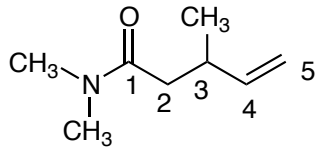
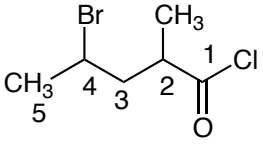
L.I.U.

Chem. 122, Final, Sections 007 + 008 250 pts, Spring, 2011

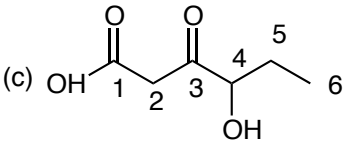
1. Name the following molecules. (15 pts)

(a) 

N,N-3-trimethyl-4-hexenamdie

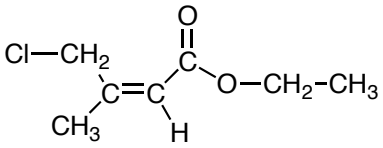
(b) 

4-bromo-2-methyl-pentaoyl chloride

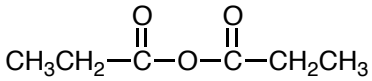
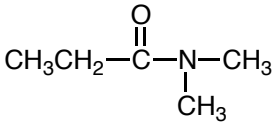
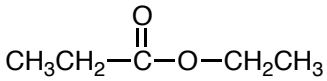
(c) 

4-hydroxy-3-oxo-hexanoic acid

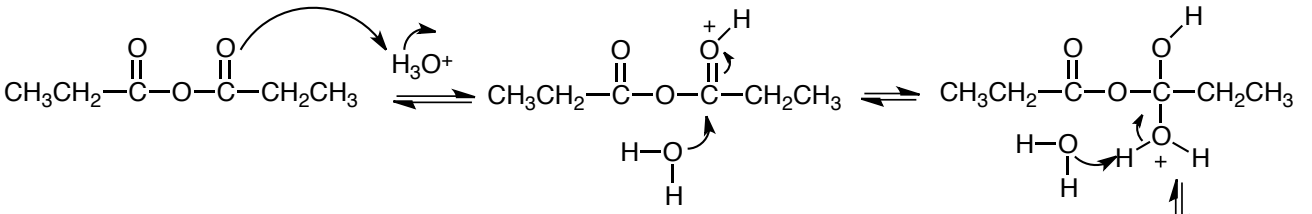
2. Find the structure of the following molecule. Formula: $C_7H_{11}O_2Cl$. IR: 1743 and 795 cm^{-1}. ^1H NMR: δ 0.9, triplet, 3H; 2.3, singlet, 3H; 3.6, singlet, 2H; 3.8, quartet, 2H; 5.4, singlet, 1H. ^{13}C: 23, 32, 48, 55, 112, 125, 173. (15 pts)

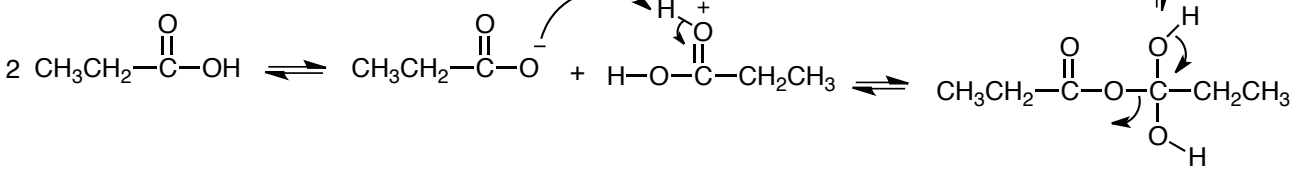


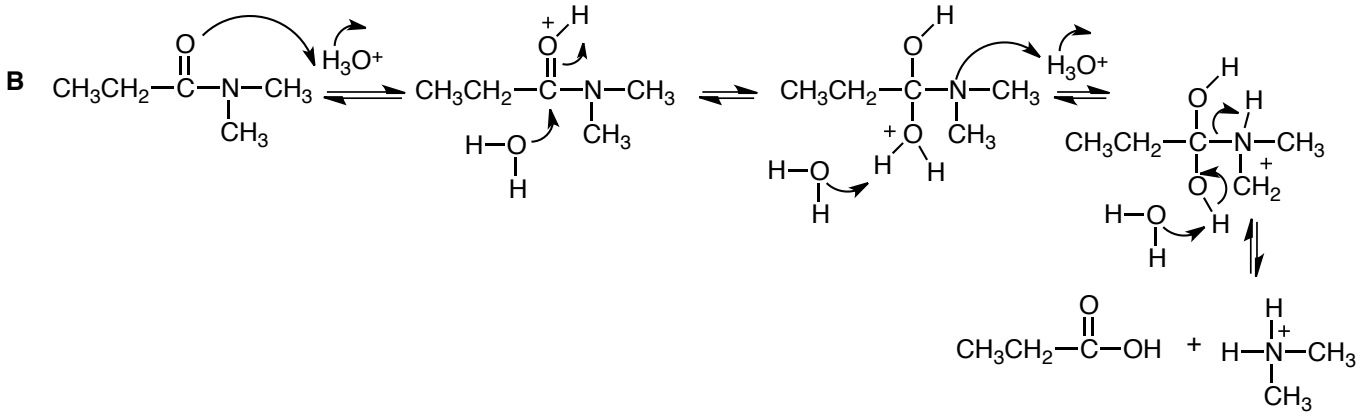
3. Which molecule would be (a) the most reactive (b) the least reactive to hydrolysis in <u>acidic conditions</u> (H_3O^+, H_2O)? Briefly explain your reasoning and show the reaction that occurs for each of the molecules you choose. (10 pts)

A  **B**  **C** 

(a) Molecule **A** is the most reactive toward hydrolysis in acidic (or basic) conditions since the carbonyl carbon is most electron deficient and therefore the most susceptible to nucleophilic attack. The oxygen is an overall electron donating group but in the anhydride **A** the lone pair has two electron withdrawing carbonyl groups to which to donate and so the oxygen donates lees than in the ester **C**. (b) Molecule **B** would be the least reactive because the amide nitrogen is less electronegative than the oxygen of the ester **C** (or the anhydride **A**) and so it has a smaller inductive effect and the C-N bond is shorter than the C-O bond, so the nitrogen lone pair is much better at donating to the carbonyl carbon of the amide, making the carbonyl carbon less electron deficient and less susceptible to nucleophilic attack.

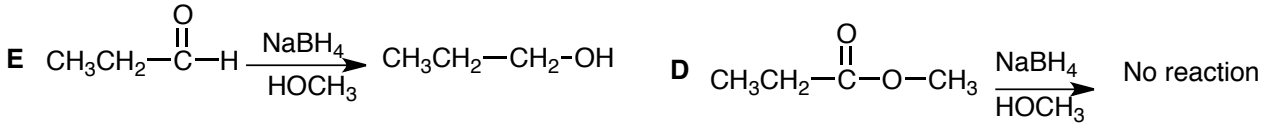
A 



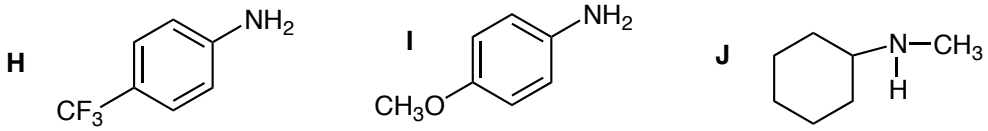


4. Which molecule would be (a) most easily reduced (b) least easily reduced by sodium borohydride? Briefly explain your answer in and in each case show the reaction that occurs. (10 pts)

(a) Molecule **E** would be most easily reduced by sodium borohydride, because the carbonyl carbon of the aldehyde is more electron deficient and therefore more susceptible to attack by the nucleophilic hydride reagent. (b) The least easily reduced molecule is **D** since it has the most electron rich carbonyl due to electron donation by the oxygen. In fact, esters are not reduced by sodium borohydride.

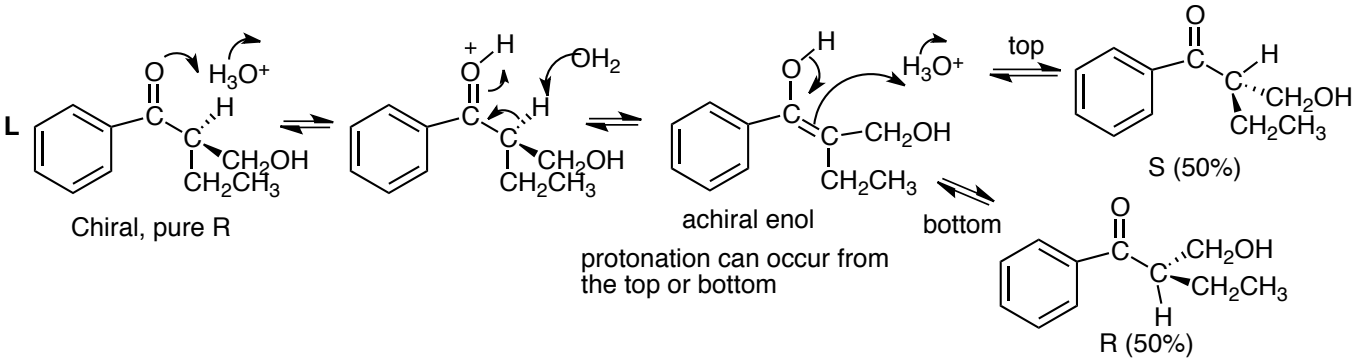


5. Which molecule is (a) the strongest base (b) the weakest base. Briefly explain your choices. (10 pts)

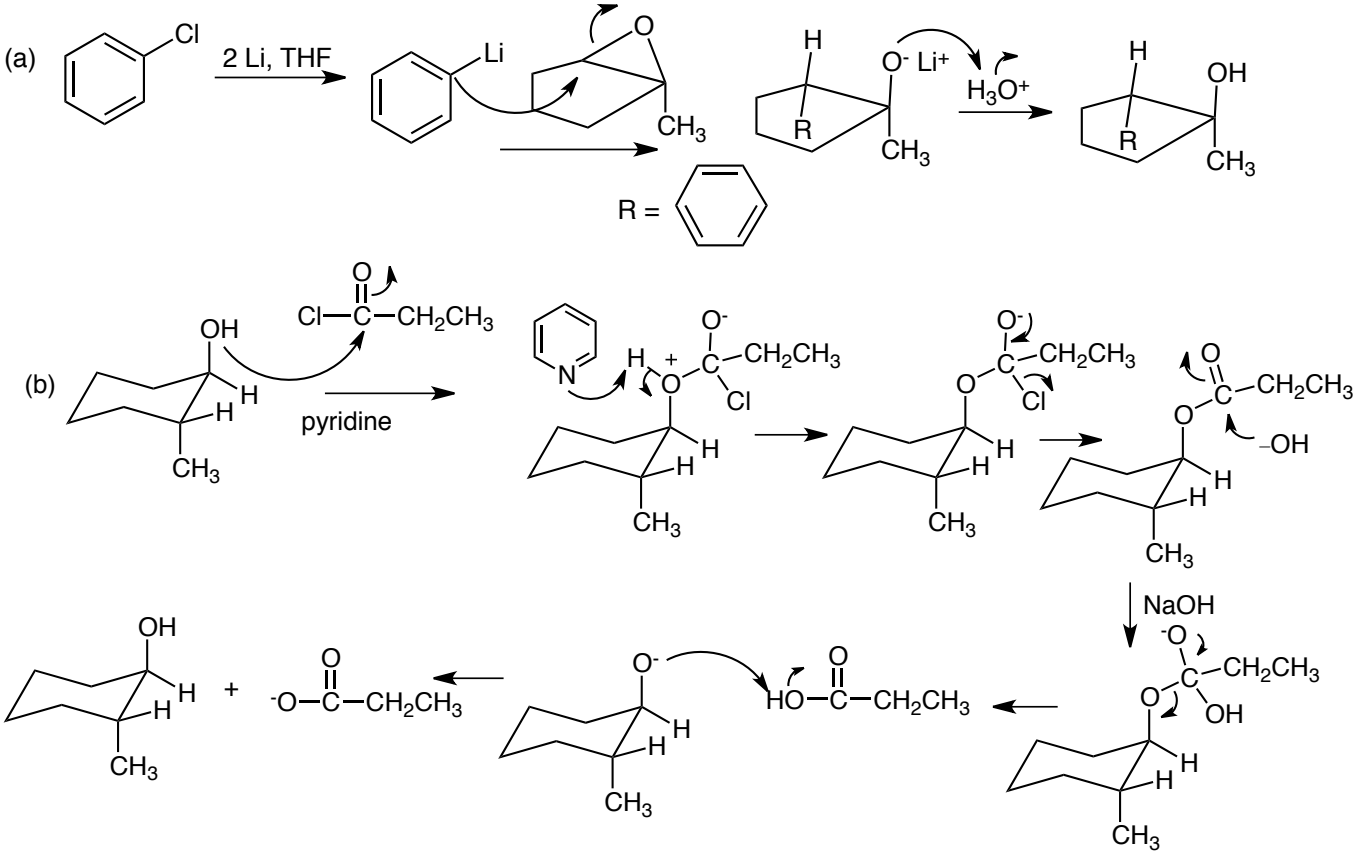


(a) The strongest base is **J** due to the electron donating ability of the two alkyl groups. The benzene ring in both **I** and **H** weaken the basicity since the nitrogen lone pair is partially delocalized onto the benzene ring. (b) **H** is weaker than **I** due to the electron withdrawing CF_3 group.

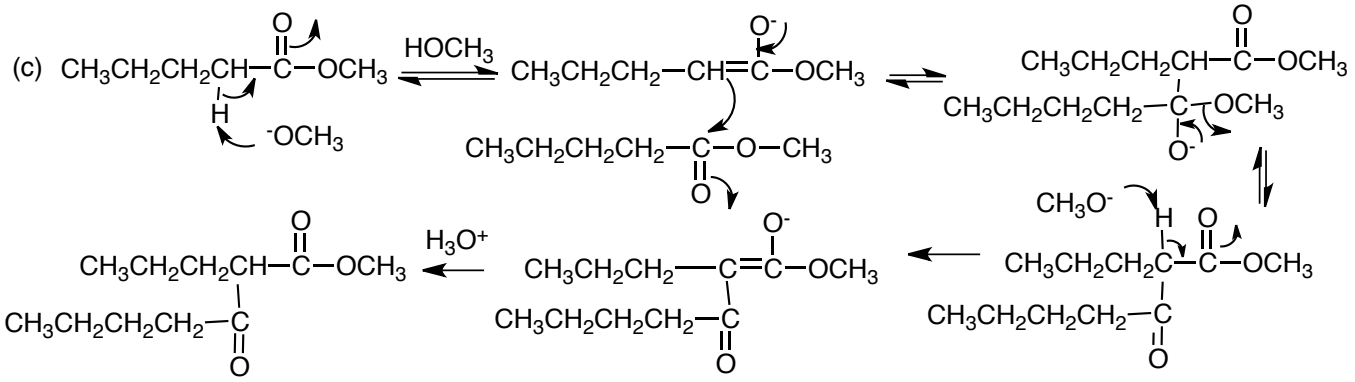
6. One of the following molecules will undergo racemization when treated with aqueous acid (H_3O^+, H_2O). Which one? Briefly explain your choice and show how the racemization occurs. (10 pts)
Only **L** will undergo racemization since it has the requisite hydrogen next to the carbonyl group.



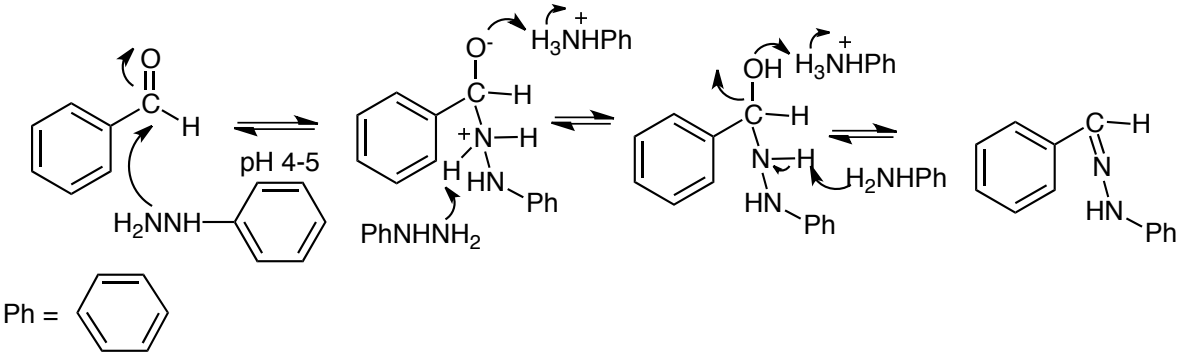
7. For the following reactions give the product and **SHOW THE COMPLETE REACTION MECHANISM**, showing all the steps. (15 pts each, 120 pts)



(c)

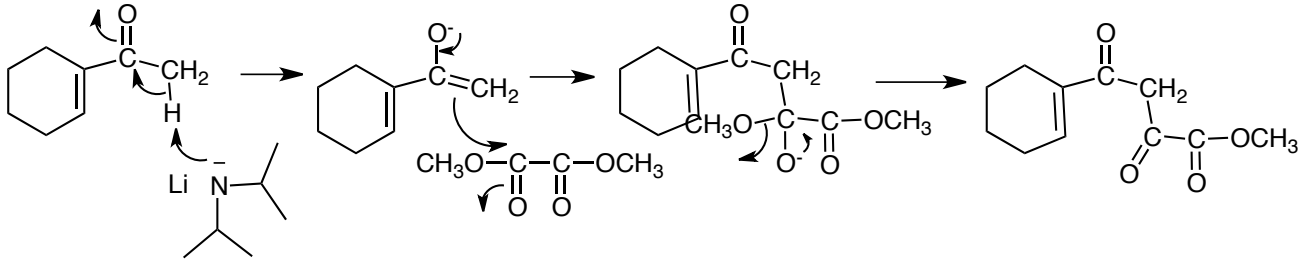


(d)

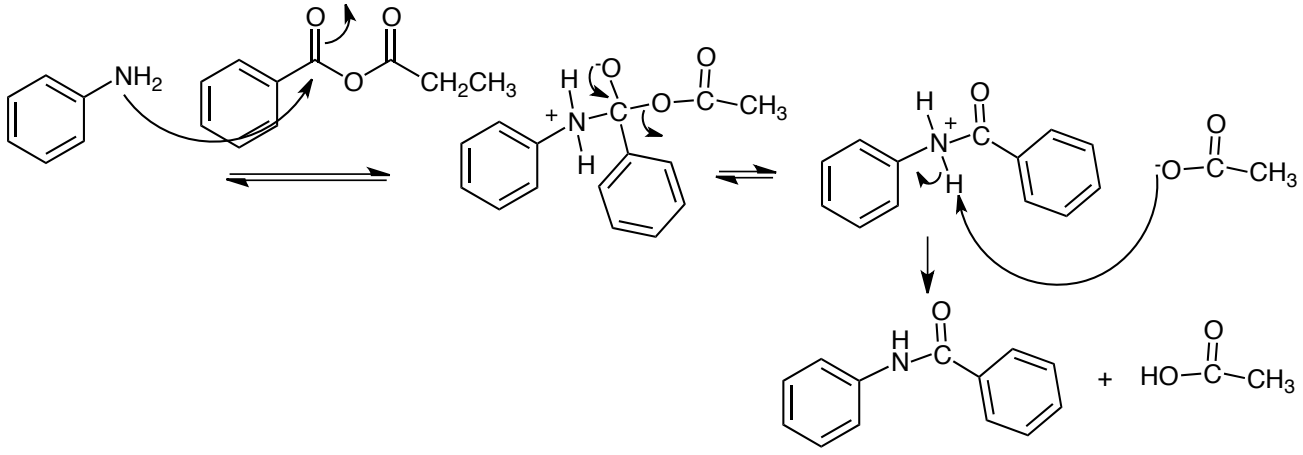


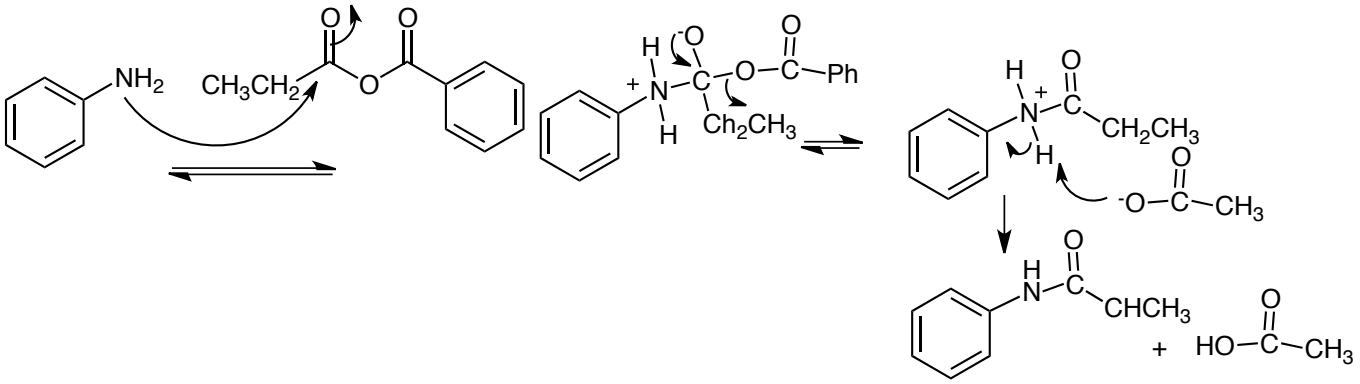
Ph =

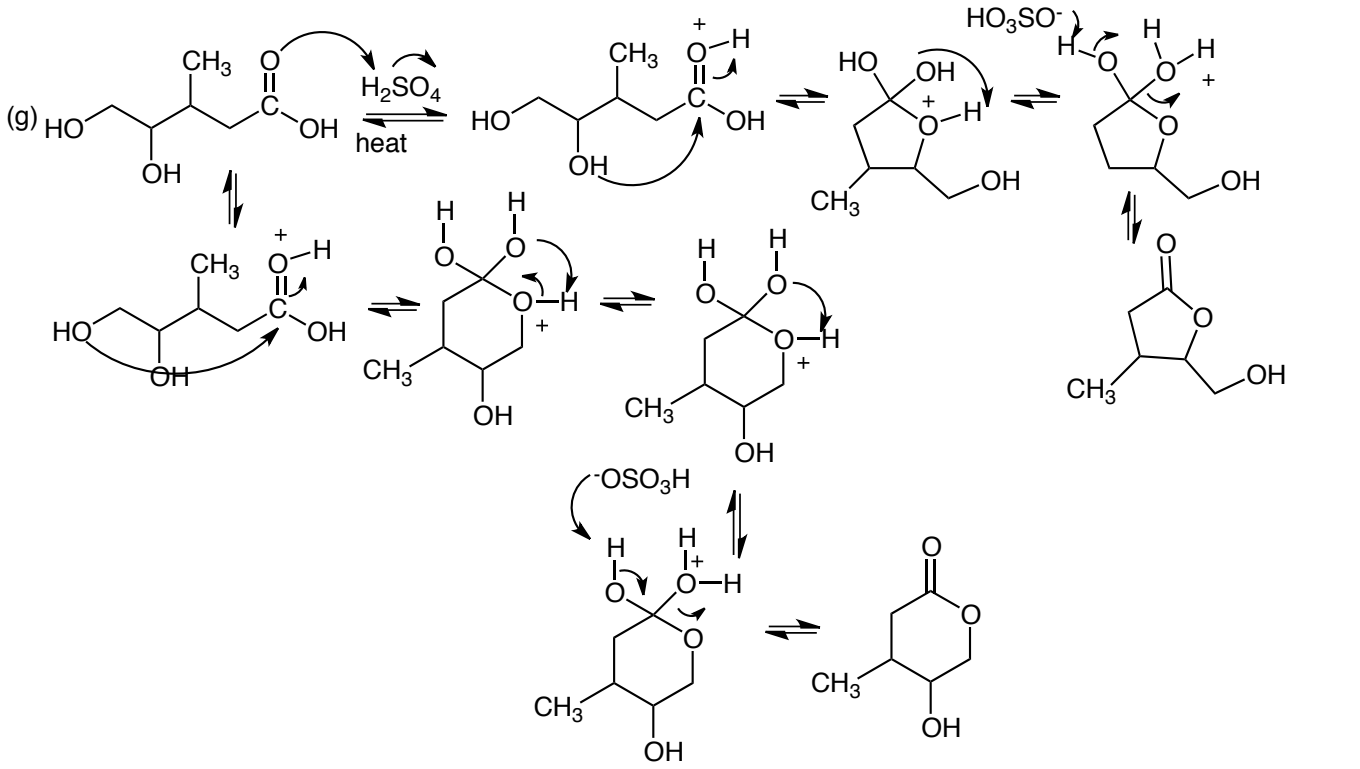
(e)

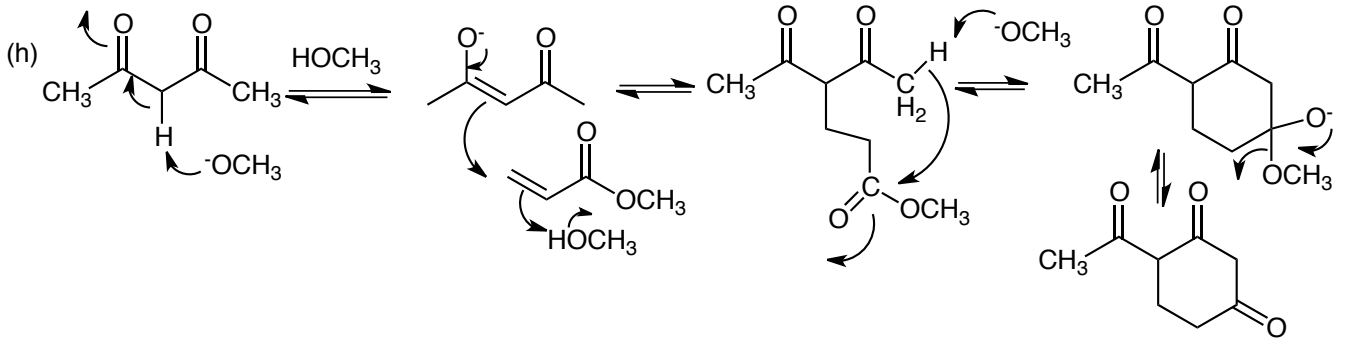


(f)



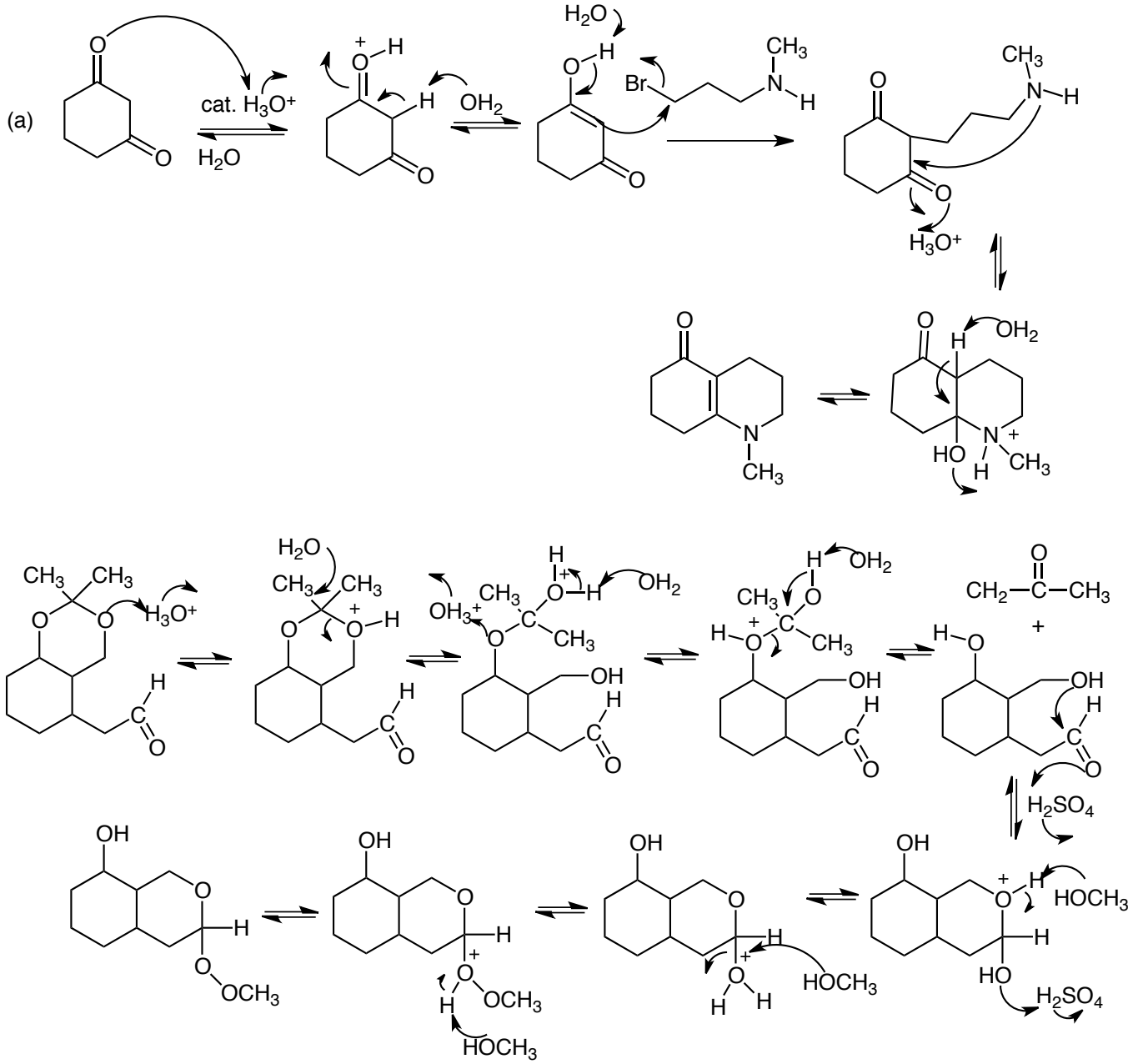



(g)
H_2SO_4
heat
HO_3SO^-
$^-OSO_3H$

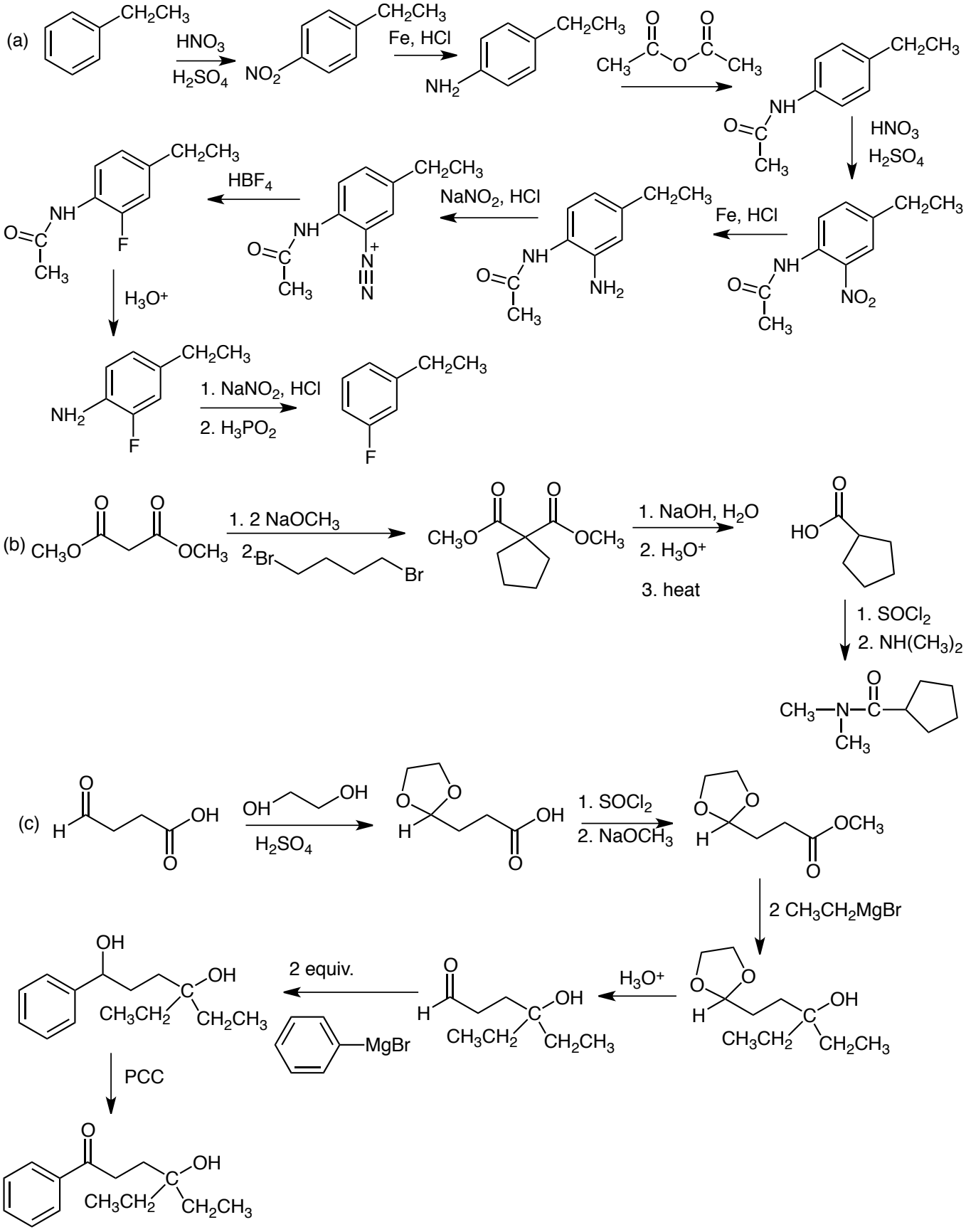

(h)
$HOCH_3$
$^-OCH_3$

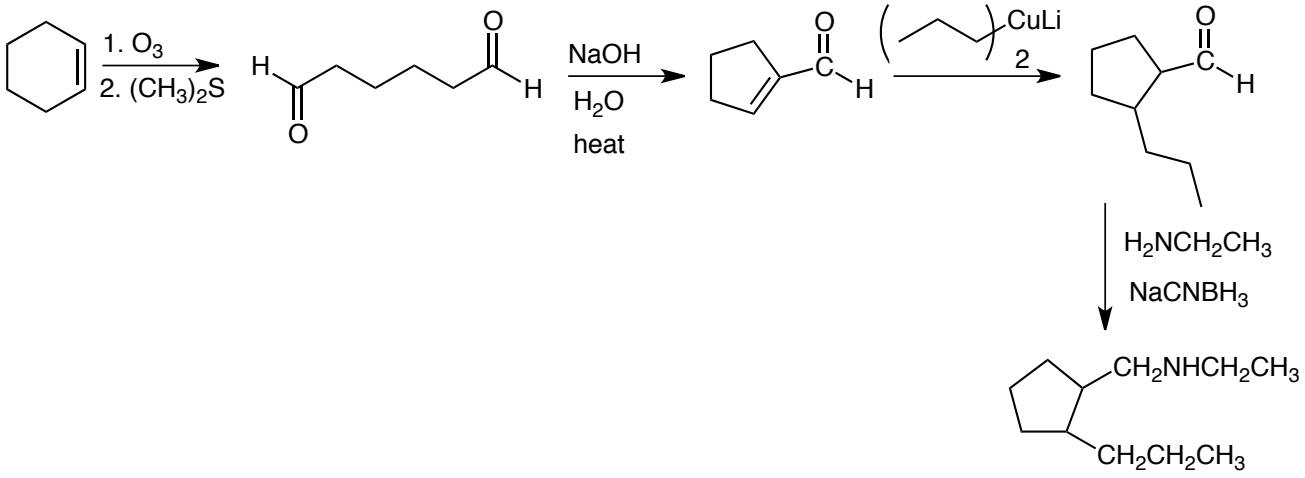
8. Show how the following transformations occur, showing all the steps of the reaction. No other reagents are needed except those given. (15 pts each, 30 pts)

(a)



9. Synthesize **three** of the following **four** molecules from the starting materials given on the left. Do all **four** for extra credit. (10 pts each)


(a)
HNO3
H2SO4
Fe, HCl
HNO3
H2SO4
Fe, HCl
NaNO2, HCl
HBF4
H3O+
1. NaNO2, HCl
2. H3PO2
(b)
1. 2 NaOCH3
2
1. NaOH, H2O
2. H3O+
3. heat
1. SOCl2
2. NH(CH3)2
(c)
H2SO4
1. SOCl2
2. NaOCH3
2 CH3CH2MgBr
H3O+
2 equiv.
MgBr
PCC

(d) 
1. O_3
2. $(CH_3)_2S$
NaOH
H_2O
heat
CuLi
2
$H_2NCH_2CH_3$
$NaCNBH_3$
$CH_2NHCH_2CH_3$
$CH_2CH_2CH_3$