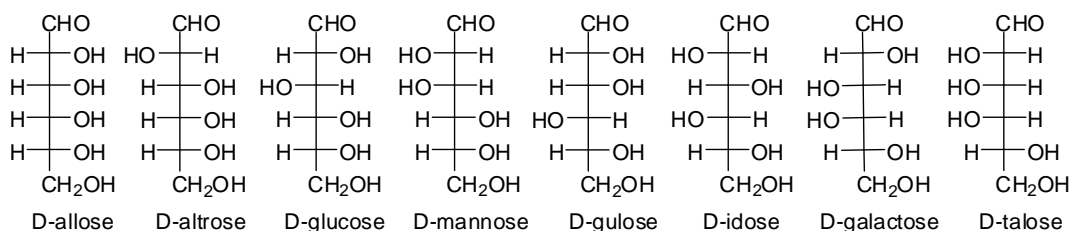


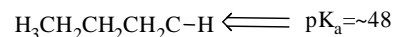
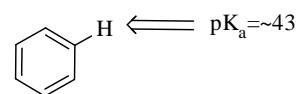
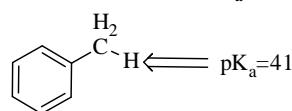
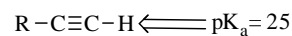
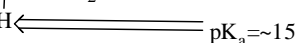
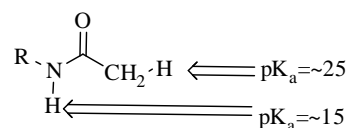
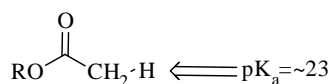
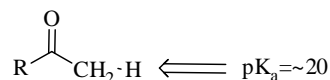
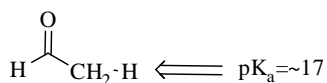
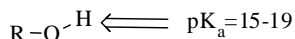
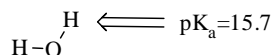
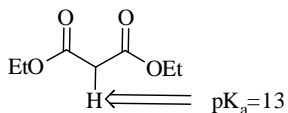
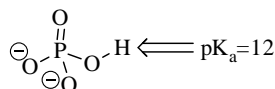
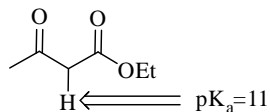
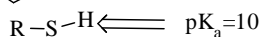
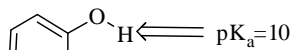
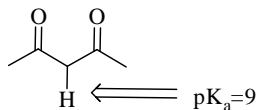
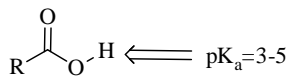
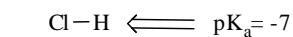
The examination has six questions on four pages. The point values for each question are found with the question. Partial credit will be given where appropriate.

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics.

In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Don't forget to include lone pairs of electrons and formal charges when appropriate.



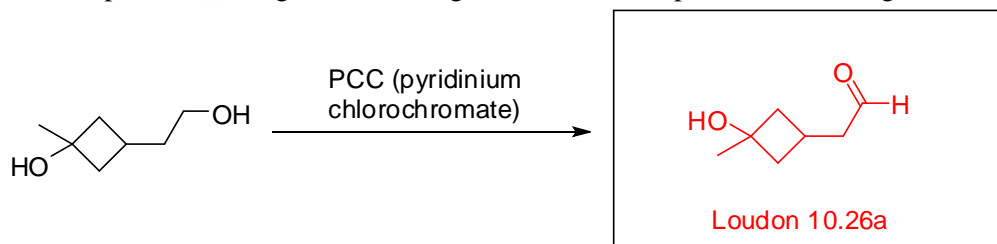
pK_a information



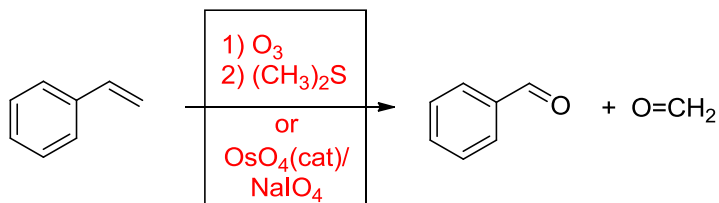
Note: R=alkyl

1. Provide the product(s), reagents or starting materials, to complete the following reactions. (4 pts. each)

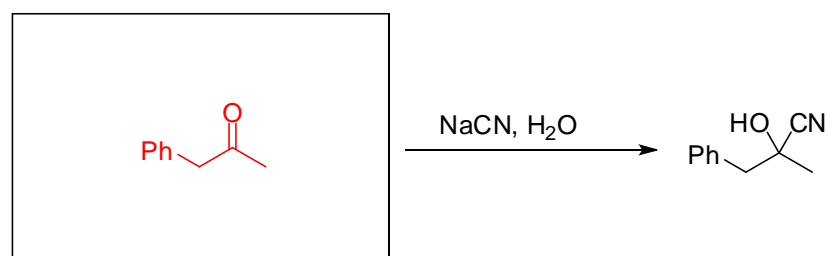
a)



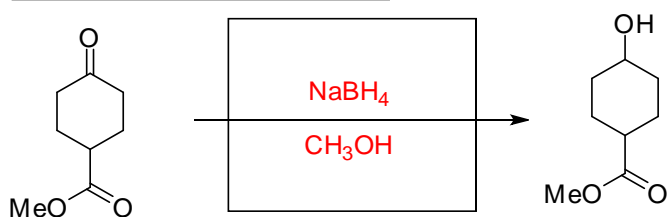
b)



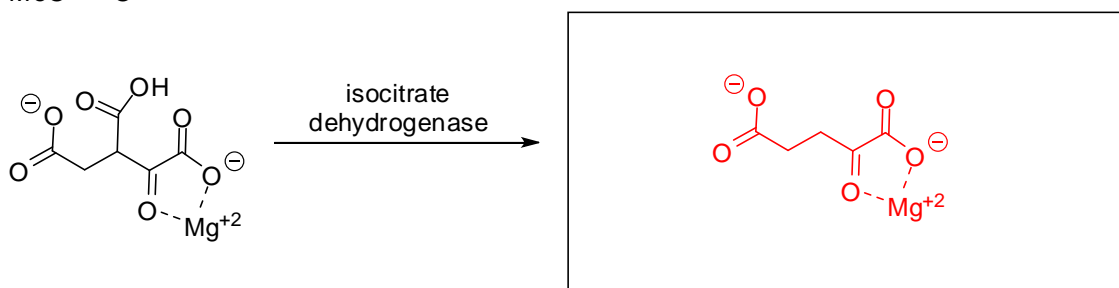
c)



d)

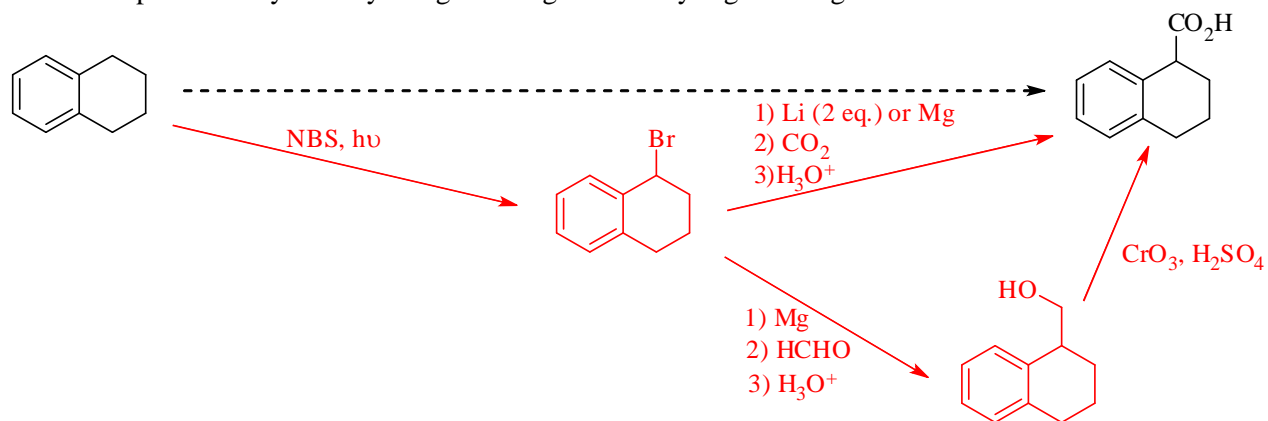


e)

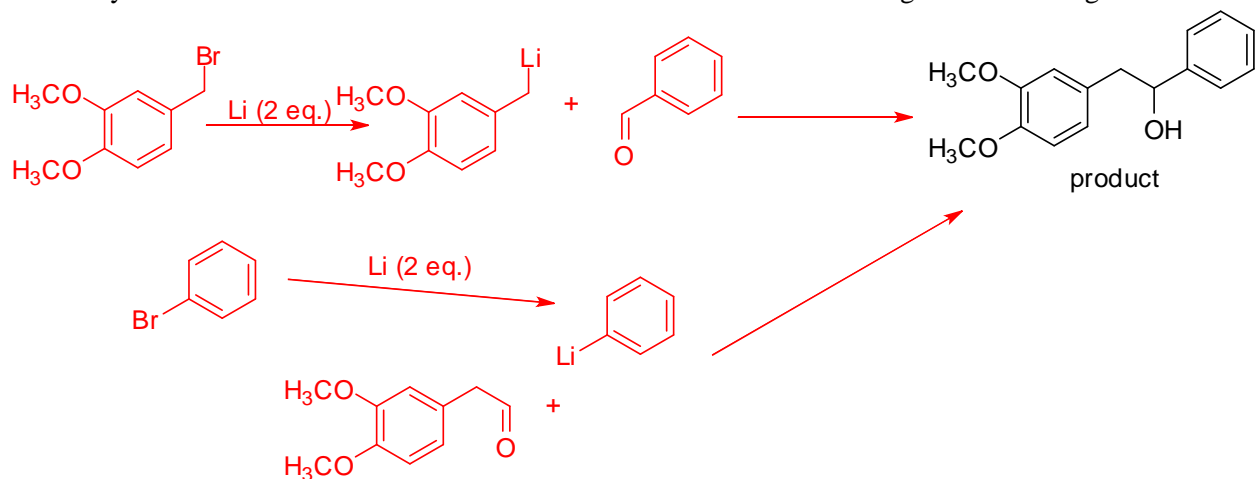


2. Synthesis questions. (8 pts. each)

a) Suggest a series of reactions to take the starting material on the left to the product on the right. This will require two or three steps. You may use any inorganic reagent and any organic reagent.



b) Show both possible combinations of organolithium reagents and carbonyl starting materials to make the following secondary alcohol. Also show the reaction that would be used to form the organolithium reagent.



3. The common tetrasaccharide core of all human blood groups (A, B and O) has the structureshown below. Answer the questions about this structure based on your understanding of carbohydrates. In all cases you should be as precise as possible to earn full credit.(8 pts.)

a) What is the glycosidic linkage between **B** and **C**?

β -1 \rightarrow 3

b) What is saccharide **A**?

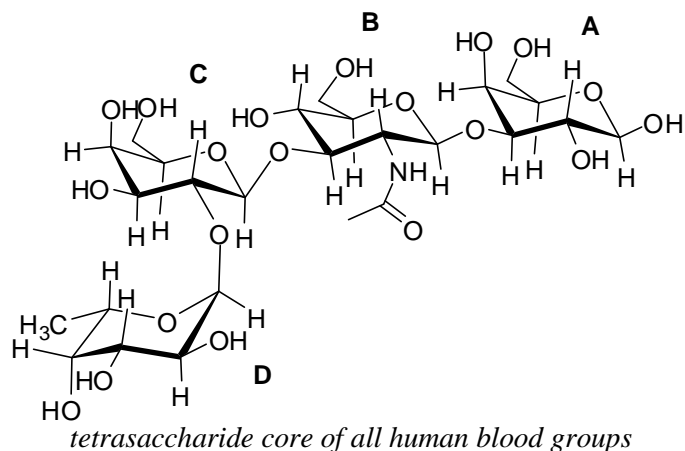
β -D-galactopyranose

c) What is saccharide **B**?

N-acetyl- β -D-glucosamine (pyranose form)

d) There are two unusual structural aspects of sugar **D** relative to our reference sugar D-glucopyranose. What are they?

D is an L sugar and it is a C-6 deoxy sugar.

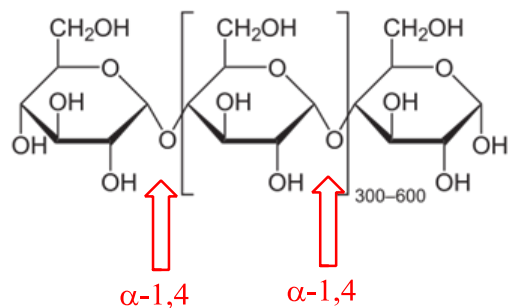


6-deoxy-L-Gal-(α -1 \rightarrow 2)-D-Gal-(β -1 \rightarrow 3)-N-acetyl-D-GlcN (β -1 \rightarrow 3)- β -D-Gal

note: 6-deoxy-L-Gal is also called fucose

4. One component of starch is amylose. Amylose is a polymer of α -D-glucopyranose with 1,4glycosidic linkages. (10 pts.)

a) Draw a Haworth projection of amylose based on this information. Although amylose typically has 300-600 monomers linked together, I'm a nice guy and I'm only asking you to draw three monomers of the polymer.



all saccharides are α -D-glucopyranose
amylose

b) Circle all the terms that apply to amylose's sugar monomers

(i) ketose

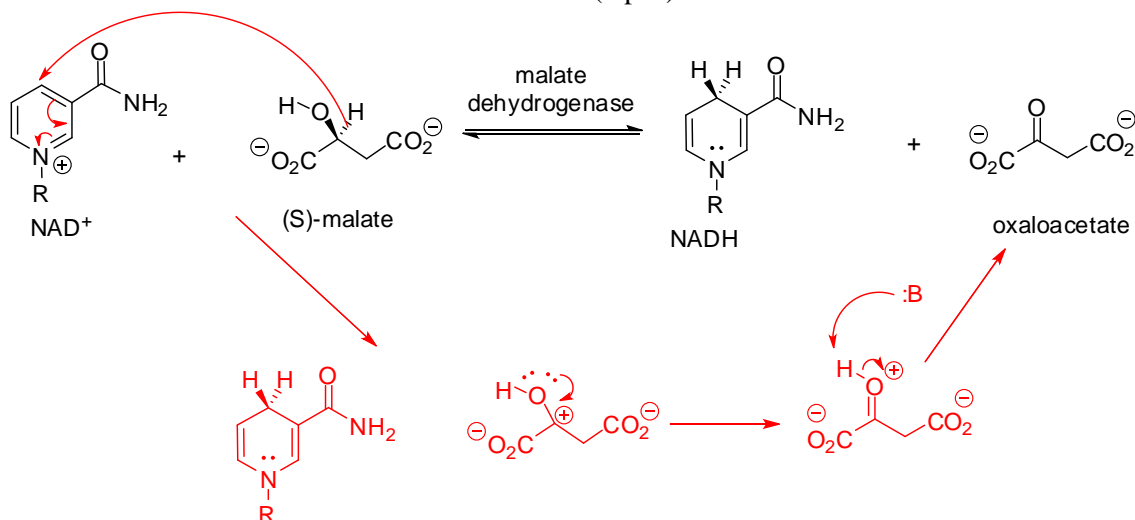
(ii) aldose

(iii) pentose

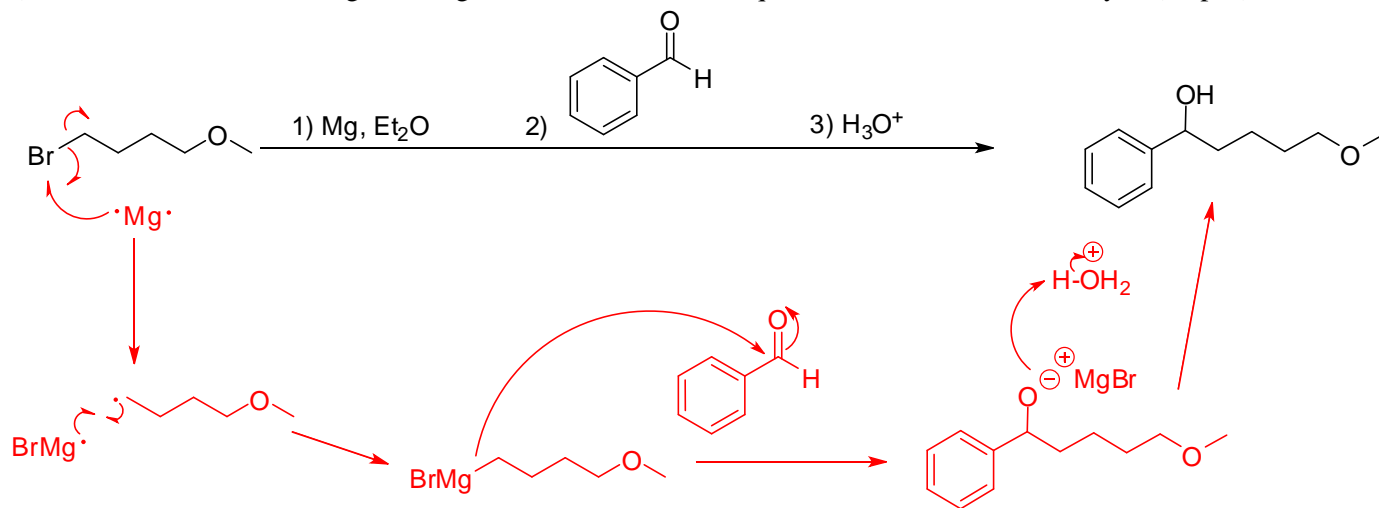
(iv) hexose

5. Draw mechanisms for the following three reactions. Show electron flow arrows and all intermediates. You do NOT need to draw any resonance forms, but you should include all formal charges where appropriate.

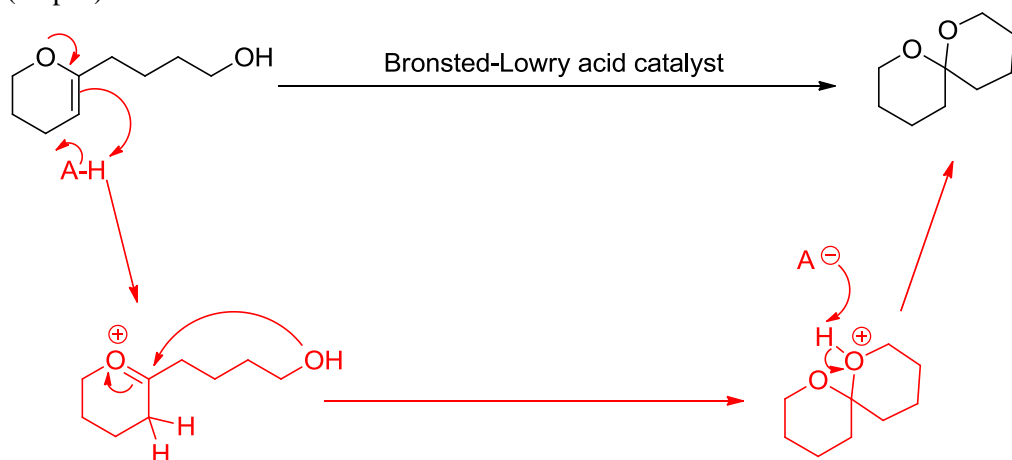
a) The NAD^+ facilitated conversion of malate to oxaloacetate. (6 pts.)



b) The mechanism of the Grignard reagent formation and subsequent reaction with benzaldehyde. (10 pts.)



c) The mechanism of the following spiroacetalization reaction, which was just reported in the journal *Nature* last week. (10 pts.)



“Asymmetric spiroacetalization catalysed by confined Brønsted acids” Ilija Čorić and Benjamin List, *Nature* 2012, 483, 315–319.

6. Circle the starting material that would react faster with the reagents shown and provide the product of this reaction in the box to the right. (5 pts. each)

