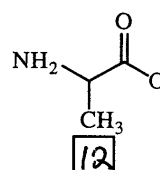
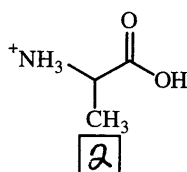
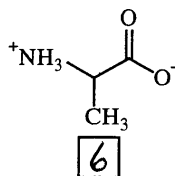
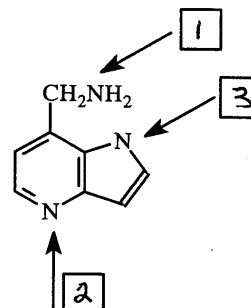
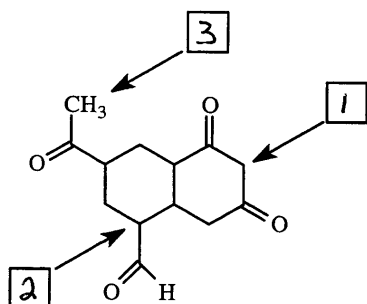


Question 1. (15 Marks)

a) In the boxes below the various forms of the amino acid alanine, place the pH (2, 6 or 12) at which the indicated structure would be the predominate form of the amino acid. (3)

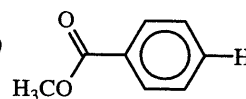
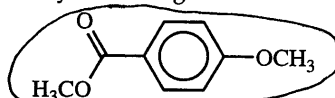
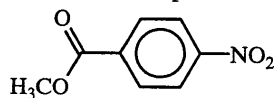


b) In the boxes place 1, 2, 3 for the H atoms of increasing pK_a value for the compound on the left; for the structure on the right, place 1, 2, 3 for the N atoms of increasing pK_b value. (6)

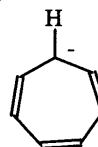
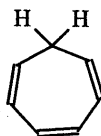
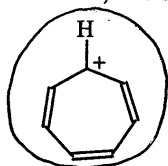


c) Circle the best answer for each of the following: (6)

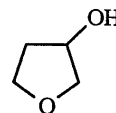
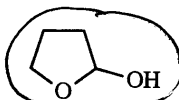
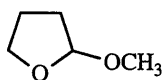
i) the compound most likely to undergo the slowest reaction with OH^-



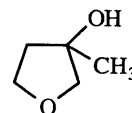
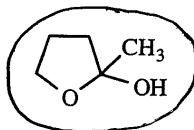
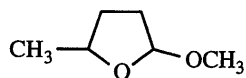
ii) the species most likely aromatic in its properties



iii) the compound which would give a positive Tollens test



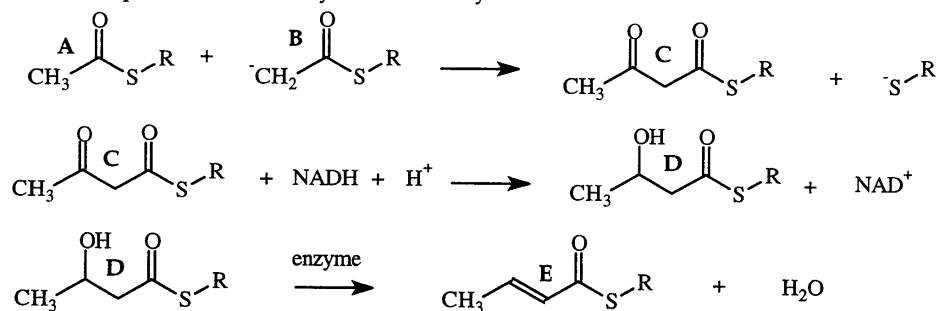
iv) the compound which would give a positive Iodoform test



Question 2.

A: <u>$\text{HNO}_3/\text{H}_2\text{SO}_4$</u>	B: <u>Cl_2/Fe</u>	C: <u>H_2/Pt</u>	D: <u>$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$</u>
E: <u>HNO_2</u>	F: <u>H_2O</u>	G: <u>KI</u>	H: <u>Cl_2/Δ</u>
I: <u>CN^-</u>	J: <u>$\text{H}_3\text{O}^+/\Delta$</u>	K: <u>$\text{SO}_3/\text{H}_2\text{SO}_4$</u>	L: <u>$\text{D}_2\text{O}/\Delta$</u>
M: <u>$\text{H}_3\text{O}^+/\Delta$</u>	N: <u>acidic KMnO_4/Δ</u>	O: <u>1. CO_2 2. H_3O^+</u>	P: <u>1. LiAlH_4 2. H_3O^+</u>
Q: <u>1. Δ 2. H_3O^+</u>	R: <u>PCl_3 or SOCl_2</u>	S: <u>PCC</u>	T: <u>$\text{CH}_3\text{CH}_2\text{OH}$</u>
U: <u>1. Δ MgBr 2. H_3O^+</u>	V: <u>1. CH_3NH_2 2. loss H_2O</u>		

Question 3. (8 Marks) Many of the reaction mechanisms that you have seen in Chemistry 2320/2420 are the same ones found when biological chemical processes occur. The following reactions are important in the biosynthesis of fatty acids.

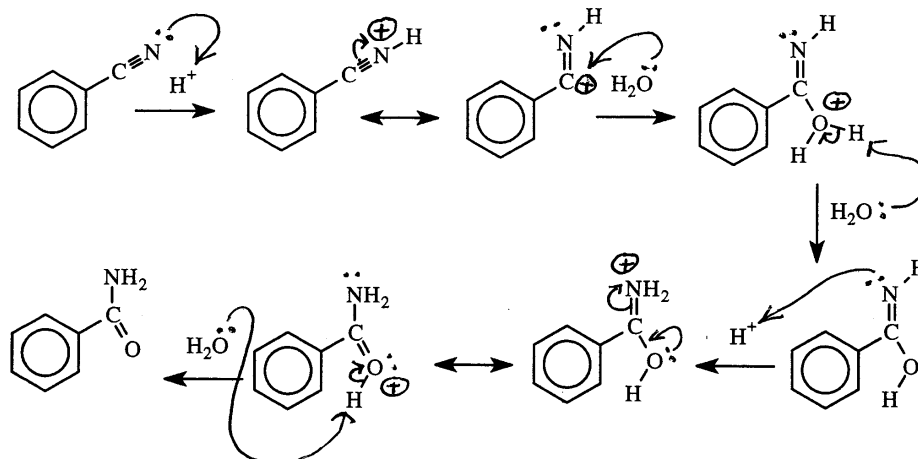


Choose the best answer for each of the following questions.

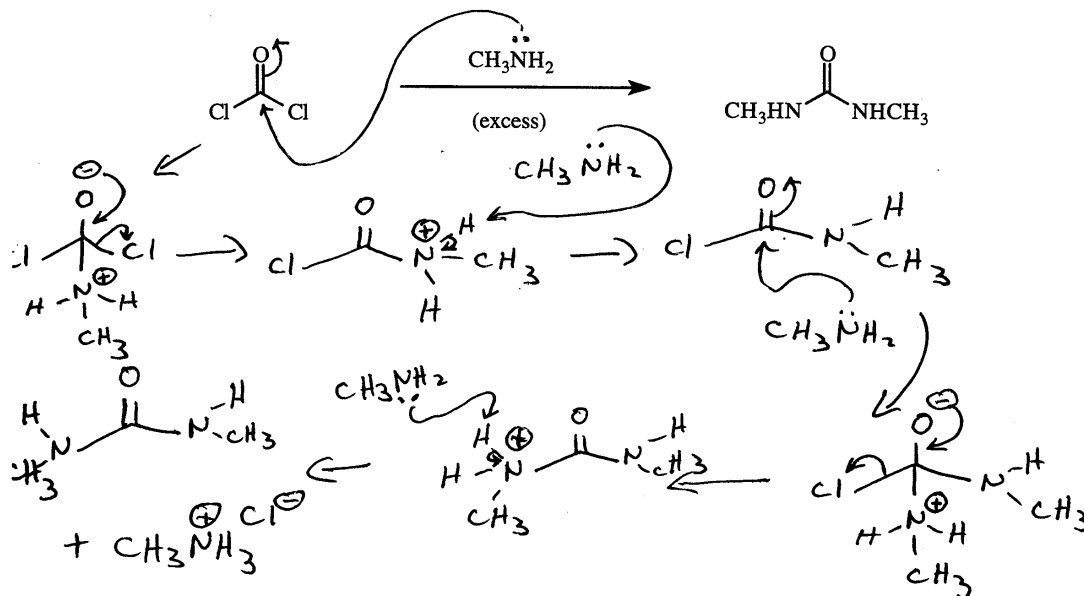
- B is best described as a(n): enol of a thioketone thioacetal enolate of a thioester
- The process $\text{A} + \text{B} \rightarrow \text{C}$ is best described as:
Aldol Condensation Claisen Condensation $\text{S}_{\text{N}}2$ Substitution
- In the process $\text{C} \rightarrow \text{D}$, compound C is being { oxidized / reduced / hydrated } and NADH is acting as the { reducing / oxidizing / hydrating } agent.
- The process $\text{D} \rightarrow \text{E}$ is best described as a { dehydration / dehydrogenation / enolization } and the most likely mechanism would be { elimination / substitution / rearrangement }.
- The process $\text{E} \rightarrow \text{D}$ requires a different enzyme and would be best described as a { 1,2 / 1,3 / 1,4 } { nucleophilic / electrophilic / radical } addition of water to the α,β -unsaturated compound E.

Question 4. (12 Marks) This question deals with the wonderful world of arrows!!

a) Provide the necessary reaction arrows/charges/lone pairs of electrons in the following mechanism involving the conversion of a nitrile to an amide.

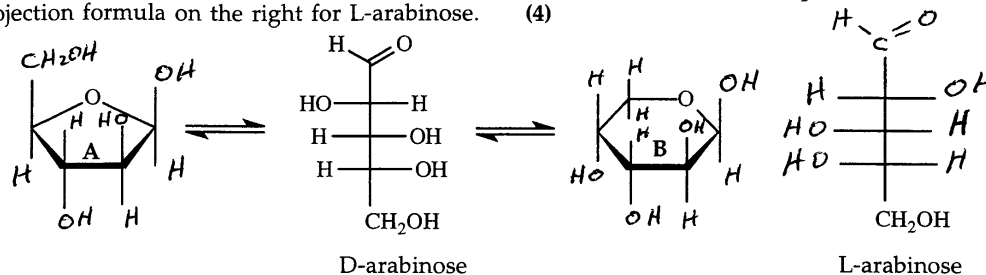


b) Supply a plausible mechanism for the following process. Indicate the flow of electrons using arrows and include all protonations and deprotonations. Provide any pertinent lone pairs of electrons and the location of any charges. Write resonance structures for any appropriate intermediates. Provide the structure of the other substance produced in the reaction.



Question 5. (20 Marks)

a) Complete the Haworth structures for two of the cyclic compounds A and B which are in equilibrium in an aqueous solution of the monosaccharide D-arabinose. Complete the Fischer Projection formula on the right for L-arabinose. (4)



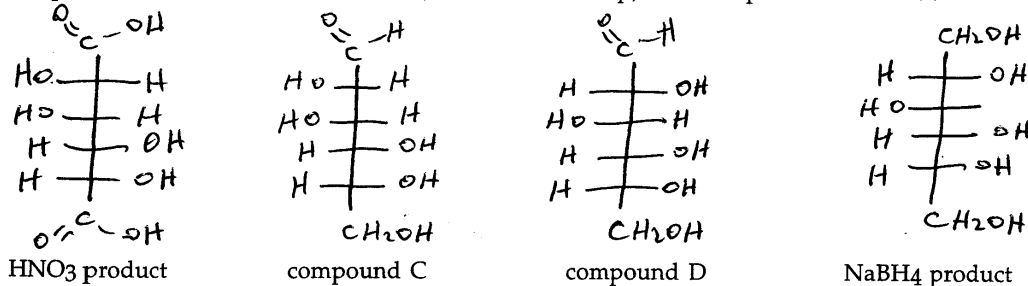
b) The structure in (a) which is a furanose is: (1)

A

B

c) The monosaccharide which is epimeric to D-arabinose at C#4 contains { 2 / 3 / 4 } stereogenic carbon atoms and is best described as a(n): { D / L } { chiral / achiral } { non-reducing / reducing } { aldo / keto } { pentose / hexose }. This monosaccharide would { undergo / not undergo } mutarotation and would give a { positive / negative } Tollens test. (4)

d) When D-arabinose is subjected to the series of reactions involved in the Kiliani-Fischer synthesis, two new monosaccharides (C and D) are isolated. Provide the Fischer Projection formulas below for monosaccharides (C and D) as well as the product from the HNO_3 reaction of compound C and the NaBH_4 reaction (after acidic workup) with compound D. (6)



The HNO_3 product is an: aldonic acid

aldaric acid

uronic acid

alditol (1)

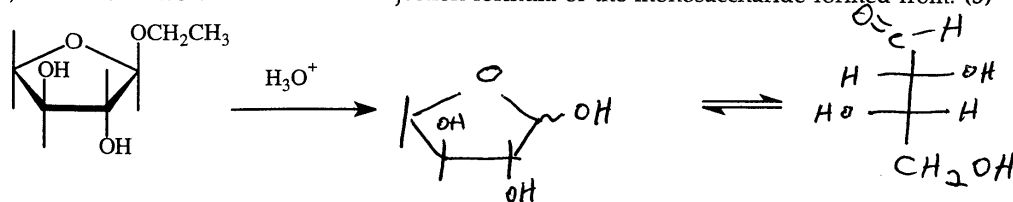
The NaBH_4 product is an: aldonic acid

aldaric acid

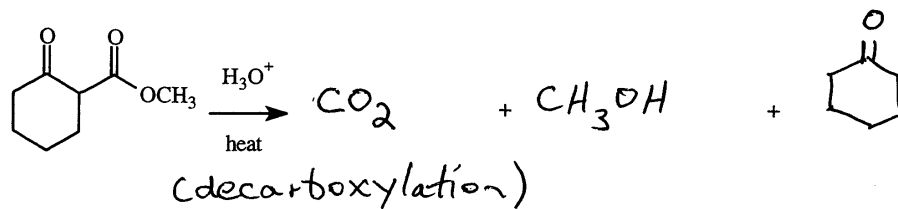
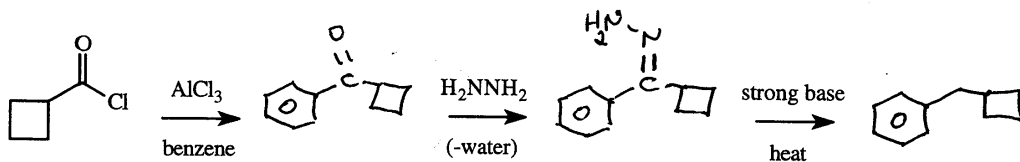
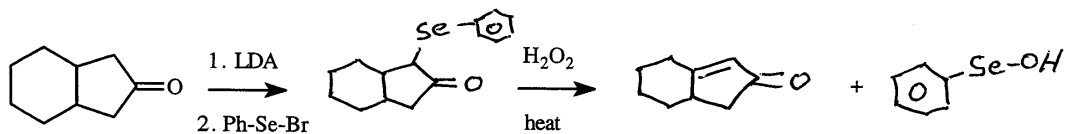
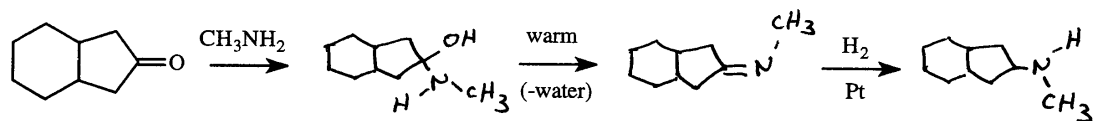
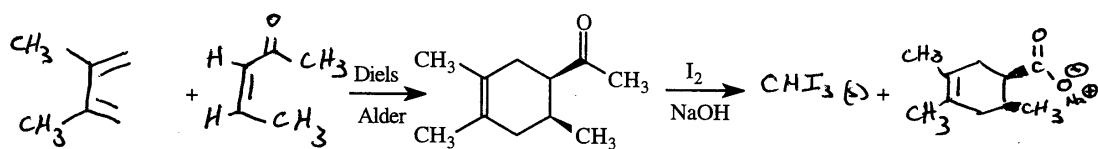
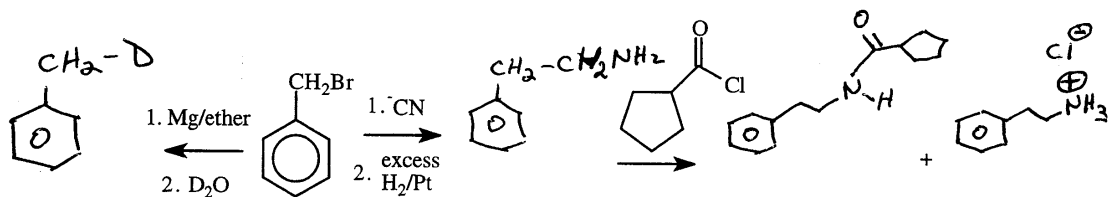
uronic acid

alditol (1)

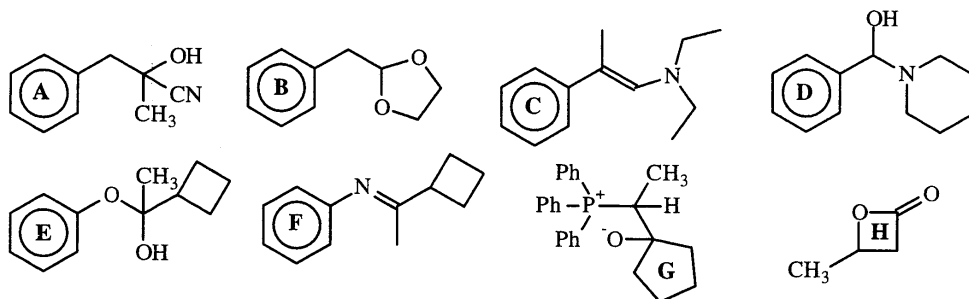
e) Give the Haworth and Fischer Projection formula of the monosaccharide formed from: (3)



Question 6. (27 Marks) Provide the structures of the organic compounds involved in the following sequences of reactions. I'll count the best 18 of 20 answers.

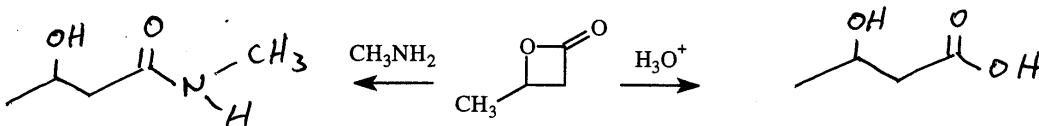
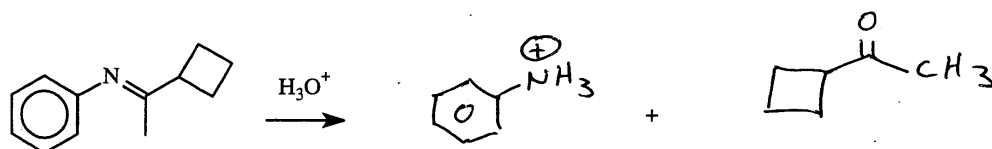
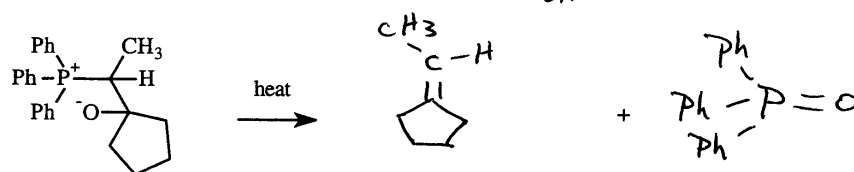
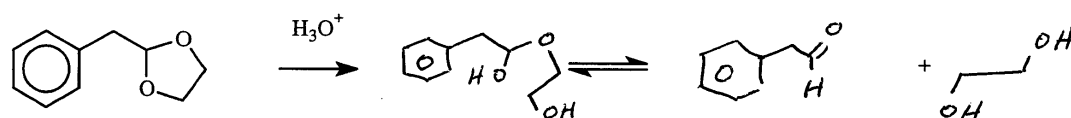


Question 7. (23 Marks) As you have seen during the past 14 weeks, the chemistry of the C=O group makes a very interesting story. Match the following structures with the correct term.
NOTE: There are more terms than structures!! (8)

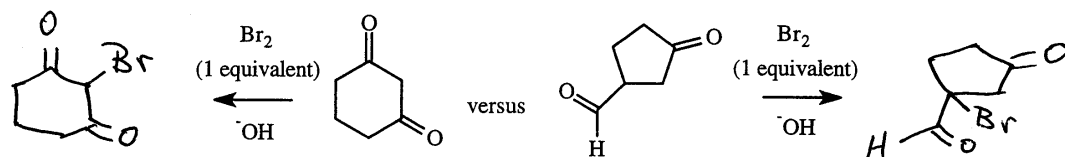
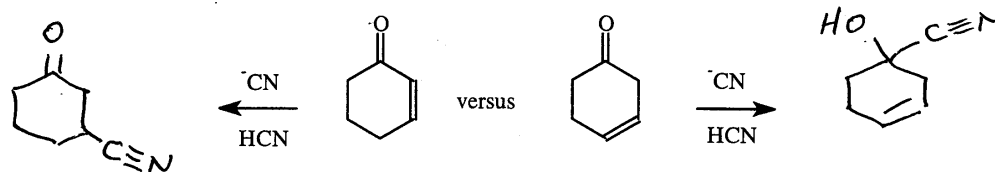
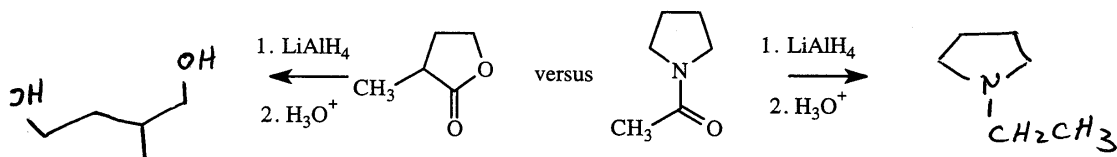
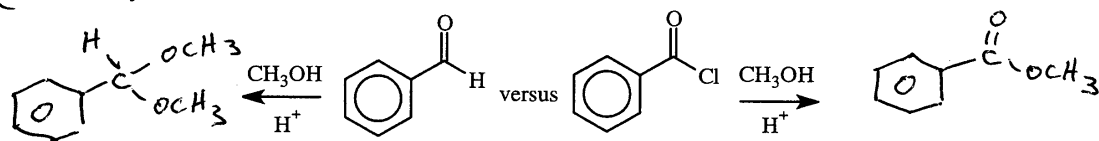
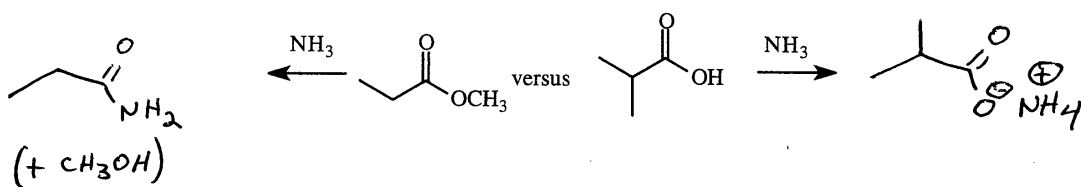
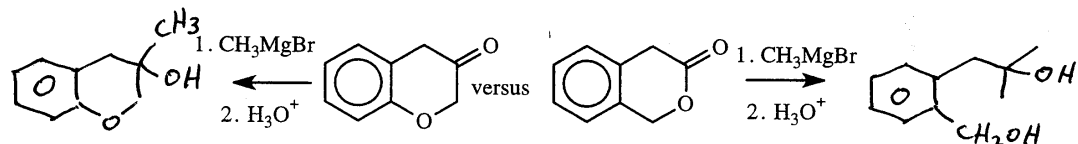


Ketal ____ Acetal B Hemiketal E Hemiacetal ____ Imine F Enamine C
 Ylid ____ Betaine G Lactam ____ Lactone H Carbinolamine D Cyanohydrin A

Provide the structure of all organic compounds formed in each of the following reactions. (15)



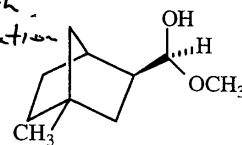
Question 8. (18 Marks) Making a small change in the structure of the starting material can result in a significant change in the structure of the products isolated in a chemical reaction. Provide the structures of the expected carbon-containing products in the following reactions. You may assume that you have as much reagent as necessary to make the reactions go to completion.



Question 9. (18 Marks) Provide a brief description of what each term means, and then provide another structure to illustrate your description. I'll count the best 6 of 7 answers.

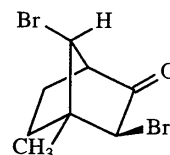
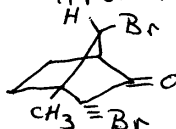
a) Anomers

- isomers that ~~differs~~ are in equilibrium with each other in a process known as mutarotation
- hemiacetals or hemiketals



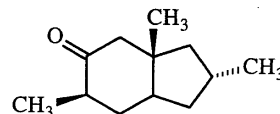
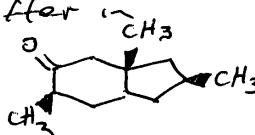
b) Diastereomers (not epimers)

- stereoisomers that are not mirror images of each other
- epimers differ in the orientation of one chirality centre



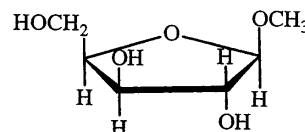
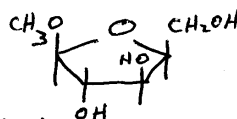
c) Epimers

- stereoisomers which differ in the orientation of one chirality centre



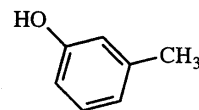
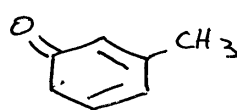
d) Enantiomers

- stereoisomers which are mirror images of each other



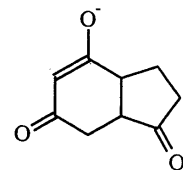
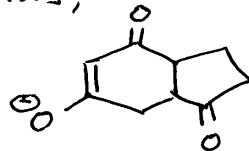
e) Tautomers

- functional isomers which are in equilibrium with each other



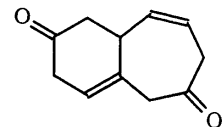
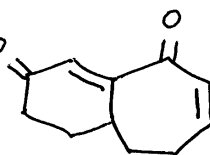
f) Resonance Structures

- localized structures which differ in the location of π -bonds, lone pairs of electrons, and charges

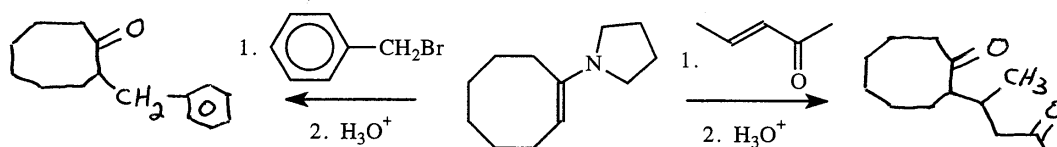
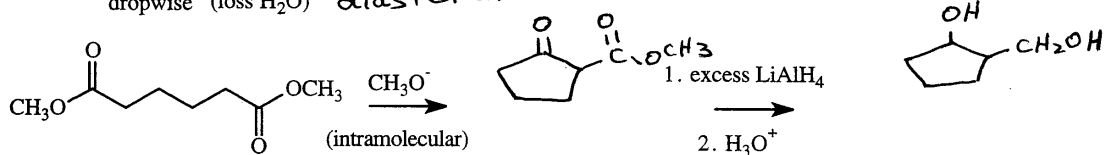
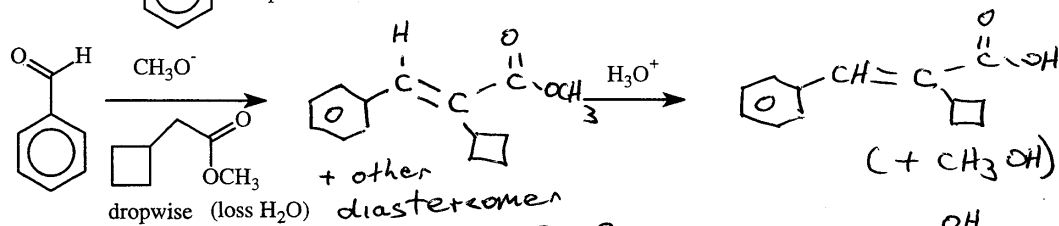
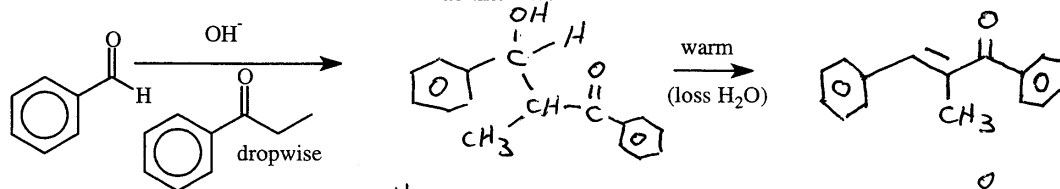


g) Conjugated Compound

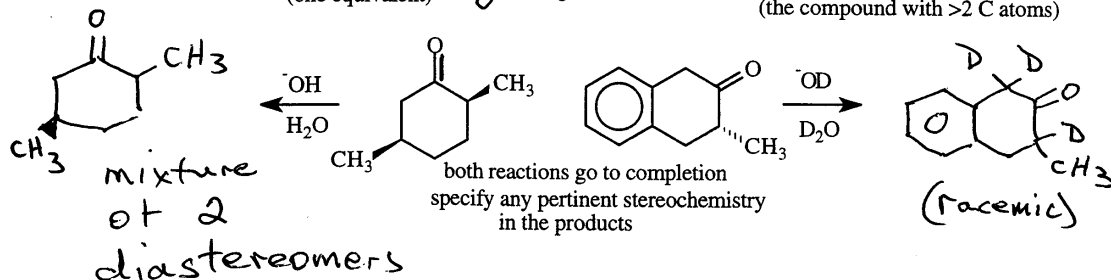
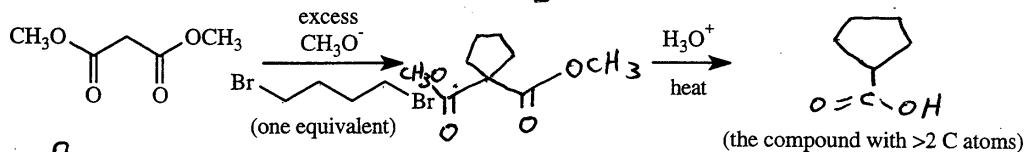
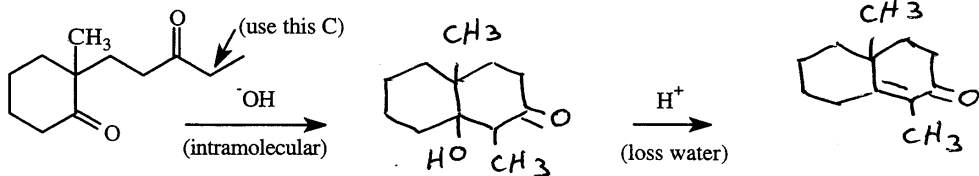
- compound with π bonds linked via a system of sp^2 hybridized carbon atoms



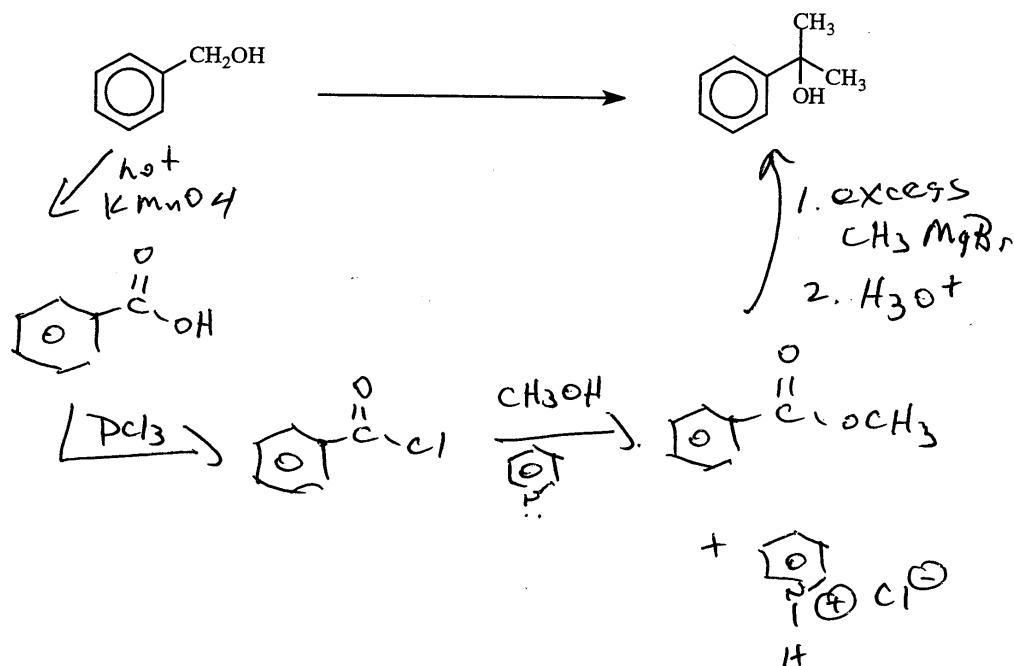
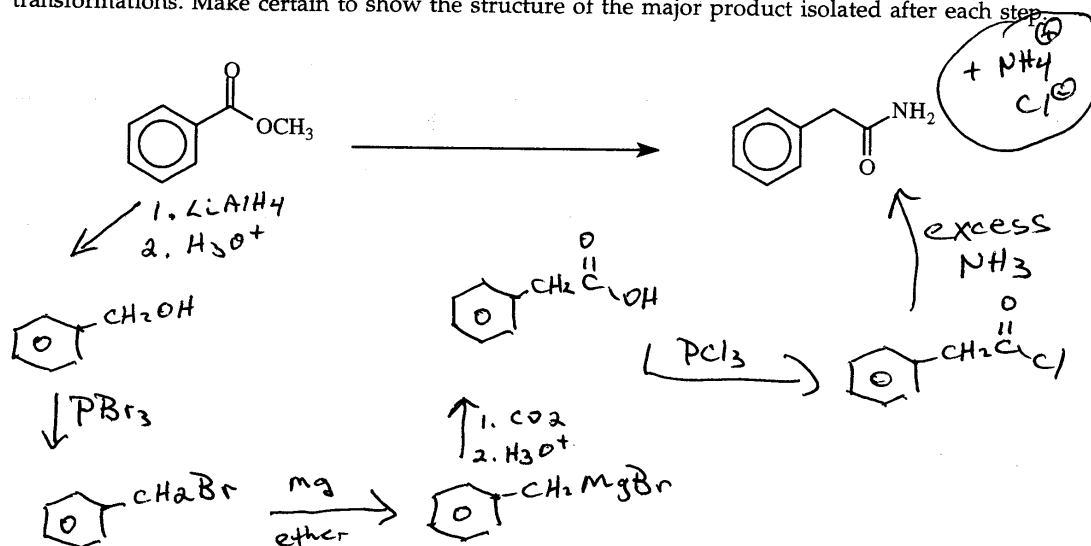
Question 10. (18 Marks) Provide the structure of the compounds formed in the following enolate reactions. I'll count the best 12 of 14 answers.



for these 2 reactions I only want the product that doesn't contain N



Question 11. (12 Marks) Provide a possible sequence of reactions for each of the following transformations. Make certain to show the structure of the major product isolated after each step.



Question 12. (16 Marks) That wacky CHEM 2420 graduate I.M. Smart is in trouble at ACME Pharmaceuticals again. He has been given the task of identifying some compounds left behind by a former research chemist. Compound A ($C_{11}H_{19}NO_2$, strong IR band at $\sim 1700\text{ cm}^{-1}$, ^1H NMR provided below) has been isolated from a reaction sequence. Compound B ($C_9H_{16}O_4$, strong IR band at $\sim 1700\text{ cm}^{-1}$, broad IR band from 2800 cm^{-1} to 3300 cm^{-1} , ^1H NMR provided below) was isolated from the acidic hydrolysis of compound A. Treatment of the aqueous filtrate from the conversion of compound A to B with NaOH(aq) resulted in the formation of compound C (C_2H_7N) which had a strong fishy aroma. Treatment of compound B with benzyl alcohol ($C_6H_5\text{-CH}_2\text{OH}$) in the presence of a catalytic amount of concentrated H_2SO_4 resulted in the formation of compound D ($C_{23}H_{28}O_4$, strong IR band at $\sim 1700\text{ cm}^{-1}$, ^1H NMR provided below). Help I.M. Smart out by providing the structures of A, B, C and D.

