Chm 222 Spring 2012
Section 1 Mr Linck
Exercises, Set One: Preliminaries Version 1.1

NOTE: Problems with a zero following a number, 5.0., are NOT part of problem 5.1. They will be assigned separately. Assignment of 5 means doing 5.1. and 5.2. If I want you to do 5.0., it will be assigned. Clearly, 6.0.1. and 6.0.2. are part of 6.0. Likewise, if problem 1 is assigned, it means doing 1.1. through 1.5.

1.1. Write the electron configuration for Li, Na, B, C, N, P, O, F, Cl, Br. Use a periodic table and appropriate abbreviations for inner shell electrons. This is not a busy work problem. You should learn to assign electronic configurations quickly and accurately.

1.2. How many valence electrons does each atom of problem 1.1. have? It should become second nature to you to know the number if valence electrons for a given atom.

1.3. Which species in problem 1.1. are "valence shell isoelectronic?"

1.4. Which of the following are "valence shell isoelectronic" with each other?
$O^{=}$, F, C, Si, N, N^{-}, N^{+}, F^{-}, Ne, O, S, O^{+}.

1.5. Which of the following are "valence shell isoelectronic" with each other?
OH^{-}, NH_2^{-}, F^{-}, OH, CH_3, NH_2, Cl, SiH_3, Br.

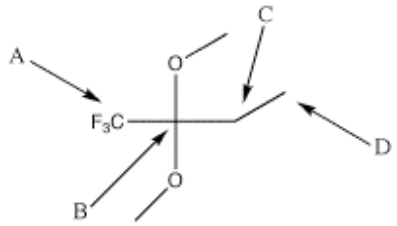
2.0. Give several groups that are isoelectronic with CH_3.

2. Write Lewis structures for C_2H_6, CH_3OH, CH_3NH_2, CH_2O, C_4H_8O.

3.1. Indicate the polarity of the bond (with the δ+ / δ- notation) for each of the following:

C-Cl	H-Cl	B-F	C-N	C-O
H-O	B-H	N-F	C-C-F	

3.2. List the carbon atoms labeled in the diagram in terms of increasing positive charge.



3.3. The dipole moment of FCl and ICl are both about 0.8 Debye. Why are they so similar.

3.4. Why is the dipole moment of CH_2Cl_2 larger than that of $CHCl_3$, when the latter has three chlorine atoms?

3.5. Find the direction of the dipole moment in CCl_2Br_2.

3.6. Carbon-oxygen bonds are more polar, larger partial charges, then sulfur-oxygen bonds, yet SO_2 has a dipole moment and CO_2 does not. Comment.

4.0. Past experience teaches me that those of you that draw sloppy Lewis structures are much more likely to be in the bottom half of the class than those of you that draw neat ones. HINT: Where is the question in that?

4.1. Draw Lewis structures of $CH_3C(O)H$, $CH_3CH(CH_3)CH_3$, CH_3CHCH_2, C_2NH_3 (cyclic), CH_3F, C_4H_9Cl (two different connectivities), CH_3OCH_3, CH_3CH_2OH, $CF_3C(O)OH$. HINT: (X) means that group X is off the main chain.

4.2. Draw a Lewis structure of CH_3CN.

5.0. Calculate the formal charge on each atom in every Lewis structure you draw. In particular, try it on:

HN_3, CH_2N_2, BH_4^-, BF_3,

5.1. Look at each structure in problem 4 and determine the number of bonds to C, to N, to O, to F, to H. Formulate a rule for the number of bonds to these atoms. Take NOTE of problem 5.2.

5.2. Take a look at the charged compounds OH^-, NH_4^+, and H_3O^+. Note that charged compounds do not obey the rule that you have formulated from 5.1. Use the concept of isoelectronic species to make sense of these.

6.0.1. Amino acids (which are used to make proteins) exist in acid solution as a cation. Draw the Lewis structure of the protonated form of glycine, $NH_2CH_2C(O)OH$.

6.0.2. Draw the Lewis structure of neutral glycine. HINT: It is a “zwitterion”, a species with both a negative charge and a positive charge in the same molecule.

6.0.3. Draw the Lewis structure of glycine in strong base where it exists as an anion.

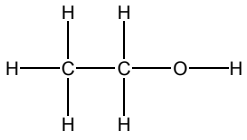
6.1. Draw a Lewis structure for $C_6H_5NO_2$ where the carbon skeleton is cyclic. Give formal charges to all atoms.

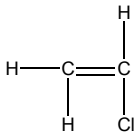
6.1.1. Does your rule of problem 5.2. work in problem 6.1.?

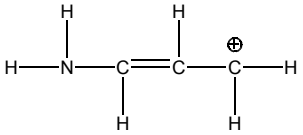
6.2. Draw a Lewis structure for $(CH_3)_2SO$. Give the formal charge on all atoms.

6.3. Draw two Lewis structures for CH_4N_2O where the two nitrogen atoms and the oxygen atom are bonded to the carbon atom.

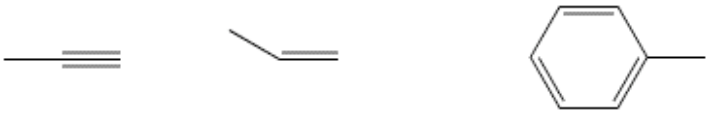
7. Use VSEPR to specify the geometry around each atom in each of the following:



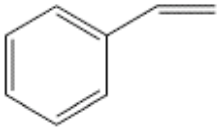


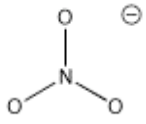


7.0. In the following, which C-C bonds are stronger? Which weaker?



7.0.1. In the following, which C-C and which N-O bonds are longer? Which shorter? HINT: In the last structure there are missing bonds and lone pairs.





8.1. Review your notes from lecture 1. Outline major topics. Rewrite your notes.

8.2. What is an aldehyde? HINT: There won't be many of you, but there will be some that by the end of the semester still do not know what an aldehyde is: Don't be one of them!

8.3. What is a ketone?

8.4. Draw a skeletal structure for an aldehyde with the formula C_4H_8O.

8.5. Draw a skeletal structure for at least four ketones with the formula $C_6H_{12}O$.

8.6. Draw a skeletal structure for a compound of formula $C_7H_{12}O$, which is **not** a ketone.

9.1. Draw the functional group associated with an carboxylic acid derivative.

9.2. Draw a skeletal structure for acetyl chloride, $CH_3C(=O)Cl$, and ethyl acetate, $CH_3C(=O)OC_2H_5$.

9.3. Draw a skeletal structure for an alkene with four carbon atoms.

9.4. How does a ketone differ from acetyl chloride?

10.1. Draw a Lewis and skeletal structure for C_5H_{12}, $C_5H_{10}O$, $C_5H_8O_2$, $C_5H_6O_3$, $C_5H_{12}O$, $C_5H_{13}N$, $C_5H_{12}S$, C_5H_{10}, and C_5H_8.

10.2. How many bonds are there to each C atom in the structures in 10.1.?

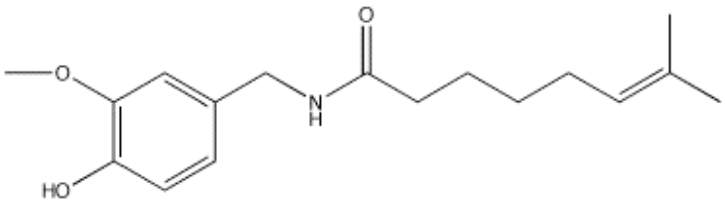
10.3. How many bonds are there to each O atom in the structures in 10.1.?

10.4. Draw a skeletal structure for $(CH_3CH_2)_2CHCH_2OCH_3$.

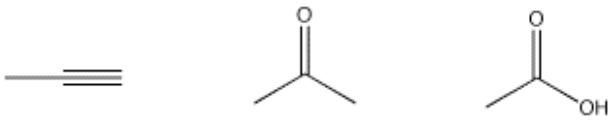
10.5. Draw a skeletal structure for $(CH_3CH_2)_2CCH_2$.

11. Draw a skeletal structure for a ketone, an aldehyde, an acid chloride (a carboxylic acid derivative), an alkene.

11.0. Find all the functional groups in capsaicin, the "hot" in hot peppers:



12.0. The following are treated with strong acid. On what atom or (atoms) will the H^+ "sit"?



12. Sketch the angular wave function for a 2s electron; a $2p_x$ electron; a $2p_z$ electron. Label your axes.

13.1. Show that a $2p_z$ orbital on one carbon atom overlaps with a $2p_z$ orbital on another carbon **if the z axis is the internuclear axis,** the axis between the two carbon atoms.

13.2. Show that a $2p_z$ orbital on one carbon atom does not have net overlap with a $2p_x$ orbital on another carbon if the z axis is the internuclear axis.

13.3. Show that a $2p_x$ orbital on one carbon atom overlaps with a $2p_x$ orbital on another carbon if the z axis is the internuclear axis. What is the magnitude of this overlap compared to that of 13.1.?

13.4. Does a $2p_z$ orbital on on carbon atom overlap with a 2s on another carbon atom if the z axis is the internuclear axis?

14.1. Add the angular wave function for a 2s electron of C to that of a $2p_z$ electron of the **same** carbon atom. Subtract one from the other. In what direction do the functions point? What orbitals are "left" on the C atom?

14.2. Add the angular wave function for a 2s electron of C to that of a $2p_y$ electron of the **same** carbon atom. Subtract one from the other. In what direction do the functions point? What orbitals are "left" on the C atom?

14.3. Add the angular wave function for a $2p_x$ electron of C to that of a $2p_y$ electron of the **same** carbon atom. In what direction does the functions point? What orbitals are "left" on the C atom?

14.4. Add a the angular wave function for a 2s electron of a C atom to the result of problem 14.3. In what direction is this function maximal?

15.1. Where in space do sp^2 hybrids point? What orbital on the atom is "left" over? Where does the "left over" orbital point relative to the sp^2 hybrids?

15.2. Where in space do sp^3 hybrids point? What orbital on the atom is "left" over?

16.0. Sketch a tetrahedral molecule in at least three ways.

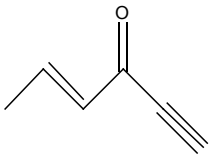
16.1. Review your notes from lecture 3.

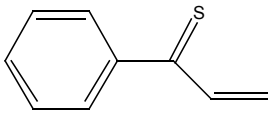
16.2. What were the main topics in lecture 3? Think about them. How do they relate to each other?

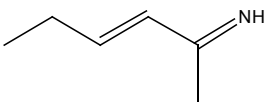
17.0.1. What happens to the overlap in a sigma bond as one atom is rotated in a clockwise fashion looking down the internuclear axis relative to the other?

17.0.2. What about a pi bond?

17.1. For each of the following skeletal structures indicate the hybridization of each C atom.

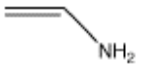






17.2. For the right hand terminal carbon in the left hand structure (above), describe the molecular orbitals used in bonding.

18.0.1. Use VSEPR to describe the structure of



18.0.2. What is the hybridization used on the left hand carbon in 18.0.1.?

18.0.3. If the C-C axis of the molecule in 18.0.1. is the y axis, and the x axis is up and down, what are the atomic orbitals used in the double part of the double bond.

18.0.4. Sketch the molecular orbital for the double part of the double bond in 18.0.1.

18.1. On which atom, C or O, does the π bond (of the C-O bond) have the largest orbital contribution?

18.2. What about the π^* (the antibond)?

18.3. On which atom, C or Cl, does the σ bond (of the C-Cl bond) have the largest orbital contribution?

18.4. On which atom, C or B, does the σ bond (of the C-B bond) have the largest orbital contribution?

18.5. In a bond between C and B, which atom is more positively charged?

18.6. In a bond between C and H, which atom is more positively charged?

18.7. In a bond between H and B, which atom is more positively charged?

19.1. Given the number of atoms attached to each carbon atom of cyclopropane, what hybridization would you use?

19.2. What is wrong with that (the hybridization of exercise 19.1.) hybridization?

19.3. Any prediction about cyclopropane?

20.1. Draw the Lewis structure of a compound with an sp hybridized C.

20.2. Draw the Lewis structure of a compound with an sp^2 hybridized C.

21.1. A carbon atom is attached to four other groups. What hybridization would it use?

21.2. A carbon atom is sp^2 hybridized. What bonding characteristics does it have (i.e., how many σ bonds? how many π?)

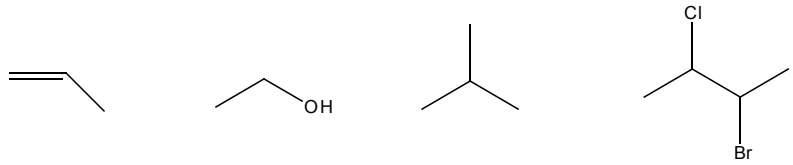
22.0.1. Assume an atom has only a p_z orbital. Draw an mo diagram for the bonding between two of these atoms if the internuclear axis is the z axis.

22.0.2. Assume an atom has only p_z and p_x orbitals. Draw an mo diagram for the bonding between two of these atoms if the internuclear axis is the z axis.

22.0.3. Assume an atom has only two sp hybrids pointing in the plus/minus z direction. Draw an mo diagram for the bonding between two of these atoms if the internuclear axis is the z axis.

22. Draw an mo diagram for the π bonding in H_2CCH_2 and in H_2CO. How do they differ?

23. Try to identify the electrons that are least tightly held in each of the following. For example, in the first compound they would be the C-C π electrons. HINT: bonding electrons are usually more stable than non-bonding electrons.



23.0.1. Which orbital is most stable, C 2s or C 2p?

23.0.2. Which hybrid orbital contains the most "s character", sp or sp^2?

23.0.3. Which hybrid orbital is the most stable , sp or sp^2? Why?

23.0.4. Which compound would be able to tolerate the negative charge easiest?

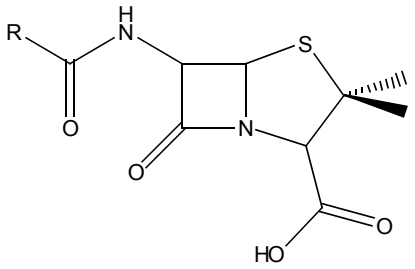
24.0.1. Build an mo diagram for the double part of a double bond (the π bond) in **1**.

24.0.2. When light interacts with the molecule and excites an electron from the π bonding orbital to the π antibonding orbital, what happens to the double bond?

24.0.3. How would you account for photoisomerization of **1** to **2**? HINT: Think about what the word photoisomerization might mean.

24. Find the following in this structure (of a penicillin):

24.1. an sp^3 hybridized carbon;
24.2. an sp^2 hybridized carbon;
24.3. an sp hybridized carbon;
24.4. an amide;
24.5. a carboxylic acid group.



24.0.1.1. Distinguish between an amide and an amine; draw examples.

24.0.1.2. Distinguish between an carboxylic acid and an alcohol; draw examples.

24.0.1.3. Distinguish between a ketone and an aldehyde; draw examples.

25.0.1. Draw the line structure of 4-methyloctane.

25.0.2. Draw the line structure of 2,4-dimethyl-5-propyldecane.

25.0.3. Draw the line structure of 4-(1,1-dimethylethyl)decane.

25.0.4. The trivial name for a propyl group attached by the central carbon is “isopropyl”. Draw the line structure for 3-isopropyldecane.

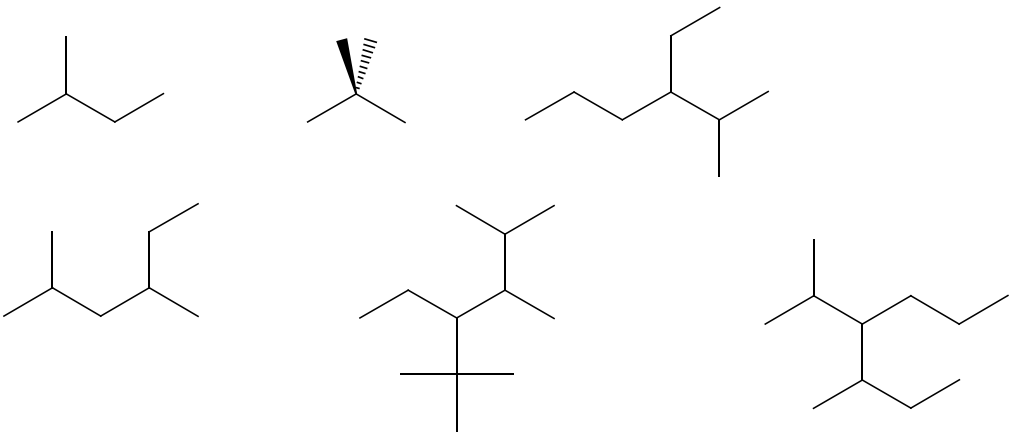
25.0.5. The trivial name for a 2-methylpropyl group is an “isobutyl” group. Draw the line structure for 5-isobutyldecane.

25.0.6. The trivial name for a 1-methylpropyl group is an “secondary butyl” group, usually abbreviated sec-butyl. Draw the line structure for 5-sec-butyldecane.

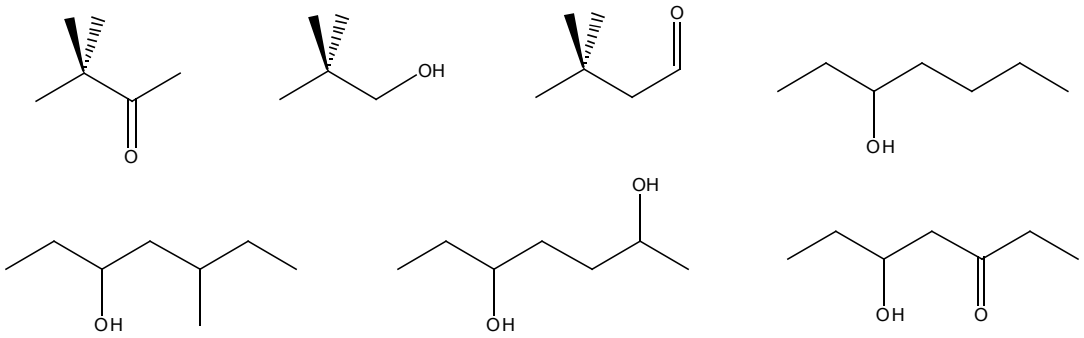
25.0.7. The trivial name for a 1,1-dimethylethyl group is an “tertiray butyl” group, usually abbreviated tert-butyl. Draw the line structure for 5-tert-butyldecane.

25.0.8. Draw the line structure for 3-ethyl-3-hexene

25. Write IUPAC name for the following:



26. Name the class of compound (the functional group) of each of the following. Then name the compounds:

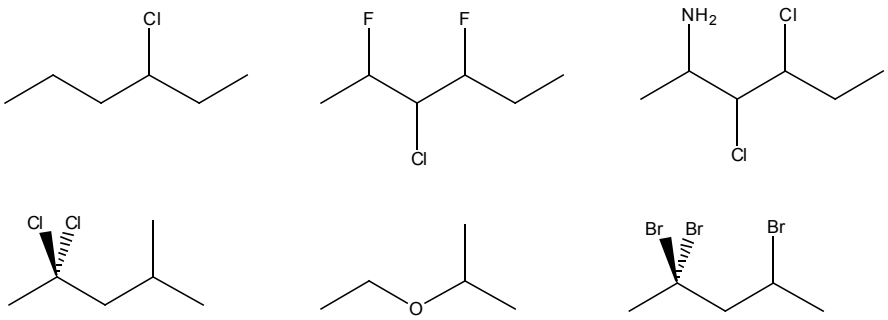


27.0.1. Draw a line structure for 1,5-dibromo-2,2-dichloro-4-ethyl-4-methyl-3-hexanol.

27.0.2. Draw a line structure for tert-butylamine.

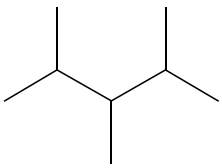
27.0.3. Draw a line structure for 3-isobutylcyclopentanol.

27. Name the following:



28. Write a skeletal structure of 4,5-diisopropylnonane; 5,5-dibromo-4-ethyloctane; 4-(1-methylethyl)decane.

29. Name the class of compound (the functional group) of each of the following. Then name the compounds.



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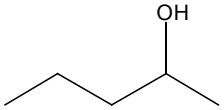

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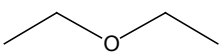

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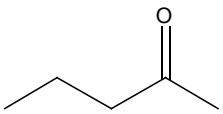

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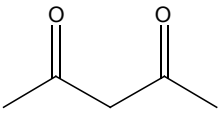

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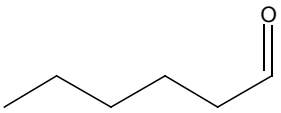

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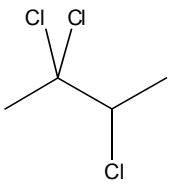

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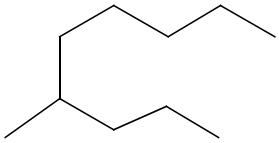

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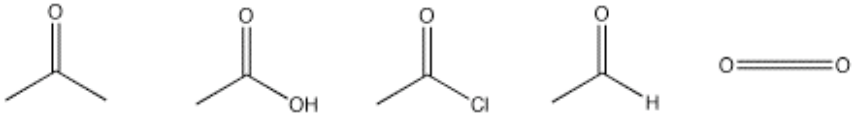
30. Find the carbon level for the carbons in each compound in problem 29.

30.0.1. Find the carbon level for the carbon atoms in each of the following compounds.

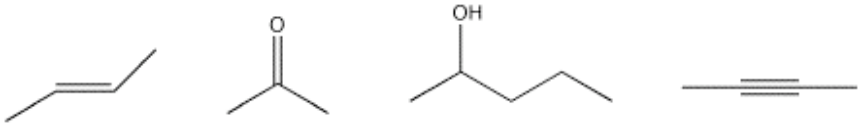


HINT: The last compound has a C in the middle (as the bond is too long compared to the others).

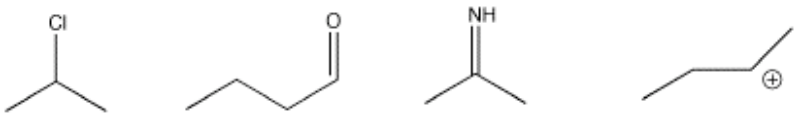
30.0.2. Find the ihd for each compound in problem 30.0.1.

30.0.3. Find the ihd for each of the following compounds: C_3H_4, $C_{10}H_8$, C_5H_9Cl, $C_6H_{10}O$, $C_5H_5NH_2$, C_4H_5N, $C_6H_{12}S$, C_5SiH_{14}.

30.0.4. If you had a positively charged species, E^+, which is called an electrophile, and it came up to each of the following, which atom would it likely attack?



30.0.5. If you had a negatively charged species, N^-, which is called a nucleophile, and it came up to each of the following, which atom would it likely attack?



30.0.6. From the name, what property does an "electrophile" have?

30.0.7. From the name, what property does a "nucleophile" have?

30.0.8. Would you classify the following as electrophiles or nucleophiles?

CH_3^-, H^-, CH_3^+, OH^-, SH^-, NH_3

31.0. Past experience teaches me that those of you that draw sloppy epwas, ones in which the electron pair being used is not obvious--the tail of the arrow--and, more importantly, in which the position in space to which the electrons move--the head of the arrow--is not clear, will generally do poorly in class. An epwa should mean something to you; it is an attempt to represent an important motion of electrons. Use the dotted line convention to make your epwas neat and concise.

31.1. What kind of reagent is hydride ion?

31.2. What is the charge on the carbon atom in a C=O bond?

31.3. Would you classify the carbon in a carbonyl bond as an electrophile or nucleophile?

31.4. What kind of reagent is a $C\text{-}O^-$ group in a molecule?

31.5. Guess the product of allowing H^- to attack butanal, followed by treatment with H^+. Use epwa/ogeda. Name the final product.

31.6. Guess why you have to do these two steps in problem 31.5. sequentially; that is, why can't you add H^-, the aldehyde, and H^+ all together? HINT: Think electrostatic attraction.

32. Find the ihd for each of the following compounds:

a. $C_6H_{10}Cl_2$ b. $C_5H_{10}O$
c. $C_6H_{14}O_2$ d. C_7H_{10}

33. Suggest a possible structure for a compound of formula $C_6H_{12}O$.

34. What is the ihd for a compound of formula C_4H_9N? Suggest a structure.

35.0.1. Draw a Newman projection of ethane.

35.0.2. Draw a Newman projection of propane looking down the C1-C2 bond.

35.0.3. Draw the gauche conformation of 1,2-dibromoethane.

35.0.4. Draw the anti conformation of 1,1,1-trifluorobutane.

35.0.5. If you did 35.0.3. and 35.0.4. using Newman projections, draw the line structures. If you did those two problems using line structures, draw the Newman projections.

35. Draw Newman projections for each of the three minimum energies of 2-bromo-1,1-dichloroethane and indicate the relative stabilities.

36.1. Review your class notes from lecture 4.

36.2. What were the major topics in the last lecture? Think about them. How can you connect them?

37. Make Newman projections for 3-methylpentane looking down the C1-C2 bond; down the C2-C3 bond. If there is more than one conformer, draw all of them.

38. Consider oxirane, show here. Make a Newman projection looking down the C1-C2 bond. Can you see any reason why this structure might have some instability?

39. Draw the zig-zag (line structure) and Newman projections (down the C1-C2 bond) of some conformations of propanal.

40. How many isomers are there of 1-chloro-2-fluoroethane? How many unique conformers?

41. For 1,2-dibromoethane the ratio of anti conformer to a gauche conformer is 89/11 at equilibrium at 298 K. Calculate ΔG^{o} for conversion of anti to the gauche conformer.

42. Draw the Newman projection of the most stable conformer of 1-cyclohexylpropane (with respect to the C_1-C_2 bond).

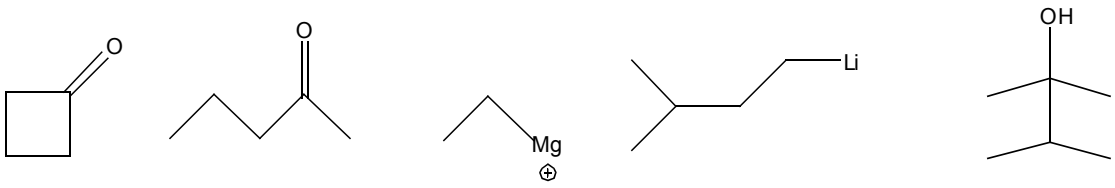
43. What is the product of the reaction of Br_2 with propene?

44.0.1. Will H^- attack the oxygen atom or the carbon atom of ethanal? Why?

44.0.2. Will H^+ attack the oxygen atom or the carbon atom of ethanal? Why?

44.0.3. If H^+ does attack the oxygen atom of ethanal, what happens to the electrophilicity of the carbonyl carbon?

44. Use epwa to show the reaction of **1** with BH_4^-, followed by treatment with H^+.



1 **2** **3** **4** **5**

45. What happens if you mix BH_4^- and excess H^+ together, and then add that mixture to **2**?

46. Use epwa to show reaction of **2** with **3** followed by treatment with H^+. Make sure you keep track of the positive charge.

47. Use epwa to show reaction of **2** with **4** followed by treatment with H^+.

48. Use epwa to show reaction of **1** with **4** followed by treatment with H^+.

49.1. Write a mechanism (use epwa) for the reaction of AlH_4^- with 2-propanone (better known as acetone), followed by treatment with H^+.

49.2. Which would you guess is a more reactive reagent, BH_4^- or AlH_4^-? Why?

50. Write a mechanism (use epwa) for the reaction of C_2H_5MgBr with ethanal followed by treatment with H^+.

51.1. What is the product of reaction of 2-iodopropane with Mg metal?

51.2. What is the product of reaction of 2-bromopropane with Mg metal?

51.3. What is the product of reaction of 2-chloropropane with Mg metal?

52. What is the product of the reaction of the product of problem 51.1. with acetone?

53.1. What happens if a Grignard reagent is treated with water? HINT: Think "C^-" looking for something positive.

53.2. What happens if a Grignard reagent is treated with CO_2? HINT: Same as 53.1.

54. How would you synthesize **3** from bromoethane?

55. How would you synthesize **5** (also known as "Molecular Woman with Lopsided Hat")?

56.0.1. How would you synthesize pentan-2-ol from 2-pentanone and any other reagent?

56.0.2. How would you synthesize pentan-2-ol from butanal and any other reagent?

56.0.3. How would you synthesize pentan-2-ol from ethanal and any other reagent?

56. How would you synthesize 2-methyl-2-butanol from acetone?