CHEM 234, Spring 2009 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 mxns 1	/28
2 acidity 1	/20	10 mxn 2	/20
3 acidity 2	/14	11 mxn 3	/22
4 basicity	/12	12 synth 1	/50
5 reaction	/10	13 synth 2	/40
6 mxn prob	/30		
7 products	/81		
8 reactions	/30		

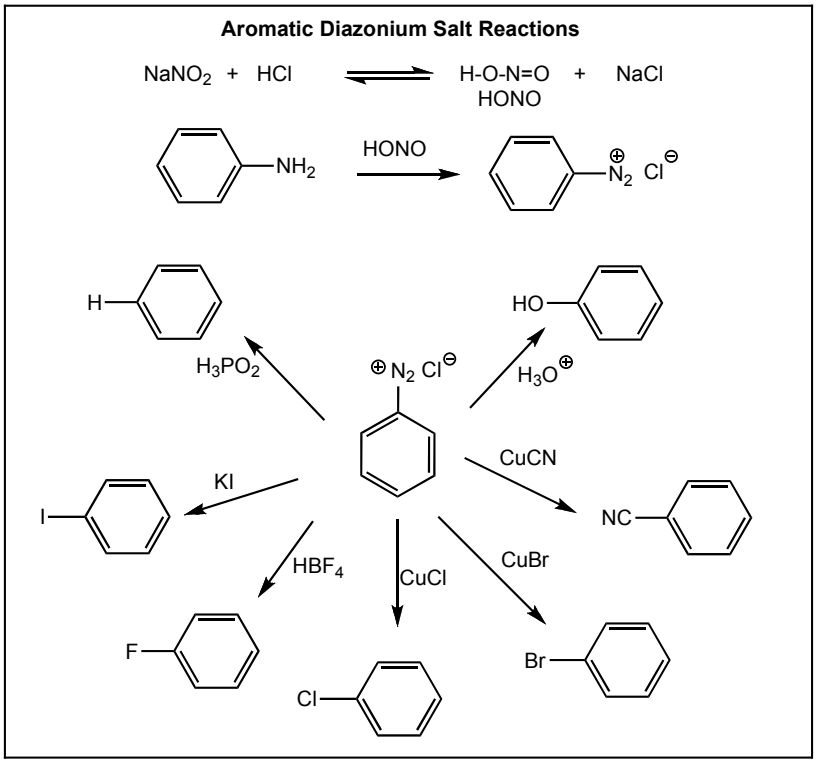
Extra Credit_____/5 **Total (incl Extra)**_____/385+5

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

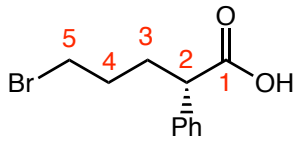
Interaction Energies, kcal/mol

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

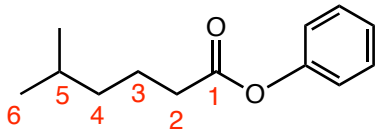
Aromatic Diazonium Salt Reactions



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

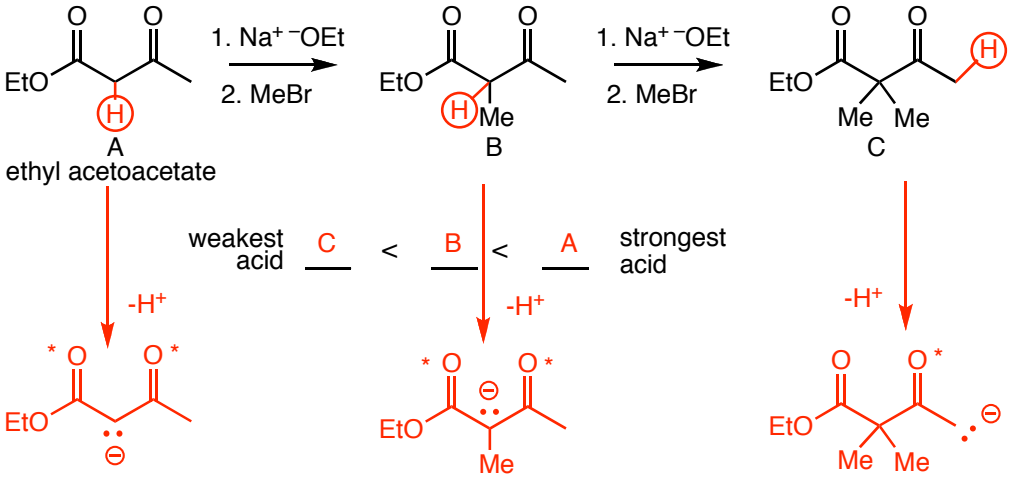
a) 

5-bromo-(2S)-phenylpentanoic acid

b) 

phenyl 5-methylhexanoate

Question 2 (20 pts.) Rank ethyl acetoacetate (A) and its methyl (B) and dimethyl (C) derivatives in order of increasing Bronsted acidity. PROVIDE AN EXPLANATION that includes drawings of the structures of the corresponding conjugate bases (all points for explanation and identifying the bases, none for just getting the order correct)



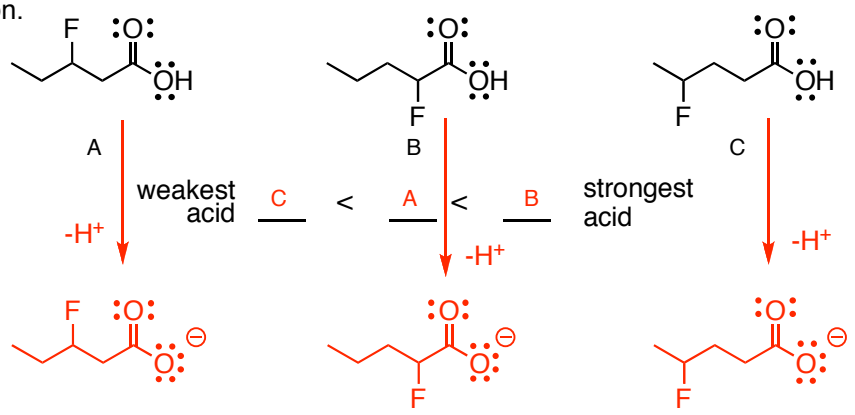
resonance stabilized enolate, 3 total resonance contributors (other anion positions indicated by *), most stable conjugate base anion

same resonance stability as anion from ethyl acetoacetate, except that the anion is destabilized by the weak donating methyl group, intermediate anion stability

only stabilized by one other resonance contributor (indicated by *), by far the least stable base

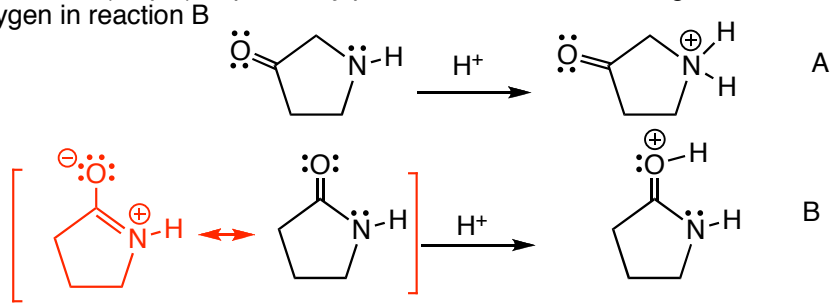
strongest acid has the weakest conjugate base anion

Question 3 (14 pts.) Rank the following in order of increasing Bronsted acidity, give a BRIEF explanation.



the electronegative fluorines stabilize the negative charge in the conjugate base anions via the inductive effect, which diminishes rapidly with increasing distance from the charge

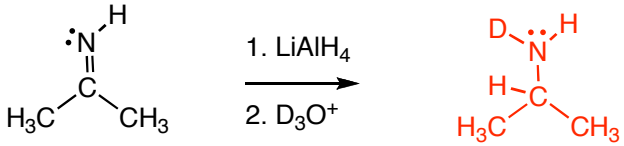
Question 4 (12 pts) Explain why protonation occurs on nitrogen in reaction A, but on oxygen in reaction B



the nitrogen is more basic in reaction A because th enon-bonding electrons are on the less electronegative element and also in an sp3 hybridized orbital

the resonance contributor shows a partial negative charge on oxygen in the structure in B and a partial positive charge on the nitrogen, reducing the basicity of the nitrogen and increasing the basicity of the oxygen

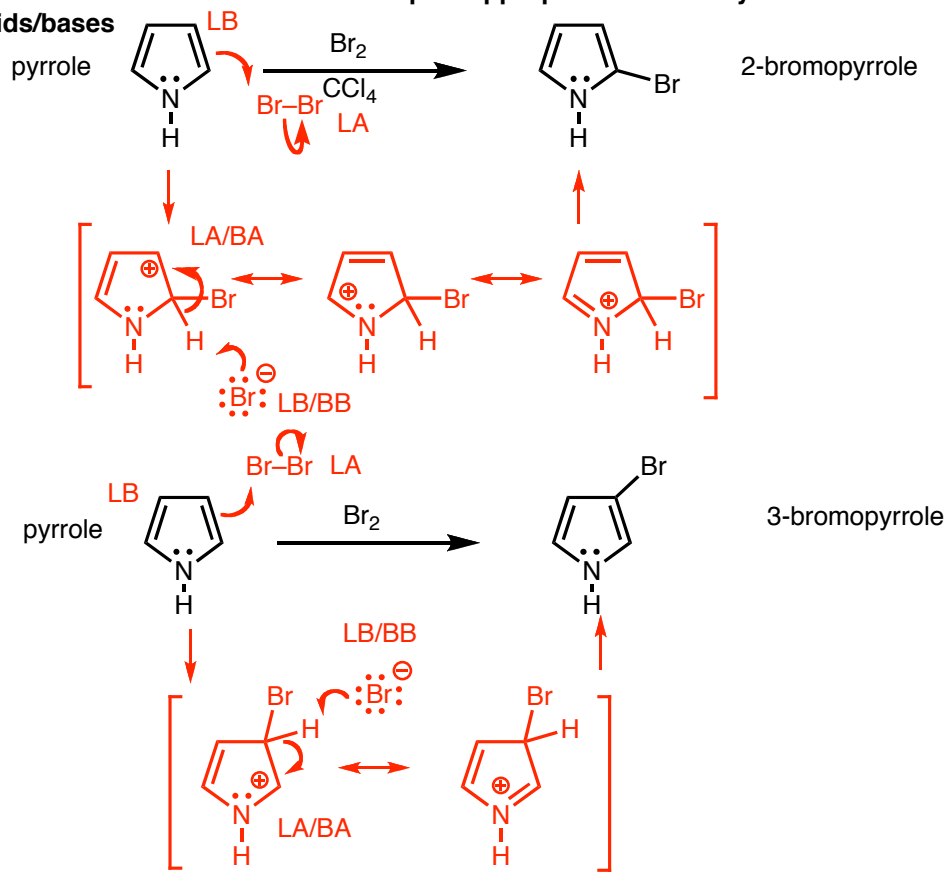
Question 5 (10 pts) Give the product of the following reaction. Remember that D represents deuterium, an isotope of hydrogen, that is used to keep track of where hydrogen atoms go in chemical reactions, but otherwise acts the same as a hydrogen atom. Your structure should be a full Lewis structure showing all atoms and non-bonding electrons.
We did not cover this reaction class, but you should be able to work it out based on what you know about the mechanisms of these reduction reactions



Question 6 (30 pts.) Pyrrole undergoes facile electrophilic aromatic substitution. The pyrrole reacts directly with the Br_2 without the need for a Lewis acid catalyst such as $FeBr_3$.

a) Draw a complete arrow pushing mechanism showing electrophilic aromatic substitution of bromine at the BOTH the 2-position and the 3-position.

- **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) Which product is more likely to be formed, the one with substitution at the 2 position, or the 3 position? Give a BRIEF explanation.

substitution at the 2 position is favored because of the larger number of resonance structures in the intermediate cation, the cation is lower in energy, it is formed faster

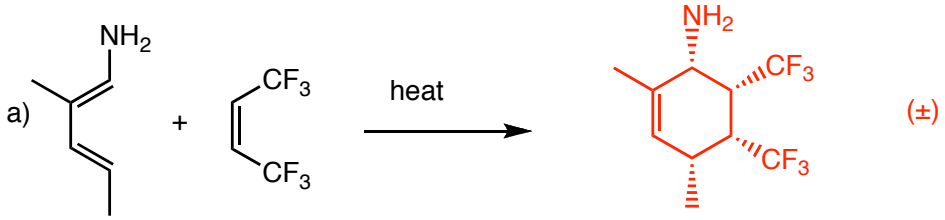
c) Suggest a reason why pyrrole reacts with Br_2 without the need for a Lewis acid catalyst, whereas benzene does require a Lewis acid catalyst

the aromatic system in pyrrole contains non-bonding electrons from N, the total electron energy is thus higher in pyrrole compared to benzene where all the electrons are bonding, higher energy electrons means more reactive, thus will react as a LB directly with Br_2

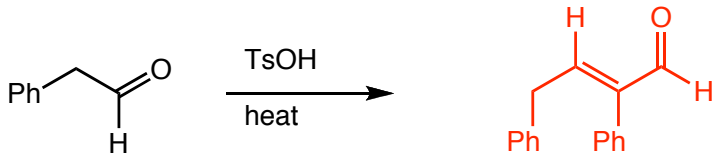
Question 7 (81 pts)

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

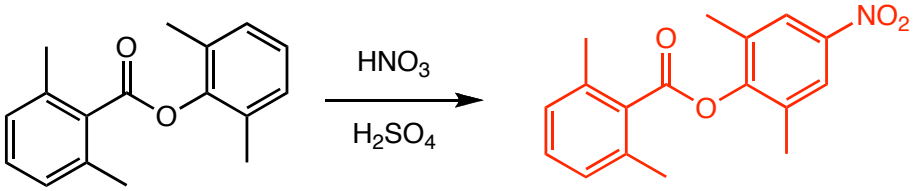
a)



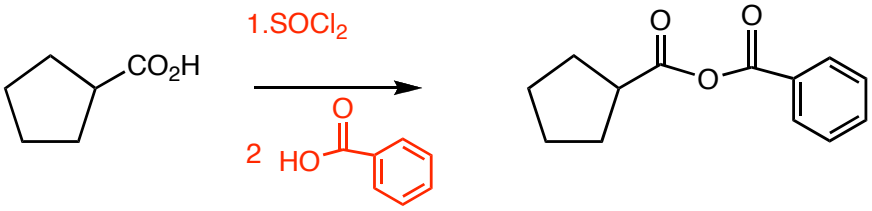
b)



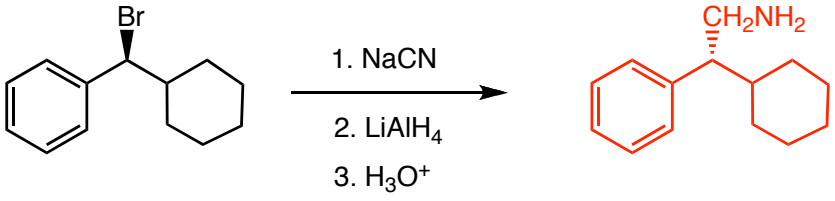
c)



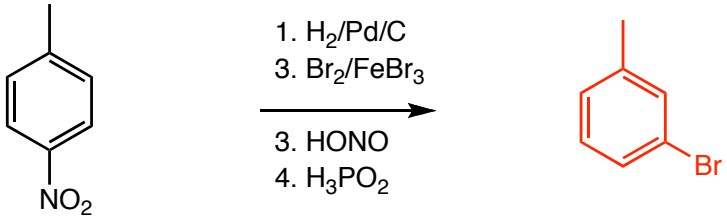
d)



e)

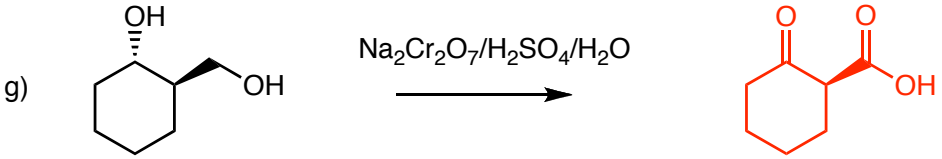


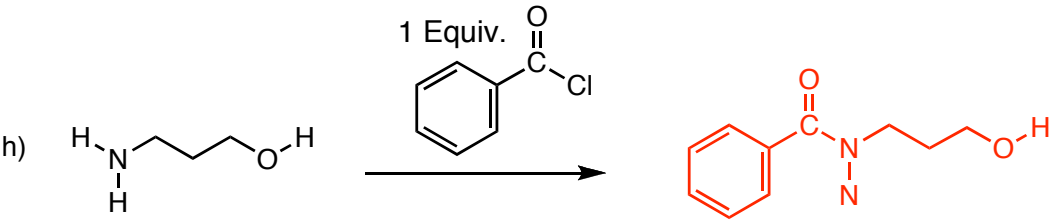
f)

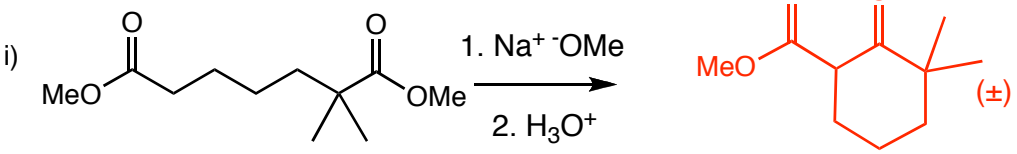


Question 7, Contd...

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

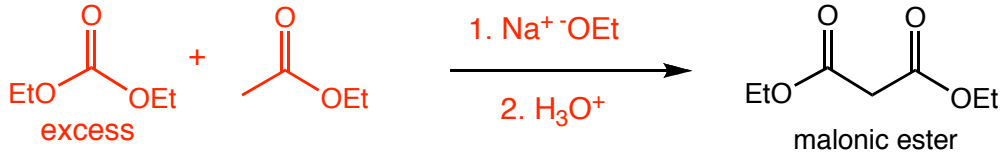
g) 

h) 

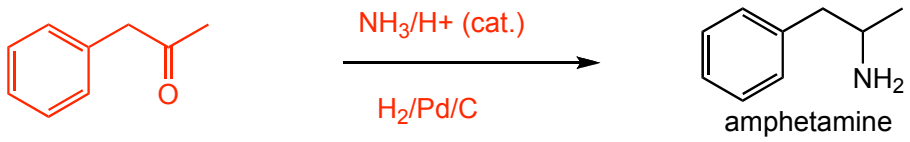
i) 

Question 8 (30 pts)

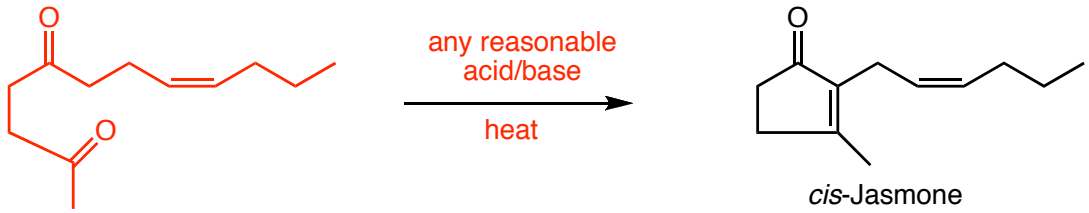
a) Give the reactants AND reagents/conditions that would allow you to synthesize malonic ester in a Claisen reaction



b) Give the reactants AND reagents/conditions that would allow you to synthesize amphetamine in a reductive amination



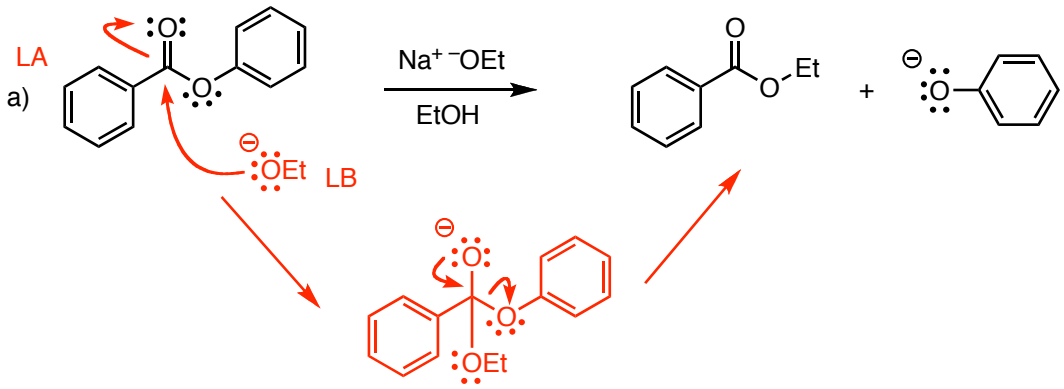
c) Give the reactants AND reagents/conditions that would allow you to synthesize *cis*-Jasmone (used in perfume industry) in an Aldol condensation.



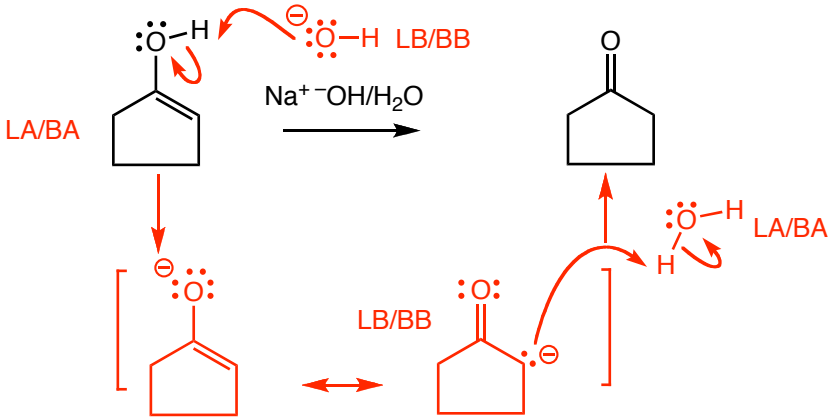
Question 9 (28 pts) Give the mechanism for
a) the transesterification, and
b) and the enol to ketone tautomerization reactions shown below

- **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**

a)

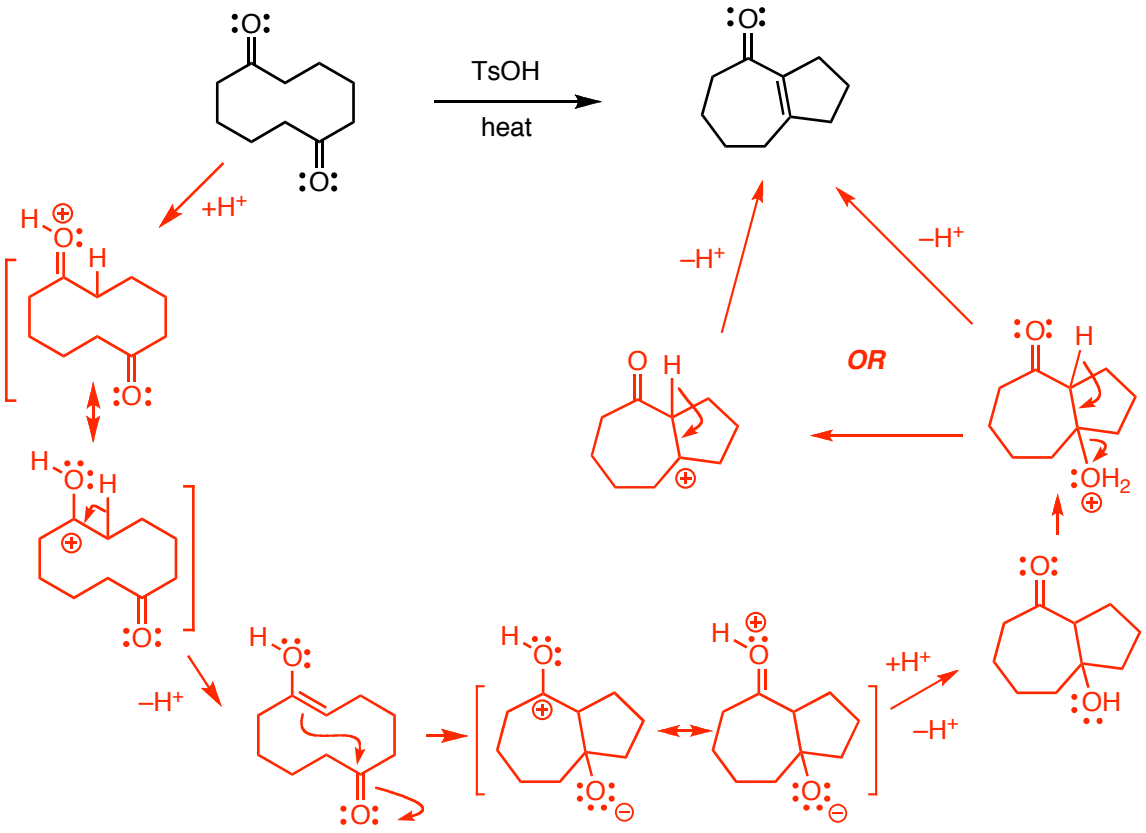


b)



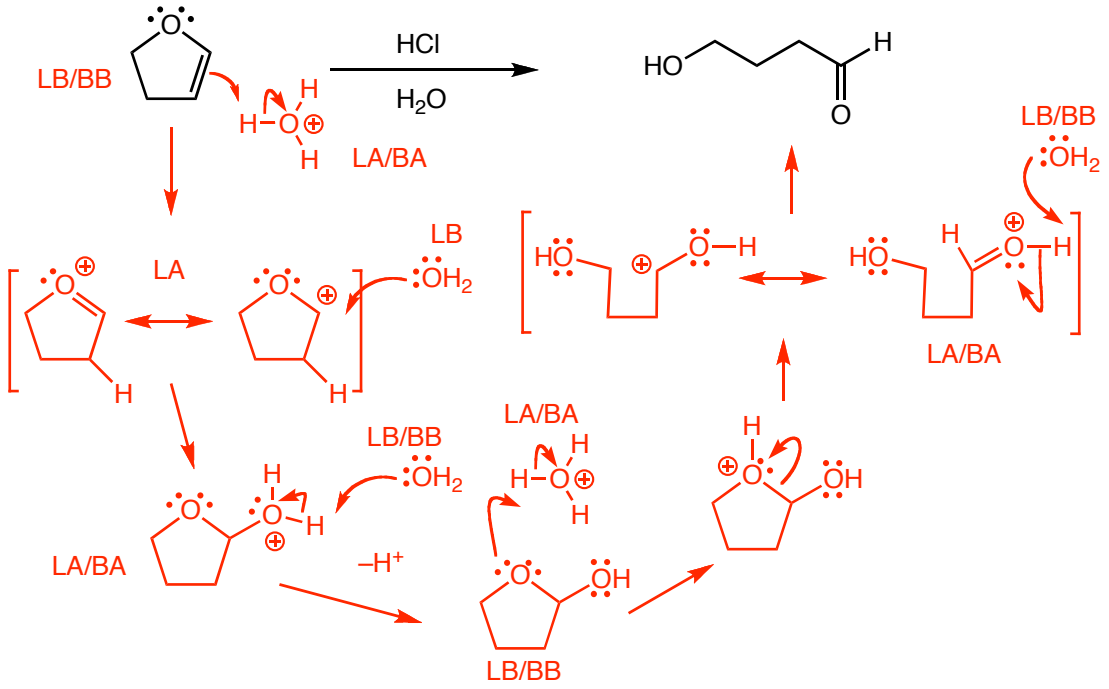
Question 10 (20 pts.) Give a curved arrow-pushing mechanism for the following reaction

- **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 11 (22 pts.) Give a curved arrow-pushing mechanism for the following reaction

- **SHOW WHERE EVERY PROTON COMES FROM AND GOES TO (no $+H^+$ or $-H^+$)**
- **DRAW ALL RESONANCE CONTRIBUTORS for the intermediates**
- **Add 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**

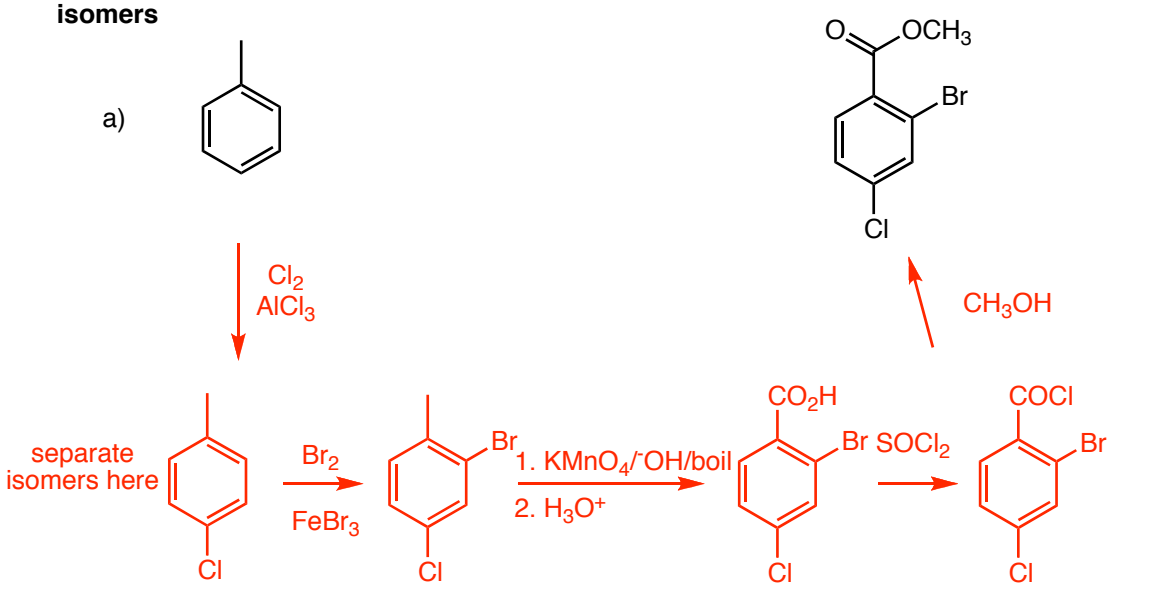


Extra Credit Question (5 pts). Which functional group formed the basis of the new "two-electron sensitizer" molecule that enhances the speed of motion picture film?

(amine) ester amide aldehyde

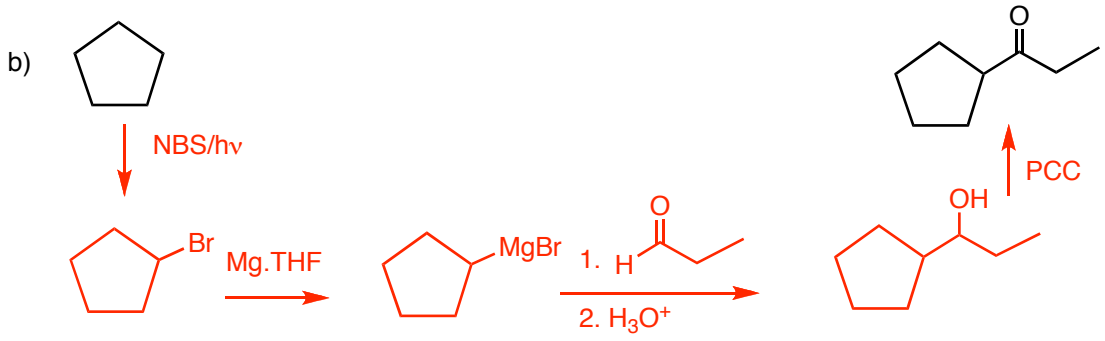
Question 12 (50 pts.) Show how you would make the target compounds on the right form the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **For question a) you must indicate steps that require separation of isomers**

a)

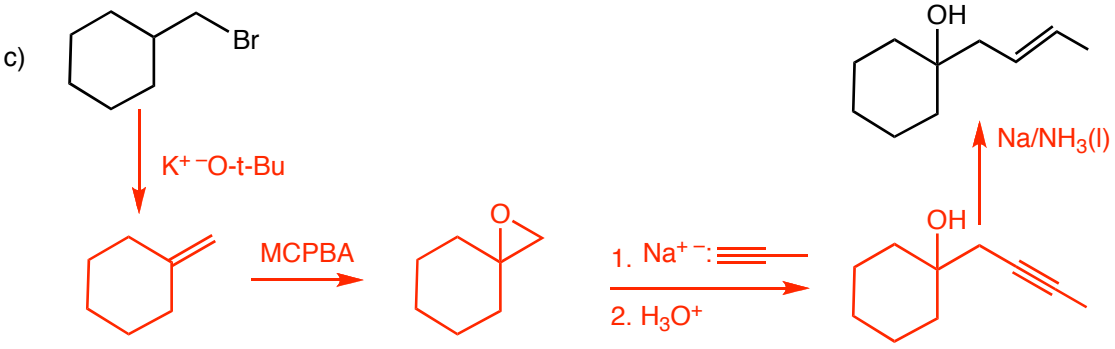


THE NEXT TWO SYNTHESIS PROBLEMS, b) and c), USE ONLY THE "SIMPLE SET OF REACTIONS" PROVIDED RECENTLY ON THE CLASS WEB PAGE!

b)

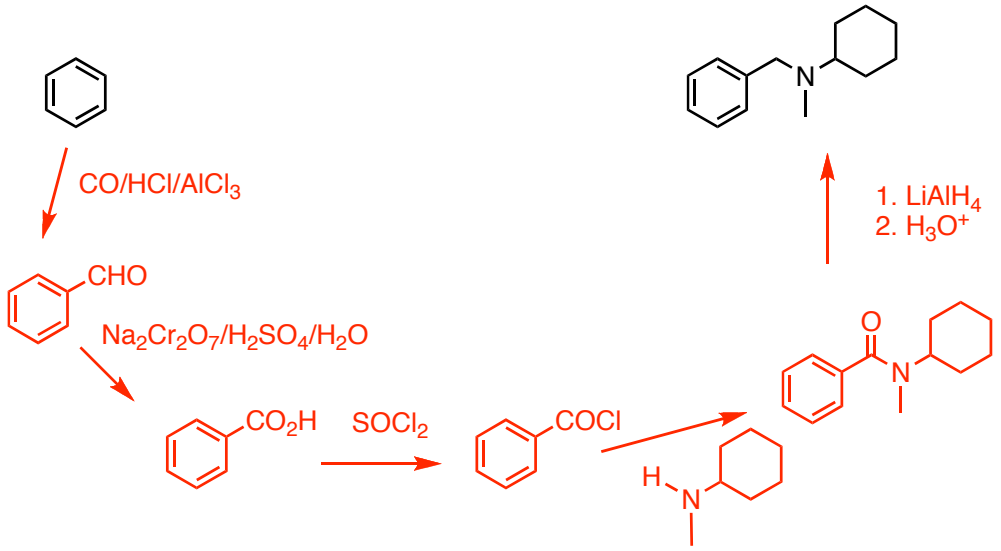


c)



Question 13 (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)