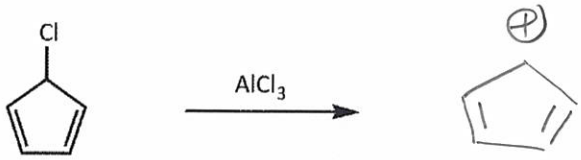
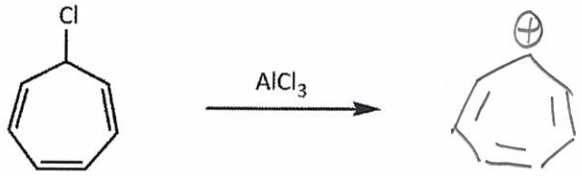
Key

1. One of the reactions below work to produce a carbocation, the other one doesn't. Show the carbocation that is expected to form and write N.R. in the one that doesn't. In terms of the stability of the resulting ion (or lack thereof), explain your answer. (10 points)

a. 

not formed since anti-aromatic ion

$4e^-$ (4π)

b. 

formed easily since it's an aromatic ion

$6e^-$ (4n+2)

2. Unlike benzene, 1,3,5,7-cyclooctatetraene has two different carbon-carbon bond lengths, 1.33 Å and 1.46 Å and it is definitely not planar. Clearly explain why (draw pictures if necessary). (6 points)

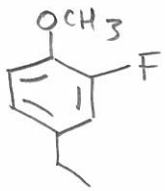
If this molecule were to lie flat it would have the property of being anti-aromatic. To alleviate the high energy of this, the molecule adopts a "tub" shape which reduces overlap of the adjacent π bonds!

} alternating single and double bonds
(1.46Å) (1.33Å)

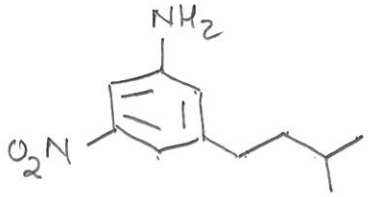
3. What are the *requirements* (conditions) for a compound to be "aromatic?" (8 points)

4. Draw the structure of the following compounds. (10 points)

a. 4-ethyl-2-fluoroanisole



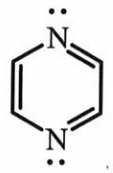
b. 3-(3-methylbutyl)-5-nitroaniline



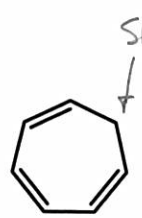
5. For each of the following molecules or ions indicate whether they are *aromatic*, *anti-aromatic* or *non-aromatic*. (16 points)

a. 

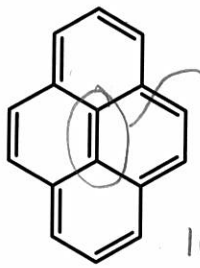
aromatic

b. 

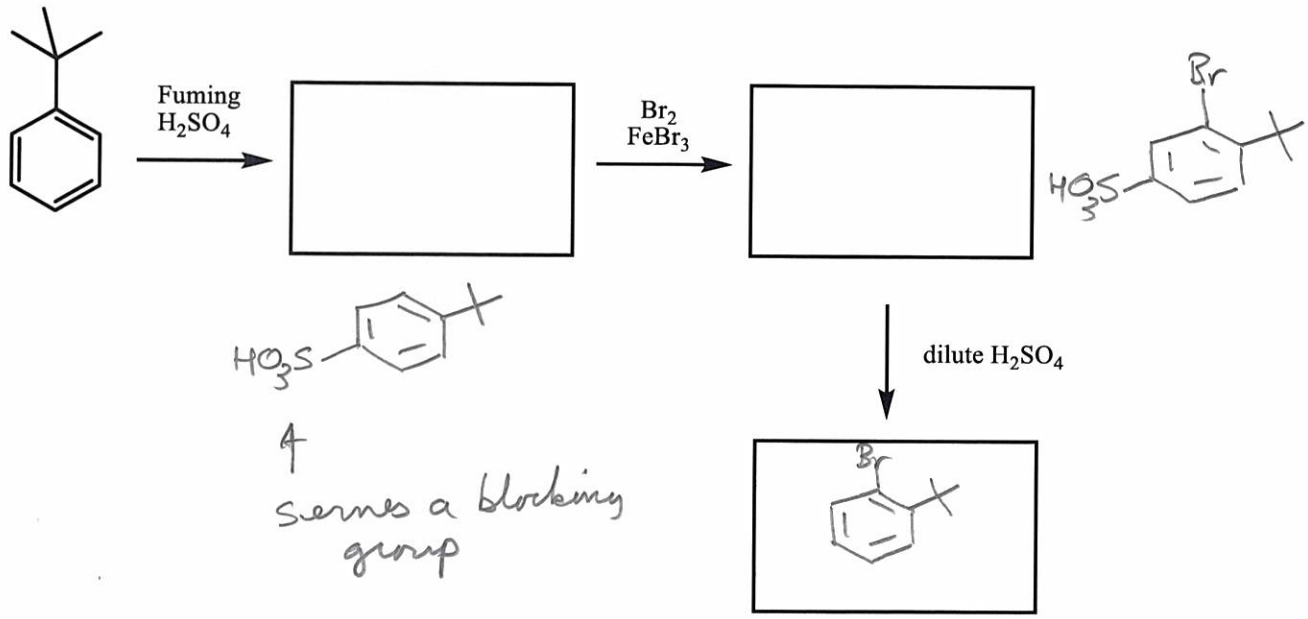
aromatic

c. 

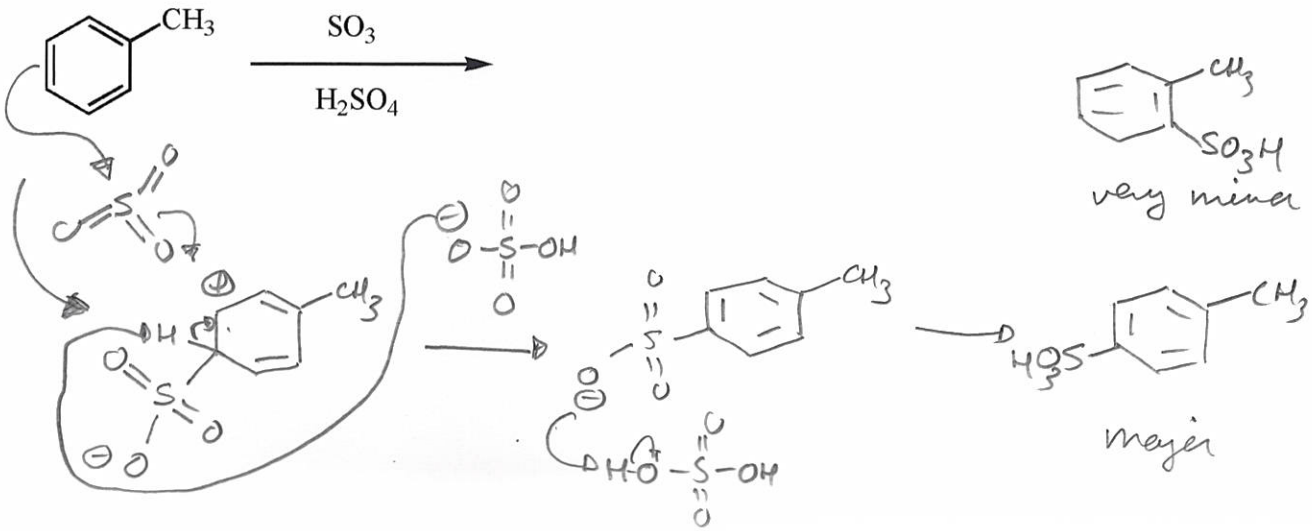
non-aromatic

d. 

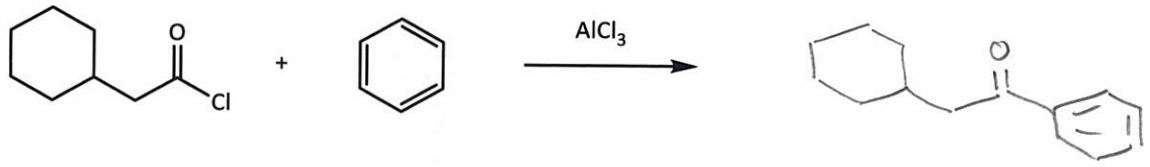
6. In the following synthesis, fill in the products or reagents. (15 points)



7. Show the product(s) and the complete *mechanism* (with electron-pushing) for the following reaction. (if more than one isomer is formed show the mechanism for only one of them, but be sure show all expected products) (20 points)

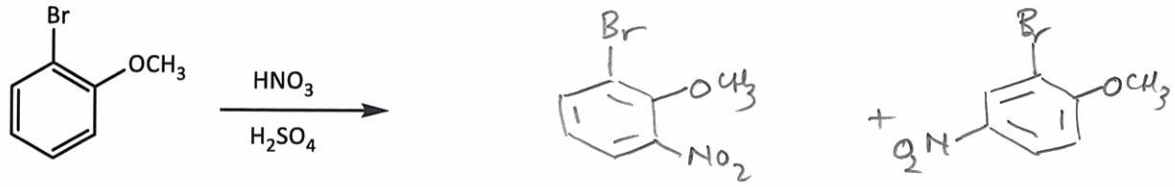


8. Show the product(s) from the following reaction. (5 points)

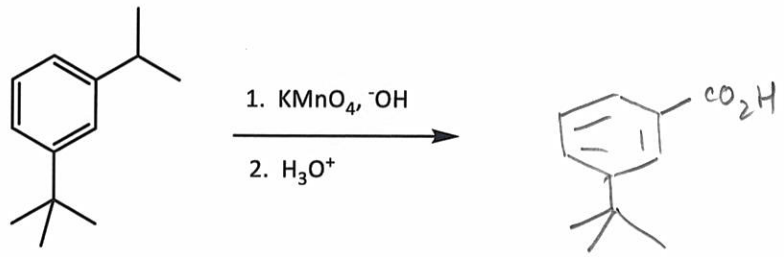


9. Show the expected product (or products) from the following reactions. (10 points)

a.



b.



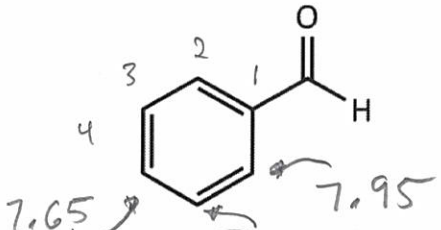
So deactivate

10. Use the NMR data sheets (from lecture) to calculate the proton and carbon chemical shifts for benzaldehyde. Explain how the chemical shift data indicate whether the aromatic substituent is an *activating* or *deactivating group* and whether it is an *ortho/para director* or a *meta director* in an Electrophilic Aromatic Substitution reaction (S_EAr). (Note: the entry in the ^1H NMR chart, Chart D.1, shows and aldehyde as CH(=O)) (15 points)

all chemical shifts are deshielded relative to benzene

C-1 = 128.5 + 8.2 = 136.7
C-2 = 128.5 + 1.2 = 129.5
C-3 = 128.5 + 0.6 = 129.1
C-4 = 128.5 + 5.8 = 134.0

most e⁻ rich carbon (not by much)

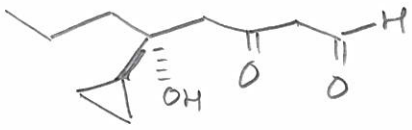


most electron rich since it's most shielded - surround by electrons

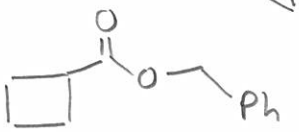
The most electron-rich region undergoes electrophilic aromatic substitution fastest, so the aldehyde group is a meta-director

11. Draw the structure of the following compounds (don't forget stereochemistry). (30 points)

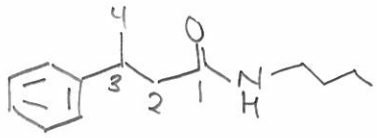
a. (*R*)-5-cyclopropyl-5-hydroxy-3-oxooctanal



b. benzyl cyclobutanecarboxylate

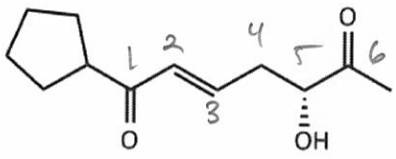


c. *N*-pentyl-3-phenylbutanamide



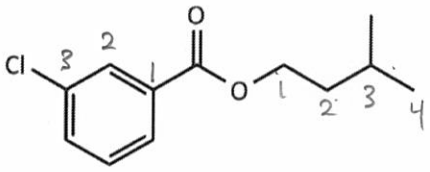
12. Provide IUPAC names for the following compounds (don't forget stereochemistry where appropriate). (30 points)

a.



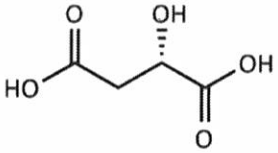
(2E, 5R)-1-cyclopentyl-5-hydroxy hept-2-ene-1,6-dione

b.



3-methyl butyl 3-chlorobenzoate

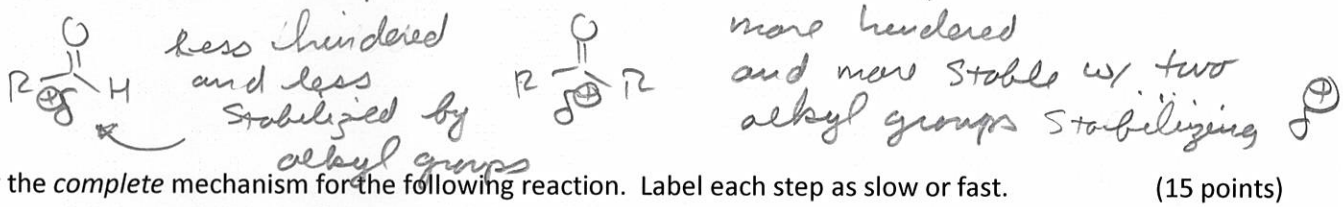
c.



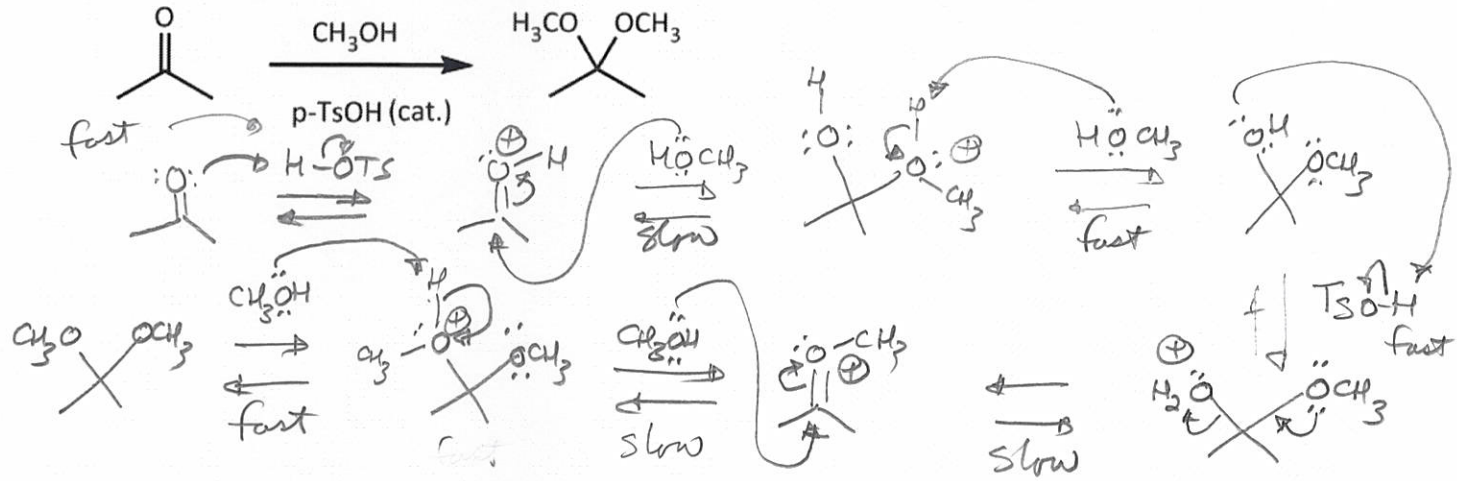
(S)-2-hydroxy butanedioic acid

(common name = (S)-malic acid (not IUPAC))

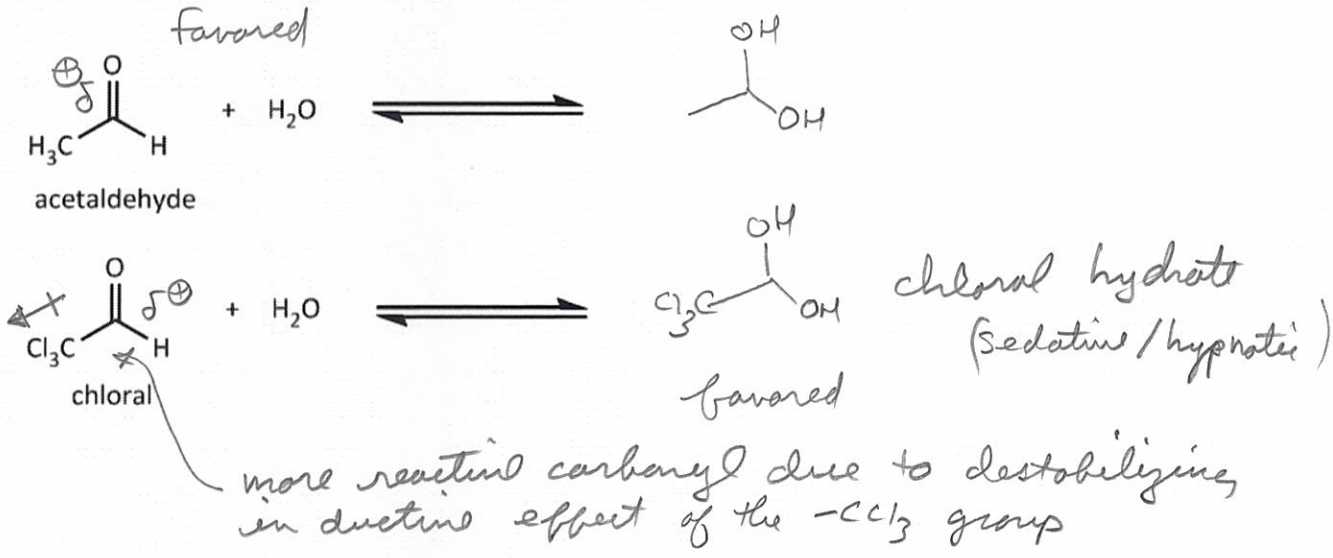
13. Which carbonyl group is more reactive toward nucleophilic attack, aldehydes or ketones? Explain. (10 points)



14. Show the *complete* mechanism for the following reaction. Label each step as slow or fast. (15 points)



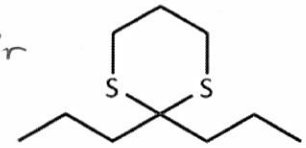
15. Show the hydrates from each aldehyde. Which equilibrium reaction is expected to favor the product more. Explain. (10 points)



16. Suggest starting materials in a. and reagents and conditions for b. and c. (15 points)

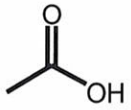
a. 

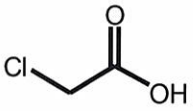
b. 1. nBuLi 2.  3. nBuLi 4. 



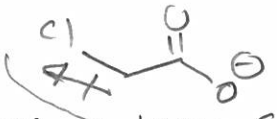
c. 1. H_3O^+, Hg^{2+} 2. $Ph_3P{=}$

17. Which carboxylic acid shown below is more acidic? Clearly explain why. (10 points)





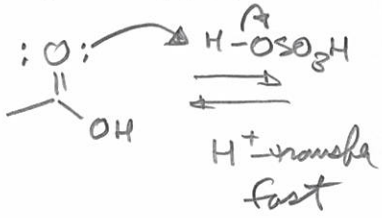
more acidic



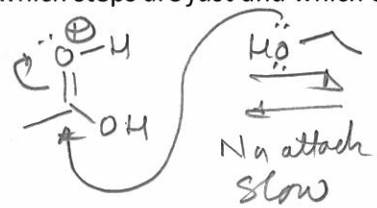
Consider (always), the conjugate base stability → stronger acid → more stable conj. base

more stable by induction

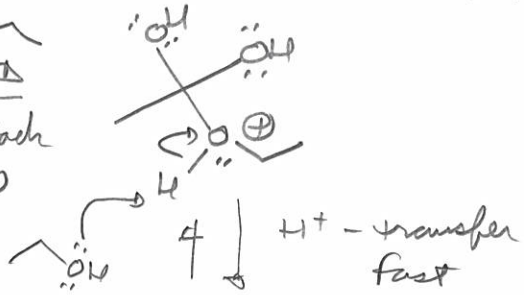
18. Show the *complete* mechanism of the Fischer esterification of acetic acid with ethanol (using a catalytic amount of H_2SO_4). For each step of the reaction, indicate whether the step is a *proton transfer*, *nucleophilic attack*, or *loss of a leaving group*. Also, show which steps are *fast* and which ones are *slow*. (20 points)



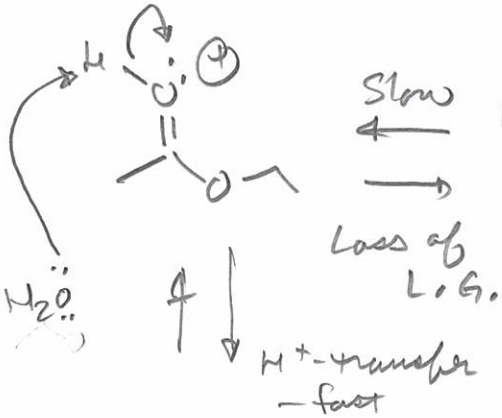
H+ transfer fast



Nu attack slow



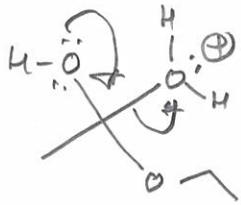
H+ - transfer fast

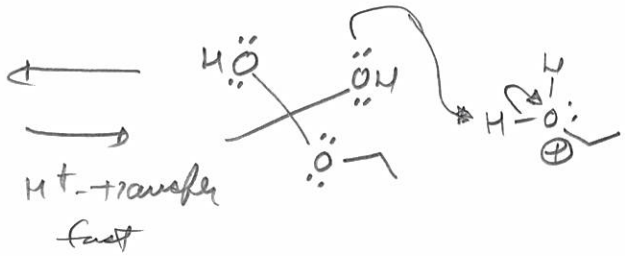


Slow

Loss of L.G.

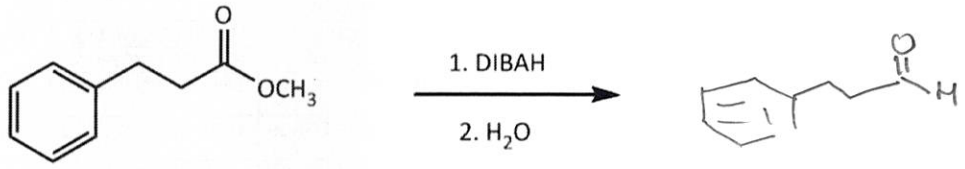
H+-transfer - fast

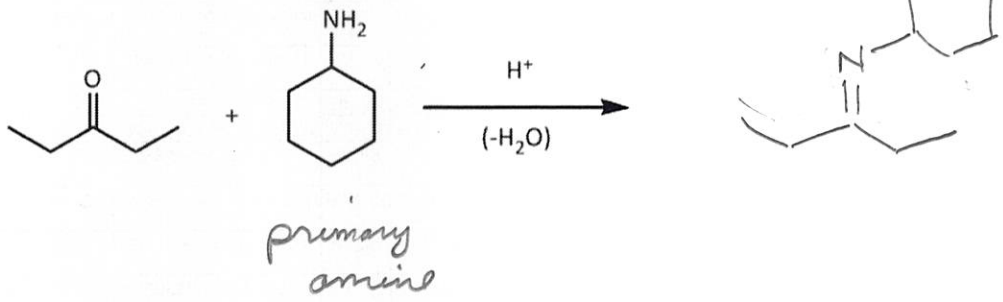




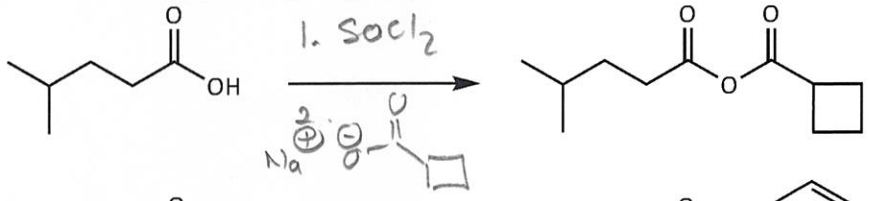
H+-transfer fast

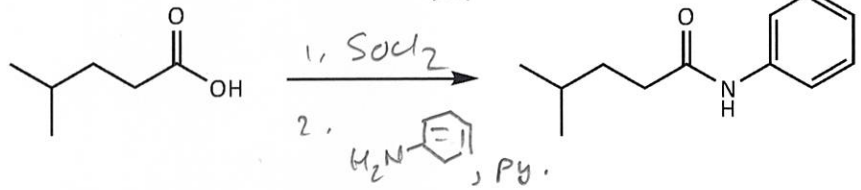
19. Show the product (or products) produced from the following synthetic transformations. (20 points)

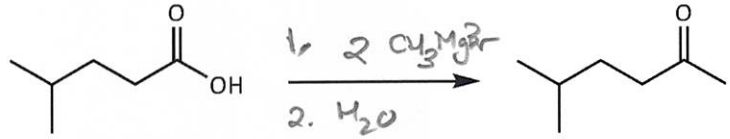
a. 

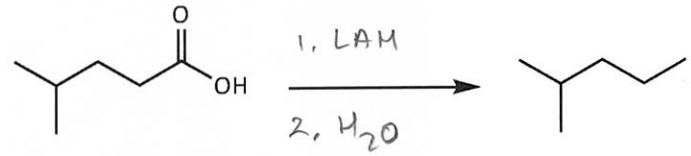
b. 

20. Show the reagents required to accomplish the following conversions. More than one step may be required. (40 points)

a. 

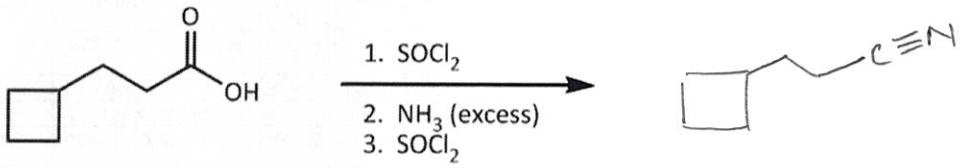
b. 

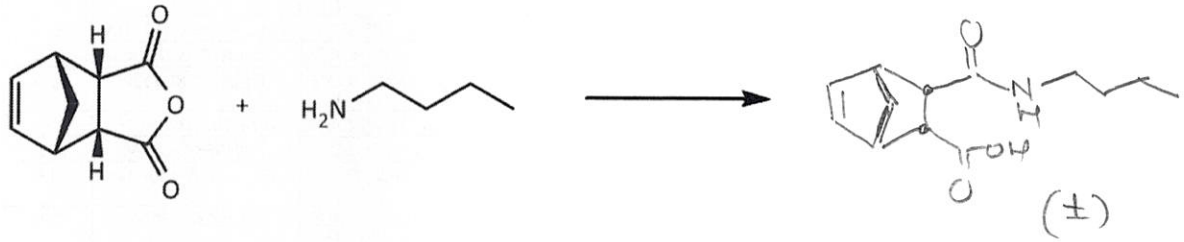
c. 

d. 

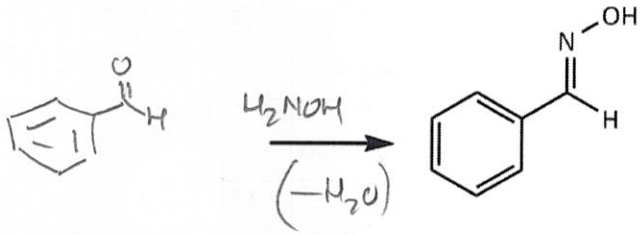
3. Ts-Cl, Py
4. $^{t}O^{\ominus}K^{\oplus}$
5. H_2, Pt

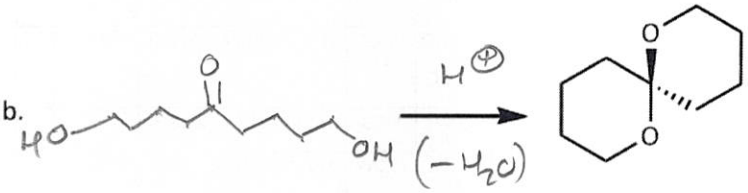
21. Show the product (or products) from each reaction shown below. (20 points)

a. 

b. 

22. Each of the following products comes from a ketone or aldehyde. Show the starting ketone or aldehyde and any other compounds or reagents needed to complete the transformation. (30 points)

a. 

b. 

c.