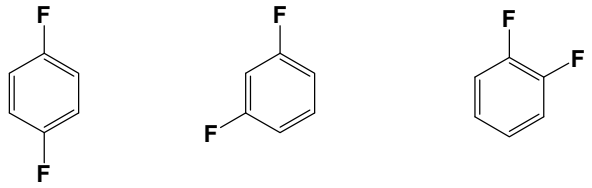
HOMEWORK PROBLEMS: POLAR BONDS, RESONANCE, ACIDS & BASES

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

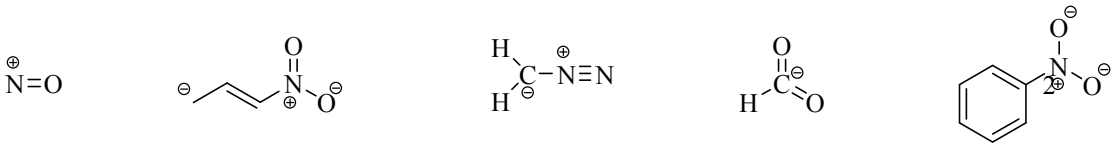


2. Trans-dichlorodifluoroethylene, $C_2Cl_2F_2$, has a number of polar bonds but no net dipole moment. Draw skeletal structure for this compound to explain this observation.

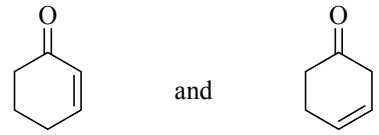
3. Draw the Lewis structures and all the possible resonance structures for the following compounds. Be sure to use curved arrows to show how these resonance structures are interconvertable for each individual compound. Indicate whether or not any of these resonance structures are equivalent and rank them from most stable (1) to least stable for each compound.

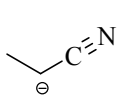
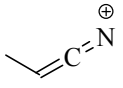
(a) NO_2^- (b) $CH_2{=}CHNO_2$ (c) $CH_3CO_2^-$ (d) $CH_2{=}CHCH_2^+$

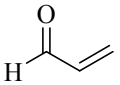
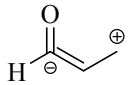
4. For each of the molecules shown below, a more stable resonance structure is possible. Draw in all lone pairs of electrons then, using curved arrows to show electron movement, draw the more stable resonance structure and state why this is more stable.



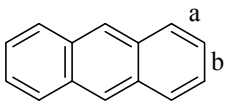
5. For each pair of compounds given below, state why they are not resonance forms of each other.

(a)  and

(b)  and 

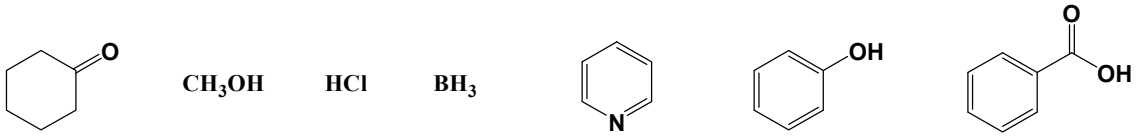
(c)  and 

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?

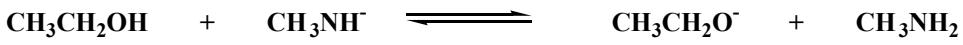


7. For the two molecules below, one is approximately 6 orders of magnitude more acidic than the other. Which compound is more acidic? Explain this difference.

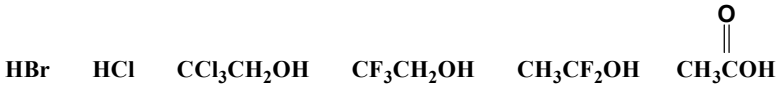
8. Circle the Lewis acids and put a box around all Lewis bases in the group of molecules below:



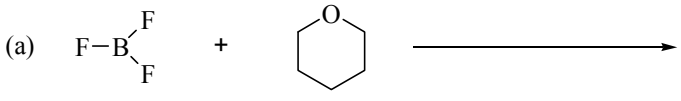
9. For the following reaction, label reactants and products as acids/bases and conjugate acid/bases. Determine which direction the equilibrium will be favored and provide curved arrows to show the flow of the electrons in the direction favored. What is the approximate Keq for this reaction? (note, you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

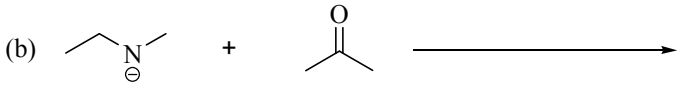


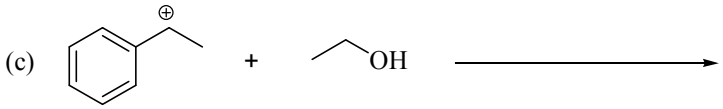
10. Rank the compounds below from strongest acid to weakest acid.



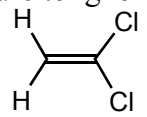
11. Predict the products from the following acid base reactions and provide curved arrows to show the movement of electrons going from reactants to products.

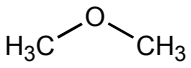




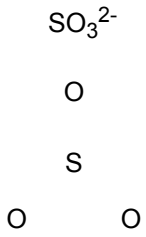


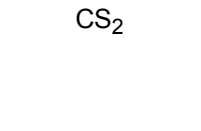
12. For the following structures, draw in all pertinent bond dipoles and show the net dipole for the molecule. Be sure to ignore C-H dipoles and consider the nonbonding electrons where appropriate.

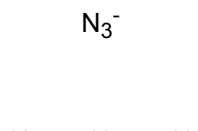




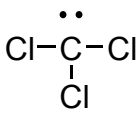
13. For the following molecules, draw a valid Lewis structure, and indicate the formal charge on each atom. Use the templates provided for the arrangement of the atoms.



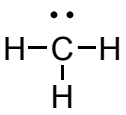




14. Consider the molecules 1 and 2 below:



1



2

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.

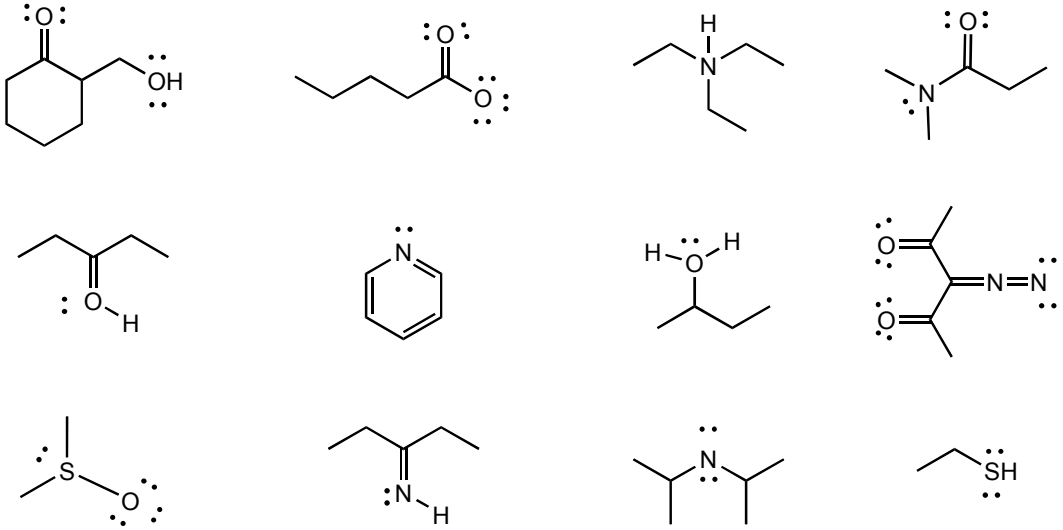
b. Given what you know about the effects of electronegative atoms, which compound is more stable? Briefly explain why.

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.
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?

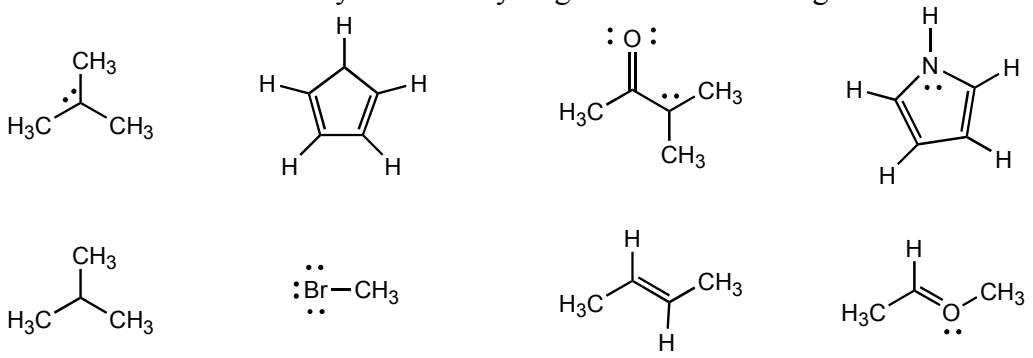
16. a. Draw a Lewis structure for carbon monoxide, CO.
b. Draw all possible resonance forms, showing formal charges.
c. What experimental method could you use to determine which resonance form is the most important? How would it help?

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

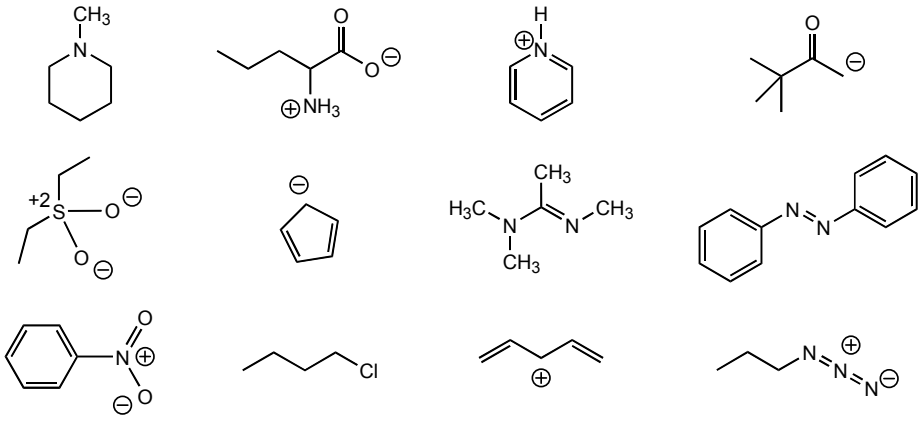
18. For the following compounds, determine the formal charge for all the heteroatoms (O, N, and S). All nonbonding electrons are shown. For carbon atoms, assume zero charge and fill in the correct number of assumed hydrogens. Note: there are no assumed electrons on carbon; they have to be explicitly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



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.



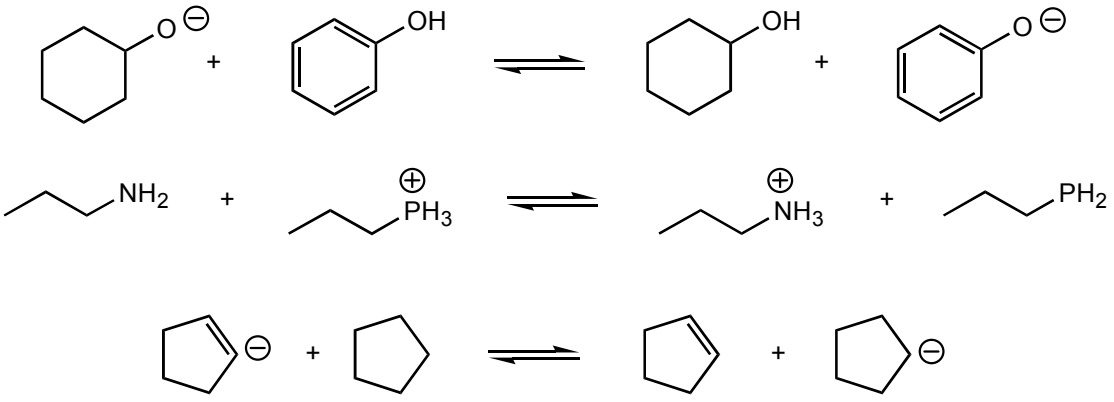
20. For the following compounds, all charges are shown as they might typically be in texts or the chemical literature. Add to these structures the correct number of normally-assumed nonbonding electrons and hydrogens *consistent with the formal charges as shown*. Recall from the drawing conventions that 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.



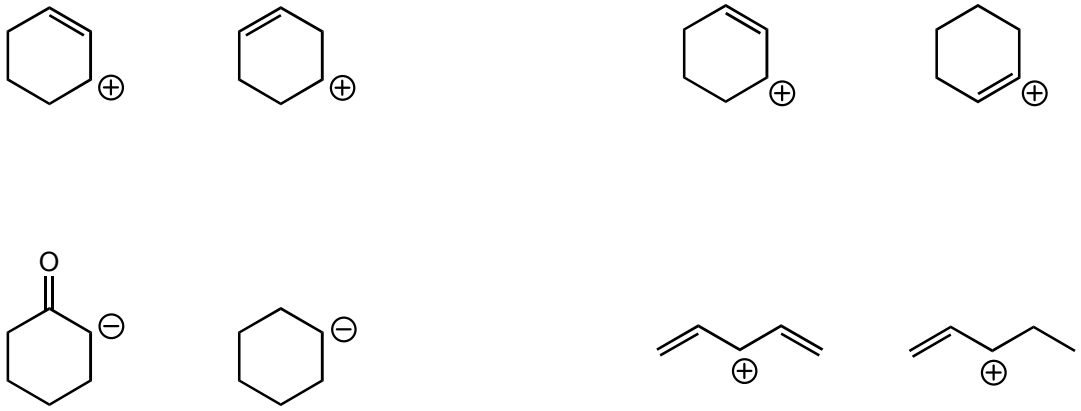
21. For the following sets of resonance structures, use mechanistic arrows to show how one can be converted to the other. Each pair has one structure listed as more stable. Give a brief explanation why it is the more stable form.

more stable more stable

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



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.

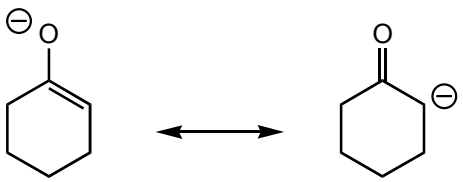


24. Give an explanation why the labeled anion of each pair is more stable.

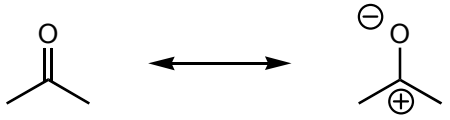
more stable

more stable

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.

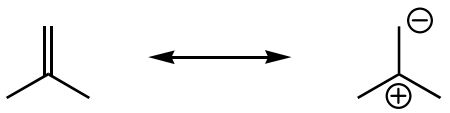


major conbributor



acetone

major conbributor

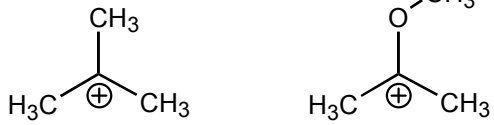


2-methylpropene

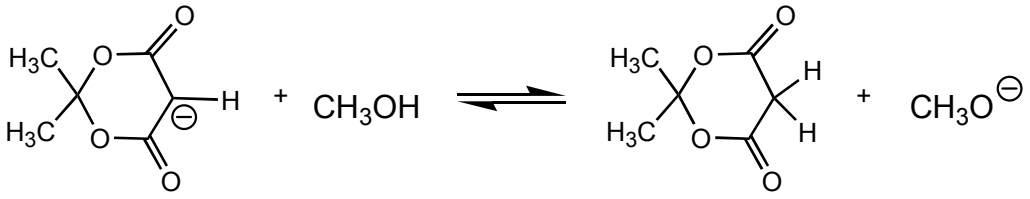
"only" conbributor

Why don't we draw this resonance form?

26. For the following carbocations, the oxygen containing molecule is significantly more stable. Explain why the -OCH3 group would be better able to stabilize the carbocation than a -CH3 group.



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



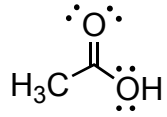
28. Use the pKa values below to answer the following questions.

HF 3.2 H_2SO_4 -5.4 CH_3CH_2OH 18 HF 3.2

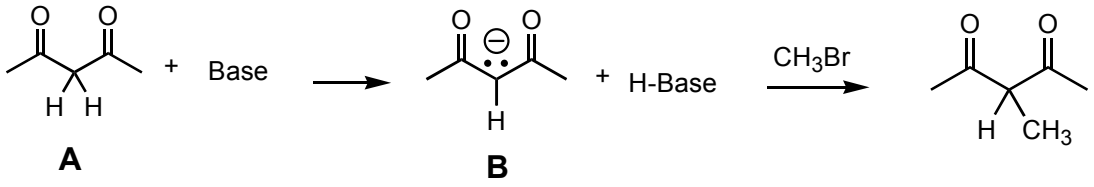
a. Which acid is the strongest? Which acid is the weakest?
b. Which of the above acids are strong enough to react with NaOH (pKa of H_2O = 15.7)?
c. Which conjugate base of any of the acids above could deprotonate acetic acid (pKa = 4.8)?

29. Trifluoromethanol, CF_3OH, has a much lower pKa than methanol, CH_3OH. Does that make CF_3OH more acidic or less acidic? Briefly explain why the pKa of trifluoromethanol is lower.

30. Draw the conjugate bases for the following acids.

Acid	pKa	Conjugate Base
	4.8	
	25	
	15.7	
	9.2	
	3.2	

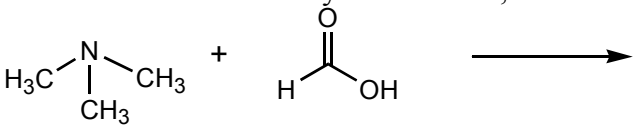
a. In the following reaction scheme, compound **A** (pKa = 10) must be deprotonated to form anion **B** with the appropriate base. Compound **B** then reacts with CH_3Br to form a new carbon-carbon bond. From the list of acids and their pKa's given above, which conjugate base(s) would you chose to deprotonate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



Draw the structure of the appropriate <u>bases</u> 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 (Lewis base) and electrophiles (Lewis acid).

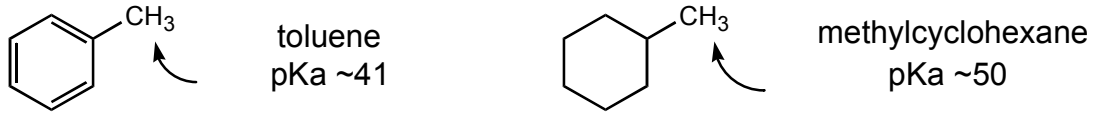
31. (a) Show the products of the following acid/base reaction and indicate whether it would occur. In addition, try to draw the mechanism of the acid-base reaction using the curved arrow notation. Show the "deprotonation" by the base taking an H^+ from the acid using a pair of electrons.
pKa: Protonated form of trimethylamine = 9.8; Formic Acid = 3.7



trimethylamine formic acid

b. Which of the following acids would react with $N(CH_3)_3$?
i) H_2S, pKa 7.0 ii) H_2CO_3, pKa 6.4 iii) CH_3CH_2OH, pKa 18 iv) NH_3, pKa 36

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

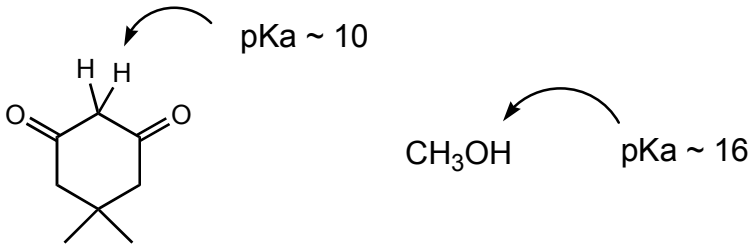


a. Draw the conjugate base for each molecule.
b. Draw all possible resonance structures for each base.
c. Why do you think toluene is so much more acidic?

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 shouold involve basic principles (not just based on the pKa's given), and you should probably include some pictures.

pKa = 10 pKa = 20 pKa = 10 pKa = 16

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



dimedone methanol

a. Draw a mechanism for the reaction.

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

c. 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?