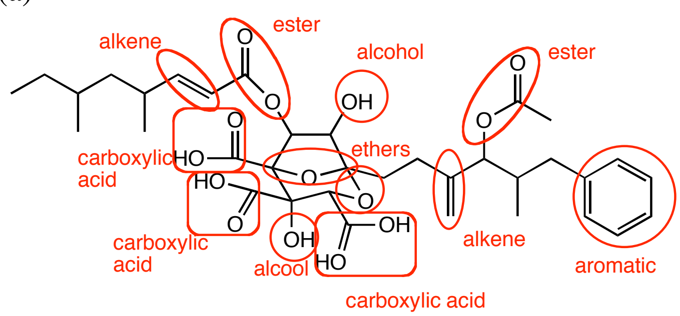
Chemistry 217
Problem Set 3

Recommended Problems from the Book: 13.6-13.14, 14.28-14.33, 2.1-2.12, 2.30-2.37
(1st ed.:14.7-14.15, 14.28-14.34, 2.1-2.11, 2.27-2.36)

Klein: Ch. 3

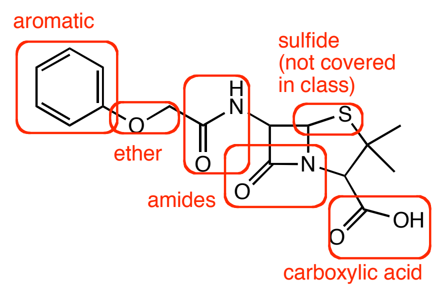
1. Circle and identify the functional groups in the following molecules.

(a)



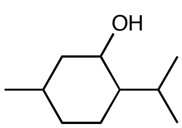
zaragozic acid: isolated from fungi, significantly reduces cholesterol, but is too toxic to be pharmaceutically viable.

(b)



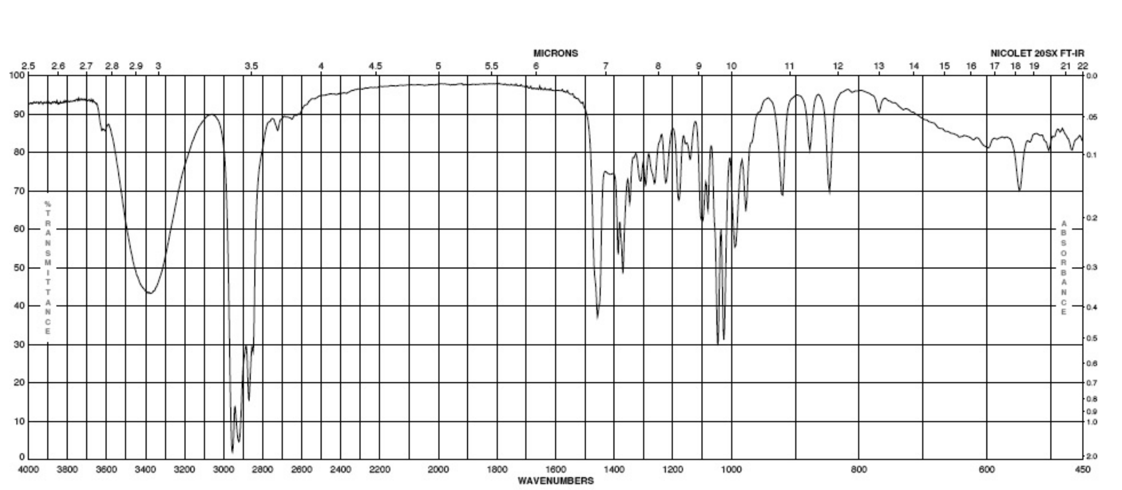
penicillin

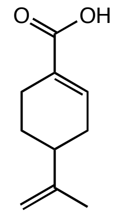
2. The following are compounds isolated from plants. Assign the important peaks in the IR spectrum of each compound.



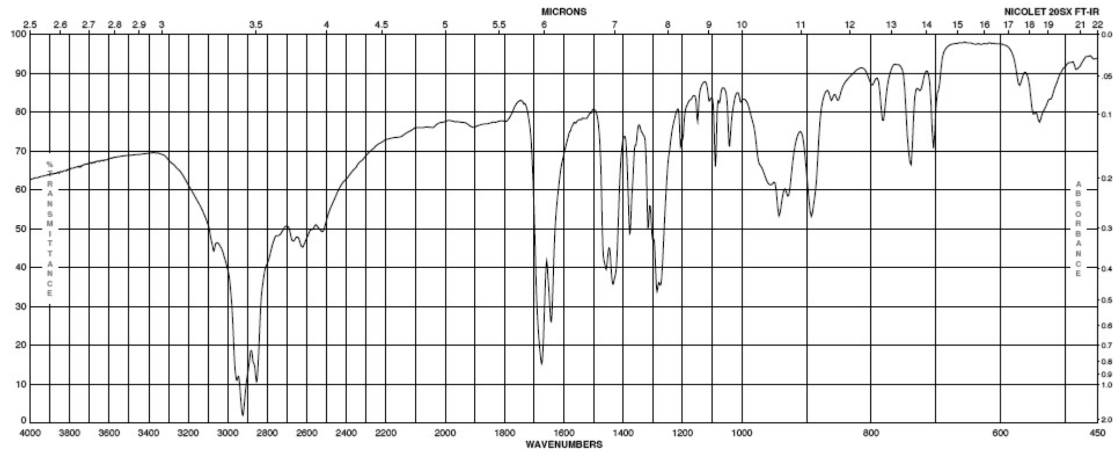
menthol

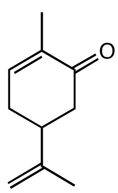
3400 cm^{-1}: O-H; 2890-2990 cm^{-1}: sp^{3}C-H



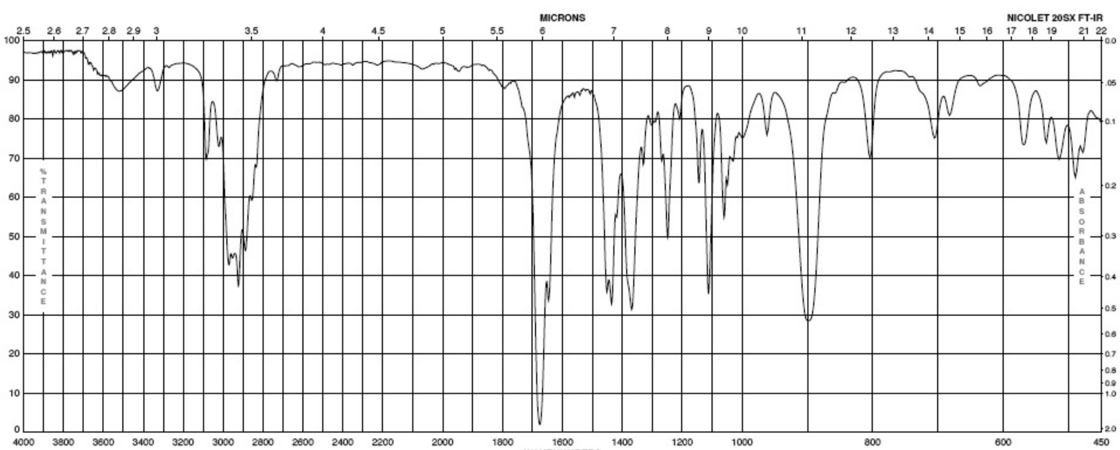


perillic acid 2300-3200 cm^{-1}: O-H; 3100 cm^{-1}: sp^{2}C-H; 2850-2980 cm^{-1}: sp^{3}C-H; 1690 cm^{-1}: C=O; 1640 cm^{-1}: C=C

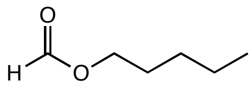




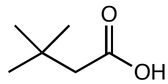
carvone 3100 cm^{-1}: sp^{2}C-H; 2850-2990 cm^{-1}: sp^{3}C-H; 1680 cm^{-1}: C=O; 1650 cm^{-1}: C=C



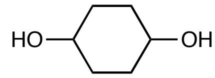
2. The IR spectra for four constitutional isomers are shown below. Match each spectrum to the correct compound. Assign the important peaks of each spectrum.



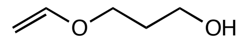
A



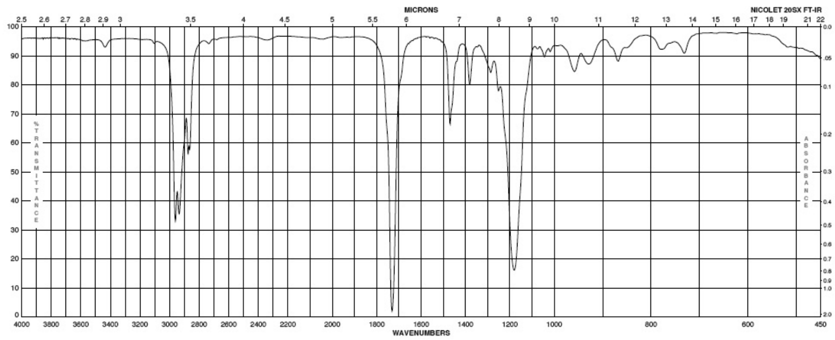
B



C

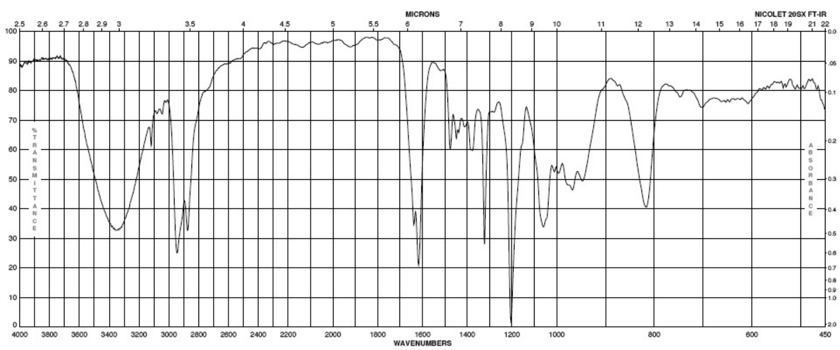


D

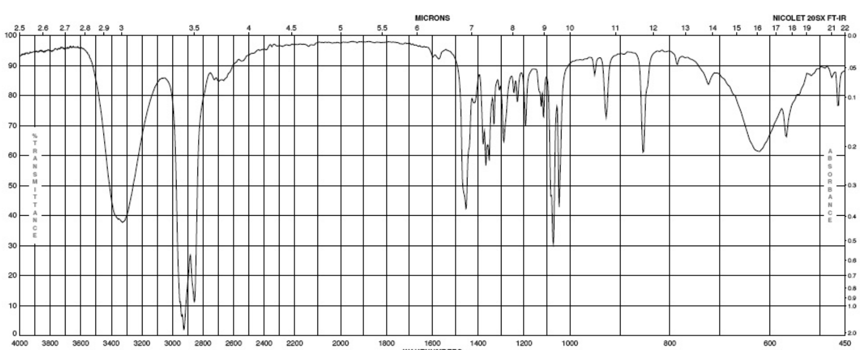


No OH, but C=C or C=O, so **A**

2850-2990 cm^{-1}: sp^3C-H
1720 cm^{-1}: C=O

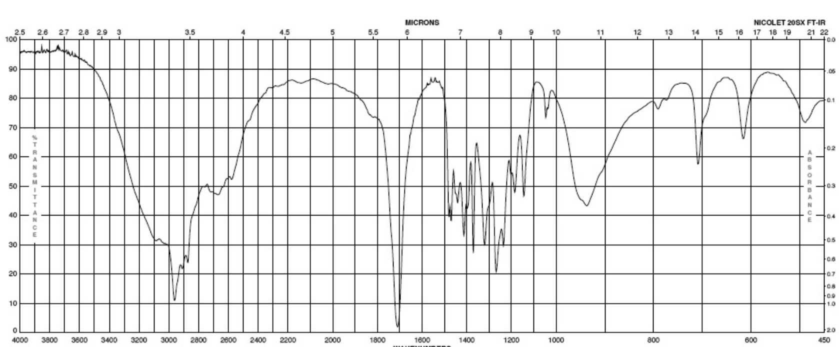


Contains an OH (not carboxylic acid because not broad enough) and a C=C or C=O, so **D**
3400 cm^{-1}: O-H
2880-2950 cm^{-1}: sp^3 C-H
1620 cm^{-1}: C=C



Contains an OH (not carboxylic acid) and no C=C or C=O, so **C**

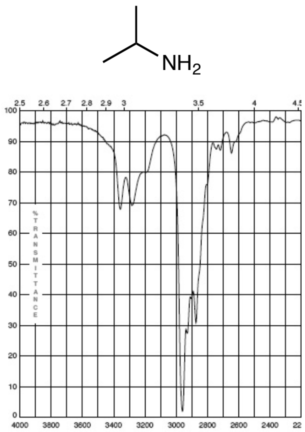
3300 cm^{-1}: O-H
2850-2950 cm^{-1}: sp^3C-H

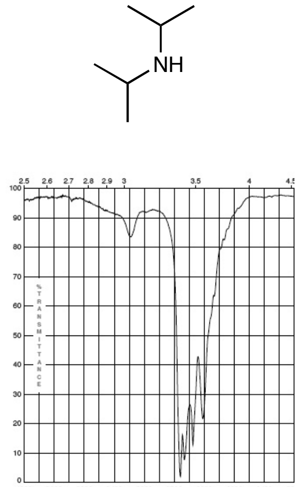


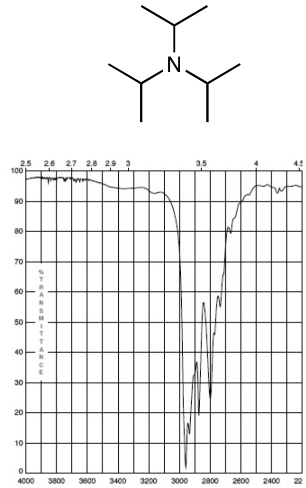
Contains a carboxylic acid, so **B**

2400-3400 cm^{-1}: O-H
2890-2990 cm^{-1}: sp^3C-H
1700 cm^{-1}: C=O

3. A portion of the IR spectrum for three different amines is shown below. Explain the differences in these spectra.

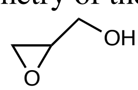






The first compound has two hydrogens attached to the nitrogen, so there are two peaks in the N-H region (these are the symmetric and asymmetric stretches H-N-H, not two N-H stretches). The second compound only has one N-H, so there is only one peak. Although the third compound is an amine, it does not have any N-H bonds, so there are no peaks in this region.

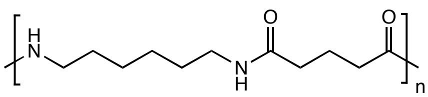
4. The IR spectrum of the molecule shown below has a peak that is slightly above 3000 cm^{-1}. Why? (hint: thnk about the geometry of the carbons in the ring)



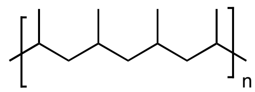
A peak slightly above 3000 cm^{-1-} is indicative of sp^{2}C-H stretches. In this molecule, all of the carbons are attached to four groups, which should make them sp^3-hybridized. However, the bond angles of the three-membered ring must be 60°, an angle more consistent with an sp^2 hybridized carbon than an sp^3, which has bond angles of 109.5°.

5. IR spectroscopy is commonly used by crime labs to determine the type of fiber found at a crime scene. Explain how you could use IR to distinguish between the following synthetic fibers. Note that these fibers are all polymers made up of repeating units between the brackets.

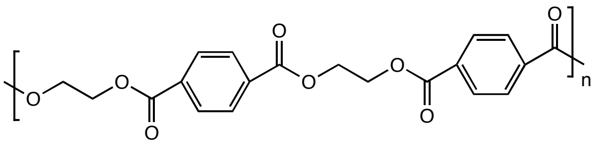
Nylon contains an amide, so it should have peaks around 3400 cm^{-1} and 1650 cm^{-1} (it is the only one that will have a peak above 3100). Except for the sp^{3}C-H peaks, polypropylene will not have any peaks above the fingerprint region. Polyester has aromatics and esters, so there will be both a C=C stretch (about 1600 cm^{-1}) and a C=O (about 1720 cm^{-1}). Acrylic contains a C≡N, which appears about 2250 cm^{-1}. None of the other compounds have a peak in this region.



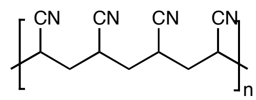
nylon



polypropylene



polyester

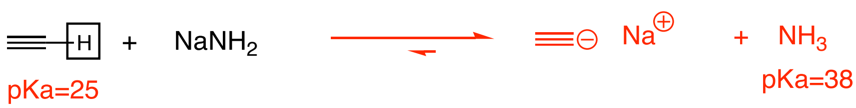


CN = C≡N

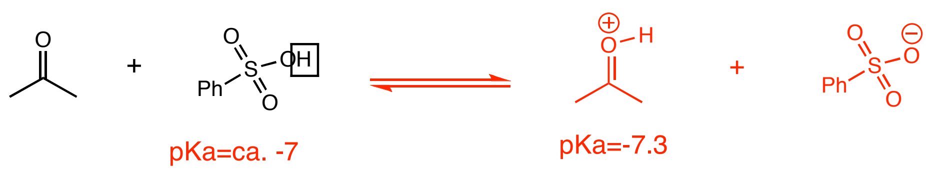
polypropylene

4. Give the products of the following acid/base reactions. The most acidic proton is shown in a box in each case. Using the pKa table on pages A1-A2 of your textbook, predict to which side of the reaction the equilibrium will lie.

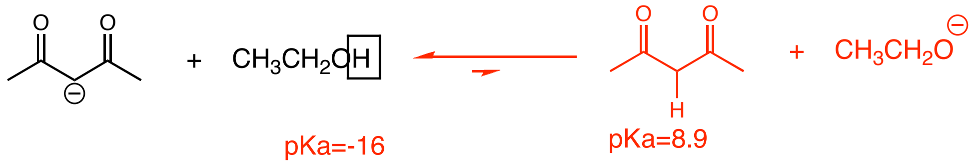
(a)



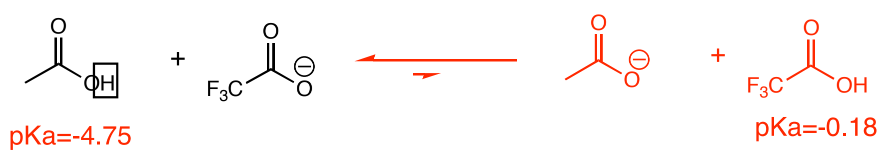
(b)



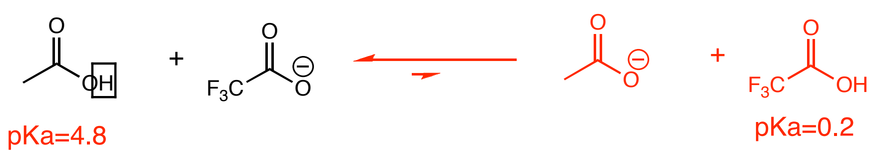
(c)



(d)

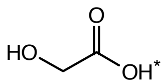
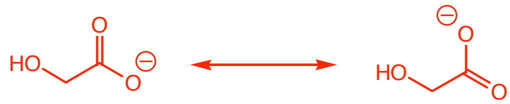


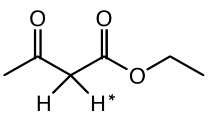
(e)

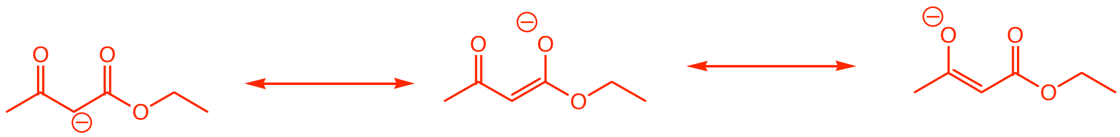


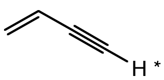
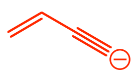
5. The most acidic proton on each of the compounds below is marked with a star. Draw the conjugate base. Draw as many resonance forms of the conjugate base as you can.

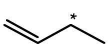
(a) CH_3OH^* c.b.: CH_3O^- (no resonance forms)

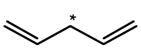
(b)  c.b.: 

(c)  c.b.:

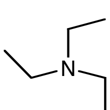
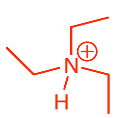


(d)  c.b.:  (no resonance forms)

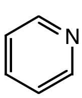
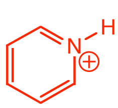
(e)  c.b.: 

(f)  c.b.:

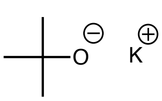
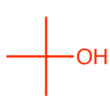
6. The following are commonly used bases among organic chemists. Draw the conjugate acid for each one. For each one, the pKa of the conjugate acid is given in parentheses. Rank all of the bases from weakest to strongest base.

(a)   (10.6)

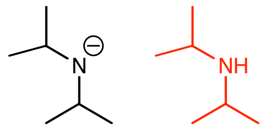
(b) $H_3C{-}O^{\ominus}$ $Na^{\oplus}$ $H_3C{-}OH$ (15.54)

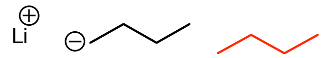
(c)   (5.21)

(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)