CHEM 234, Spring 2010 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!***

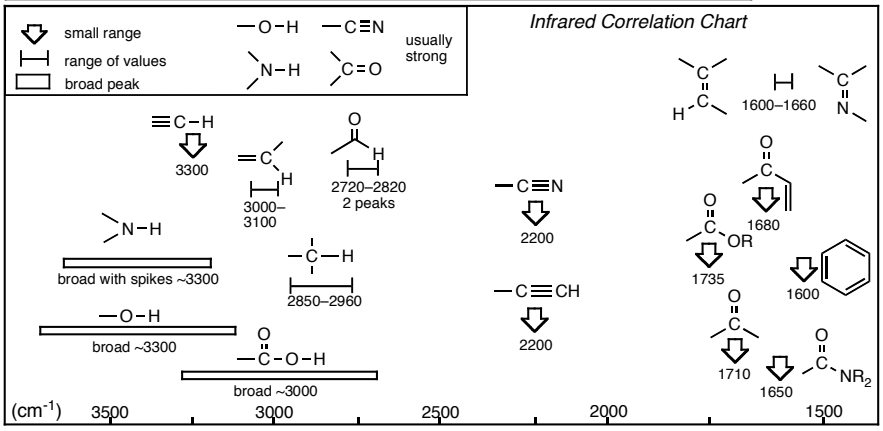
1	/16	9	/18
2	/10	10	/16
3	/14	11	/20
4	/14	12	/20
5	/14	13	/25
6	/14	14	/20
7	/24	15	/40
8	/72	16	/40

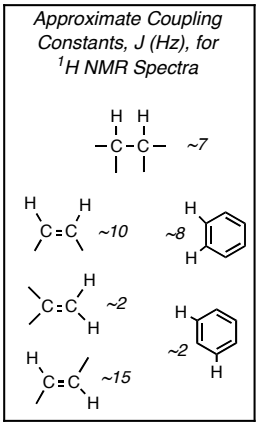
Extra Credit _____/5 **Total (incl Extra)** _____/375+5

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

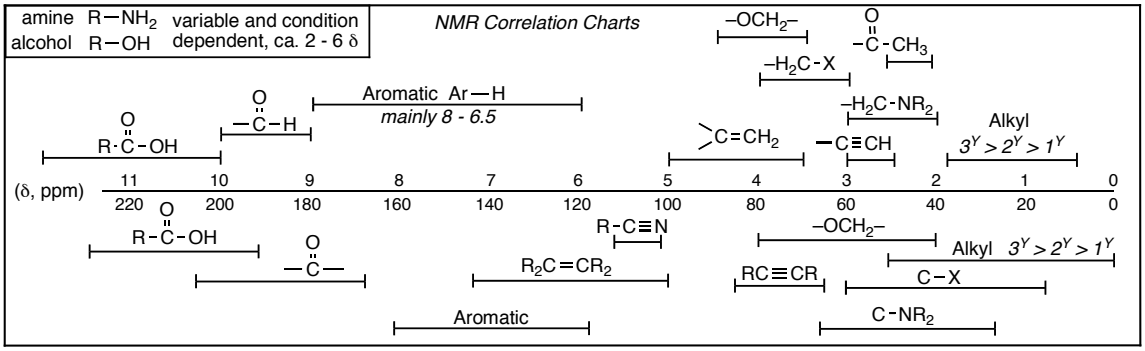
Interaction Energies, kcal/mol

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

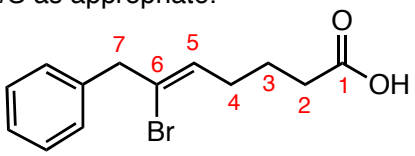




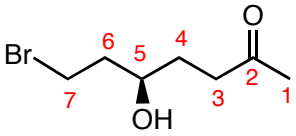
amine R—NH_2 variable and condition
alcohol R—OH dependent, ca. 2 - 6 δ



Question 1 (16 pts.) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

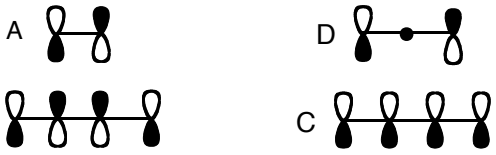
a) 

6-bromo-7-phenylhept-(5Z)-enoic acid

b) 

7-bromo-(5R)-hydroxyheptan-2-one

Question 2 (10 pts.) Rank the energies of an electron in each of the following π-molecular orbitals. Give a BRIEF explanation for your choice.

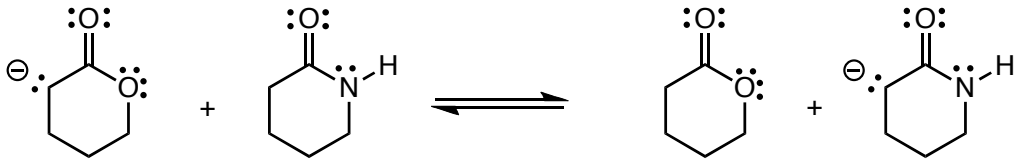


C < D < A < B

lowest energy highest energy

an electron will be lower in energy the bonding interactions in the molecular orbital, and higher in energy the more antibonding interactions, orbital D is non-bonding

Question 3 (14 pts.) On each side of the following equilibrium, identify the stronger and weaker acid and base, identify which acid would have the LOWER pKa, indicate on which side the equilibrium would lie, and give a brief explanation for your choices.

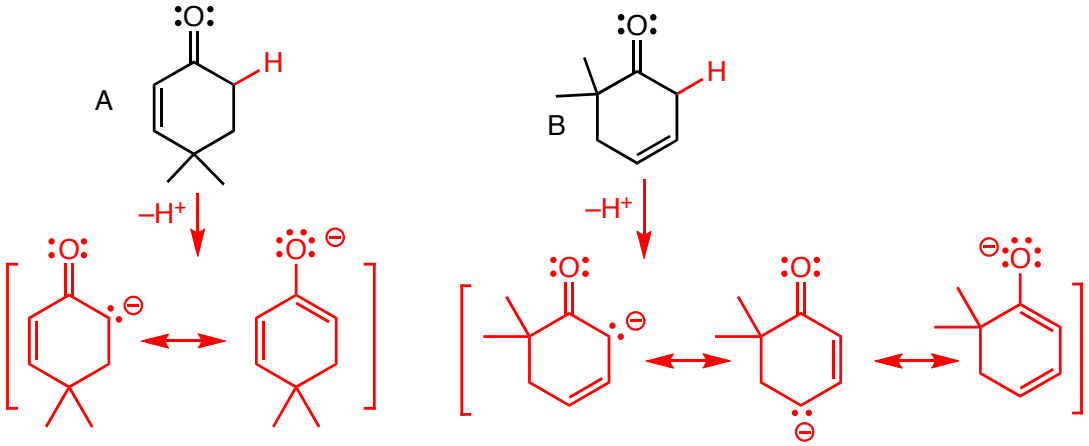


weaker base | weaker acid larger pKa | stronger acid smaller pKa | stronger base

The second pair of nonbonding electrons on the deprotonated amide are stabilized by conjugation into the C=O bond, lowering their energy and stabilizing the anion. This ion is thus the weaker base, corresponding to the stronger acid.

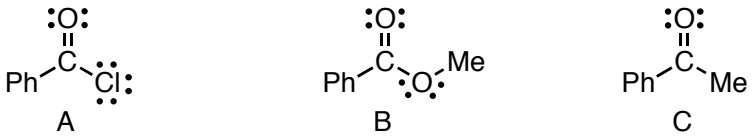
the stronger base is stronger because of the presence of the nitrogen that acts as a strnger donating group to destabilize the enolate anion, compared to the weaker oxygen donating group in the ester

Question 4 (14 pts.) Which is the stronger acid, A or B? Give a BRIEF explanation, including the drawings of all relevant structures and ALL resonance contributors as appropriate.



The anionic conjugate base has more resonance structures, is more stable, thus B is more acidic.

Question 5 (14 pts.) Rank in order of increasing rate of reaction with a Grignard reagent, give a BRIEF explanation.



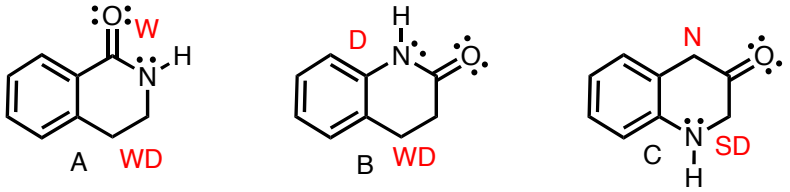
slowest B < C < A fastest

The Grignard is a nucleophile/Lewis base, the carbonyls are the electrophiles/Lewis acids, the electrophilic atom is teh C of the C=O, in A the electrophilic Cl activates this carbon towards nucleophilic attach and in B the -OMe is resonance electron donating and deactivates this carbon towards nucleophilic attack

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 6 (14 pts.) Rank in order of increasing rate of electrophilic aromatic substitution, e.g. $Br_2/FeBr_3$.

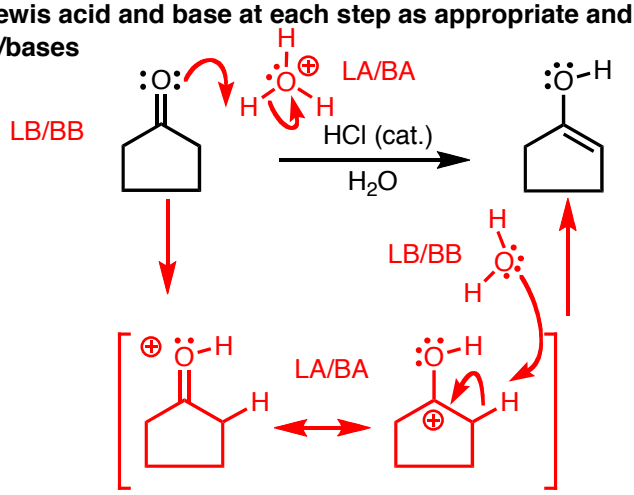


slowest A < B < C fastest

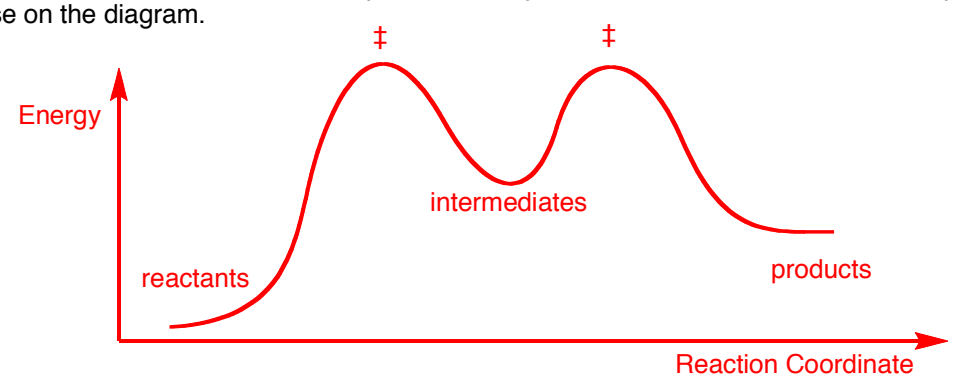
In electrophilic aromatic substitution the benzene ring is a Lewis base/nucleophile, donating substituents activate towards reaction and withdrawing substituents deactivate towards reaction, thge substituents are as indicated (W = withdrawing, WD = weak donating, D= strong donating, SD = strong donating, N = neutral, neither withdrawing or donating)

Question 7 (24 pts.) For the following reaction, give a curved arrow-pushing mechanism

- **Draw all of the resonance contributors for important intermediates.**
- **Do NOT use $+H^+/-H^+$ notation, show exactly where each proton goes to and comes from**
- **Indicate the Lewis acid and base at each step as appropriate and if they are also Bronsted acids/bases**



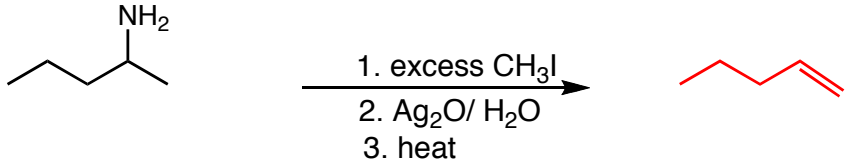
b) Draw a properly labelled reaction energy diagram, indicated the positions of the reactants, intermediates, transition states and products, but you do not draw the structures of any of these on the diagram.



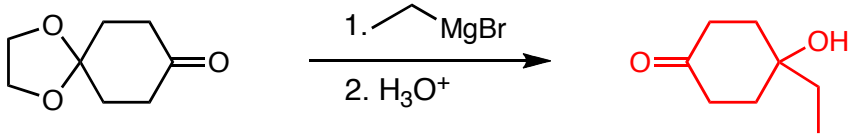
Question 8 (72 pts)

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

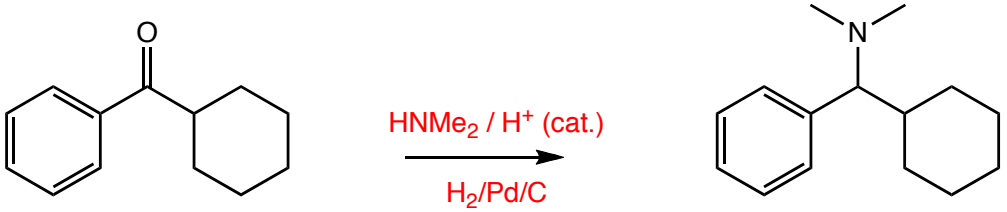
a)



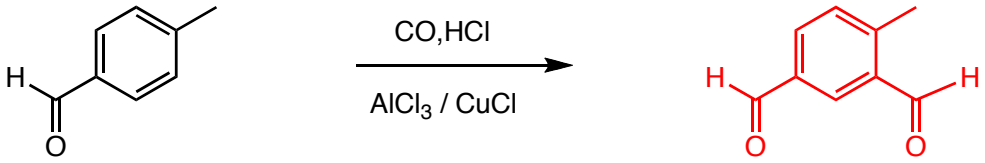
b)



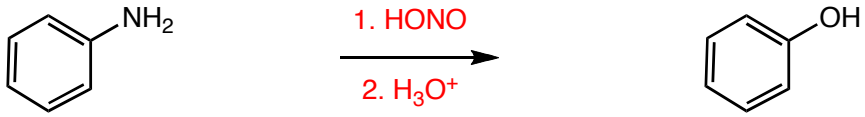
c)



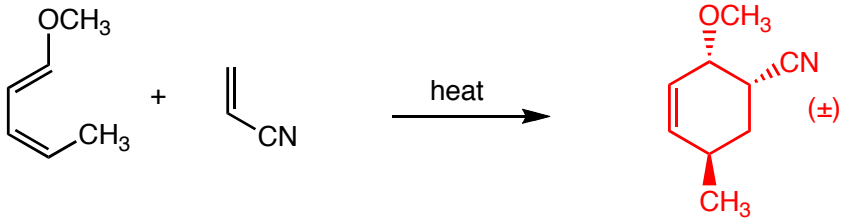
d)



e)

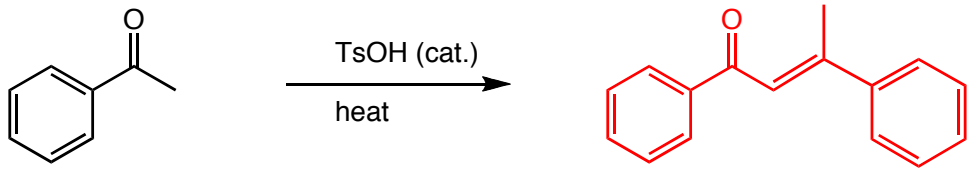


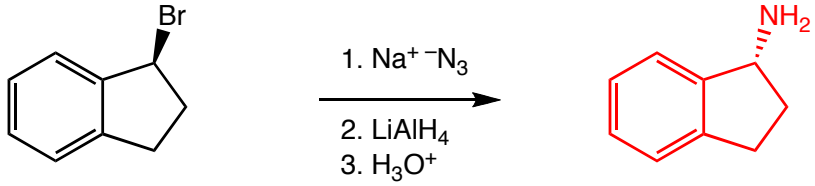
f)

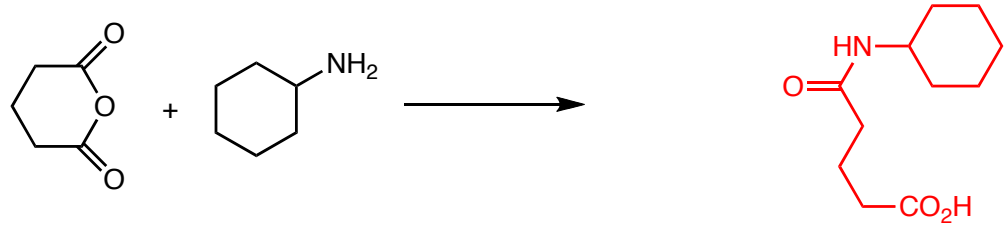


Question 8, Contd...

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

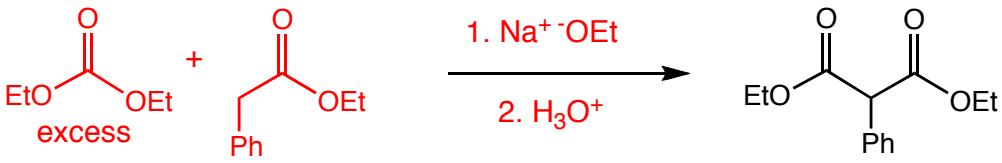
g) 

h) 

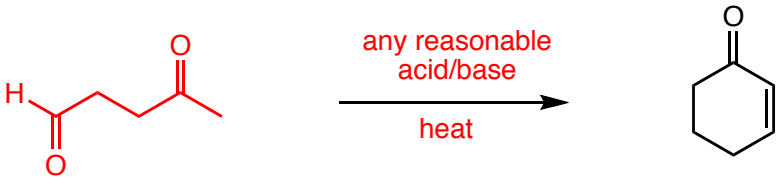
i) 

Question 9 (18 pts)

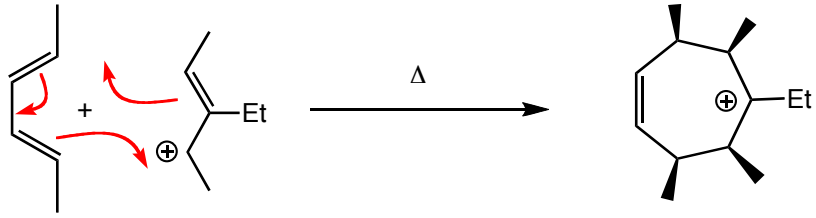
a) Give the reactants AND reagents/conditions that would allow you to synthesize the provided structure in a Claisen reaction



b) Give the reactants AND reagents/conditions that would allow you to synthesize the following structure in an Aldol condensation.



Question 10 (16 pts) For the following cycloaddition reaction:
a) Give the curved arrow-pushing describing product formation



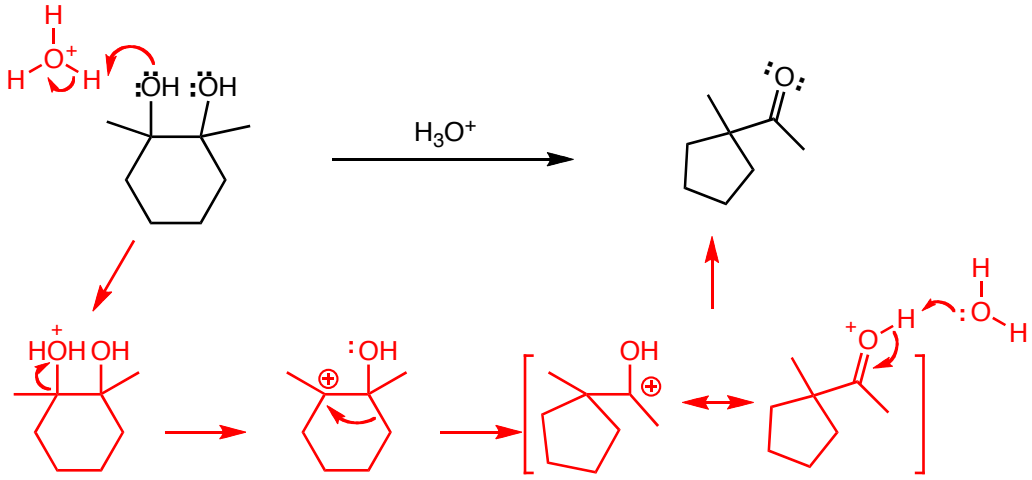
b) On TOP OF THE structures below, draw the HOMO for reactant A and the LUMO for reactant B

c) USING F.M.O. theory, explain whether the provided product is allowed or forbidden, include the terms suprafacial and/or antarafacial in your explanation

the reaction is suprafacial on both reactants, the product is thius allowed since suprafacial/suprafacial results in both bonding interactions in the transition state according to the HOMO/LUMO overlap

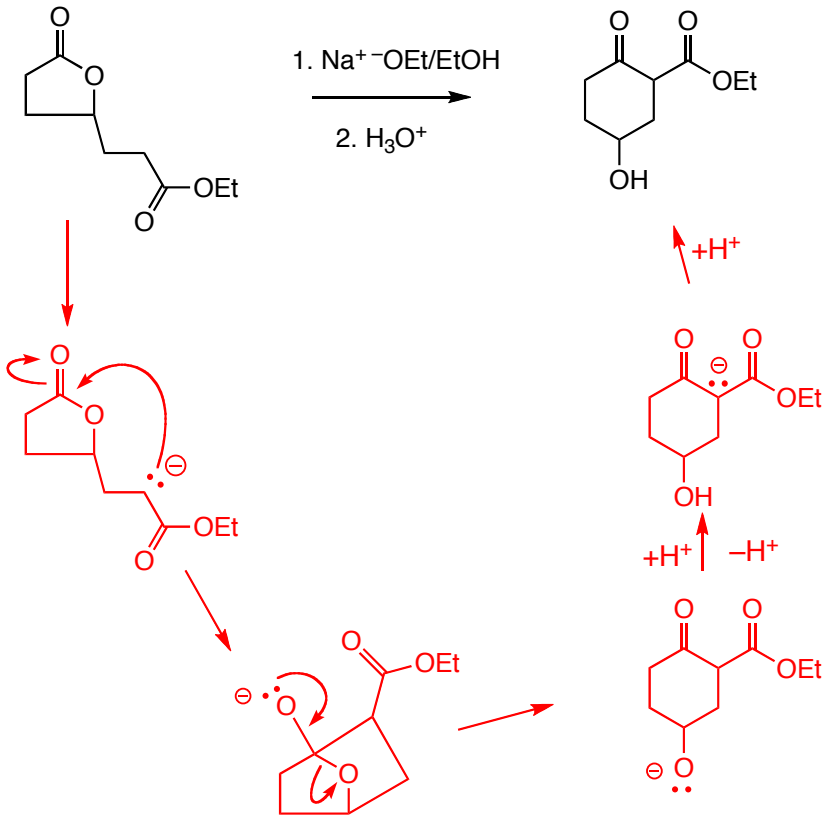
Question 11 (20 pts) Give the mechanism for the following reaction

- **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 12 (20 pts.) Give a curved arrow-pushing mechanism for the following reaction

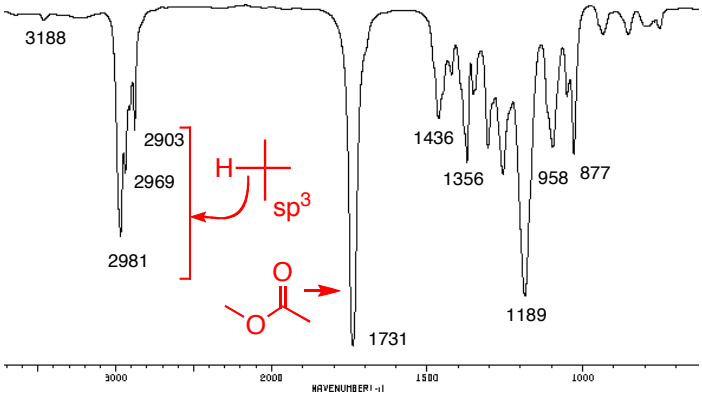
- **You can give an "abbreviated mechanism, i.e. you may use $+H^+$ and $-H^+$**
- **IT IS NOT NECESSARY TO INDICATE THE LEWIS/BRONSTED ACID/BASE AT EACH STEP**
- **<u>BUT, draw all resonance structures for the intermediates</u>**
- **Add non-bonding electrons and C–H bonds as necessary**



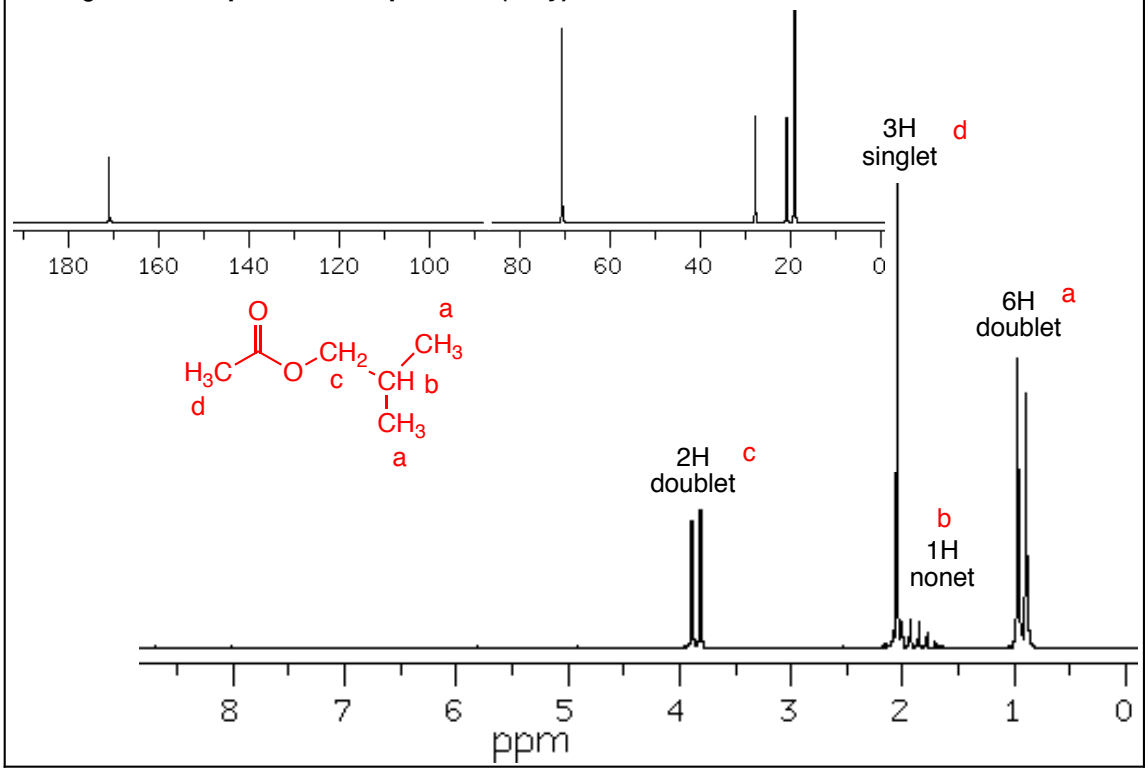
Question 13 (25pts) Provided are spectra for a compound with molecular formula **$C_6H_{12}O_2$**

a) Give the degrees of unsaturation 0 degrees of unsaturation

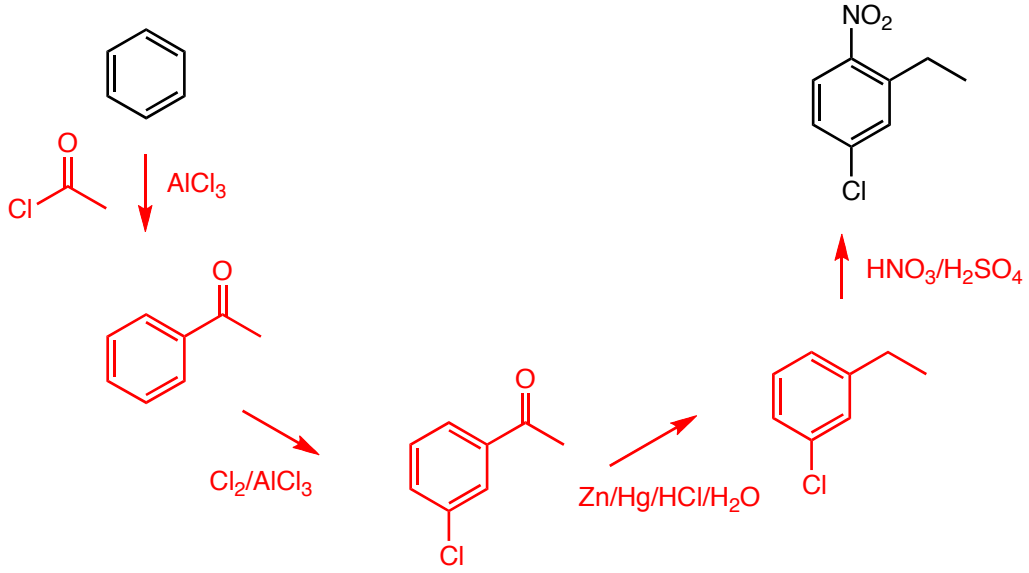
b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp^3)-H). Indicate **BOTH the functional group**, and where appropriate, **the specific BOND** in the functional group that corresponds to the peak.



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

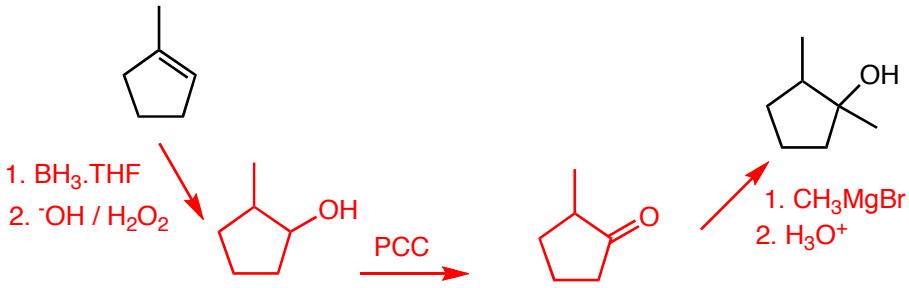


Question 14 (20 pts.) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**

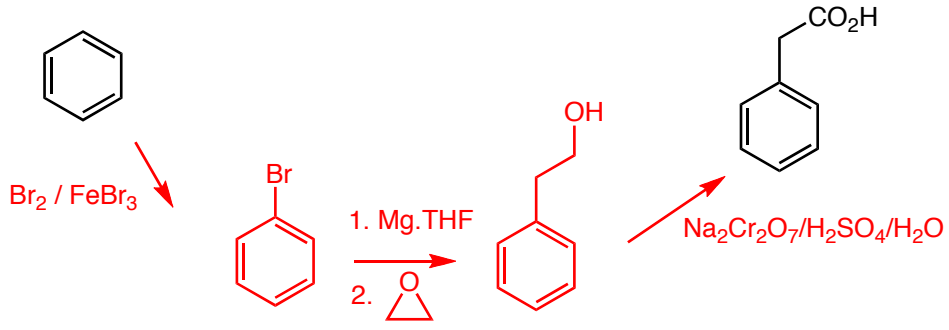


Question 15 (40 pts) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. These 2 questions use only reactions from the basic sets that were provided on the class website

a)

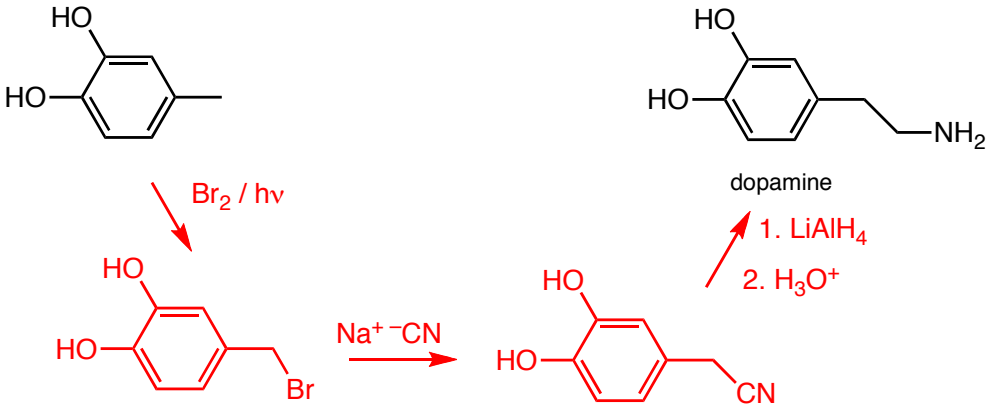


b)



Question 16 (40 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)