CHEM 3311, Fall 2011
Professor Walba
First Hour Exam
September 22, 2011

scores:

1) 20

2) 20

3) 20

4) 25

5) 15

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CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Name (printed): Key ______________________

Signature: ______________________

Recitation TA Name: ______________________

Recitation day and time: ______________________

This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear ziplock bag. Please put all you answers on the test. Use the backs of the pages for scratch.

PLEASE read the questions very carefully!

Partial Periodic Table

1A	2A	3A	4A	5A	6A	7A	8A
1 H							2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
						35 Br	
						53 I	

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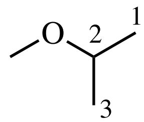
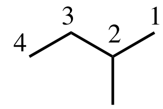
1. (20 pts) The structures of 2-methoxypropane (**1**) and 2-methylbutane (2) are given below.



1



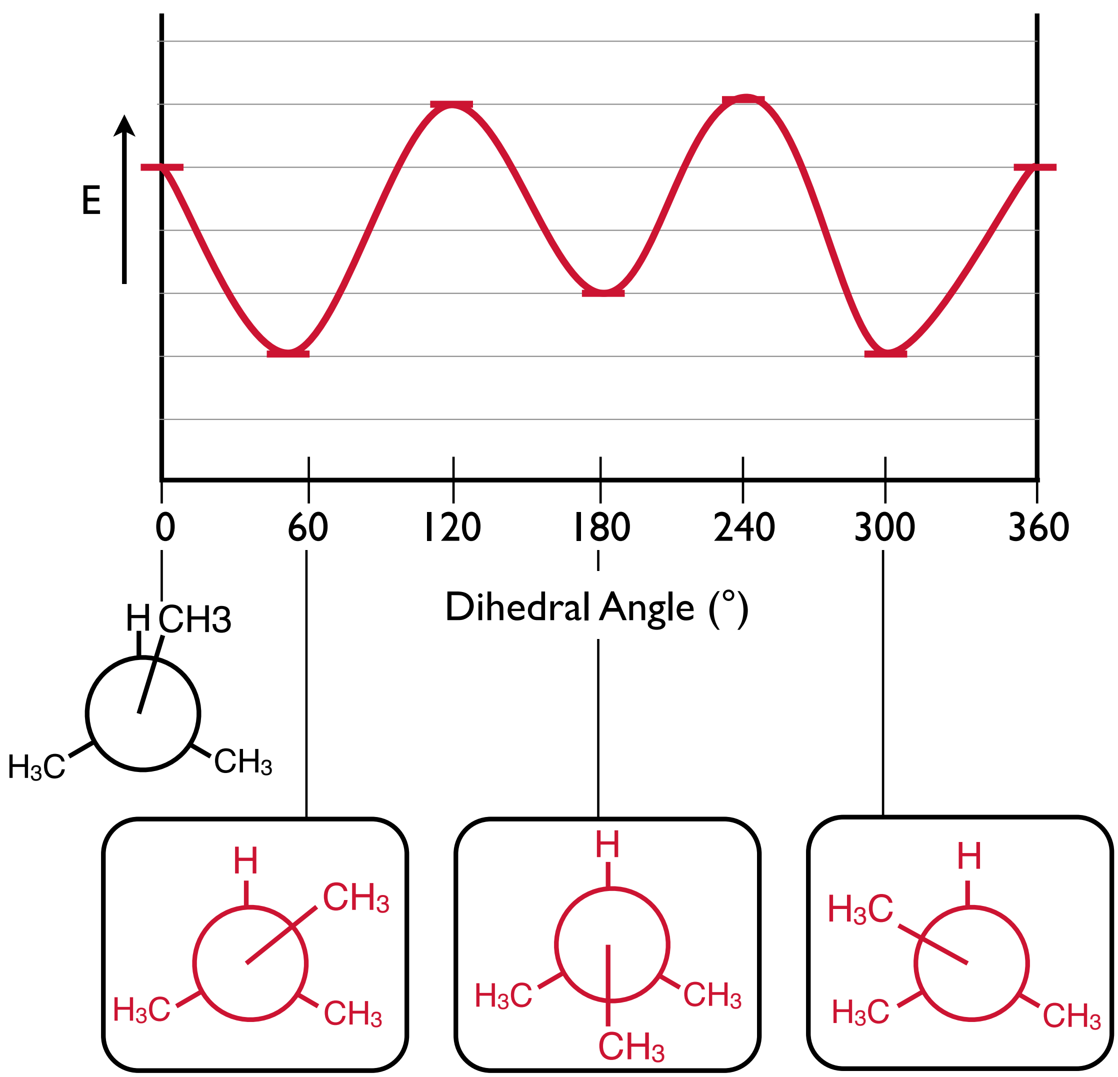
2

a) Is the O-C(2) bond of **1** longer or shorter than the C(2)-C(3) bond of **2**? Check the appropriate box at right to indicate your answer.

longer ☐ shorter ☑ √

b) Perform a conformational analysis for rotation **clockwise** of the methyl group on oxygen, around the O-C(2) bond of 2-methoxypropane (**1**) by completing the energy diagram below. Sight down the O-C(2) bond with the oxygen atom in front. Define the conformation where the CH_3 on O is eclipsing the H atom on C(2) as having the 0° dihedral angle, as indicated by the Newman projection on the energy diagram (the CH_3 group on oxygen is rotated slightly so you can see the H atom behind it, lone pairs on oxygen are not shown).

Carefully draw Newman projections for the three staggered conformations in the appropriate boxes, and complete the energy diagram showing the relative energies of all the staggered and eclipsed conformations.



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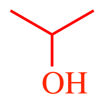
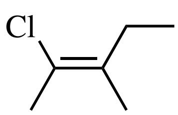
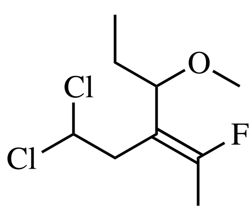
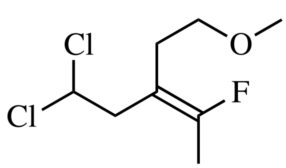
2) (20 pts) a) Draw the structure using skeletal formulas (molecular graphs) for all possible stable isomers of C_3H_8O. Make your structures valid valence bond structures showing all lone pairs. Be careful to draw each isomer only once – points will be taken off for both missing and redundant structures.


For each of the following alkenes, indicate the stereochemical configuration (E or Z).

b) 
Z

c) 
Z

d) 
E

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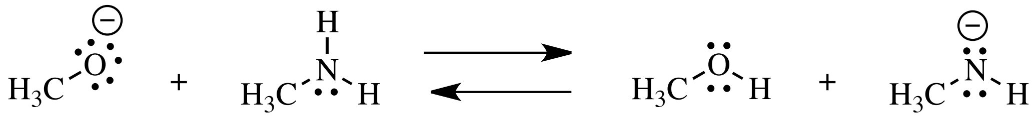
3) 20 pts) For the following equilibrium:



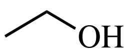
Base Acid Conjugate acid Conjugate base

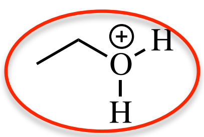
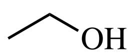
a) Label each structure above as an acid, a base, a conjugate acid, or a conjugate base (there is one of each).

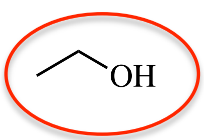
b) Is K_{equ} greater than 1, or less than 1? Less than 1

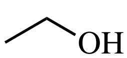
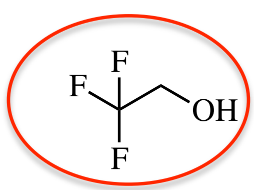
c) Which has lower energy, the starting materials or the products? Starting materials

For each of the following pairs of structures, circle the stronger Brønsted acid.

d)  

e)  

f)  

g)  

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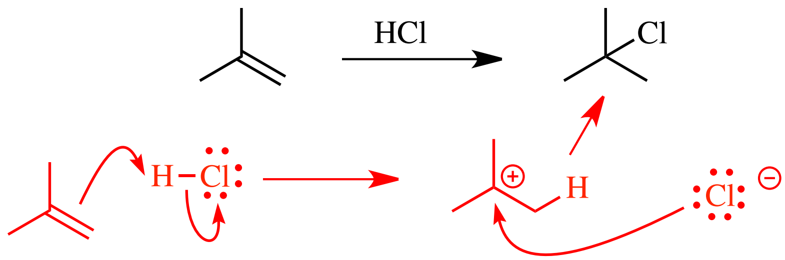
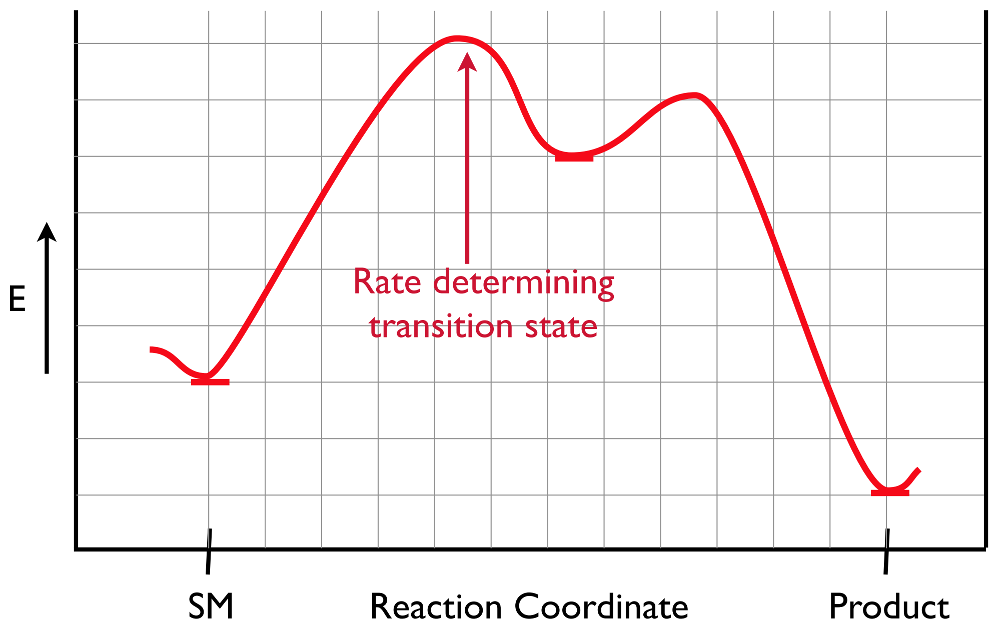
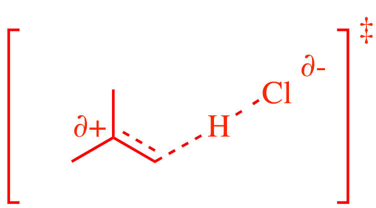
4) (25 pts) a) Propose an arrow-pushing mechanism for the following reaction. Show all intermediates in your mechanism, but do not show transition states. Be sure all structures are complete valid valence bond structures, including all lone pairs and formal charges.



b) Complete the reaction coordinate diagram below for the reaction in part a) of this question.



c) Draw a structure for the rate determining transition state for this reaction in the space below, and clearly indicate using an arrow where it lies on the reaction coordinate diagram.



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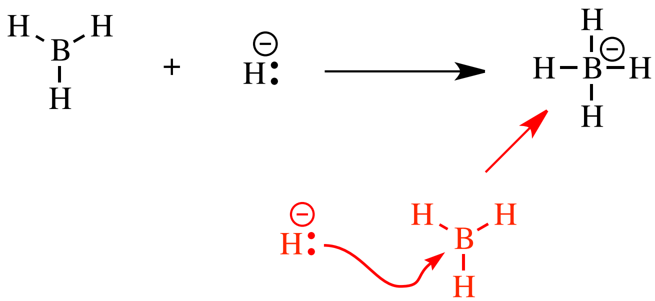
4) –continued-

Borane (BH_3) reacts with sodium hydride ($Na^+ H^-$) to give sodium borohydride ($Na^+ BH_4^-$).

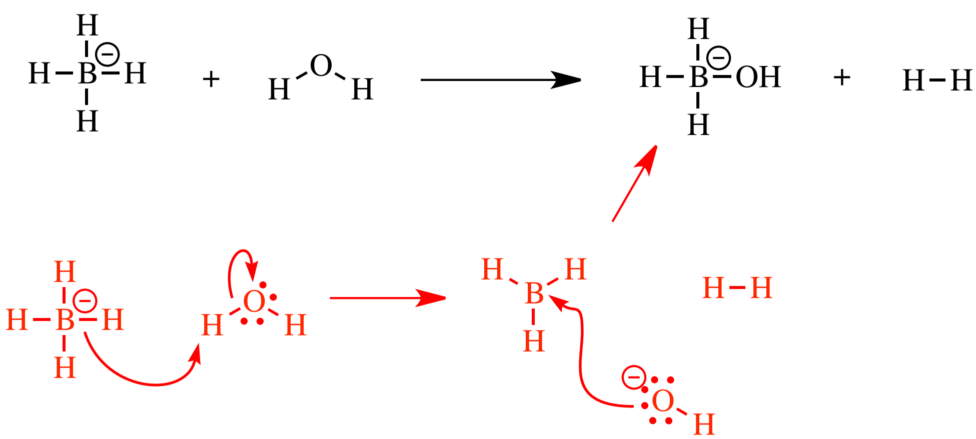
d) Propose an arrow-pushing mechanism for this reaction. Show all intermediates in your mechanism, but do not show transition states. Be sure all structures are complete valid valence bond structures, including all lone pairs and formal charges. Following a typical convention, the Na^+ ion is not shown, and is not needed in your mechanism.



e) What is the name of this type of reaction? [hint: it's a kind of acid/base reaction]

Lewis acid/base association reaction

f) Sodium borohydride reacts with water to give hydrogen gas and "hydroxyborohydride," as shown in the equation below (again, the Na^+ ion is not shown). Give an arrow-pushing mechanism for this reaction, using valid valence bond structures with all lone pairs and formal charges correctly indicated.



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5) (15 pts) Based upon what you've learned, it's not possible to decide which of the following molecules is the stronger Brønsted acid. However, it is possible to make an argument for either molecule being the stronger acid.

CF_3CH_2OH CH_3CH_2SH

1 **2**

a) In the space just below this sentence, make a **concise** argument for why 2,2,2-trifluoroethanol (**1**) would be a stronger acid than ethanethiol (**2**).

Trifluoroethanol (**1**) is the stronger acid because the conjugate base of **1** is the weaker conjugate base, being stabilized relative to the conjugate base of **2** by the electronegativity of the oxygen and the delocalization of charge onto the fluorine atoms (the polar effect).

[More explanation, not needed in answer] Relative stability of the ions (in this case conjugate bases) is usually not the most important effect on relative acidities for acids where the protons are donated from atoms in the same column but different rows of the periodic table, but the combination of electronegativity of oxygen and the fluorine atoms makes **1** more acidic than **2**.

b) In the space below, make a **concise** argument for why ethanethiol (**2**) would be a stronger acid than 2,2,2-trifluoroethanol (**1**)

Oxygen and sulfur are in the same column but different rows of the periodic table. Ethanthiol is the stronger acid because the S-H bond is weak relative to an O-H bond, and this increases the acidity of protons donated from sulfur, an atom in the third row, relative to protons donated from oxygen, an atom in the second row.

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Which molecule is actually more acidic?
The pKa of trifluoroethanol is reported in the literature to be ~11 – 12.5
The pKa of ethanthiol is reported to be ~10.6

According to this data, the second row acid is still weaker than the third row acid, even with the three fluorines. So, the weak bond strength of the ethanethiol is more important than the stabilization of negative charge in the trifluoroethanol conjugate base in this case.

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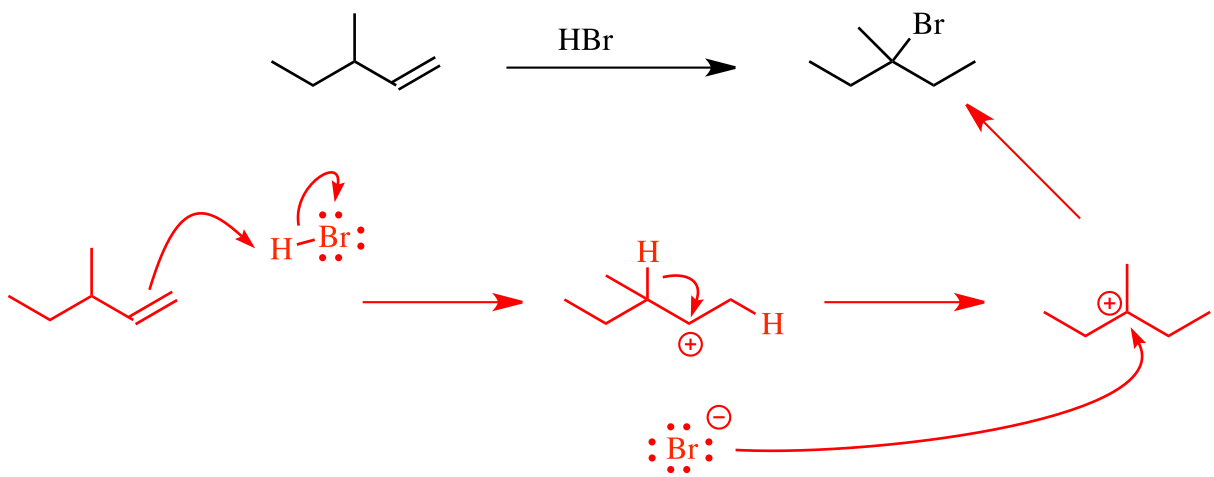
5) – Continued

c) Give an arrow-pushing mechanism for the following reaction. Show all intermediates in your mechanism, but do not show transition states. Be sure all structures are complete valid valence bond structures, including all lone pairs and formal charges.



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