

**YOU MUST COMPLETE THIS PAGE WITH YOUR NAME
(EVEN THOUGH YOU ALREADY DID THIS ON THE COVER PAGE)
AND ALSO GIVE YOUR ASU OR POSTING ID NUMBER**

we need this information because we will not be able to read the names of many students!

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

Points by question

1 _____ /13

12a _____ /9

2 _____ /14

12b _____ /9

3 _____ /16

13 _____ /16

4 _____ /20

14 _____ /22

5 _____ /8

15a _____ /20

6a _____ /22

15b _____ /13

6b _____ /12

15c _____ /13

7a _____ /8

16a _____ /20

7b _____ /8

16b _____ /20

7c _____ /8

7d _____ /8

7e _____ /8

Points Removed for cover errors ____/2

7f _____ /8

Extra Credit ____/5

7g _____ /8

Total (incl Extra) ____/375+5

7h _____ /8

8 _____ /12

9 _____ /10

10a _____ /8

10b _____ /2

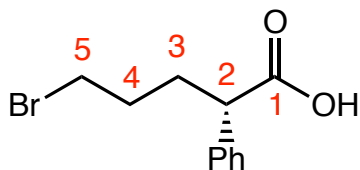
10c _____ /2

10d _____ /4

10e _____ /6

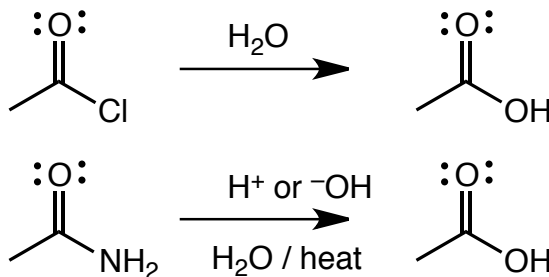
11 _____ /20

Question 1 (13 pts.) Provide a IUPAC name for the following structure, do not forget to use E/Z and R/S as appropriate.



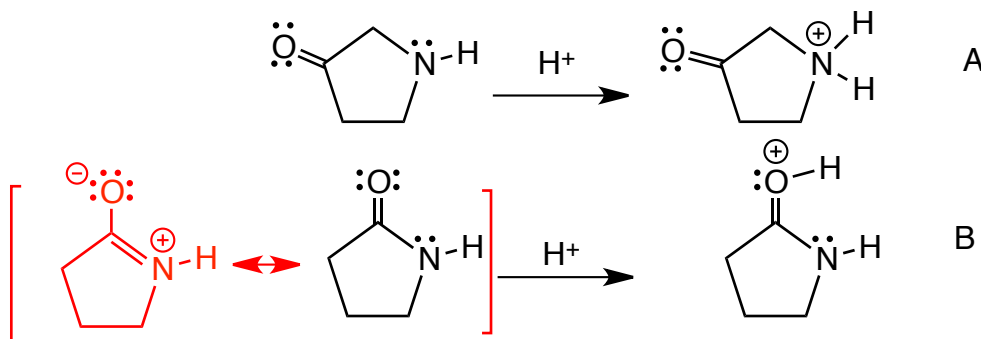
5-bromo-(2S)-phenylpentanoic acid

Question 2 (14 pts.) Give TWO reasons why an acid chloride hydrolyzes to a carboxylic acid in pure water at room temperature, but an amide requires strong acid or base catalysis and heat



the reaction involves nucleophilic addition to the C=O bond, the amide has a donating group attached to this carbon, the chloride a withdrawing group, also the amide anion is a poor leaving group whereas chloride is a good leaving group

Question 3 (16 pts) Using a drawing of a minor resonance contributor, explain why protonation occurs on nitrogen in reaction A, but on oxygen in reaction B



the nitrogen is more basic in reaction A because the non-bonding electrons are on the less electronegative element and also in an sp^3 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

Extra Credit Question (5 pts). What kind of functional group is hydrolyzed to form soap?

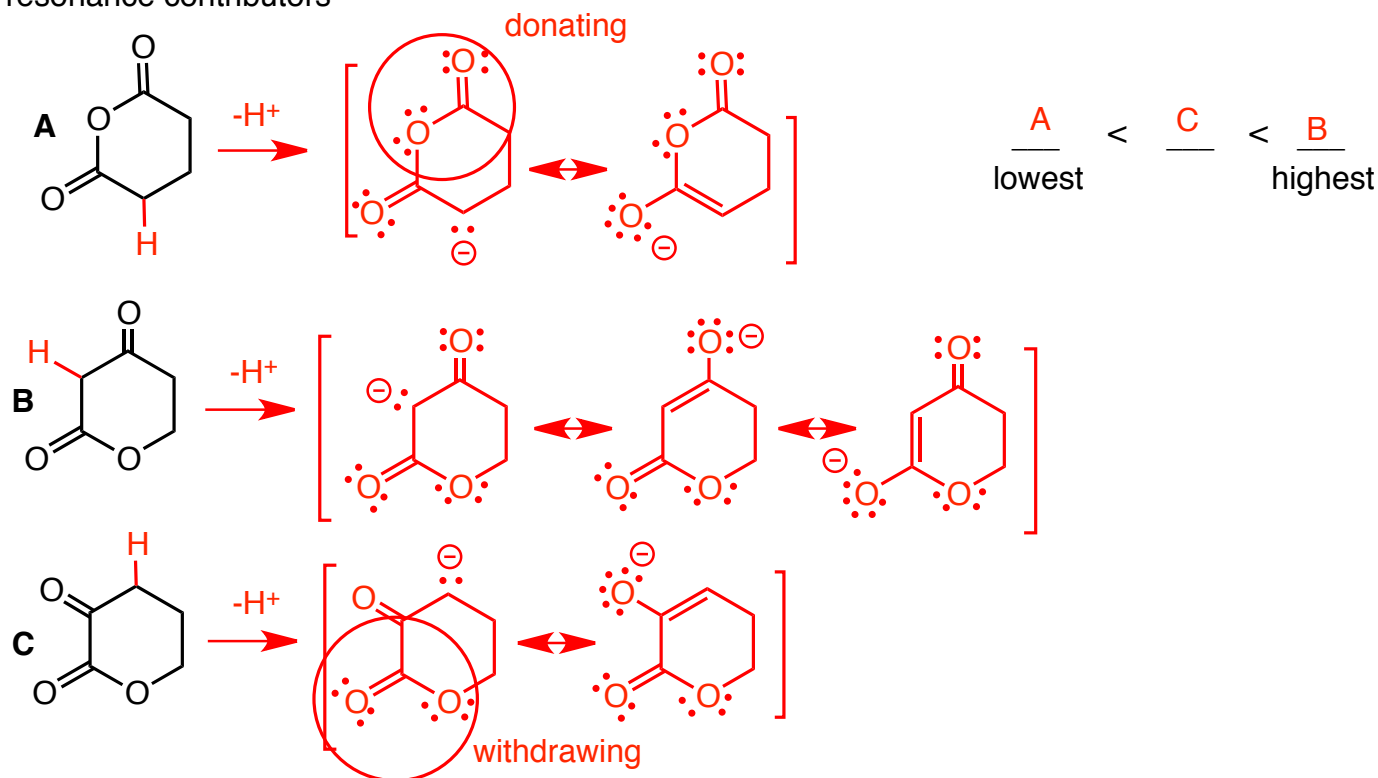
carboxylic acid

ester

amide

aldehyde

Question 4 (20 pts.) Rank the following in order of increasing Bronsted acidity. Give a BRIEF explanation that includes drawings of the conjugate base anions, including ALL relevant resonance contributors



acidity is determined by the stability of the enolate anions formed by deprotonation of the indicated hydrogens

the anion for B is stabilized by 3 resonance contributors, it is the most stable base, its acid is the strongest

the anions for both A and C are stabilized by 2 resonance contributors, in C the anion is stabilized by the weak W group and in A the anion is destabilized by the donating group, A is the weakest acid

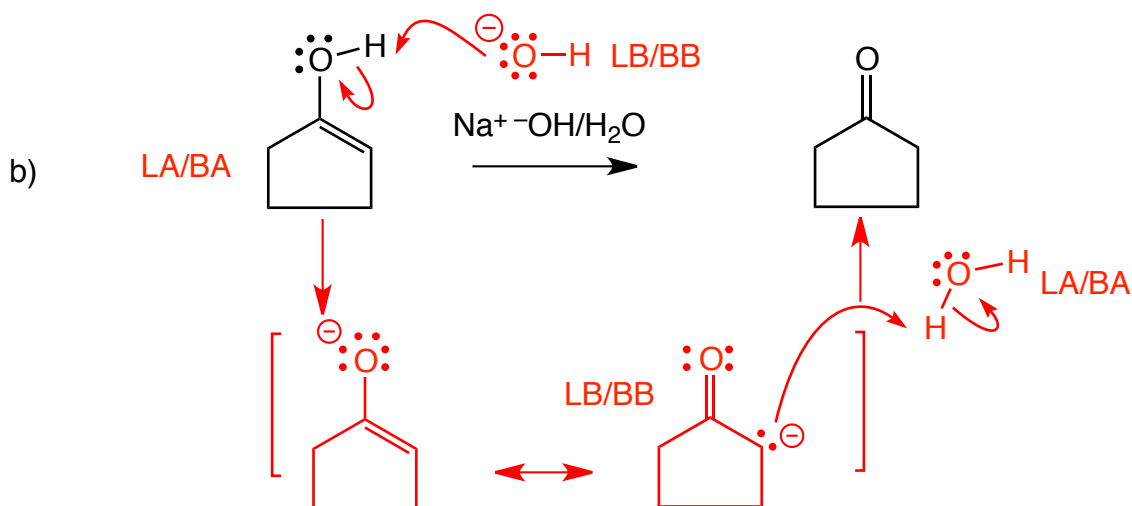
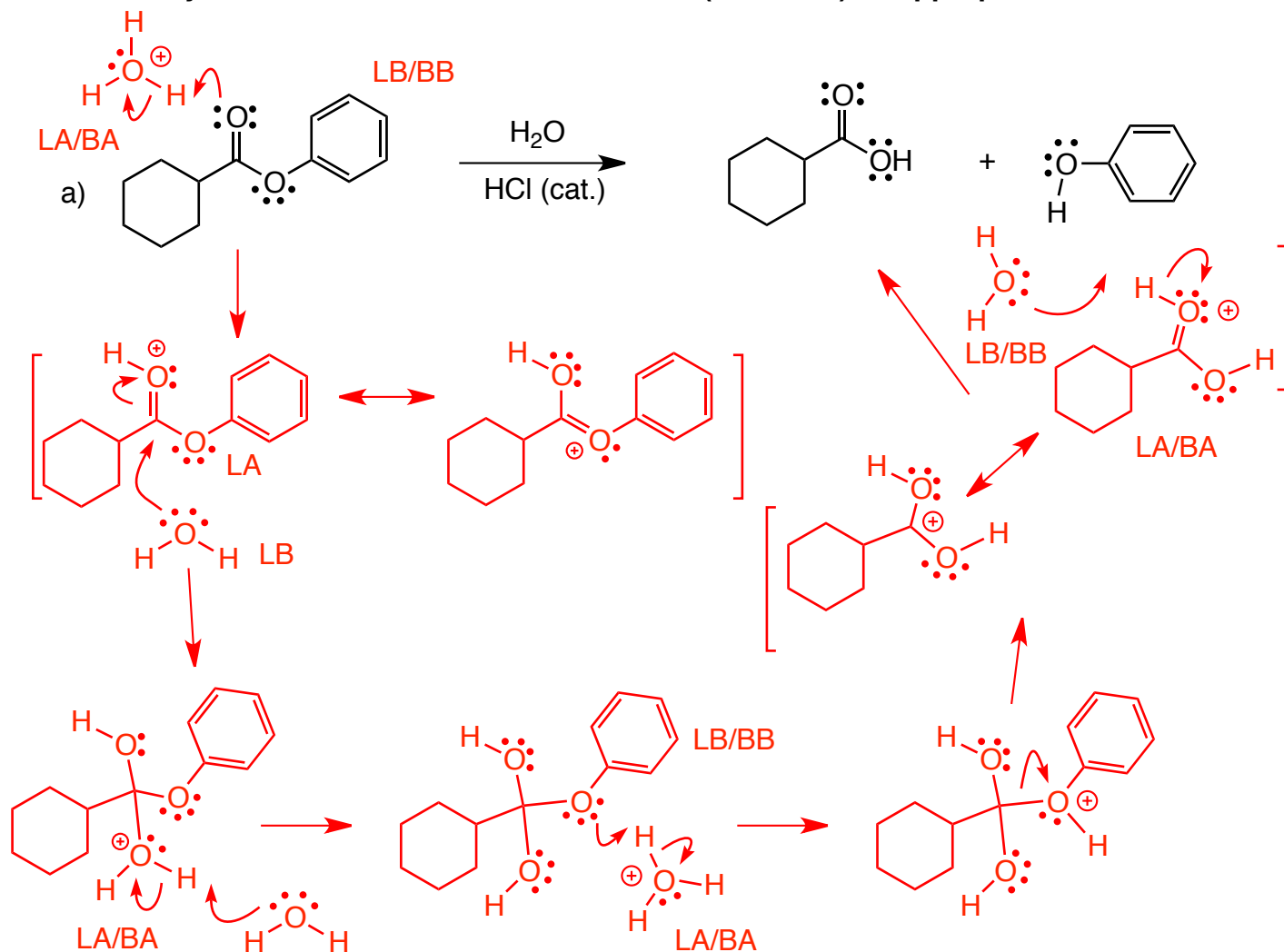
Question 5 (8 pts.) Which would you expect to be the stronger Bronsted Base? Give a BRIEF explanation that includes the term "energy of electrons" and "chemical reactivity"



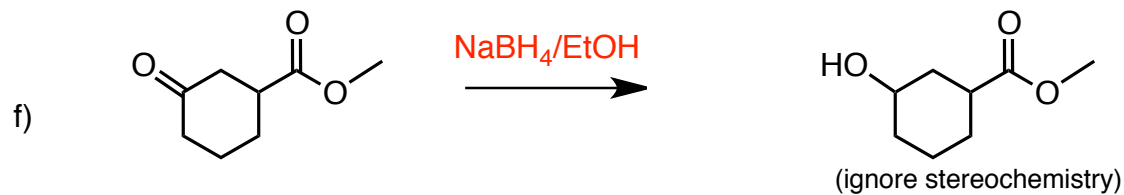
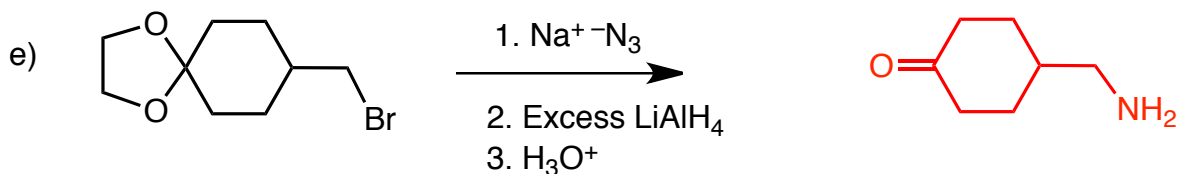
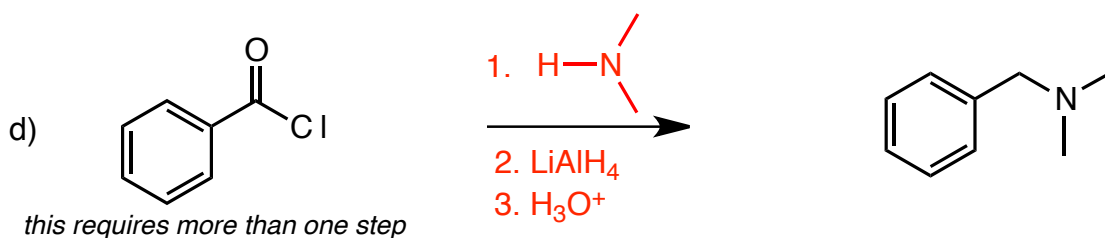
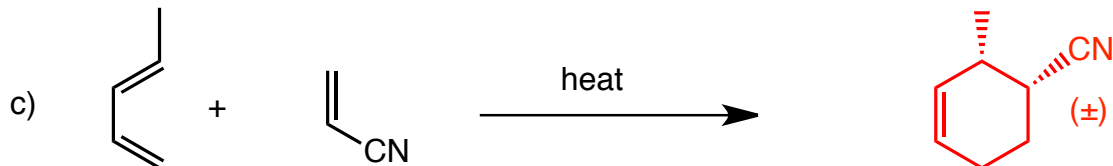
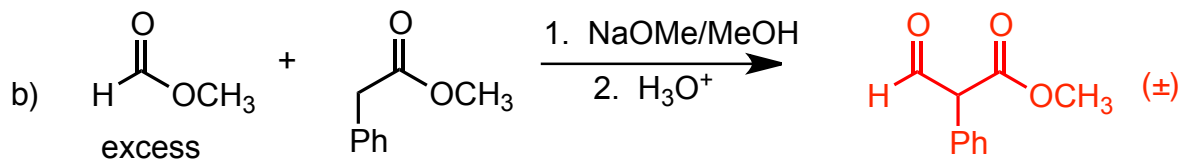
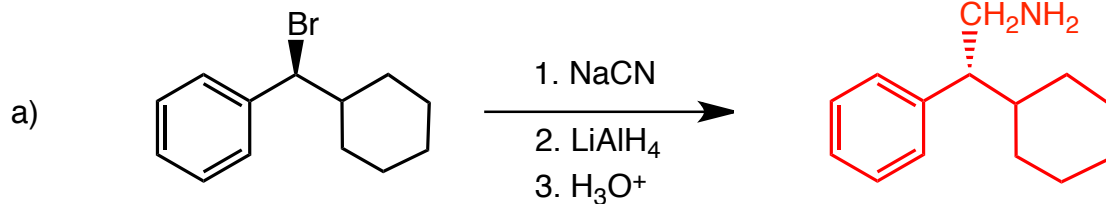
the non-bonding electrons in A are stabilized by resonance delocalization, the electrons are thus lower in energy and are thus less chemically reactive, A is the weaker Bronsted base

Question 6 (34 pts) Give a curved arrow pushing mechanism for the following reactions

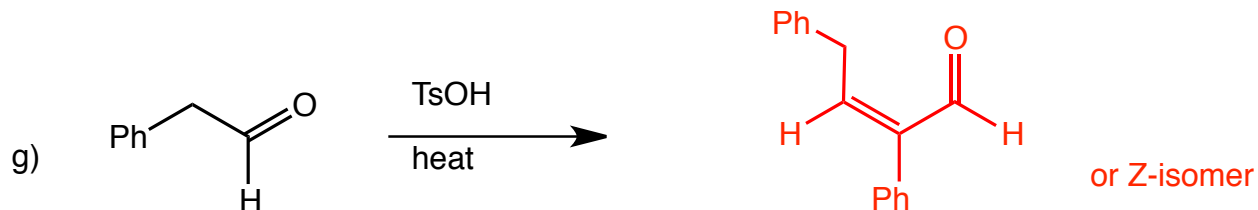
- AS APPROPRIATE, SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no +H⁺/⁻H⁺)
- DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate
- At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate



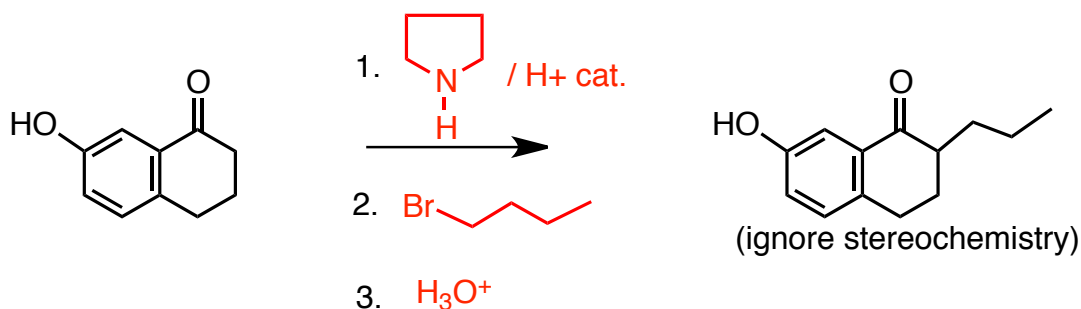
Question 7 (64 pts) Provide the missing major organic products or reagents/conditions for the following reactions. **Do not forget to include stereochemistry as appropriate** and INDICATE ANY RACEMIC MIXTURES.



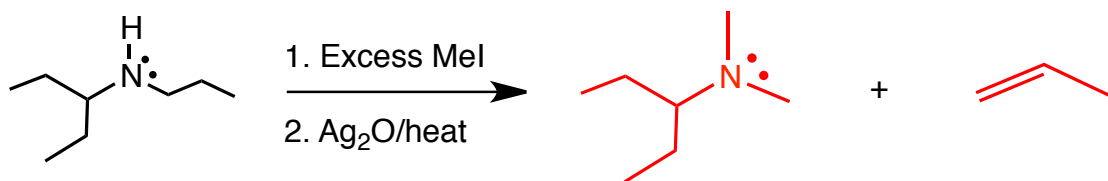
Question 7, Contd... Provide the missing major organic products for the following reactions. **Do not forget to include stereochemistry as appropriate** and INDICATE ANY RACEMIC MIXTURES.



Question 8 (12 pts.) The following is a Stork enamine synthesis. There are 3 steps. Add the relevant reagents/conditions for each of the 3 steps.

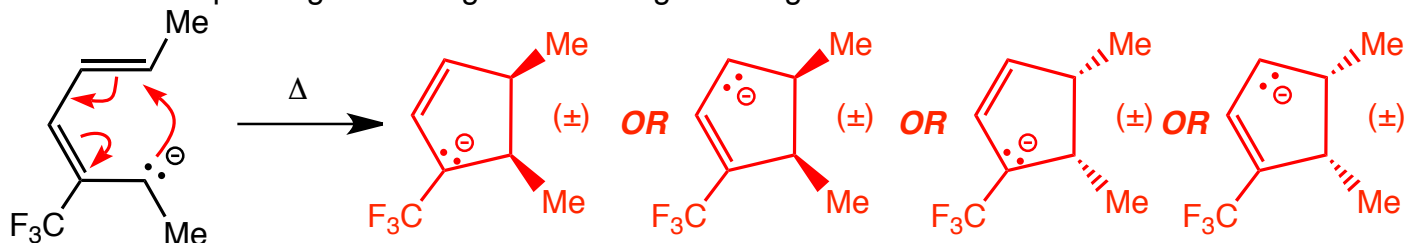


Question 9 (10 pts.) Give the TWO organic products expected for the following Hoffman elimination



Question 10 (22 pts)

a) Give the allowed product of the electrocyclic ring closure reaction shown below and give the curved arrow-pushing describing bond making/breaking



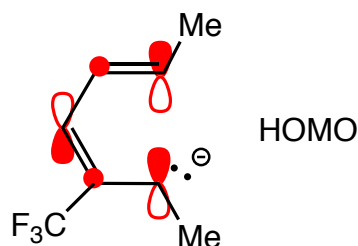
b) How many electrons are involved in this reaction **6**

c) Does the ALLOWED reaction proceed via a disrotatory or a conrotatory ring closure **disrotatory**

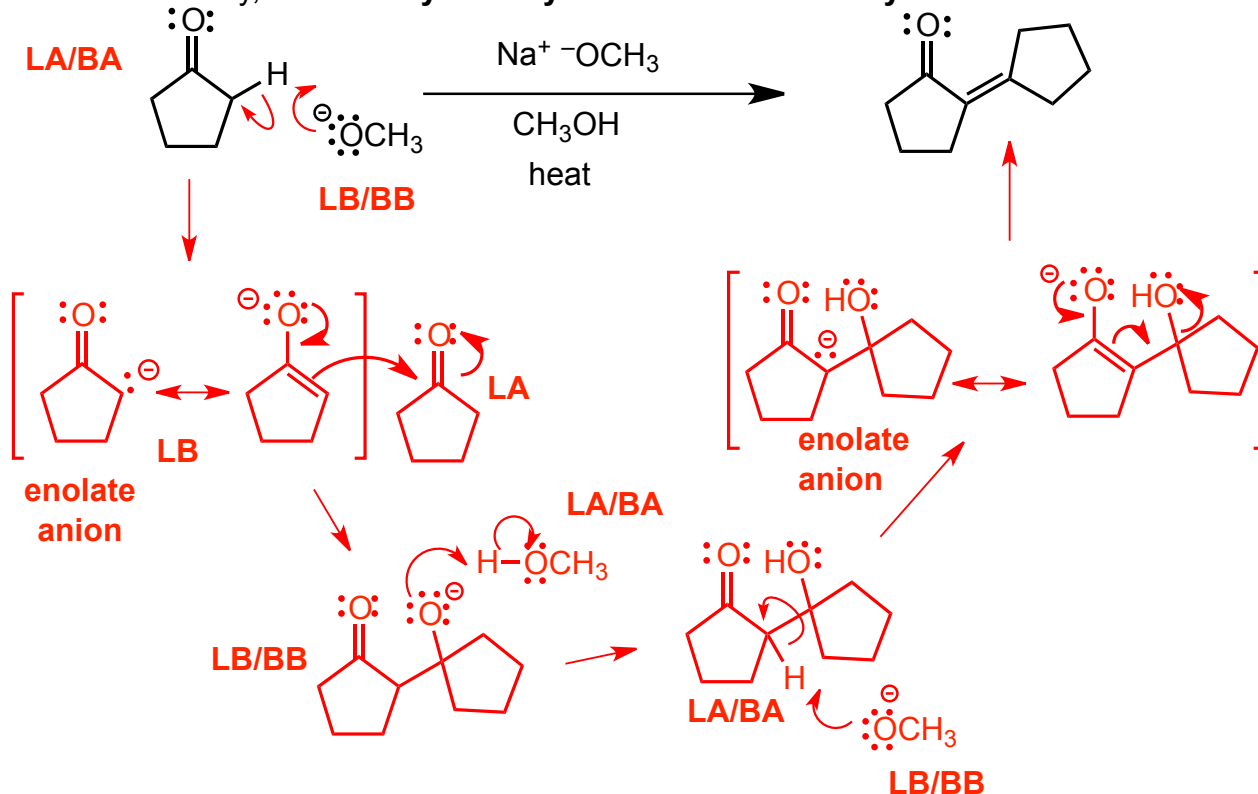
d) Does the allowed reaction proceed via a Huckel or a Mobius transition state? Give a BRIEF explanation that includes the term "aromatic"

Huckel, because 6 electrons in a cyclic loop Huckel transition state are aromatic and lower in energy than a Mobius transition state

e) Draw the HOMO of the reactant anion ON TOP of the structure to the right



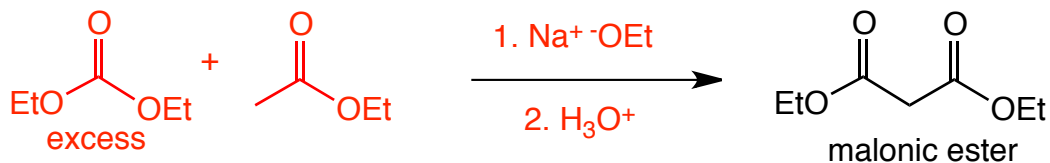
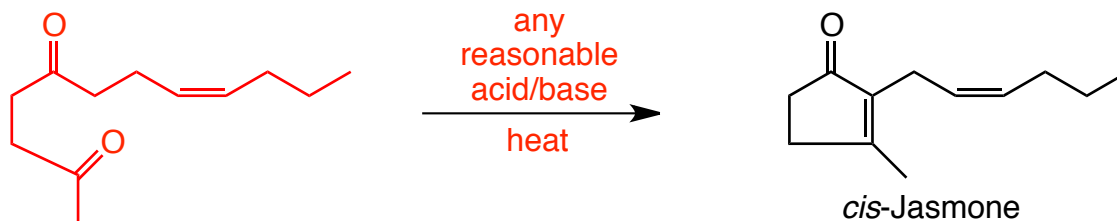
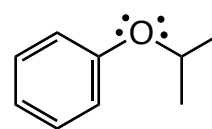
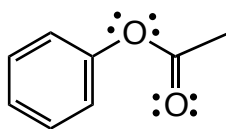
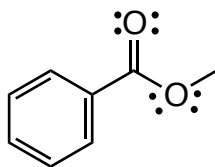
Question 11 (20 pts.) Give the arrow pushing mechanism for the following reaction. Show where each proton goes and comes from (no H^+/H^-), indicate the LB/BB and LA/BA, and show all reasonable resonance contributors for the intermediates, add H atoms and non-bonding electrons as necessary, and **Clearly identify all enolate anions in your mechanism!**



How many steps are in your mechanism? **5**

Question 12 (18 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 *cis*-Jasmone (used in perfume industry) in an Aldol condensation.Question 13 (16 pts) Rank the following in order of increasing rate of electrophilic aromatic substitution, for example, reaction with $\text{Br}_2/\text{FeBr}_3$. Provide a BRIEF explanation that includes the terms activating and deactivating.

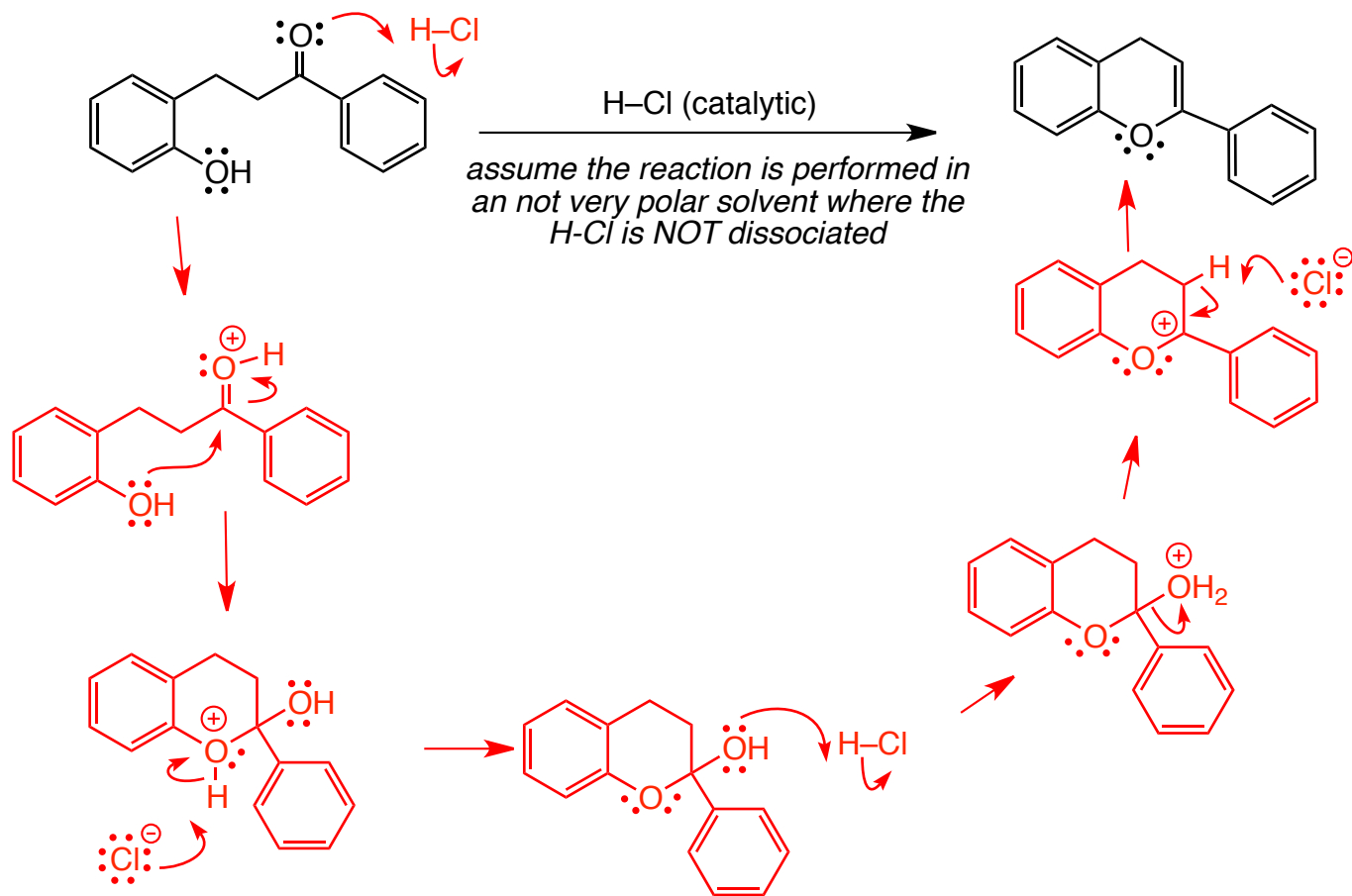
electrophilic aromatic substitution is faster with stronger donating more activating substituents

the substituent in A is withdrawing and deactivating, it is slowest

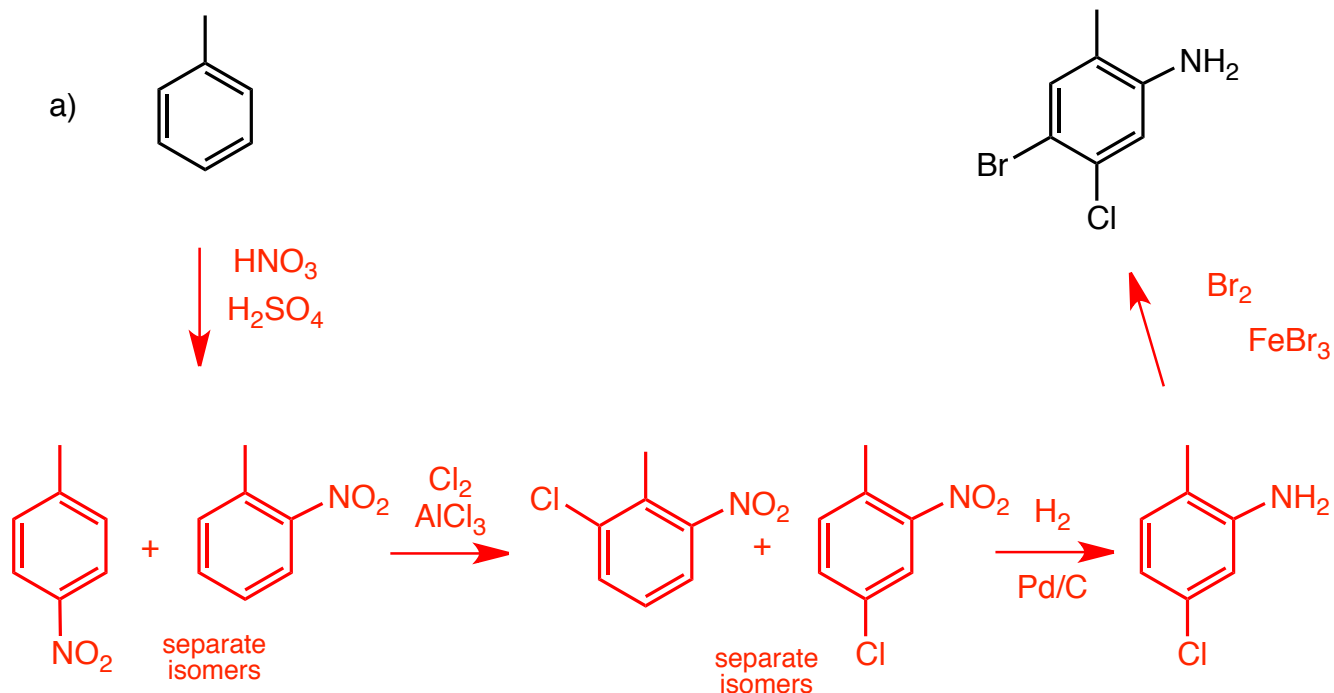
the substituent in B is donating and activating, but the substituent in C is stronger donating and more activating, thus C is fastest

Question 14 (22 pts.) Give a curved arrow-pushing mechanism for the following reaction

- **SHOW WHERE EVERY PROTON COMES FROM AND GOES TO (no $+H^+$ or $-H^+$)**
- **DO NOT DRAW RESONANCE STRUCTURES for the intermediates**
- **Add non-bonding electrons and C–H bonds as necessary**
- **Indicate the Lewis acid/bases (LA or LB) and Bronsted acids/bases (BA or BB) for each INTERMOLECULAR step**



Question 15 (46 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. **For question a) you must indicate steps that require separation of isomers and ALSO GIVE THE STRUCTURES OF THE OTHER ISOMER(S)**



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

