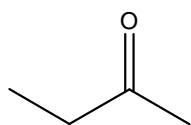
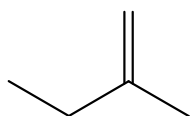


7. Match the given boiling points with the structures below and give a short reason for your answers.
 (-7°C, +31°C, +80°C, +141°C, 1420°C)



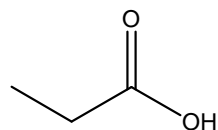
2-butanone

MW = 72 g/mol



2-methyl-1-butene

MW = 70 g/mol



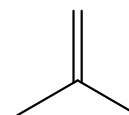
propanoic acid

MW = 74 g/mol

KCl

potassium chloride

MW = 74.5 g/mol

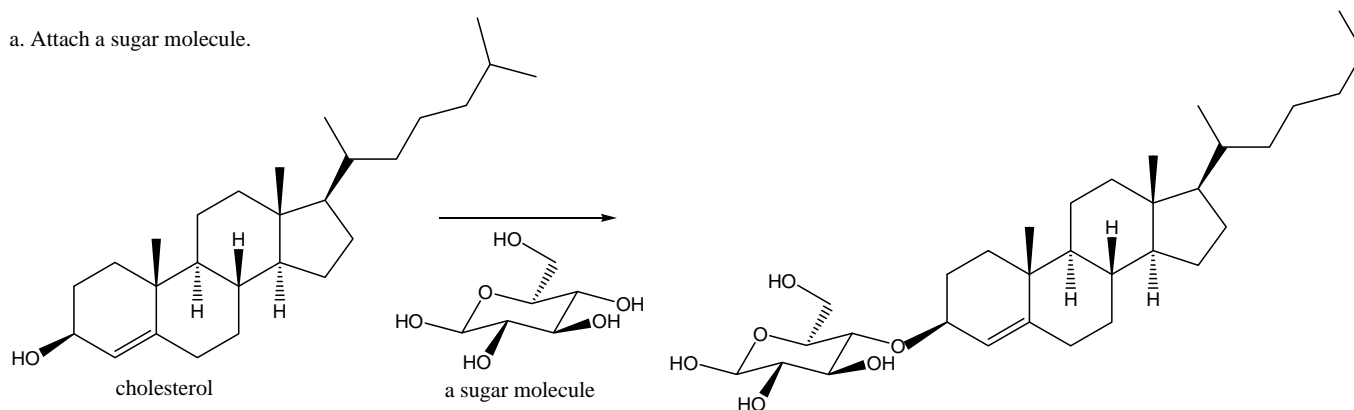


2-methylpropene

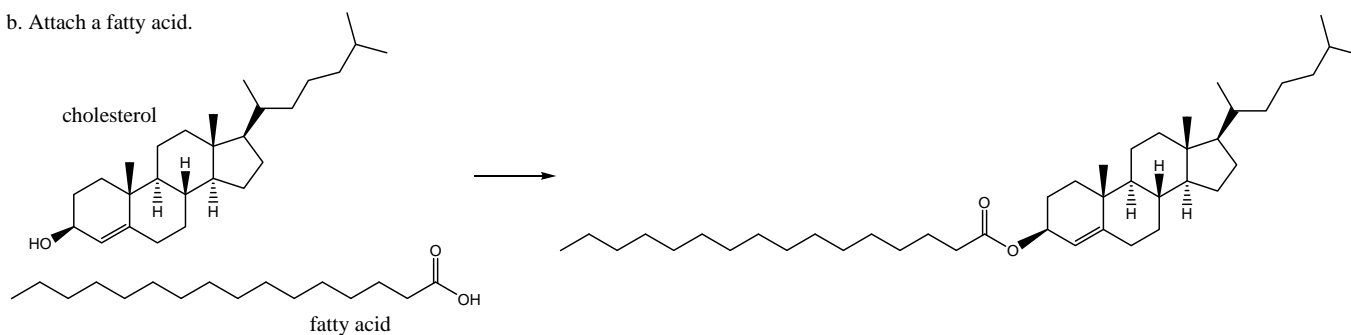
MW = 56 g/mol

8. Different groups can be connected to the “O-H” substituent of cholesterol. What effect on water solubility do you expect for each of the following changes. Why?

- a. Attach a sugar molecule.



- b. Attach a fatty acid.



9. Draw all possible chair conformations of phenylcyclohexane. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the less stable conformation using the C₂→C₁ and C₄→C₅ bonds to sight along. Point out any gauche interactions shown in your Newman projection. Use the axial energy of a phenyl to determine what are the relative percents of each conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes.

Substituent	ΔG° (A value)	Substituent	ΔG° (A value)
-H	0.0	-CH ₂ OH	1.8
-CH ₃	1.7	-CH ₂ Br	1.8
-CH ₂ CH ₃	1.8	-CF ₃	2.4
-CH(CH ₃) ₂	2.1	-O ₂ CCH ₂ CH ₃	1.1
-C(CH ₃) ₃	> 5.0	-OH	0.9
-F	0.3	-OCH ₃	0.6
-Cl	0.5	-SH	1.2
-Br	0.5	-SCH ₃	1.0
-I	0.5	-SC ₅ H ₆	1.1
-CH=CH ₂	1.7	-SOCH ₃	1.2
-CH=C=CH ₂	1.5	-SO ₂ CH ₃	2.5
-CCH	0.5	-SeC ₅ H ₆	1.0
-CN	0.2	-TeC ₅ H ₆	0.9
-C ₅ H ₆ (phenyl)	2.9	-NH ₂	1.2(C ₆ H ₅ CH ₃), 1.7(H ₂ O)
-CH ₂ C ₅ H ₆ (benzyl)	1.7	-N(CH ₃) ₂	1.5 (C ₆ H ₅ CH ₃), 2.1(H ₂ O)
-CO ₂ H	0.6	-NO ₂	1.1
-CO ₂ [⊖]	2.0	-HgBr	0.0
-CHO	0.7	-HgCl	-0.2
		-MgBr	0.8

10. Use a Newman projection of the C₃→C₄ bond of 2-methyl-4-phenylhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight.

2D structure

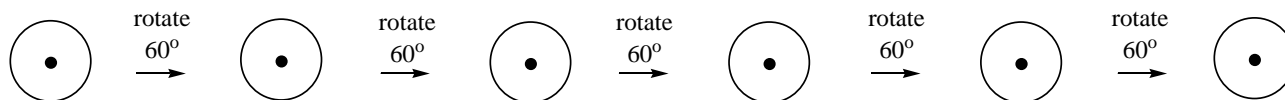
Approximate Eclipsing Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.4	1.5	1.6	3.0	1.7
Me	1.4	2.5	2.7	3.0	8.5	3.3
Et	1.5	2.7	3.3	4.5	10.0	3.8
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5
Ph	1.7	3.3	3.8	8.1	13.5	8.3

$$\Delta G \approx \Delta H$$

$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$$

Approximate Gauche Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.2
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.6	3.0	1.5
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9
Ph	0.2	1.4	1.5	2.1	3.9	2.3

most stable
conformation
↓



$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

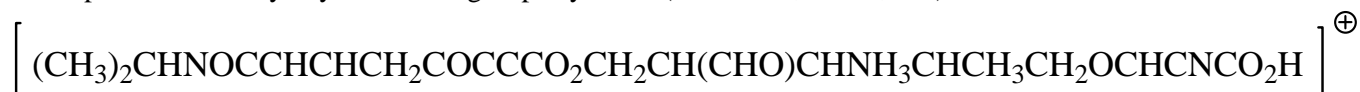
$\Delta H^\circ =$

$\Delta H^\circ =$

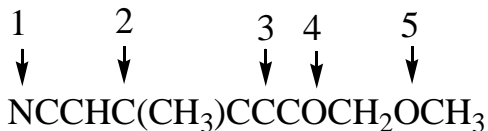
$\Delta H^\circ =$



11. Draw an acceptable Lewis structure (2D) for each of the following. Show all single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atom where present. Identify any functional groups by name (i.e. ketone, amide, etc.)



12. Draw a 3-D structure for the following molecule. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms.



Atom	Shape	Hybridization	Bond Angles	# σ bonds	# π bonds	# lone pairs
------	-------	---------------	-------------	------------------	---------------	--------------

1

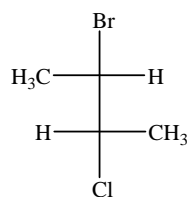
2

3

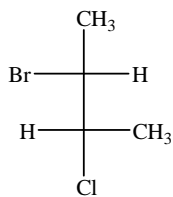
4

5

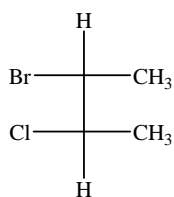
13. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration and write an acceptable name for that isomer.



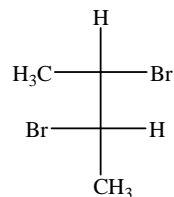
A



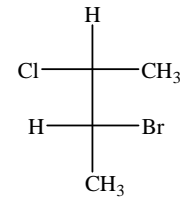
B



C



D

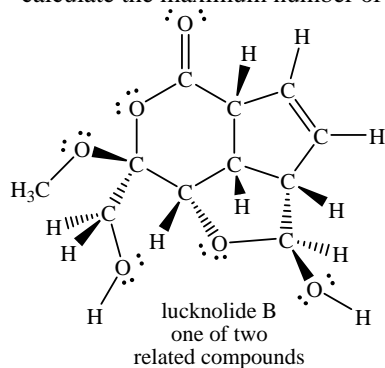


E

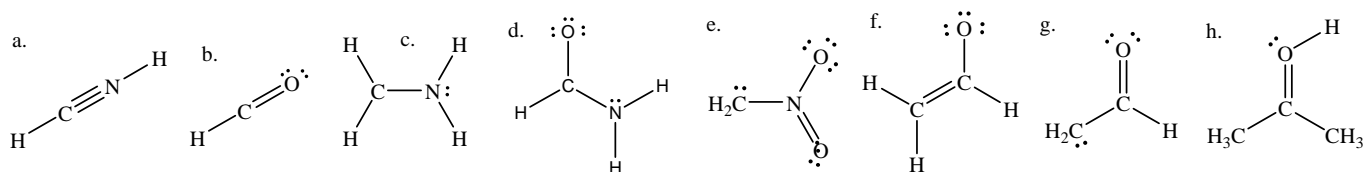
- a. Which are optically active? A B C D E
- b. Which are meso? A B C D E
- c. Which is not an isomer with the others? A B C D E
- d. Which pairs are enantiomers? AB AC AD AE BC BD BE CD CE DE
- e. Which pairs are identical? AB AC AD AE BC BD BE CD CE DE
- f. Which pairs are diastereomers? AB AC AD AE BC BD BE CD CE DE
- g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE BC BD BE CD CE DE
- h. Draw any stereoisomers of 2-bromo-3-chlorobutane as Fischer projections, which are not shown above. If there are none, indicate this.

- i. Would anything change if, in compound D, the Br was replaced with a Cl group? How about compound A?

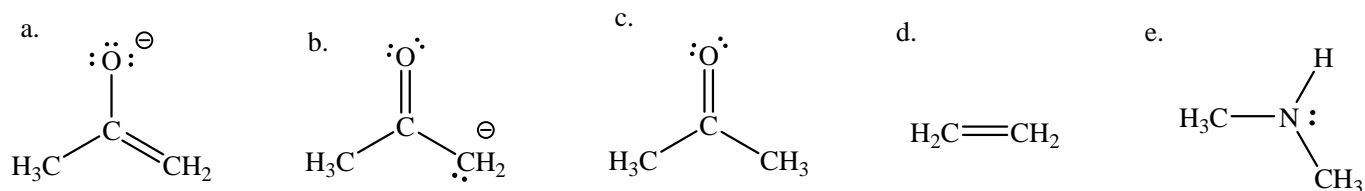
- j. The structure of lucknolide B was recently determined (and the absolute configuration of all chiral centers!). It was isolated from the terrestrial bacteria, *Streptomyces* sp. ANK-289, in screenings for new medicinal lead compounds (Org. Lett. p.3800, 2010). Circle all chiral centers and any other stereochemical features, and calculate the maximum number of stereoisomers possible.



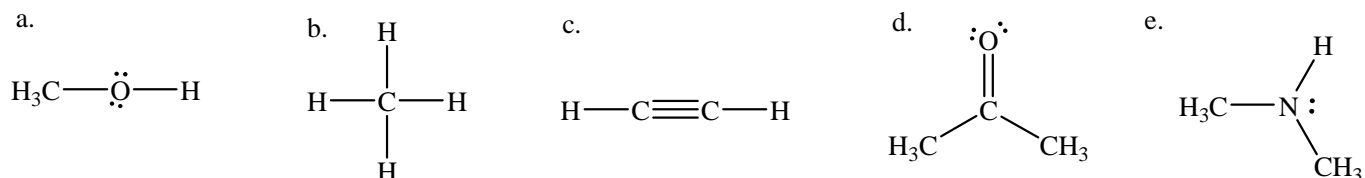
14. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw one additional resonance structure using the proper arrow conventions.



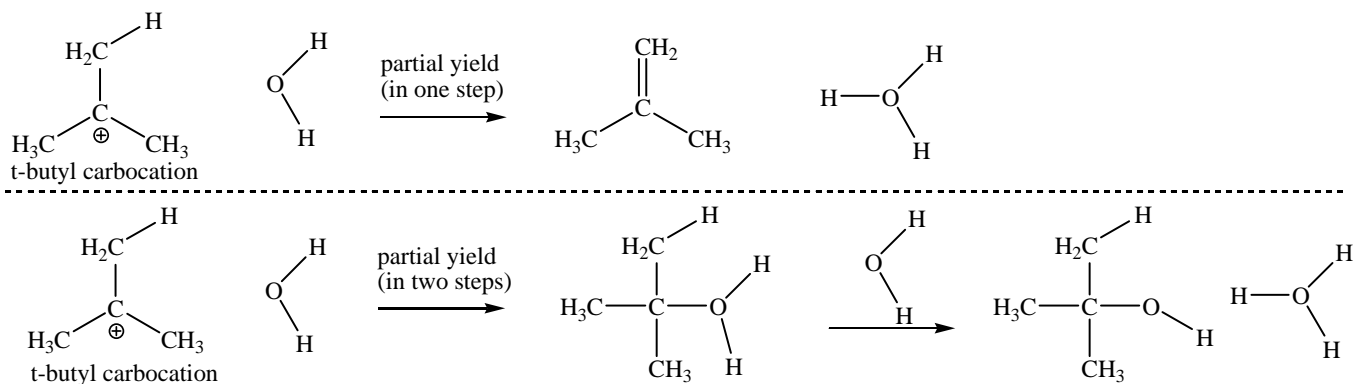
15. Write an equation showing each of the following structures reacting as a Bronsted base, using HA as the acid. If structures do not have any lone pairs of electrons, you will have to use the pi electrons as the base where one carbon atom of the pi bond will lose its share of the electron pair when the pi bond is broken and a new sigma bond is made using the other carbon atom and the proton. What will be the formal charge on the carbon atom losing the electrons? Hint: That carbon atom will become a carbocation.



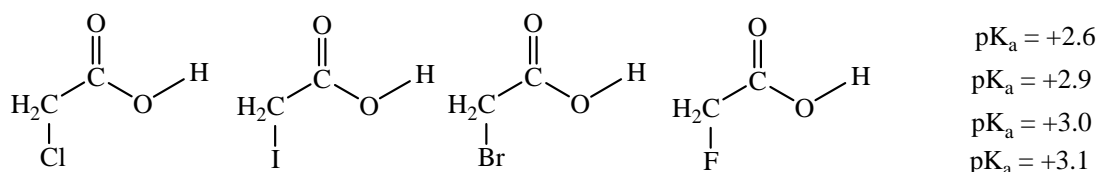
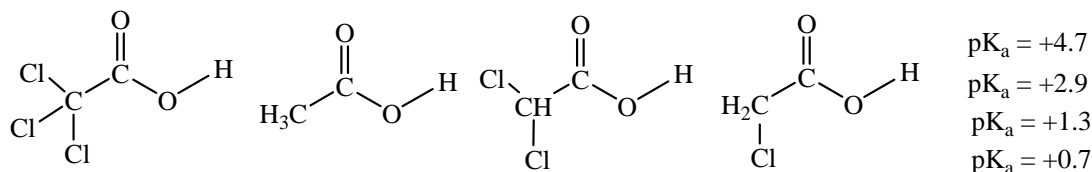
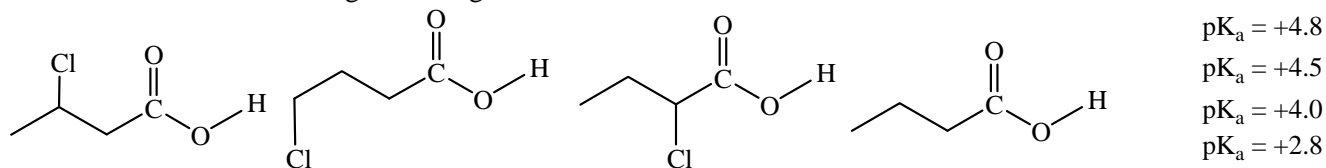
16. Write an equation showing each of the following reacting as a Bronsted acid, using B: as the base (neutral). Use correct formal charge. You are going to have to leave two electrons behind and pay attention to formal charge.



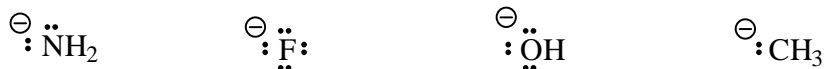
17. There are two reasonable choices for a water molecule reacting with a t-butyl carbocation. One answer involves water acting as a Bronsted base and the other involves water acting as a Lewis base (which equation goes with each term?). Write in the necessary lone pairs of electrons, curved arrows and formal charge to show the mechanism for each of these possibilities. What are other terms that could be used to describe the water and carbocation reactants? Match those terms with the appropriate reactant structures. This problem illustrates a common competition for electron pair donors in organic chemistry: react with a hydrogen atom or react at a carbon atom.



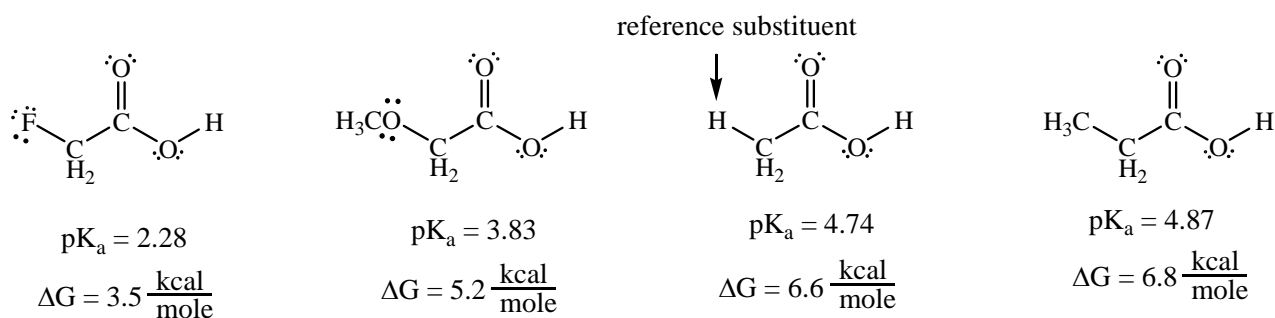
18. Match the pK_a 's with the correct acid and explain your reasoning. Show the reaction with generic base, B:, using curved arrow formalism using the strongest acid.



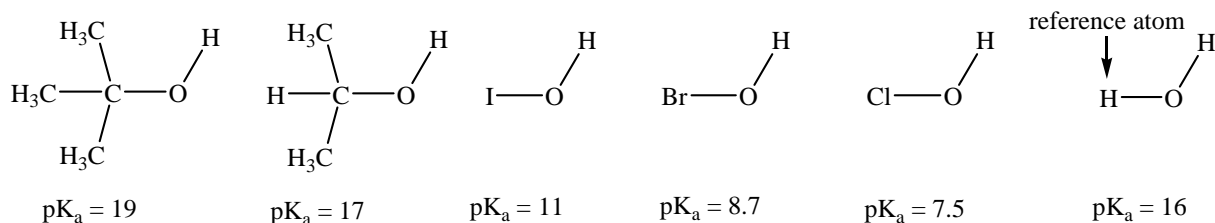
19. Order the following bases in increasing strength below (1=strongest). Are these differences big or small? Provide an explanation for your choice. Show the reaction with the strongest base using H-A using curved arrow formalism.



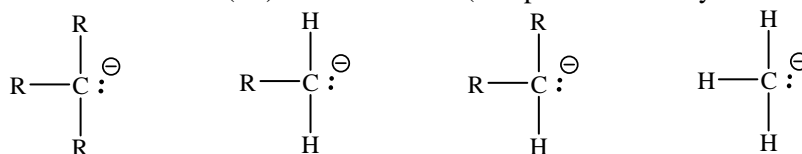
20. Order these acids from strongest (=1) to weakest. What do the pK_a and ΔG values indicate about the inductive effects of the substituents relative to the reference substituent (H)?



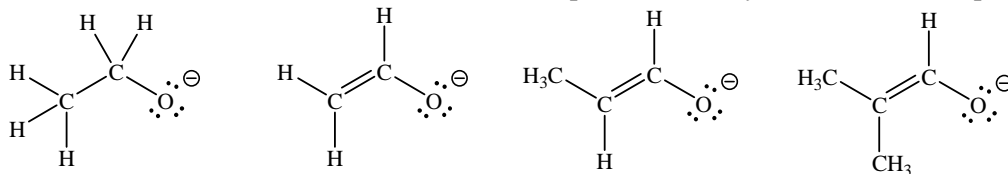
21. Order the substituents below, from most (=1) to least electron withdrawing, according to their apparent inductive effect based on the pK_a for the given acids (of the O-H bond). Are any of the substituent groups electron donating relative to the hydrogen atom (the reference atom)? Provide a possible explanation for the relative order of acidities.



22. a. Order the carbanions below from most (=1) to least stable. (R represents an alkyl substituent.). Explain your order.



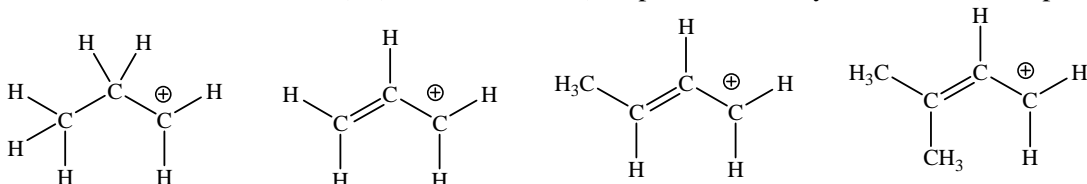
b. Order the anions below from most (=1) to least stable. (R represents an alkyl substituent.). Explain your order.



b. Order the carbocations below from most (=1) to least stable. (R represents an alkyl substituent.). Explain your order.

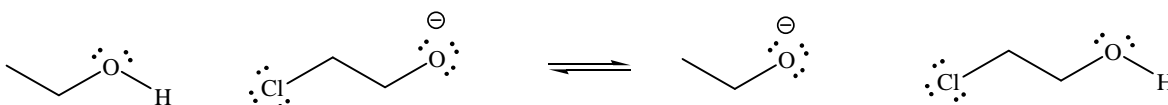


d. Order the carbocations below from most (=1) to least stable. (R represents an alkyl substituent.). Explain your order.

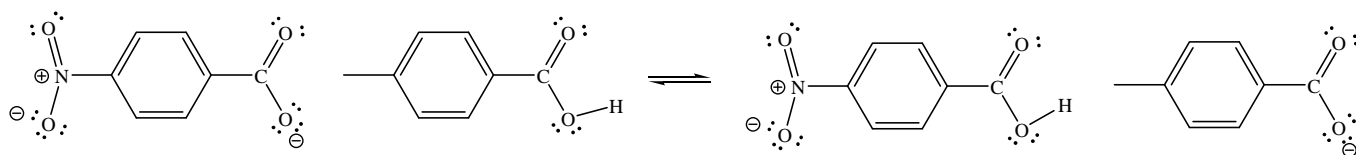


23. Qualitatively predict whether reactants or products would be favored in the equations below. Write in the arrow-pushing details. Do not use a K_a/pK_a table and explain your choices. Does the equilibrium lie to the left (favor reactants) or to the right (favor products)? Explain your answers.

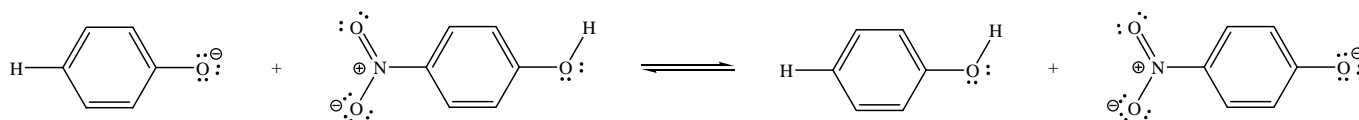
a.



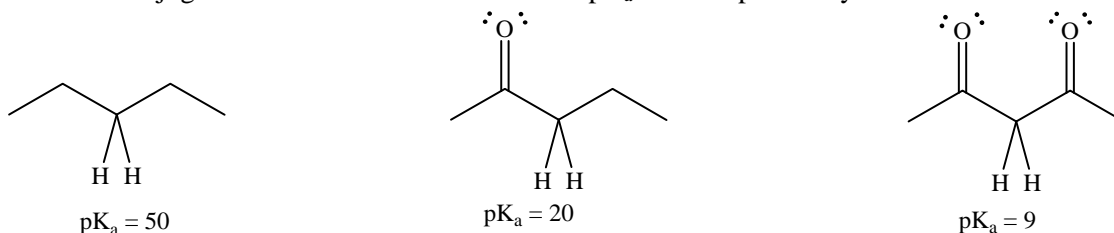
b.



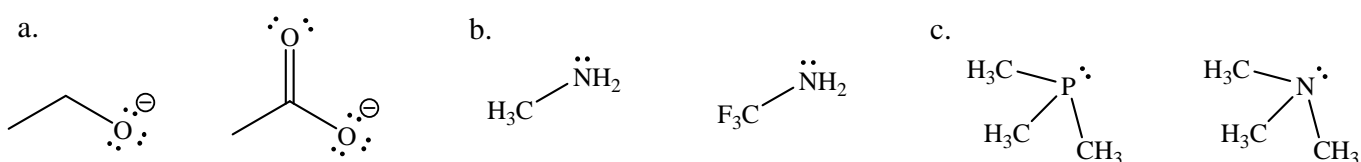
c.



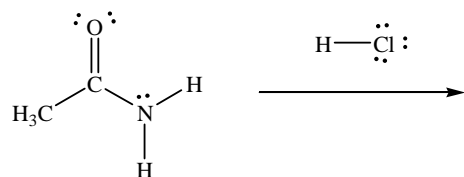
24. Each of the carbon acids below has a pK_a listed with it. Indicate the relative order of acidities (1 = strongest) and provide an explanation for the indicated differences. Write an arrow-pushing equation for each example using a general base, $B:^-$. Include curved arrows to show electron movement, include formal charge and all lone pairs. Can you tell which conjugate acid is more stable from their pK_a 's and explain why?



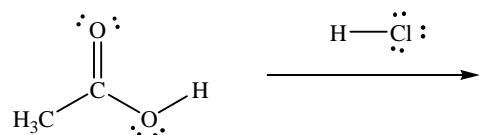
25. Which is the weaker base in each pair below. Explain your answers. A more stable base is usually a less reactive base (weaker). Electrons are more stable when they are balanced by a greater positive charge, or are closer to positive charge, or are more delocalized.



26. a. Is protonation of an amide more likely on the oxygen atom or the nitrogen atom. Show the reaction for both and examine any possible resonance structures for clues that explain the difference.



- b. Predict the more basic oxygen in a carboxylic acid. Show both oxygen atoms acting as a base and explain your choice (just like the amide in part a).



- c. Is the amide or the carboxylic acid more basic, or are they similar in basicity? Explain your answer.