

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!

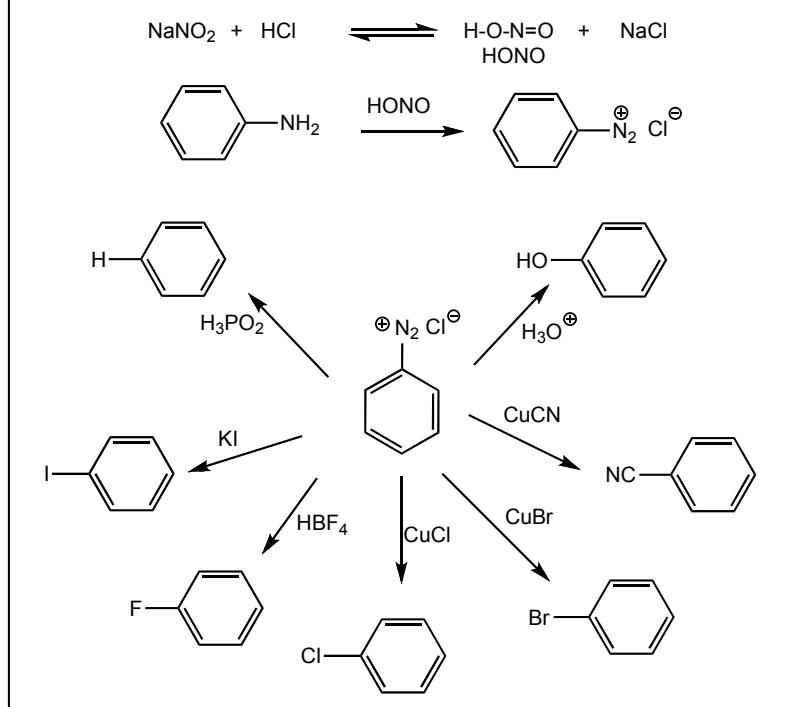
1 _____ /18 9 _____ /28.....
 2 _____ /20..... 10 _____ /20.....
 3 _____ /14..... 11 _____ /22.....
 4 _____ /12..... 12 _____ /50.....
 5 _____ /10 13 _____ /40.....
 6 _____ /30
 7 _____ /81
 8 _____ /30

Extra Credit _____ /5

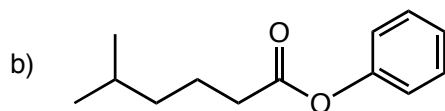
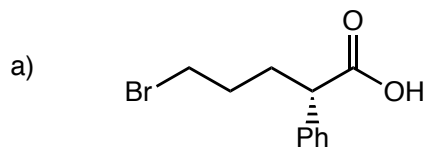
Total (incl Extra) _____ /385+5

H																He																Interaction Energies, kcal/mol			
Li	Be															B	C	N	O	F	Ne	Eclipsing		Gauche											
Na	Mg															Al	Si	P	S	Cl	Ar	H/H	-1.0	Me/Me	-0.9										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	H/Me	-1.4	Et/Me	-0.95														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Me/Me	-2.6	i-Pr/Me	-1.1														
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Me/Et	-2.9	t-Bu/Me	-2.7														

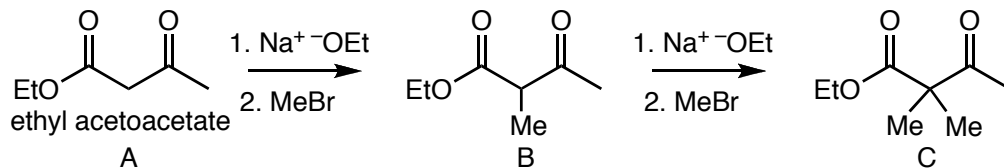
Aromatic Diazonium Salt Reactions



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

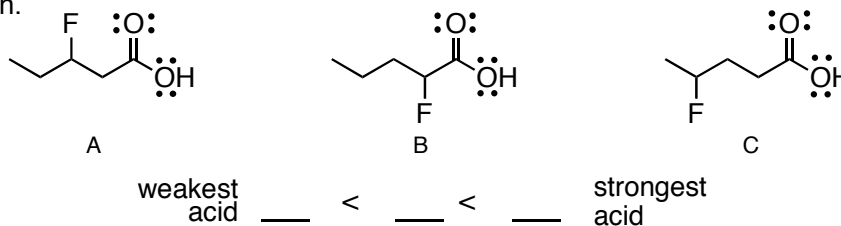


Question 2 (20 pts.) Rank ethyl acetoacetate (A) and its methyl (B) and dimethyl (C) derivatives in order of increasing Bronsted acidity. PROVIDE AN EXPLANATION that includes drawings of the structures of the corresponding conjugate bases (all points for explanation and identifying the bases, none for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

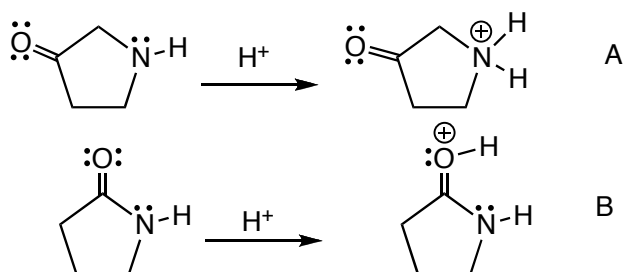


weakest acid ___ < ___ < ___ strongest acid

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

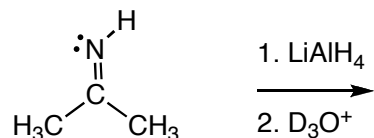


Question 4 (12 pts) Explain why protonation occurs on nitrogen in reaction A, but on oxygen in reaction B



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 .

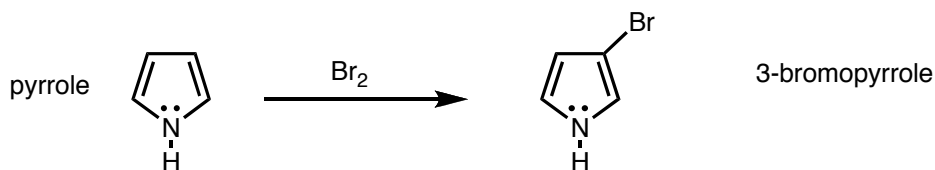
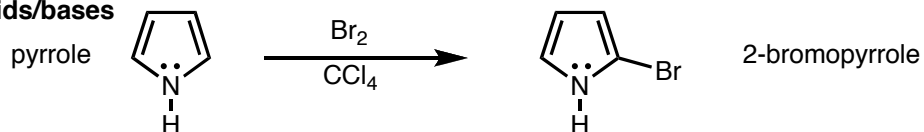
a) Draw a complete arrow pushing mechanism showing electrophilic aromatic substitution of bromine at the BOTH the 2-position and the 3-position.

• Draw all of the resonance contributors for important intermediates.

• Do NOT use $+\text{H}^+/-\text{H}^+$ 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

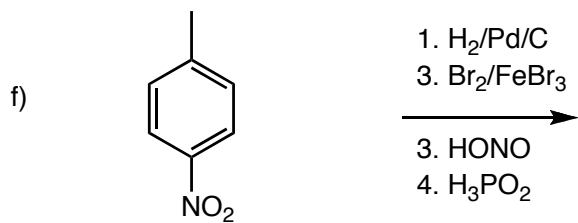
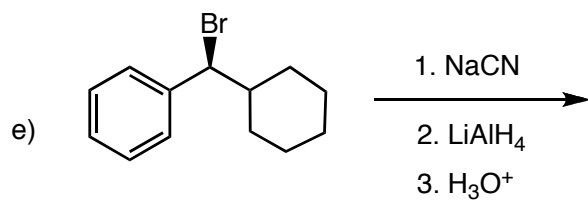
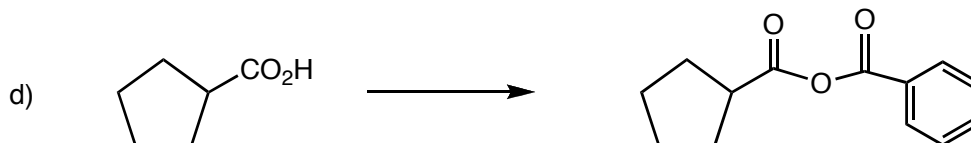
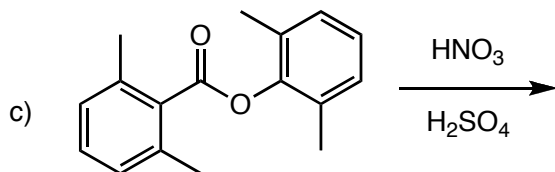
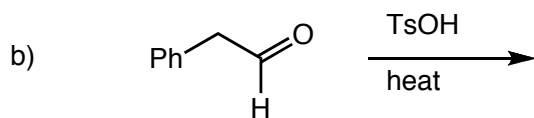
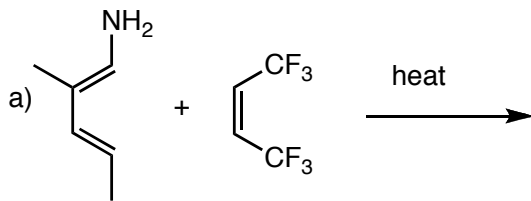


b) Which product is more likely to be formed, the one with substitution at the 2 position, or the 3 position? Give a BRIEF explanation.

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

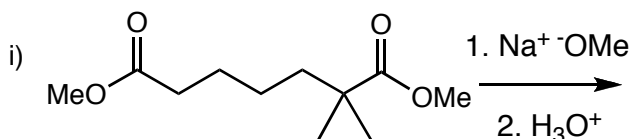
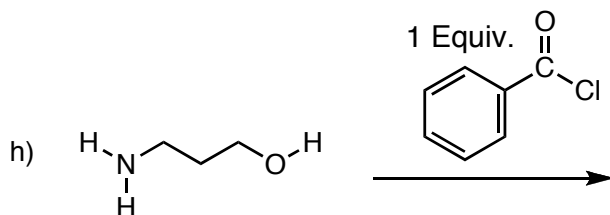
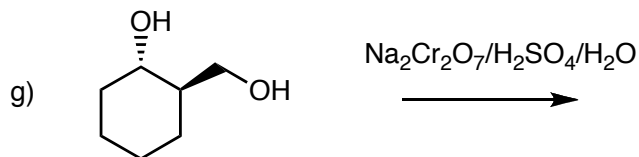
Question 7 (81 pts)

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



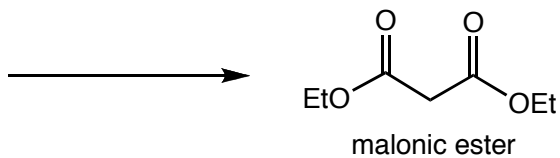
Question 7, Contd...

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

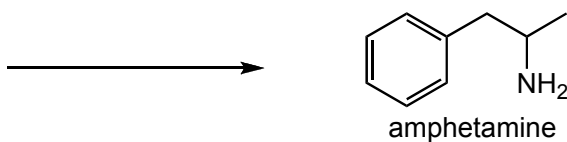


Question 8 (30 pts)

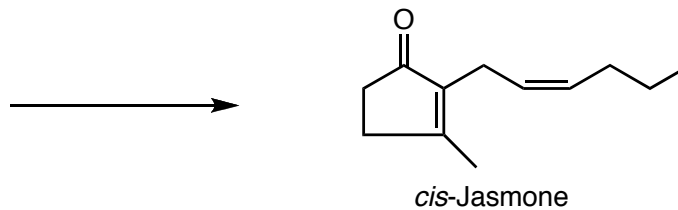
a) Give the reactants AND reagents/conditions that would allow you to synthesize malonic ester in a Claisen reaction



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

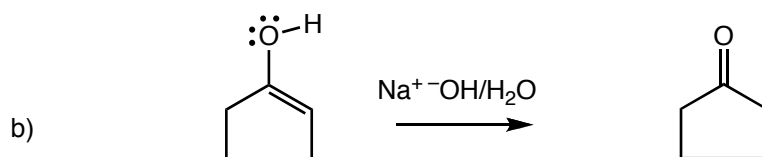
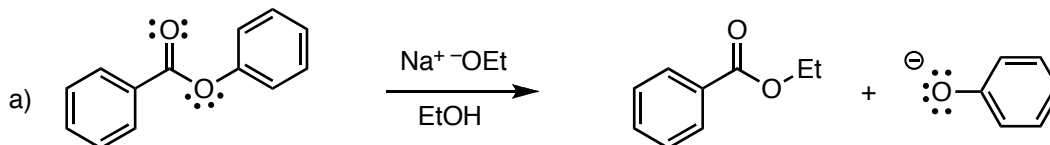
a) the transesterification, and

b) and the enol to ketone tautomerization reactions shown below

• **AS APPROPRIATE, SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no +H⁺/-H⁺)**

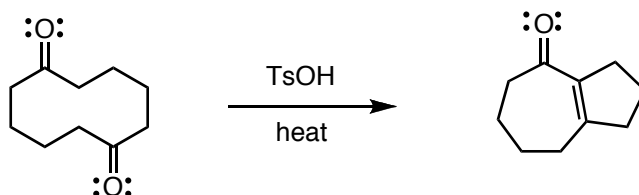
• **DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate**

• **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**



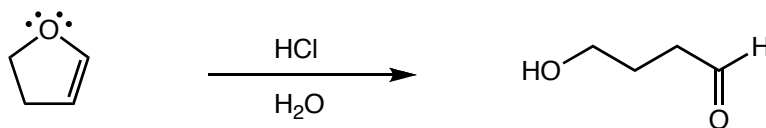
Question 10 (20 pts.) Give a curved arrow-pushing mechanism for the following reaction

- 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
- **BUT, draw all resonance structures for the intermediates**
- 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?

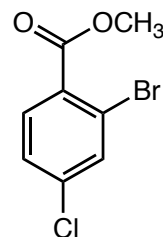
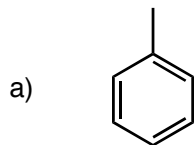
amine

ester

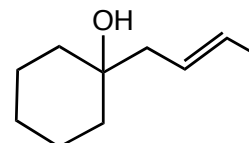
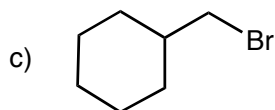
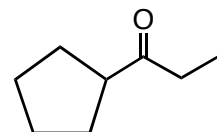
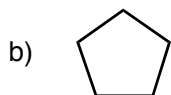
amide

aldehyde

Question 12 (50 pts.) Show how you would make the target compounds on the right 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**



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



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.

