CHEM 233, Fall 2018 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) _____

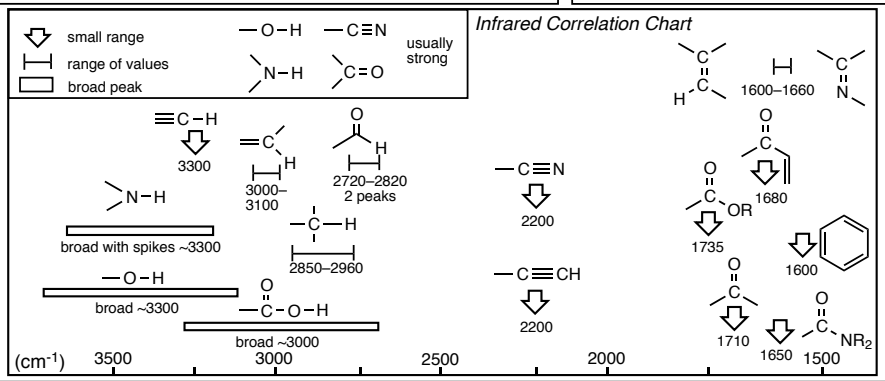
*****YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM*****

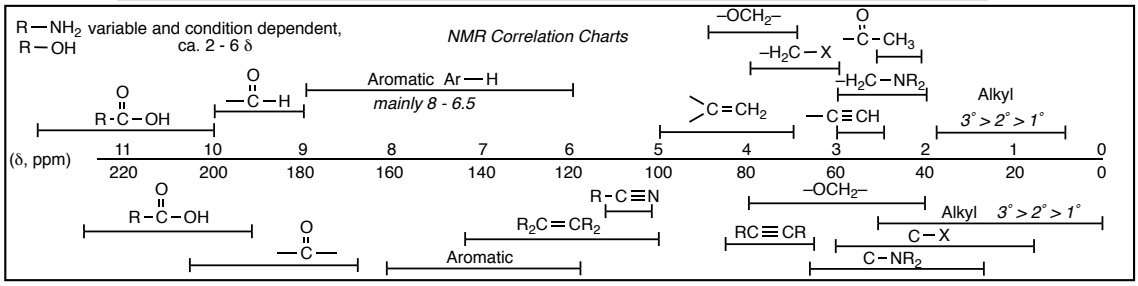
- *PRINT YOUR NAME ON EACH PAGE!*
- *READ THE DIRECTIONS CAREFULLY!*
- *USE BLANK PAGES AS SCRATCH PAPER*
  work on blank pages will not be graded...
- *WRITE CLEARLY!*
- *MOLECULAR MODELS ARE ALLOWED*
- *DO NOT USE RED INK*
- *DON'T CHEAT, USE COMMON SENSE!*

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

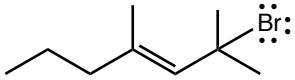
Interaction Energies, kcal/mol

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





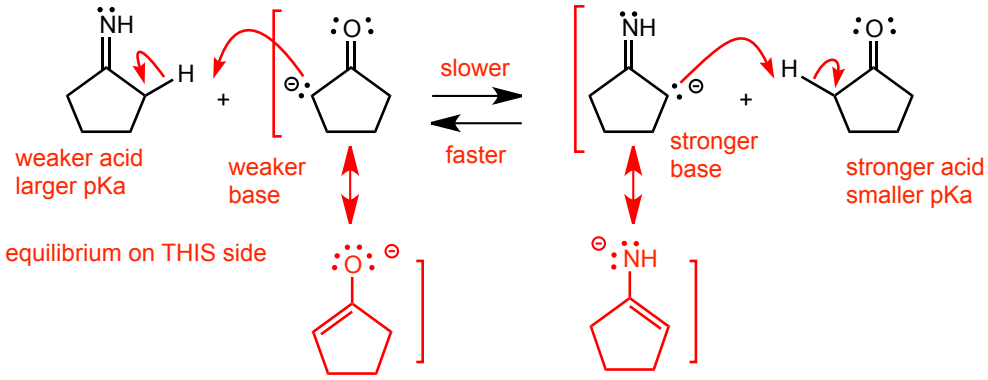
Question 1 (14 pts.) Give the IUPAC name for the following structure.



2-bromo-2,4-dimethylhept-(3E)-ene
or...
2-bromo-2,4-dimethyl-(3E)-heptene
or...
(E)-2-bromo-2,4-dimethyl-3-heptene

etc.

Question 2 (20 pts) For the following Bronsted acid/base equilibrium
a) add the curved arrow pushing for reaction in **both** directions and **ADD ALL REASONABLE MISSING RESONANCE CONTRIBUTORS AS APPROPRIATE**
b) indicate the stronger and weaker acid and base on each side and give a brief explanation for your choice
c) indicate which reaction is faster **AND** on which side the equilibrium lies
d) indicate which acid has the smaller and which the larger pKa



the base on the left is weaker because the electron energy is lower, the charge is delocalized onto the more electronegative oxygen, compared to nitrogen on the right

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

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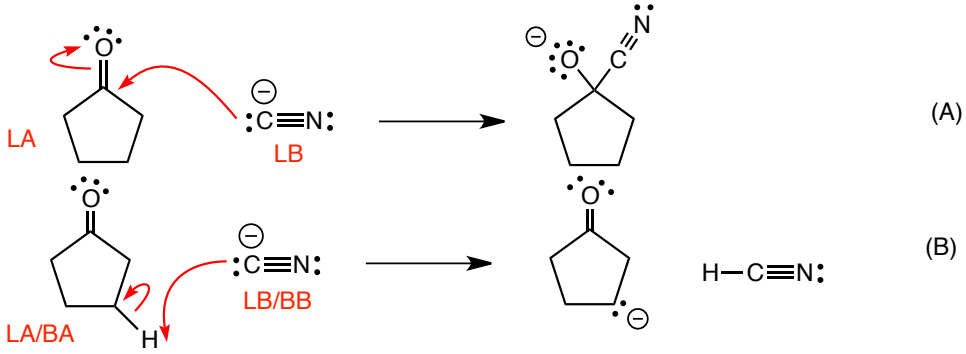
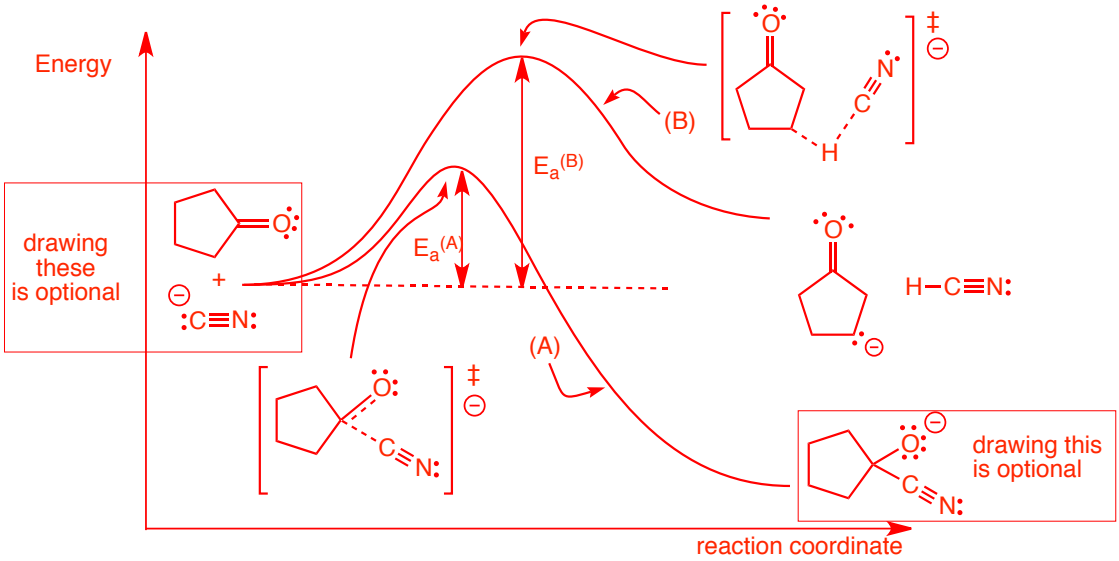
Question 3 (32 pts.) For reactions (A) and (B) shown.

a) 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) Reaction (A) is exothermic and reaction (B) is endothermic. Draw a reaction energy diagram for both reactions ON THE SAME DIAGRAM (do not draw 2 diagrams) and label the axes. Indicate which curve is for which reaction and indicate the activation energies for each reaction and include a **drawing of both transition states** and indicate their **positions** on the diagrams.



c) Briefly explain why reaction (A) is exothermic and reaction (B) is endothermic

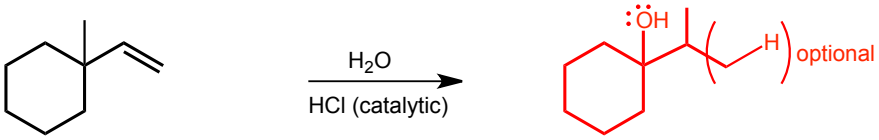
Reaction A is exothermic since it breaks a pi-bond and makes a sigma-bond and it puts the negative charge on the more electronegative oxygen
Reaction B is endothermic since it breaks a sigma bond and puts the negative charge on carbon, AND, the charge was on an sp hybridized carbon in the reactant and sp3 hybridized carbon in the product, the charge in the reactant is also stabilized by the electronegative nitrogen

d) Briefly explain which reaction is faster and which has the EARLIER transition state in terms of the Hammond postulate.

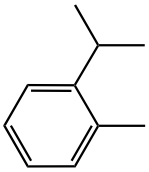
reaction A is faster because it is more exothermic, the Hammond postulate says that the more exothermic reactions have smaller activation energies and earlier transition states

Question 4 (16 pts.) Give the missing major organic products OR reagents/conditions as appropriate for each of the following reactions, include all non-bonding electrons.

a) 

b) 

Question 5 (8 pts.) How many signals would be observed in a proton decoupled ^{13}C NMR spectrum of the following molecule?



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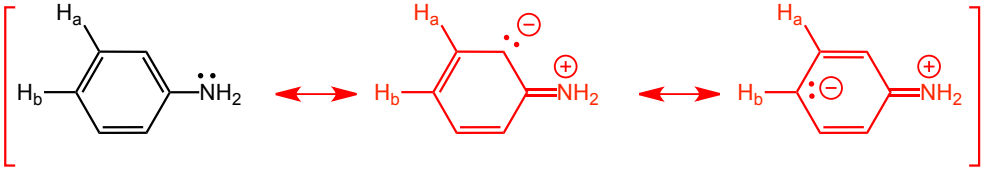
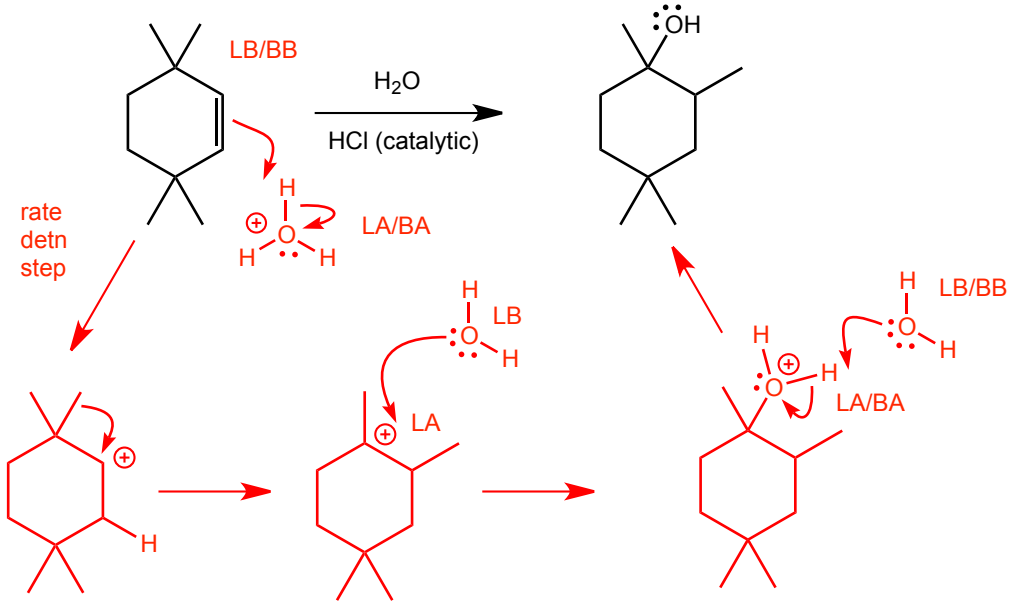
Question 6 (25 pts.) Which of the hydrogen atoms H_a or H_b would have the SMALLER chemical shift in a proton NMR spectrum? Give a brief explanation that includes the terms "electron density" and "shielding" and "deshielding", and include drawings of MINOR RESONANCE contributors to support your arguments.



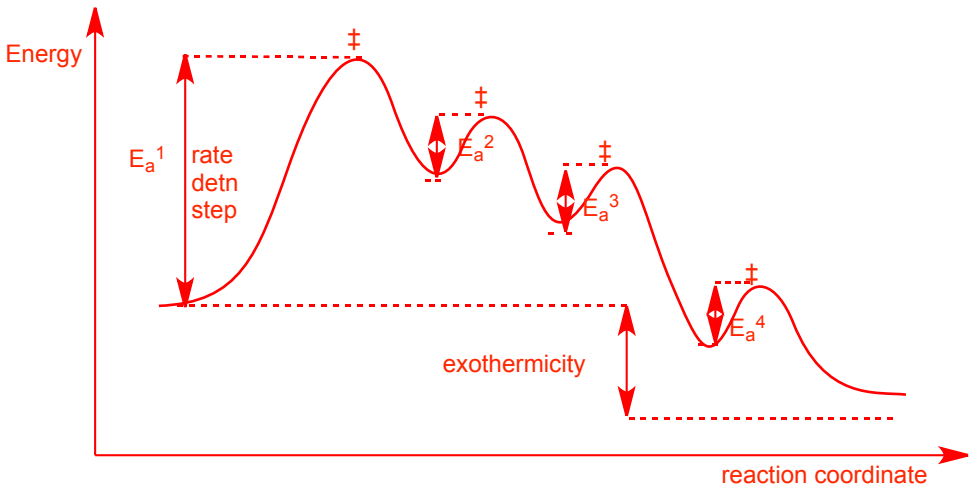
the minor resonance contributors show that the carbon with H_b has increased electron density compared to the carbon with H_a, H_b will experience more shielding, less deshielding and will thus have a smaller chemical shift.

Question 7 (34 pts.) For the following reaction:

a) Give a curved arrow-pushing mechanism for the following reaction. Indicate the Lewis acid and base (LA, LB) for each intermolecular step, and whether they are also Bronsted acids and bases (BA, BB). Indicate the RATE DETERMINING STEP for the mechanism.



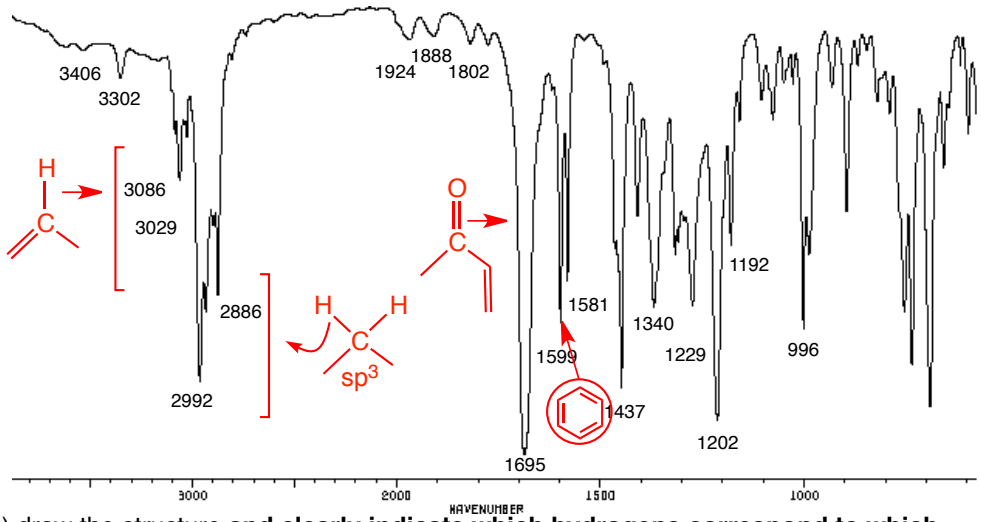
b) Draw reaction energy diagram with properly labelled axes for the mechanism that you drew, Indicate the **ACTIVATION ENERGY FOR EACH STEP**, indicate the **POSITIONS OF THE TRANSION STATES FOR EACH STEP (but do NOT draw the transition states)**, indicate the **REACTION EXOTHERMICITY** and the **RATE DETERMINING STEP**



Question 8 (26 pts) Provided are spectra for a compound with molecular formula **$C_{10}H_{12}O$**

a) Give the degrees of unsaturation **5 degrees**

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)**