

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	/20	9	/24
2	/20	10	/20
3	/27	11	/24
4	/10	12	/24
5	/38	13	/24
6	/64	14	/28
7	/8	15	/32
8	/12			
Extra Credit /5			Total (incl Extra) /375+5		

H Li Be Na Mg K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd Cs Ba Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn	He Ne Ar Kr Xe Rn	Interaction Energies, kcal/mol <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th colspan="2">Eclipsing</th> <th colspan="2">Gauche</th> </tr> </thead> <tbody> <tr> <td>H/H</td> <td>-1.0</td> <td>Me/Me</td> <td>-0.9</td> </tr> <tr> <td>H/Me</td> <td>-1.4</td> <td>Et/Me</td> <td>-0.95</td> </tr> <tr> <td>Me/Me</td> <td>-2.6</td> <td>i-Pr/Me</td> <td>-1.1</td> </tr> <tr> <td>Me/Et</td> <td>-2.9</td> <td>t-Bu/Me</td> <td>-2.7</td> </tr> </tbody> </table>	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
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↙ small range
┌───┐ range of values
 broad peak

-O-H -C≡N usually strong
>N-H >C=O

Infrared Correlation Chart

Approximate Coupling Constants, J (Hz), for ¹H NMR Spectra

amine R-NH₂ variable and condition dependent, ca. 2 - 6 δ

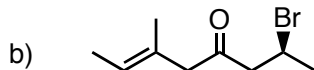
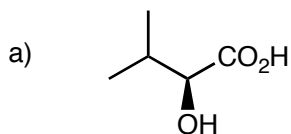
alcohol R-OH

NMR Correlation Charts

Alkyl 3^Y > 2^Y > 1^Y

Alkyl 3^Y > 2^Y > 1^Y

Question 1 (20 pts.) Provide IUPAC names for the following structures, do not forget to use E/Z and R/S as appropriate.

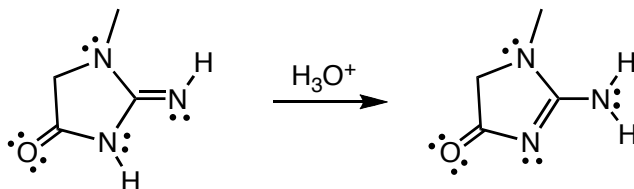


Question 2 (20 pts.) Serum creatinine levels are used to measure renal function. Creatinin exists in several tautomeric forms, two are shown below. Write a curved arrow-pushing mechanism that shows how the structure on the left is converted into the one on the right.

Show where all protons come from and go to (no $+H^+/-H^+$)

Show all resonance contributors to the intermediate structures

Label the Lewis acid/base and and Bronsted acids/bases as appropriate

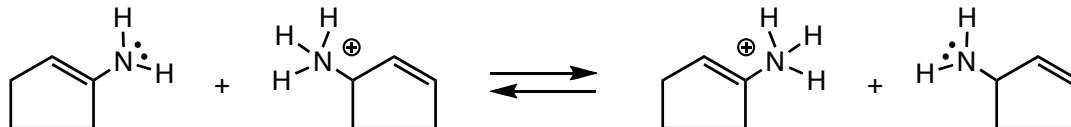


Question 3 (27 pts.) For the following acid/base equilibrium:

a) draw the curved arrows showing bond making/breaking

b) indicate which is the STRONGER and the WEAKER acid and base on each side

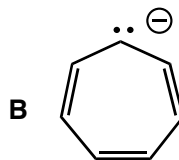
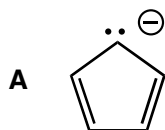
c) give a BRIEF explanation for your choice of stronger/weaker that includes the phrase "energy of the electrons"



d) Indicate which reaction (left to right or right to left) is faster and which is slower and indicate on which side the equilibrium lies

e) Draw a PROPERLY labelled reaction energy diagram, indicate the position of the transition state and include a drawing of the transition state

Question 4 (10 pts.) Indicate which of the following two structures **A** and **B** you would expect to be the stronger Bronsted **BASE**, and give a brief explanation **that includes the term "energy of the electrons"**. Assume that both structures are completely FLAT.



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

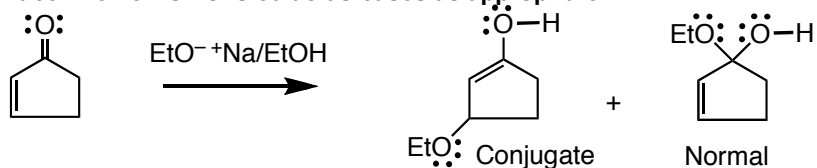
ester

amide

aldehyde

Question 5. (38 pts.) Give the mechanisms for formation of the "Normal" and the "Conjugate" addition products in the following reaction.

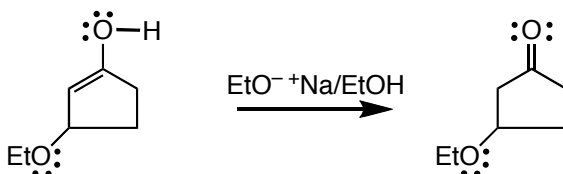
Show all resonance structures of the intermediates, show where all protons come from and go to (no $+H^+/-H^+$) and label the Lewis/Bonsted acids/bases as appropriate



b) Both products form with the same exothermicity, draw a reaction energy diagram for both reactions **ON THE SAME DIAGRAM**, label the activation energy for the rate determining step for each reaction

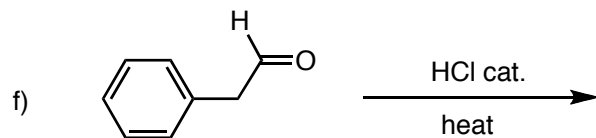
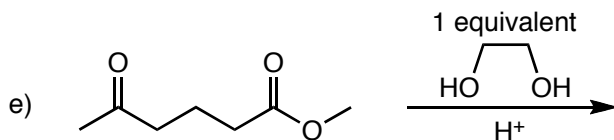
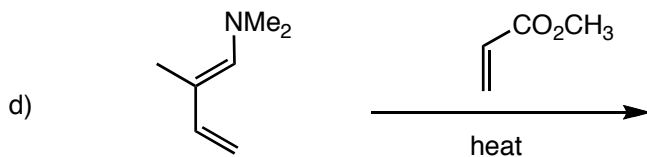
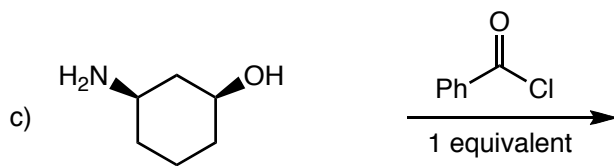
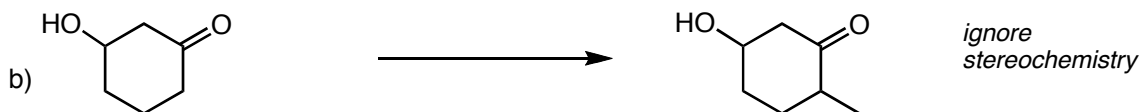
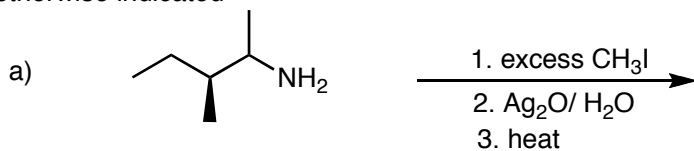
c) Under the reaction conditions, the conjugate product will tautomerize back into a ketone, give the curved arrow-pushing mechanism for this reaction

Show all resonance structures of the intermediates, show where all protons come from and go to (no $+H^+/-H^+$) and label the Lewis/Bonsted acids/bases as appropriate



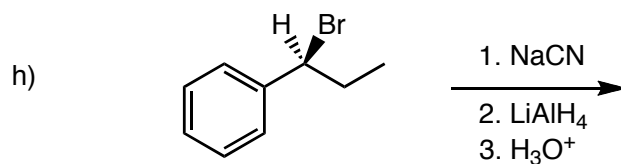
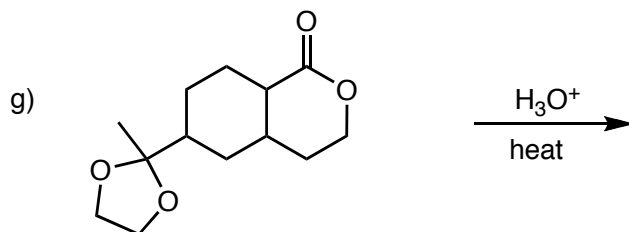
Question 6 (64 pts)

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

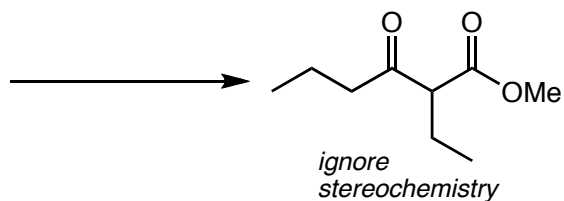


Question 6, Contd...

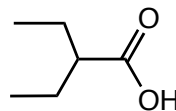
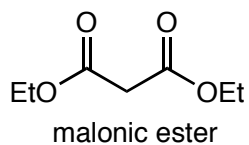
Provide the missing products, reagents/conditions or reactants, as required. **Do not forget to include stereochemistry as appropriate.**



Question 7 (8 pts) Give a reactants and reagents/conditions that will give the following structure in a Claisen reaction

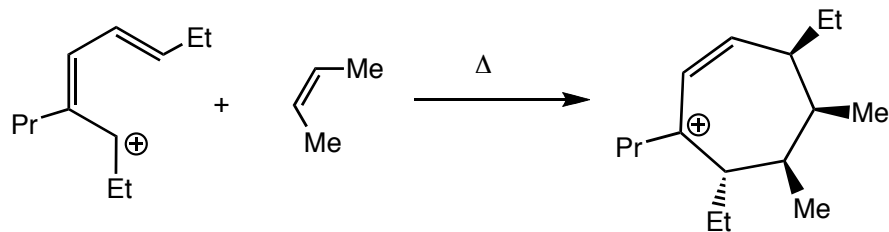


Question 8 (12 pts) Give a synthesis of the provided carboxylic acid from malonic ester. TREAT THIS AS A SYNTHESIS QUESTION. This is a FIVE STEP synthesis, give reagents/conditions and the intermediate molecules AT EACH STEP.



Question 9 (24 pts.) For the cycloaddition reaction below

a) Draw the curved arrow-pushing that describes the bond-making and breaking processes.



b) Draw the HOMO and LUMO of the reactants as requested, ON TOP of the structures that are redrawn below



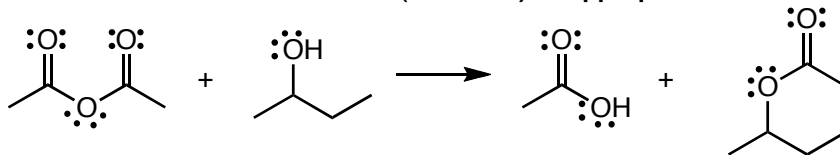
c) Is the cycloaddition reaction shown above allowed or forbidden. Give a BRIEF explanation that includes the words suprafacial and/or antarafacial as appropriate

Question 10 (20 pts) Give the mechanism for the following reaction

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

• DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate

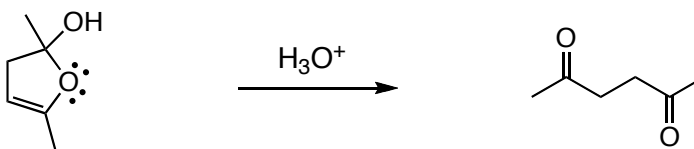
• At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate



Question 11 (24 pts.) Give a curved arrow-pushing mechanism for the following reaction **Show where all protons come from and go to (no $+H^+/-H^+$)**

Show all resonance contributors to the intermediate structures

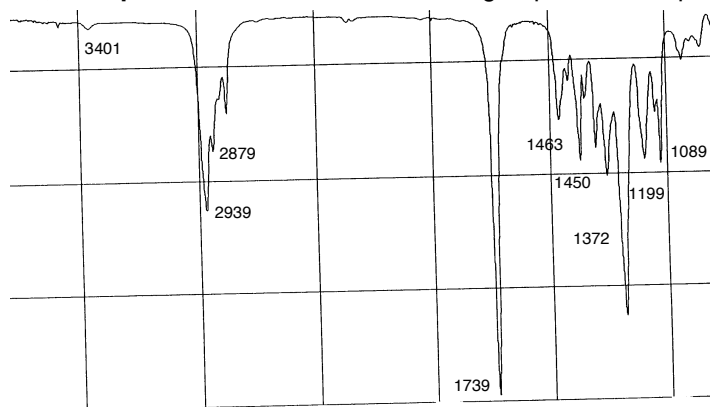
Label the Lewis acid/base and and Bronsted acids/bases as appropriate



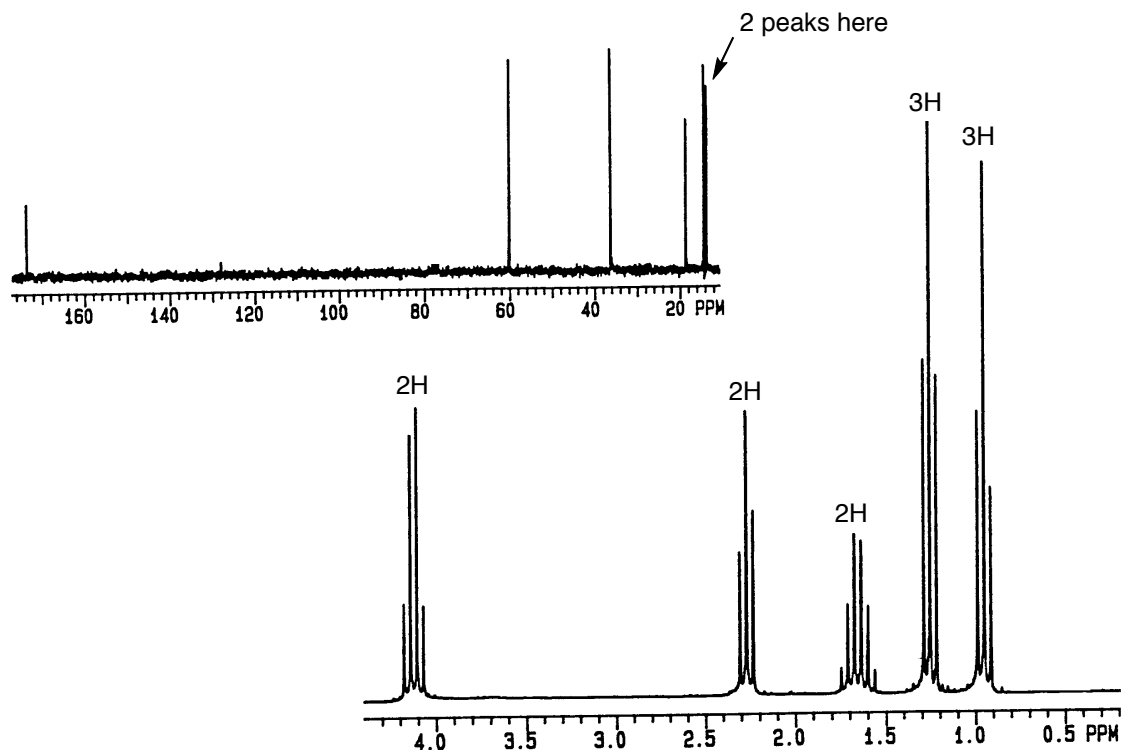
Question 12 (24 pts) Provided are spectra for a compound with molecular formula $C_6H_{12}O_2$

a) Give the degrees of unsaturation _____

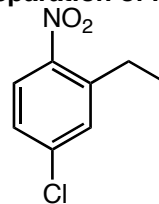
b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including $C(sp^3)-H$). Indicate **BOTH the functional group**, and where appropriate, **the specific BOND** in the functional group that corresponds to the peak.



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

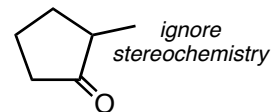
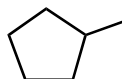


Question 13 (24 pts.) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**

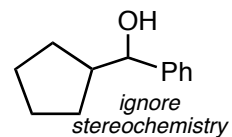
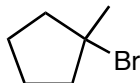


Question 14 (28 pts) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **These 2 questions use only reactions from the basic sets that were provided on the class website**

a)

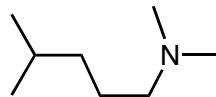


b)



Question 15 (32 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)

