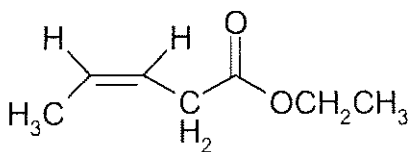


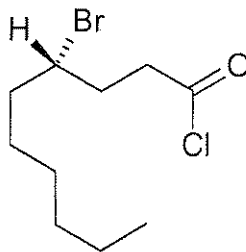
1. (12 pts, 3 each) Give the IUPAC name of the following compounds (except c). (Be sure to use R/S and E/Z when necessary).

a)



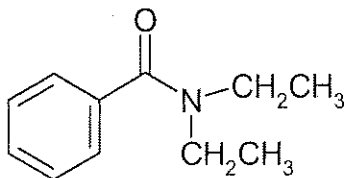
ethyl (Z)-3-pentenoate

b)



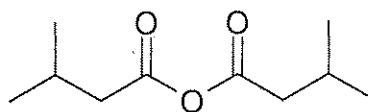
(S)-4-bromodecanoyl chloride

c)



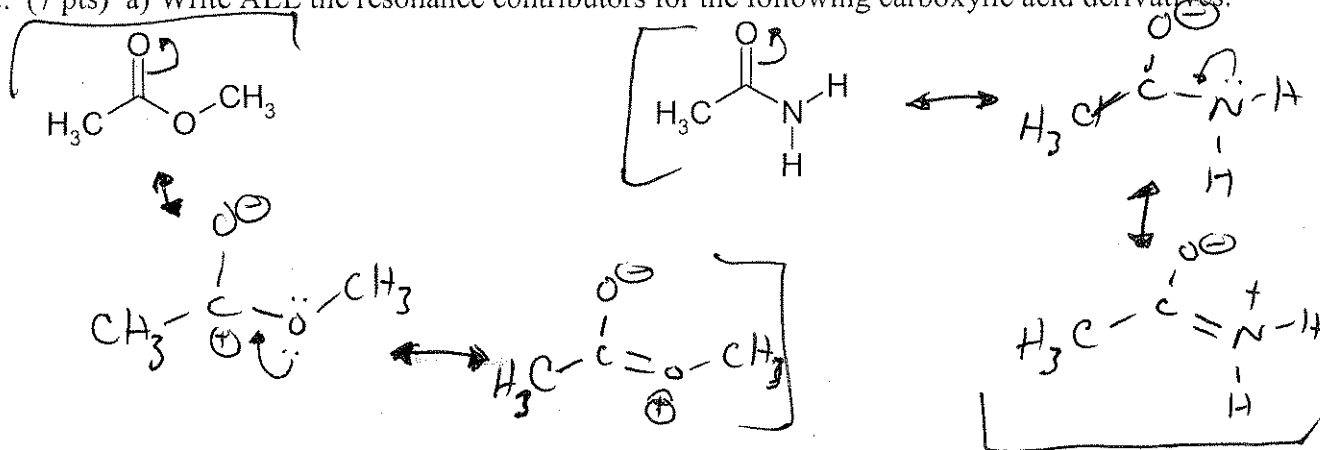
N,N-diethylbenzamide

d)



3-methylbutanoic anhydride

2. (7 pts) a) Write ALL the resonance contributors for the following carboxylic acid derivatives:



b) Explain why an amide is more resistant to nucleophilic attack (and is consequently more stable) than an ester.

Oxygen is more electronegative than nitrogen and therefore the carbonyl in the ester has a larger  $\delta^+$  charge. Consequently, a nucleophile is more attracted to it compared to an amide carbonyl. In addition, the  $2^\circ$  resonance structures shown below reduce the  $\delta^+$  charge on the carbonyl groups.

(see back page for rest of answer)

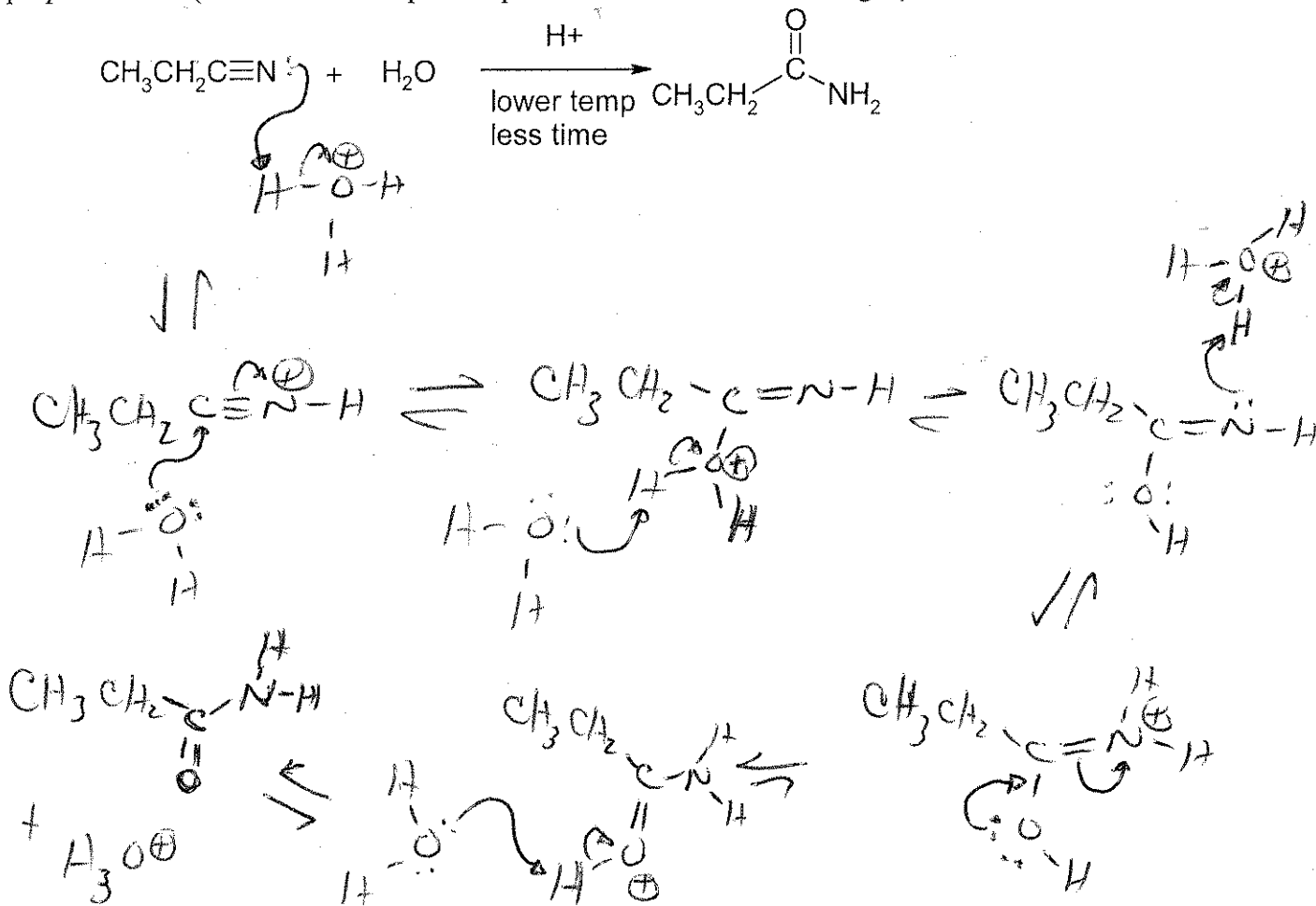
3. (5 pts) A chemist carried out an oxidation reaction of heptanol and produced heptanoic acid. Unfortunately, the reaction didn't go as well expected. There was a fair amount of the starting material that was left unreacted. (Both the product and starting material were dissolved in the organic solvent that was used for the reaction). The chemist wanted to separate the product carboxylic acid from the alcohol starting material. Briefly explain how this separation could be accomplished.

The chemist could remove the heptanoic acid from the heptanol by extracting the organic solvent containing these compounds with an aqueous solution of a base like NaOH or NaHCO<sub>3</sub>. The base would deprotonate the carboxylic acid forming sodium heptanoate which is more soluble in the aqueous layer. He/she could separate the two layers in a separatory funnel and reacidify the aqueous layer to form heptanoic acid. The heptanol would remain mostly in the organic layer.

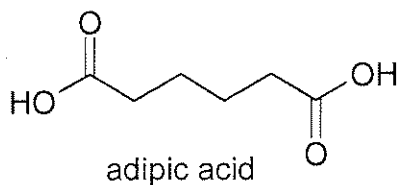
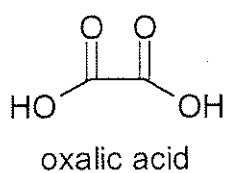
4. (4 pts) What is the isoelectric point of an amino acid?

It is the pH where the amino acid exists mainly as the zwitterion  $H_3N^+ - C(H) - COO^-$  which has no net charge. At this pH the amino acid will not migrate in an electric field because it has no net charge.

5. (9 pts) Write a complete mechanism for the acid-catalyzed hydrolysis of propanenitrile to propanamide. (Note: the first step is the protonation of the nitrile nitrogen)



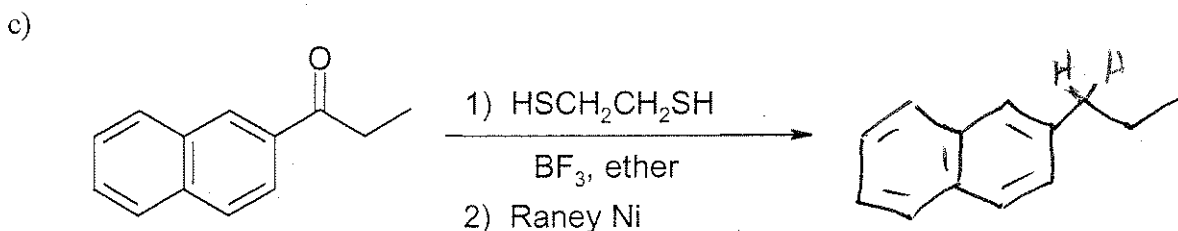
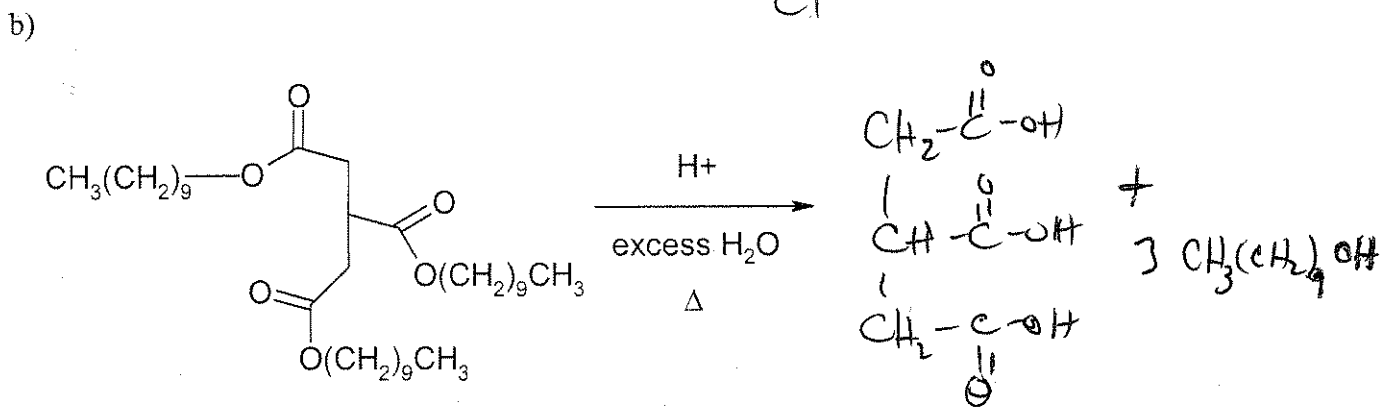
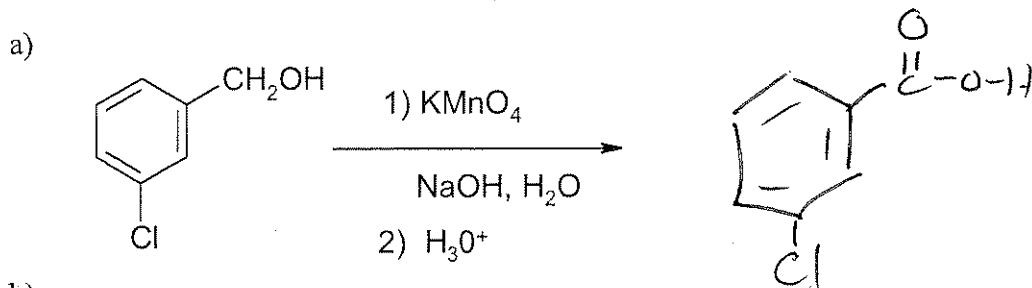
6. (5 pts) Oxalic acid has 2 acidic protons with pKa's of 1.27 and 4.27. Adipic acid also has 2 acidic protons with pKa values of 4.43 and 5.41. (See structures below). Briefly explain why the 1<sup>st</sup> pKa value for oxalic acid (pKa = 1.27) is so much lower than the 1<sup>st</sup> pKa value for adipic acid (pKa = 4.43).

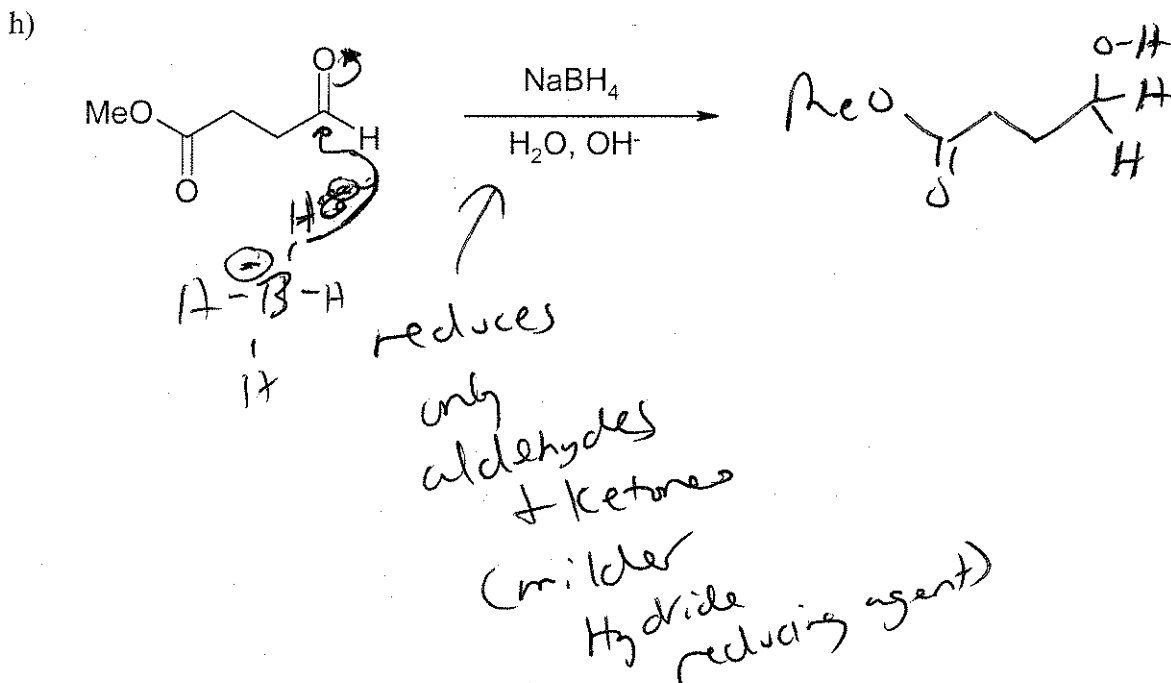
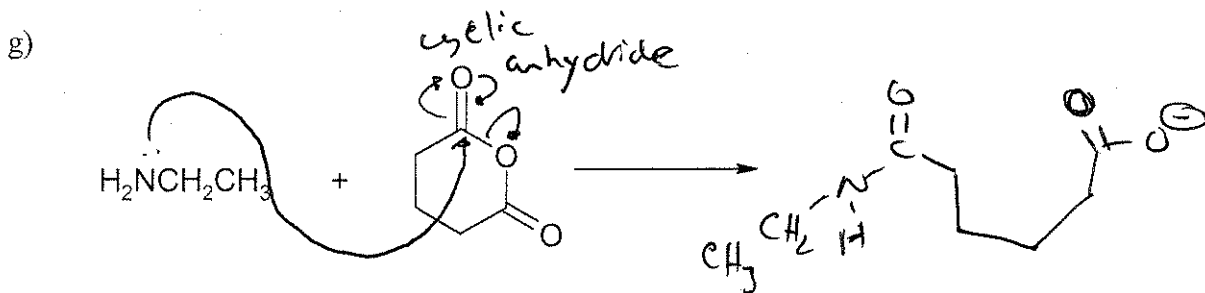
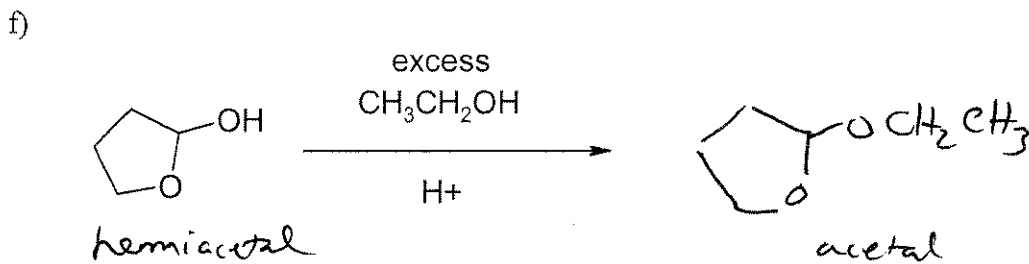
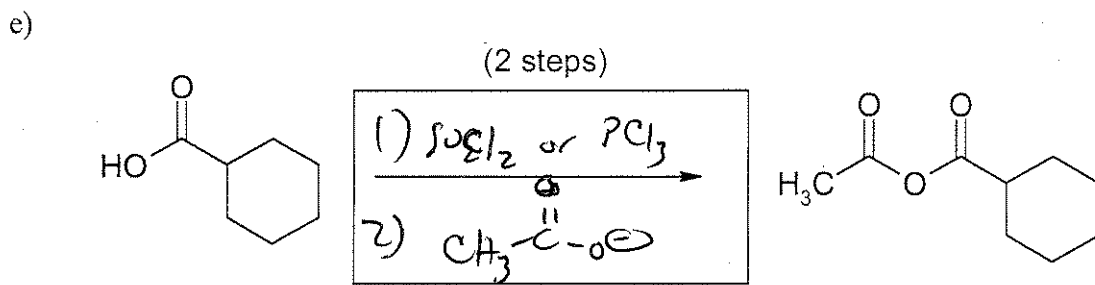
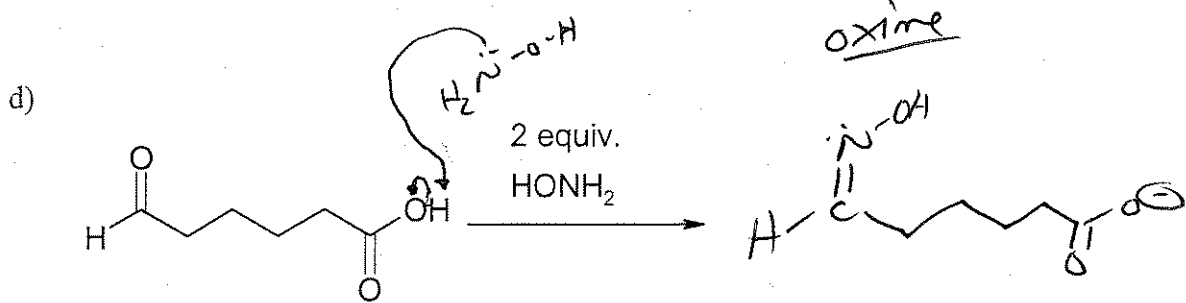


The 1<sup>st</sup> pKa for oxalic acid is much lower than the 1<sup>st</sup> pKa of adipic acid because

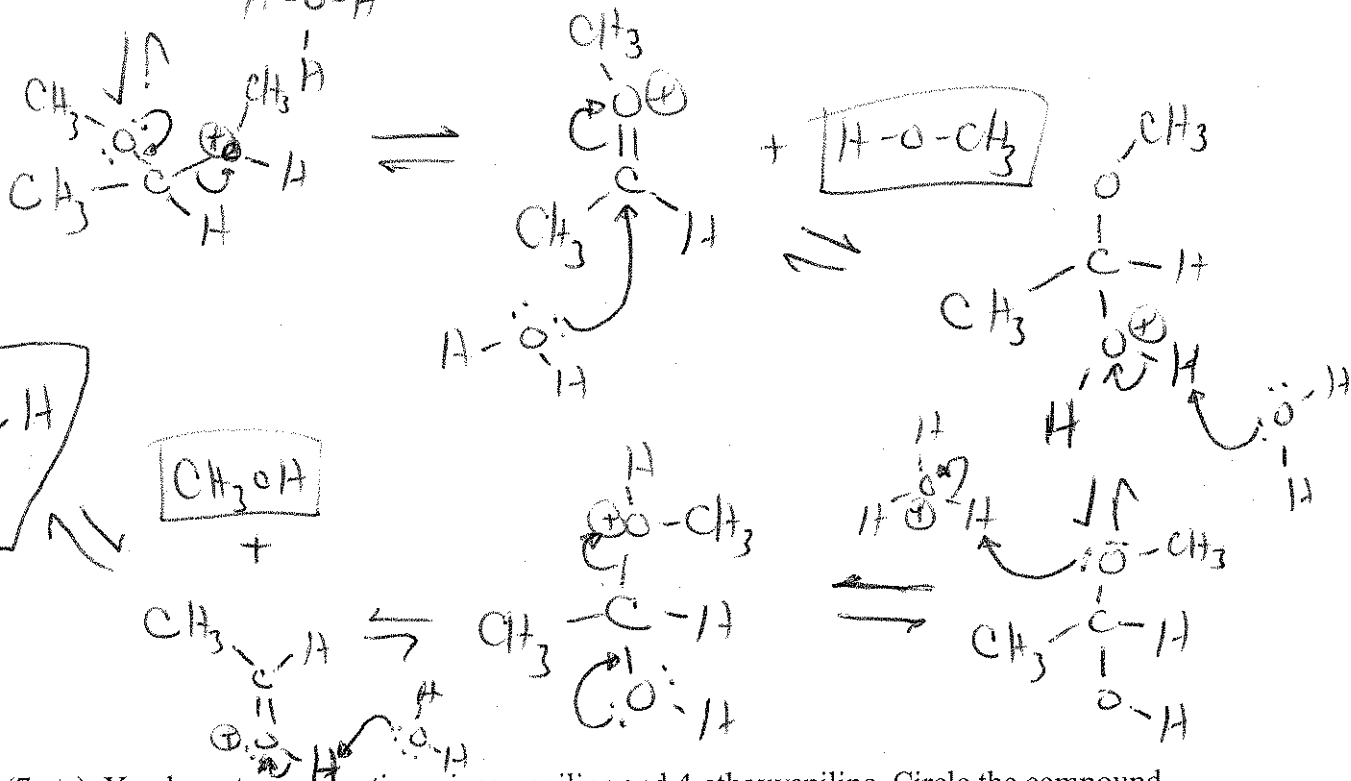
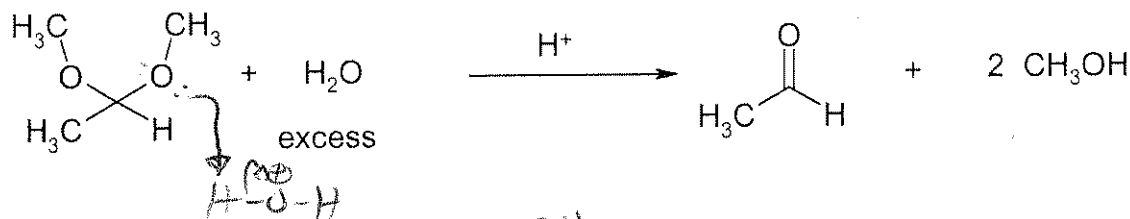
The negative charge on the mono deprotonated oxalate  $\text{H}-\text{O}-\overset{\ominus}{\text{C}}(\text{O})-\overset{\ominus}{\text{C}}(\text{O})-\text{H}$  is stabilized by the inductive effect of the carbonyl group of the adjacent  $\text{C}_2\text{H}$ . In the case of adipic acid, the 2<sup>nd</sup>  $\text{C}_2\text{H}$  group is much farther away, so the negative charge can't be stabilized well by this distant group.

7. (32 pts, 4 each) Give the structures for the **major product** or the **reagents needed** for the following transformations. If no reaction occurs, write **NO RXN**.

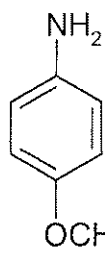
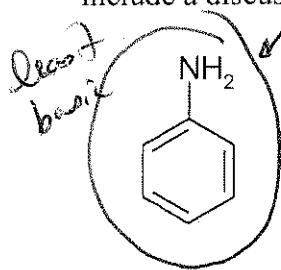




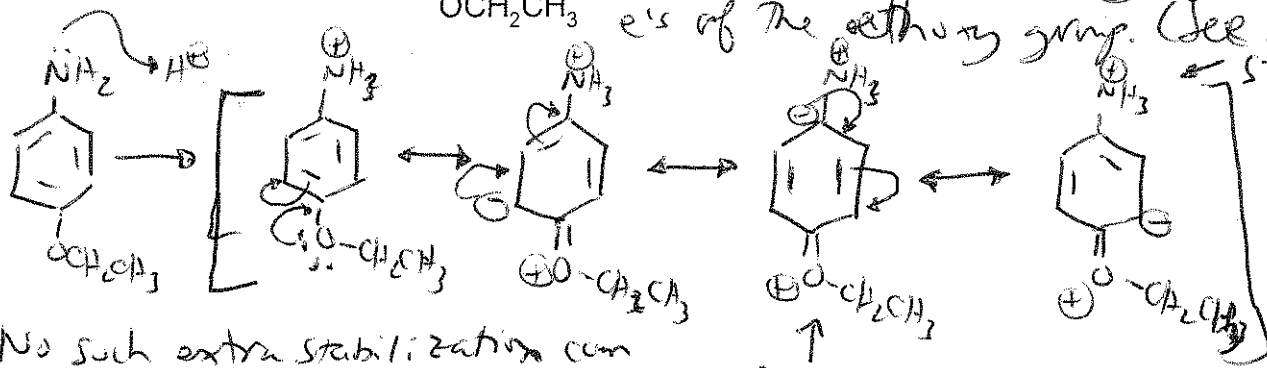
8. (11 pts) Give the complete mechanism for the following acid-catalyzed hydrolysis of an acetal.



9. (7 pts) You have two aromatic amines - aniline and 4-ethoxyaniline. Circle the compound which is **least basic** of the two, and briefly explain why you chose your answer. (Be sure to include a discussion of resonance effects in your explanation).



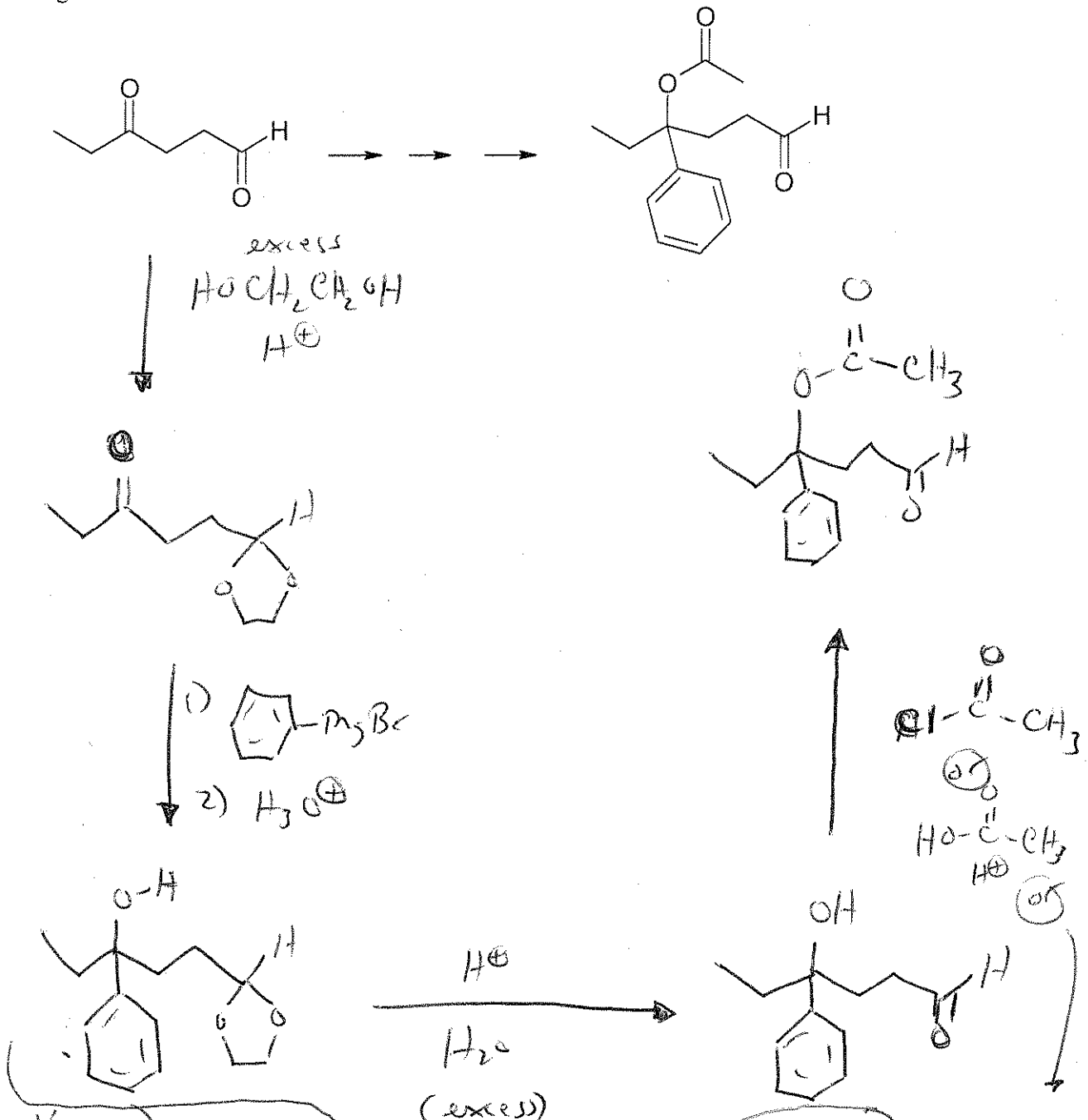
4-ethoxy aniline is a stronger base than aniline because the conjugate acid of 4-ethoxy aniline can be stabilized by delocalization of  $\pi$  density of the lone pair of the ethoxy group. (See resonance structures)



No such extra stabilization can occur w/ aniline itself, so aniline is **less basic** than 4-ethoxyaniline.

(This structure especially important to stabilize conj. acid)

10. (8 pts) **Multistep synthesis.** Give the **reagents needed** as well as the structures of the **intermediate products** on the pathway to synthesize the following product from the given starting material.



± 2b (continued)

The 2° resonance structure for the amide ( $\text{CH}_3-\overset{\ominus}{\text{C}}=\overset{\oplus}{\text{N}}-\text{H}$ ) is more stable than that of an ester ( $\text{CH}_3-\overset{\ominus}{\text{C}}=\overset{\oplus}{\text{O}}-\text{CH}_3$ ) because nitrogen is less electronegative than oxygen + holds a  $\oplus$  charge more easily. Since the amide 2° resonance structure is more stable, it makes a larger contribution to the overall hybrid structure of the amide which causes the amide to be less reactive w/ nucleophiles, compared to esters.