CHEM 234, Spring 2008 | Third Midterm | 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!***

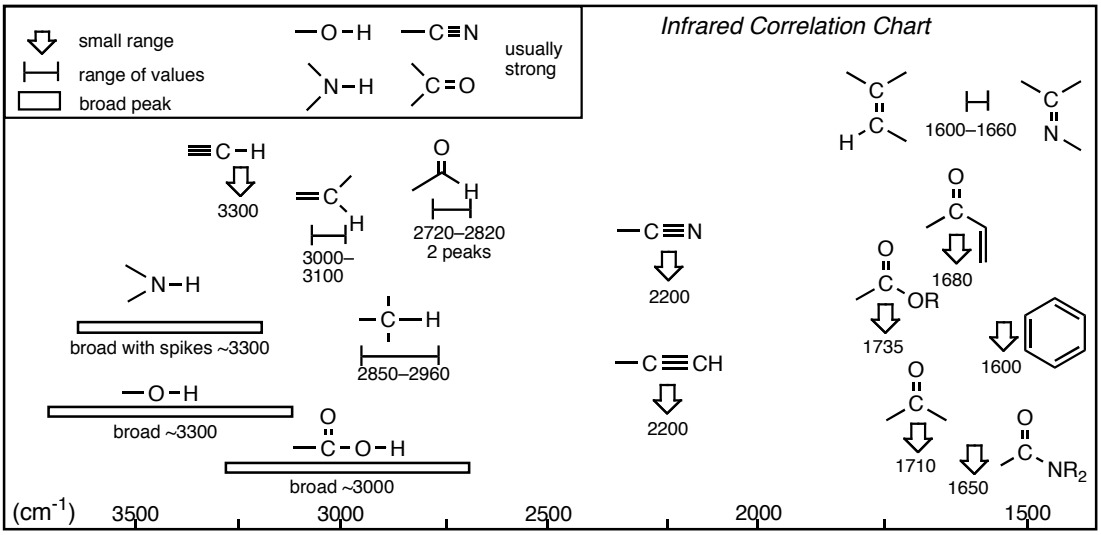
| | | | | | |
|---|---|---|---|---|---|
| 1 | nomen | /9 | 9 | Mxn | /20 |
| 2 | EAS | /15 | | | |
| 3 | Keq | /12 | | | |
| 4 | Stork | /14 | | | |
| 5 | Reactions | /32 | | | |
| 6 | Retro | /38 | | | |
| 7 | Benene R | /20 | | | |
| 8 | Claisen Mxn | /20 | | | |

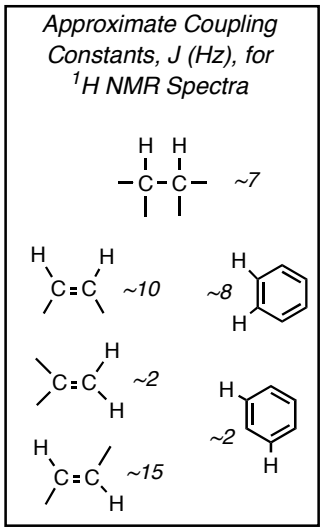
**Extra Credit** _____/5 **Total (incl Extra)** _____/180+5

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 |

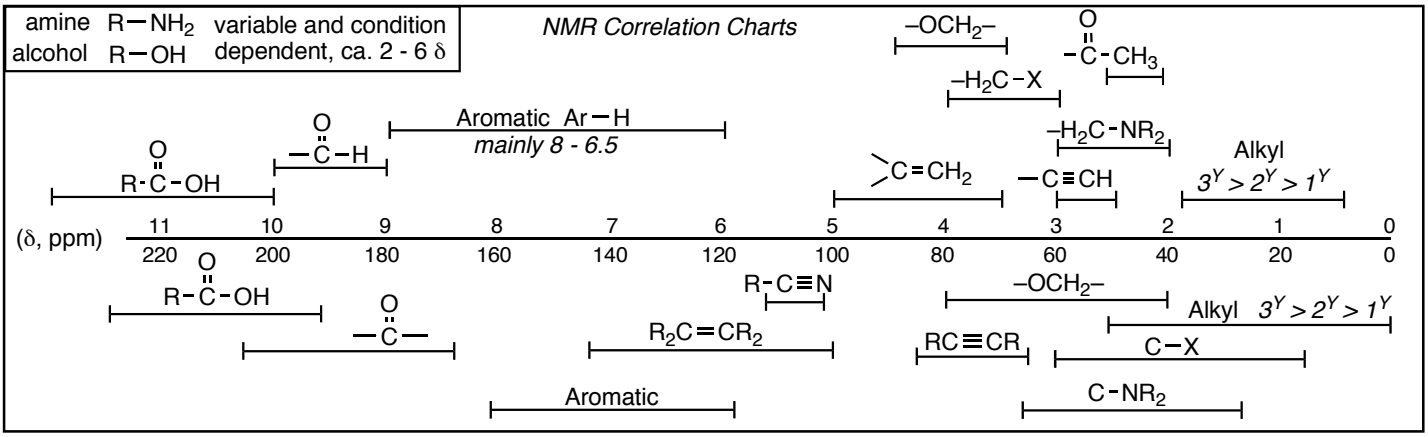
**Interaction Energies, kcal/mol**

| 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 |

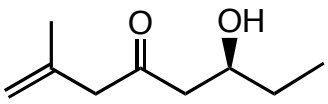



amine R–$NH_2$ variable and condition dependent, ca. 2 - 6 δ
alcohol R–OH

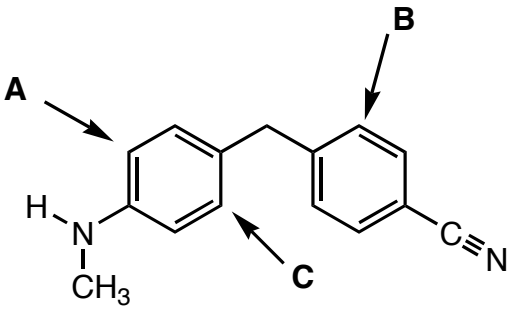


Question 1 (9 pts.) Give an unambiguous IUPAC or common name for the following compounds. Be sure to use cis/trans, E/Z or R/S where appropriate.




[6S]-hydroxy-2-methyloct-1-en-4-one

Question 2 (15 pts). Rank in order of increasing rate of electrophilic aromatic substitution at the carbons indicated by the arrows. Give a BRIEF explanation.



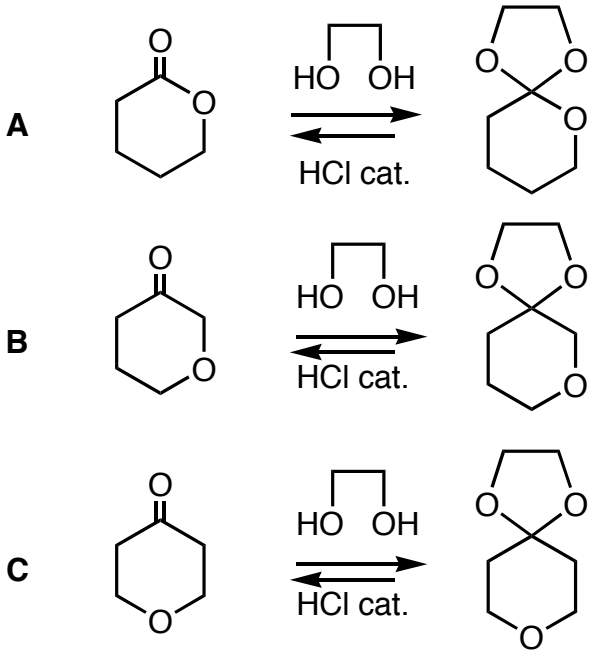

B < C < A

slowest fastest

Reaction at both A and C is faster than at B, because both are activated by strong (amine) and weak (aryl) donating groups on the ring. Reaction at A is activated more than at C because the donating group stabilizes the intermediate more at this position it is o- and p-directing). Reaction at B is deactivated by the by the strongly withdrawing nitrile group.

Question 3 (12 pts).

a) Rank the following reactions in order of increasing equilibrium constant for formation of product and give a BRIEF explanation

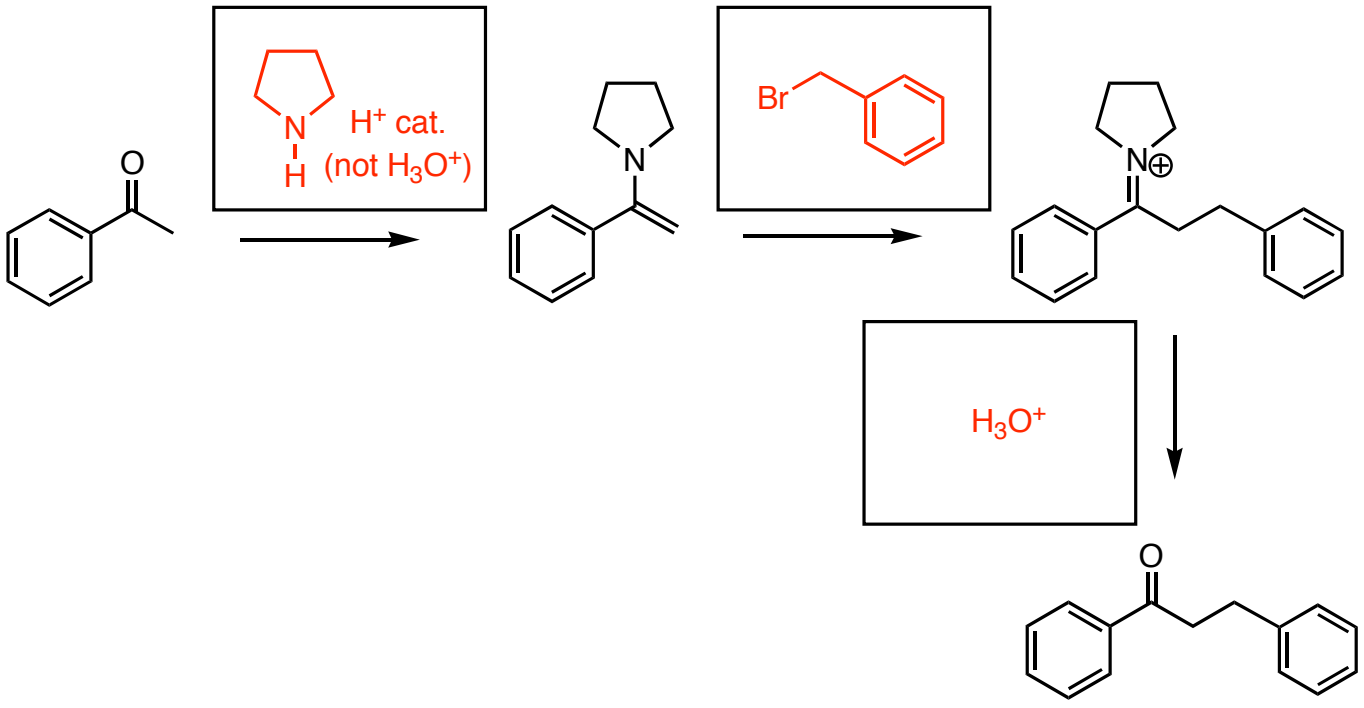



A < C < B

smallest largest

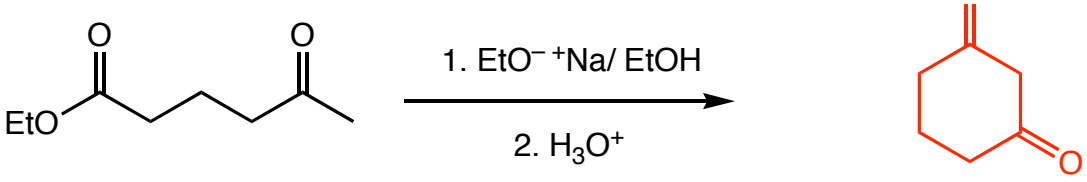
as far as the C=O is concerned, the O in A is strongly donating which decreases reactivity, the O in B is mildly withdrawing due to the inductive effect which increases reactivity, in C the O effect is negligible and the alkyl groups are weakly donating, intermdiate reactivity

Question 4 (14 pts) In the boxes, fill in the missing reagents/conditions in the following reaction sequence

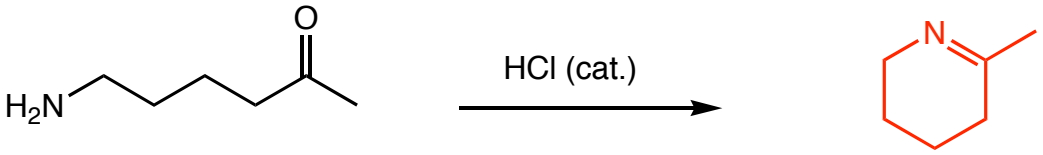


Question 5 (32 pts.) provide the reaction products or reagents/conditions as required

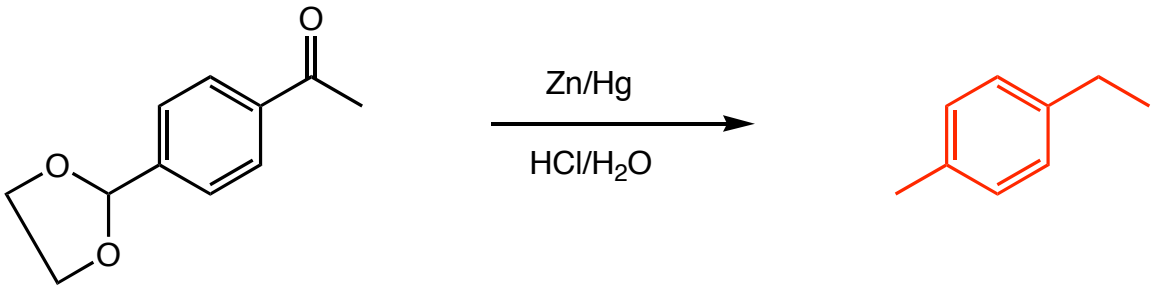
a)



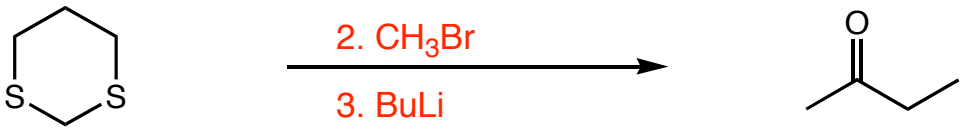

b)




c)

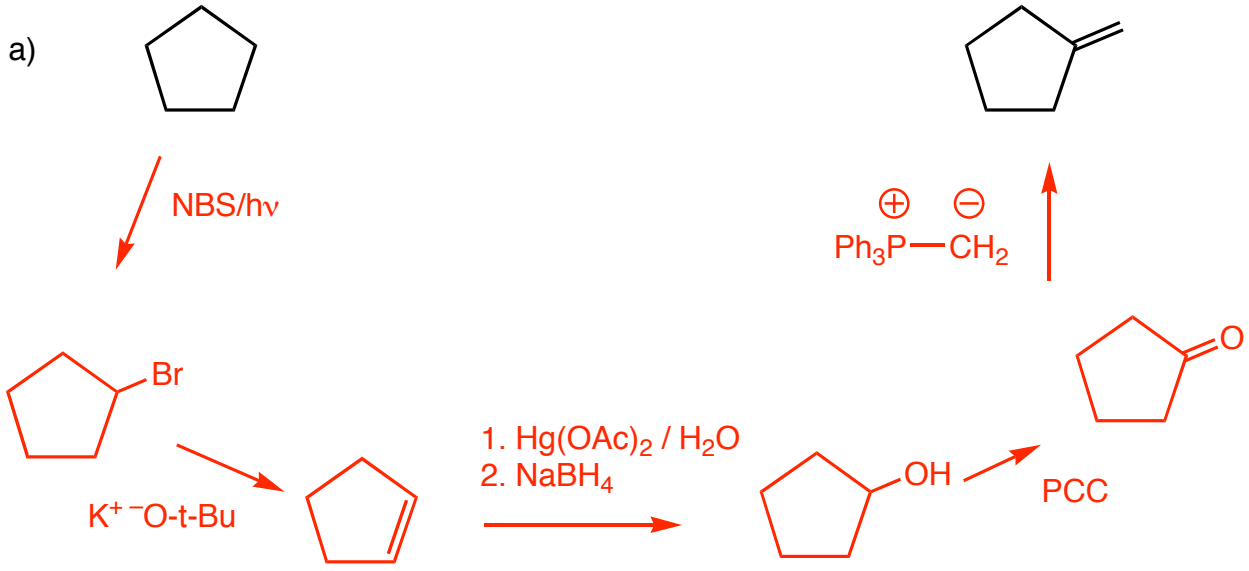



d)

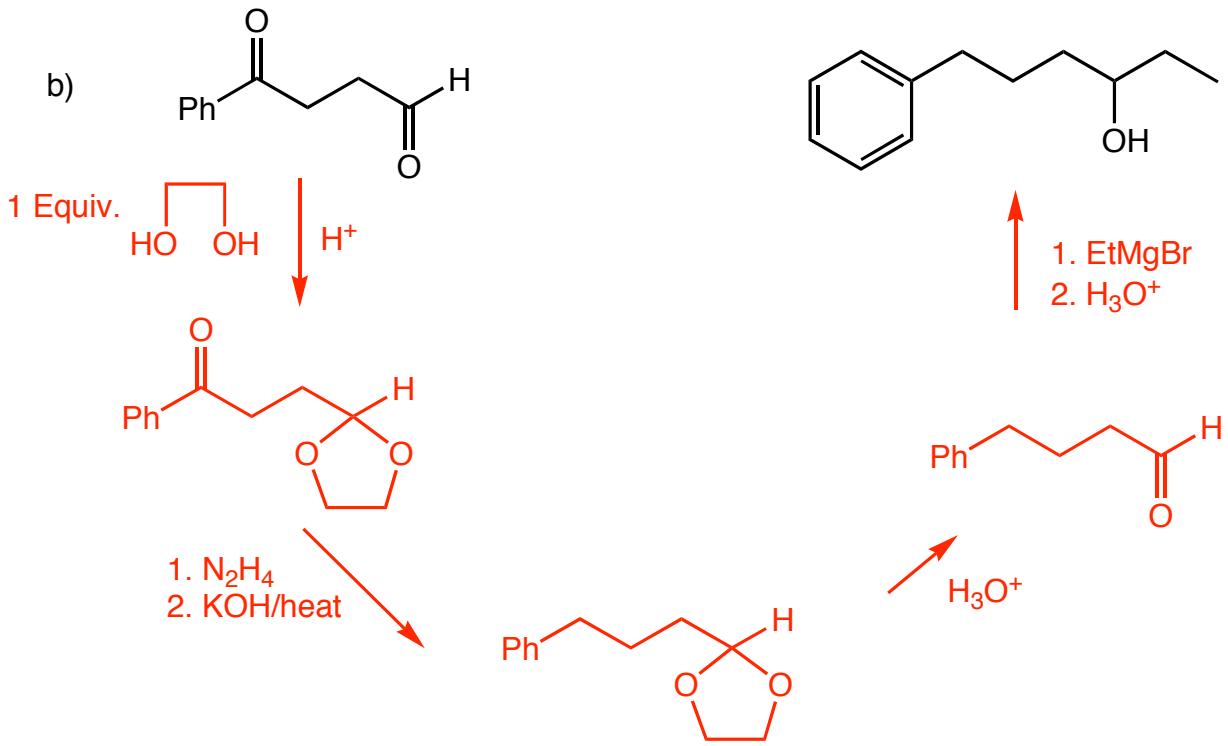


Question 6 (38 pts.) In each case, synthesize the (target) molecules on the right from the starting molecules the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.

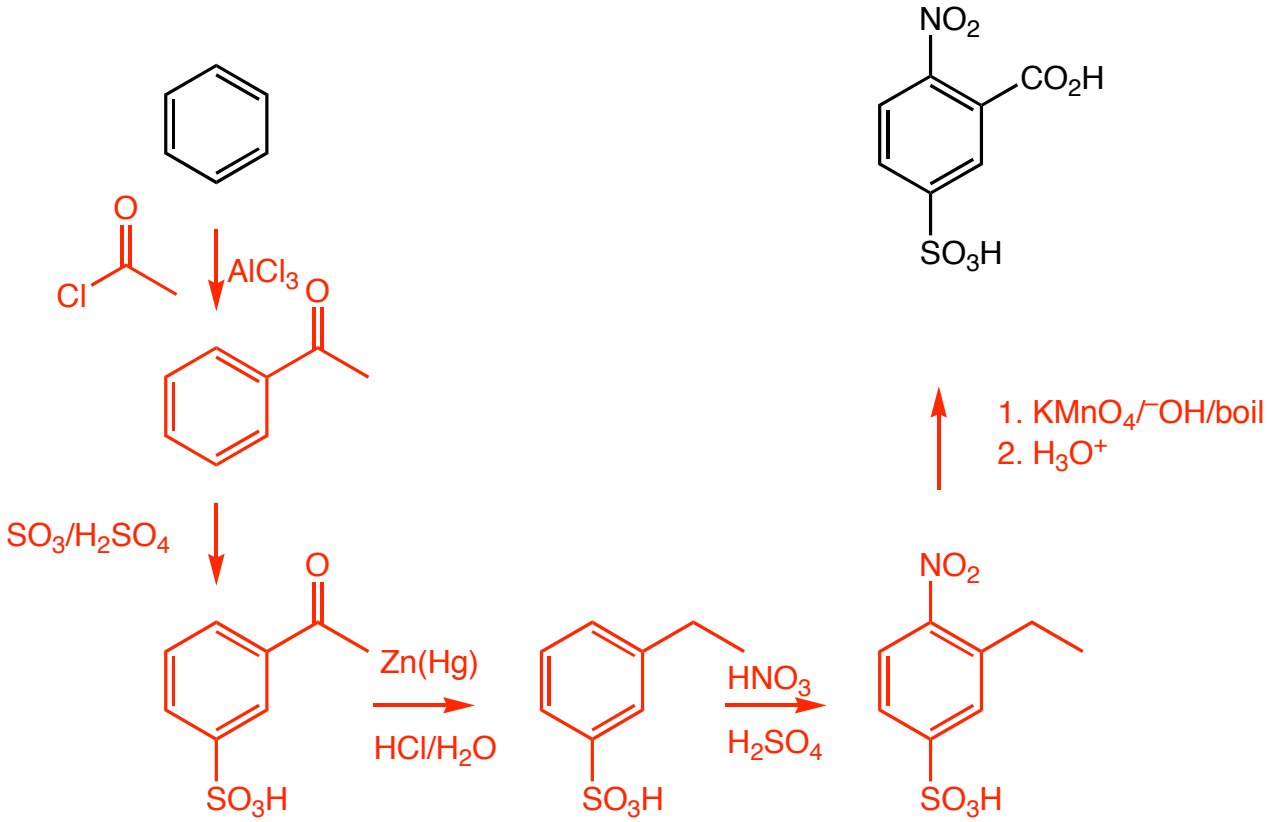
a)




b)



Question 7 (20 pts.) Synthesize the (target) molecule on the right from the starting molecule 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.




Extra credit question (5 pts). A photochemical 2 + 2 cycloaddition reaction occurs in

(DNA) Hemoglobin Vitamin C peroxidase

from weekly work #12

 NAME _____

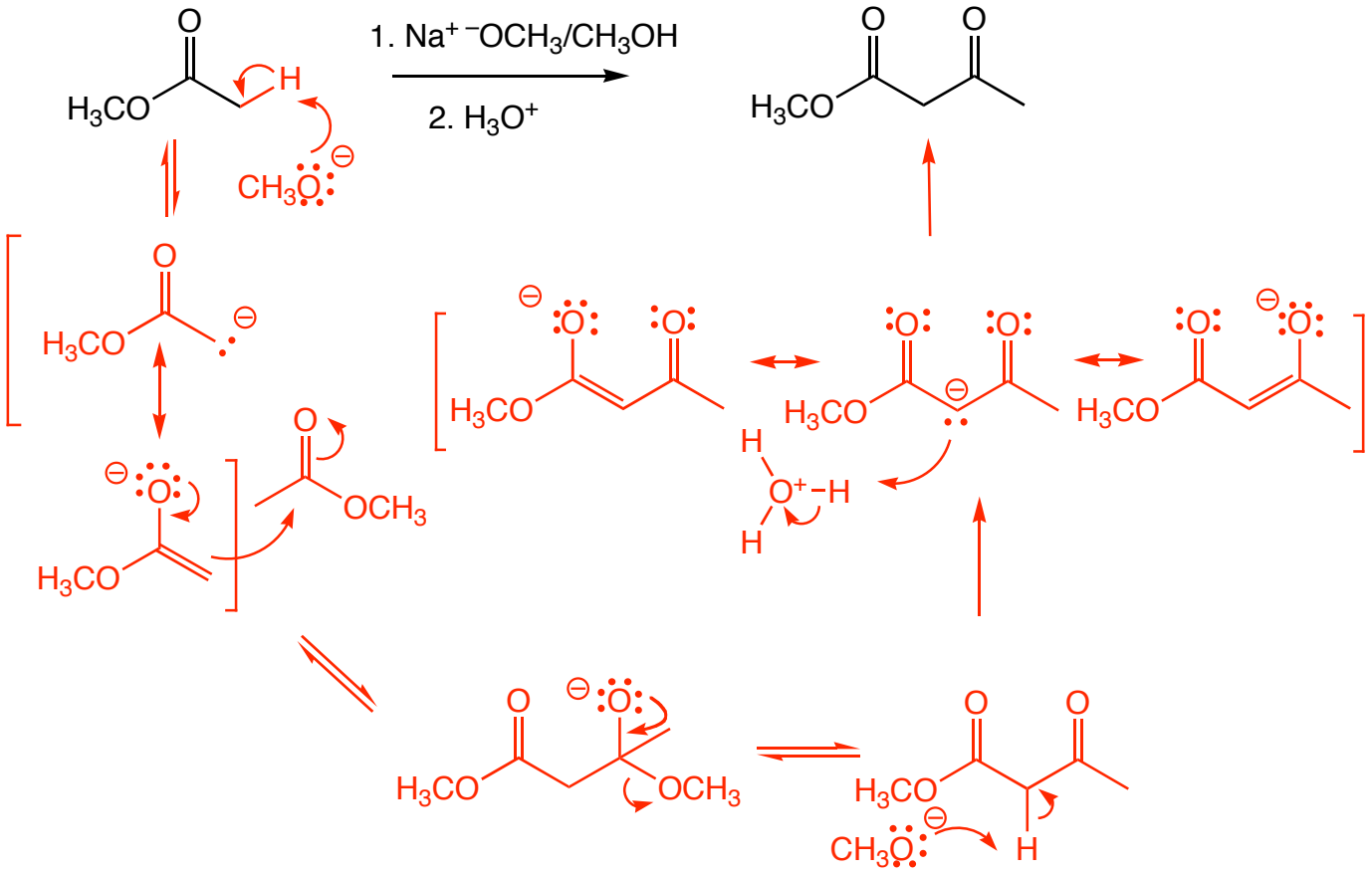
Question 8 (20 pts.) Give a complete arrow-pushing mechanism for the following TWO reactions.

***Show exactly where each proton comes from and goes to.***

***Add non-bonding electrons and hydrogen atoms as necessary***

***Indicate the lewis acid/base for each INTERmolecular step (LB or LA) and whether they are also Brønsted bases/acids (LB/BB or LA/BA)***

**SHOW ALL RESONANCE STRUCTURES OF THE INTERMEDIATES**



Question 9 (20 pts.) Give a complete arrow-pushing mechanism for the following reaction.

***Show exactly where each proton comes from and goes to.***

***Add non-bonding electrons and hydrogen atoms as necessary***

***Indicate the lewis acid/base for each INTERmolecular step (LB or LA) and whether they are also Brønsted bases/acids (LB/BB or LA/BA)***

**SHOW ALL RESONANCE CONTRIBUTORS OF THE INTERMEDIATES**