CHEM 233, Fall 2017 Midterm #3 Ian R. Gould

COMPLETE THIS SECTION : Up to TWO POINTS will be removed for incorrect/missing information!

PRINTED **FIRST** NAME answer key PRINTED **LAST** NAME _____

Person on your **LEFT** (or **Empty** or **Aisle**) _____

Person on your **RIGHT** (or **Empty** or **Aisle**) _____

Class you are REGISTERED FOR (onground or hybrid) _____

The room where most students will take the test for your class, i.e. LS A-191 for onground and PS H-152 for hybrid) _____

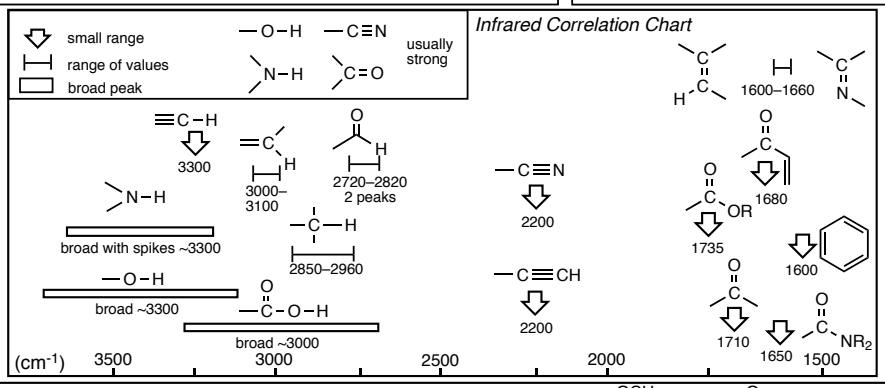
*****YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM*****

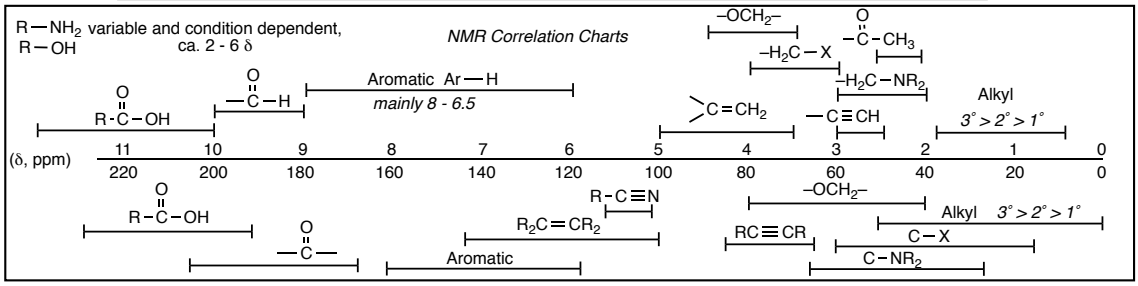
- *PRINT YOUR NAME ON EACH PAGE!*
- *READ THE DIRECTIONS CAREFULLY!*
- *USE BLANK PAGES AS SCRATCH PAPER*
  work on blank pages will not be graded...
- *WRITE CLEARLY!*
- *MOLECULAR MODELS ARE ALLOWED*
- *DO NOT USE RED INK*
- *DON'T CHEAT, USE COMMON SENSE!*

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

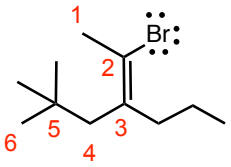
Interaction Energies, kcal/mol

Eclipsing		Gauche	
H/H	~1.0	Me/Me	~0.9
H/Me	~1.4	Et/Me	~0.95
Me/Me	~2.6	i-Pr/Me	~1.1
Et/Et	~3.1	t-Bu/Me	~2.7





Question 1 (12 pts.) Give the IUPAC name for the following structure.

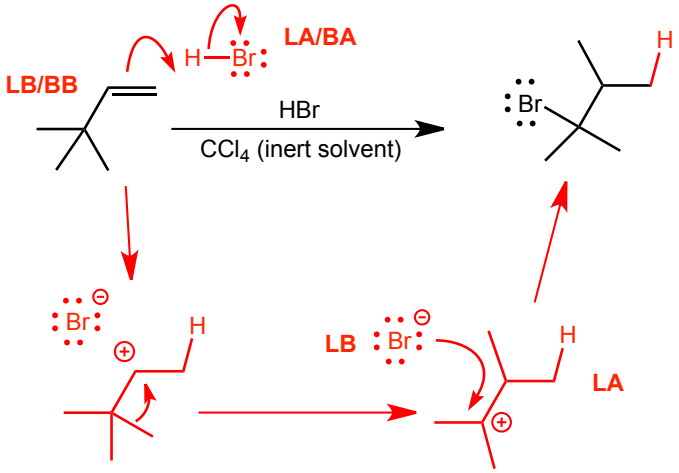


2-bromo-5,5-dimethyl-3-propyl-(2E)-hexene

Question 2 (35 pts.)

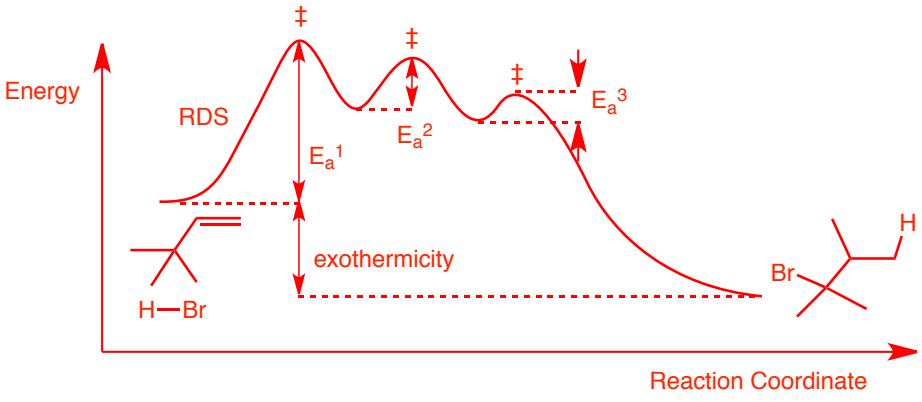
a) Give a full curved-arrow pushing mechanism for the following reaction, indicate the Lewis acid/base (LA/LB) and Bronsted acid/base (BA/BB) at each step as appropriate.

CLASSIFY THE OVERALL REACTION as addition, elimination, substitution or rearrangement. **GIVE THE NUMBER of transition states and the number of sets of intermediates in your mechanism.**



# of sets of intermediates 2 **# of transition states** 3 **classification** addition

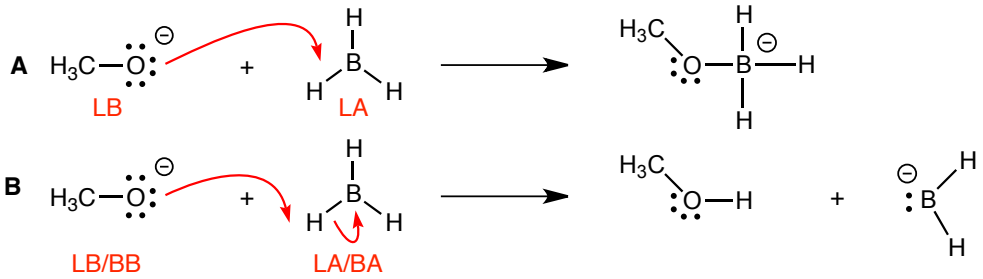
b) Draw a reaction energy diagram with properly labelled axes for the reaction above. Draw on the diagram **the activation energy for EVERY STEP of the mechanism**, and clearly indicate **which one is the rate determining step**. Also draw on the diagram the overall reaction exothermicity or endothermicity. Indicate the positions of the transition states (but do not draw the structures of the transition states).



CHEMISTRY 233, Fall 2017 MIDTERM 3 NAME _____

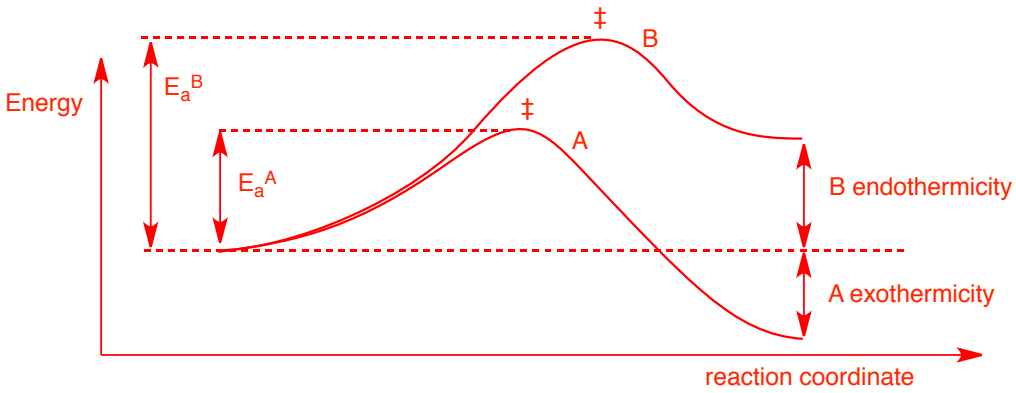
Question 3 (30 pts)

a) For the reactions **A** and **B**, add the curved arrows that illustrate bond-making and bond-breaking, indicate the Lewis acids bases (LA/LB) and whether they are also Brønsted acids/bases (BA/BB)



b) One of these reactions is exothermic, the other is endothermic. Decide which is which and give an explanation. Draw a reaction energy diagram for A and B **ON THE SAME DIAGRAM** (so that they can be compared, do not draw 2 different diagrams). Do not forget to properly label the axes and clearly indicate which diagram refers to which reaction!

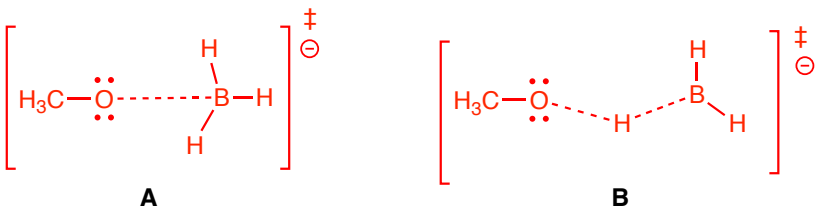
reaction A is exothermic because it makes one sigma bond, no bonds are broken
reaction B is endothermic because it makes one sigma bond, breaks one sigma bond, but the negative charge goes from being on the electronegative oxygen to the non-electronegative boron



c) Indicate the activation energies for the two reactions on your energy diagram, and also indicate the exothermicity or endothermicity as appropriate. State which reaction, A or B would be FASTER, and **BRIEFLY (one sentence) explain why.**

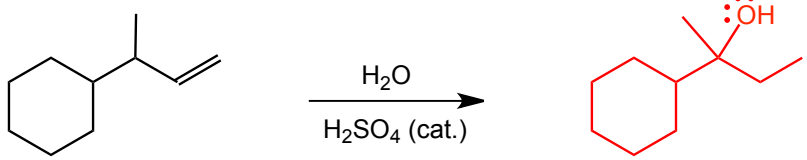
reaction A is faster because it has a smaller activation energy because it is exothermic

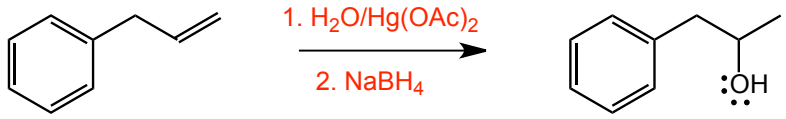
d) Below, draw structures for the transition states for each reaction **A** and **B**.

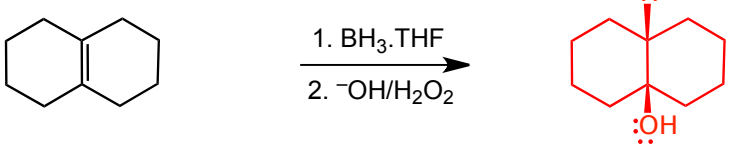


Question 4 (24 pts.) Give the missing major organic products OR reagents/conditions as appropriate for each of the following reactions, include all non-bonding electrons.

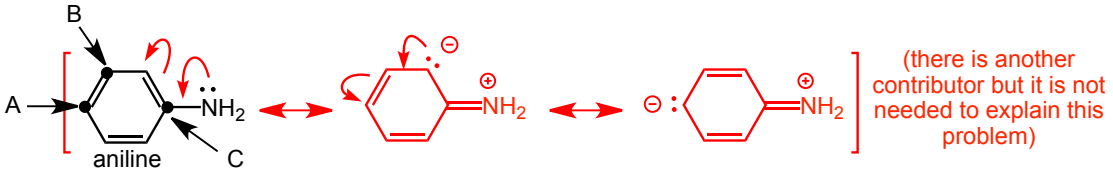
clearly indicate sterochemistry in the products where relevant

a) 

b) 

c) 

Question 5 (20 pts.) The structure of aniline is shown below. Rank the carbon atoms labelled A, B and C in order of decreasing chemical shift in a 13C (carbon) nmr spectrum. You will need to draw minor resonance contributors in order to get the correct answer to this question. Give an explanation for your answer that includes the following terms, "electron density" and "shielding and/or deshielding" (you do not need to mention local magetic field, although it will not be incorrect if you do)



C > B > A

C: largest chemical shift

A: smallest chemical shift

C is most deshielded because it is attached to the electronegative nitrogen, it has the largest chemical shift

the minor resonance contributors indicate that A has a partial negative charge, which increases electron density on this carbon, which increases shielding, or decerases deshielding, A has the smallest chemical shift

C is closest to the electronegative N, it has the largest chemical shift

A does not have the smallest chemical shift because it is farthest from the N, but that answer is worth partial credit

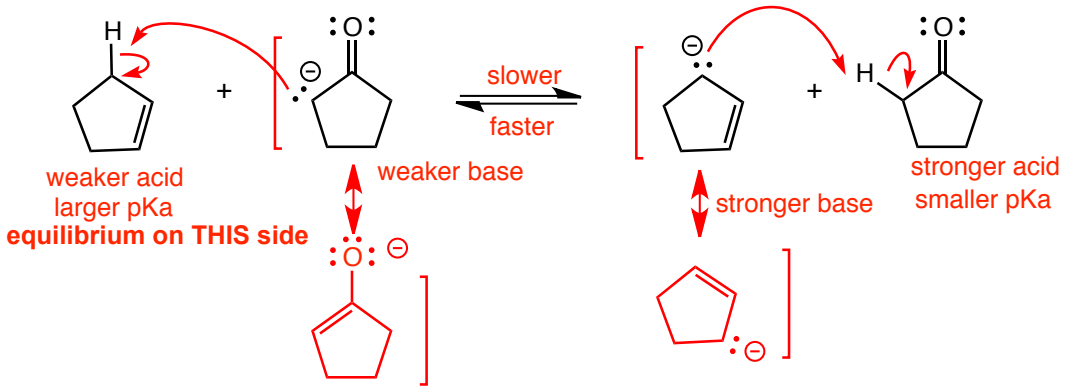
Question 6 (30pts.) For the following Bronsted acid/base equilibrium (not all of the H atoms are specifically shown in the line-angle structures):

a) Draw the curved arrows for reaction in both directions

b) Add any missing important resonance contributors for the anions on both sides of the equilibrium

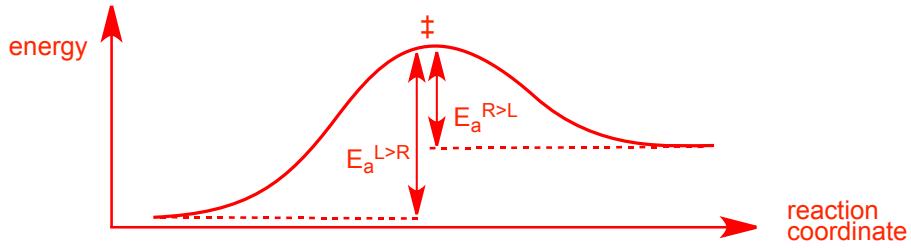
c) Identify the stronger acid and base on each side, indicate which acid would have the smaller pKa, indicate which reaction would be faster and give a brief explanation for your choices

d) Indicate on which side the equilibrium would lie



although both anions are resonance stabilized, the weaker base anion delocalizes the negative charge onto the more electronegative oxygen, lowering the electron energy, reducing the chemical reactivity of the electrons, the base is easier to make and thus has the stronger conjugate acid

e) Draw an energy diagram with properly labelled axes for the equilibrium shown above, showing the activation energy in BOTH directions, do NOT draw the transition state



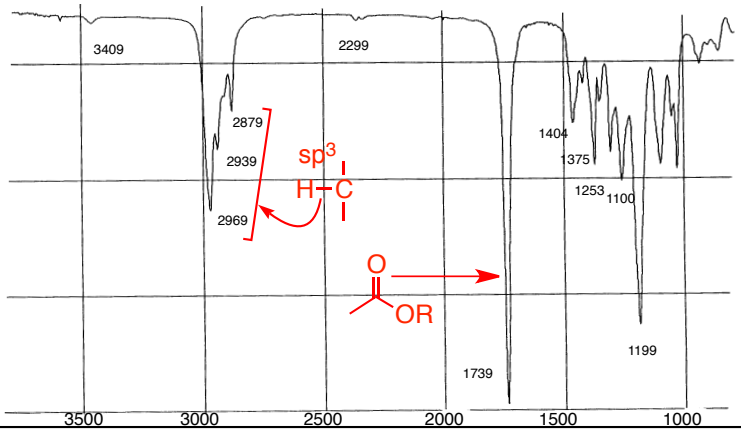
Extra Credit (5 pts) Dr. Gould had a conversation with his daughter about which topic?

cis- and trans-	saturated and unsaturated	(acids and bases)	Markovnikov and Anti-Markovnikov

Question 7 (24 pts) Provided are spectra for a compound with molecular formula $C_6H_{12}O_2$

a) Give the degrees of unsaturation one degree

b) On the infrared spectrum, indicate which peaks correspond to which functional groups (including C(sp^3)-H). Indicate **BOTH the functional group**, and where appropriate, **the specific BOND** in the functional group that corresponds to the peak.



c) draw the structure **and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY**