Easily Legible Printed Name:_____

CHEM 3311 (300), Fall 2014
Professor Walba
First Hour Exam
September 23, 2014

scores:

1) 20

2) 20

3) 20

4) 20

5) 20

_____
100

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

Signature: Key

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 in the appropriate place. Use the backs of the pages for scratch (there are two additional blank scratch sheets after the last page of the exam). DO NOT PUT ANSWERS ON THE SCRATCH SHEETS.

PLEASE read the questions very carefully!

PLEASE legibly print your name on each page of the exam.

Partial Periodic Table

1A							8A
1 H	2A	3A	4A	5A	6A	7A	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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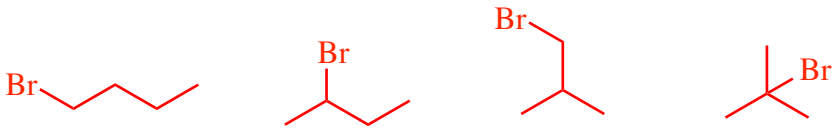
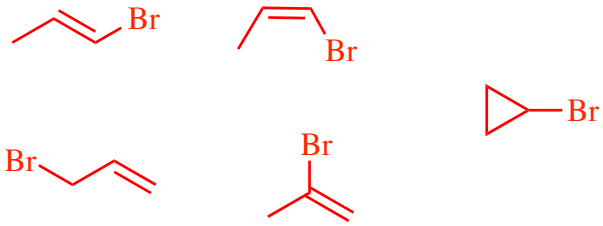
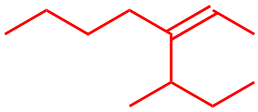
1 (20 pts) a) Draw the molecular graphs (skeletal formulas – showing no H atoms, indicating C atoms as vertices, and explicitly indicating the Br atom) for all the possible constitutional isomers with molecular formula C_4H_9Br (bromobutane). Draw each isomer only once. Points will be deducted for leaving out an isomer, AND for drawing the same isomer multiple times.



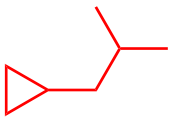
b) Draw the molecular graphs for all of the possible isomers (both constitutional isomers and stereoisomers) with molecular formula C_3H_5Br. Again, points will be deducted for leaving out an isomer, AND for drawing the same isomer multiple times.



c) Draw the molecular graph of (Z)-3-sec-butyl-2-heptene, carefully showing the stereochemistry.



d) Draw the molecular graph of isobutyl-cyclopropane



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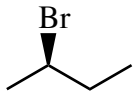
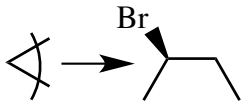
2) (20 pts) A "wedges and dashes" structure for one conformation of 2-bromobutane is given below – following the usual convention that H atoms are not shown, but are assumed to be present.



a) Sighting down the C2—C3 bond, let the dihedral angle of the conformation where the C1 and C4 methyl groups are eclipsed be defined as 0° as shown below.



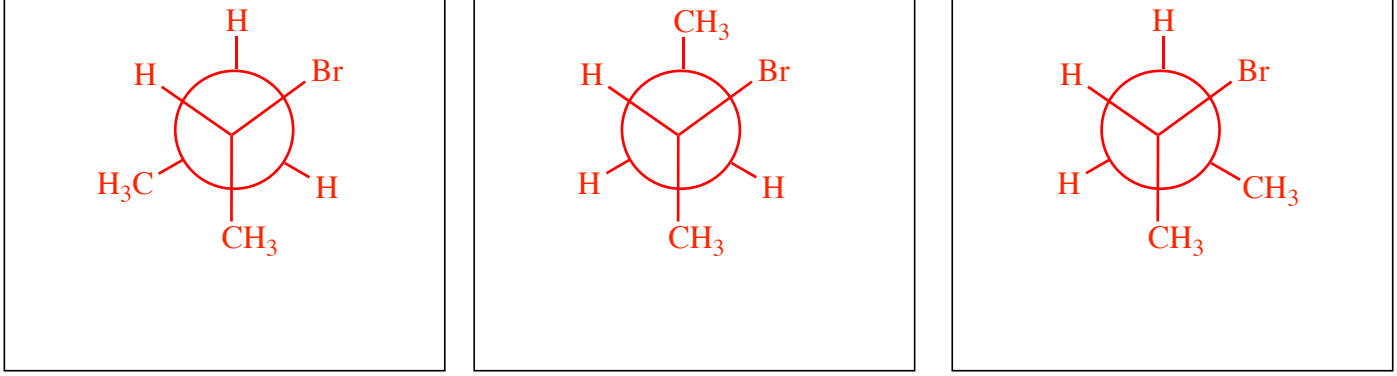
Defined as 0° conformation

Sighting down the C2–C3 bond, and rotating C3 (the "back" carbon) clockwise starting from the 0° conformation, carefully draw Newman projections of the three **staggered** conformations in the boxes below. Be sure to include all the atoms (including H atoms) in your Newman projections.

60°

180°

300°



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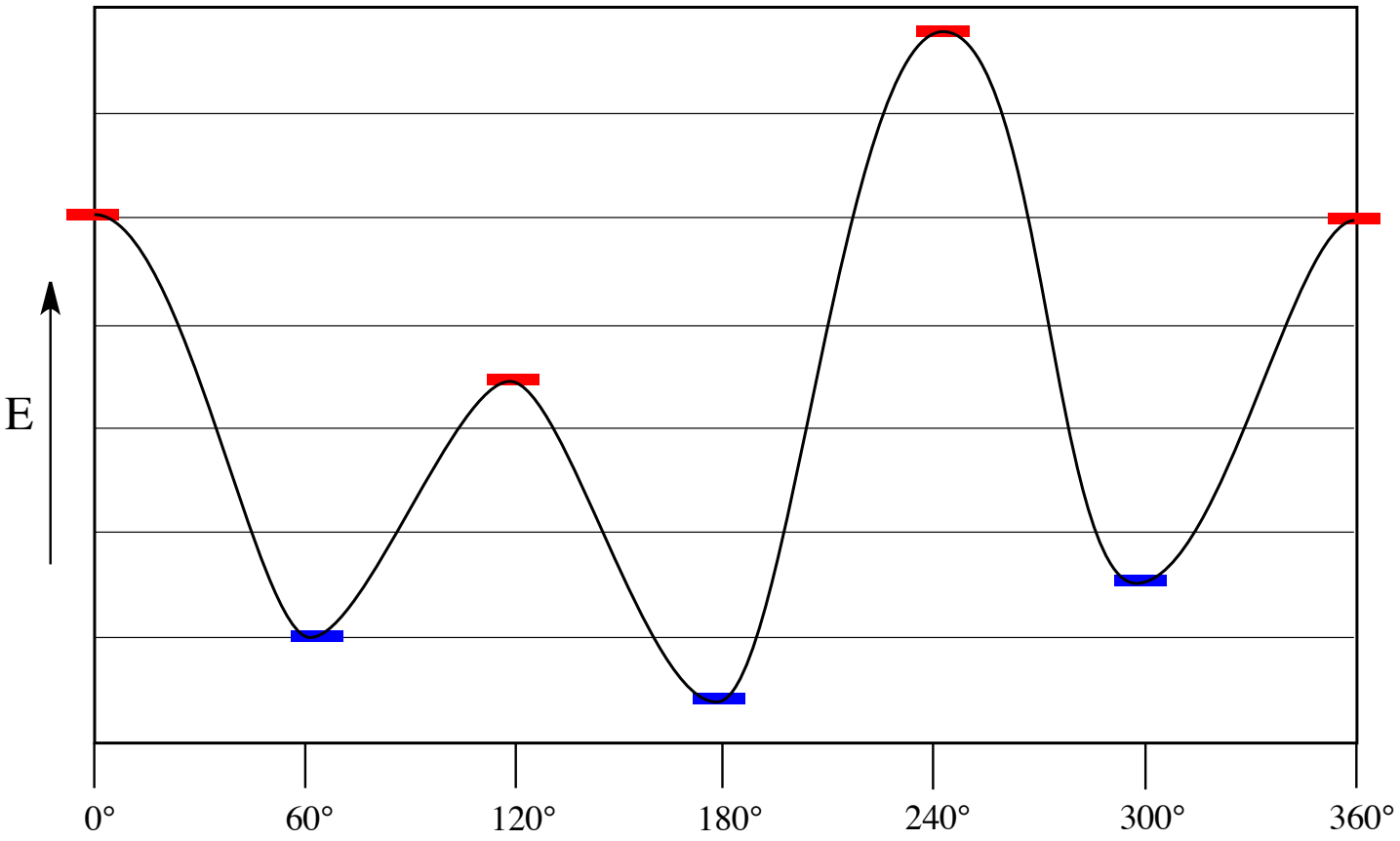
2 – continued

b) A bromine atom is quite large, but the conformational analysis of alkyl halides is complex. Assume the following: When bromine is eclipsed with a methyl group, it behaves as if it were larger (has more "steric demand") than a methyl group. However, if the bromine atom is staggered with respect to a methyl group, it behaves as if it were smaller than a methyl (has less steric demand, due to the long C–Br bond).

Given this assumption, complete the conformational energy diagram below. Be sure to clearly indicate the relative energies of all of the barriers and wells on the energy hypersurface, and connect them with smooth curves, following the standard convention for conformational energy diagrams obtained by rotation around single bonds.



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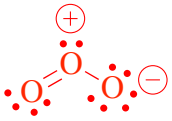
3) 20 pts) a) Two of the smallest common molecules, ozone (O_3), and carbon monoxide (CO), are somewhat complicated with respect to their valence bond structures. Given that the three oxygen atoms of ozone are bonded in a chain (O–O–O), and that carbon monoxide has the C and the O bonded, write valid valence bond structures for ozone and for carbon monoxide, **which show an octet on each atom**. Be sure to include all the lone pairs in your structures, and be sure to show the correct formal charges on all the atoms.



b) For each of the following pairs of molecules, circle the stronger Brønsted acid, and indicate with a check mark the best reason for your choice. Note: In general stronger bonds are shorter bonds.

		charge effect	relative electronegativities	relative bond strengths
NH_4^+	H_3O^+	☐	X	☐
H_2S	H_2O	☐	☐	X
H_2O	H_3O^+	X	☐	☐
HBr	HCl	☐	☐	X
H_2O	NH_3	☐	X	☐

Total points for this page: ☐

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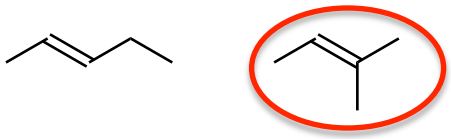
4) (20 pts) a) If hypothetical compounds A and B are isomers, and compound A is more stable than compound B, check the box next to the compound with the higher heat of combustion (also must have the higher standard heat of formation).

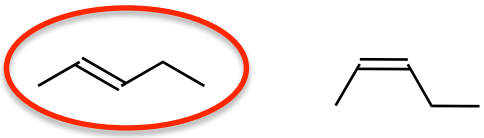
Compound A ☐

Compound B ☐

For each of the following pairs of structures, circle the structure representing the more stable compound, and give a **brief** explanation for why your choice is more stable.

b) 

Trisubstituted double bonds are more stable than disubstituted double bonds because there are more sp^2–sp^3 carbon-carbon bonds in the trisubstituted isomer, and they are stronger.

c) 

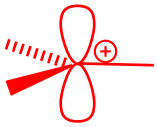
The cis alkene has steric strain no present in the trans isomer, which makes the cis isomer less stable.

The structure of the tert-butyl cation is given here ➜ 

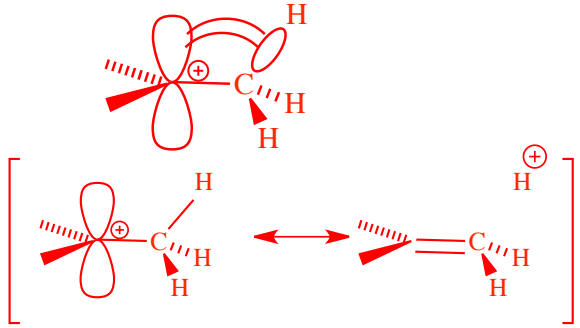
d) Give the hybridization of the central carbon of this cation, and name the geometry.

sp^2, trigonal

e) Draw a wedges and dashes structure for the tert-butyl cation, showing the p orbital (the four carbons must be in a plane perpendicular to the plane of the paper). Be sure to include the formal charge in your structure.



f) Draw another wedges and dashes structure for the tert-butyl cation indicating how and why hyperconjugation stabilizes the ion. (Hint: For this question you will need to include a σ bonding orbital in your drawing).



The electrons in a C–H sigma bond overlap with the empty p orbital on the cation carbon. This puts positive charge on the H, delocalizing the charge, and stabilizing the ion. The resonance picture for this effect would also be correct.

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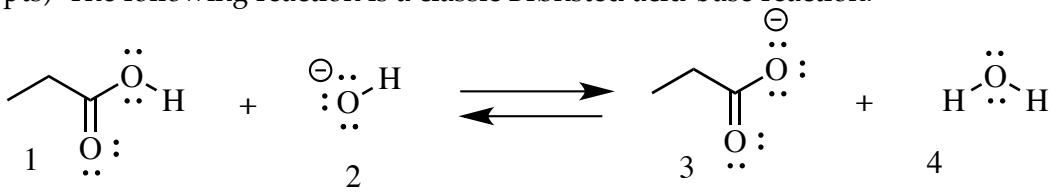
5) (20 pts) The following reaction is a classic Brønsted acid-base reaction.



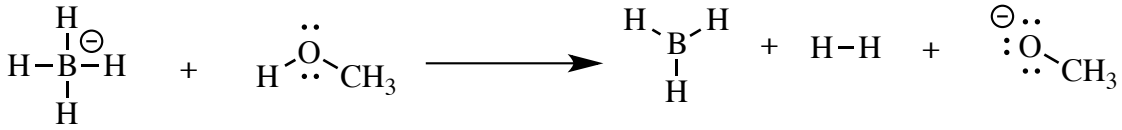
a) Does the equilibrium favor the products (**3** + **4**) or the starting materials (**1** + **2**)? Product

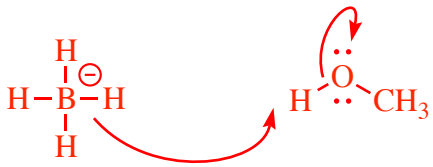
b) Compound **1** has two C–O bonds (ignoring bond order). Are the these bonds the same length, or different length? Different

c) Compound **3** also has two C–O bonds (ignoring bond order). Are these bonds the same length, or different length? The same

For each of the following reactions, propose an arrow-pushing mechanism, and characterize the reaction as a **Brønsted acid-base electron pair displacement**, a **Lewis acid-base association**, or a **Lewis acid-base dissociation.**

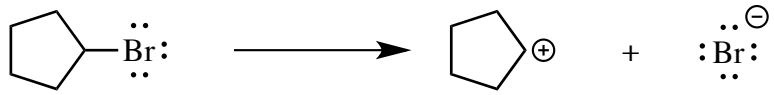
d)

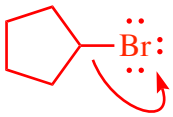




Brønsted acid-base electron pair displacement

e)





Lewis acid-base dissociation

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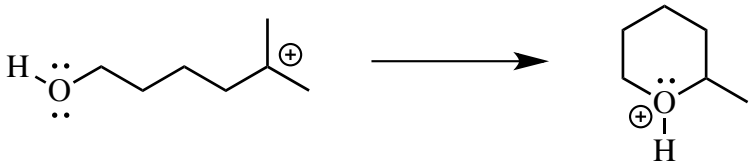
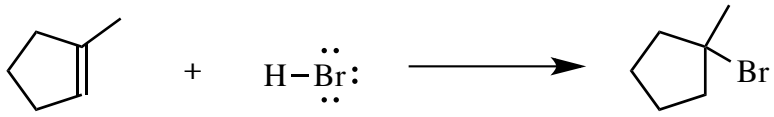
5 – continued

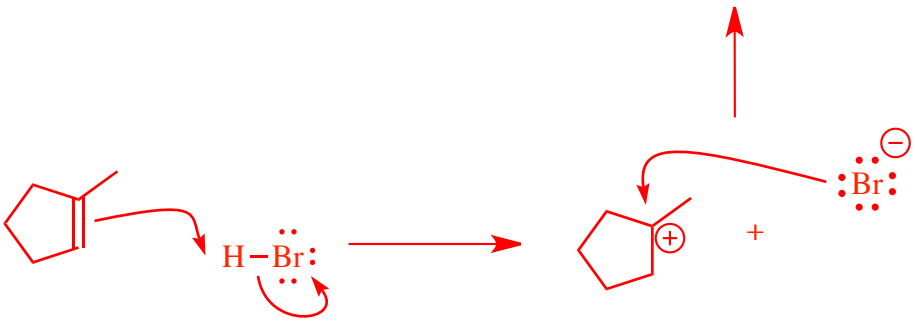
f)



Lewis acid-base association

g) NOTE – this reaction requires two steps. Show both steps in the mechanism, and characterize each step separately.





Brønsted acid-base electron pair displacement

Lewis acid-base association

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