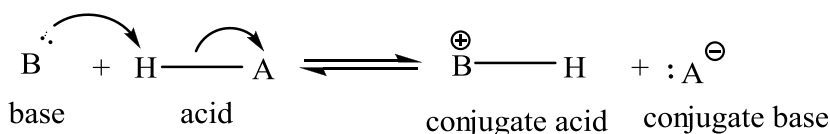


RESONANCE, USING CURVED ARROWS AND ACID-BASE REACTIONS

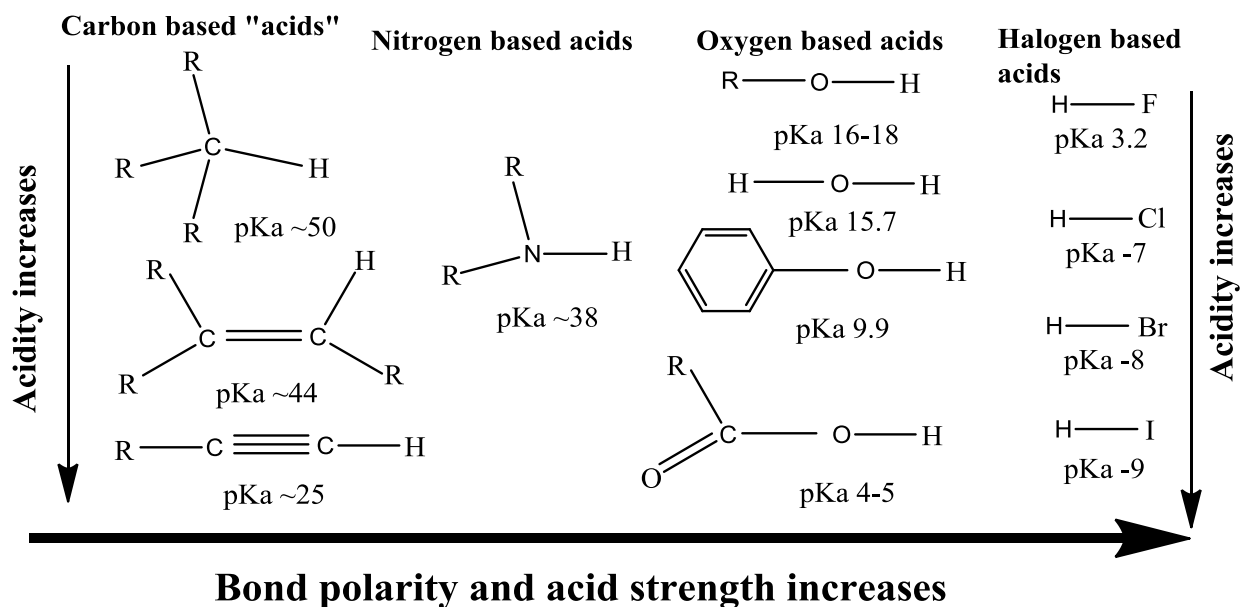
A STUDENT SHOULD BE ABLE TO:

- Properly use curved arrows to draw resonance structures: the tail and the head of every arrow must be drawn in exactly the proper location. The tail shows where the electrons are coming from, and the head shows where the electrons are going. Recognize "bad arrows." Identify insignificant resonance structures.
When drawing resonance structures: *avoid breaking a sigma bond; never exceed an octet for second-row elements; recognize and properly notate formal charges.*
- Define terms "resonance", "resonance stabilization", "delocalization" and "resonance hybrid". Be able to identify allylic and vinylic positions in a molecule. Also identify delocalized lone pairs, including allylic, and differentiate them from localized lone pairs. Identify lone pairs that appear to be allylic, however they are not delocalized because of the geometry of their orbitals.
- Define Bronsted-Lowry acids (proton donors) and bases (proton acceptors); conjugate acids and conjugate bases. Bronsted-Lowry acids are all protic: have an ionizable proton. Be able to draw a conjugate base for any acid and conjugate acid for any base.



Use arrows to show how an acid loses proton with the help of a base. Note that this process, called proton transfer, is shown with at least two arrows. Proton transfers play an integral role in reaction mechanisms.

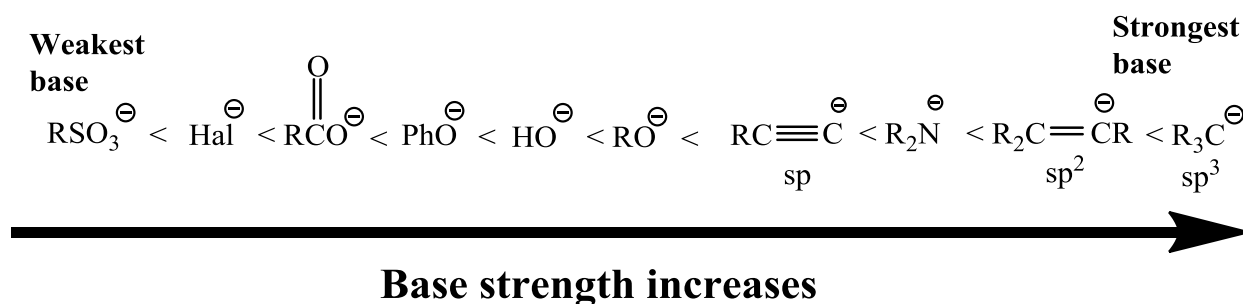
Define pKa and be able to predict the acidity of different hydrogens, using it.



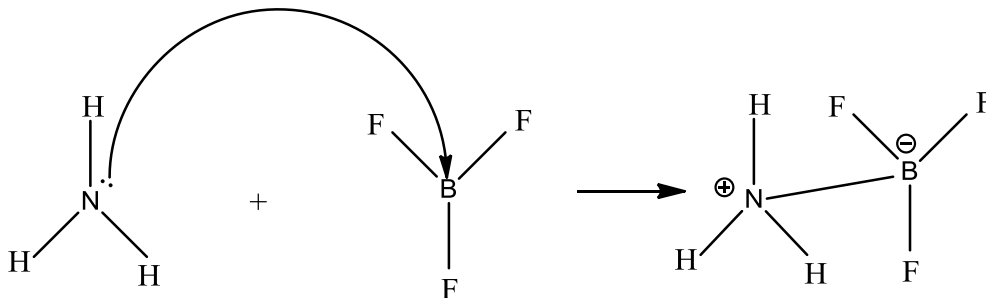
4. Write acid-base reactions, keeping in mind that reactions will proceed in the direction from a stronger to a weaker base formation. Remember that the strongest acid would form the weakest conjugate base, and the weakest acids would form the strongest conjugate base. Consider factors affecting the stability of negative charges: (1) which atom the charge is on: more electronegative and larger atoms stabilize negative charge better; (2) resonance effect: resonance stabilized bases are more stable and therefore weaker; (3) inductive effect: electron withdrawing atoms and groups stabilize negative charge better, and (4) hybridization: orbitals with more s-character stabilize negative charge better (that is negative charge is most stable on sp-orbital, then sp², then sp³).

Predict the position of an equilibrium based on comparative strength of acids or bases, or using pKa values. Also be able to predict which base would be suitable for removal of a particular proton (deprotonating). Keep in mind: bases that are stronger than hydroxide cannot be used when the solvent is water. Counterions (cations) always accompany negatively charged bases and can be ignored: NaOH, LiOH, KOH are all the same base – hydroxide.

Use the following series for comparative strength of bases:



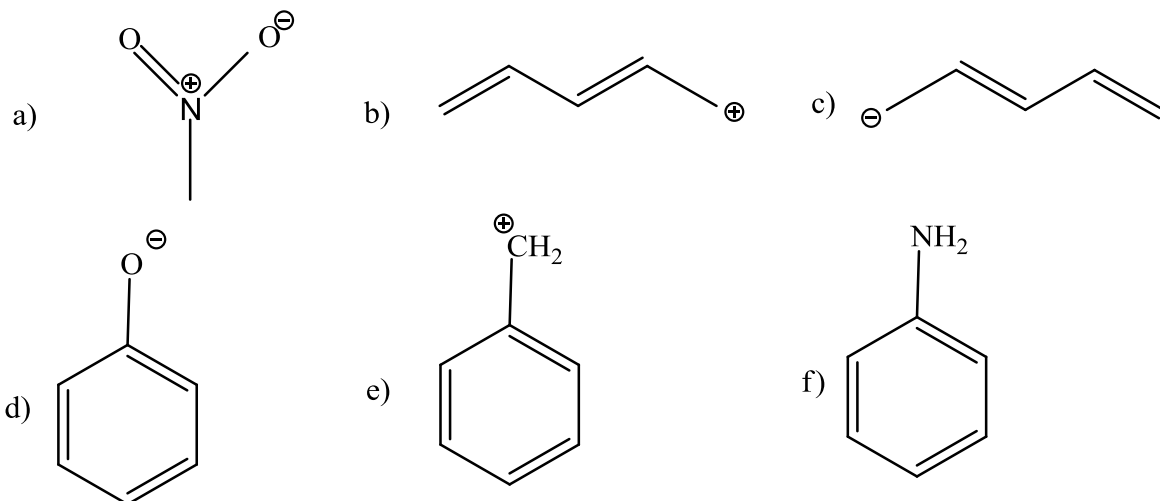
5. Define Lewis bases (electron pair donors) and Lewis acids (electron pair acceptors). Lewis acids may be protic (have an ionizable proton) or aprotic (do not have an ionizable proton). Be able to show Lewis Acid-Base reactions with curved arrows. Different from Bronsted Acid-Base reactions, Lewis Acid-Base reactions can be shown with one arrow:



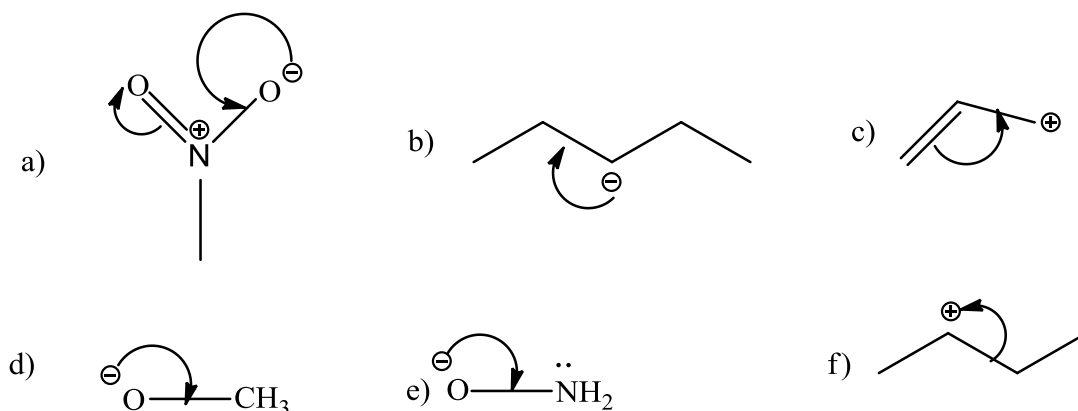
To best prepare for this module, please work Chapter 2 (2.7-2.12) and Chapter 3 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGES SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

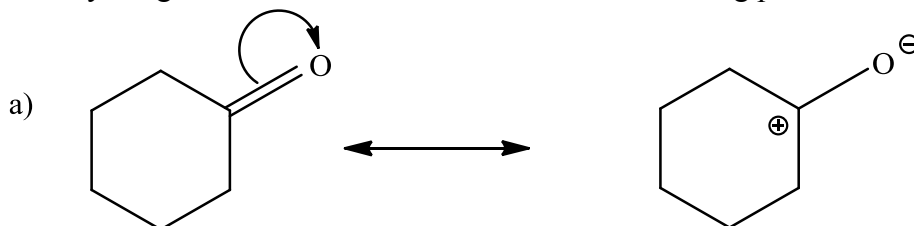
1.1 Using curved arrows draw resonance structures for the following:



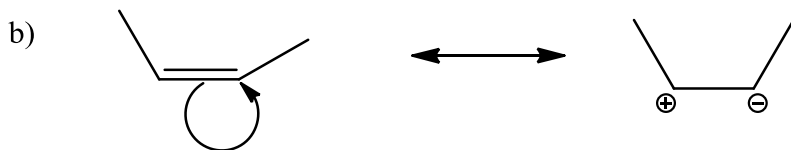
1.2 Identify bad arrows in the following drawings:



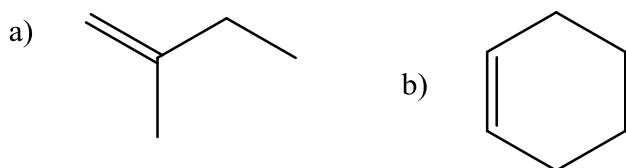
1.3 Identify insignificant resonance structures in the following pairs:



1.3

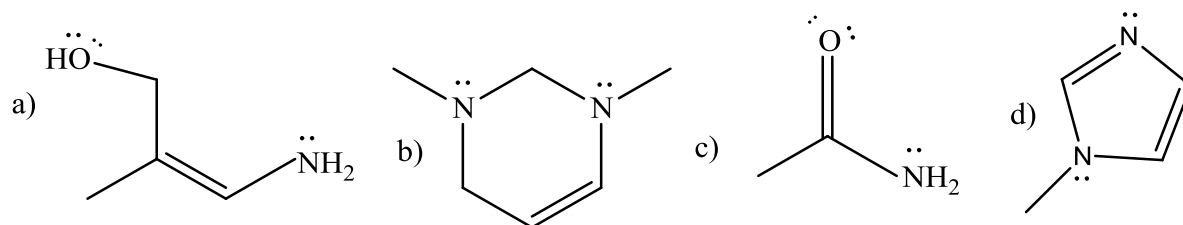


2.1 Identify **all** allylic positions in the following molecules:



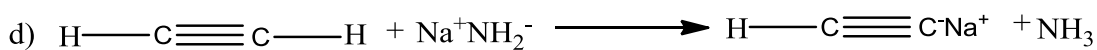
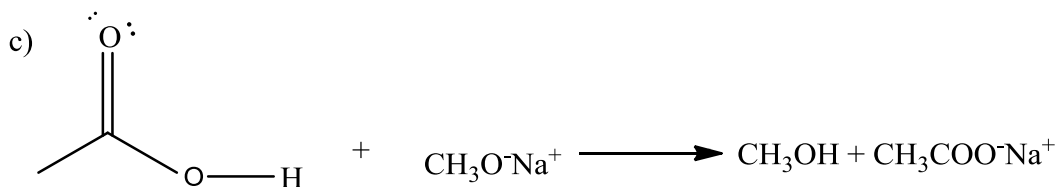
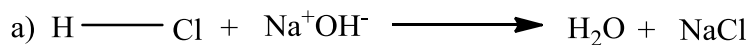
2.2 How many vinylic hydrogens do the structures above contain?

2.3 Identify delocalized lone pairs of electrons, including allylic, in the following structures.



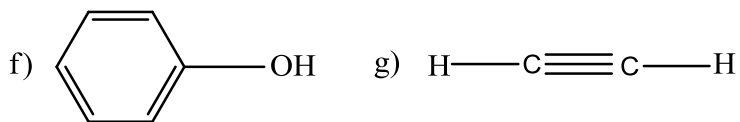
2.4 Draw resonance structures for each of the molecules in 2.3 that show delocalization of the lone pairs identified in 2.3.

3.1 Use arrows to show how the following acids lose their proton with the help of base in the following acid-base reactions:

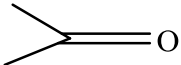


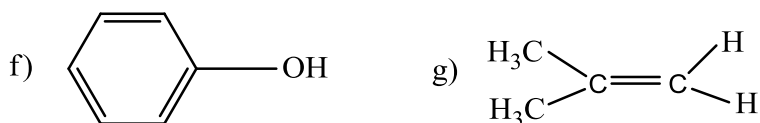
3.2 Draw conjugate bases for the following compounds:

- a) H_2O b) NH_3 c) HCl d) H_2SO_4 e) $\text{C}_2\text{H}_5\text{OH}$

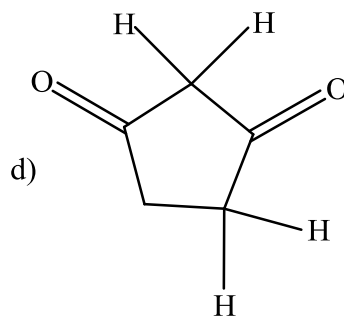
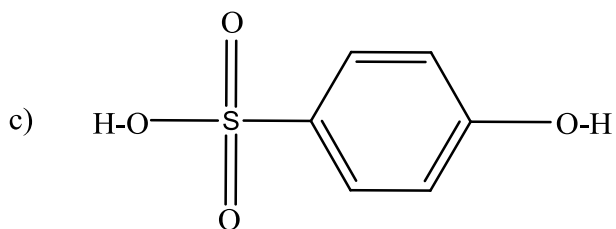
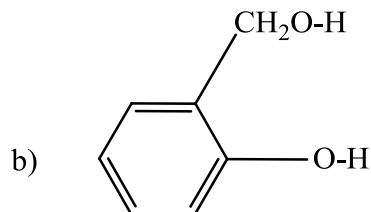
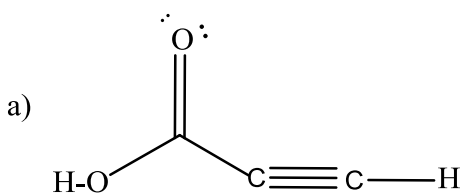


3.3 Draw conjugate acids for the following compounds:

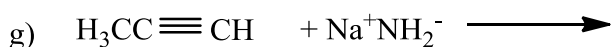
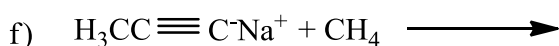
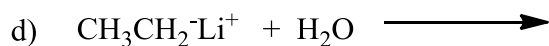
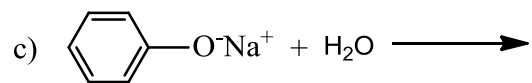
- a) H_2O b) NH_3 c) $\text{C}_2\text{H}_5\text{OH}$ d)  e) CH_3NH_2



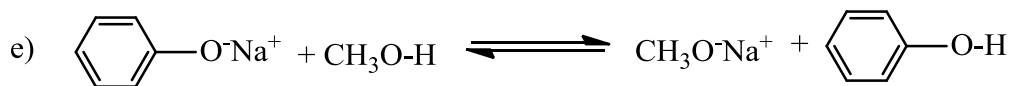
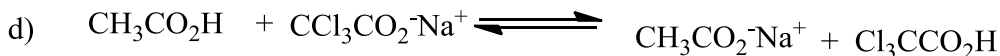
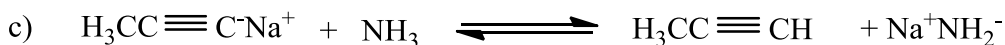
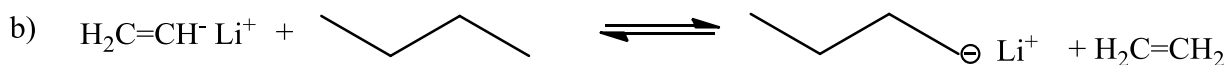
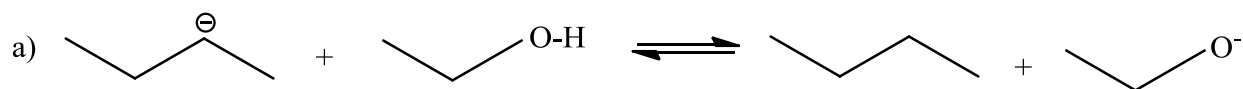
3.4 Using Table 3.1 in your textbook identify the most acidic hydrogen in each of the following compounds:



4.1 For each of the following reactions, write the acid/base reaction product or indicate no reaction. (Hint: use base strength series).




4.2 Predict the position of the equilibrium for each of the following reactions: Verify your answers with pKa values where possible.



4.3 Identify whether the reagent shown would be suitable to accomplish the task described. Explain why or why not.

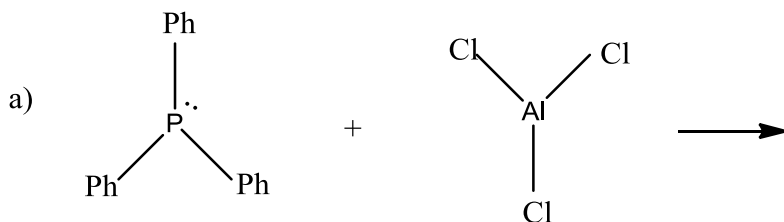
a) To deprotonate $\text{H}_2\text{C}=\text{CH}_2$ using NaOH

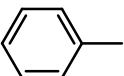
b) To protonate Na^+NH_2^- using water

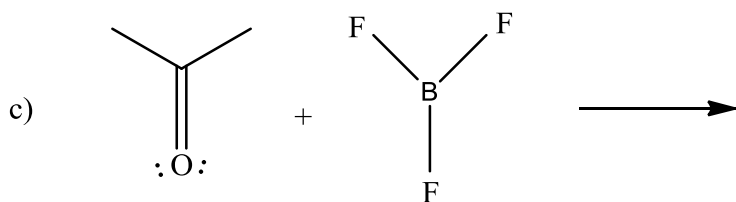
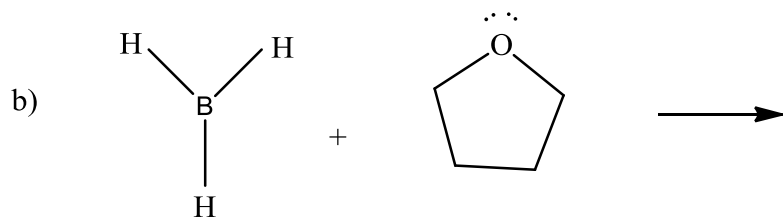
c) To deprotonate  using NaOH

d) To protonate $\text{H}_3\text{CC}\equiv\text{C}^-\text{Na}^+$ using ethane

5. In each case identify the Lewis acid and the Lewis base. Show with curved arrows how the base attacks the acid, and draw the reaction products.

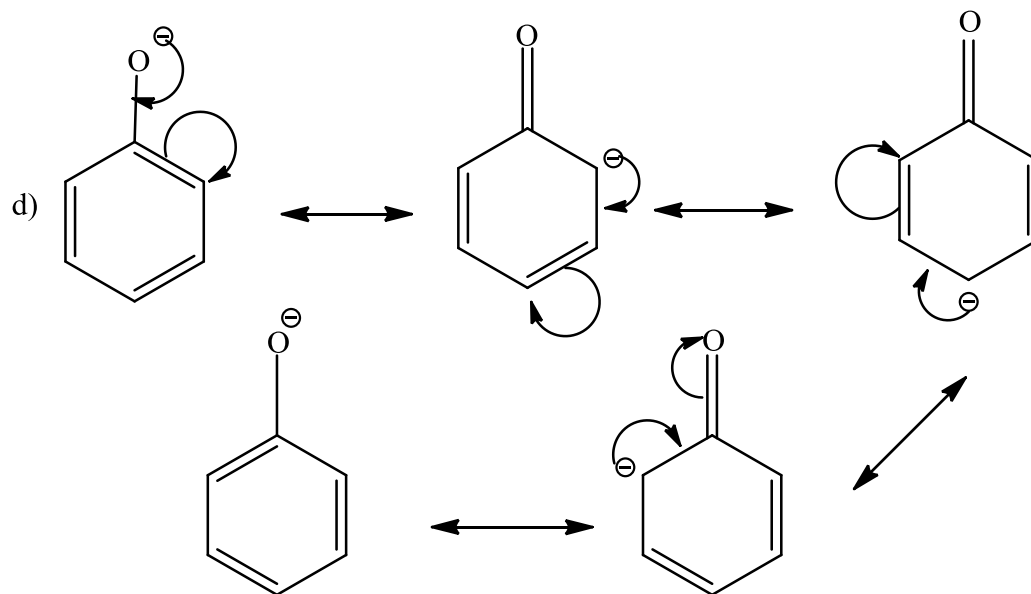
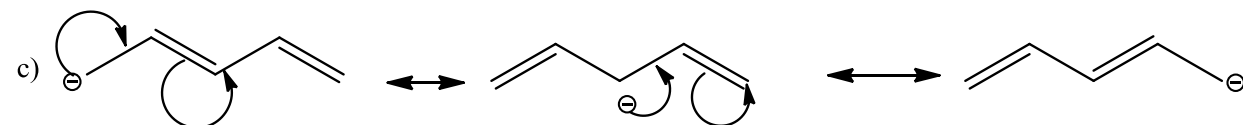
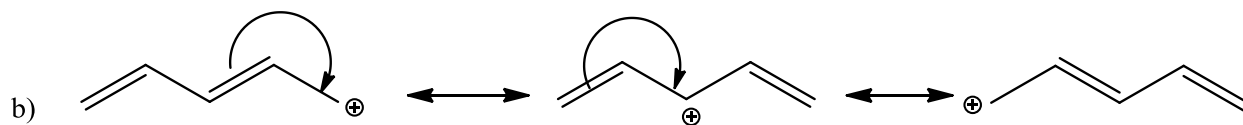
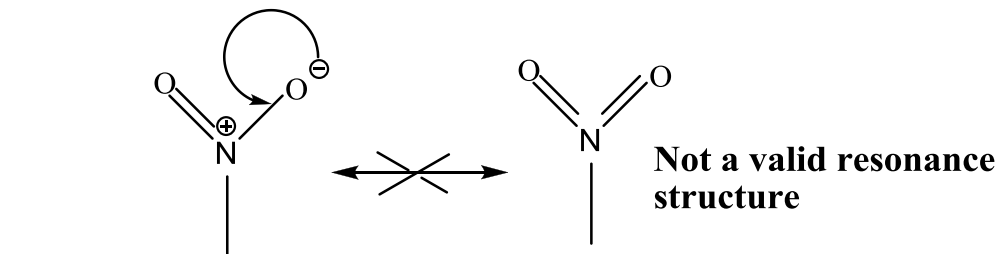
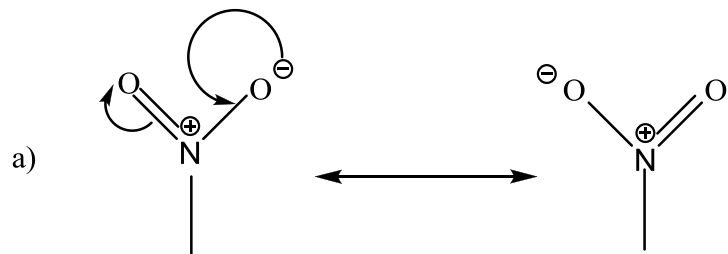


Note: Ph is 

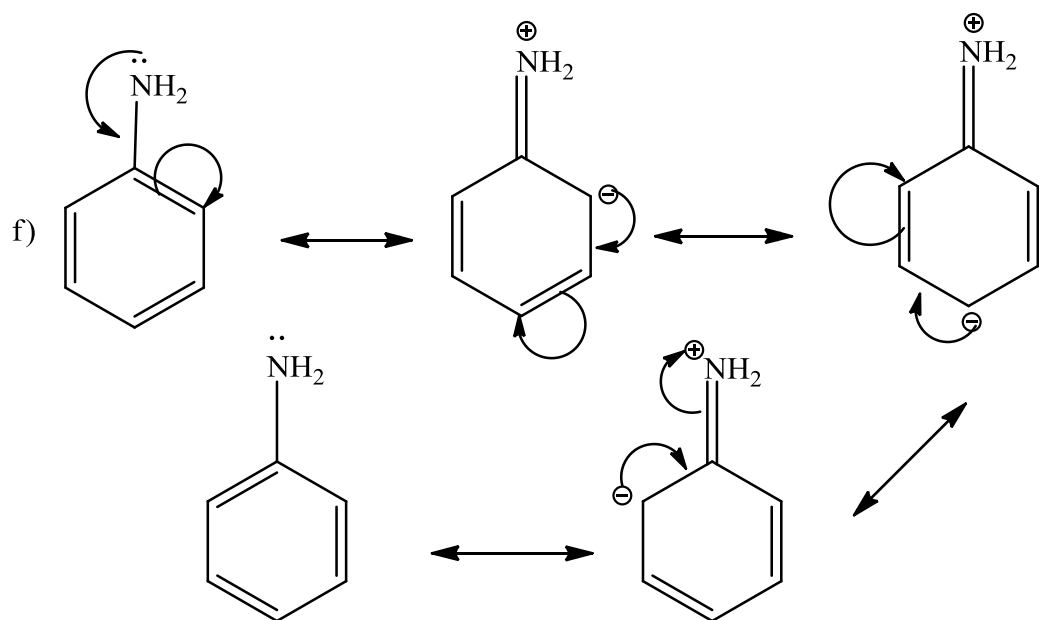
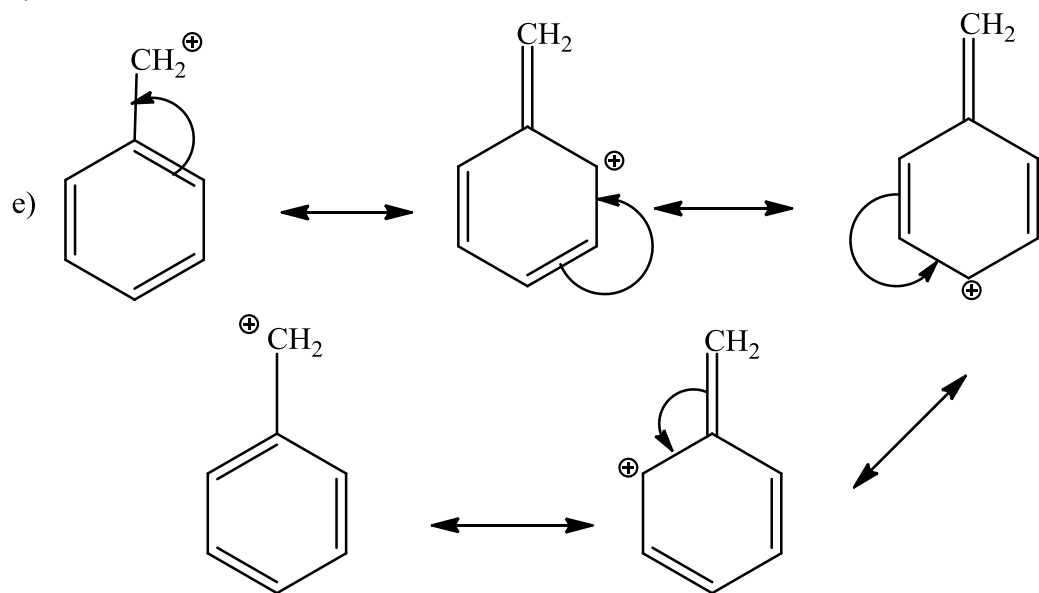


SOLUTIONS TO SAMPLE PROBLEMS:

1.1



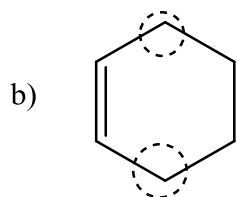
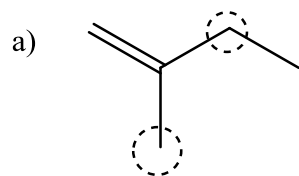
1.1



1.2 Arrows a) and c) are good. Arrows b), d), e) and f) are bad.

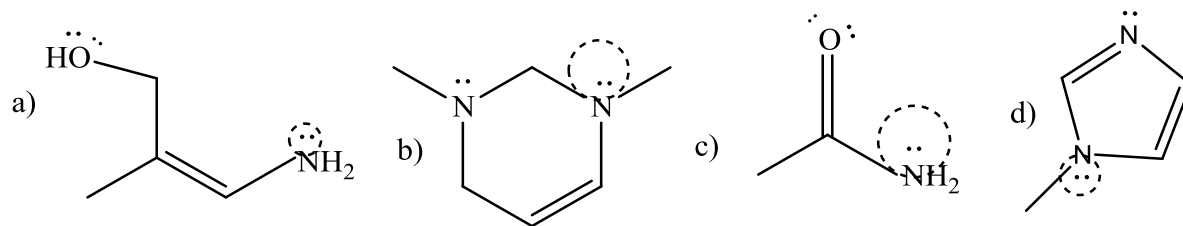
1.3 Resonance structure on the right is insignificant in each pair.

2.1 Circled positions are allylic:



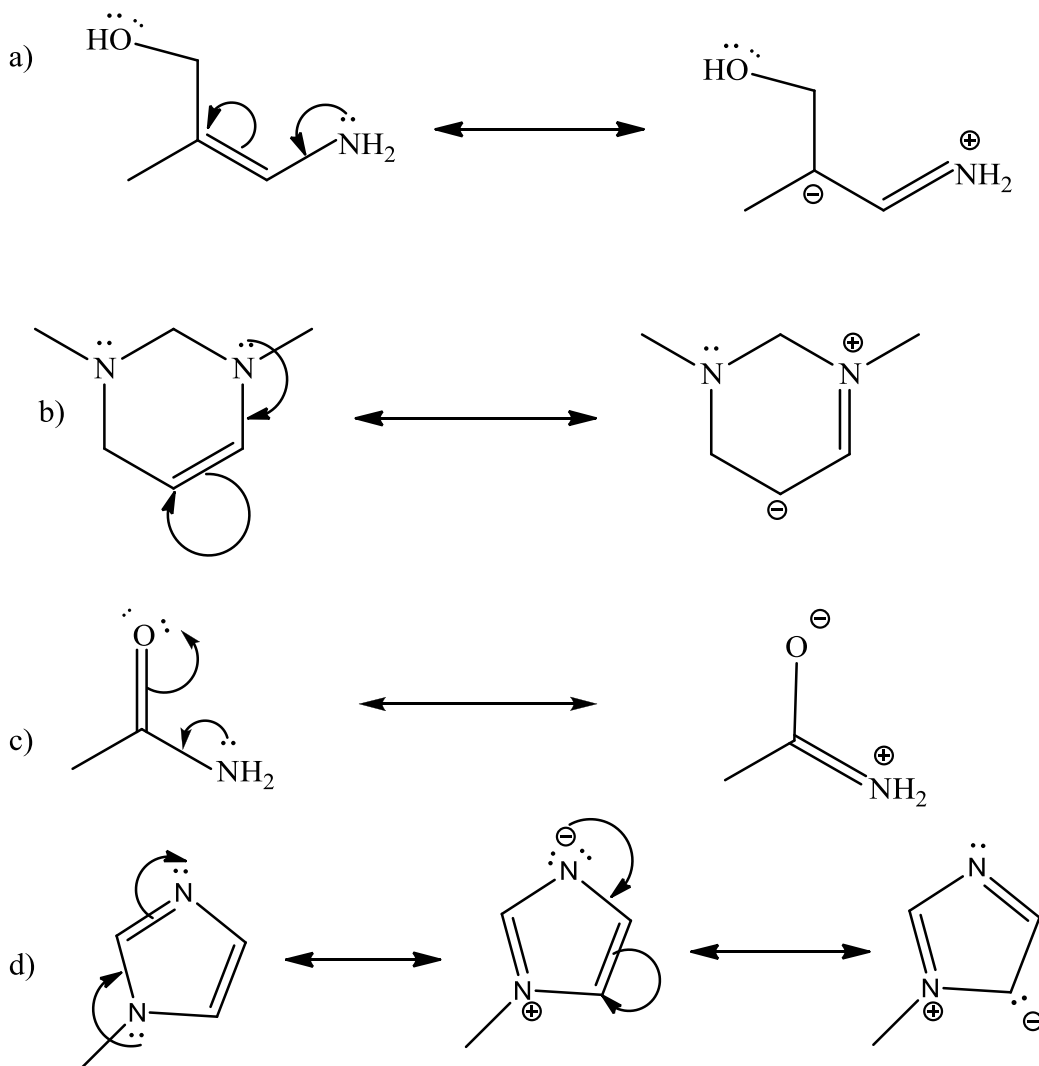
2.2 Structure a) has two vinylic hydrogens; structure b) has two vinylic hydrogens.

2.3 Delocalized lone pairs of electrons are circled. Circled lone pairs in a), b) and d) are allylic.



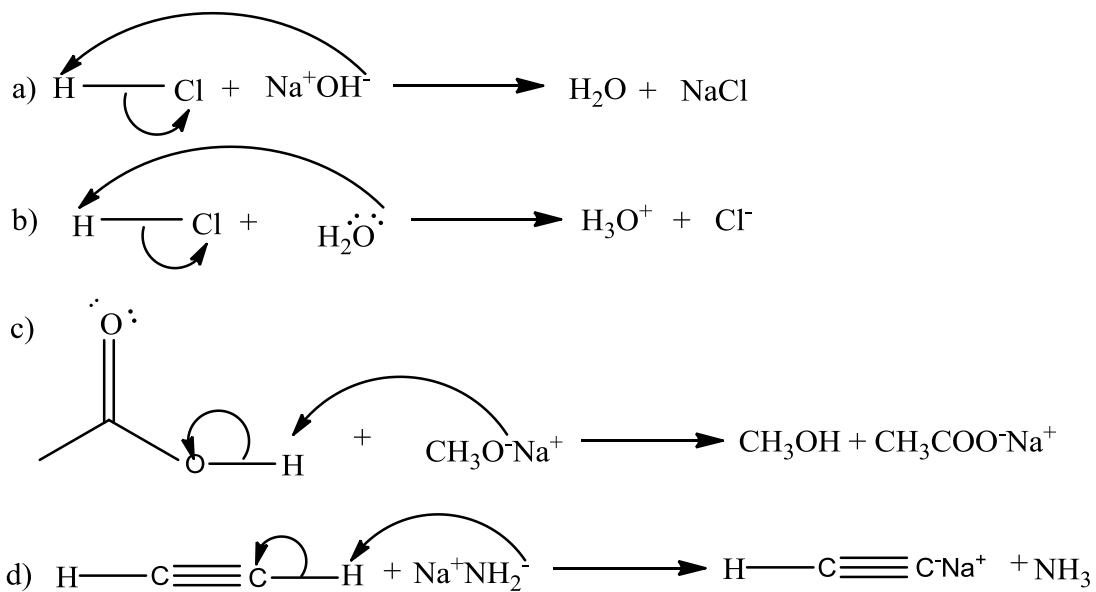
Note that in structure d) the lone pair on the second nitrogen appears to be allylic, however that nitrogen already has a double bond, so the lone pair occupies a perpendicular orbital, and therefore cannot be delocalized and participate in resonance, as the orbital of the π -bond already does.

2.4

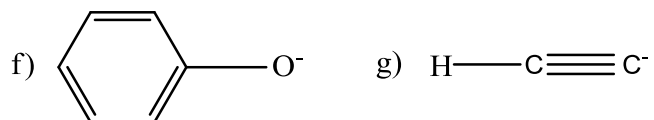


Also see the solution to 1.1 f, which shows delocalization of the lone pair on the nitrogen atom.

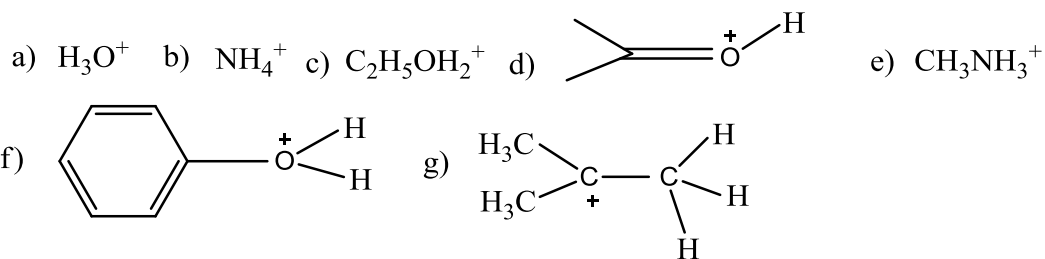
3.1



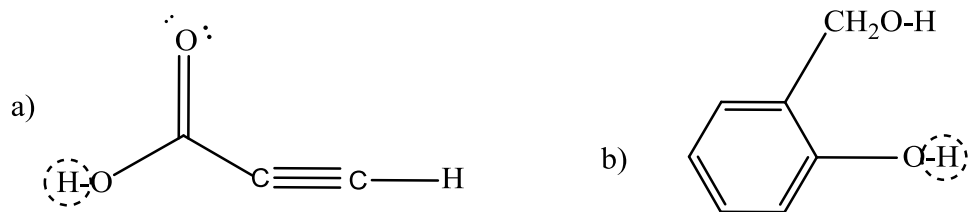
3.2



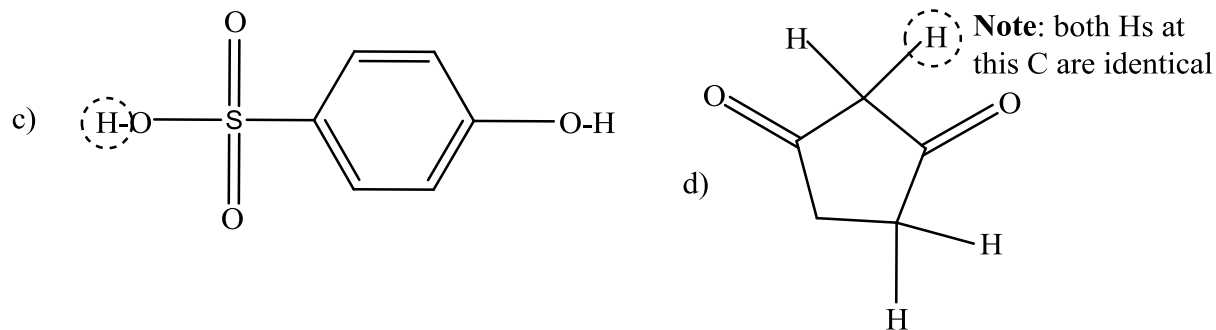
3.3



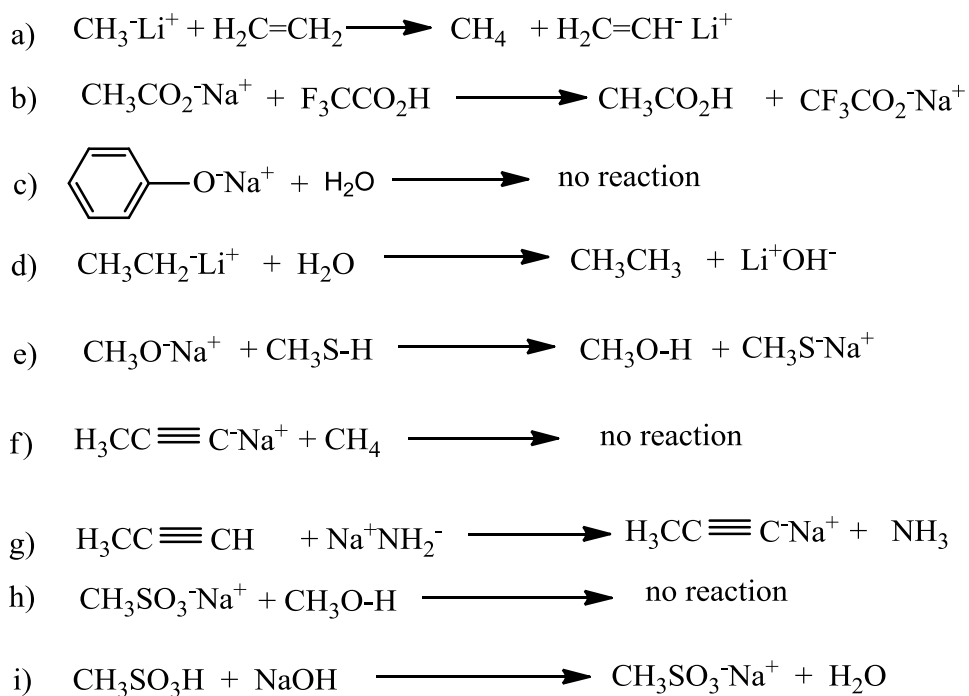
3.4



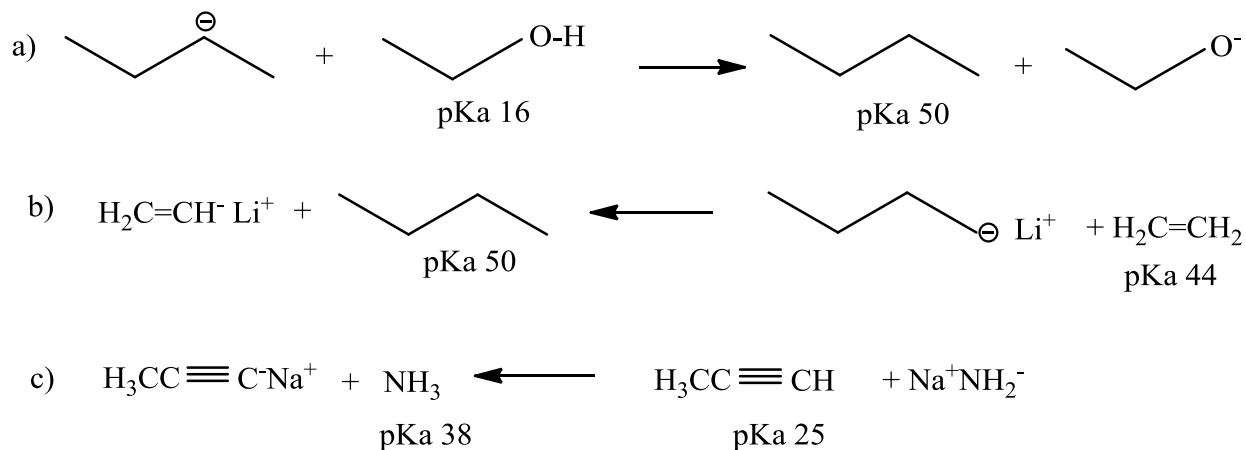
3.4



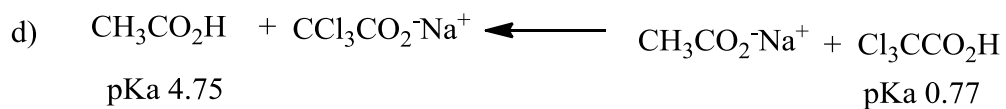
4.1



4.2 Equilibrium always favors a weaker acid (greater pKa) and weaker base. There is no need to check both acids and bases. Checking only acids or only bases is enough.



4.2



4.3

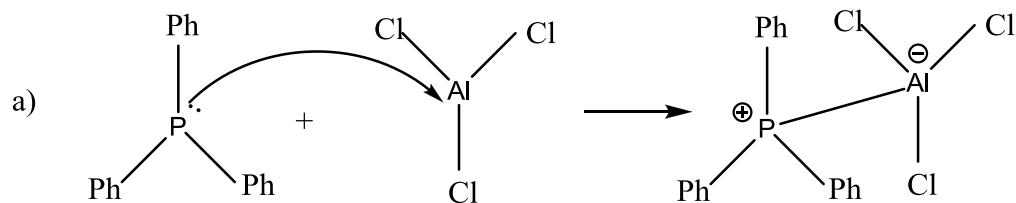
a) No, because hydroxide is a weaker base than $\text{H}_2\text{C}=\text{CH}^-$

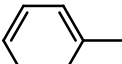
b) Yes, because hydroxide is a weaker base than amide.

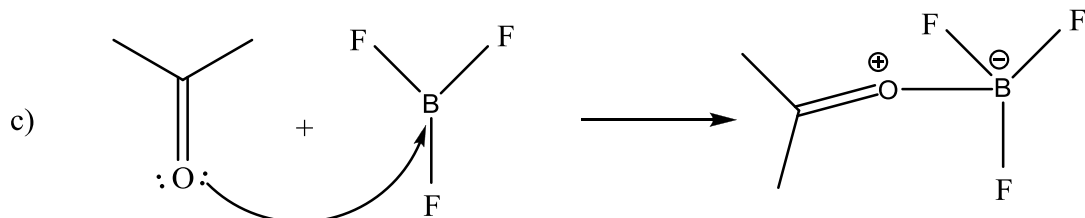
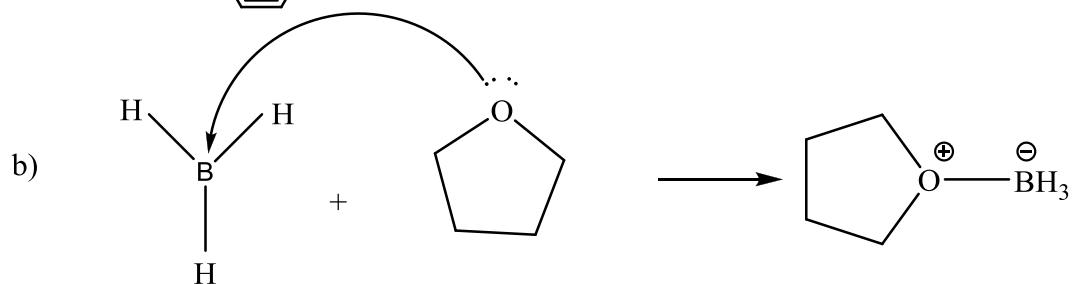
c) Yes, because hydroxide is a stronger base than phenolate (PhO^-)

d) No, because stronger base cannot be produced

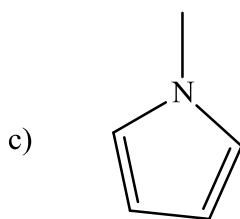
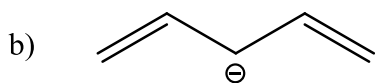
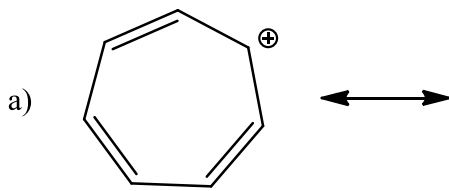
5.



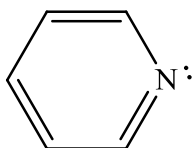
Note: Ph is 



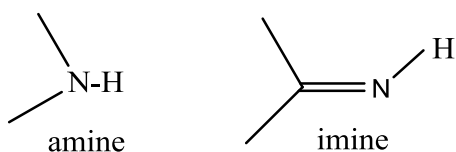
1. Using curved arrows draw all resonance structures for each of the following. Where possible, indicate which of the structures is least significant and explain why. (Hint: you may want to label each atom first and keep all atoms in the same place in each structure).



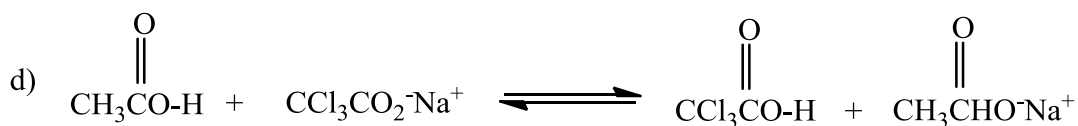
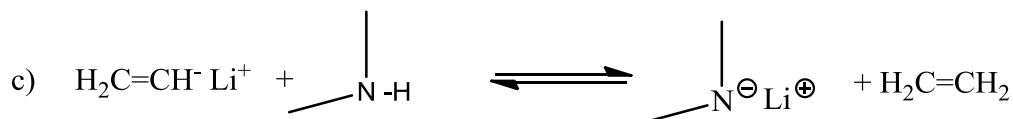
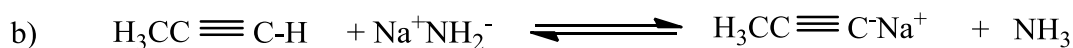
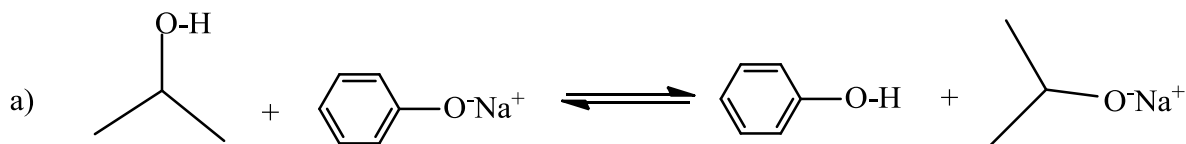
2. The electron pair on nitrogen in pyridine appears to be allylic. However it is not delocalized. Explain why. Hint: consult your textbook, Chapter 2.



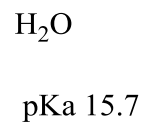
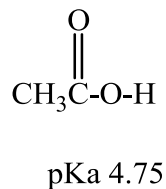
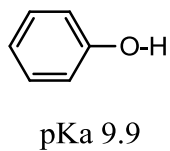
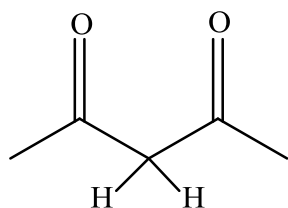
3. Amines contain single C-N bonds, and imines contain double C=N bonds. Based on factors that affect the stability of a negative charge predict which conjugate base will be stronger. Explain your prediction. Hint: first draw both conjugate bases, then analyze the difference between them.



4. Predict the position of the equilibrium in the following reactions. Show with curved arrows how the base deprotonates the acid to form products according to your conclusion about the equilibrium position.



5. You are assigned to deprotonate a compound **A** using one of the available bases: sodium phenolate ($\text{PhO}^- \text{Na}^+$), sodium hydroxide (NaOH), and sodium acetate ($\text{CH}_3\text{COO}^- \text{Na}^+$). Based on the following pK_a data, identify which of the bases you could use to complete the task. (Hint: the weakest acid produces the strongest conjugate base). Write the corresponding acid-base reaction and show with curved arrows how the base would deprotonate compound **A**.

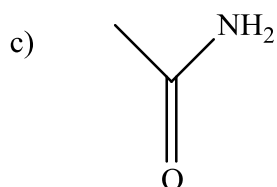
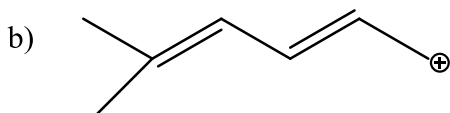
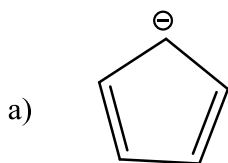


Compound A pK_a 9

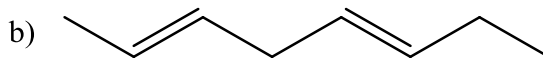
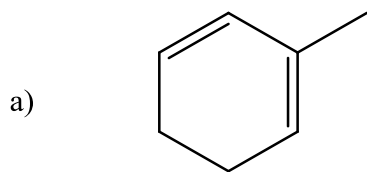
6. Use curved arrows to derive products of the following Lewis acid-base reactions. Draw the products and make sure to show charges where they belong.



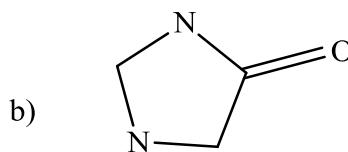
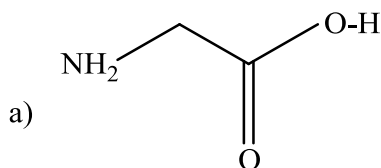
1. Using curved arrows draw all resonance structures for each of the following. Where possible, indicate which of the structures is least significant and explain why. (Hint: you may want to label each atom first and keep all atoms in the same place in each structure).



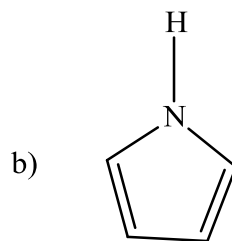
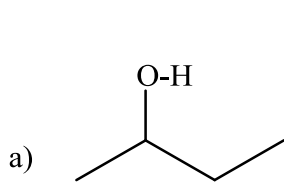
2. How many allylic hydrogens do the following structures have? Show them on the structures.
How many vinylic hydrogens are there in the following molecules? Show them in a separate picture.



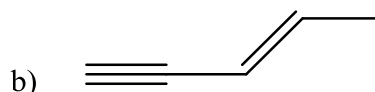
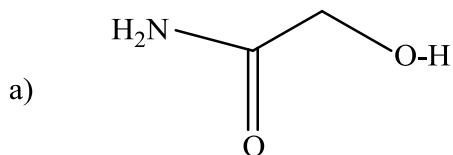
3. Find delocalized electron pairs in the following structures and show with arrows how each one can be delocalized. Draw corresponding resonance structure(s):



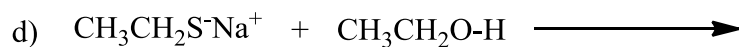
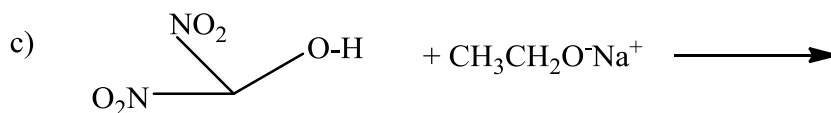
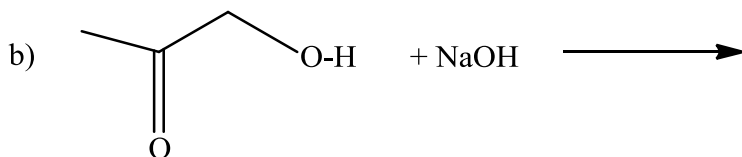
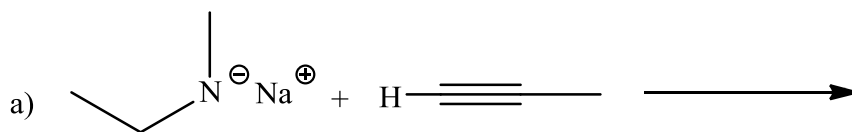
4. Draw conjugate acids and conjugate bases for the following compounds:



5. Identify the most acidic hydrogen in each of the following molecules:



6. Use curved arrows to derive products of the following acid-base reactions or indicate where there will be no reaction.



7. Label Lewis acids and Lewis bases among the following compounds:

