CHM 2120 – Assignment #1
ANSWERS

Additions/corrections:

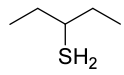
- Question 4 now includes hybrid resonance structures

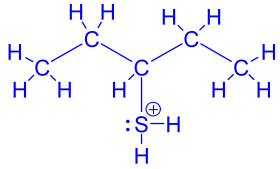
In this assignment:

- Lewis structures, formal charge
- Electronegativity, dipoles
- Resonance
- Acid/base

1. Draw the following molecules as full Lewis structures. Many molecules below possess a charge that is not shown—calculate the formal charge on each atom and indicate the location of the charge where applicable.

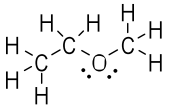
   Hint: each atom has a full octet, so start by adding electrons to each atom to complete its octet. The only atoms we will encounter in this course that lack an octet are carbon (a carbocation lacks an octet) and metals (B, Al, Mg, Li, etc).

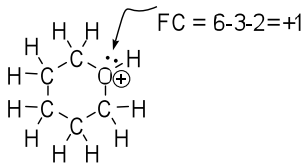
example: 

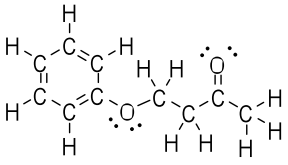


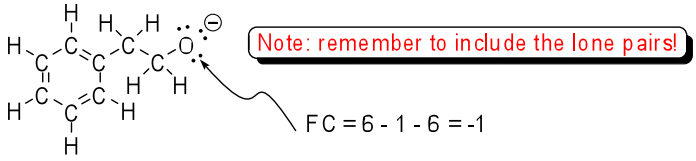
Formal charge (FC) = # valence electrons in neutral atom - # bonds - # lone electrons

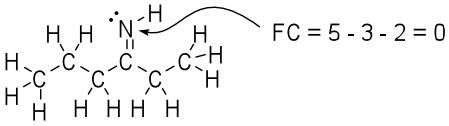
For the carbons: FC = 4 - 4 - 0 = 0 (the carbons are all neutral in this molecule)
For the sulfur: FC = 6 - 3 - 2 = +1 (so a "+" is placed beside the S)

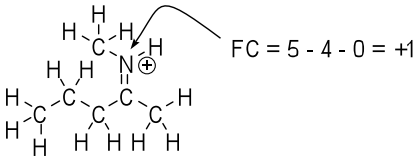
a) 

b) 

c) 

f) 

g) 

h) 

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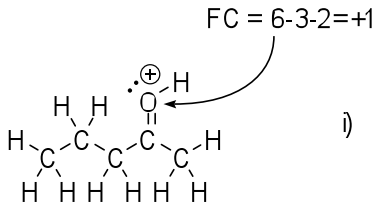

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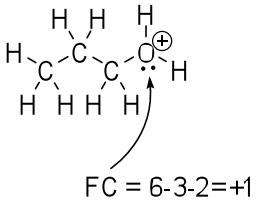
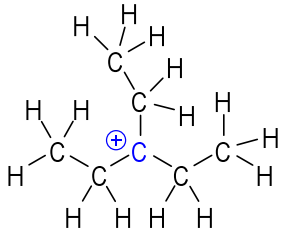
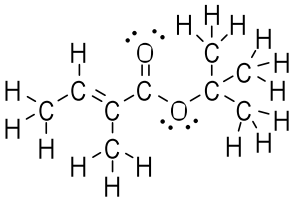


i)

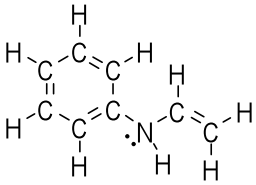


j)



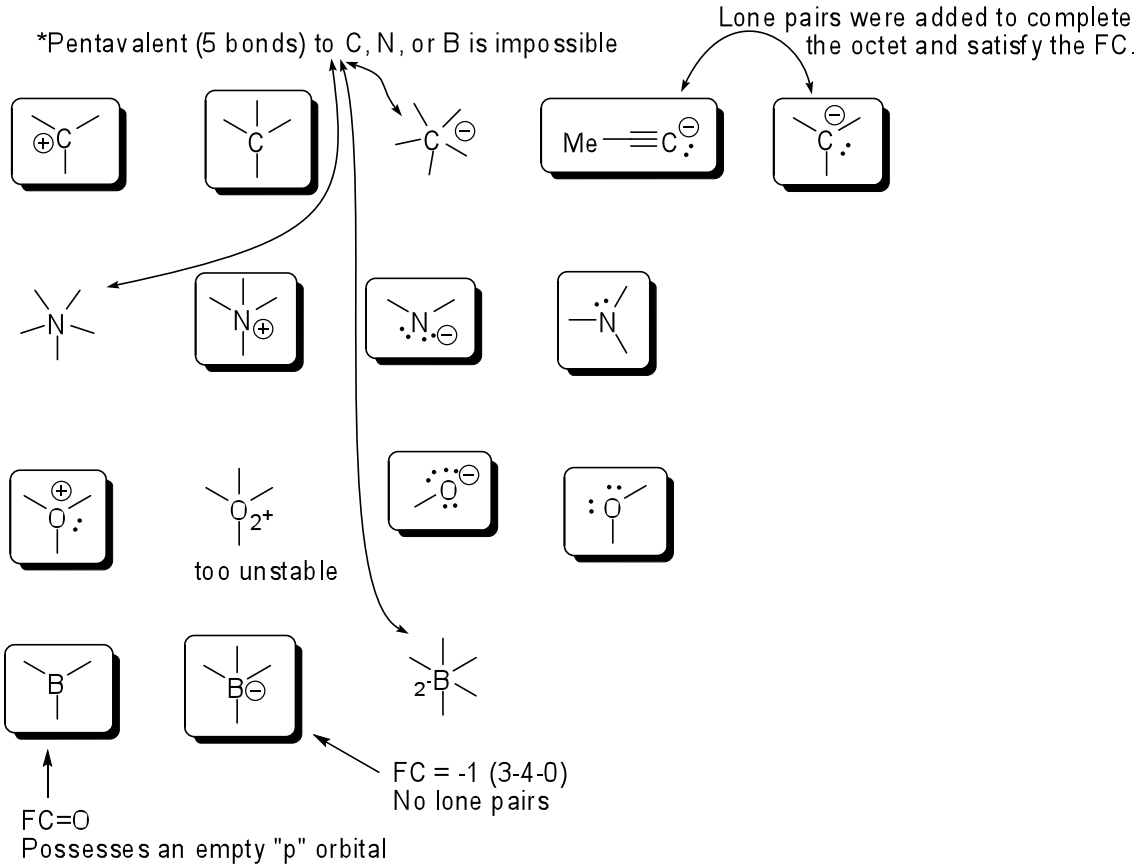
all atoms are neutral

k)



all atoms are neutral

2. Circle the plausible structures and put an "X" through the impossible structures below:



3. For the following bonds,
   a. Show the direction of the dipole moment using two methods.
   b. Is the bond ionic or polar covalent?

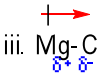
Example: C-H

$\overset{\delta^-}{C}-\overset{\delta^+}{H}$ Method 1: δ^- and δ^+ indicate PARTIAL negative and PARTIAL positive charges; the formal charge of each atom is ZERO.

$\longleftarrow\!\!+$ Method 2: an arrow points toward the more electronegative atom; there is a "+" sign at the base of the arrow, under the more electropositive atom

i. 

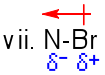
ii. 

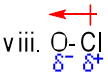
iii. 

iv. 

v. 

vi. 

vii. 

viii. 

ix. 

x. 

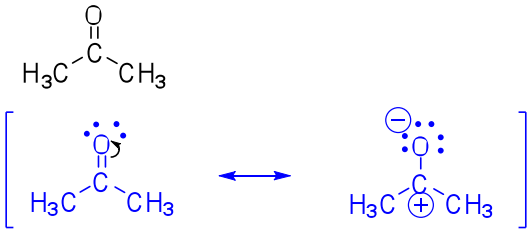
xi. 

All the bonds are polar covalent with the exception of the Li-O bond (ionic).

4. For the following molecules:
    a. Draw the important resonance forms using arrows to show the movement of electrons
    b. Identify the major, minor, and intermediate resonance structures, and explain your choices.
    c. Draw the hybrid structure.

Note: when identifying and explaining major, minor, and intermediate resonance structures, apply the criteria given in class IN ORDER. The explanation can stop as soon as you find a point of difference.

(a)

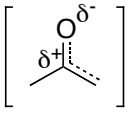


MAJOR
- all atoms have full octets

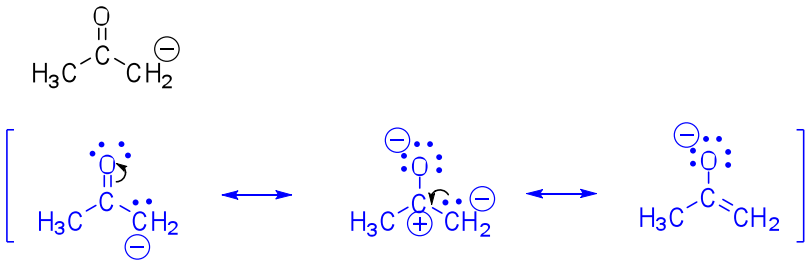
MINOR
- The C+ lacks an octet

Note: an explanation about charges is unecessary since there is a difference between the two structures based on the first criteria (i.e. full octets = good)

Hybrid:



(b)

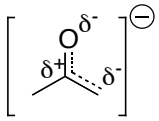


INTERMEDIATE
- all atoms have full octets
- The negative charge is on the least electronegative atom (not good)

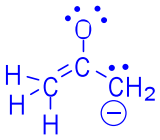
MINOR
- The C+ lacks an octet

MAJOR
- All atoms have a full octet
- The negative charge is on the most electronegative atom (good).

Hybrid:

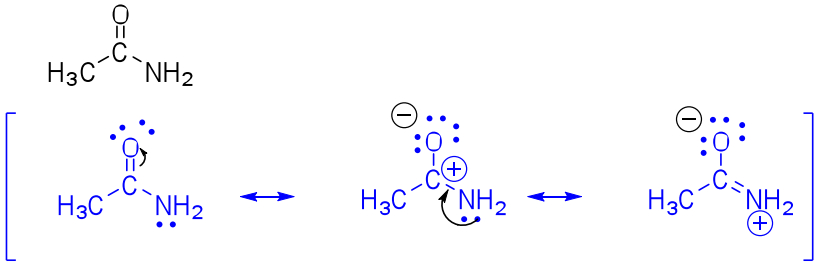


Note: Draw all atoms and lone pairs that are involved in electron movement (this will help avoid errors such as drawing pentavalent carbons):



Impossible structure: the CH_3 bears 5 bonds. This is physically impossible

(c)



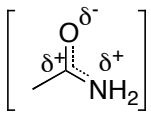
MAJOR
- All atoms have full octets
- No charges on the atoms (good)

MINOR
- The C+ lacks an octet

INTERMEDIATE
- All atoms have full octets

BUT
- Two atoms bear charges (bad)

Hybrid:



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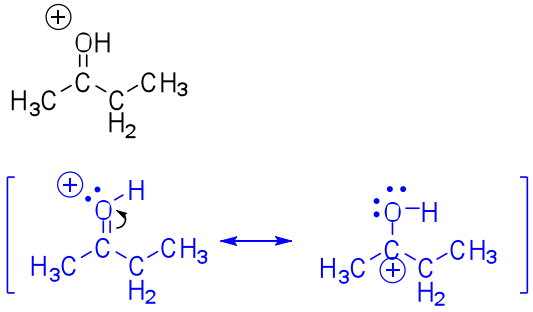
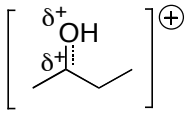


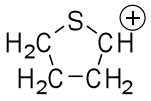
MAJOR
- All atoms have ful octets

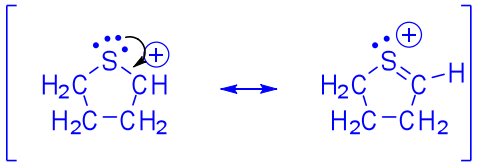
MINOR
- The C+ lacks an octet

Hybrid:



(e)

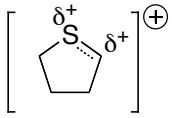




MINOR
- The C+ lacks a full octet (bad)

MAJOR
- All atoms have a full octet

Hybrid:



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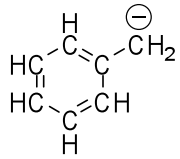
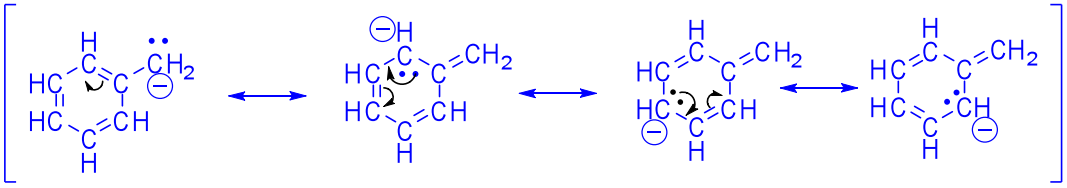
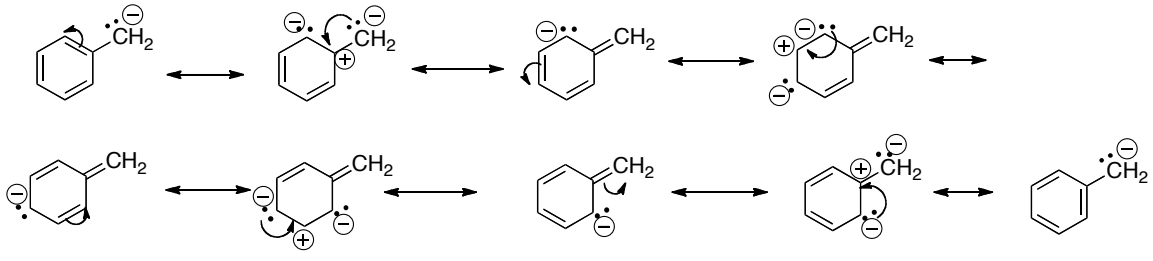


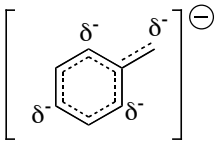


All roughly equivalent (all atoms have a full octet and the charge is always on a carbon

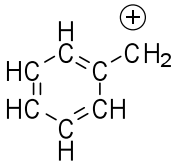
For aromatic molecules (benzene, etc), you can either draw just the major resonance structures (see above) or also include the minor structures (see below).

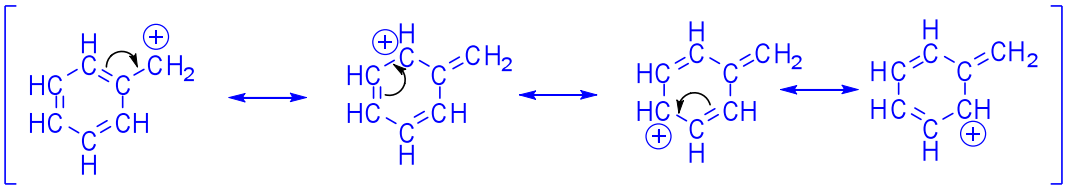


Hybrid:



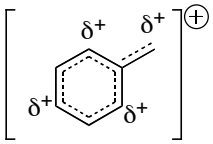
(g)





All roughly equivalent

Hybrid:



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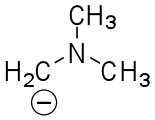
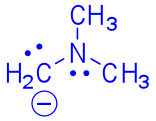
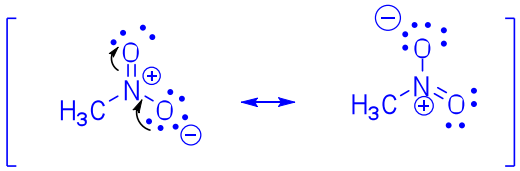




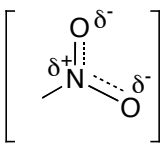
octets full - no resonance possible

(i) CH_3NO_2

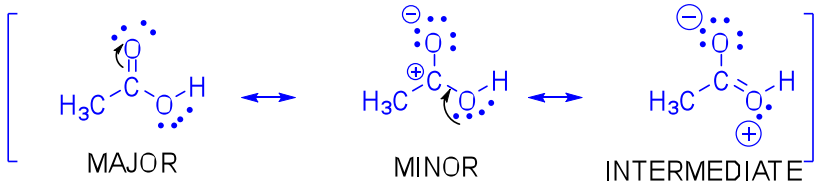


Equivalent

Hybrid:



(j) CH_3COOH

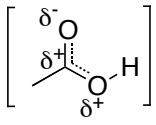


MAJOR
- All atoms have a full octet
- There are no charges (good)

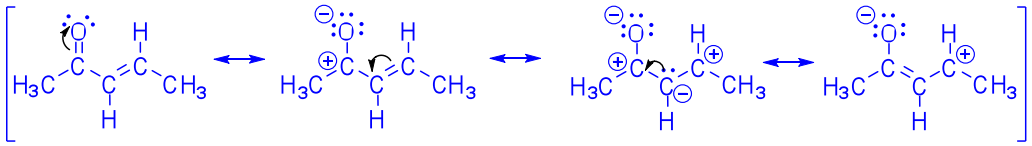
MINOR
- The C+ lacks a full octet (bad)

INTERMEDIATE
- All atoms have a full octet
- There are 2 charged atoms (less good)

Hybrid:



(k)



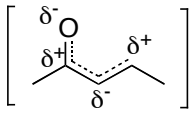
MAJOR
- All atoms have full octets

INTERMEDIATE
- The C+ lacks an octet
- Least separation of unlike (+ and -) charges (better than structure 4)

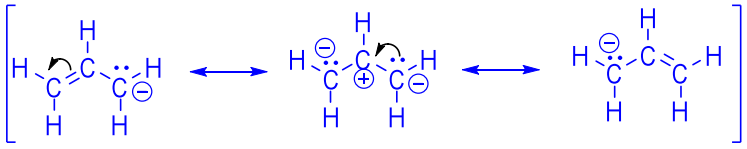
VERY MINOR
- 2 atoms lack octets

MINOR
- The C+ lacks an octet
- Most separation of unlike charges (bad)

Hybrid:



(l)

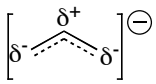


MAJOR
- all atoms have a full octet

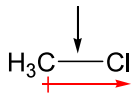
MINOR
- The C+ lacks an octet

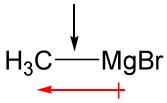
MAJOR
- all atoms have a full octet

Hybrid:

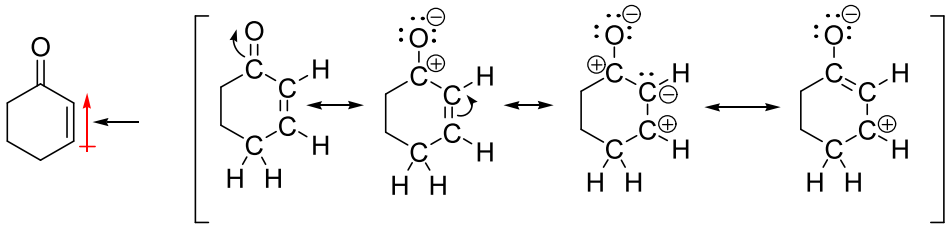


5. Draw the direction of the dipole in the indicated bonds in each of the following molecules.

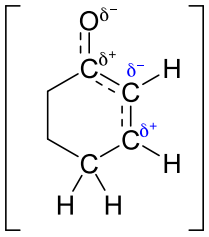
a) 

b) 

c)

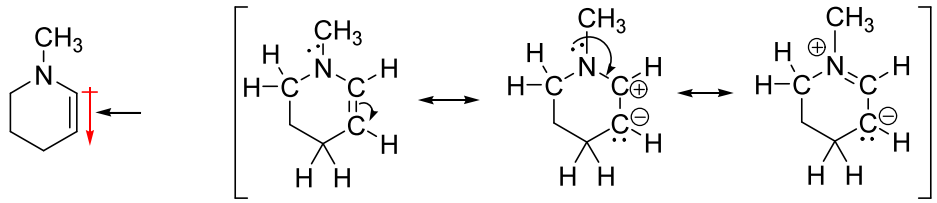


Resonance Hybrid:

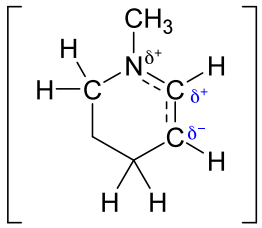


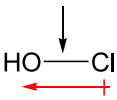
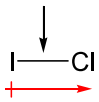
By drawing resonance structures, we can see where the partial charges reside in the molecule. The partial charges show the dipole of the C-C bond.

d)



Resonance hybrid:



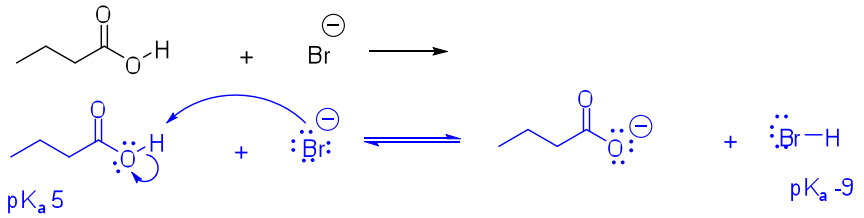
e)  f) 

6. Write equations for the following reactions using arrow notation. Predict whether the reaction will favor the starting materials or products and justify your choice.

Note: Either a comparison of the physical properties of the base and conjugate base OR the comparison of pKa strengths can be used for the explanation. If pKa strengths are used, you MUST quote the pKa values of the acid and conjugate acid to obtain full marks.

Note: A comparison of base strength can be done when comparing two identical atoms (i.e. part e or h) or two atoms of the same hybridization in the same row or in the same column of the periodic table (i.e. part b)

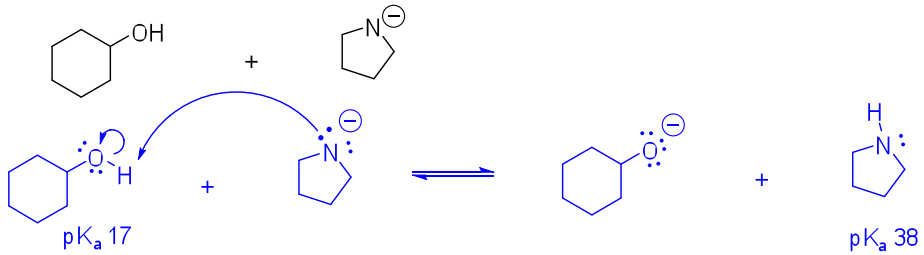
a)



Reaction will favor the starting materials

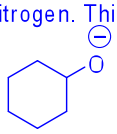
HBr is a much stronger acid than butanoic acid (HBr has a lower pK$_a$). This shifts the equilibrium to the left favoring the starting materials

b)

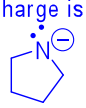


Reaction will favor the products

oxygen is more electronegative than nitrogen. This means that the negative charge is better stabilized on oxygen than on nitrogen. Therefore



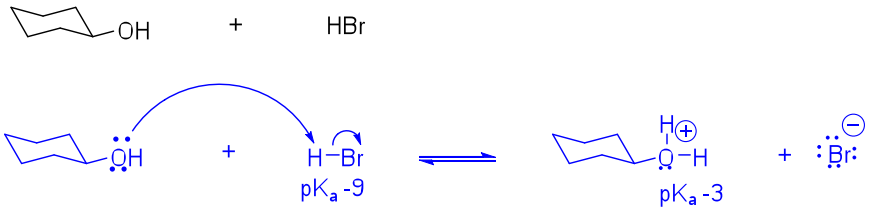
is a weaker base than



and so the reaction must favor the products.

An alternate explaination involves pK$_a$. R-OH (pKa ~17) is a stronger acid that R_2NH (pKa ~ 38) (ROH has a lower pK$_a$). Therefore the reaction will favor products.

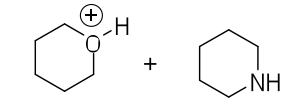
c)

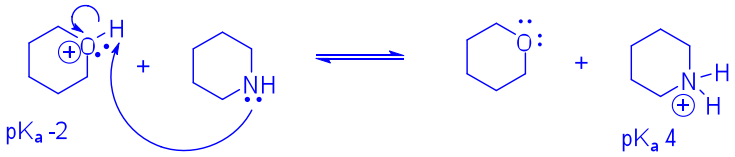


Reaction will favor the products

HBr is a much stronger acid than oxonium (HBr has a lower pK$_a$). This shifts the equilibrium to the right favoring the products

d)

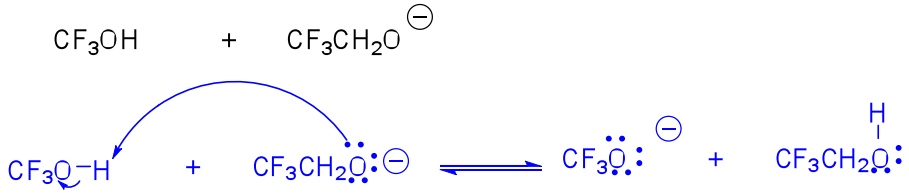




Reaction favors the products

Oxygen is more electronegative than nitrogen. Therefore positively charged oxygen will be less stable than a positively charged nitrogen. This means that a protonated oxygen compound like R_2OH^+ will be a stronger acid than the corresponding protonated nitrogen compound

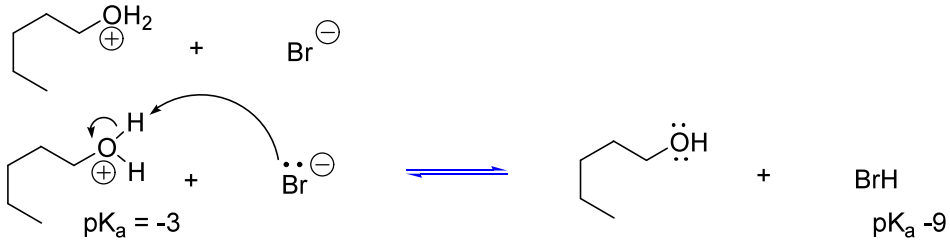
e)



Reaction favors the products

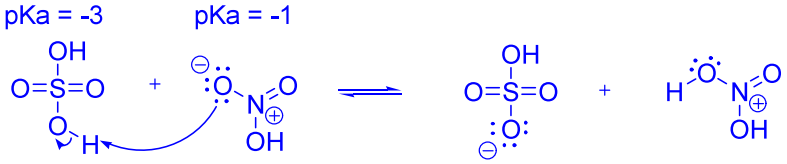
The fluorines are closer to the oxygen in CF_3OH than in CF_3CH_2OH. Therefore the inductive effect from the electronegative fluorines will be stronger for CF_3O- than for CF_3CH_2O-. This means that the negaitive charge on CF_3O- will be more stabilized by the inductive effect that the negative charge on CF_3CH_2O-. Because CF_3O- is more stable, the reaction will favor the products.

f)



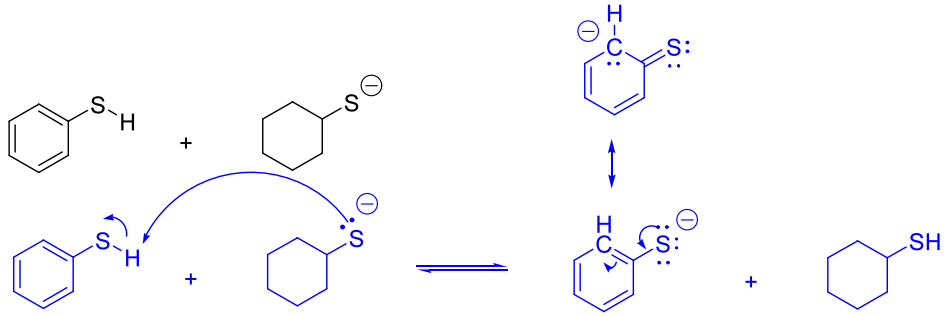
Reaction favors the starting materials
HBr is a stronger acid than the alcohol (pKa is lower). Therefore the equilibrium will be shifted to the left and the starting materials will be favored

g) Sulfuric acid and nitric acid are both strong acids. Which will act as the acid, and which will act as the base? Use pKa values to decide:



Sulfuric acid (pKa = -3) is a stronger acid than nitric acid (pKa = -1), so H_2SO_4 will act as the acid, and HNO_3 will act as the base.

h)



reaction favors the products

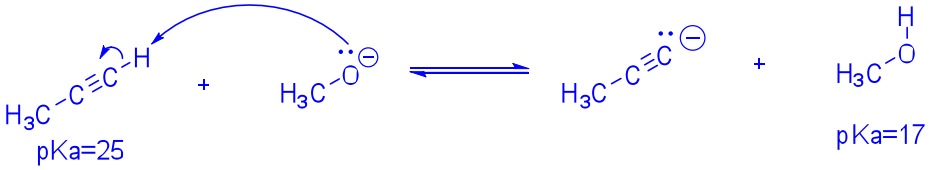
The anion in PhS^- is stabilized by resonance and is therefore a weaker base than the anion of cyclohexylthiol. This means that the acid in the starting materials is stronger than that in the products. This forces the reaction to favor the products.

Note: At least one resonance structure must be shown for full marks.

i) $CH_3CO_2^-$ + CF_3CO_2H

The conjugate base $CF_3CO_2^-$ is a weaker base than $CH_3CO_2^-$. This is because the CF_3 goup is a stong electron withdrawing group (inductive effect). This stabilizes the negative charge in $CF_3CO_2^-$ by dispersing the negative charge. This means that CF_3CO_2H is the strongest acid and therefore this equilibrium will lie towards the products.

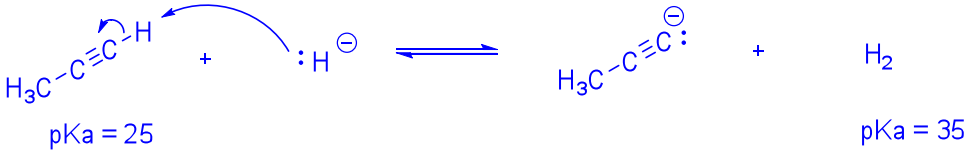
j)



The equilibrium will lie to the left since methanol is a stronger acid (lower pKa) than propyne.

The moral of the story? Methoxide cannot be used to deprotonate a terminal alkyne

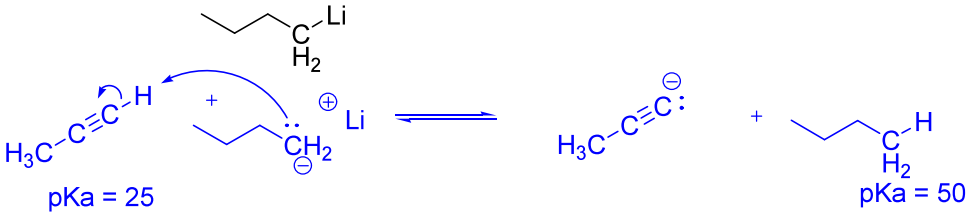
k)



The equilibrium lies to the right since H_2 is a weaker acid (higher pKa) than propyne.

A hydride (like sodium hydride, NaH) can be used to deprotonate a terminal alkyne.

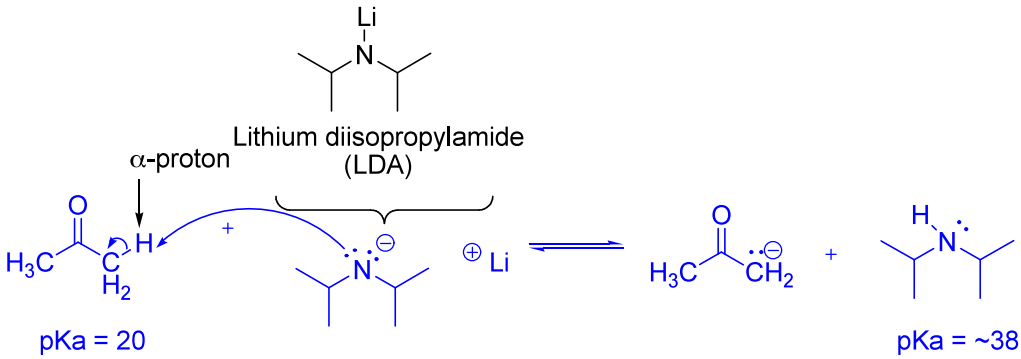
l)



The equilibrium lies to the right since n-butane is a weaker acid (higher pKa) than propyne.

n-butyl lithium can be used to deprotonate a terminal alkyne.

m)



The equilibrium lies to the right since diisopropylamine is less acidic (higher pKa) than the protons alpha (α) to a ketone.