CHEM 234, Spring 2011 FINAL EXAM Ian R. Gould

PRINTED **FIRST** NAME **ANSWER** *PRINTED* **LAST** NAME **KEY** *ASU ID or Posting ID* _____

*Person on your **LEFT** (or **Aisle**)* *Person on your **RIGHT** (or **Aisle**)*

- ***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!***

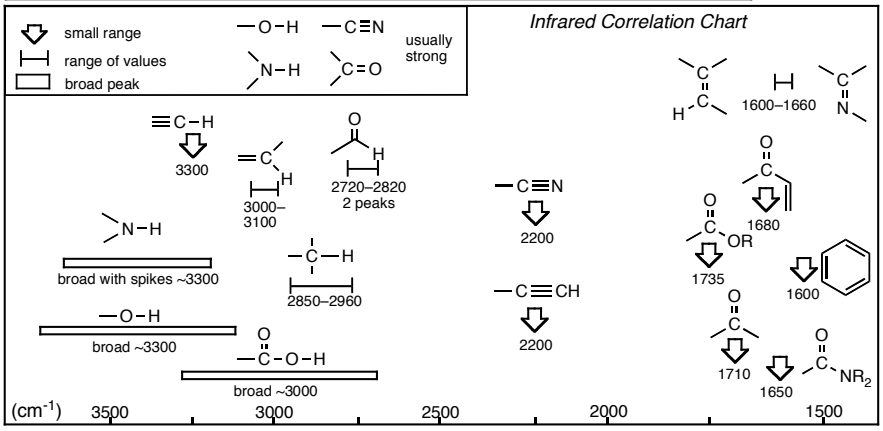
1 _____	/20	9 _____	/24
2 _____	/20	10 _____	/20
3 _____	/27	11 _____	/24
4 _____	/10	12 _____	/24
5 _____	/38	13 _____	/24
6 _____	/64	14 _____	/28
7 _____	/8	15 _____	/32
8 _____	/12		

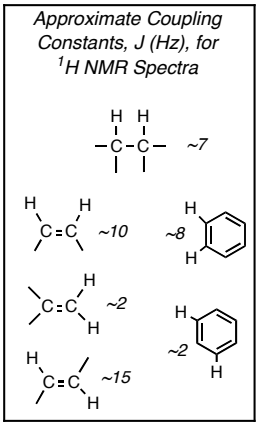
Extra Credit _____ /5 **Total (incl Extra)** _____ /375+5

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

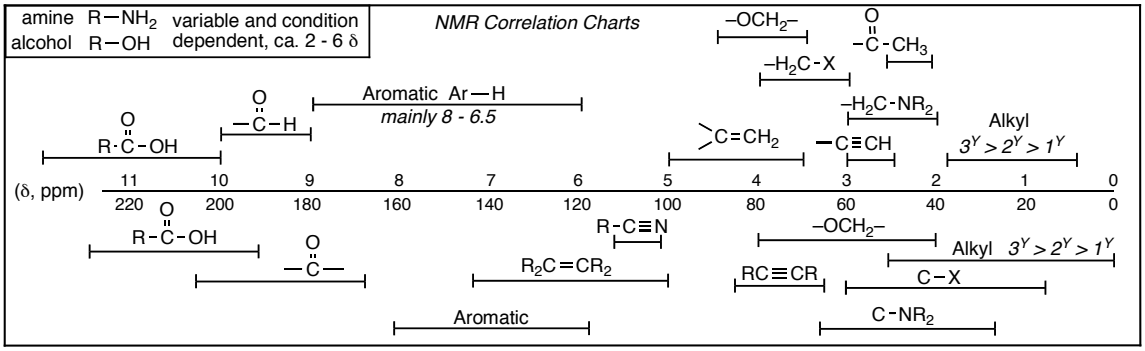
Interaction Energies, kcal/mol

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
Me/Et	~2.9	t-Bu/Me	~2.7

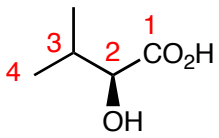




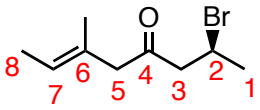
amine R–NH2 variable and condition
alcohol R–OH dependent, ca. 2 - 6 δ



Question 1 (20 pts.) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

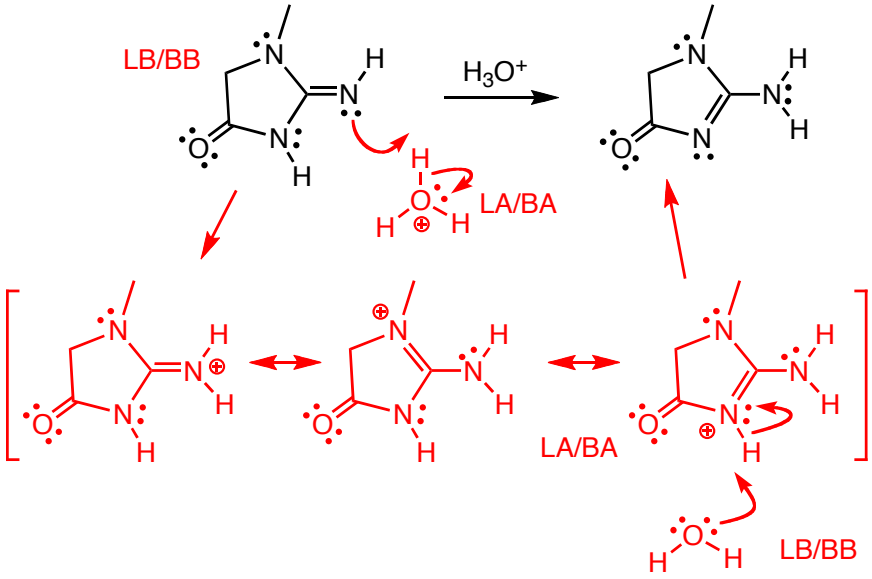
a) 

(2S)-hydroxy-3-methylbutanoic acid

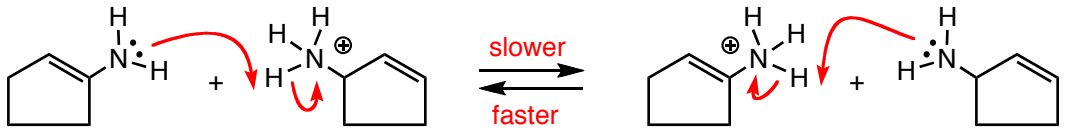
b) 

(2S)-bromo-6-methyloct-(6E)-en-4-one

Question 2 (20 pts.) Serum creatinine levels are used to measure renal function. Creatinin exists in several tautomeric forms, two are shown below. Write a curved arrow-pushiung mechanism that shows how the structure on the left is converted into the one on the right.
Show where all protons come from and go to (no $+H^+/-H^+$)
Show all resonance contributors to the intermediate structures
Label the Lewis acid/base and and Bronsted acids/bases as appropriate



Question 3 (27 pts.) For the following acid/base equilibrium:
a) draw the curved arrows showing bond making/breaking
b) indicate which is the STRONGER and the WEAKER acid and base on each side
c) give a BRIEF explanation for your choice of stronger/weaker that includes the phrase "energy of the electrons"



weaker base

weaker acid
larger pKa

equilibrium lies on THIS side

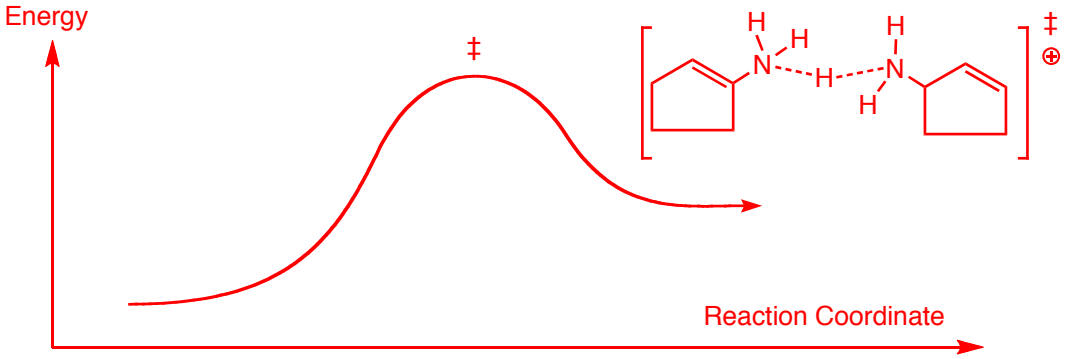
stronger acid
smaller pKa

stronger base

the weaker base has the lower energy electrons, the non-bonding electrons in A are stabilized by resonance, are this lower in energy

d) Indicate which reaction (left to right or right to left) is faster and which is slower and indicate on which side the equilibrium lies

e) Draw a PROPERLY labelled reaction energy diagram, indicate the position of the transition state and include a drawing of the transition state



Question 4 (10 pts.) Indicate which of the following two structures **A** and **B** you would expect to be the stronger Bronsted **BASE,** and give a brief explanation **that includes the term "energy of the eletrons". Assume that both structures are completely FLAT.**

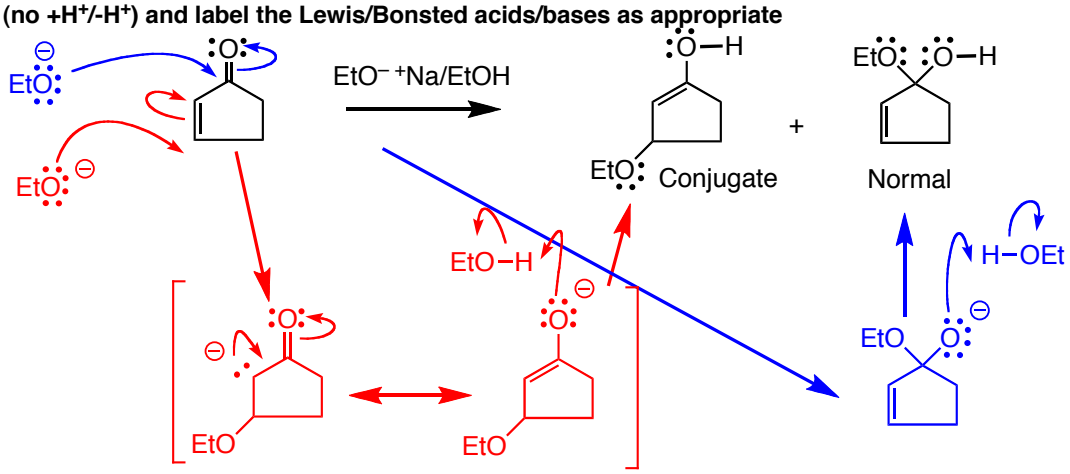
In A the electrons are in an aromatic system and are thus stabilized and lower in nergy, less reactive, and thus a weaker base, in B the electrons are in an antiaromatic system

Extra Credit Question (5 pts). Which kind of molecule was used in the new Two-Electron Sensitization Process for Photography that Dr. Gould worked on when at Kodak?

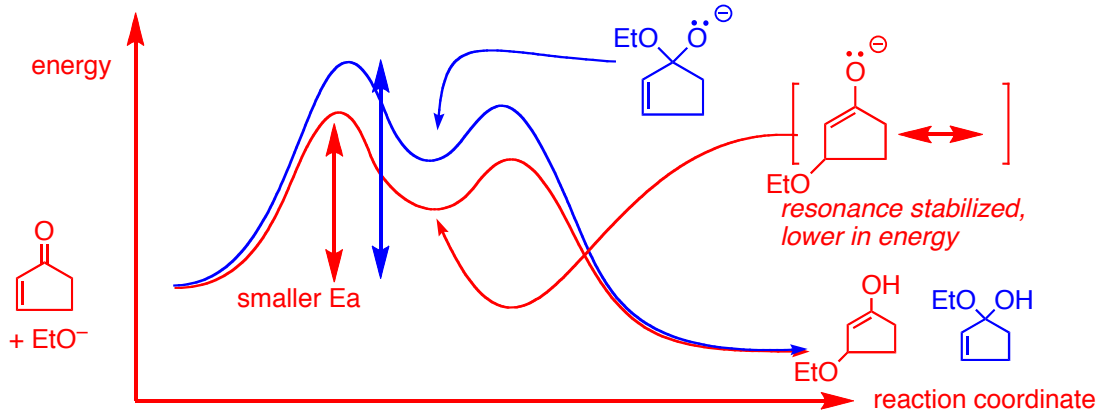
(amine) ester amide aldehyde

Question 5. (38 pts.) Give the mechanisms for formation of the "Normal" and the "Conjugate" addition products in the following reaction.

Show all resonance structures of the intermediates, show where all protons come from and go to (no $+H^+/-H^+$) and label the Lewis/Bonsted acids/bases as appropriate

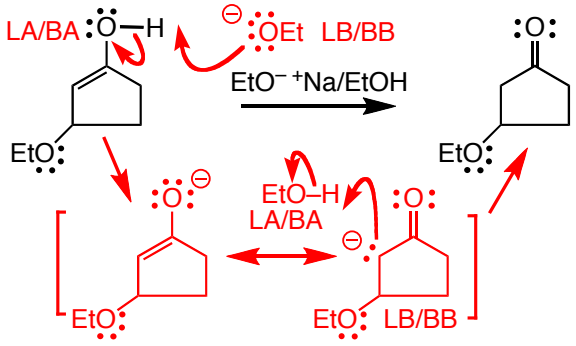


b) Both products form with the same exothermicity, draw a reaction energy diagram for both reactions ***ON THE SAME DIAGRAM***, label the activation energy for the rate determining step for each reaction



c) Under the reaction conditions, the conjugate product will tautomerize back into a ketone, give the curved arrow-pushing mechanism for this reaction

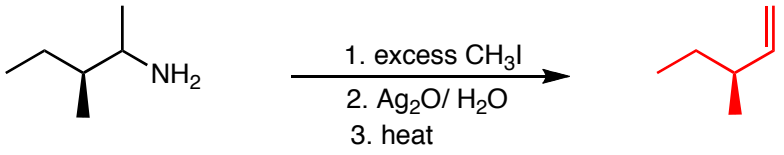
Show all resonance structures of the intermediates, show where all protons come from and go to (no $+H^+/-H^+$) and label the Lewis/Bonsted acids/bases as appropriate



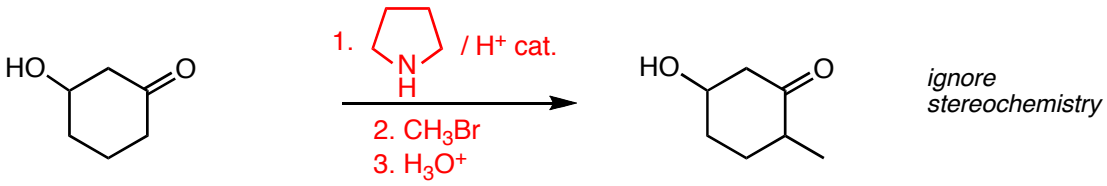
Question 6 (64 pts)

Provide the missing products, reagents/conditions or reactants, as required. **Do not forget to include absolute and relative stereochemistry as appropriate** unless otherwise indicated

a)

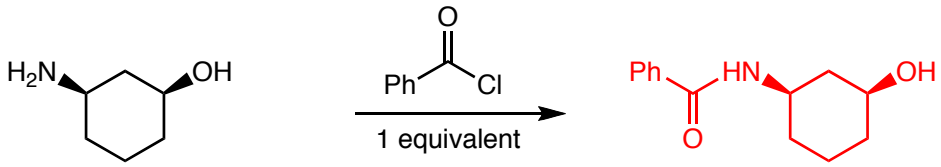


b)

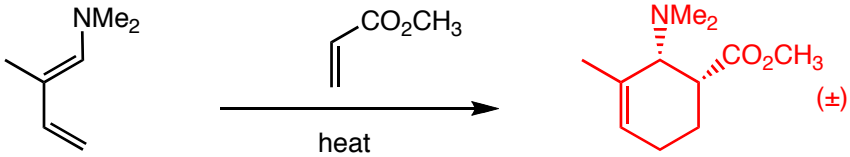


ignore stereochemistry

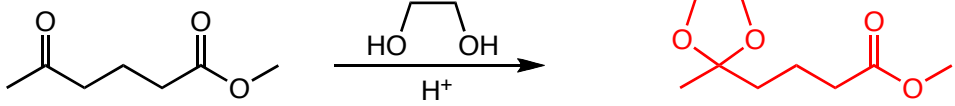
c)



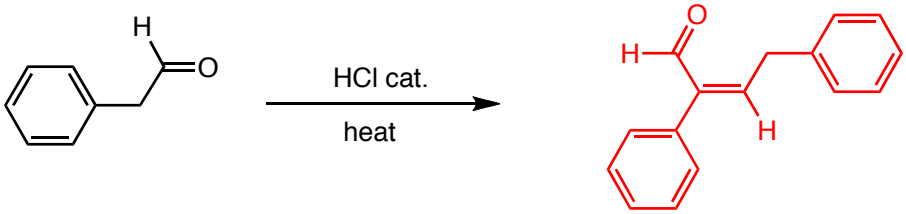
d)



e)



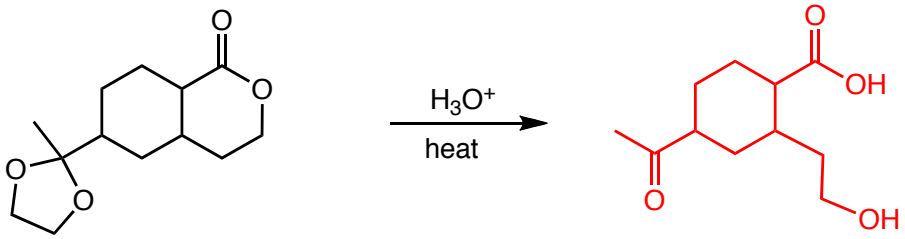
f)



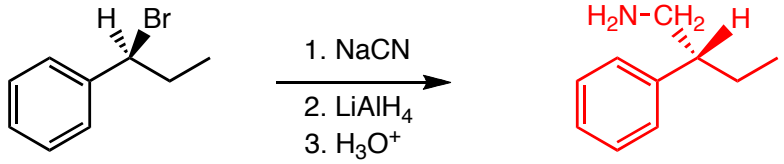
Question 6, Contd...

Provide the missing products, reagents/conditions or reactants, as required. **Do not forget to include stereochemistry as appropriate**.

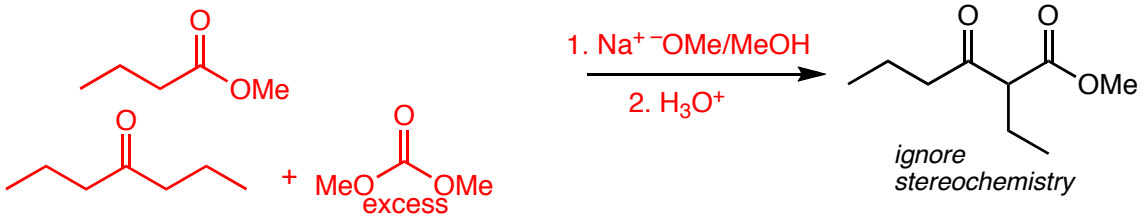
g)



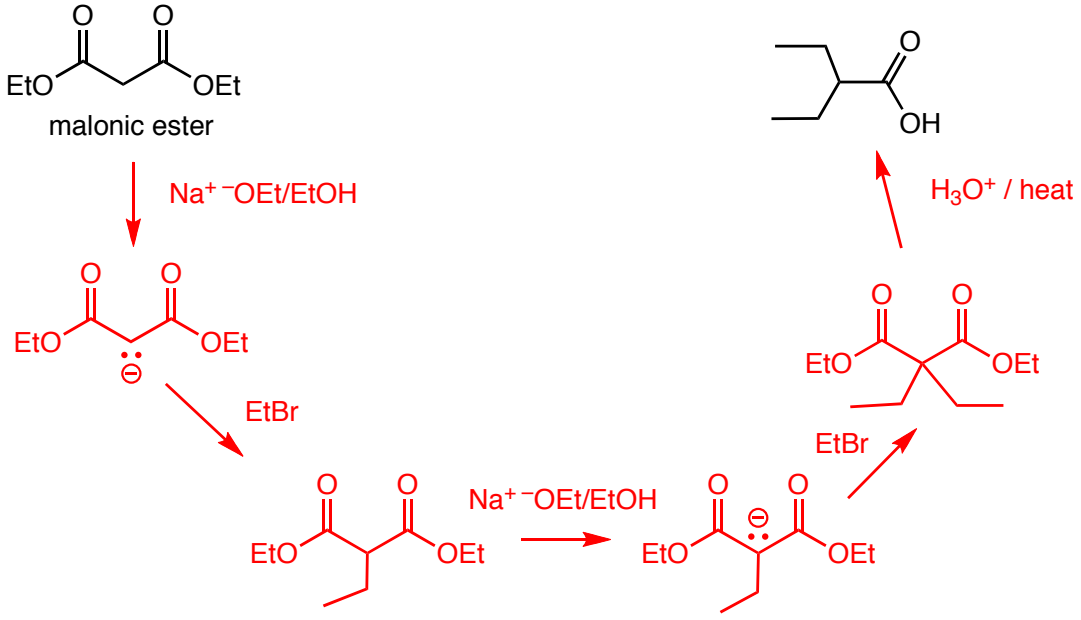
h)



Question 7 (8 pts) Give a reactants and reagents/conditions that will give the following structure in a Claisen reaction

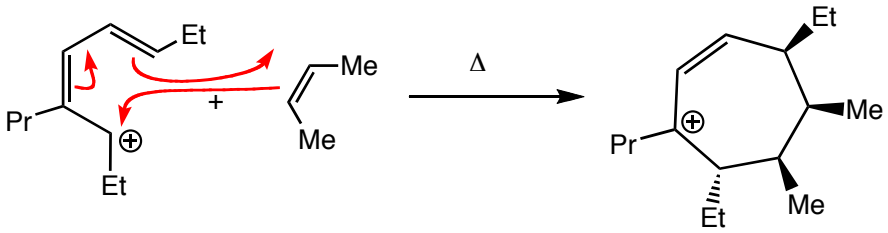


Question 8 (12 pts) Give a synthesis of the provided carboxylic acid from malonic ester. TREAT THIS AS A SYNTHESIS QUESTION. This is a FIVE STEP synthesis, give reagents/conditions and the intermediate molecules AT EACH STEP.

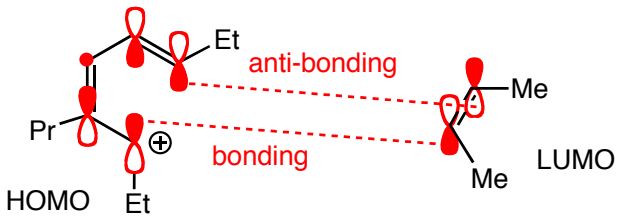


Question 9 (24 pts.) For the cycloaddition reaction below

a) Draw the curved arrow-pushing that describes the bond-making and breaking processes.



b) Draw the HOMO and LUMO of the reactants as requested, ON TOP of the structures that are redrawn below

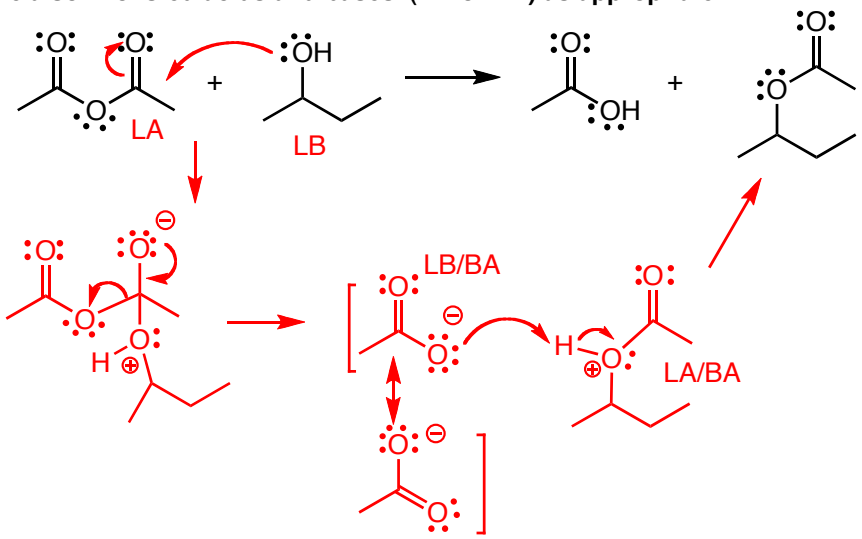


c) Is the cycloaddition reaction shown above allowed or forbidden. Give a BRIEF explanation that includes the words suprafacial and/or antarafacial as appropriate

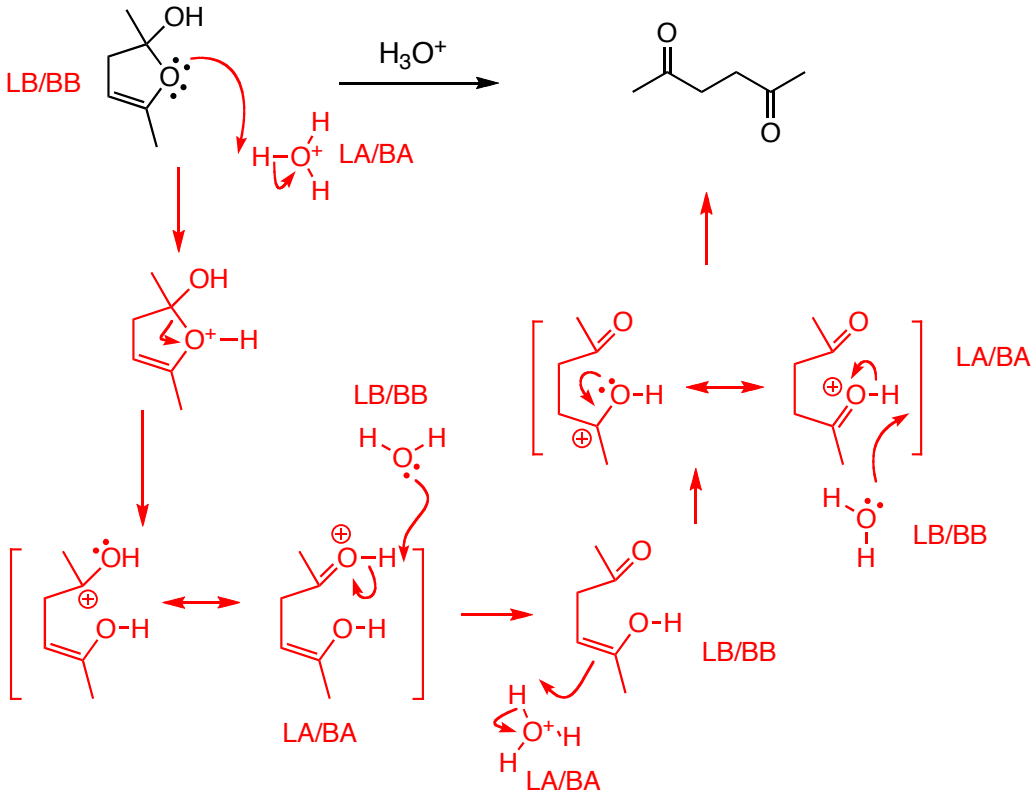
this is antarafacial on the cation and suprafacial on the alkene, which is forbidden based on FMO theory since there is a bonding and an anti-bonding interaction interaction between the pairs of atoms involved in making the two new sigma bonds

Question 10 (20 pts) Give the mechanism for the following reaction

- **AS APROPRIATE, SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no $+H^+/-H^+$)**
- **DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as approriate**
- **At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate**



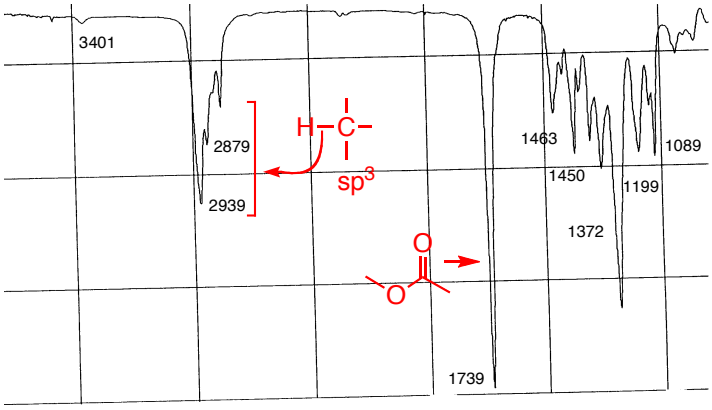
Question 11 (24 pts.) Give a curved arrow-pushing mechanism for the following reaction**Show where all protons come from and go to (no $+H^+/-H^+$)**
Show all resonance contributors to the intermediate structures
Label the Lewis acid/base and and Bronsted acids/bases as appropriate



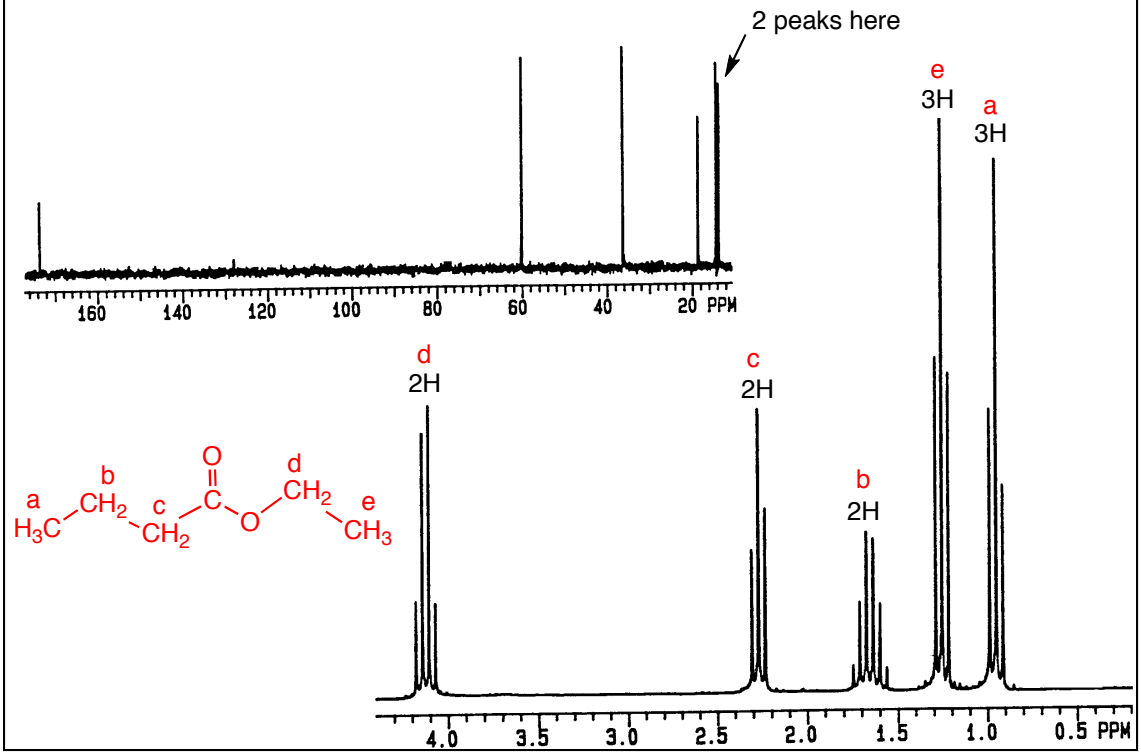
Question 12 (24 pts) Provided are spectra for a compound with molecular formula $C_6H_{12}O_2$

a) Give the degrees of unsaturation 1 degree of unsaturation

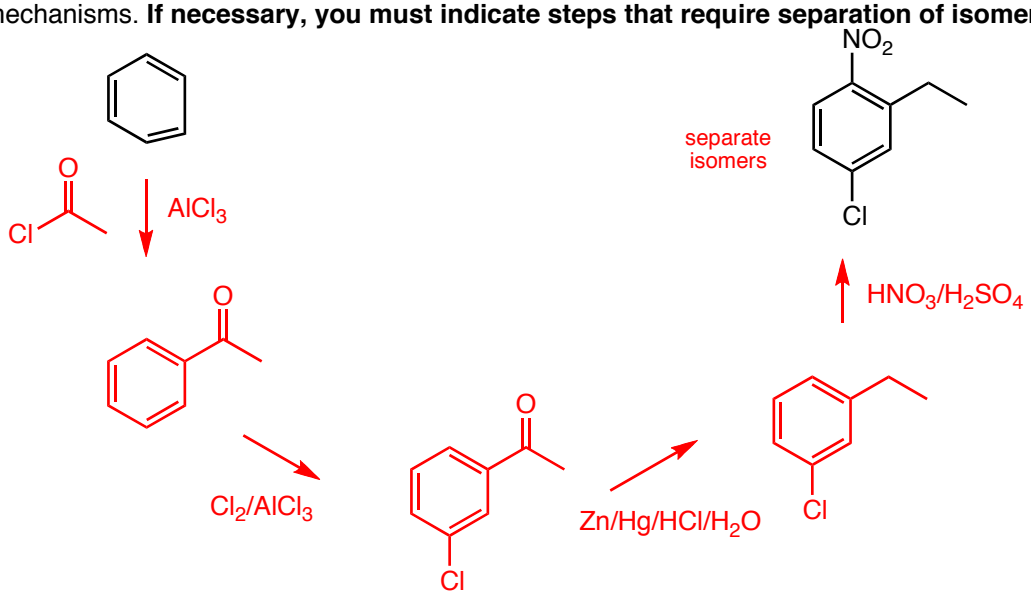
b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp^3)-H). Indicate **BOTH the functional group**, and where appropriate, **the specific BOND** in the functional group that corresponds to the peak.



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

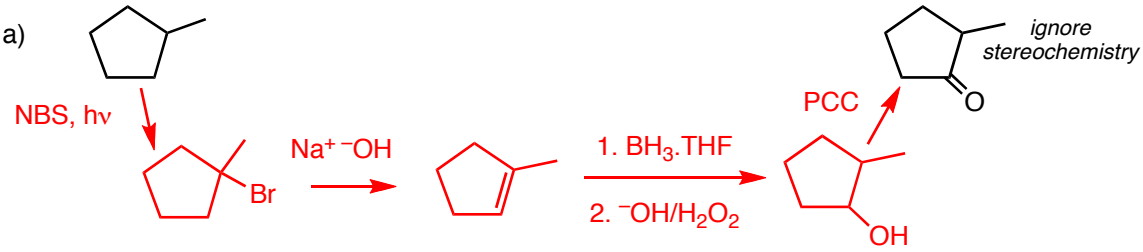


Question 13 (24 pts.) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**



Question 14 (28 pts) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. These 2 questions use only reactions from the basic sets that were provided on the class website

a)



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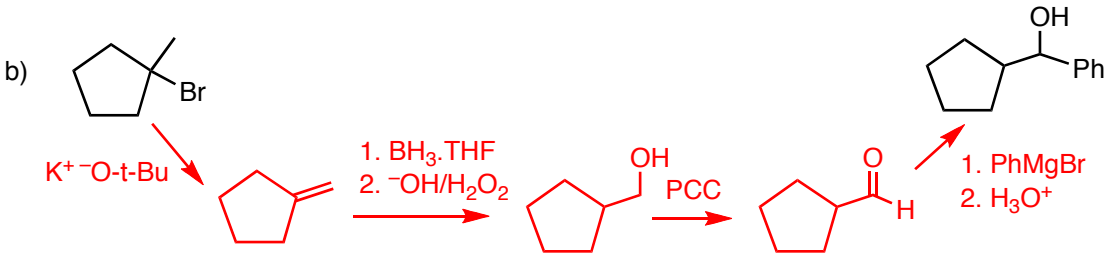
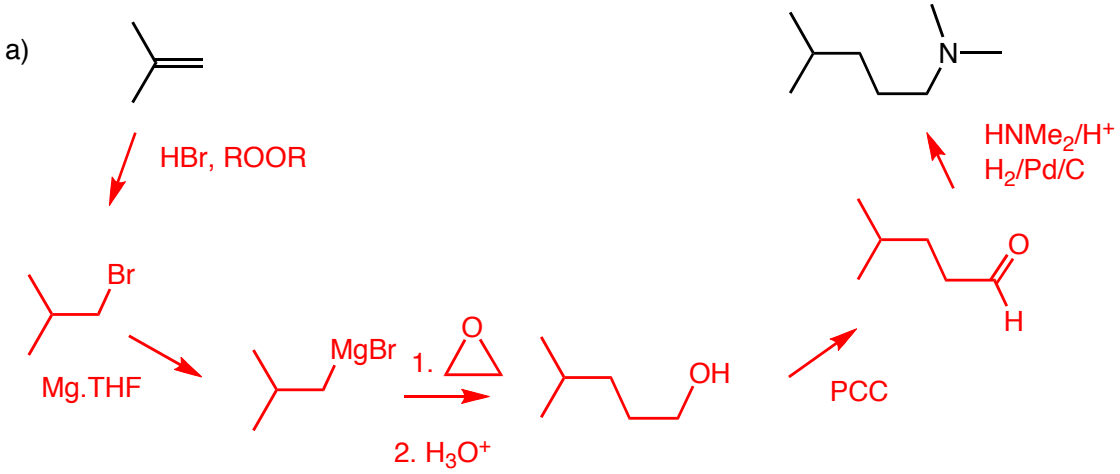


Question 15 (32 pts.) In each case, synthesize the (target) molecules on the right from the starting molecules the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.

a)



b)