

**Biological Molecules.**

1. Draw a three dimensional structure of the dipeptide: Ala-Gly.
2. The amino acid lysine has  $pK_a$  values of 2.16, 9.18, and 10.79. What is the predominate form of lysine at pH 7? At what pH is the form of lysine shown in the figure at the right predominate?
3. Protein structures are quite complex and are described in different ways. Explain what is meant by each of the following terms.
  - a. Primary structure
  - b. Secondary structure
  - c. Tertiary structure.
4. Which has the higher melting point, a saturated fat or an unsaturated fat? Explain.
5. What are the differences between RNA and DNA? What is the complementary strand to a DNA molecule of sequence AGTTCACTA?

**From exam 1.**

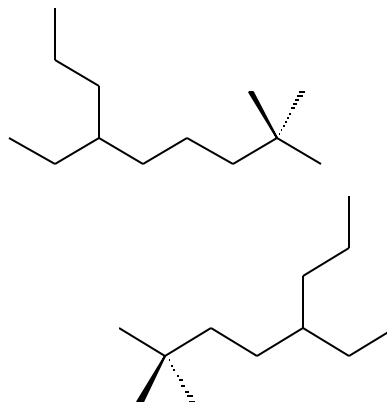
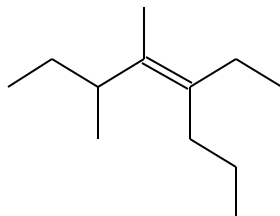
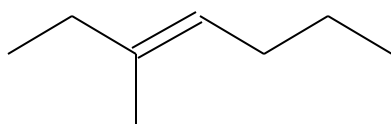
Draw Lewis structures. Name hydrocarbons and draw structures from names. Identify functional groups. Draw MOs of diatomics:  $p$  systems of organics, intermolecular forces.

**From exam 2.** Review thermodynamics of solutions, colligative properties, hydrophobic effect. Organic reactions: additions to alkenes, oxidations. Kinetics, first, second order.  $C^{14}$  dating,  $S_N1$   $S_N2$ , energy profile diagrams. Draw mechanisms for addition and substitution reactions.

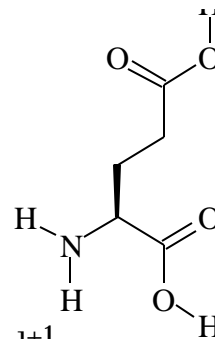
**From exam 3.** Carbon-carbon bond forming reactions, eliminations, organic synthesis, polymer synthesis, transition metals, orbital splitting diagrams, color, magnetic properties. Structure and isomers, 18 electron rule.

**Questions from past final exams:**

6. Draw Lewis structures, including formal charges and all important resonance structures for each of the following
  - a.  $HCO_3^-$
  - b.  $SOCl_2$
  - c.  $H_2NNH_2$
  - d.  $CH_3NO$  (the simplest amide)
  - e.  $C_2H_6PO_4^{-1}$  (dimethyl ester of phosphoric acid at pH 7)
  - f.  $H_3NO$  (hydroxylamine)
7. Draw structures of each of the following molecules.
  - a. 3,4-dimethyl-4-propyloctane
  - b. *cis*-1,2-dimethylcyclobutane
  - c. (Z)-4-ethyl-6-methyl-3-heptene
8. Name each of the following molecules

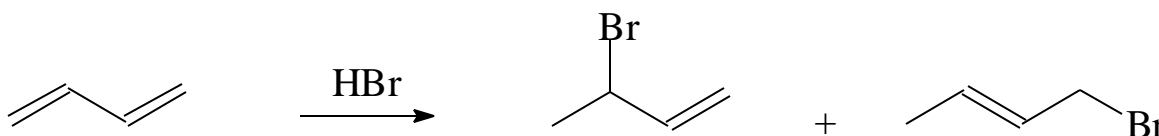


9. A representation of the amino acid glutamic acid is shown  
The pKa values for glutamic acid are: 2.10, 4.07, and 9.47
- Draw the predominant structure of glutamic acid at pH 1.0.
  - Draw the predominant structure of glutamic acid at pH 7.0.
  - Draw the predominant structure of glutamic acid at pH 11.0.



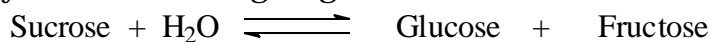
10. draw all isomers of the transition metal complex  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Br}_2]^+$
11. Consider the following ions,  $\text{CrCl}_4^{-2}$ ,  $\text{V}(\text{H}_2\text{O})_6^{+3}$ ,  $\text{CuCl}_4^{-3}$ ,  $\text{Ti}(\text{H}_2\text{O})_6^{+4}$ ,  $\text{FeCl}_4^{-1}$ ,  $\text{Cu}(\text{H}_2\text{O})_6^{+2}$ .  
Some of them show little if any color. Which would you expect to be colorless?

12. The molecule 1,3-butadiene is allowed to react with HBr. In addition to the expected product, 3-bromo-1-butene, a smaller amount of 1-bromo-2-butene was formed as an unexpected biproduct.



- Draw a mechanism for the addition of HBr to 1,3-butadiene to give 3-bromo-1-butene. Be sure to show all important electrons. Use arrows to show how the important arrows move in each step of the reaction.
  - Now draw a mechanism showing how the second product, 1-bromo-2-butene, is formed as an unexpected biproduct.
6. The drug atropine is an ester. In water solution the ester bond is hydrolyzed to an acid and an alcohol. At a temperature of  $25^\circ\text{C}$  this rate was found to be first order with a rate constant,  $k = 4.5 \times 10^{-5} \text{ min}^{-1}$ .
- What is the half-life for the hydrolysis of a solution of atropine at  $25^\circ\text{C}$  ?
  - How many days would it take for 90% of the drug to be hydrolyzed at  $25^\circ\text{C}$ ?
  - If the energy of activation for the reaction was  $75 \text{ kJ/mol}$  what would be the half life for the hydrolysis if the drug was stored at  $0^\circ\text{C}$ ?
13. Chemists commonly use a rule of thumb that an increase of  $10^\circ\text{C}$  in temperature doubles the rate of a reaction. Obviously this rule is not always valid because there is a wide range in activation energies for different reactions. However it is still a reasonable rule for many reactions.  
What must the activation energy be for this statement to be true for a temperature rise from  $25^\circ\text{C}$  to  $35^\circ\text{C}$ ?
14. Suppose you were living in the mid 19th century in a cabin in the middle of the wilderness. You need some soap, but the nearest supermarket is several decades away.
- Explain how you would make the soap. What raw materials would you use?
  - Explain the chemistry of the process.
  - Explain how the soap actually works when you use it to wash something (or someone).
15. Hexane will not dissolve in water even though the enthalpy of solution is negative. Explain this observation.
16. Draw d orbital splitting diagrams and predict the electron occupancies for each of the following species.  $[\text{Fe}(\text{CN})_6]^{3-}$   $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$   $[\text{FeCl}_4]^{-2}$  (tet)  $[\text{NiCN}_4]^{-2}$  (square planar)

17. A study of the hydrolysis of sucrose to give glucose and fructose was conducted

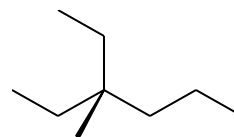
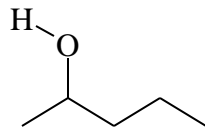
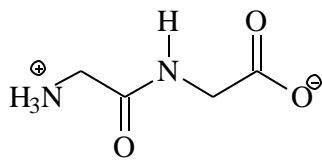


The following concentrations of sucrose were recorded.

Time (minutes)	sucrose concentration (M)
0	1.000
30	.899
60	.805
90	.723
120	.648
180	.532

- What is order of this reaction for sucrose?
  - What is the rate constant?
  - How long will it take for 99.0 percent of the sucrose to be consumed?
18. Hexane will not dissolve in water even though the enthalpy of solution is negative. Explain this observation.
19. Indicate if the following molecules are chiral? (10 pts)

*cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+1</sup>    *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+1</sup>

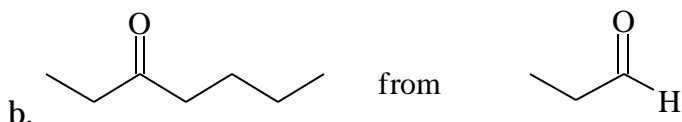
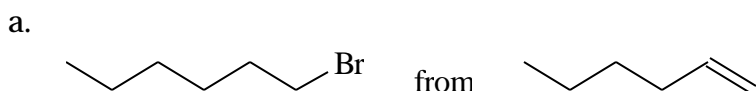


20. Draw a molecular orbital energy level diagram for the molecule NO. Be sure to indicate which levels contain electrons. What are the bond orders for NO<sup>+</sup>, NO and NO<sup>-</sup>? Which would have the longest bond length? Which would have the shortest bond length?

21. Each of the following compounds contain a first row transition metal and they obey the 18 electron rule. Identify the metal.

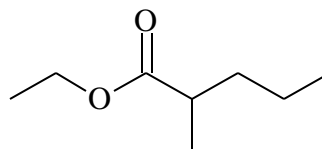
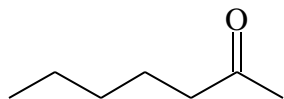
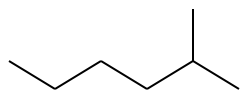
- M(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>
- a. M(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>
- c. M(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>
- d. M(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>

22. Show how you could synthesize the following molecules from the indicated starting materials. You may use any other reagents you want. Note: the syntheses may require more than one step. (12 pts)

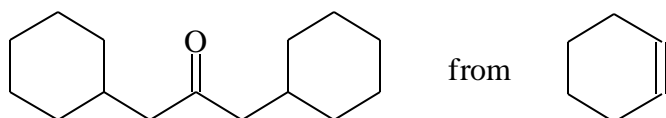


23. Give a synthesis for each of the following molecules. All carbon starting materials must have four carbons or less.

a



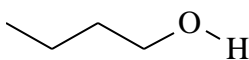
24. Show how you could synthesize the following molecule.



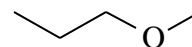
plus any other reagents you want as long as they contain no more than four carbon atoms.

25. For each of the following select the proper molecule and give a short explanation.

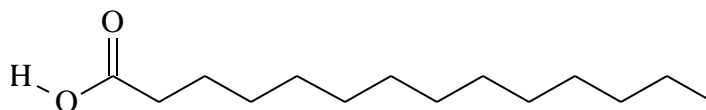
a. Which has the higher boiling point?



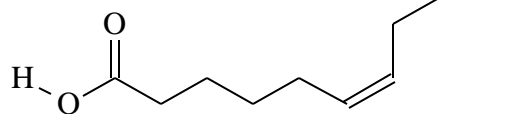
or



b. Which has the higher melting point?

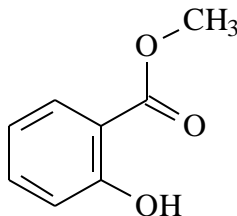


or

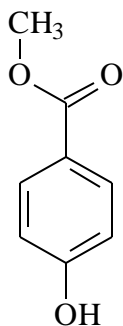


c. Which has the higher melting point?

Hint: the melting points are very different,  $-8^{\circ}\text{C}$  and  $+127^{\circ}\text{C}$ , so your explanation better be good.

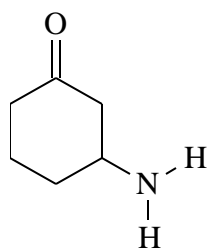


or

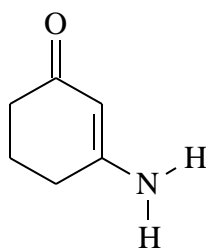


26. Consider the following two molecules.

In one of these molecules the nitrogen atom is expected to be trigonal planar, in the other is expected to be trigonal pyramidal. Explain.



a.

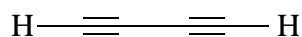


b.

27. Conjugated polymers are very interesting molecules which may be used in various electronic or optical applications.

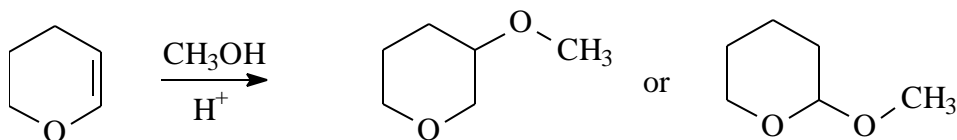
a. Draw the structure of the polymer polyacetylene, the polymer of acetylene.

b. Draw the structure of polydiacetylene obtained via the 1,4-polymerization of diacetylene.



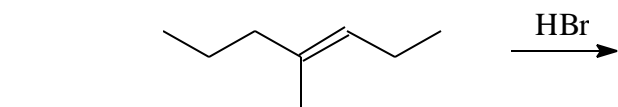
diacetylene

28. The following reaction is carried out under acid catalyzed conditions. Two possible products could be formed, but only one is observed. Predict the product, draw a mechanism and explain why the one you chose is favored.

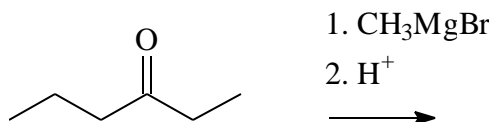


29. Give a product for each of the following reactions.

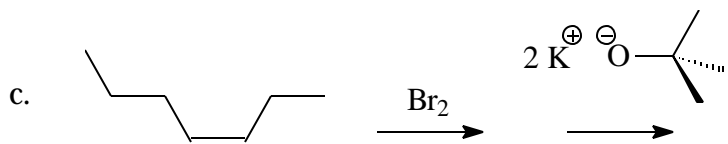
(12 pts)



a.

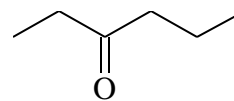
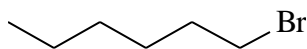
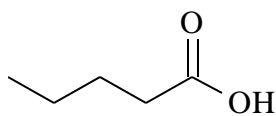


b.

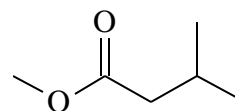
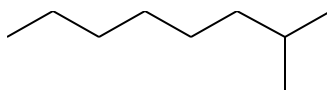
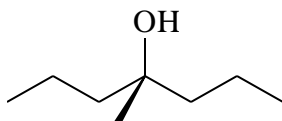


c.

30. Show how you could synthesize each of the following compounds starting with any alkene of any length. In some cases there may be more than one way to make the compound. In such cases chose the method you think best.

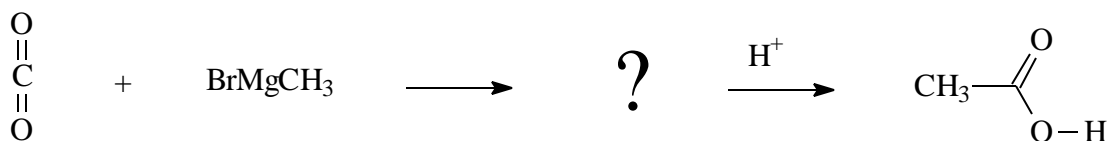


31. Give a synthesis of each of the following molecules. Your carbon containing starting materials should have no more than four carbon atoms.



32. The most important part of learning organic chemistry is the ability to apply the general principles you learn to new circumstances.

For example: One reaction that we did not discuss in class is the reaction of a Grignard reagent with carbon dioxide. This reaction can be used to synthesize carboxylic acids.

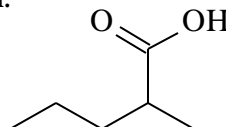
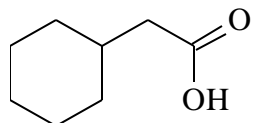


a. Use the curved arrow formalism and draw a mechanism for this reaction?

33. Give a synthesis of the following molecule. Your carbon containing starting materials should have no more than four carbon atoms.

b. Show how you could use this new reaction to synthesis the following carboxylic acids.

You can start with any alkyl bromide you wish.



34. Give a synthesis of the following molecule. Your carbon containing starting materials should have no more than four carbon atoms.

