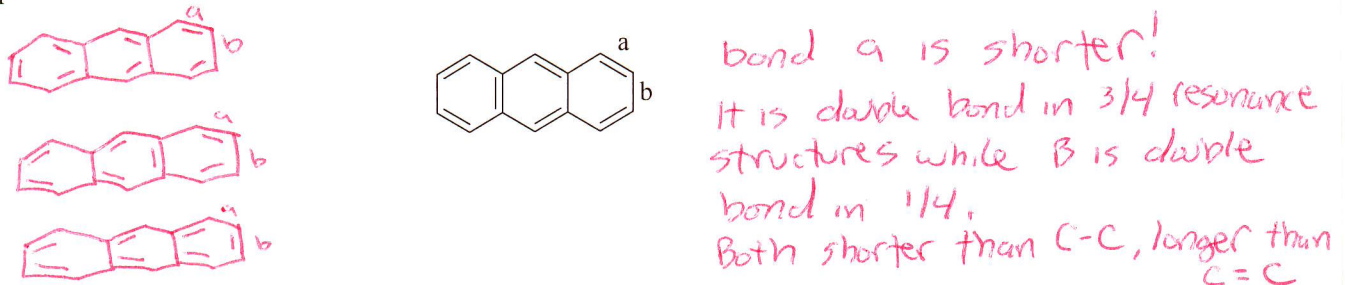
4. For each of the molecules shown below, a more stable resonance structure is possible. Draw in all lone pairs of electrons then, using curved arrows to show electron movement, draw the more stable resonance structure and state why this is more stable.



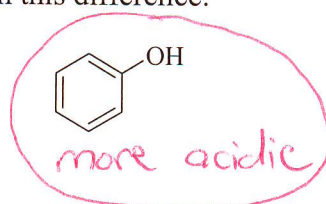
5. For each pair of compounds given below, state why they are not resonance forms of each other.



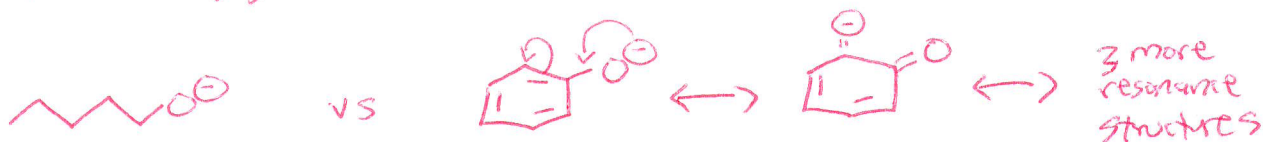
6. Shown below is the structure of anthracene. There are three more degenerate resonance structures that can be drawn for this compound. Draw them. Using your resonance forms, which bond do you predict to be shorter, bond a or bond b? Are either bond a or b shorter than a typical carbon-carbon double bond? Than a carbon-carbon single bond?



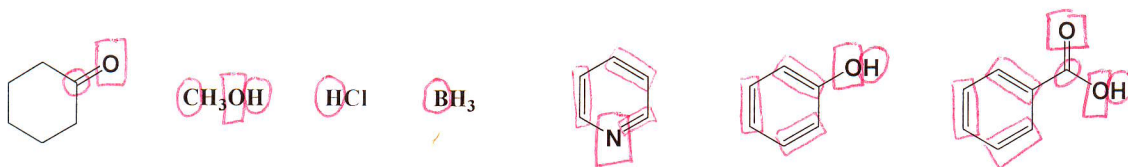
7. For the two molecules below, one is approximately 6 orders of magnitude more acidic than the other. Which compound is more acidic? Explain this difference.



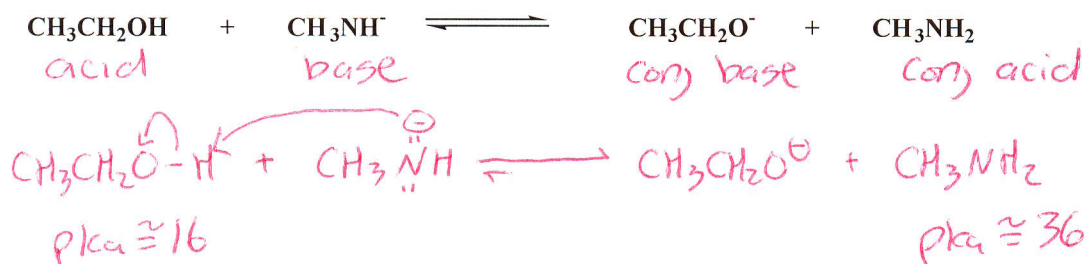
Consider conjugate bases:



8. Circle the Lewis acids and put a box around all Lewis bases in the group of molecules below:

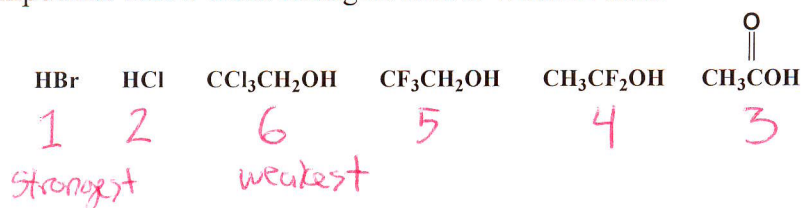


9. For the following reaction, label reactants and products as acids/bases and conjugate acid/bases. Determine which direction the equilibrium will be favored and provide curved arrows to show the flow of the electrons in the direction favored. What is the approximate K_{eq} for this reaction? (note, you should redraw the reaction showing bonds and lone pairs)

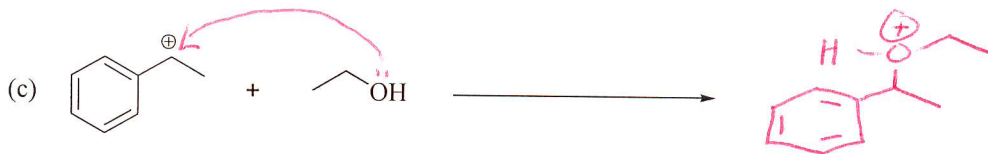
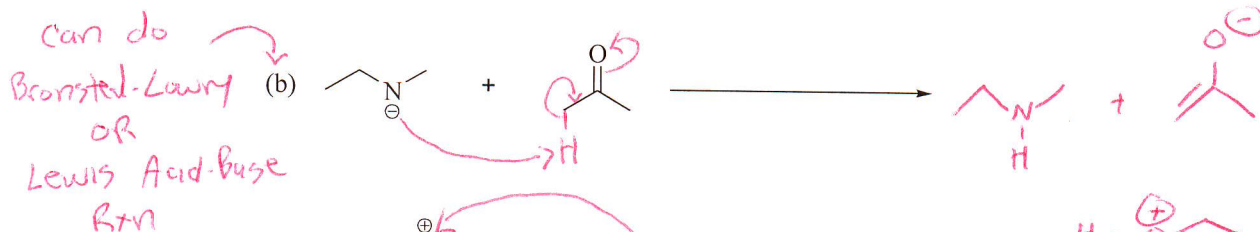
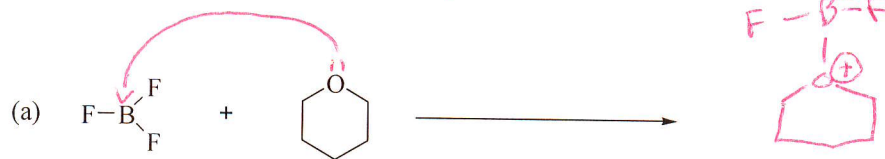


Favored
 $K \approx 10^{20}$

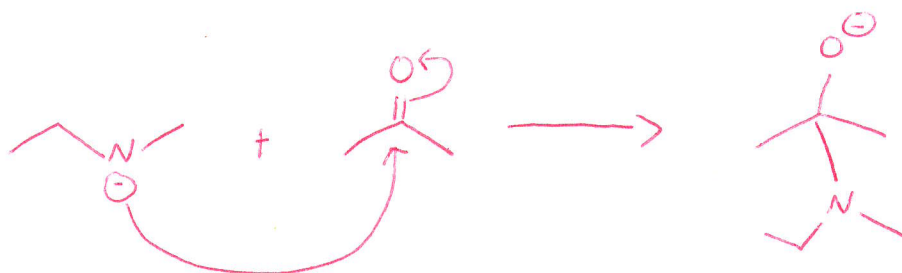
10. Rank the compounds below from strongest acid to weakest acid.



11. Predict the products from the following acid base reactions and provide curved arrows to show the movement of electrons going from reactants to products.

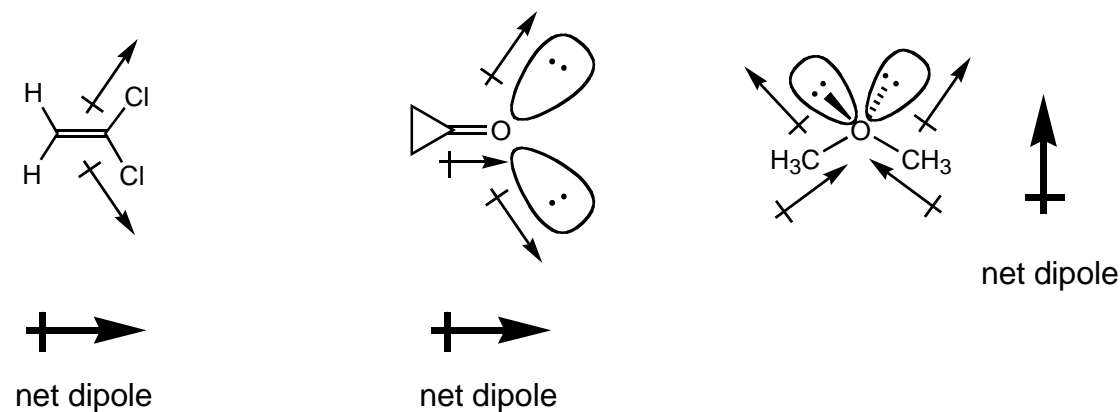


For (b), can also do the following:

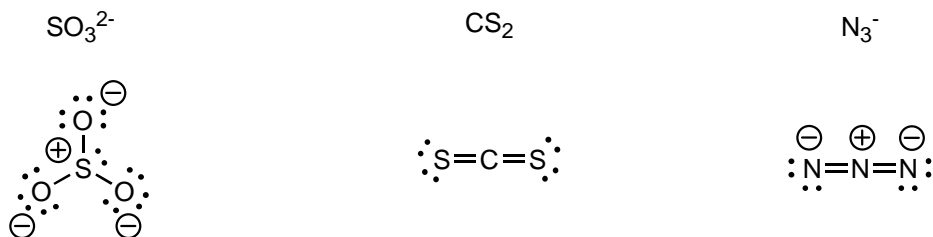


this would be classified as a Lewis Acid-Base reaction

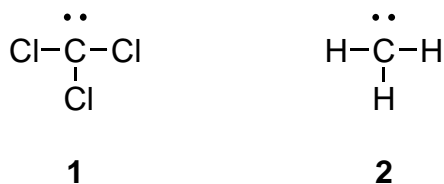
12. For the following structures, draw in all pertinent bond dipoles and show the net dipole for the molecule. Be sure to ignore C-H dipoles and consider the nonbonding electrons where appropriate.



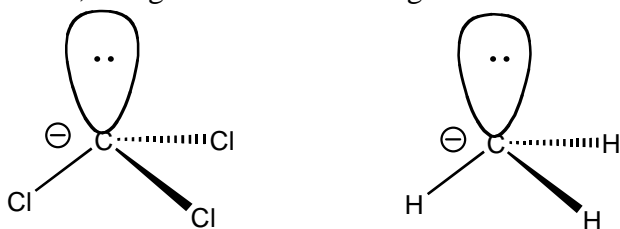
13. For the following molecules, draw a valid Lewis structure, and indicate the formal charge on each atom. Use the templates provided for the arrangement of the atoms.



14. Consider the molecules 1 and 2 below:

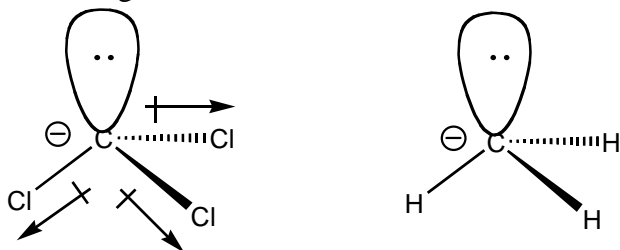


a. Draw a three-dimensional picture of 1 and 2 using wedges and dashes. Show any nonbonding electrons residing in an orbital, and give the formal charge on carbon.



b. Given what you know about the effects of electronegative atoms, which compound is more stable? Briefly explain why.

The first compound is more stable -- anion is more stable on a carbon that is electron poor due to the effects of the highly electronegative Cl atoms attached.

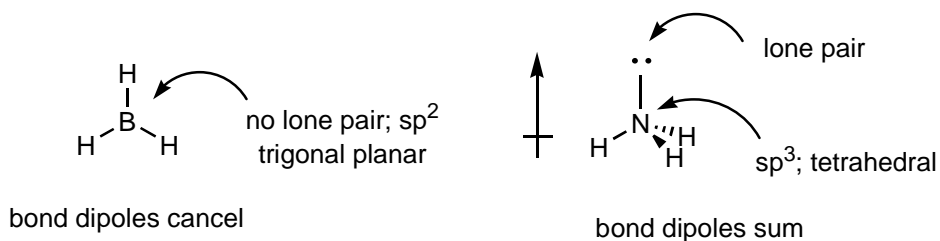


15. BH_3 and NH_3 have similar formulas and might be expected to have similar properties. However, BH_3 has no observed dipole moment but NH_3 has an observed dipole moment of 1.47 D.

a. Use your knowledge of structure and bonding to explain this difference. Draw pictures.

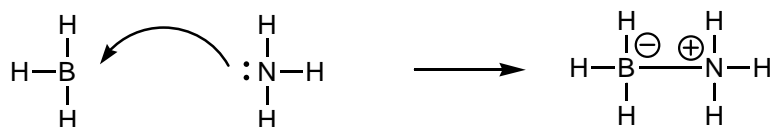
Boron has three valence electrons and normally forms three bonds with no lone pairs left over. With three "things" attached, we describe it as sp^2 -hybridized. As a result, all the B-H bonds are in a plane -- we have trigonal planar geometry. Any dipoles for these bonds would cancel each other, so it is not a surprise that BH_3 has no overall dipole moment.

Nitrogen has five valence electrons and normally forms three bonds with one lone pair left over. With four "things" attached, we describe it as sp^3 -hybridized. As a result, we have tetrahedral geometry. Any dipoles for the N-H bonds would not cancel each other. Moreover, the lone pair is on one side of the molecule. We would expect an overall dipole moment.



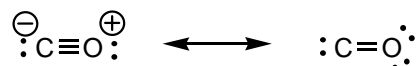
b. If you mixed BH_3 and NH_3 together, what would you expect to happen? Would they react with each other or remain inert? Explain your answer. Would you want to store them in the same cabinet?

This question is a preview of acid-base chemistry. Boron would like to have a full octet, and therefore it is a lone pair acceptor (Lewis acid). The nitrogen of ammonia has a lone pair that can be donated (Lewis base). If I mixed BH_3 and NH_3 , I would see the lone pair donated to form a bond from the nitrogen to the boron. Although I have formal charges, the new complex provides each atom with a full octet. I've illustrated it in pictures below. Needless to say, I wouldn't want to store mutually reactive substances in the same cabinet.



16. a. Draw a Lewis structure for carbon monoxide, CO. $\ominus \text{:C}\equiv\text{O:}^{\oplus}$

b. Draw all possible resonance forms, showing formal charges.



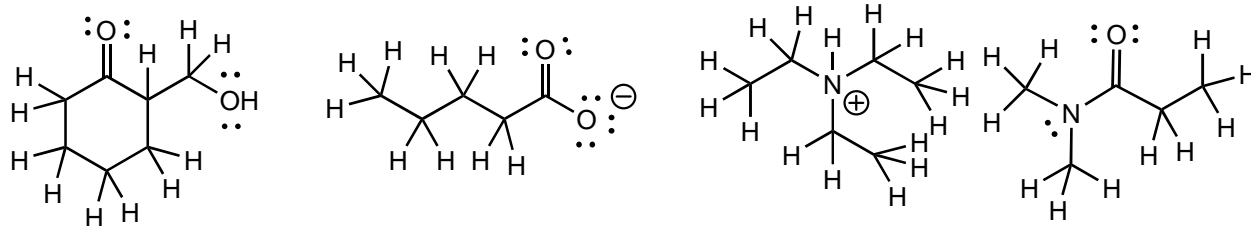
c. What experimental method could you use to determine which resonance form is the most important? How would it help?

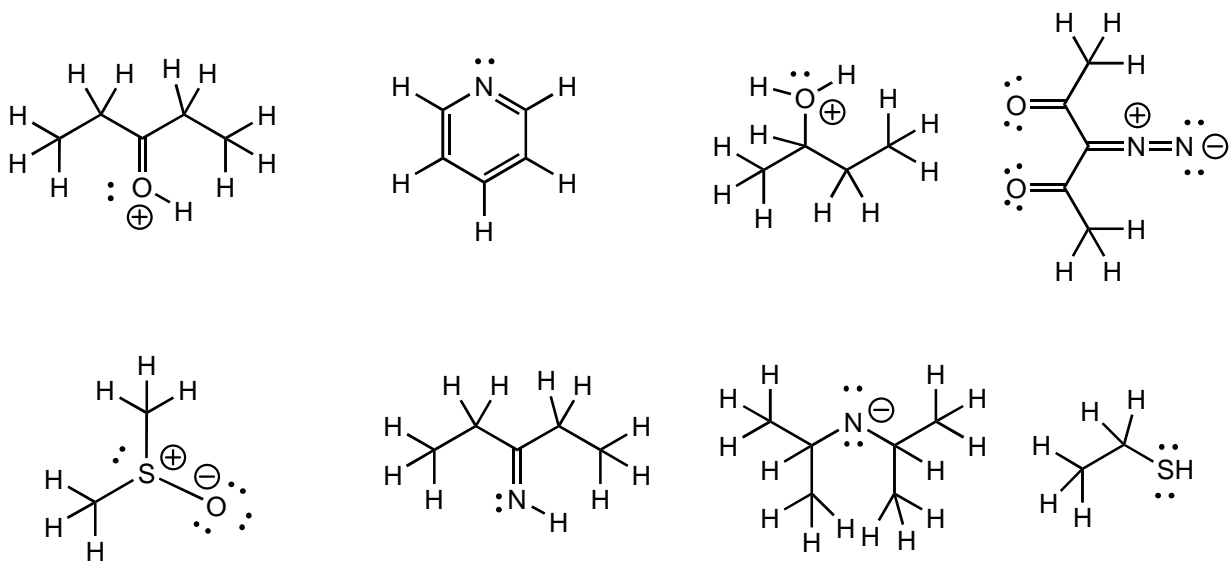
You could determine the dipole moment. In the resonance structure on the left, the dipole would point toward the carbon. In the structure on the right, the dipole would point toward the oxygen. Measuring the actual dipole moment and its direction would indicate where the electrons really lie and which resonance form is the bigger contributor.

17. Do you expect AlBr_3 to be a weaker or stronger Lewis acid than AlCl_3 ? Explain.

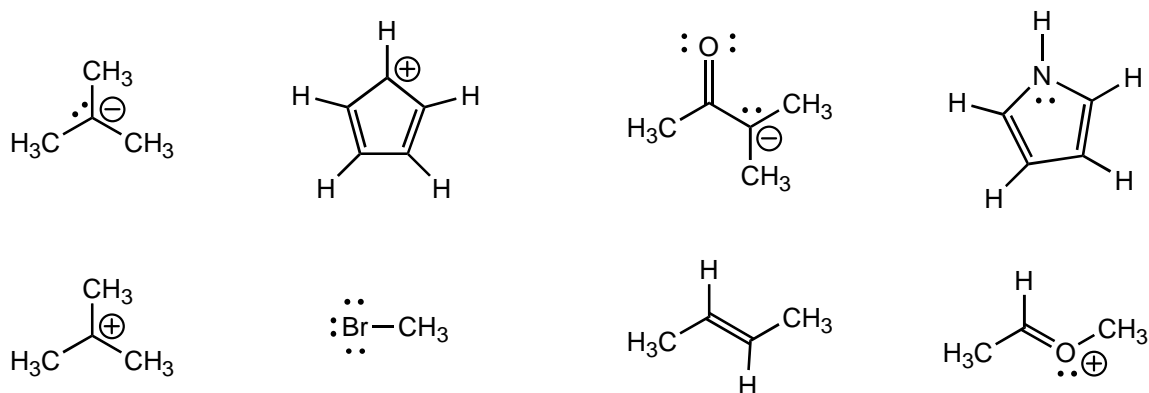
A Lewis acid is an electron pair acceptor. Here the Al is electron deficient because it has three bonds and no lone pairs. It is disposed to accept an electron pair. The attached halogen atoms also pull electrons away from the Al and make it an even better electron pair acceptor. The more electronegative halogen will be better at pulling electrons away. Cl is more electronegative than Br and will cause the Al to be more electron deficient. The more deficient, the more it wants a lone pair, and the better the Lewis acid it is. AlCl_3 is stronger.

18. For the following compounds, determine the formal charge for all the heteroatoms (O, N, and S). All nonbonding electrons are shown. For carbon atoms, assume zero charge and fill in the correct number of assumed hydrogens. Note: there are no assumed electrons on carbon; they have to be explicitly shown with nonbonding electrons and/or with a charge notation. heteroatoms with no indicated formal charge have a charge of 0.

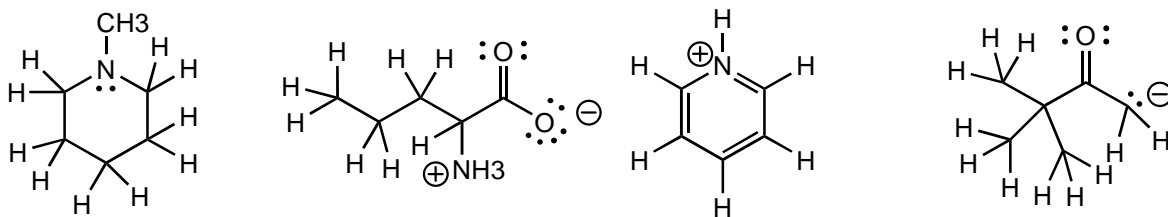


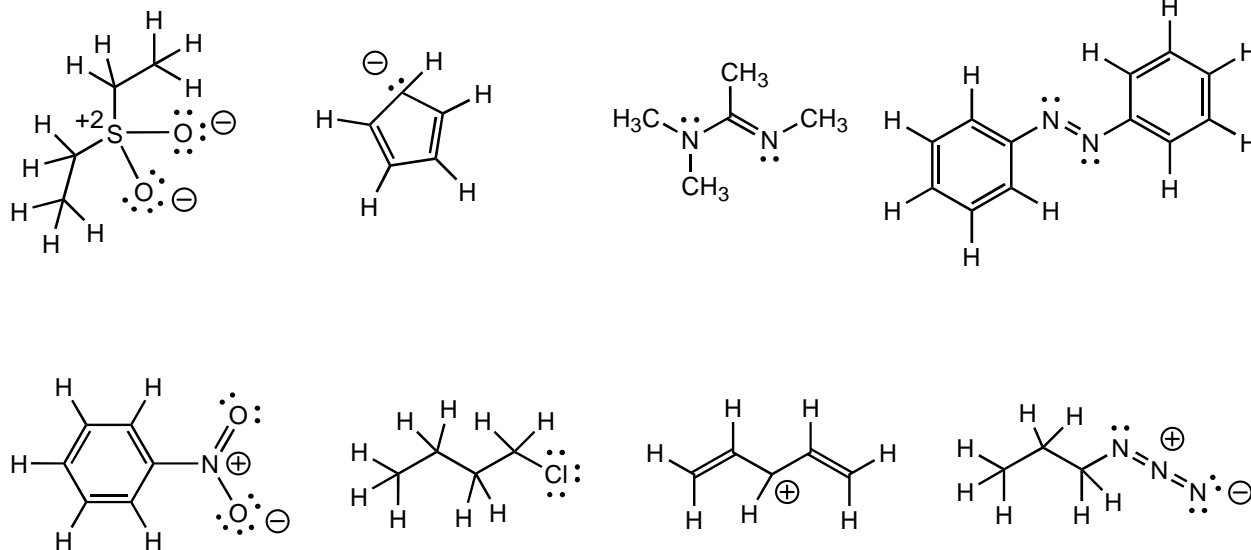


19. For the following compounds, determine the charge for all the atoms, and assign formal charges to any atoms that need them. All normally-assumed hydrogens and nonbonding electrons are shown.

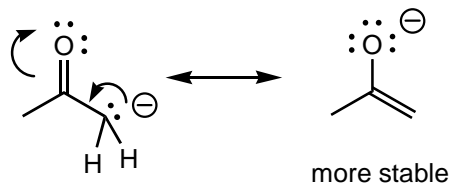


20. For the following compounds, all charges are shown as they might typically be in texts or the chemical literature. Add to these structures the correct number of normally-assumed nonbonding electrons and hydrogens *consistent with the formal charges as shown*. Recall from the drawing conventions that hydrogens are always shown on heteroatoms (O, N, and S); only hydrogens on carbons are assumed and need to be added to the structures below. As always, assume zero charge unless a charge is shown.

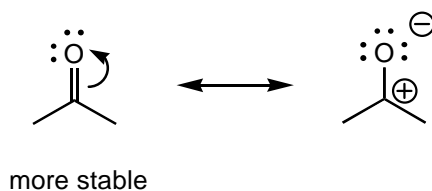




21. For the following sets of resonance structures, use mechanistic arrows to show how one can be converted to the other. Each pair has one structure listed as more stable. Give a brief explanation why it is the more stable form.

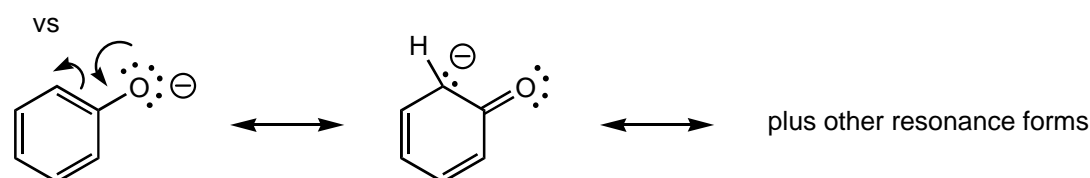
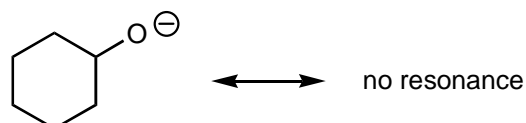
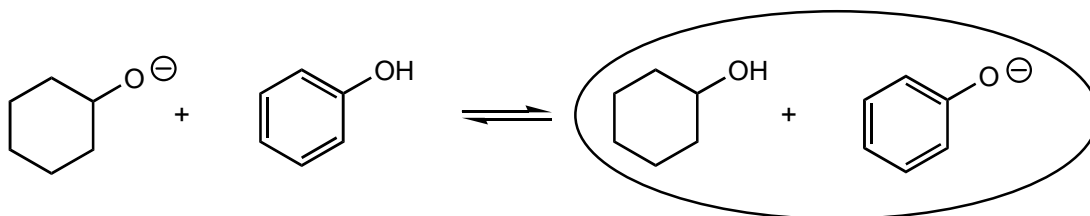


Because oxygen is more electronegative than carbon, having a negative charge on the oxygen is better than having it on the carbon. The resonance form on the right should be a bigger contributor to the overall picture.

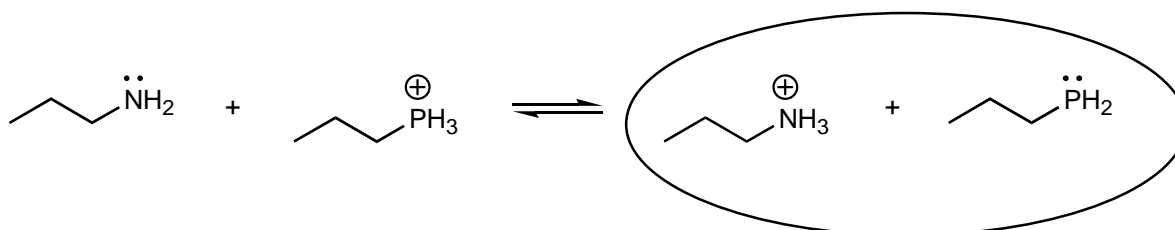


The resonance form on the left is better because all the atoms have full octets with 8 electrons. The resonance form on the right is reasonable because the lone pair goes to the more electronegative atom, but the carbon has only 6 electrons. Note that a resonance form with the lone pair moving to the carbon would be unreasonable -- it has essentially no contribution to the overall picture.

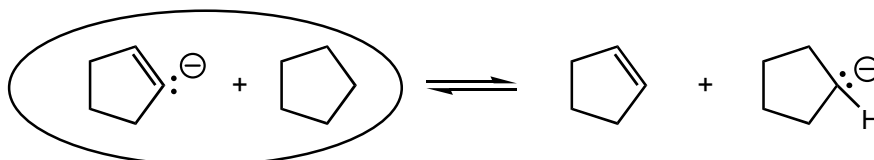
22. For the following reactions, predict on which side the equilibrium should lie. Give a brief explanation for your reasoning.



The extra electrons on the oxygen are better stabilized when they have additional places to go -- which is what occurs by resonance. That makes the bottom (or right side) base more stable than the top (or left side) base. Equilibrium should be on the right.



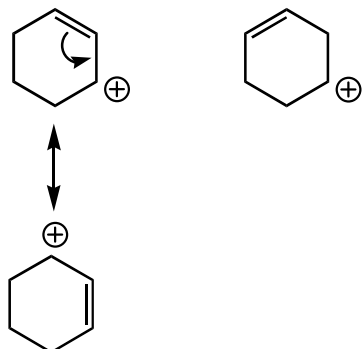
Here the base and conjugate base are the neutral molecules. Is the lone pair better on the phosphorous or the nitrogen? Phosphorous is bigger, more diffuse, and better stabilizes electron pairs (more kids to start with). It is less likely than nitrogen to feel the need to donate its lone pair to a proton. Use the periodic trend. It is less basic, and the equilibrium lies on the right.



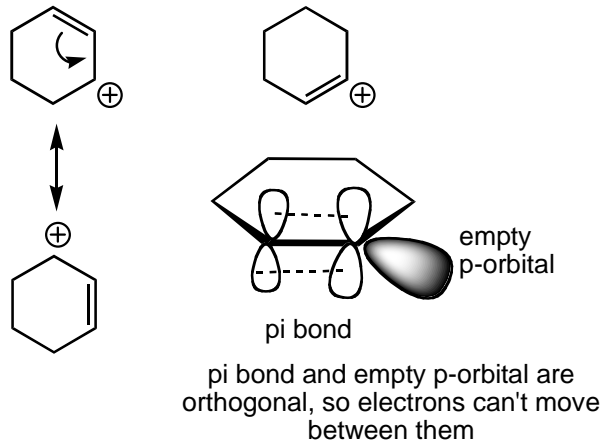
The difference in the two bases here is whether the lone pair is held in an sp^2 orbital (left) or an sp^3 orbital (right). The more s-character, the more stable the lone pair. An sp^2 orbital at 33% s is better than an sp^3 orbital at 25% s. Equilibrium lies on the left.

23. For the following pairs of compounds, decide which one is more stable, and briefly explain why. Draw out any structures that would justify your selection.

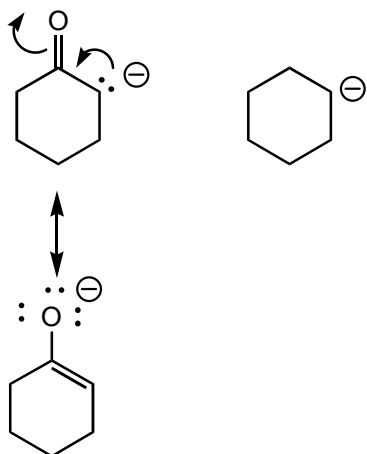
more stable
resonance



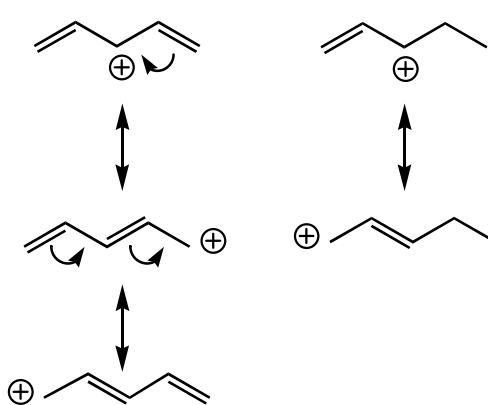
more stable
resonance



more stable
resonance

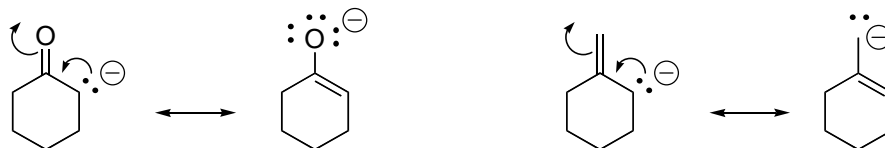


more stable
more resonance

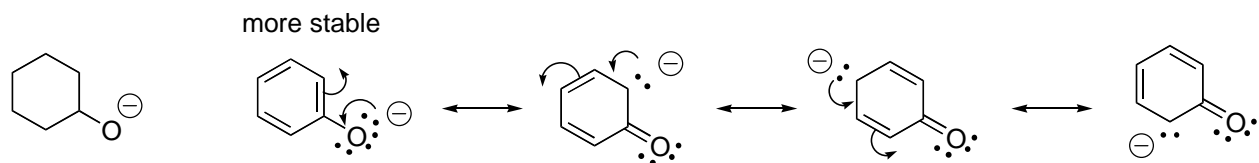


24. Give an explanation why the labeled anion of each pair is more stable.

more stable

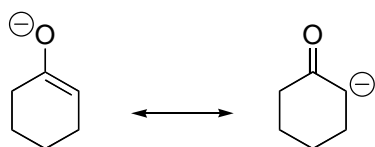


Both structures have resonance, but the one on the left can delocalize the lone pair to a more electronegative atom (O more electronegative than C).



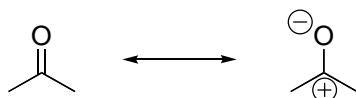
no resonance for the one on the left, lots of resonance for the one on the right.

25. The major contributor is labeled in each set of resonance structures. Explain why that resonance form is "better" than the other. Although a resonance form is shown for 2-methylpropene, we generally consider it so "bad" that we don't bother to draw it. Explain why we don't draw the second resonance form for 2-methylpropene but we do consider a similar resonance form for acetone.



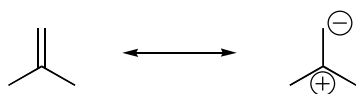
major contributor has the negative charge on the more electronegative atom

major contributor



major contributor avoids charge separation; the only reason that the minor one isn't silly is that it puts a negative charge on the more electronegative atom, and we know the bond is polarized to start. (We'll see that it also explains a lot of the reactivity of ketones.)

major contributor

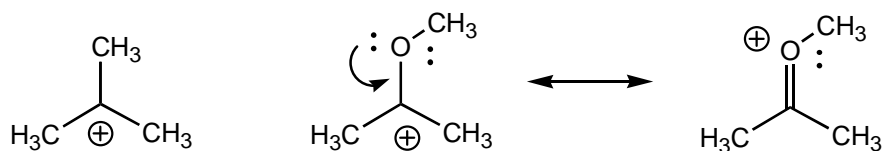


"only" contributor

Why don't we draw this resonance form?

Simultaneously creating carbon anions and cations from a neutral structure is so bad it sends shivers down our spines. Bond has no polar character to make us think this structure would appear in anything other than our nightmares.

26. For the following carbocations, the oxygen containing molecule is significantly more stable. Explain why the $-\text{OCH}_3$ group would be better able to stabilize the carbocation than a $-\text{CH}_3$ group.

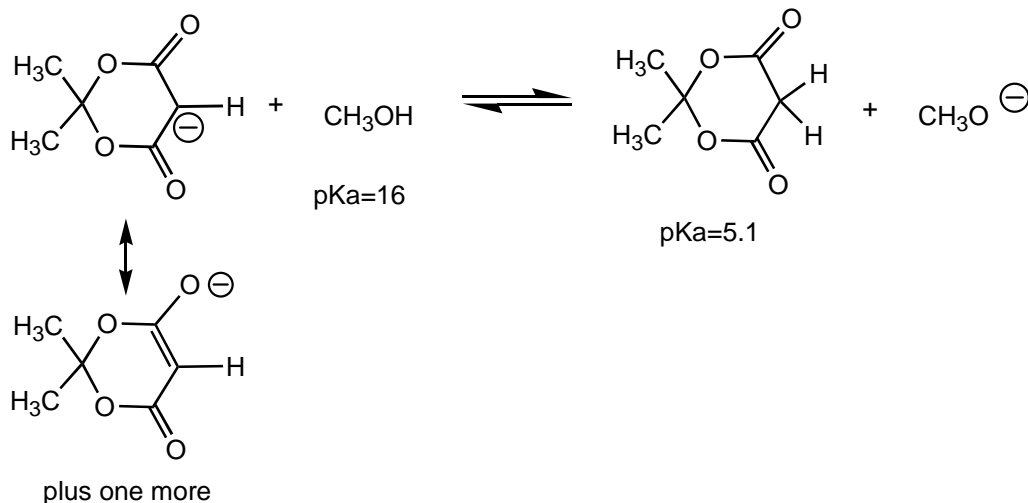


no resonance

cation is stabilized by resonance

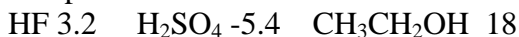
The lone pairs of the oxygen can be donated by resonance to stabilize the cation. Nothing similar is possible with just a methyl group.

27. Indicate where the equilibrium would lie for the following reaction. Explain your answer briefly.

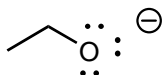


A simple answer is that reactions favor to the weaker acid/base, which correlates with higher pKa's, so the equilibrium must be on the left. Could you do it if we hadn't given you the pKa's? It's a tougher call because the initial anion is on carbon vs. oxygen. However, the anion on the left is stabilized by multiple resonance forms, including two where the charge is on an oxygen. At a minimum, this assessment allows us to make sense of the experimental data.

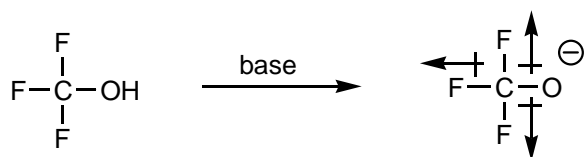
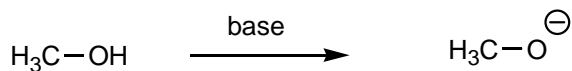
28. Use the pKa values below to answer the following questions.



- Which acid is the strongest? Which acid is the weakest?
strongest, H₂SO₄ weakest, CH₃CH₂OH
- Which of the above acids are strong enough to react with NaOH (pKa of H₂O = 15.7)?
HF and H₂SO₄
- Which conjugate base of any of the acids above could deprotonate acetic acid (pKa = 4.8)?
only, the conjugate base of ethanol,



29. Trifluoromethanol, CF₃OH, has a much lower pKa than methanol, CH₃OH. Does that make CF₃OH more acidic or less acidic? Briefly explain why the pKa of trifluoromethanol is lower.

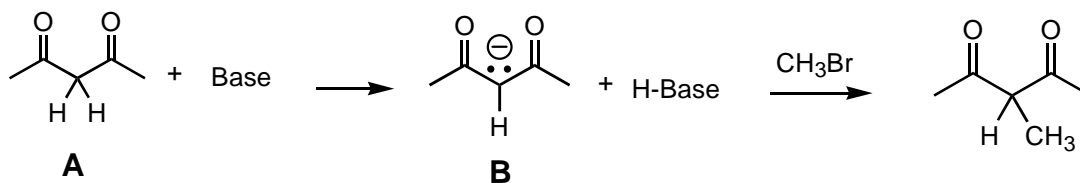


The strongly electronegative fluorines withdraw electrons from the carbon and inductively stabilize the anion on oxygen, so trifluoromethanol is more acidic. Note that this example is really just theoretical because the anion shown would immediately decompose to other products. Trifluoromethanol itself is highly unstable.

30. Draw the conjugate bases for the following acids.

Acid	pKa	Conjugate Base
$\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \\ \text{H}_3\text{C}-\text{C}-\ddot{\text{O}}\text{H} \end{array}$	4.8	$\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \\ \text{H}_3\text{C}-\text{C}-\ddot{\text{O}}\text{:}^- \end{array}$
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	25	$\text{H}-\text{C}\equiv\text{C}\text{:}^-$
$\text{H}_2\ddot{\text{O}}\text{:}$	15.7	$\text{H}\ddot{\text{O}}\text{:}^-$
NH_4^+	9.2	:NH_3
$\text{H}-\ddot{\text{F}}\text{:}$	3.2	$\text{:}\ddot{\text{F}}\text{:}^-$

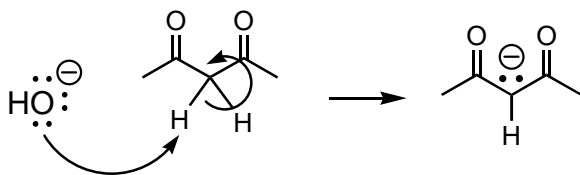
a. In the following reaction scheme, compound **A** (pKa = 10) must be deprotonated to form anion **B** with the appropriate base. Compound **B** then reacts with CH_3Br to form a new carbon-carbon bond. From the list of acids and their pKa's given above, which conjugate base(s) would you choose to deprotonate **A**? Be sure to give all the bases that would be appropriate for this reaction.



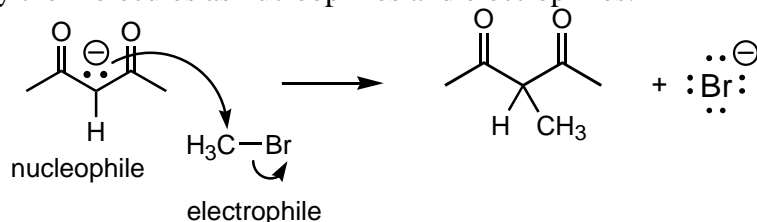
Draw the structure of the appropriate **bases** below:



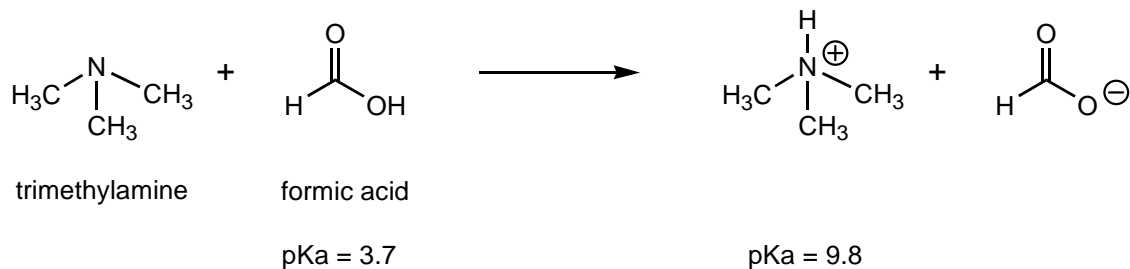
b. Draw out the acid-base reaction using one of the bases you chose. Use mechanistic arrows to show the flow of electrons.



c. Draw the subsequent mechanism for the substitution reaction using mechanistic arrows. Identify the molecules as nucleophiles and electrophiles.



31. a. Show the products of the following acid/base reaction and indicate whether it would occur. pKa: Protonated form of trimethylamine = 9.8; Formic Acid = 3.7



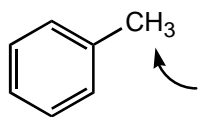
Reactions go to the weakest acid and base. The trimethylammonium ion is a much weaker acid than formic acid. Difference of 6 pK units corresponds to an equilibrium constant of about 10^6 . The reaction will definitely occur.

b. Which of the following acids would react with $\text{N}(\text{CH}_3)_3$?

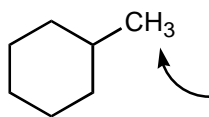
i) H_2S , pKa 7.0 ii) H_2CO_3 , pKa 6.4 iii) $\text{CH}_3\text{CH}_2\text{OH}$, pKa 18 iv) NH_3 , pKa 36

We will get a reasonable reaction with anything that is at least a few pKa units below 9.8, the pKa for the trimethylammonium ion. That means H_2S and H_2CO_3 , but neither of the other two.

32. Toluene (methylbenzene) has a pKa of 41, while methylcyclohexane has a pKa ~ 50.

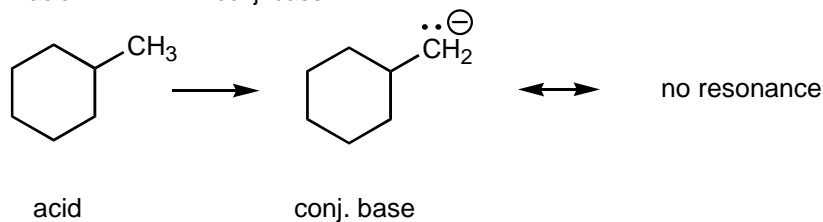
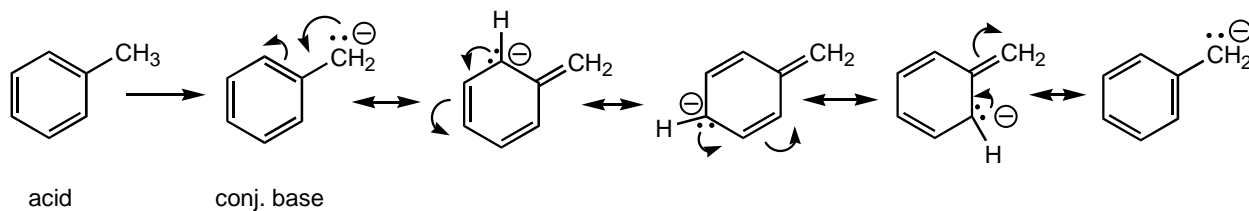


toluene
pKa ~41



methylcyclohexane
pKa ~50

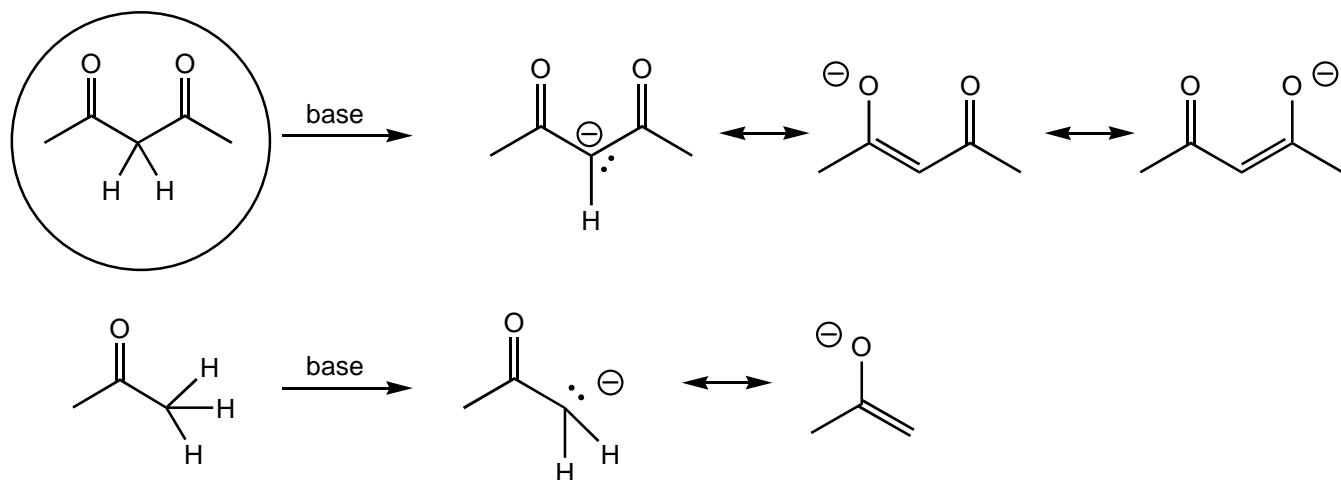
- Draw the conjugate base for each molecule.
- Draw all possible resonance structures for each base.



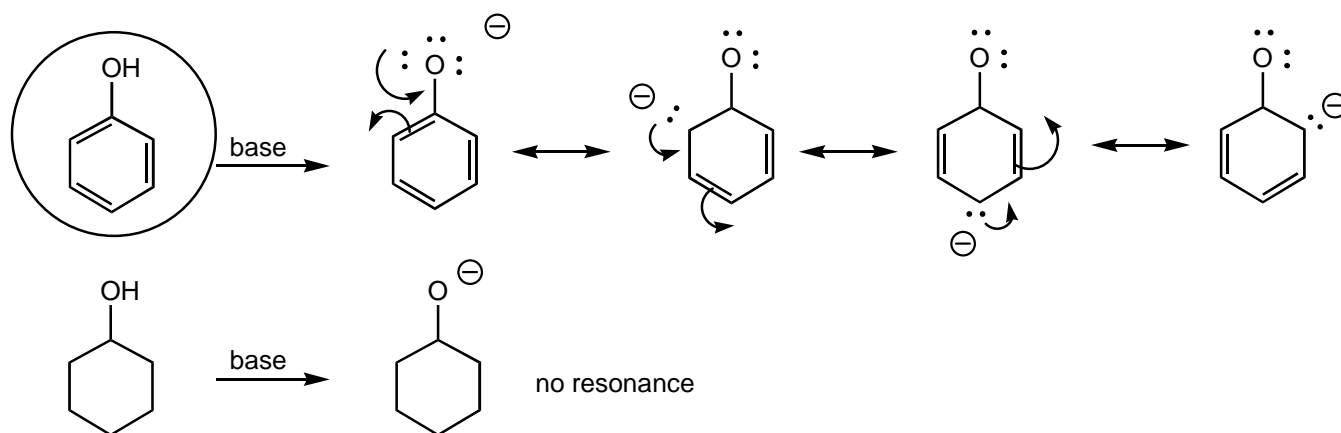
c. Why do you think toluene is so much more acidic?

The conjugate base of toluene is stabilized by resonance, while the conjugate base of methylcyclohexane is not. The better stabilized the conjugate base, the stronger the corresponding acid.

33. For each pair of compounds, circle the one that is more acidic. Briefly explain why your choice is the more acidic one. Your answer should involve basic principles (not just the pKa's given), and you should probably include some pictures.

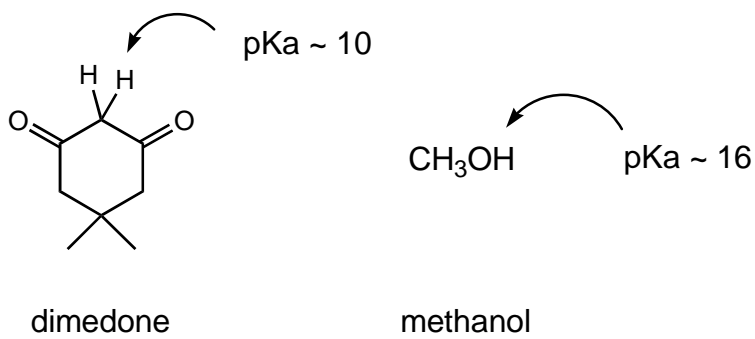


Resonance forms are similar, so the more the better. Resonance with two carbonyls is better than one.

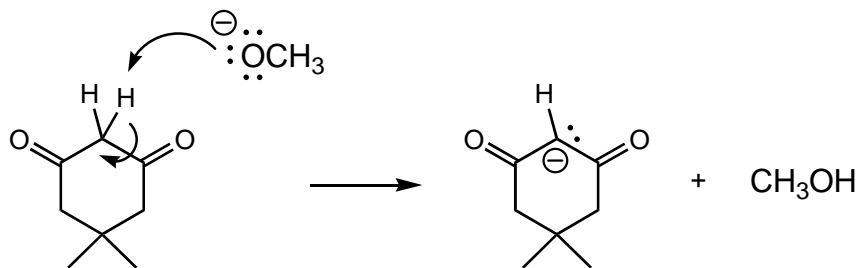


One anion is stabilized by resonance, and the other isn't

34. Consider an acid/base reaction between dimedone and sodium methoxide (NaOCH_3).



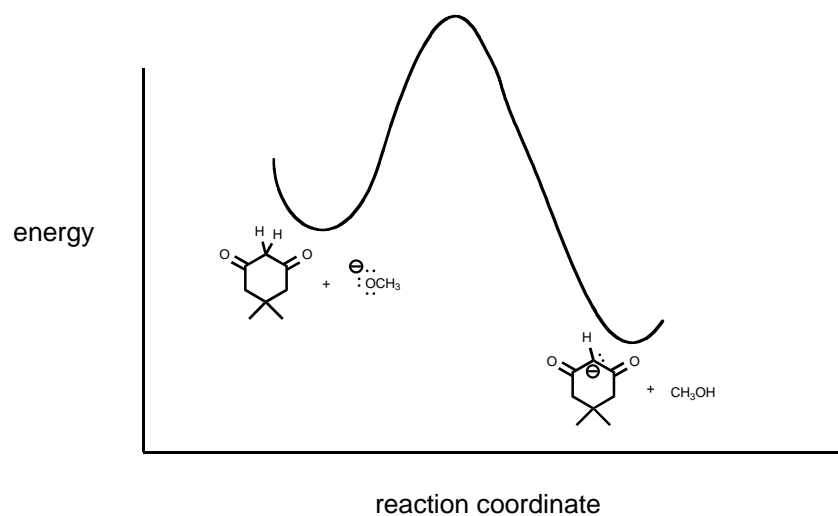
a. Draw a mechanism for the reaction.



b. Do you expect this reaction to go to completion? Explain.

Reactions go to the weakest acid and base. Methanol is a much weaker acid than dimedone. Difference of 6 pK units corresponds to an equilibrium constant of about 10^6 . The reaction will definitely occur and go to completion.

c. (Preview to future topic) Draw an energy diagram that represents your reaction mechanism. Give an estimate for the energy difference between the reactants and products. Is it exothermic or endothermic?



The reaction is exothermic. An equilibrium constant of 10^6 corresponds to an energy decrease of about 40 kJ/mol from reactants to products.