

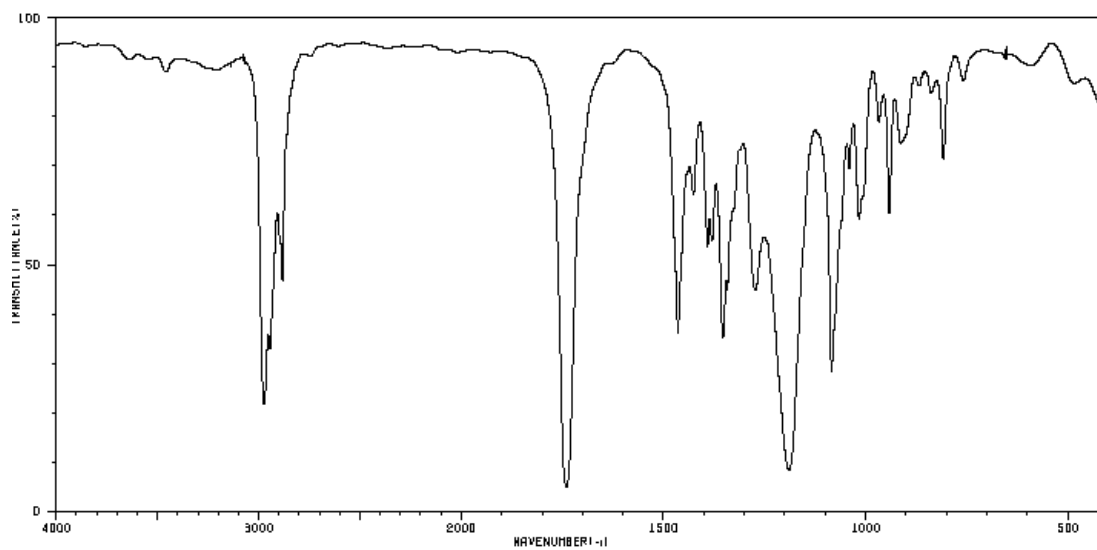
Chemistry Department

University of Alberta

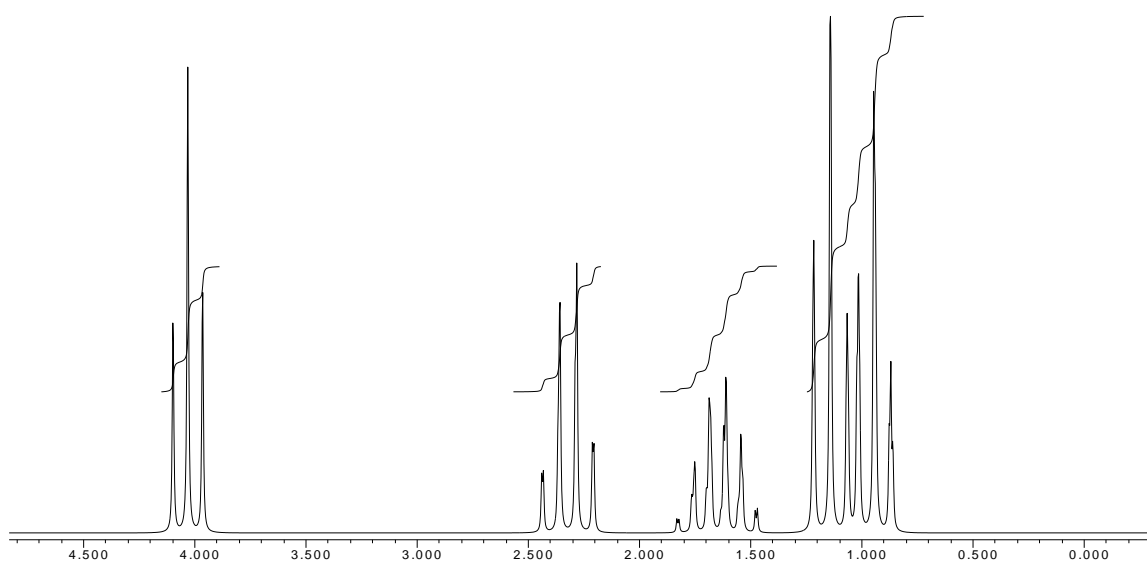
CHEM 263
Final Exam

April 16, 2009

1. The IR and ^1H NMR spectra of a compound of molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$ are given below.



SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/> (18-11-08)



- a. Calculate the degree of unsaturation. (1 point)

$$(2 \times 6 - 12 + 2)/2 = 1$$

- b. List the possible functional groups using the molecular formula and your calculated degree of unsaturation. (2 points)

Carboxylic acid

Ester

Alcohol

Aldehyde

Ether

Ketone

(Note that Phenol is not a possibility)

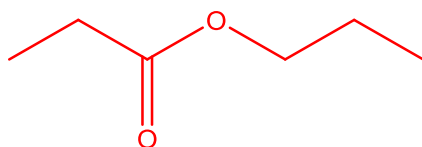
- c. What are the oxygen-containing functional groups listed in your answer to part "b" that the IR spectrum shows to be absent in the unknown? (1 point)

Carboxylic acid

Alcohol

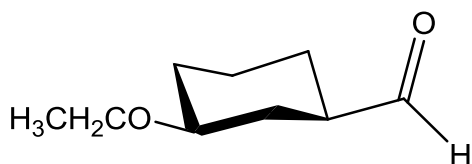
Aldehyde

- d. Draw a table that lists chemical shifts and multiplicity. Then propose a structure for this compound. (11 points)



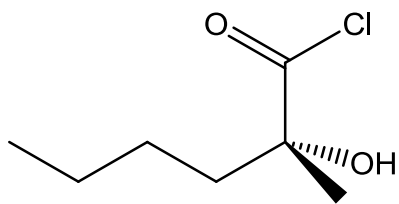
2. Name five (5) of the following structures: (15 points)

- a.



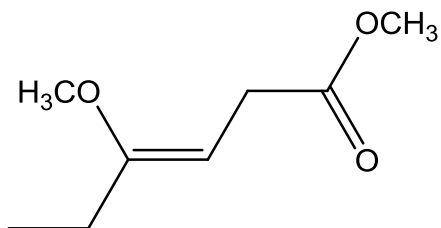
cis-3-ethoxycyclohexanecarbaldehyde

- b.



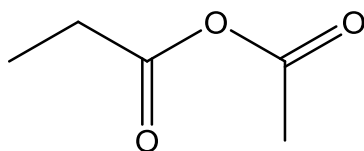
(R)-2-hydroxy-2-methylhexanoyl chloride

c.



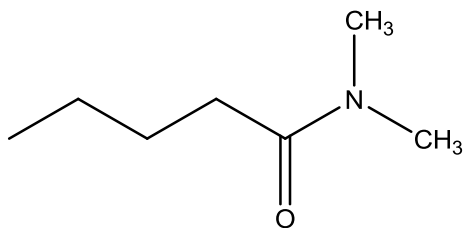
methyl (Z)-4-methoxy-3-hexenoate

d.



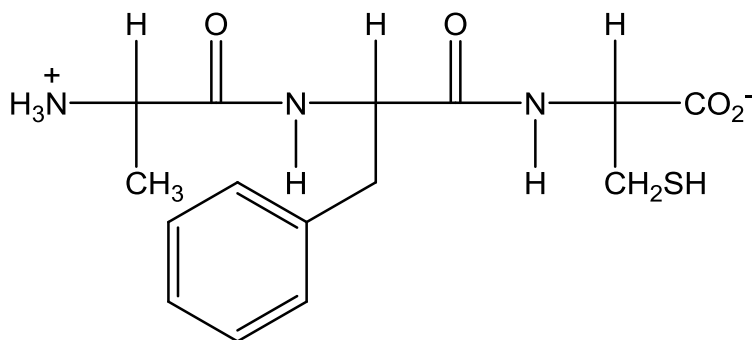
acetic propionic anhydride or ethanoic propanoic anhydride

e.



N,N-dimethylpentanamide or *N,N*-dimethylvaleramide

f.



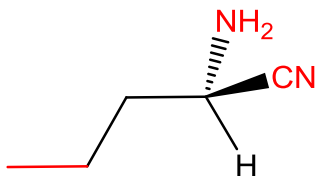
alanylphenylalanyl-L-cysteine

3. Give the structural formula of five (5) of the following compounds. Where given, complete the partial structures: (15 points)

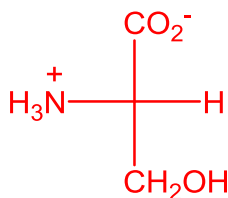
a. glycerol



b. (R)-2-aminopentanenitrile



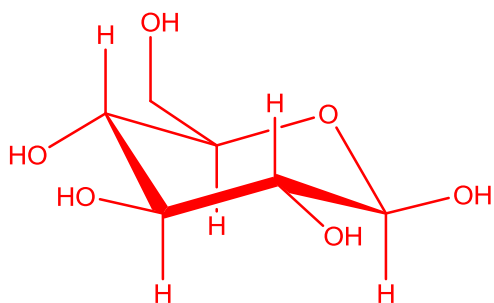
c. L-serine (as a zwitterion)



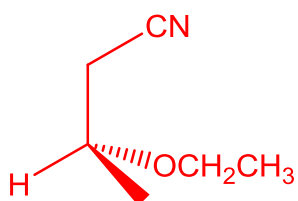
d. *cis*-3-methylaminocyclohexanecarboxylic acid



e. β -D-glucopyranose

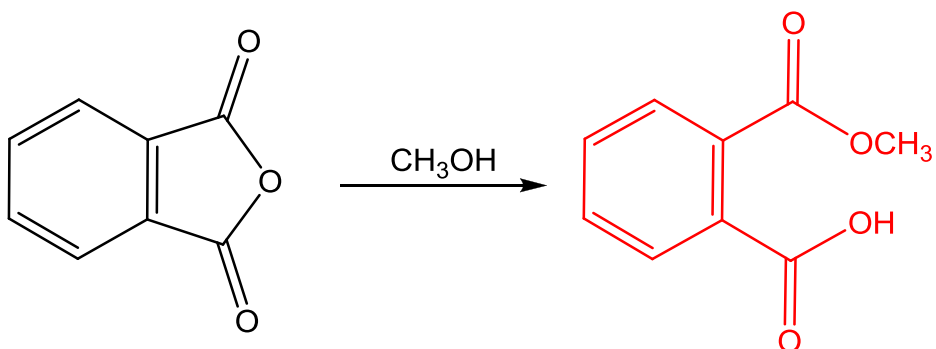


f. (S)-3-ethoxybutanenitrile

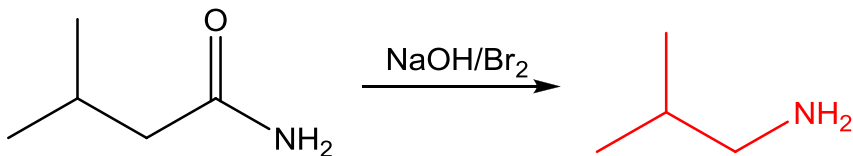


4. Give the structure(s) of the principle organic products of ten (10) of the following reactions: (30 points)

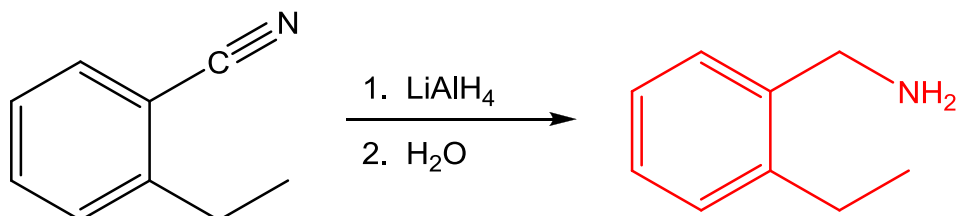
a.



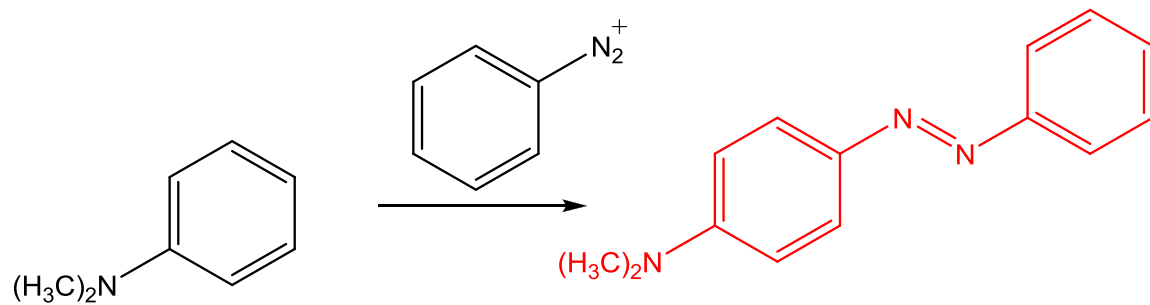
b.



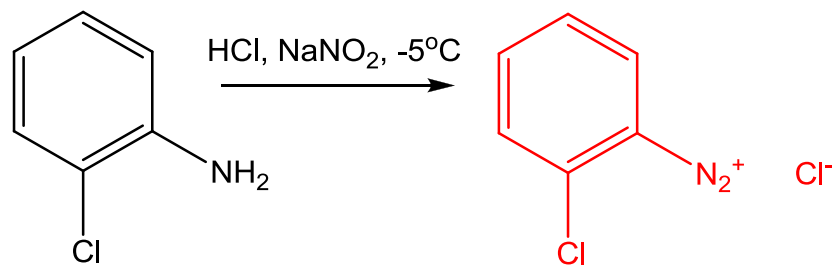
c.



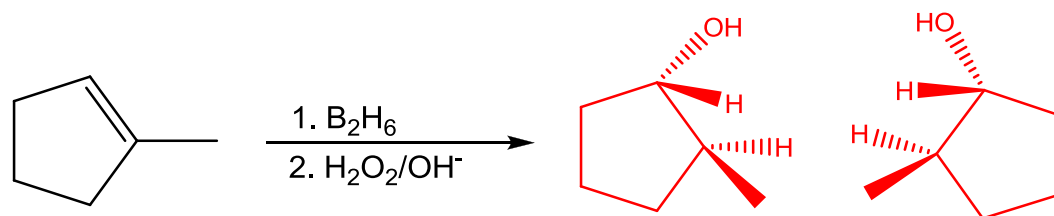
d.



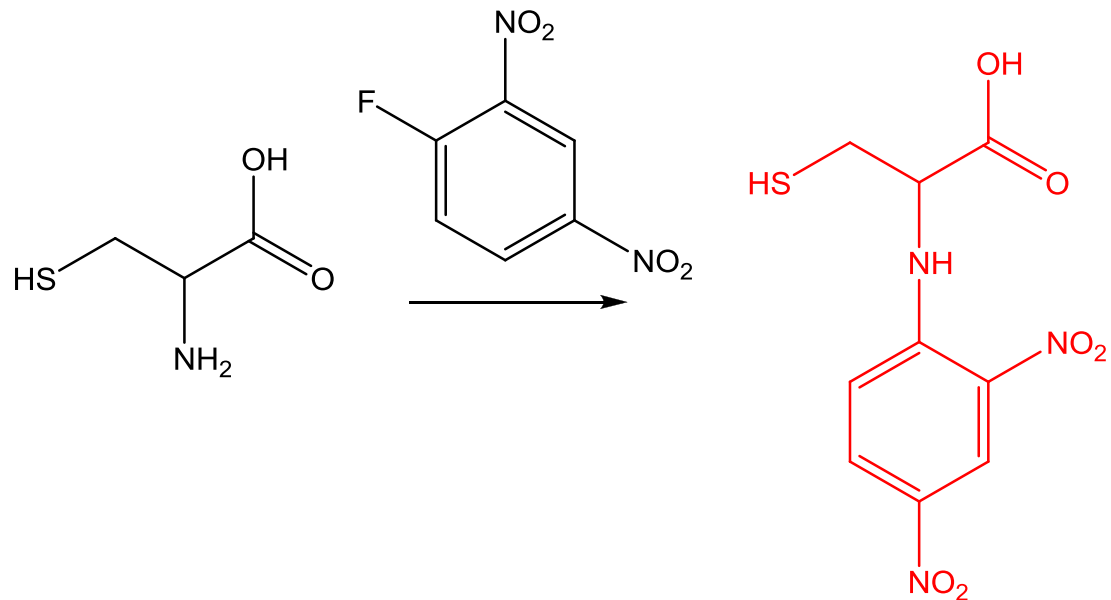
e.



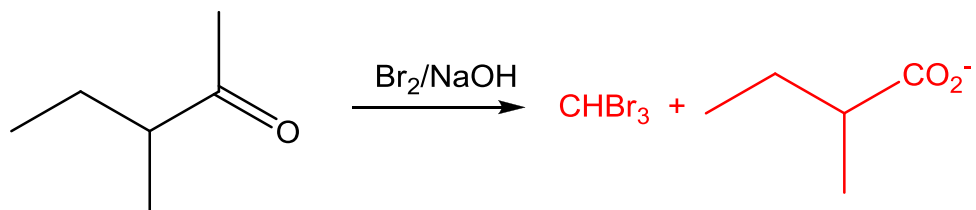
f.



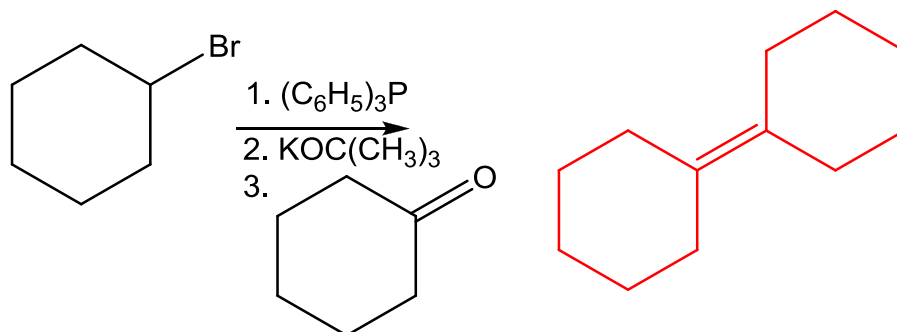
g.



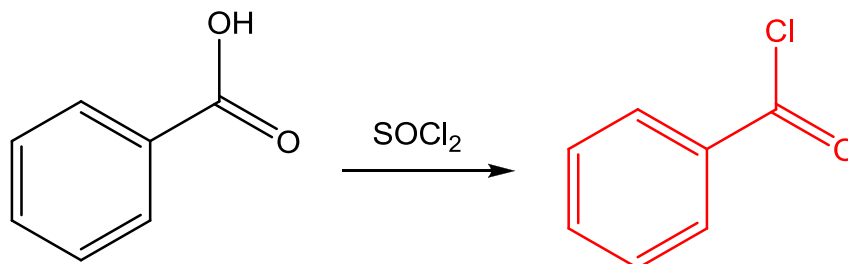
h.



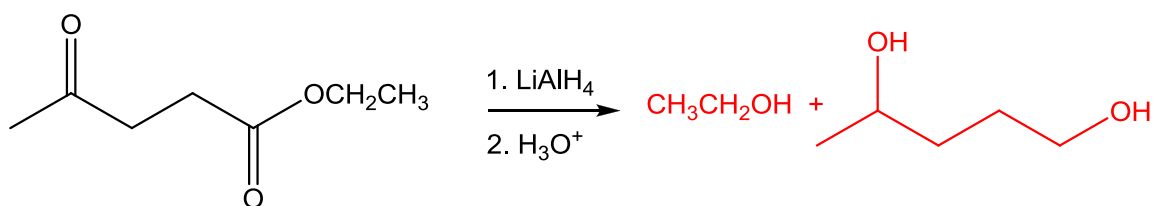
i.



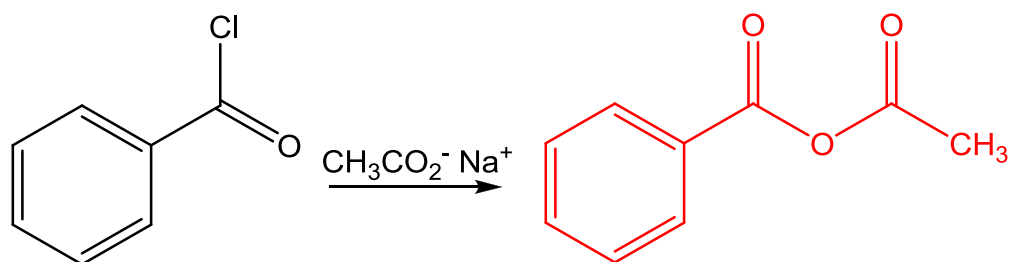
j.



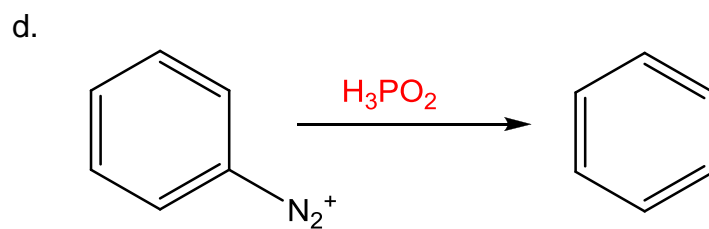
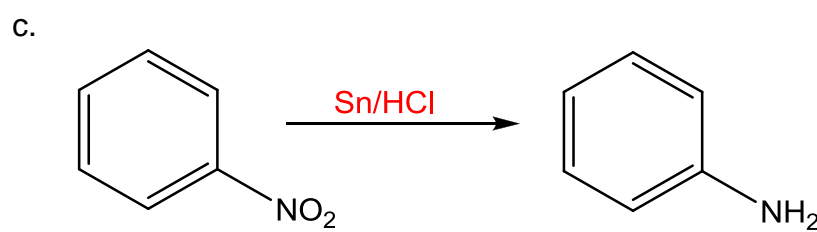
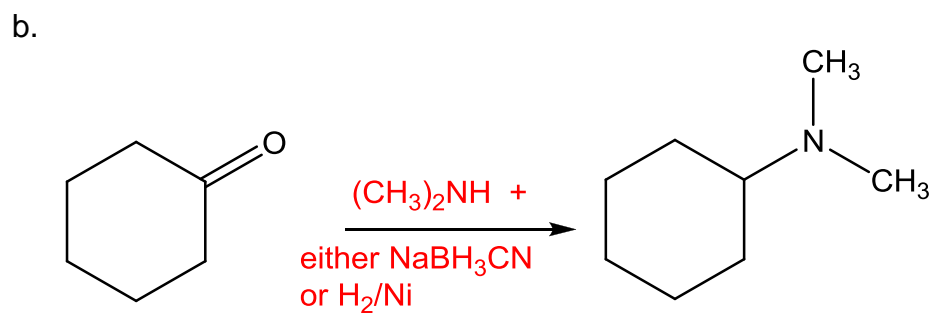
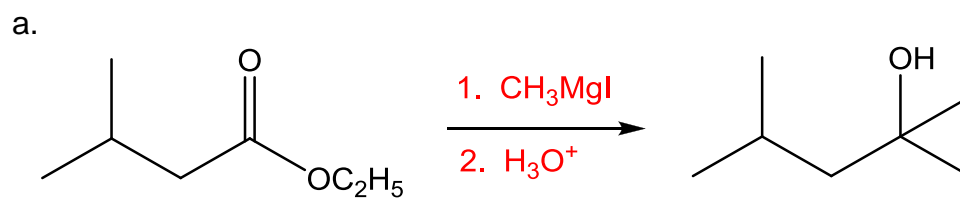
k.



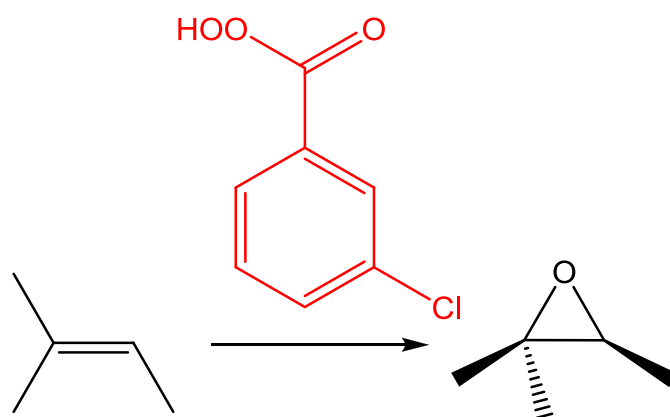
l.



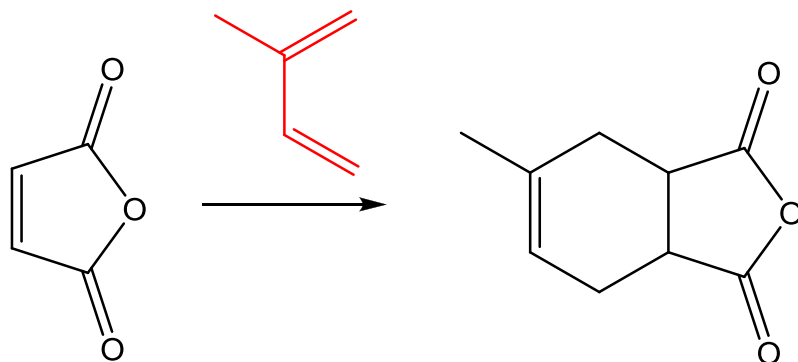
5. What reagent(s) would you use to effect ten (10) of the following conversions? (30 points)



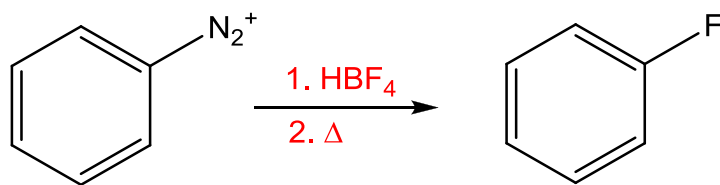
e.



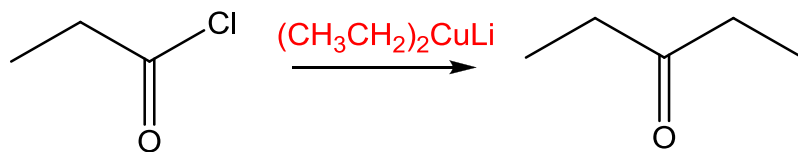
f.



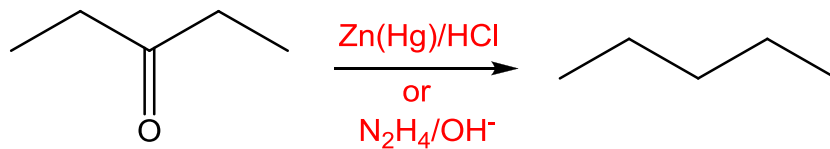
g.



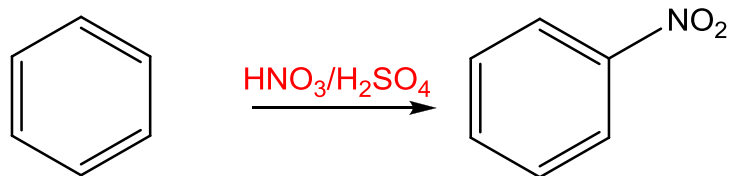
h.



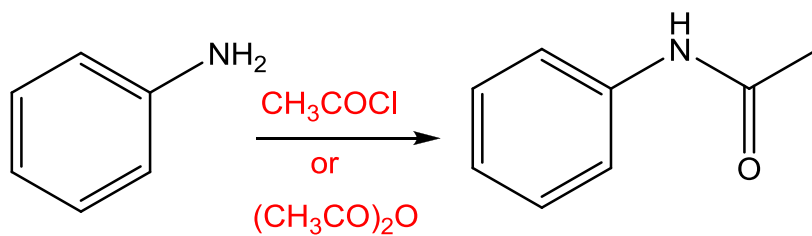
i.



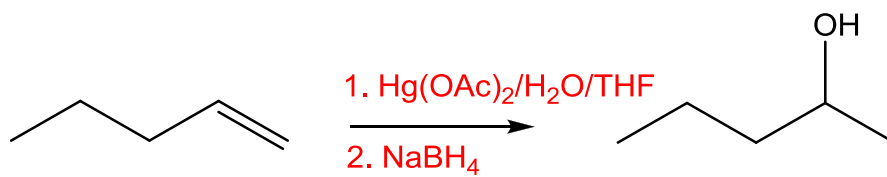
j.



k.

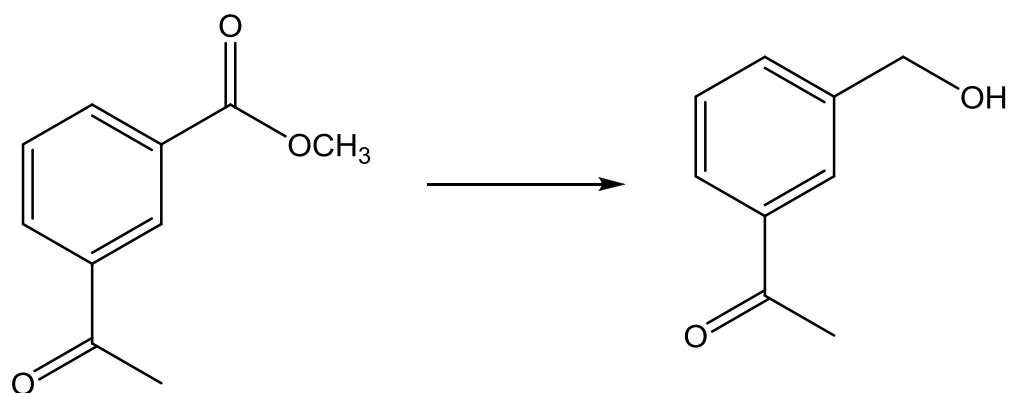


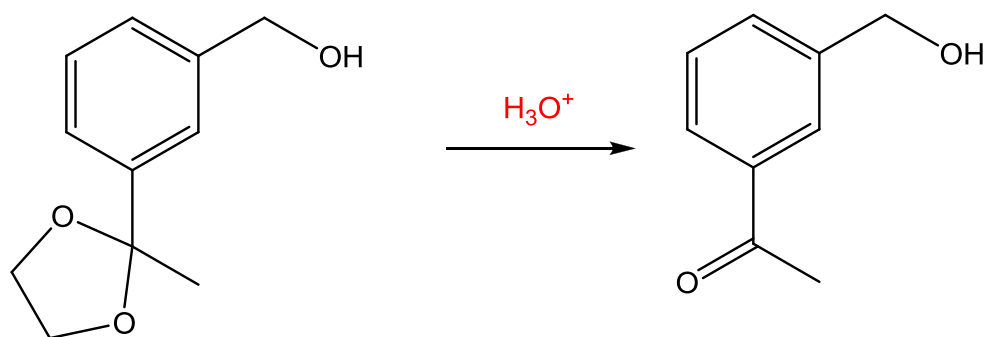
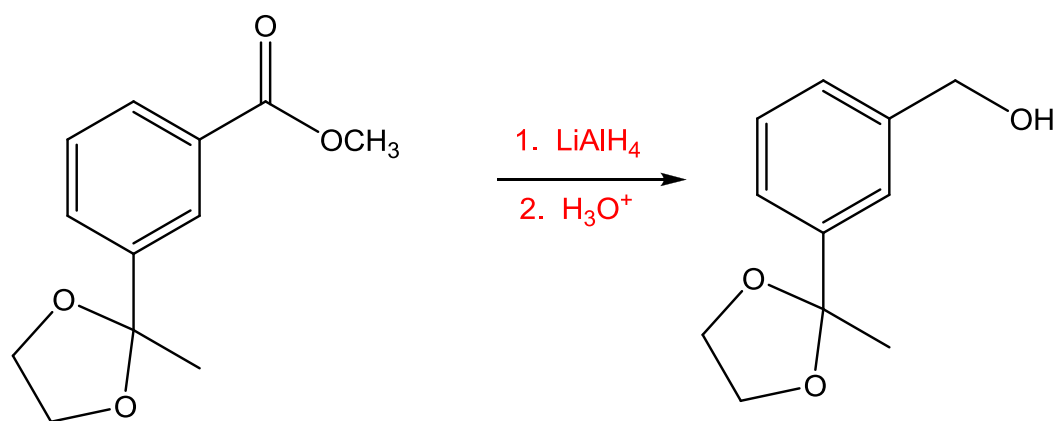
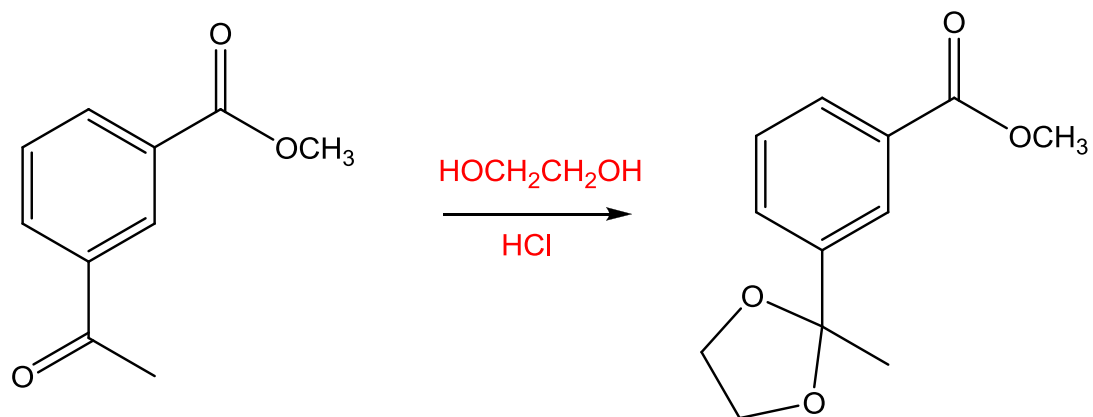
l.



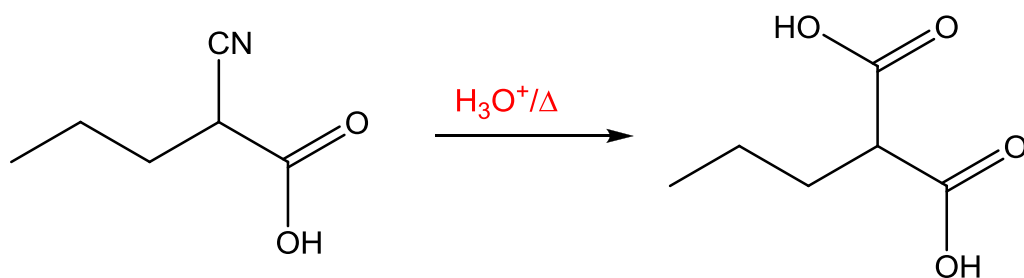
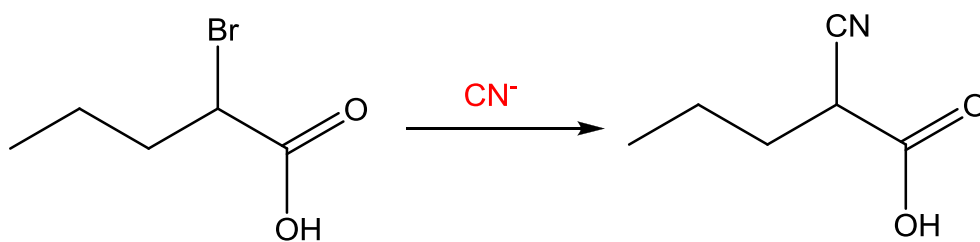
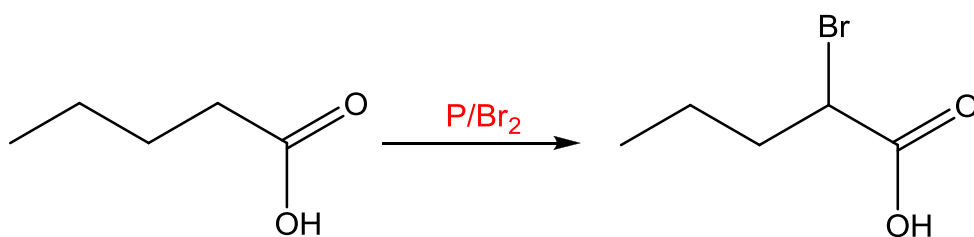
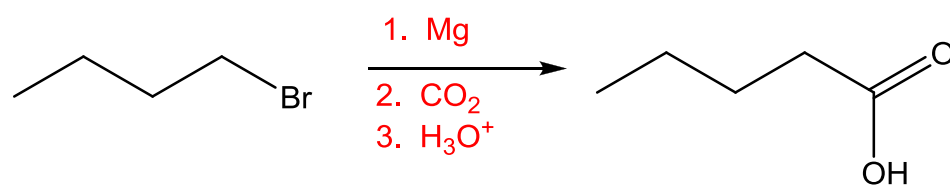
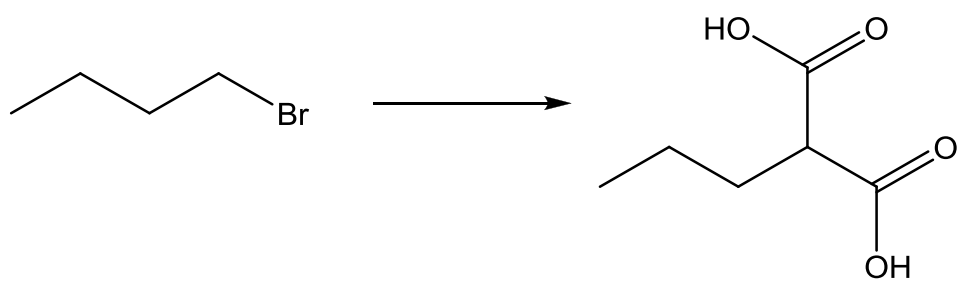
6. Provide synthetic pathways for three (3) of the following transformations (30 points):

a.

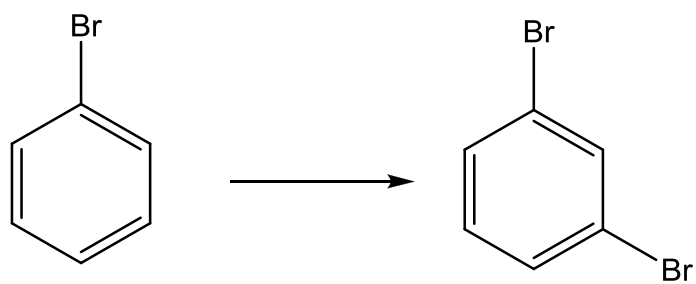


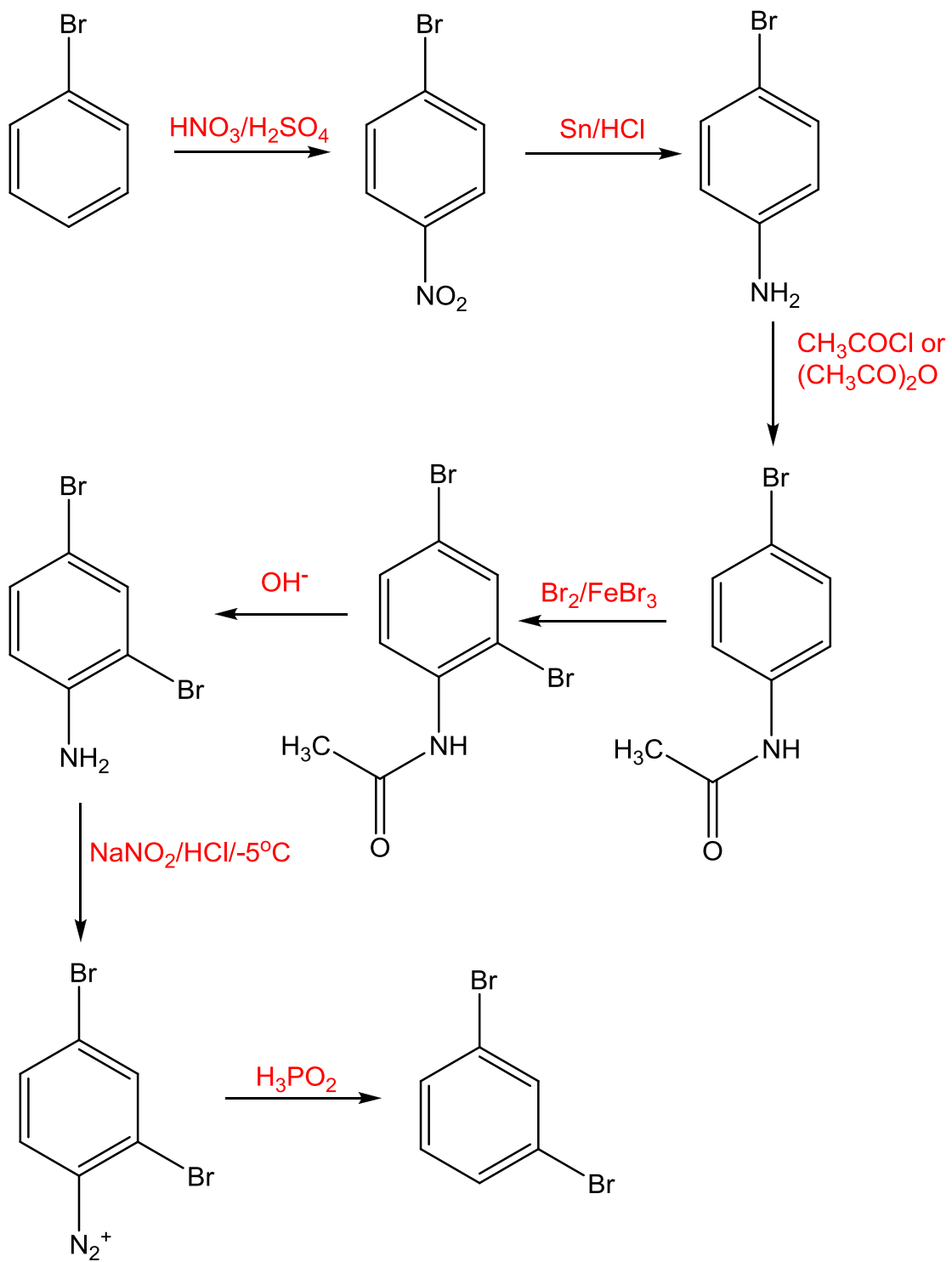


b.

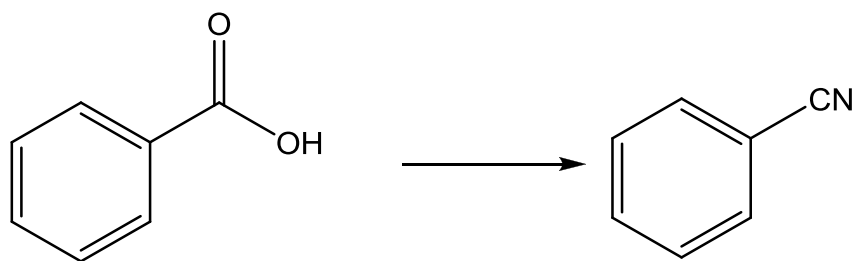


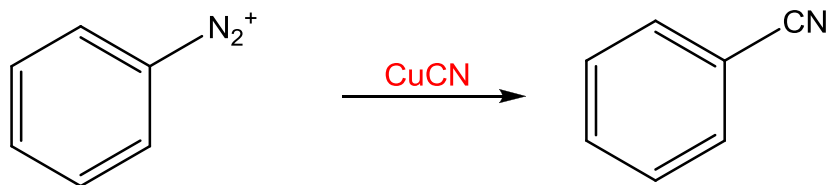
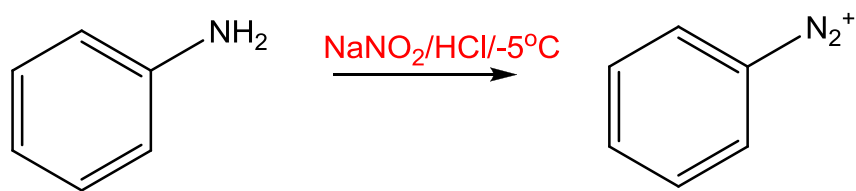
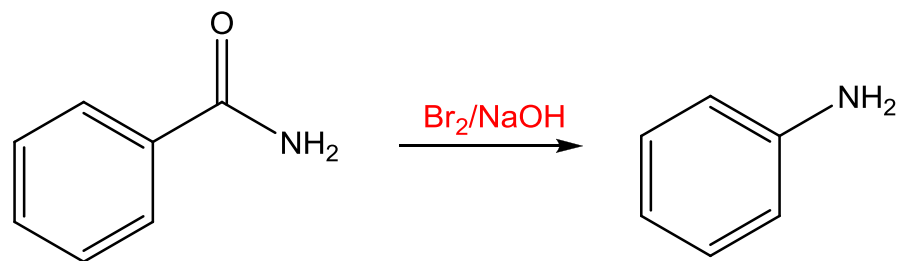
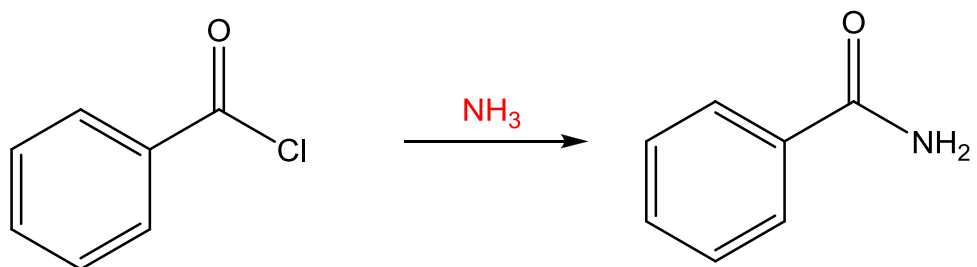
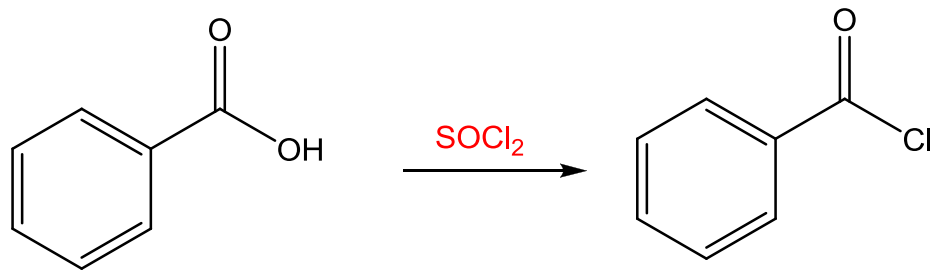
c.





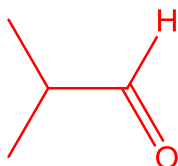
d.



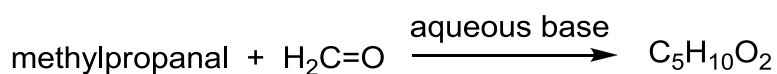


7. Pantothenic acid, a B vitamin, is an important intermediate in the synthesis of coenzyme A and can be synthesized from methylpropanal.

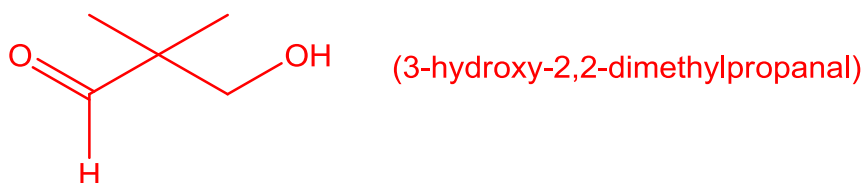
a. Draw the structure of methylpropanal. (3 points)



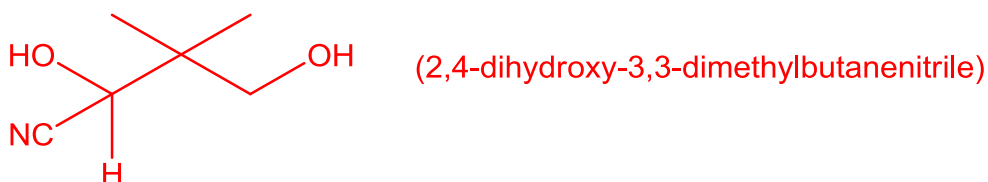
b. The first step involves the following reaction:



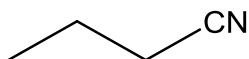
Draw the product of this crossed aldol reaction. (3 points)



c. Reaction of this product with HCN gives $\text{C}_6\text{H}_{11}\text{NO}_2$. Give the structure of this new compound. (3 points)

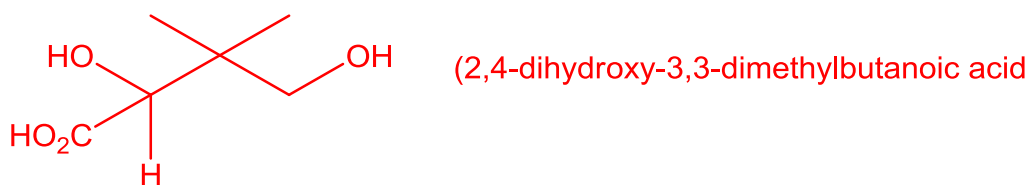


d. Name the following compound: (3 points)

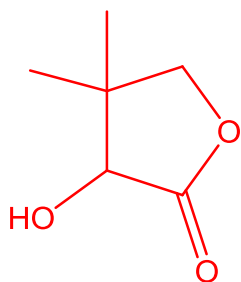


butanenitrile

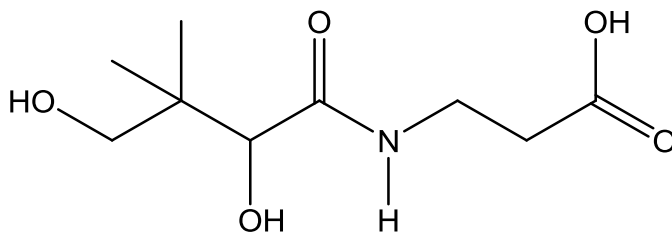
e. Heating the product from part c with aqueous acid gives $\text{C}_6\text{H}_{12}\text{O}_4$. Give the structure of this compound. (3 points)



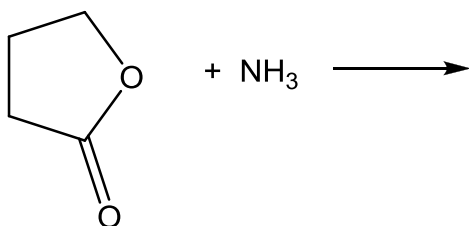
- f. Compound $C_6H_{12}O_4$ reacts to form a γ -lactone, $C_6H_{10}O_3$. Draw the structure of the lactone. (3 points)

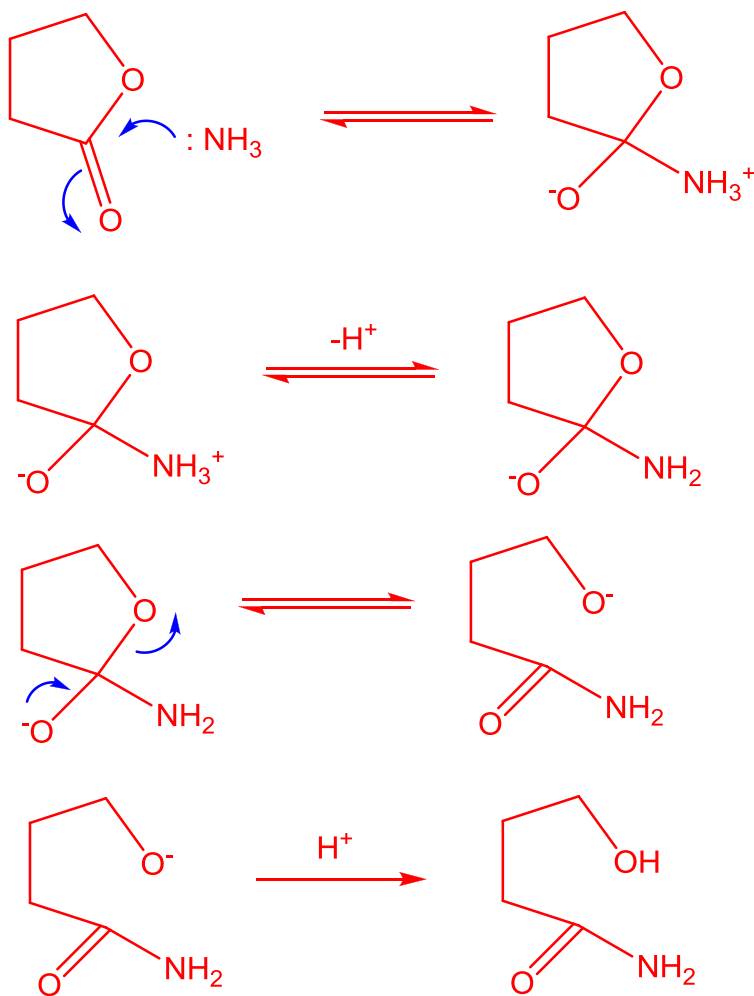


- g. The lactone then reacts with $H_2NCH_2CH_2CO_2H$ to give pantothenic acid:



Using the following structures to represent the lactone and the amine, draw the mechanism of this reaction. (8 points)



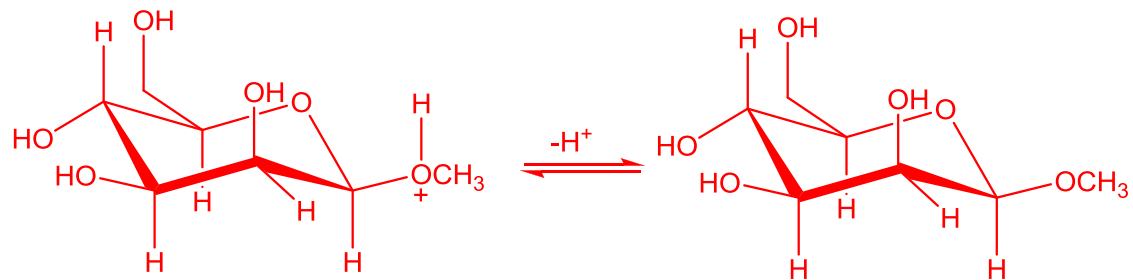
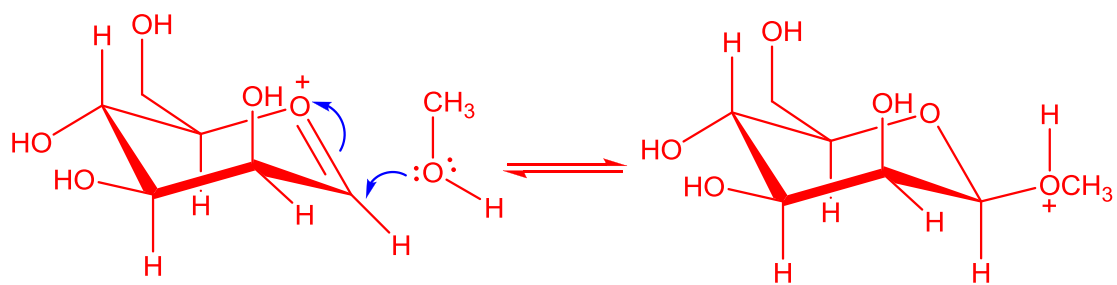
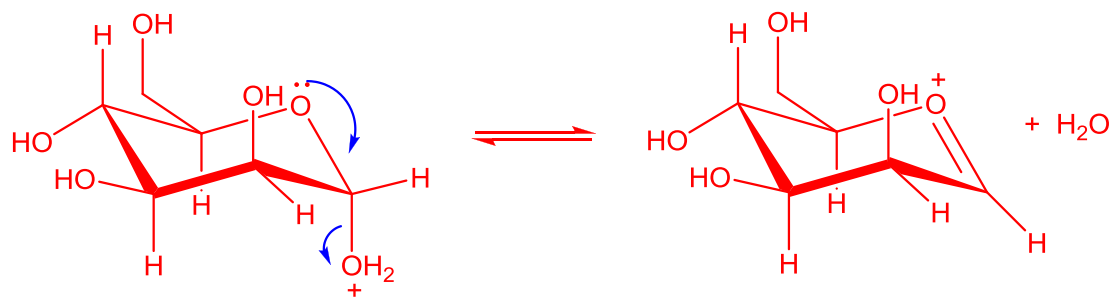
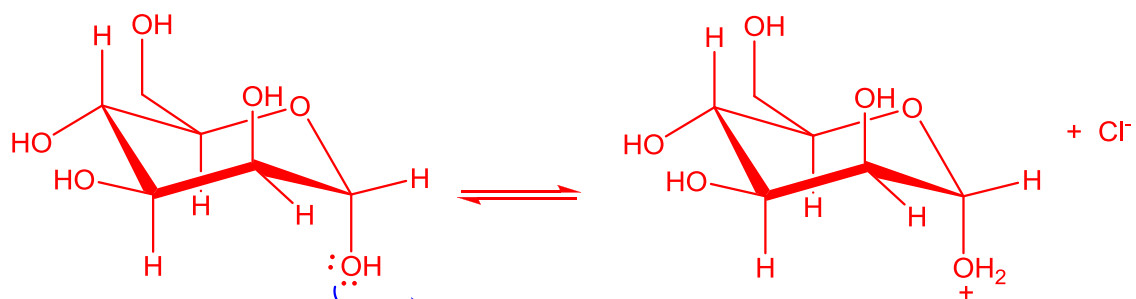
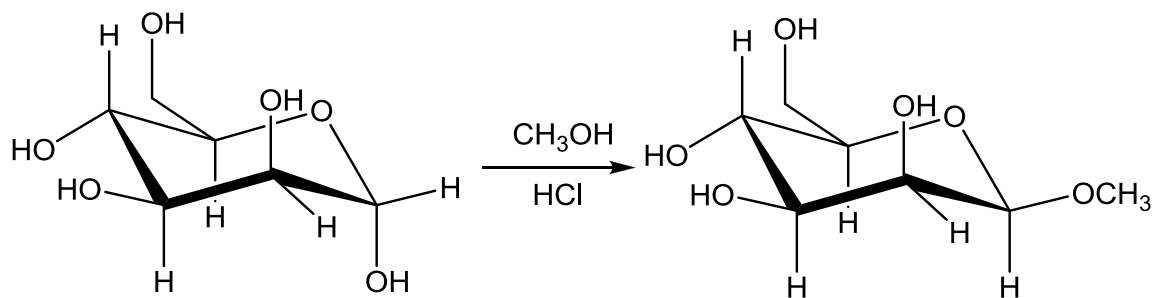


8.

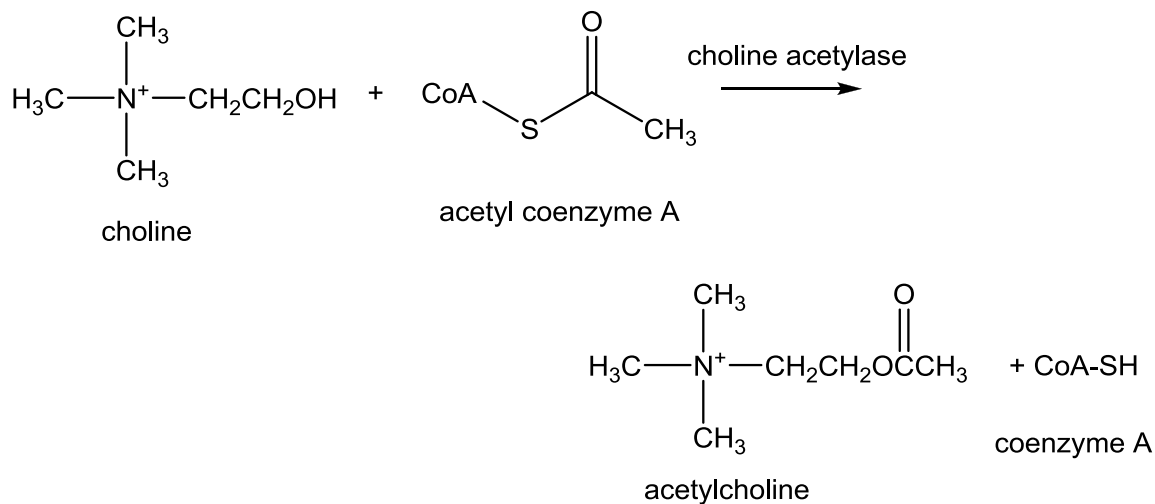
a. What is meant by the term anomer? (3 points)

Stereoisomers which only differ in the configuration about the hemiacetal carbon are called **anomers**.

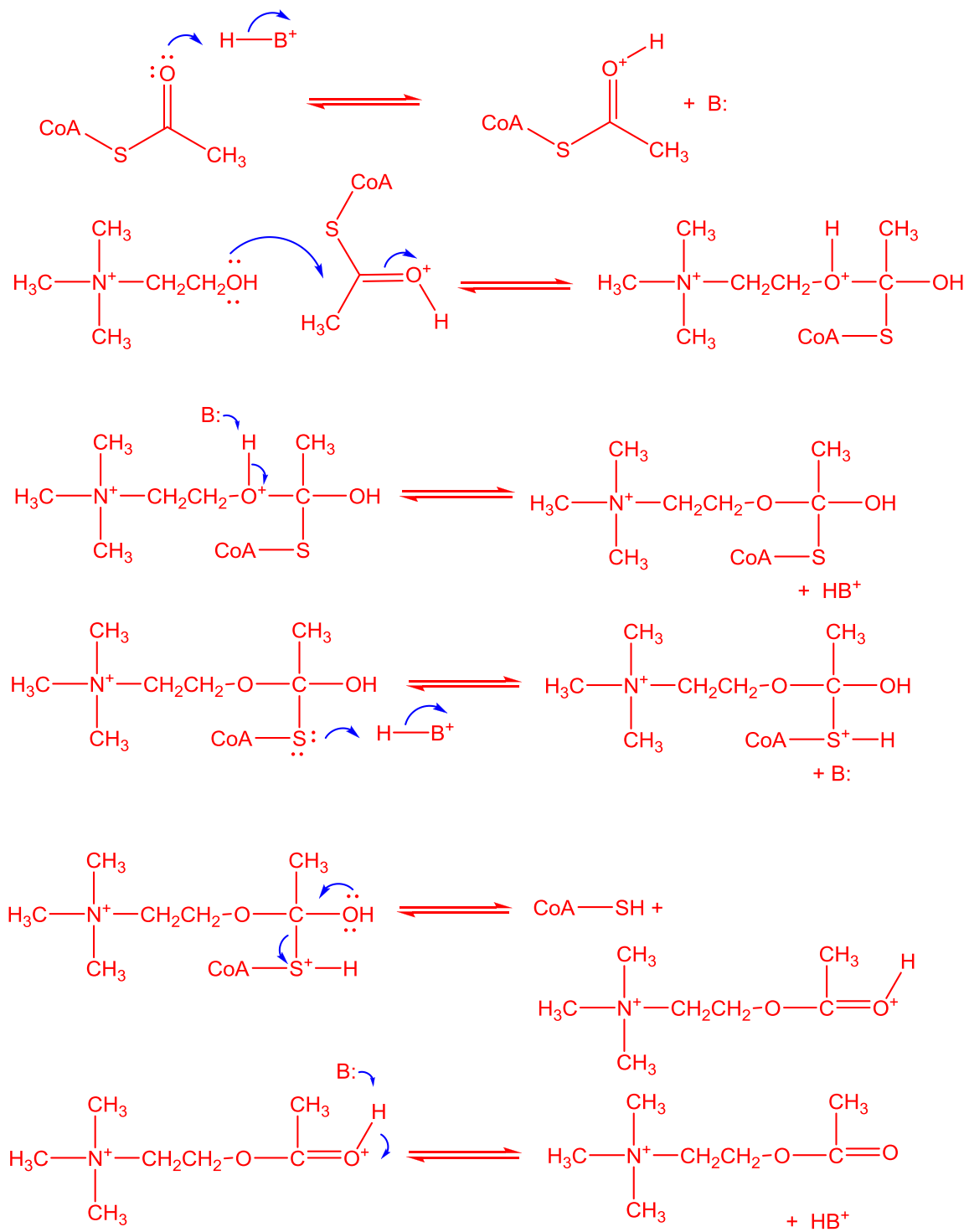
b. α -D-Mannopyranose reacts with methanol in the presence of a small amount of HCl to give methyl β -D-mannopyranoside according to the following equation. Propose a mechanism that accounts for this transformation. (8 points)



9. Thioesters are compounds in which a sulphur atom has replaced the alkoxy oxygen of an ester. Acetyl coenzyme A is an important thioester and is central to the following reaction that synthesizes acetylcholine at the nerve synapses:



Assuming that choline acetylase is a good source of protons, HB^+ , and of bases to remove protons, B^- , write a complete mechanism for this reaction. Don't forget to use curved arrows. (12 points)



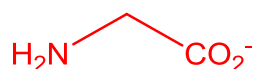
10. a. Explain what is meant by the term essential amino acid. (1 point)

These are the amino acids that higher animals cannot synthesize and must obtain from their diet.

- b. Explain the term isoelectric point. (1 point)

The pH at which the concentration of the zwitterion is at its maximum.

- c. The isoelectric point of glycine is 6.0. What is the structure of this acid at pH 10.0? (2 points)



- d. Complete hydrolysis of a decapeptide followed by an analysis of the amino acids produced shows that the peptide contains 2 Ala, 1 Arg, 1 Cys, 1 Glu, 1 Gly, 1 Leu, 1 Lys, 1 Phe, and 1 Val fragments. Edman degradation yields a lysine phenylthiohydantoin. Partial hydrolysis yields the following peptides:

Cys-Glu-Leu
 Gly-Arg-Cys
 Leu-Ala-Ala
 Lys-Val-Phe
 Val-Phe-Gly

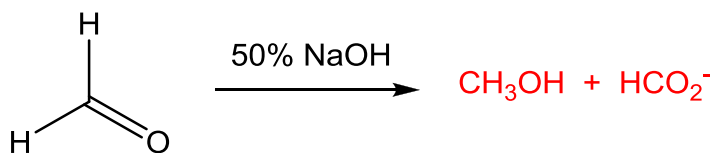
What is the sequence of amino acids in this peptide? (3 points)

Lys-Val-Phe-Gly-Arg-Cys-Glu-Leu-Ala-Ala

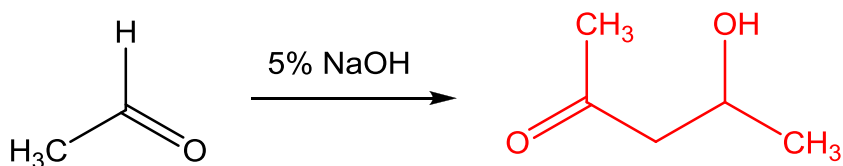
11. Pentaerythritol, a compound used to make explosives, can be prepared by reacting ethanal with methanal in a basic solution. The reaction successively yields three compounds of formulae $\text{C}_3\text{H}_6\text{O}_2$, $\text{C}_4\text{H}_8\text{O}_3$, and $\text{C}_5\text{H}_{10}\text{O}_4$. Compound $\text{C}_5\text{H}_{10}\text{O}_4$, in the presence of concentrated NaOH, is converted into two compounds, pentaerythritol, $\text{C}_5\text{H}_{12}\text{O}_4$, and a sodium salt, $\text{C}_5\text{H}_9\text{O}_5\text{Na}$.

- a. Give the structure(s) of the principle organic products of the following reactions: (6 points)

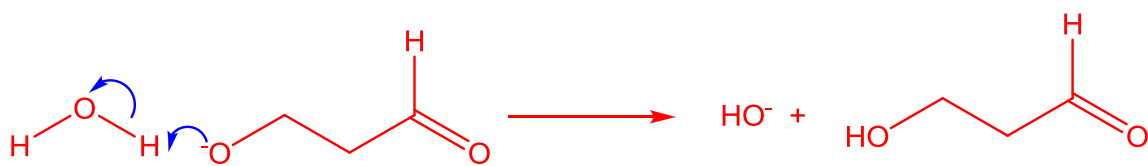
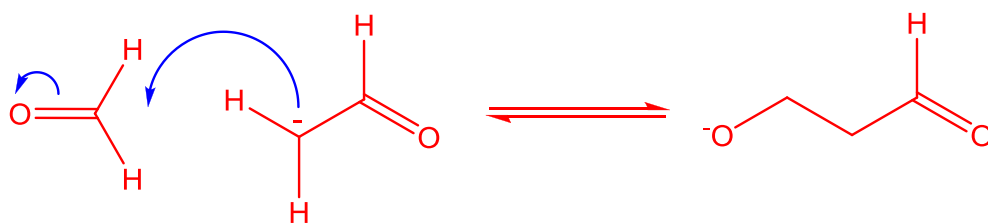
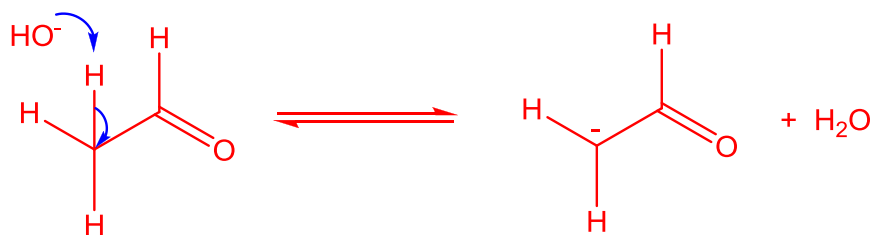
i.



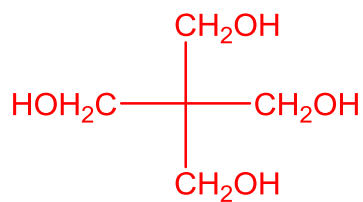
II.



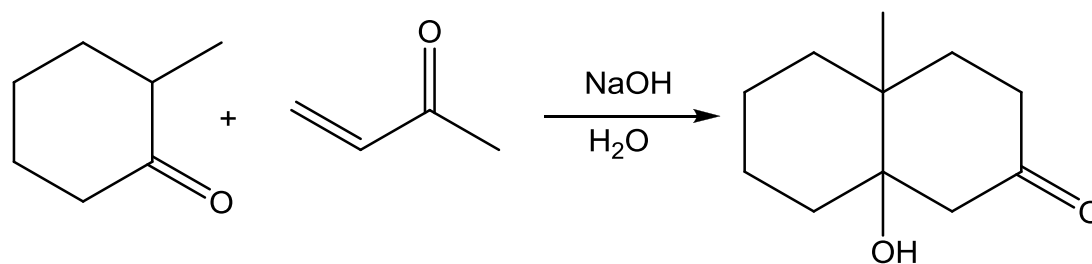
b. Draw the mechanism for the formation of compound $\text{C}_3\text{H}_6\text{O}_2$ via the reaction of ethanal and methanal in a basic solution. (6 points)

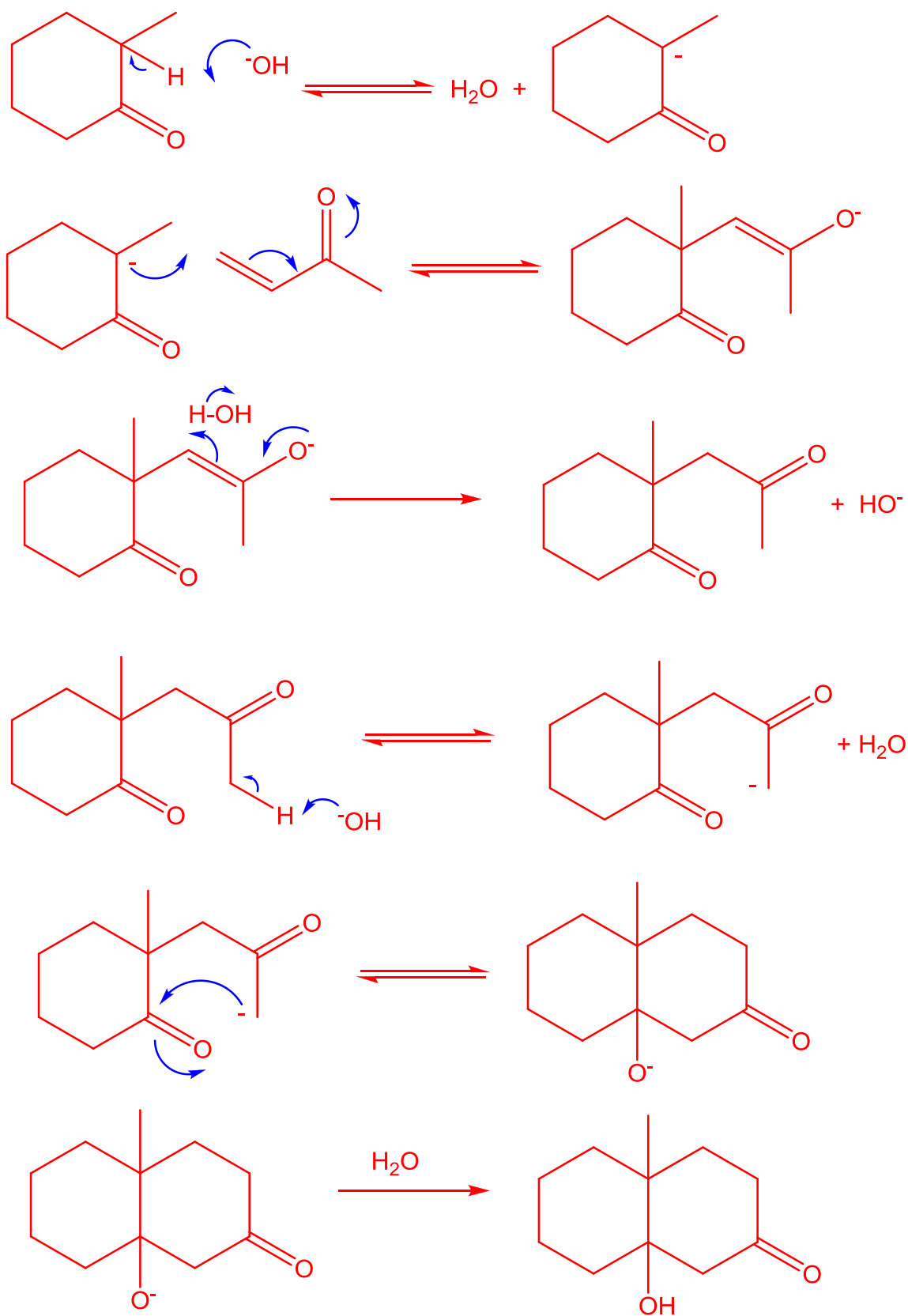


c. Draw the structure of pentaerythritol? (3 points)

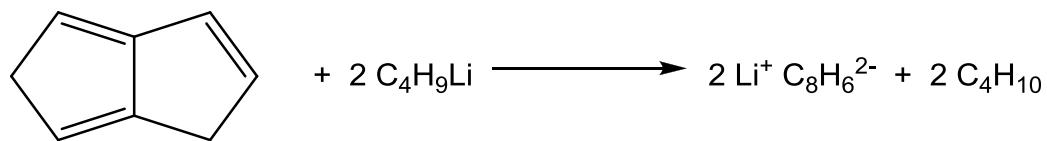


- d. The Robinson Ring Annulation is a process that fuses a cyclohexanone ring onto a cyclic ketone. Propose a mechanism for the following example of such an annulation: (12 points)

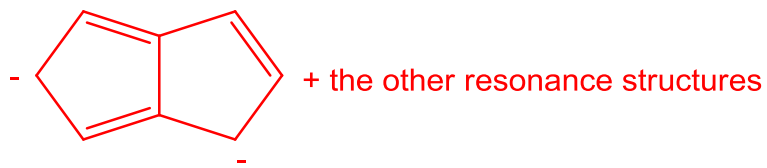




12. In 1964 Katz obtained a stable dianion, $C_8H_6^{2-}$, using butyllithium as the base:



Propose a reasonable structure for the product and explain why it is stable. (6 points)



The dianion is aromatic as it is cyclic, planar, and has 10π electrons delocalised over the ring system.