

CHEMISTRY 313-02

MIDTERM # 1

October 06, 2009

Name

The total number of points in this midterm is 100. The total exam time is 120 min (2 h). Good luck!

1. (12 pts) Mark as true (T) or false (F) the following statements. Do not explain!

- Single bonds are always σ -bonds;
- Constitutional isomers have different molecular formulas;
- The conformations of a particular substance are stereoisomers;
- The chair conformation of cyclohexane is a global minimum;
- Cyclopropane suffers from *van der Waals* strain;
- Molecules with polar bonds are always polar;
- All *Brønsted* bases are also *Lewis* bases;
- Nucleophiles are *Lewis* bases;
- Increasing oxidation number indicates an oxidation process;
- Intermediates are not formed in concerted reactions;
- The *Hammond* postulate relates the energies and structures of two species on the energy diagram;
- Carbocations are electron-deficient species;

2. (4 pts) Provide the structural formula for each of the following molecules.



sec-butyl alcohol



tetrahydropyran

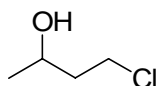
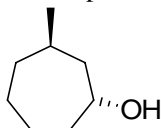


isobutyl bromide



trans-2-methylcyclobutanol

3. (3 pts) Provide an acceptable name for each of the following:

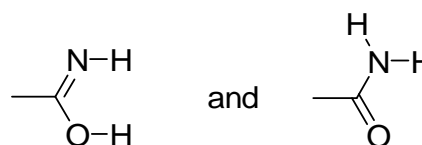
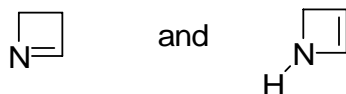
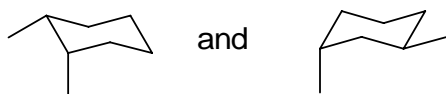


4. (2 pts) Provide a structure for each of the following compounds:

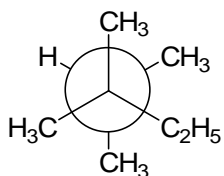
a. *Trans*-decalin.

b. Bicyclo[1,1,1]pentane.

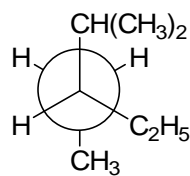
5. (4 pts) What is the relationship of the molecules or ions in each of the following pairs? Classify them as resonance structures, constitutional isomers, or neither.



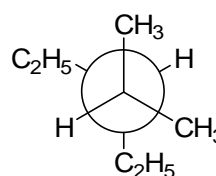
6. (2 pts) Within the set below, which two *Newman* projections represent the same compound?



A



B



C

7. (3 pts) Provide examples of the following:

a. A compound with one quaternary C;

c. A fused bicyclic compound;

b. A tertiary carbocation;

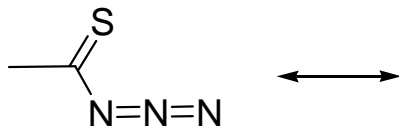
8. (7 pts) Consider the species below.

a. Complete the Lewis structure

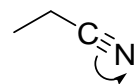
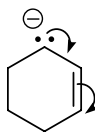
b. Provide two additional valid resonance structures and use the curved arrow formalism to show the flow of electrons.

c. Rank the resultant resonance structures.

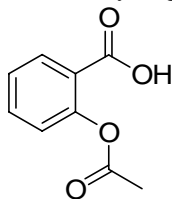
d. Assign hybridization to each non-hydrogen atom in the structure below.



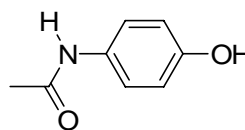
9. (3 pts) Consider the compounds and ions drawn below. When the curved arrows give a second valid resonance structure, draw that resonance structure. When the curved arrows generate an invalid resonance structure, explain why the structure is unacceptable.



10. (2 pts) Indicate the most acidic hydrogen in the structure of each of the following drugs.



Acetylsalicylic acid (Aspirin)



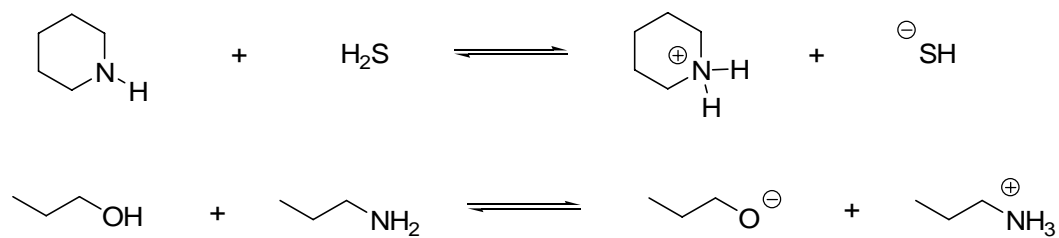
Acetaminophen (Tylenol)

11. (4 pts) For each of the molecules below, draw both the conjugate acid and the conjugate base:

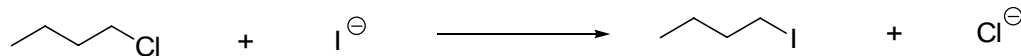
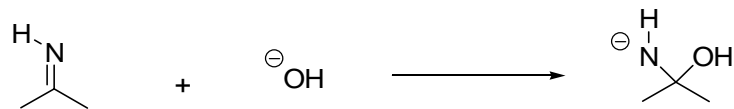
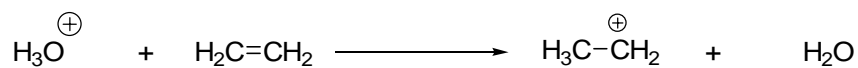
a. 1-Propanol;

b. $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{SH}$

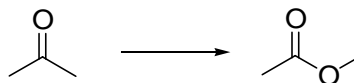
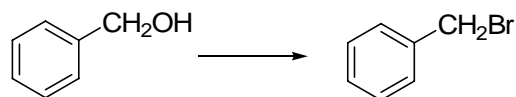
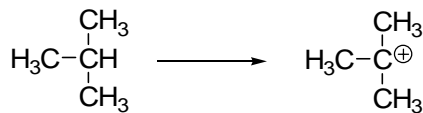
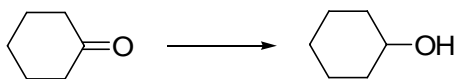
12. (4 pts) Predict the shift of equilibrium (to the left or right) for the following acid – base reactions.



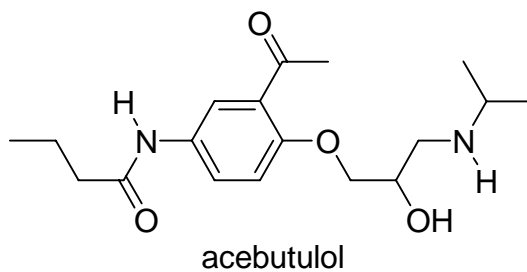
13. (6 pts) Label the reactants in the following reactions as *Lewis* acids or *Lewis* bases.



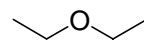
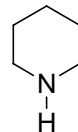
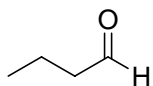
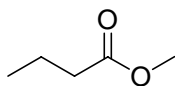
14. (4 pts) Classify each of the following transformations as a **reduction, oxidation** or **not redox**.



15. (5 pts) Identify and name the functional groups present in acebutulol, a drug that blocks certain part of the nervous system.



16. (4 pts) For each of the following compounds, draw an isomer that has the same functional group.



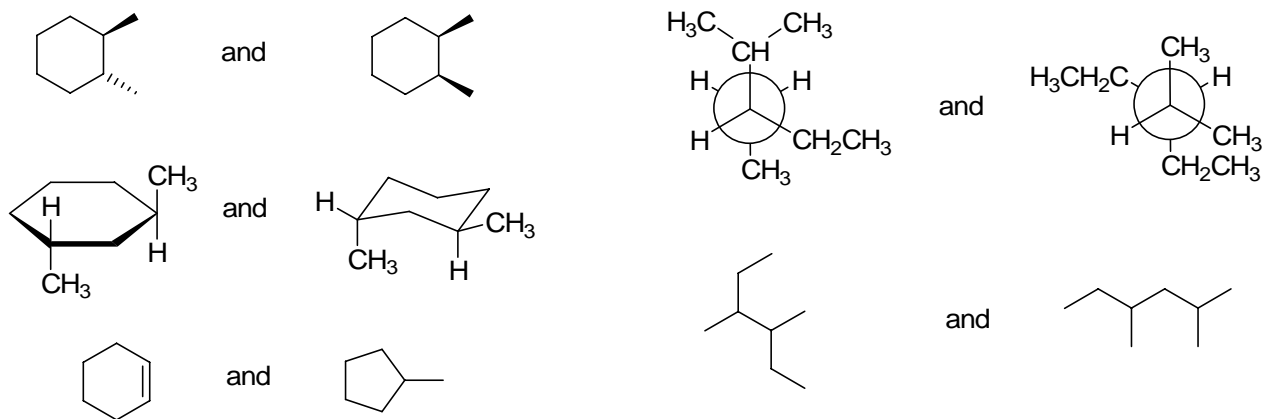
17. (4 pts) Propose structures for the following:

a. An aldehyde with molecular formula C_4H_8O ;

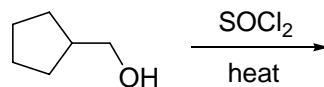
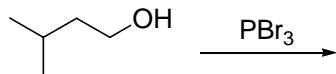
c. A carboxylic acid with molecular formula $C_4H_8O_2$;

b. A thiol with molecular formula $C_4H_{10}S$;

18. (6 pts) Give the relationship between the following pairs of structures. There are four (4) possible relationships: **same compound**, **constitutional isomers**, **cis-trans isomers**, **not isomers** (i.e. different molecular formula).



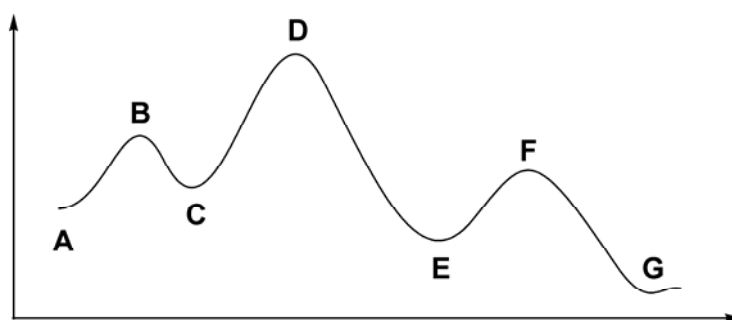
19. (4 pts) Draw the structure of the principle organic product of each of the following reactions.



20. (6 pts) Using *Newman* projections, draw the conformations arising upon a full 360° turn (in 60° steps) around the **C3 – C4** bond in 2,2,4-trimethylpentane. Represent the energy changes on a qualitative energy/dihedral angle diagram. Assign the proper term (i.e. minimum, transition state, etc.) to each conformation.

21. (4 pts) Using detailed chair conformation analysis, find out if *cis*-3-methylcyclohexanol or *trans*-3-methylcyclohexanol is the more stable stereoisomer.

22. (4 pts) Consider the energy diagram shown below and answer the following questions:



a. Does the diagram represent a concerted or a stepwise process? If stepwise, how many steps does it have?

c. Which transition states are reactant-like?

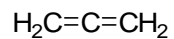
d. Which transition states are product-like?

b. What is the rate-determining step?

e. Which elementary steps are exothermic?

23. (3 pts) Write the rate-determining step in the reaction of 3-methyl-3-pentanol with HBr.

24. (2 pts) **BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!)**. In class, as part of our discussion in Chapter 2, we considered the bonding models of the various carbon – carbon bonds, i.e. single, double and triple. Using the same approach, construct a bonding model for allene (see below). Indicate hybridization for all C – atoms and show how bonds are formed using hybrid or unhybridized orbitals as necessary. Predict the geometry of the molecule.



allene