CHEM 234, Spring 2008 Final Exam Ian R. Gould

PRINTED **FIRST** NAME _____ *PRINTED* **LAST** NAME _____ *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!***

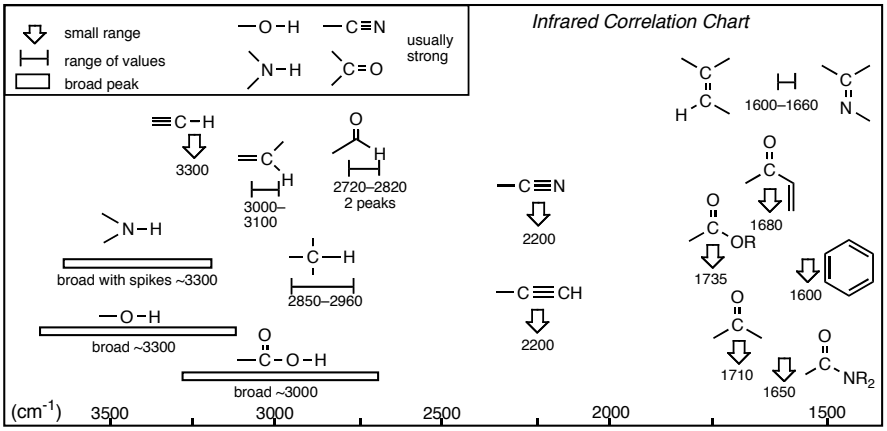
1 nomen	/18	9 reactions	/72
2 acidity 1	/14	10 synthons	/22
3 acidity 2	/10	11 pericyclic	/20
4 basicity	/12	12 mxns 1	/40
5 reactivity	/12	13 mxns 2	/25
6 basicity 2	/12	14 synth 1	/50
7 malonics	/20	15 synth 2	/40
8 Stork	/18		

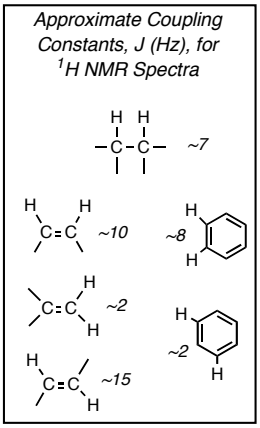
Extra Credit _____/5 **Total (incl Extra)** _____/385+5

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

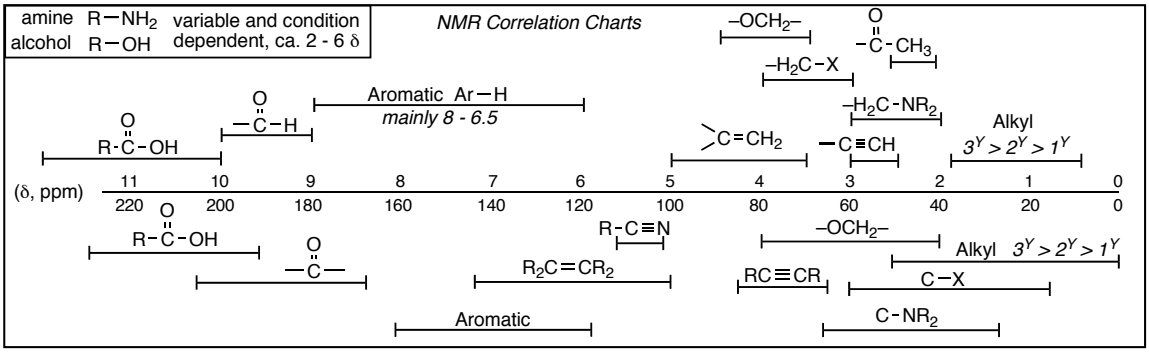
Interaction Energies, kcal/mol

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

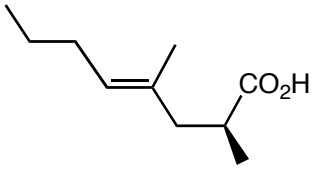




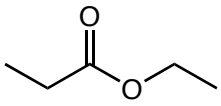
amine R–NH_2 variable and condition
alcohol R–OH dependent, ca. 2 - 6 δ



Question 1 (18 pts.) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

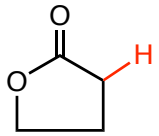
a) 

(2S),5-dimethyloct-(5E)-enoic acid

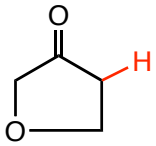
b) 

ethyl propanoate

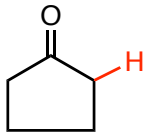
Question 2 (14 pts.) For the following three structures:
a) Clearly indicate the location of the most acidic hydrogen atom on the line-angle structures
b) Indicate the order of increasing Bronsted acidity for A, B and C. Give a BRIEF explanation.



A



B

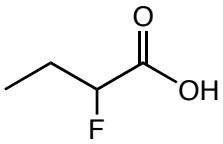


C

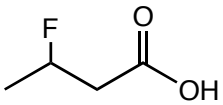
least acidic A < C < B most acidic

the anion in A is destabilized by the O of the ester, which acts as a resonance donating group to the enolate anion, the oxygen in B acts as a weak inductive withdrawing group to the enolate

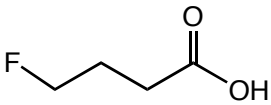
Question 2 (10 pts.) Rank the following three structures in order of increasing Bronsted acidity. Give a BRIEF explanation.



A



B

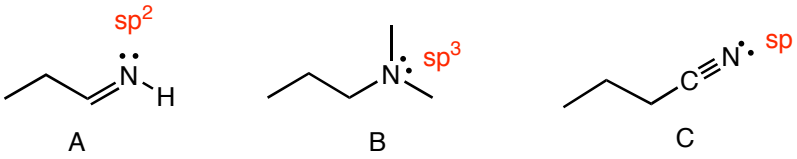


C

least acidic C < B < A most acidic

the carboxylate is stabilized by the fluorines via the inductive effect, the further the F from the anion, the weaker the inductive effect

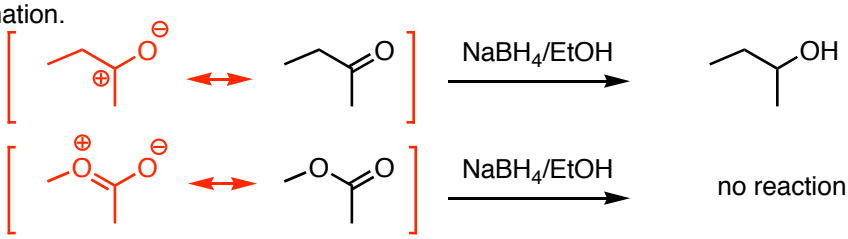
Question 4 (12 pts.) Rank the following in order of increasing basicity, give a BRIEF explanation.



least basic C < A < B most basic

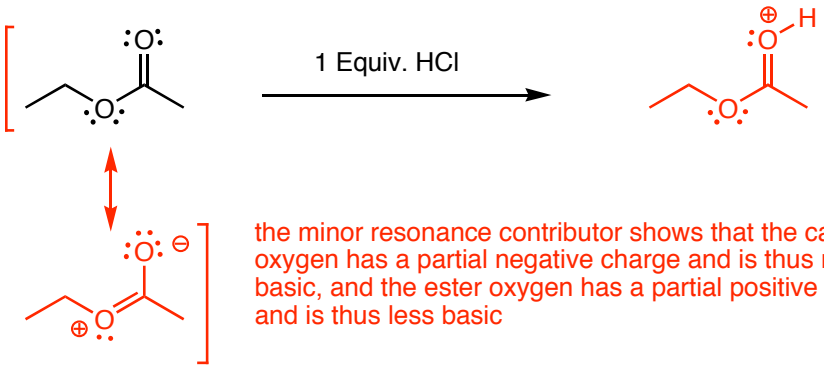
non-bonding electrons are lower in energy the more s-character the A.O., lower in energy means less reactive, less basic

Question 5 (12 pts) Explain why sodium borohydride ($NaBH_4$) will reduce a ketone but will not reduce an ester. Draw minor resonance structures of the ketone and ester to support your BRIEF explanation.



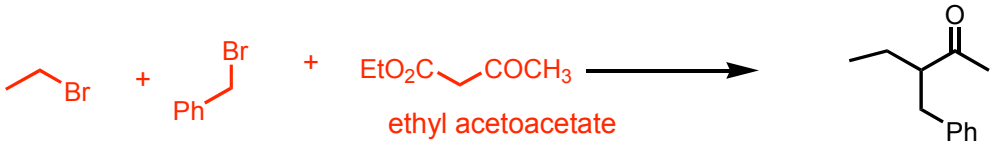
BH_4^- is a Lewis base, the carbonyl carbon is Lewis acidic in the ketone (see resonance structure), the carbonyl carbon is less Lewis acidic in the ester due to the presence of the oxygen.

Question 6 (12 pts) Give the product of the following acid/base reaction, give a BRIEF explanation for your choice of product

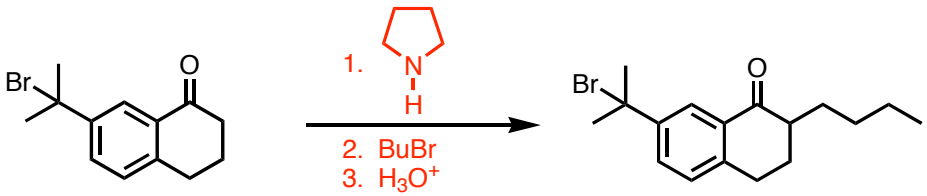


the minor resonance contributor shows that the carbonyl oxygen has a partial negative charge and is thus more basic, and the ester oxygen has a partial positive charge and is thus less basic

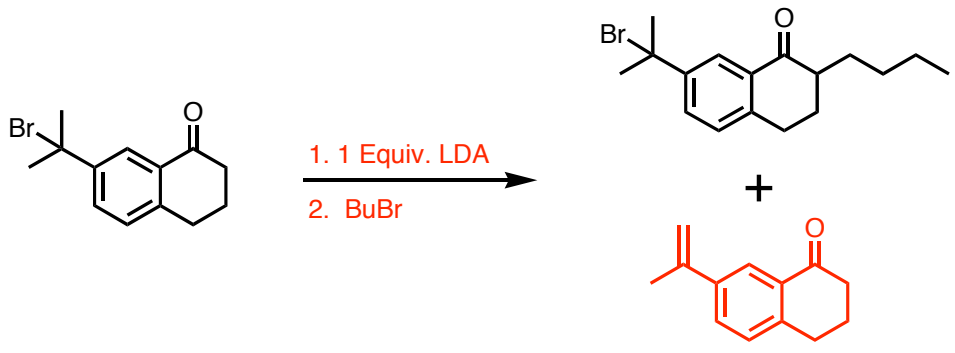
Question 7. (20 pts.) Provide the reactants that can be used to synthesize the following two structures using a malonic ester or ethylacetoacetate synthesis, i.e. give the structure of malonic ester or ethyloacetoacetate and give the structures of the two bromides.



Question 8 (18 pts.) Give the reagents/conditions to perform the following alkylation using a Stork enamine reaction



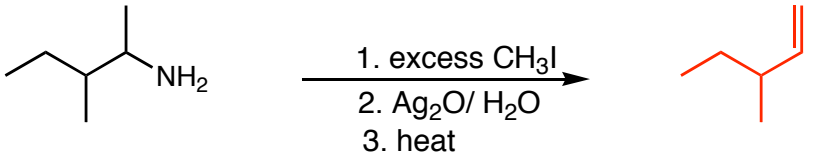
b) Give the reagents/conditions to perform the following alkylation using the LDA method, AND give the unwanted side-product that you would also expect to form under these conditions



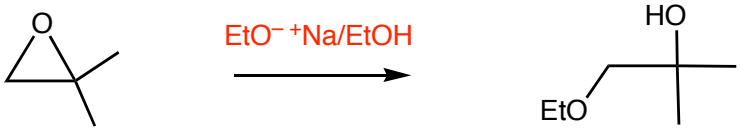
unwanted side-product

Question 9 (72 pts)
Provide the missing products, reagents/conditions or reactants, as required. **Do not forget to include stereochemistry as appropriate**.

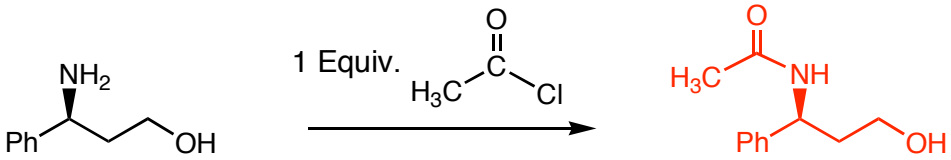
a)



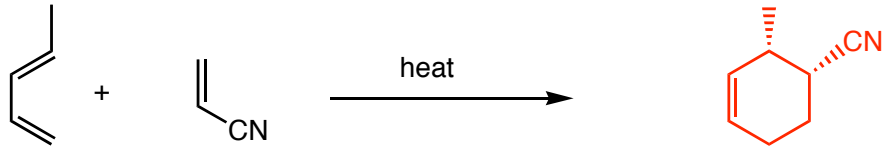
b)



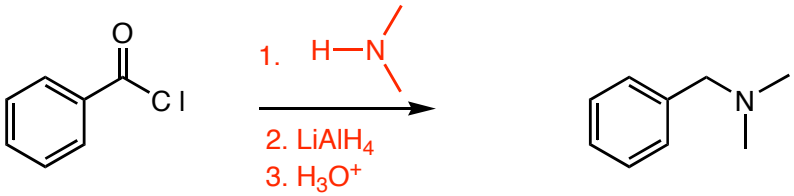
c)



d)

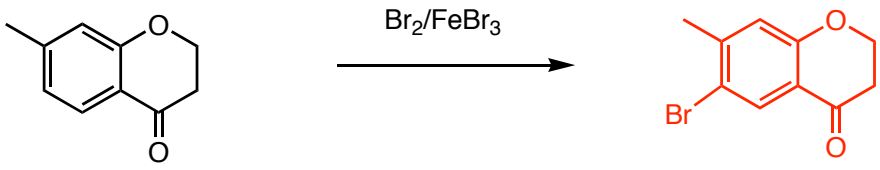


e)

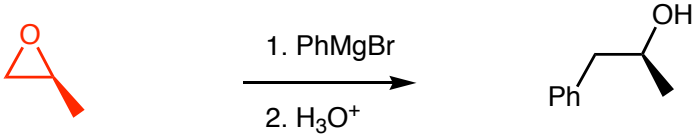


Question 9, Contd...
Provide the missing products, reagents/conditions or reactants, as required. **Do not forget to include stereochemistry as appropriate**.

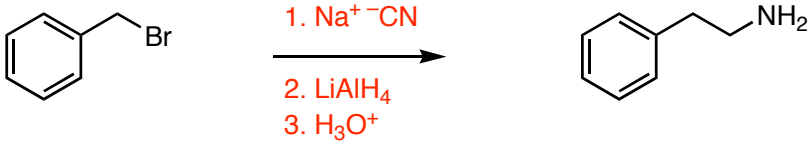
f)



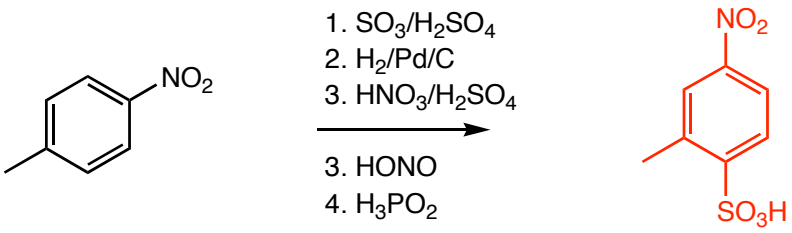
g)



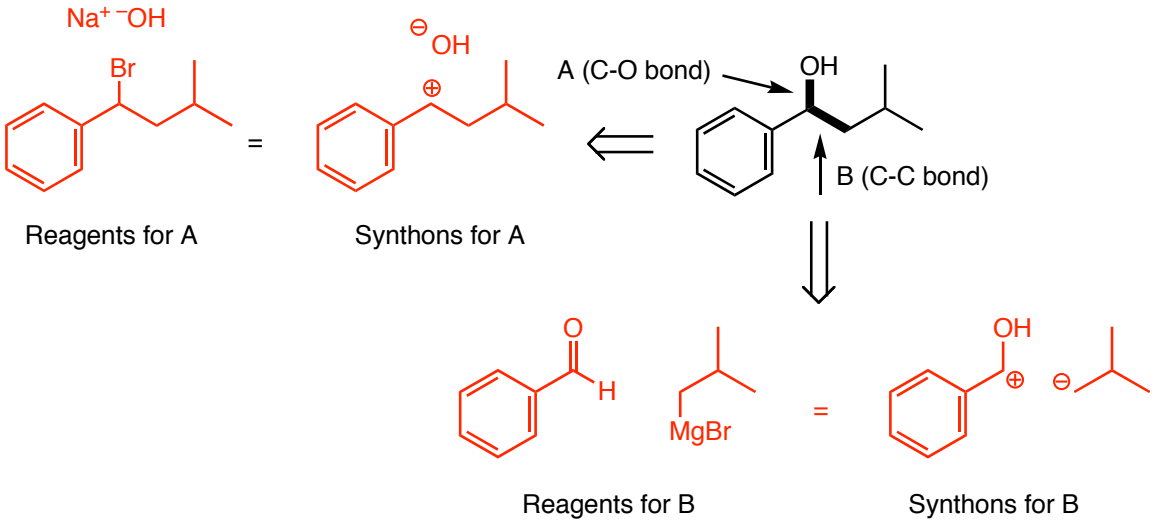
h)



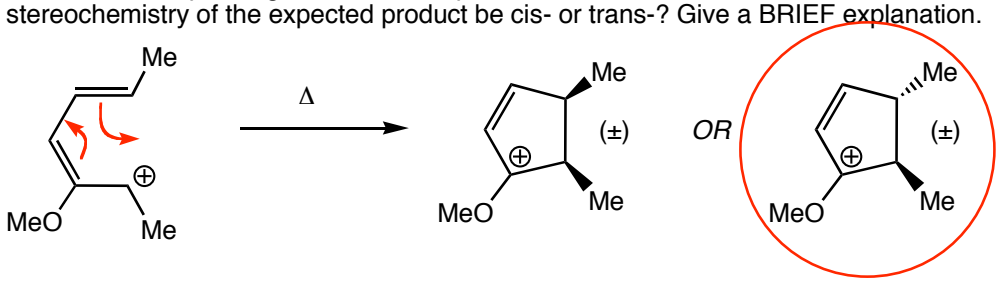
i)



Question 10 (22 pts) For EACH of the TWO bonds indicated, A and B, provide the best SYNTHONS, and also appropriate "actual reagents"

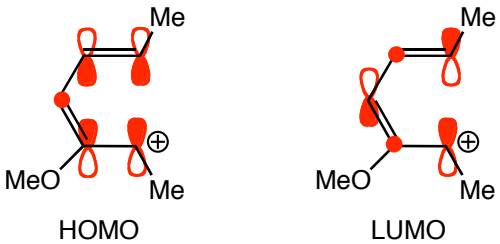


Question 11 (20 pts) For the cycloaddition reaction below:
a) Draw the curved arrow-pushing that describes product formation
b) will the stereochemistry of the expected product be cis- or trans-? Give a BRIEF explanation.



TRANS-, this is a 4-electron reaction, the allowed reaction proceeds via a conrotatory Mobius transition state which puts the methyl groups on opposite sides of the cyclic product

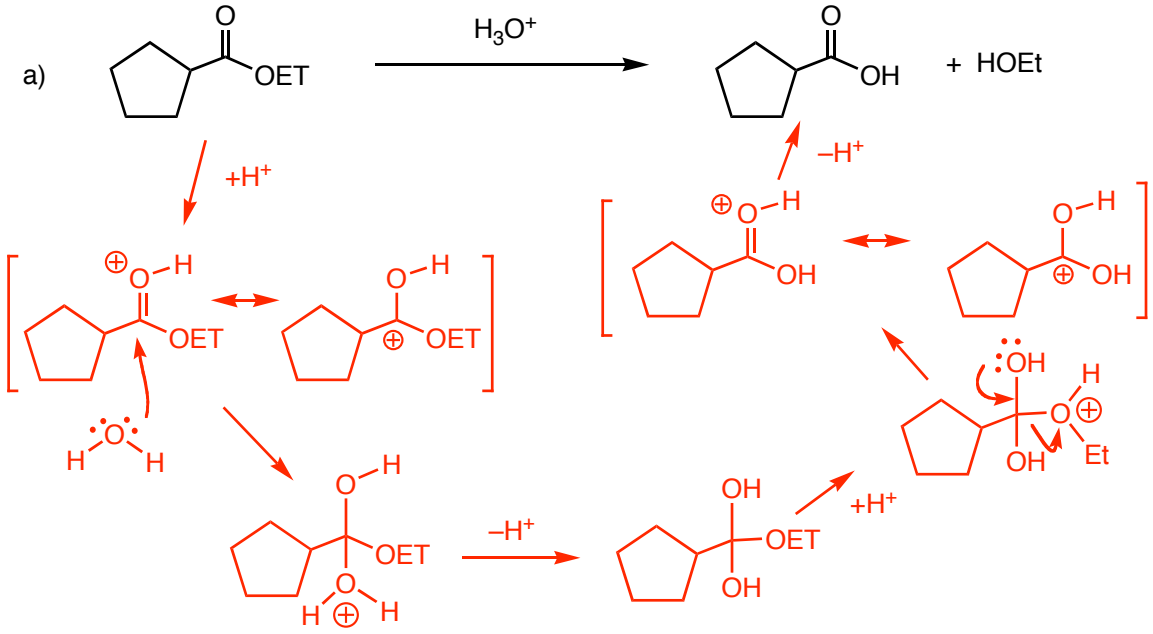
c) Draw the HOMO and LUMO of the reactant cation ON TOP of the structures that are redrawn below



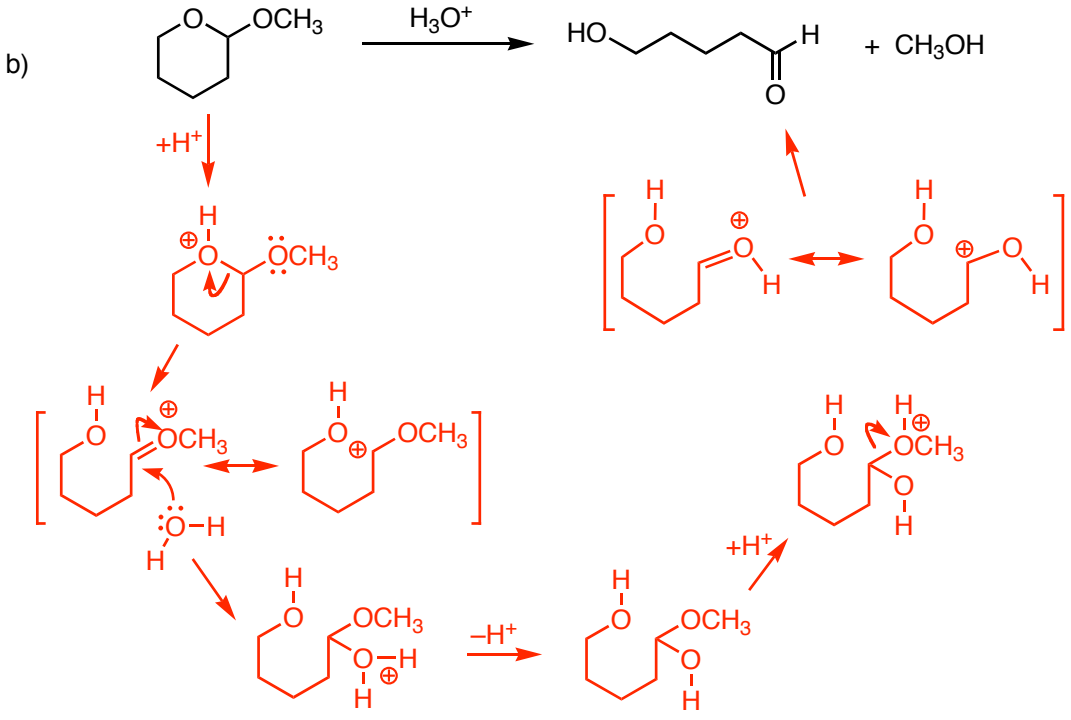
Question 12 (40 pts.) a) Give a curved arrow-pushing mechanism for the following reactions

- **You can give an "abbreviated mechanism, i.e. you may use $+H^+$ and $-H^+$**
- **<u>BUT, draw all resonance structures for the intermediates</u>**
- **Add non-bonding electrons and C–H bonds as necessary**

a)

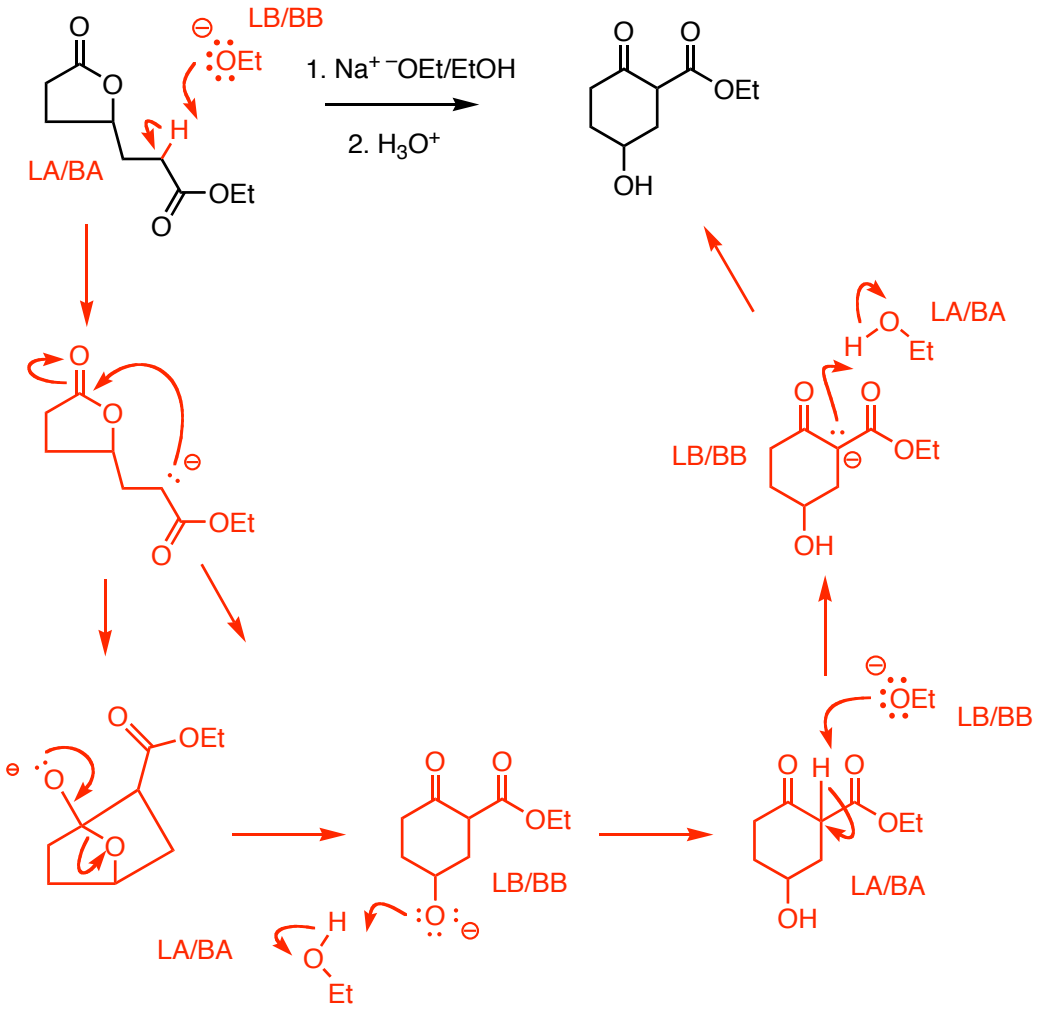


b)



Question13 (25 pts.) b) Give a curved arrow-pushing mechanism for the following reaction

- **SHOW WHERE EVERY PROTON COMES FROM AND GOES TO (no $+H^+$ or $-H^+$)**
- **DO NOT DRAW RESONANCE STRUCTURES for the intermediates**
- **Add non-bonding electrons and C–H bonds as necessary**
- **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**

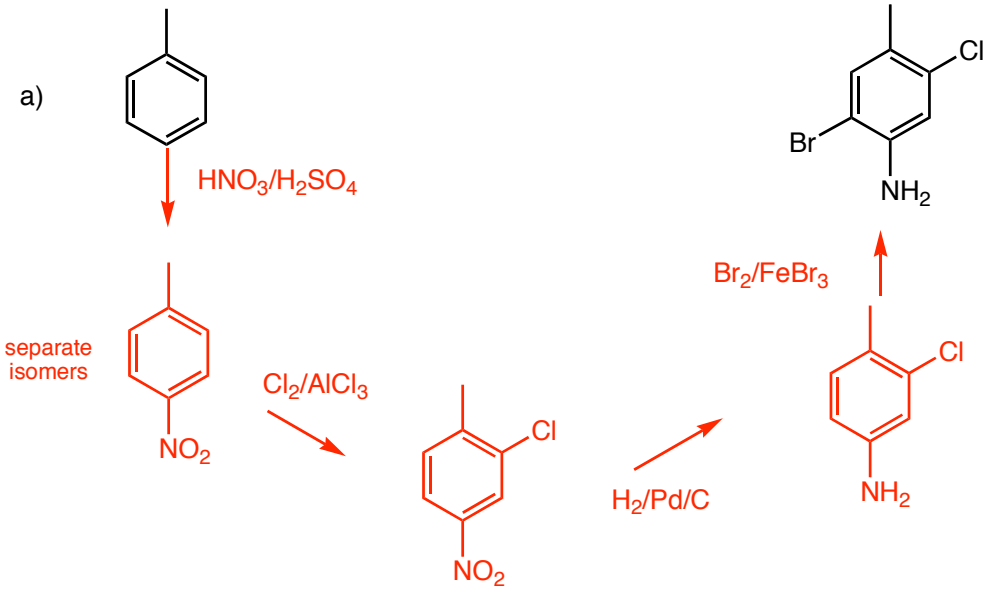


Extra Credit Question (5 pts). Hydrolysis of which functional groups is used to make soap?

amine ester amide aldehyde

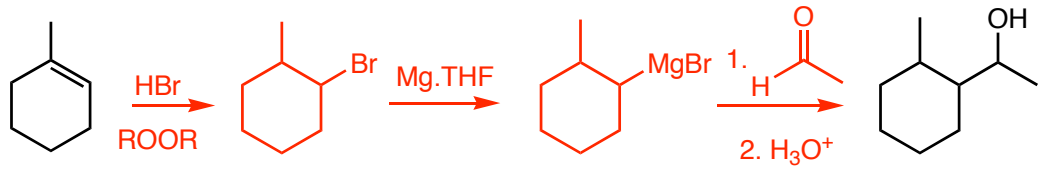
Question 14 (50 pts.) Show how you would make the target compounds on the right form the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **For question a) you must indicate steps that require separation of isomers**

a)

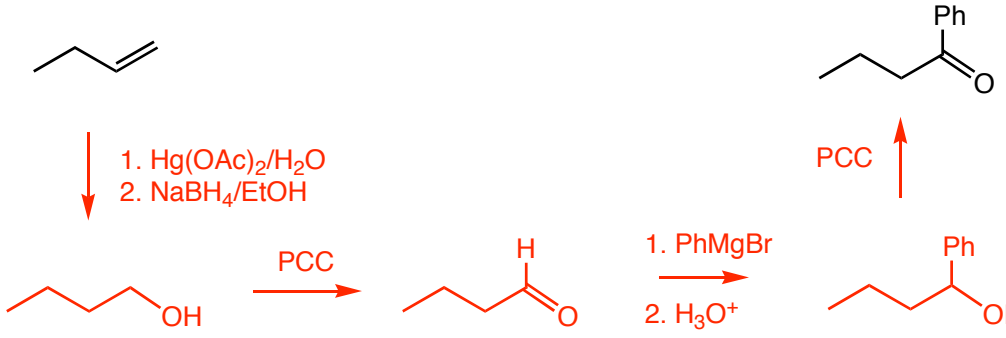


THE NEXT TWO SYNTHESIS PROBLEMS, b) and c), USE ONLY THE "SIMPLE SET OF REACTIONS" PROVIDED RECENTLY ON THE CLASS WEB PAGE!

b)

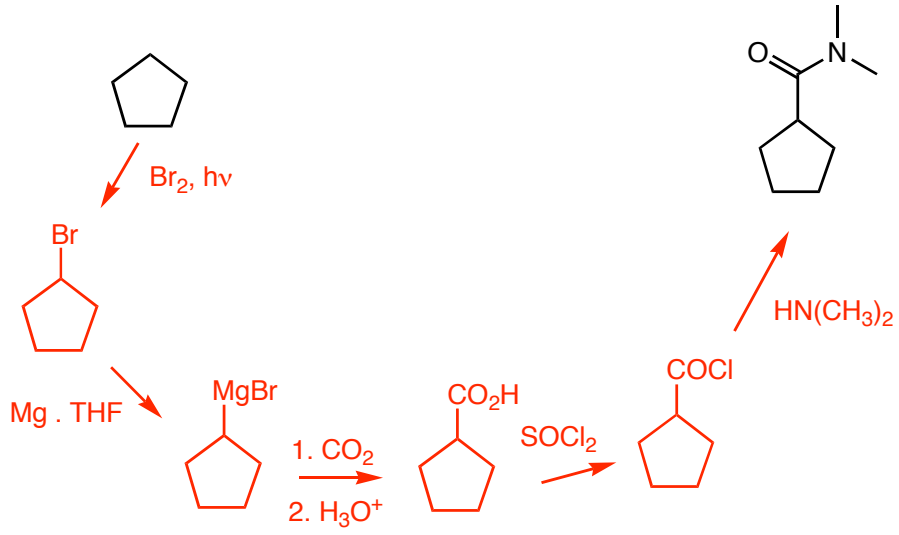


c)



Question 15 (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)