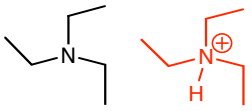
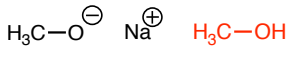
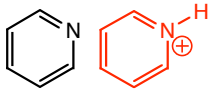
Chemistry 217
Problem Set 4

Recommended Problems from the Book: 2.13-2.27, 2.38-2.48, 2.49-2.54, 2.56 (1st ed.: 2.12-2.26, 2.37-2.46, 2.47-2.51, 2.53)
Klein: Ch. 3

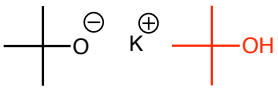
1. The following are commonly used bases among organic chemists. Draw the conjugate acid for each one. For each one, the pKa of the conjugate acid is given in parentheses. Rank all of the bases from weakest to strongest base.

(a)  (10.6)

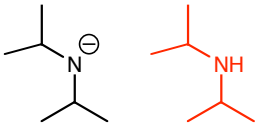
(b)  (15.54)

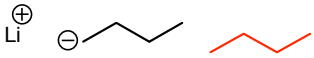
(c)  (5.21)

(d) NaH H_2 (36)

(e)  (17)

(f) $NaNH_2$ NH_3 (38)

(g)  (36)

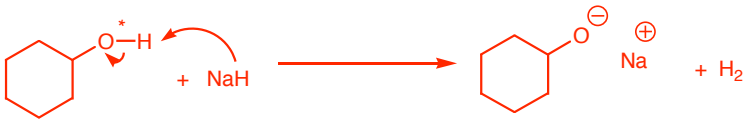
(h)  (50)

You are given the pKa of the conjugate acid for each base. Since strong bases have weak conjugate acids and vice versa, the base whose conjugate acid has the LARGEST pKa is the strongest base and the base whose conjugate acid has the SMALLEST pKa is the weakest base. Therefore, from weakest to strongest:

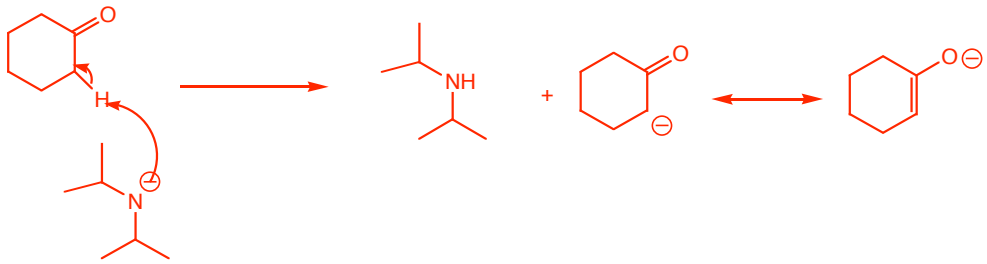
(c), (a), (b), (e), (d)=(g), (f), (h)

2. Choose an appropriate base from those in question 1 to deprotonate the most acidic proton in each of the following compounds (you probably will need to consult a pKa table). For each one, draw the mechanism of the reaction and the product.
There are many possibilites for which base to use. I have given one for each part. Just be sure that the conjugate acid of the base you choose has a pKa at least 3-4 units higher than the proton you are deprotonating.

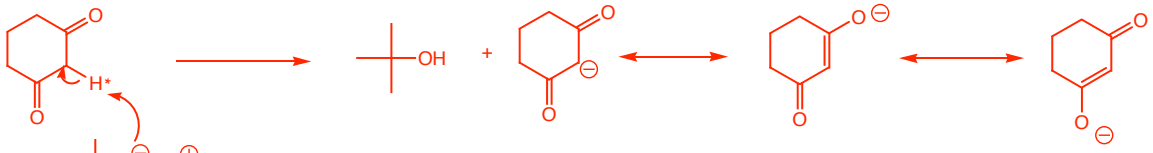
(a)



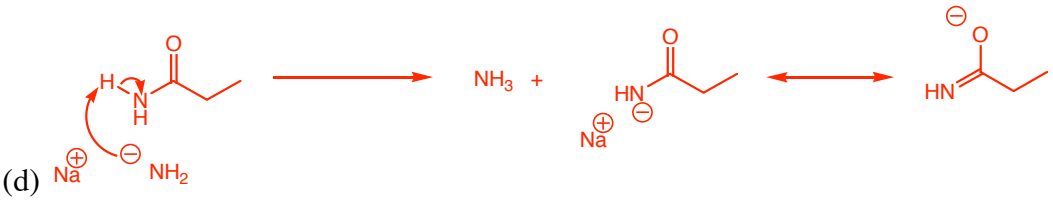
(b)



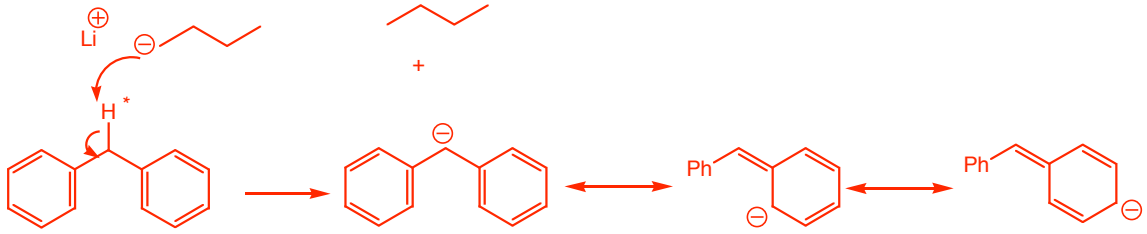
(c)

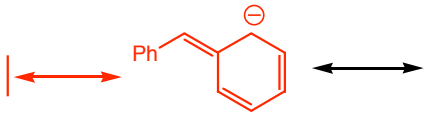


(d)



(e)

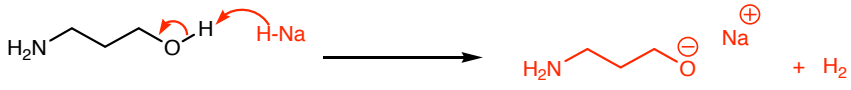




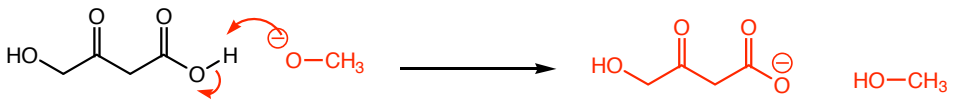
same resonance structures on the other ring

(f)

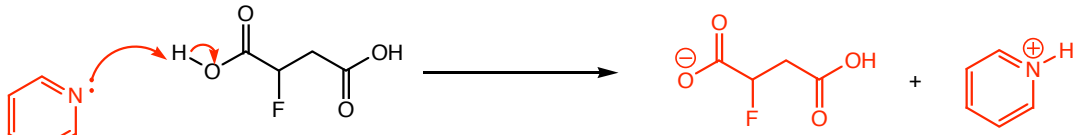
(g)



(h)

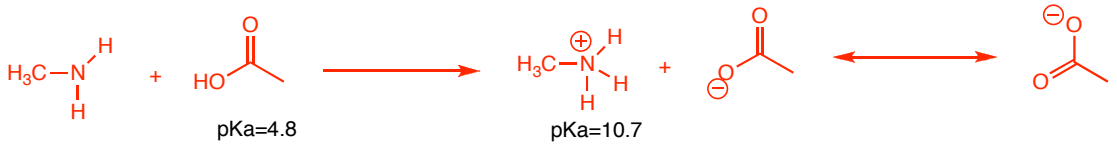


(i)

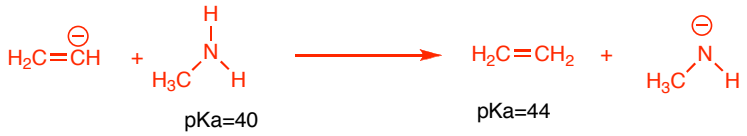


3. Amines can be EITHER bases or acids. Draw a reaction in which methyl amine (CH_3NH_2) acts as a base, and a second reaction in which it acts as an acid. Which is a stronger acid, a protonated amine or a neutral amine? Which is a stronger base, a deprotonated amine or a neutral amine?

As a base: remember that in order to fully deprotonate, the pKa of the conjugate acid must be 3-4 units higher than the acid. The conjugate acid of CH_3NH_2 is $CH_3NH_3^+$, which has a pKa of 10.7 (page A-4). Therefore, the acid cannot have a pka greater than 7.6. Acetic acid has a pKa of 4.8, so that would be a good choice (there are others):



As an acid: pKa of methyl amine is 40, so it can only protonate a base whose conjugate acid has a pKa of at least about 43. The pKa of ethylene is 44, so that would be a good choice:

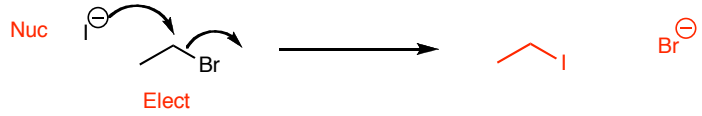


The protonated amine has a pKa of 10.7, while the neutral amine has a pKa of 40. Therefore, the protonated amine is stronger.

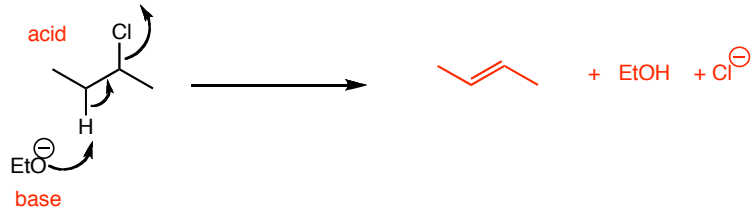
The conjugate acid of the deprotonated amine is the neutral amine (pKa=40), while the conjugate acid of the neutral amine is the ammonium ($CH_3NH_3^+$, pKa=10.7). Because a strong base has a weak conjugate acid, the deprotonated amine is a stronger base.

4. Follow the curved arrows to give the product(s) of the following reactions. For parts a-c, label the species on the left of the arrow as Brønsted-Lowry acid or base, nucleophile, or electrophile.

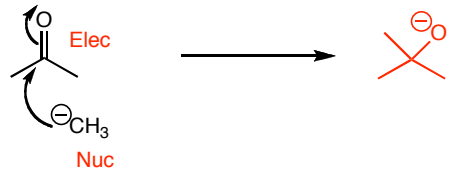
(a)



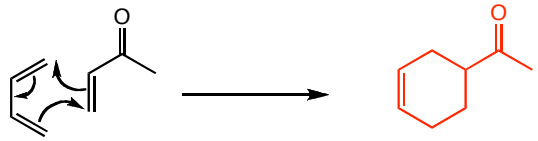
(b)



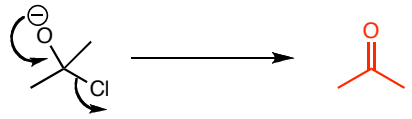
(c)



(d)

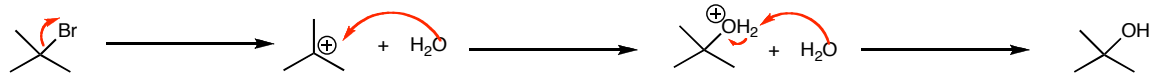


(e)



5. Propose a mechanism for each step of the following reactions:

(a)



(b)