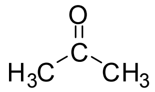
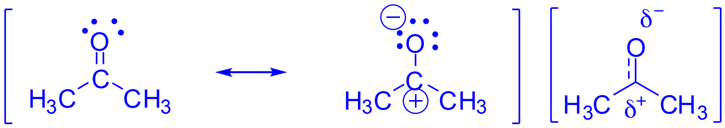
CHM 1321
Problem set 6 Answers

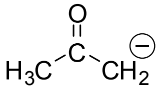
1) Draw the important resonance forms and show the resonance hybrid structures for the following:

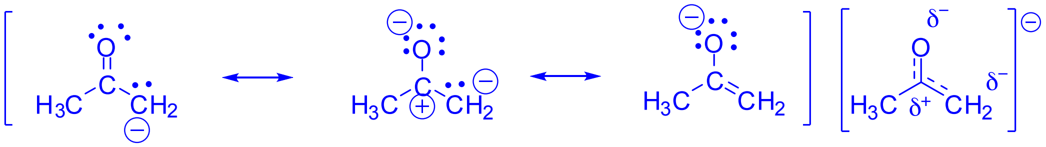
(a)



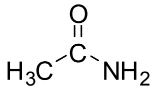


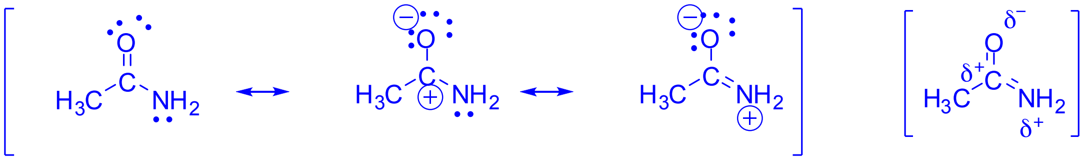
(b)



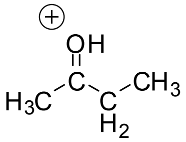


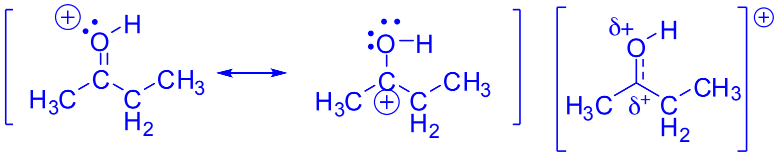
(c)



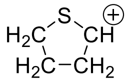


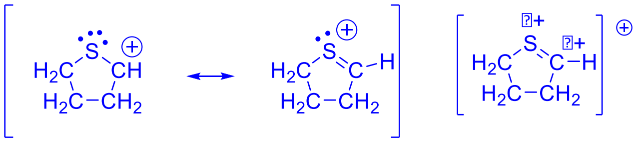
(d)



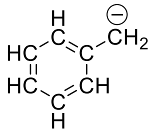


(e)

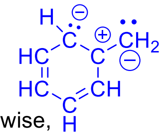


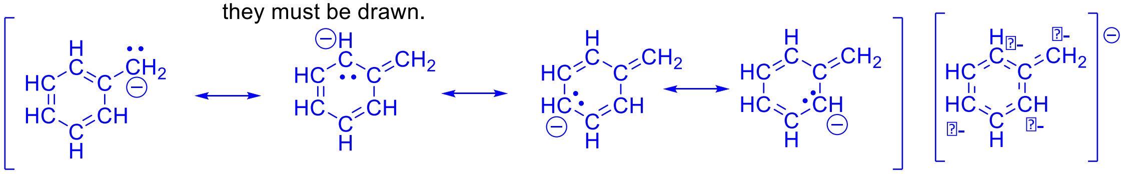


(f)

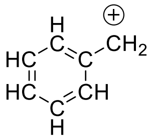


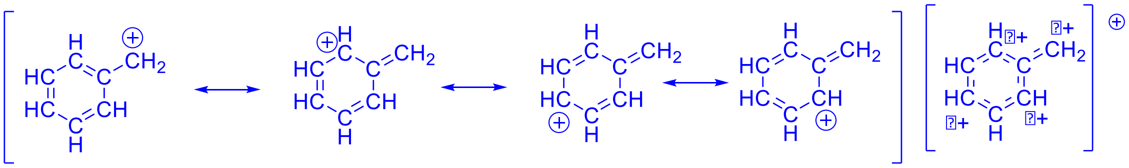
Note: the very minor resonance structures such as: have not been shown in order to simplify the answer. Only in questions such as this (more than 3 double bonds) can you omit the very minor structures. Otherwise, they must be drawn.



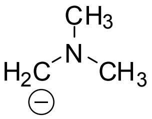


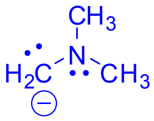
(g)





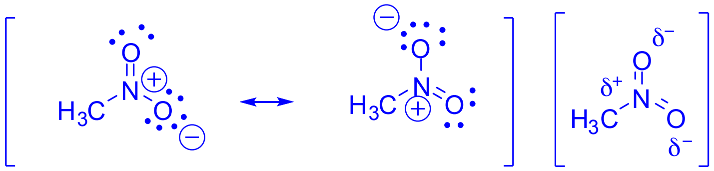
(h)



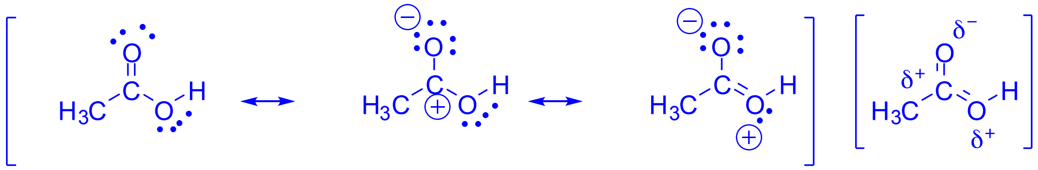


octets full - no resonance possible

(i) CH_3NO_2

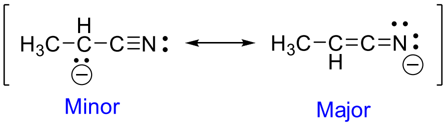


(j) CH_3COOH



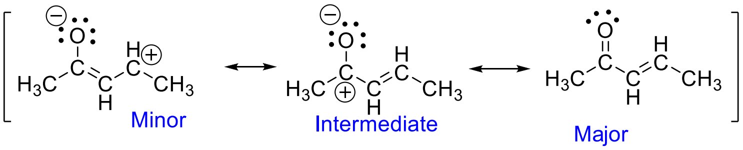
2) For the following resonance forms, label the major and minor resonance forms, and show which ones are of equal energy. Justify your choices.

(a)



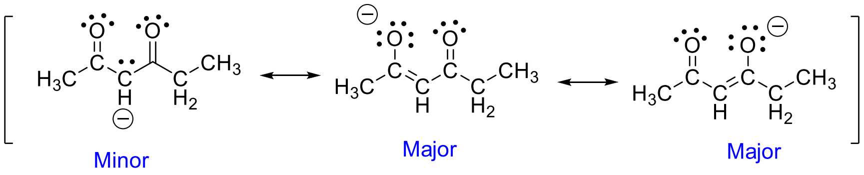
All atoms have a full Octet and have the same number of charges. In the second structure, the negative charge is located on the more electronegative atom.

(b)



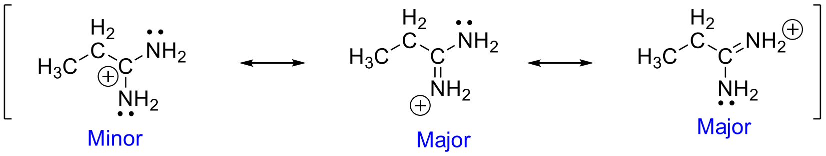
In the Major resonance structure, all atoms have a full octet.
In the minor and intermediate resonance forms, one carbon is lacking an octet.
In the intermediate and minor resonance structures, there is the same number of charges and the negative charge is on the most electronegative atom. In the intermediate structure has less separation between opposite charges than does the minor structure.

(c)



All atoms in all structures have a full octet and have the same number of charges.
In the Major (2 equivalent) resonance forms, the negative charge resides on the more electronegative oxygen atom.
In the Minor resonance form, the negative charge resides on the less electronegative carbon.

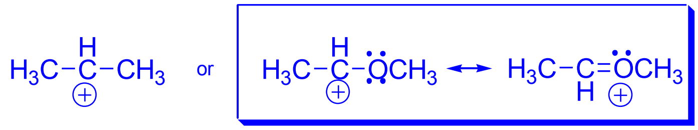
(d)



In the Major (2 equivalent) resonance forms, all atoms have an octet (this criterion overides having a positive charge on a more electronegative atom).
In the minor resonance form, the positively charged carbon atom (carbocation) is lacking an octet.

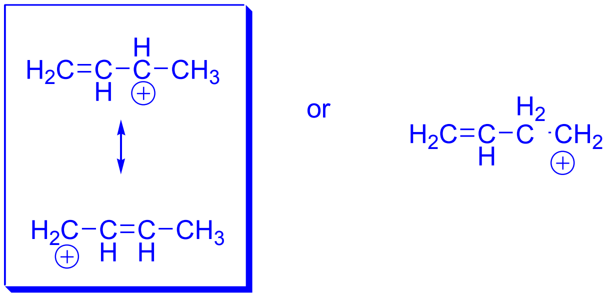
3) For each pair of ions, determine which is more stable. Justify your answer in each case.

a)



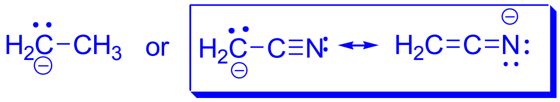
Delocalization with the lone pairs of the oxygen stabilizes the second compound.

b)



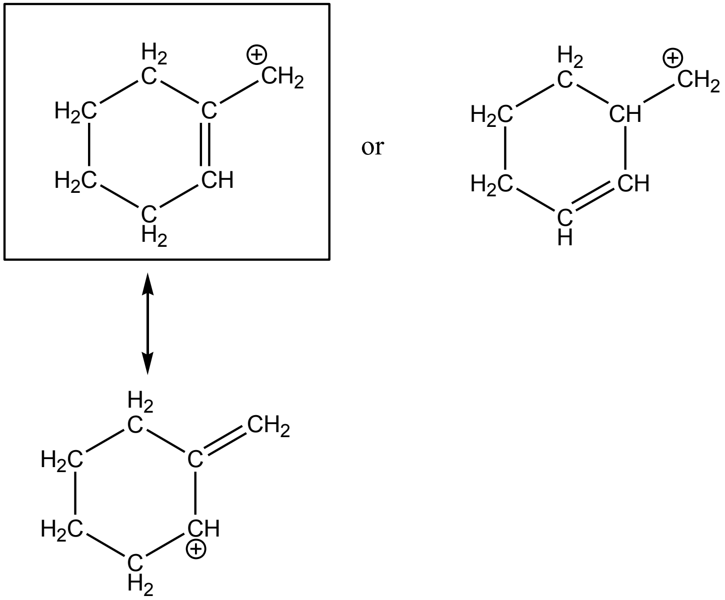
Delocalization with the electrons in the double bond stabilizes the first compound. In the second compound, the double bond is too far away. The CH_2 carbon has no lone pairs to donate to the positively charged carbon.

c)



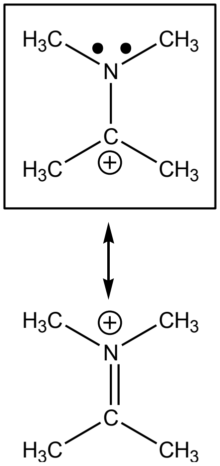
Delocalization with the lone pairs of the nitrogen stabilizes the second compound.

d)

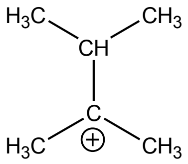


Delocalization with the electrons in the double bond stabilizes the first compound. In the second compound, the double bond is too far away. The CH_2 carbon has no lone pairs to donate to the positively charged carbon.

e)

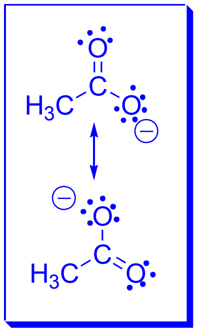


or



Delocalization with the lone pairs of the nitrogen stabilizes the first compound.

f)

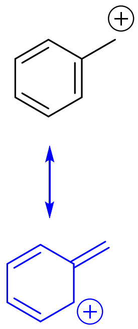


or

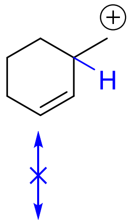
CH_3CH_2O

Delocalization with the lone pairs of both oxygens stabilizes the first compound.

(g)



or

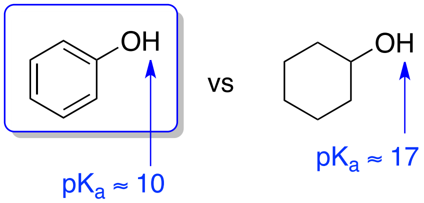


Many resonance structures (at lease one must be shown) help to stabilize the positive charge

No resonance possible through the sp^3-hybridized atom

4) For the following pairs of compounds, predict which one will be the strongest acid and justify your choice. Hint: Use table 3.1 (Solomons) to justify your choices. This table is also available in the content section of the virtual campus site under Required downloads.

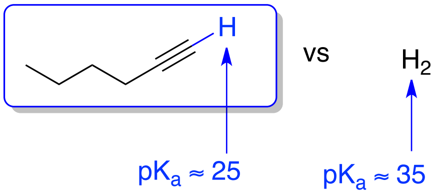
(a)



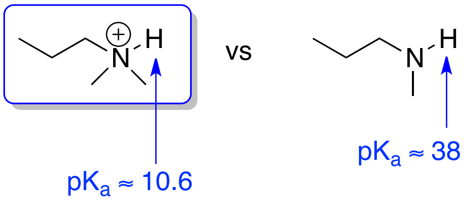
Explanation (not required as part of your answer; only the above would be for this question): to answer this type of question,

- **First identify the most acidic proton in each molecule**.
    - For example, in the phenol (molecule on left), there are alkene protons which have pK_as of approximately 44 (find the most similar functional group in the table. Alkene protons are listed under $CH_2=CH_2$) and there is the phenolic proton (alcohol on benzene ring) with a pK_a of approx. 9.9 (see C_6H_5OH). The phenolic proton has the lowest pK_a and so is therefore the most acidic proton in that molecule. For cyclohexanol, compare the alkyl protons (pK_a of ~50) with the alcohol proton (pK_a of ~17). The alcohol is most acidic.
- **Second, compare the most acidic protons on each molecule**.
    - In this case, compare the phenolic proton with pK_a of ~10 with alcoholic proton with pK_a of ~17.
- **Conclusion:** The phenol has the lowest pK_a and is therefore the strongest acid.

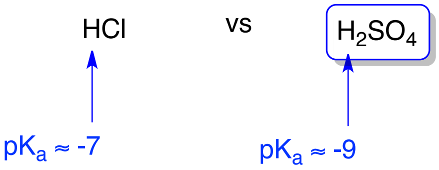
(b)



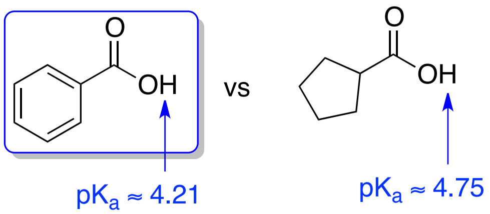
(c)



(d)



(e)



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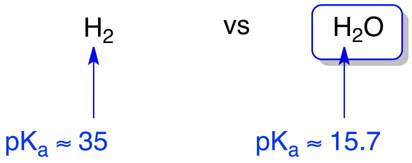

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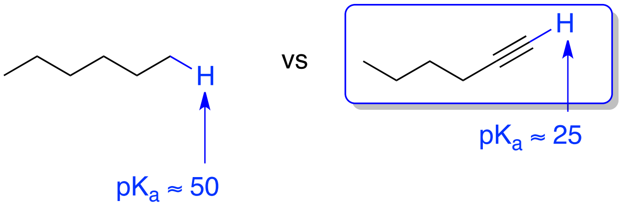
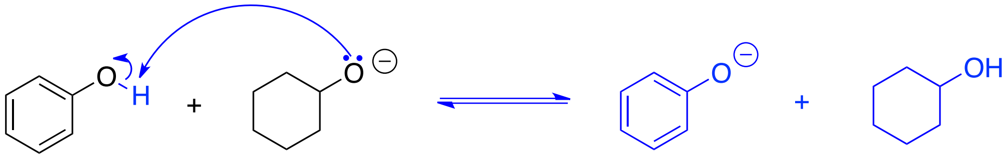


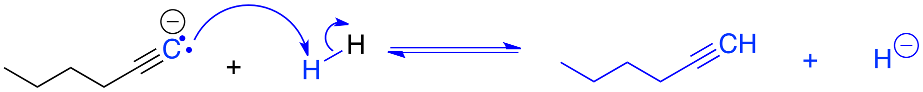
5) Draw the mechanism and products for each of the following reactions:

(a)

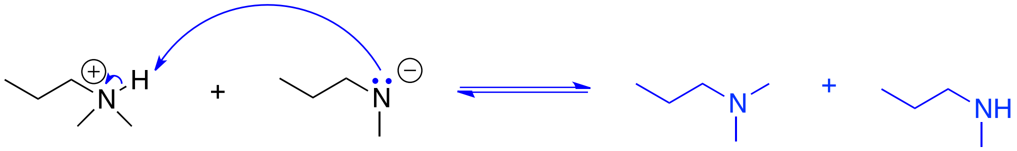


Note: as part of the mechanism, you must show all electrons involved in the reaction. For this case, that means that you would have to draw the lone pairs on the O- and the bond between the O and H in the starting materials.

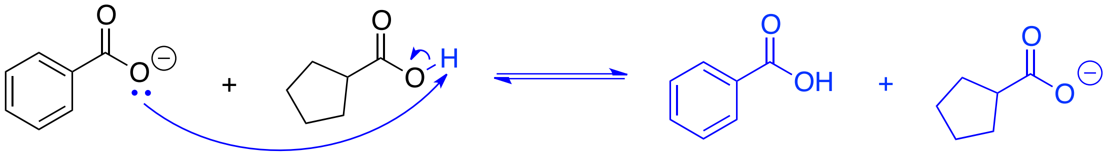
(b)



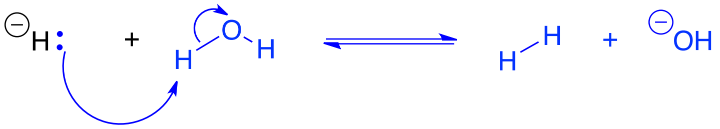
(c)



(d)



(e)



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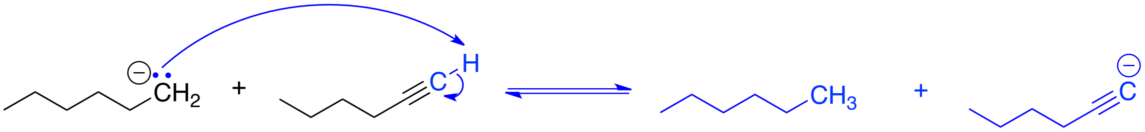
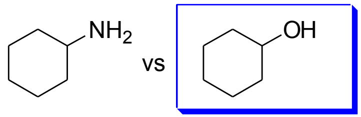
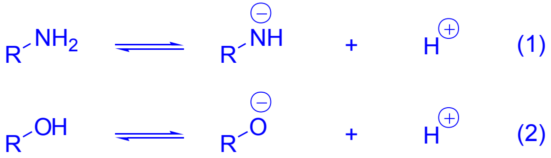


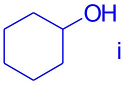
6) For the following pairs of compounds, predict which one will be the strongest acid and justify your choice.

a)



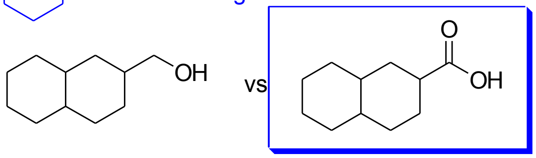


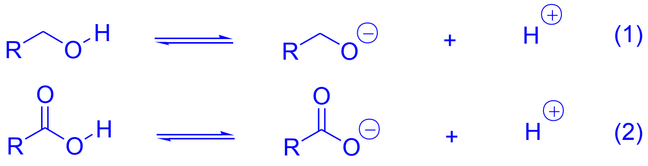
look at the conjugate bases:
-in equation 2 the atom bearing the negative charge is more electronegative than the atom holding the negative charge in equation 1. Therefore the negative charge will be more stabilized in the conjugate base of equation 2
-this means that this conjugate base will be more stable and a weaker base than the conjugate base in equation 1
- since the conjugate base in equation 2 is weaker, the corresponding acid will be stronger
So



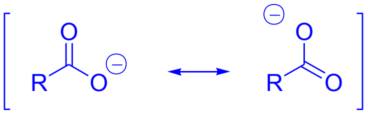
is the stronger acid

b)

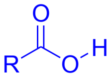




The conjugate base in equation 2 is stabilized by resonance.

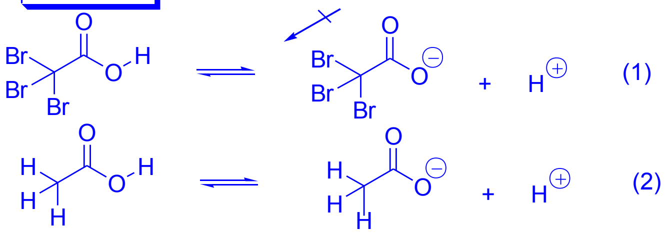


this conjugate base is more stabilized than that in equation 1, therefore this is the weaker conjugate base and

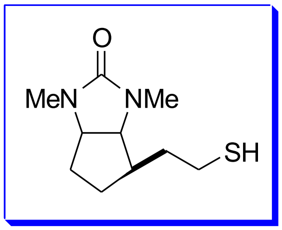


is the stronger acid

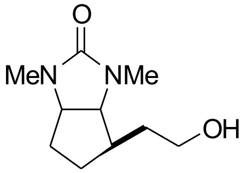
c) $\boxed{CBr_3CO_2H}$ vs CH_3CO_2H

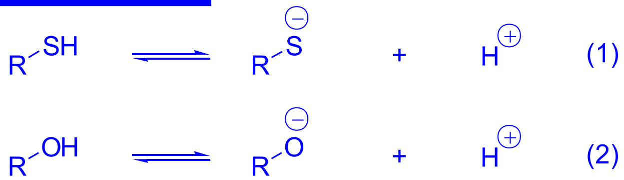


The bromines in equation 1 are more electronegative than the corresponding hydrogens in equation 2. The stronger electron withdrawing power of the bromines stabilize the conjugate base in (1) by the inductive effect. Since the conjugate base in (1) is more stable than in (2) it is a weaker base and therefore the acid in equation (1) is the stronger acid d)



vs



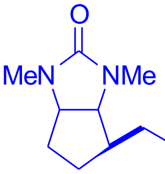


-in equation 1 the atom bearing the negative charge is larger (lower in the periodic table) than the atom holding the negative charge in equation 2. Therefore the negative charge will be more dispersed in the conjugate base of equation 1

-the dispersion of negative charge in the conjugate base in equation 1 results in better stabilization of the negative charge, therefore this conjugate base will be more stable and a weaker base than the conjugate base in equation 2

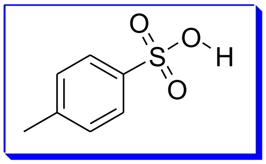
- since the conjugate base in equation 1 is weaker, the corresponding acid will be stronger

So

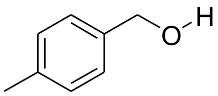


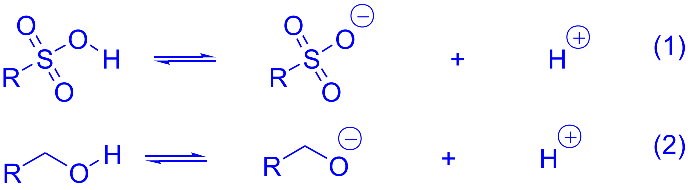
is the stronger acid

e)

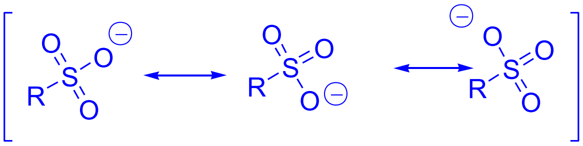


vs

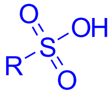




The conjugate base in equation 1 is stabilized by resonance

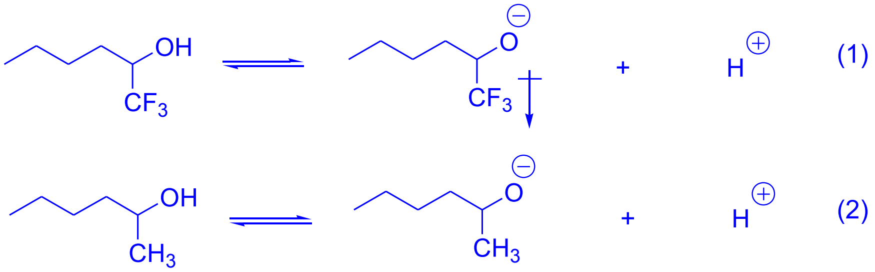


this stabilizes this conjugate base more than that in equation 2, therefore this is the weaker conjugate base and



is the stronger acid

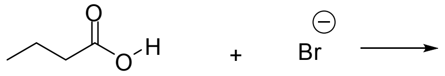
f)

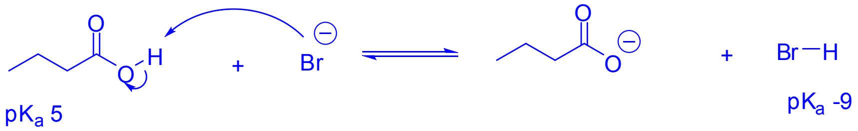


The flourines in equation 1 are more electronegative than the corresponding hydrogens in equation 2. The stronger electron withdrawing power of the flourines stabilize the conjugate base in (1) by the inductive effect. Since the conjugate base in (1) is more stable than in (2) it is a weaker base and therefore the acid in equation (1) is the stror acid

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

a)

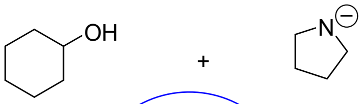


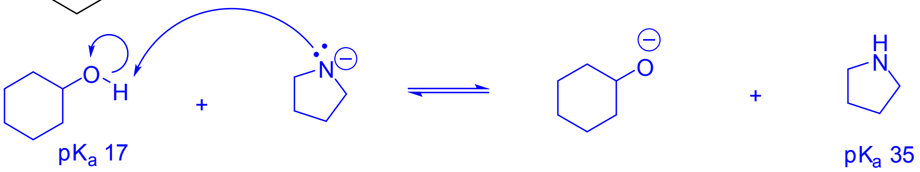


Reaction will favor the starting materials

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

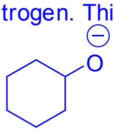
b)



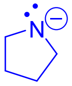


Reaction will favor the products

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



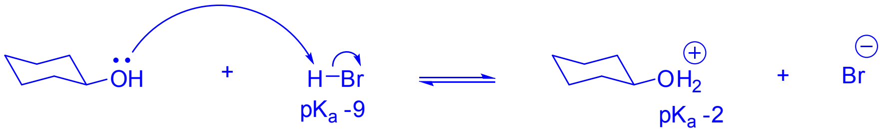
is a weaker base than



and so the reaction must favor the products.

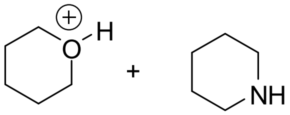
An alternate explaination involves pK_a. R-OH is a stronger acid that R_2NH (ROH has a lower pK_a). Therefore the reaction will favor products

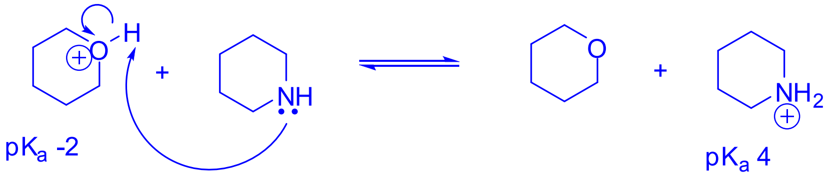
c)



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)

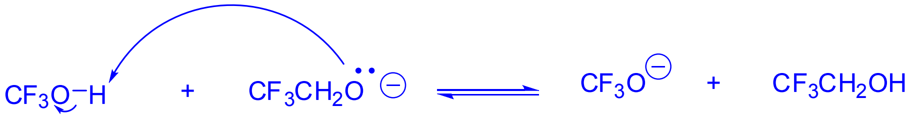




Reaction favors the products

oxygen is more electronegative than nitrogen. Therefore positively charged oxygen will be <u>less</u> 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

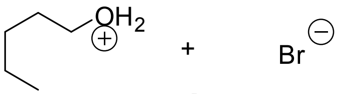
e) CF_3OH + $CF_3CH_2O^{\ominus}$

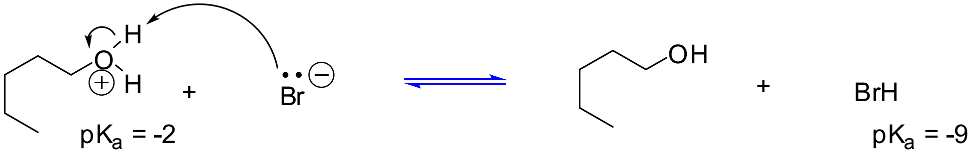


Reaction favors the products

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 negative charge on CF_3O- will be more stabilized by the inductive effect that then negative charge on CF_3CH_2O-. Because CF_3O- is more stable, the reaction will favor the products.

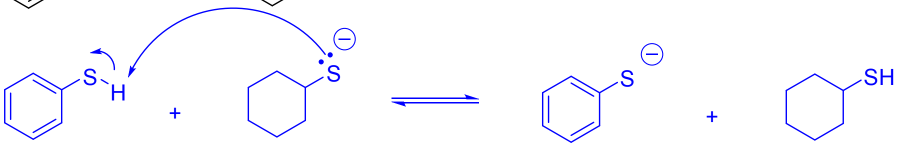
f)





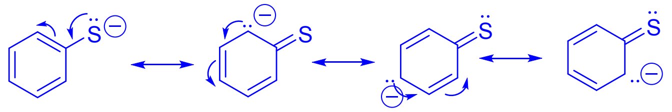
Reaction favors the starting materials
HBr is a stronger acid than the alcohol (pKa is lower). Therefore the equilibrium will be shifted to the left and the starting materials will be favored

g)



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



at least one resonance structure must be drawn

h) $CH_3CO_2^{\ominus}$ + CF_3CO_2H

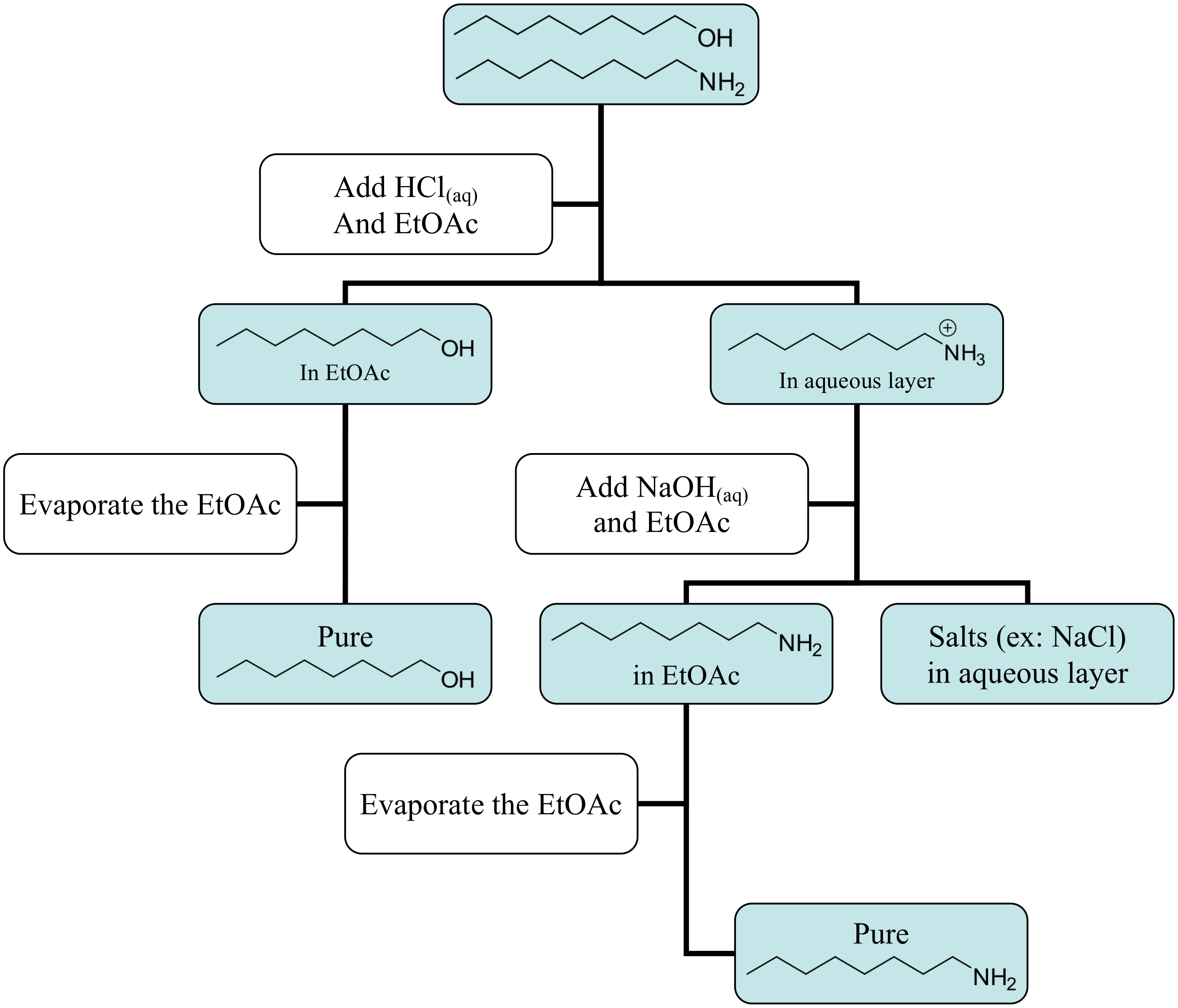
$$CH_3CO_2^{\ominus} + CF_3CO_2H \rightleftharpoons CH_3CO_2H + CF_3CO_2^{\ominus}$$

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.

8) How would you separate the following mixtures of compounds?

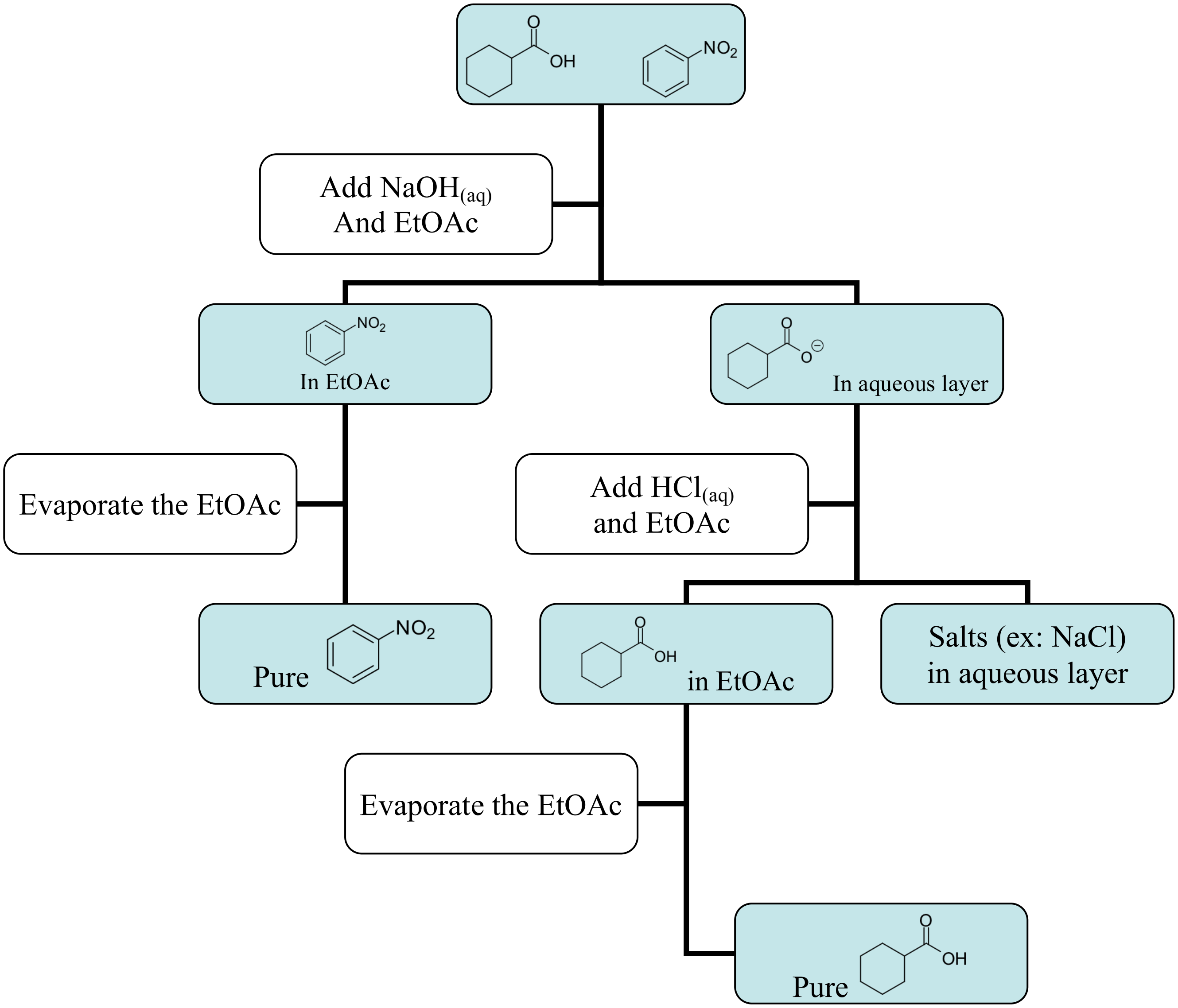
a. Octan-1-ol and octan-1-amine

Dissolve both in EtOAc. Add a 10% HCl solution in H_2O, which protonates the amine. Now the octan-1-ol is in the EtOAc, and the protonated (charged) amine is in the aqueous layer. Separate the organic and aqueous layers. Evaporate the organic layer to obtain pure octan-1-ol. Deprotonate the amine to make it neutral by adding a 10% NaOH solution in H_2O. Extract the aqueous layer with EtOAc. The neutral amine dissolves best in the organic layer. Separate the layers and evaporate the EtOAc to obtain pure octan-1-amine.

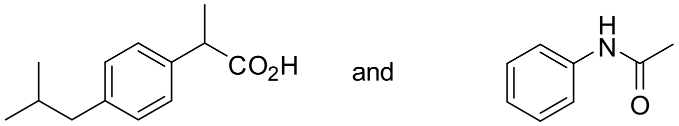


b. Cyclohexanecarboxylic acid from nitrobenzene

Dissolve both in EtOAc. Add a 10% NaOH solution in H_2O, which deprotonates the carboxylic acid. Now we have nitrobenzene in the organic layer, and the deprotonated (charged) cyclohexanecarboxylic acid (a carboxylate) in the aqueous layer. Separate the organic and aqueous layers. Evaporate the organic layer to obtain pure nitrobenzene. Protonate the carboxylate by adding a 10% HCl solution in H_2O. Extract the aqueous layer with EtOAc. The neutral acid dissolves best in the organic layer. Separate the layers and evaporate the EtOAc to obtain pure cyclohexanecarboxylic acid.



c.



Ibuprofen (advil)

Same procedure as in part B.