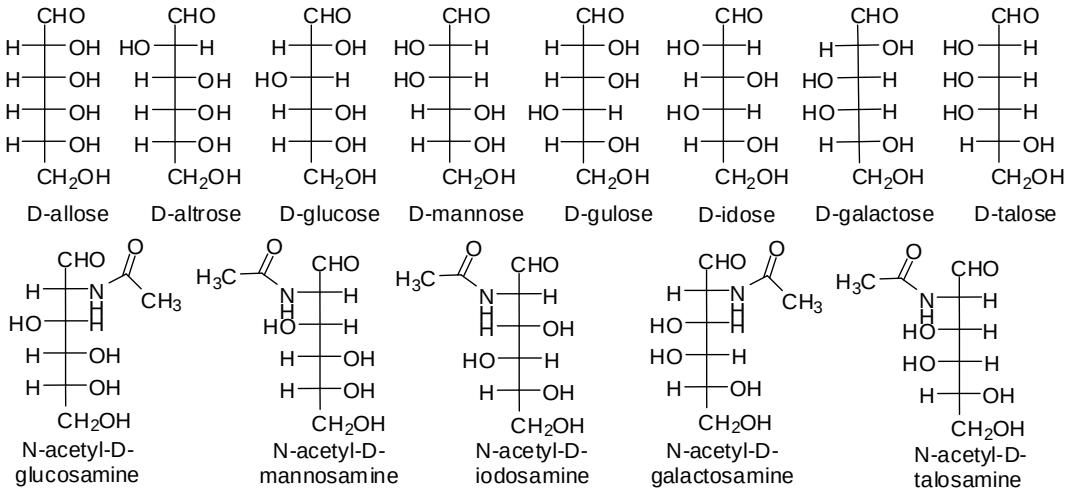
Organic Chemistry 2
Second Examination
March 26, 2010
Prof. Malachowski

Name:_____Jody Williams_____

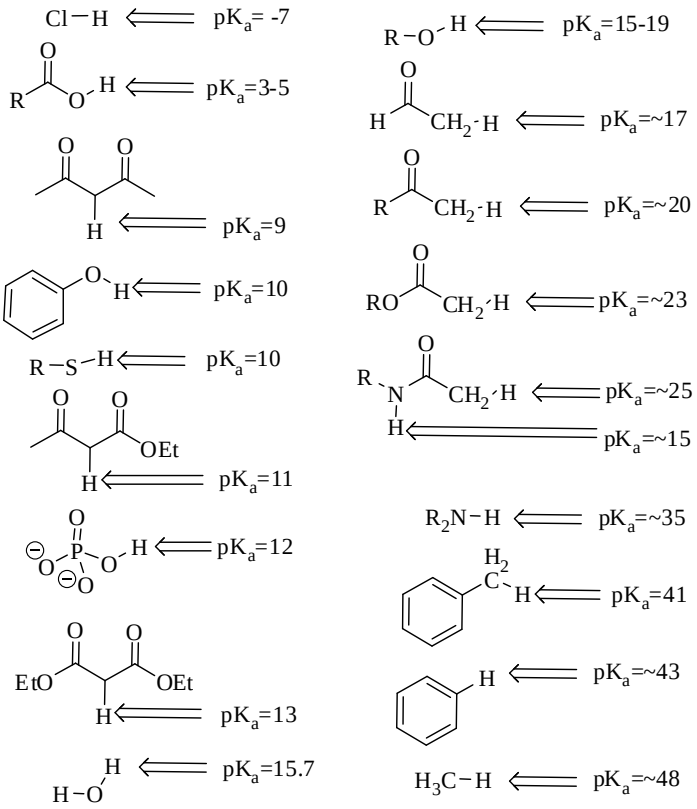
The examination has eight questions on five pages. The point values for each question are found with the question. Partial credit will be given where appropriate.

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. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include lone pairs of electrons and formal charges when appropriate.



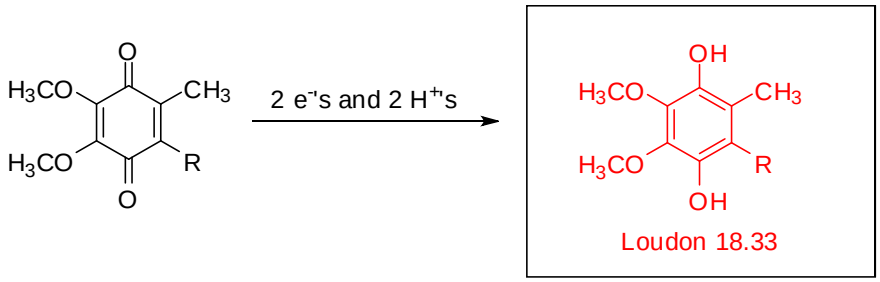
pK_a information



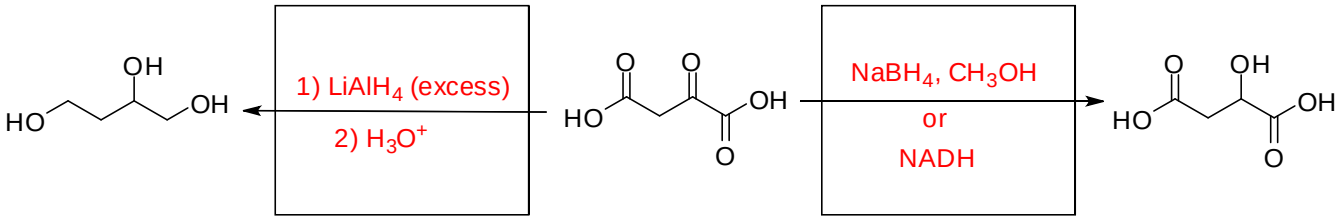
Note: R=alkyl

1. Provide the necessary information, product(s), reagents or starting materials, to complete the following reactions. (15 pts.)

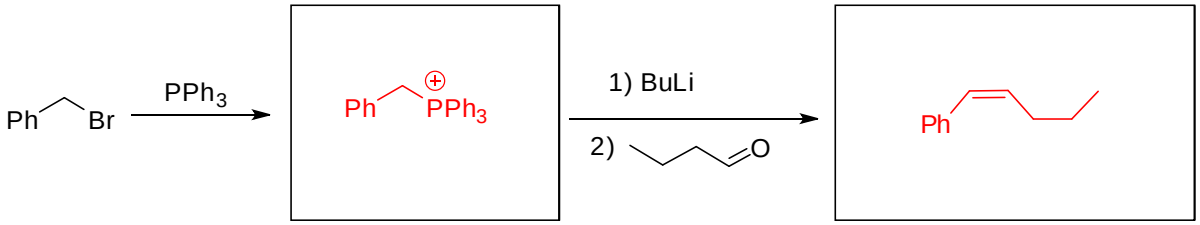
a)



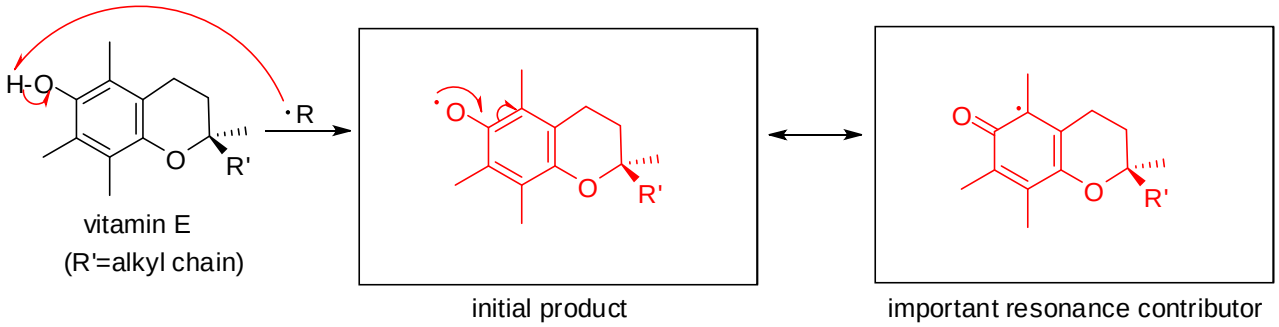
b)



c)



2. Provide the product of the following reaction between vitamin E and a free radical species, ˙R. Show curved electron flow arrows to get to the initial product. Show an important resonance form of the initial product in the next box. Draw electron flow arrows indicating how the initial product is transformed into this important resonance contributor. (7 pts.)



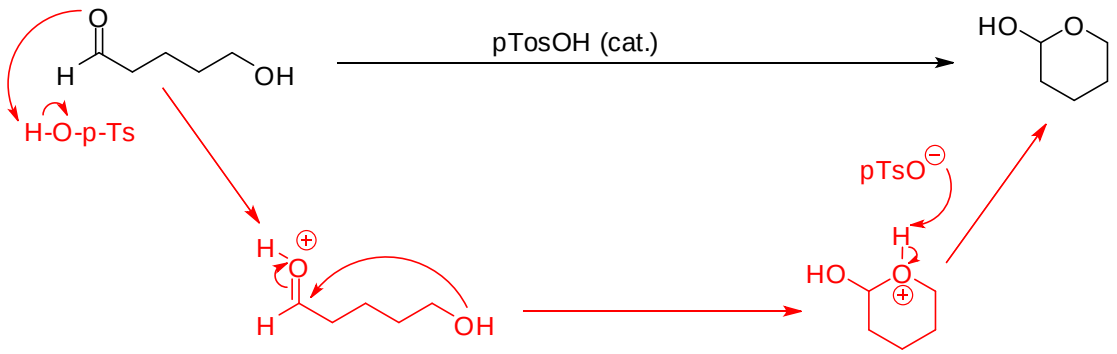
3. Provide two reasons why ketones react more slowly and to a lesser extent with nucleophiles than aldehydes. (4 pts.)

Ketones are more sterically hindered with two alkyl groups around the electrophilic carbon versus just one carbon and one hydrogen for aldehydes. Secondly, ketones are less electrophilic due to the two alkyl groups which donate more electron density through hyperconjugation to the ketone carbonyl carbon than the hydrogen and alkyl group donate to the aldehyde carbonyl carbon.

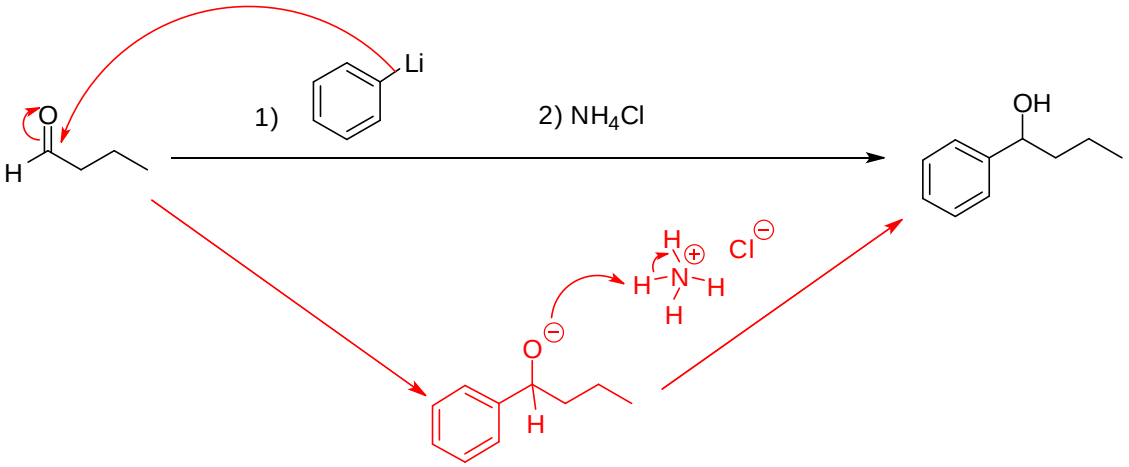
/26 pts.

4. Draw the mechanism of the three reactions shown below. You do NOT need to include resonance structures. You should include all formal charges and curved electron flow arrows. You may use general acids, H-A, and general bases, B:, as necessary. (8 pts. each)

a)



b)



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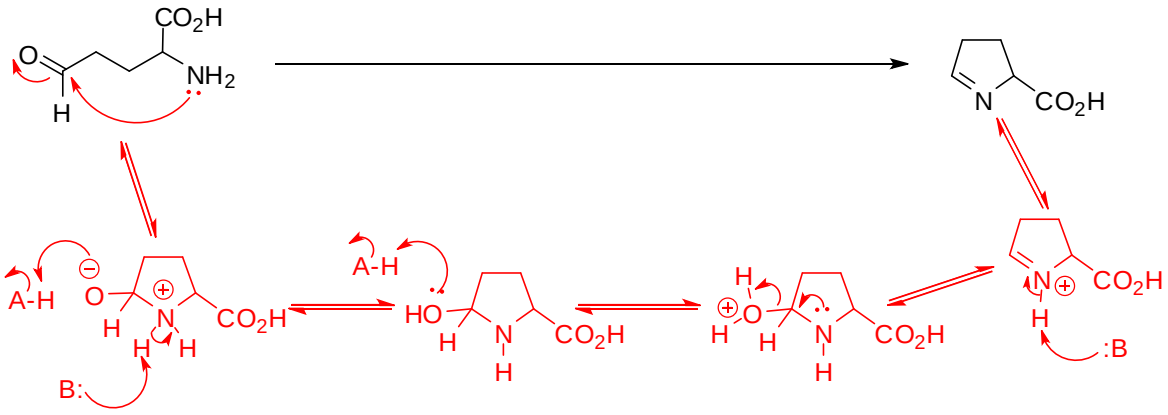
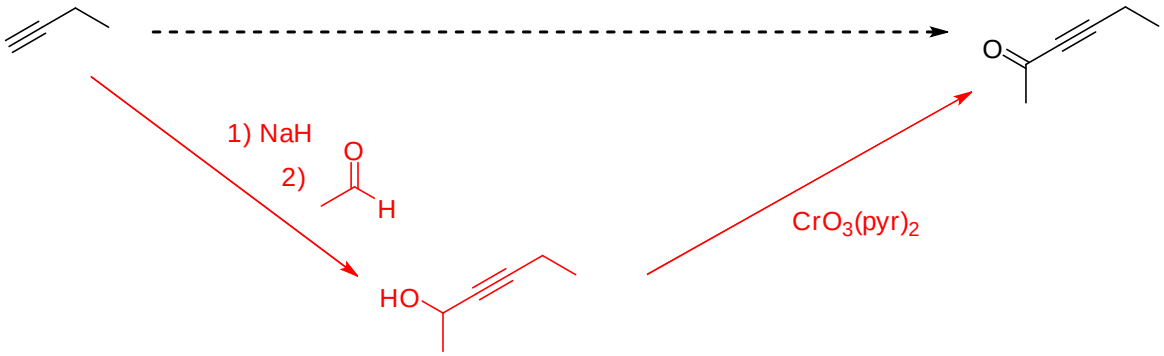


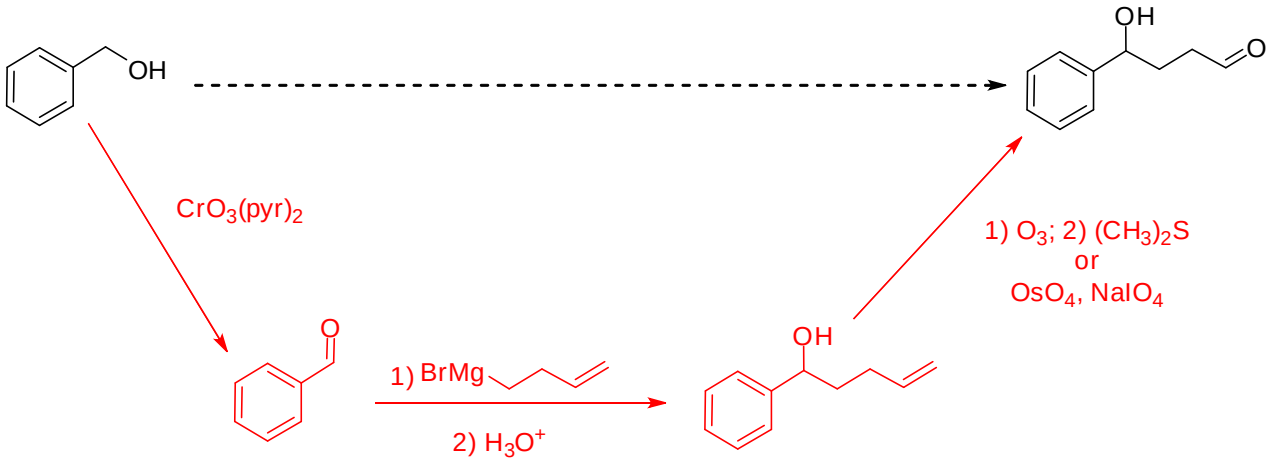
/24 pts.

5. 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 of seven carbons or less. (7 pts. each)

a)



b)



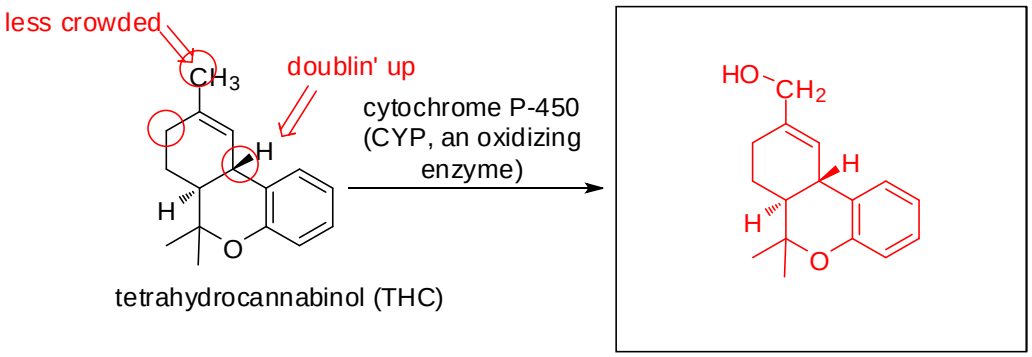
6. Once a foreign chemical enters your body, there is a concerted effort to remove it. One of the most common pathways to remove foreign chemicals is through oxidation of an allylic or benzylic position by the liver enzyme cytochrome P-450 (CYP). Tetrahydrocannabinol (THC), the active ingredient in marijuana, is one such foreign chemical and it has a variety of allylic and benzylic positions where CYP can react. (10 pts.)

a) Identify all the allylic and benzylic positions of THC by circling them on the structure shown below.

b) One of these positions should be more reactive than the others because it is doubly activated with two allylic/benzylic activations. Identify this position by writing 'doublin' up' or 'double dippin' next to it.

c) One allylic/benzylic position is the least hindered. Identify this with 'less crowded' or 'rural'.

d) The product of THC reaction with CYP is usually the reaction at the less crowded allylic/benzylic site. Show any oxidation product of a CYP reaction at this less crowded site in the box. *Hint: I'm just looking for you to show me you know what an oxidation product of THC looks like.*

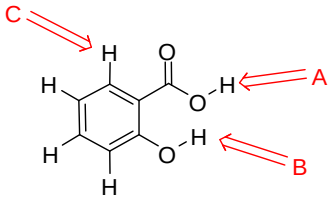


tetrahydrocannabinol (THC)

/24 pts.

7. Salicylic acid is a plant hormone and a pain reliever related to aspirin. There are three types of protons on salicylic acid shown below.

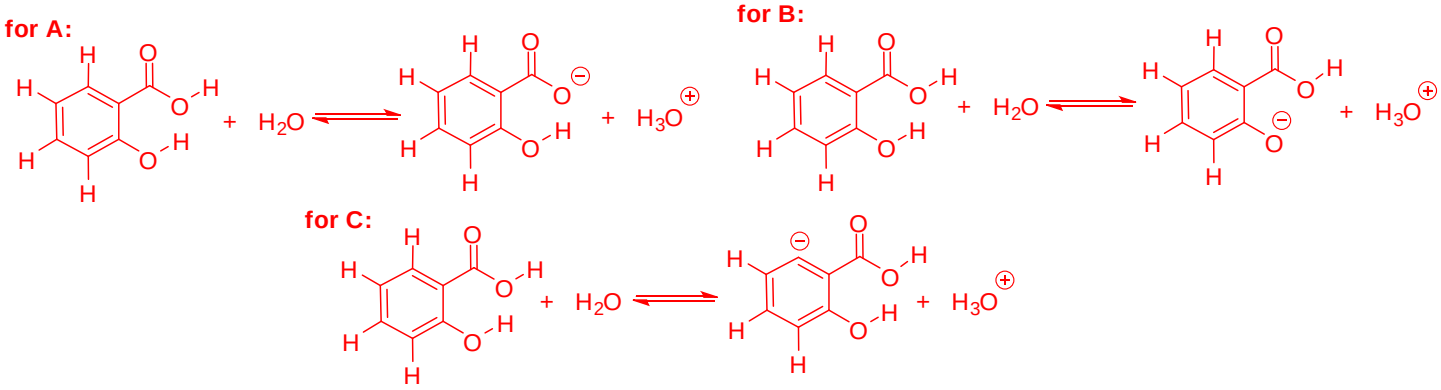
a) Identify and then rank the three types of protons based on their acidity. (5 pts.)



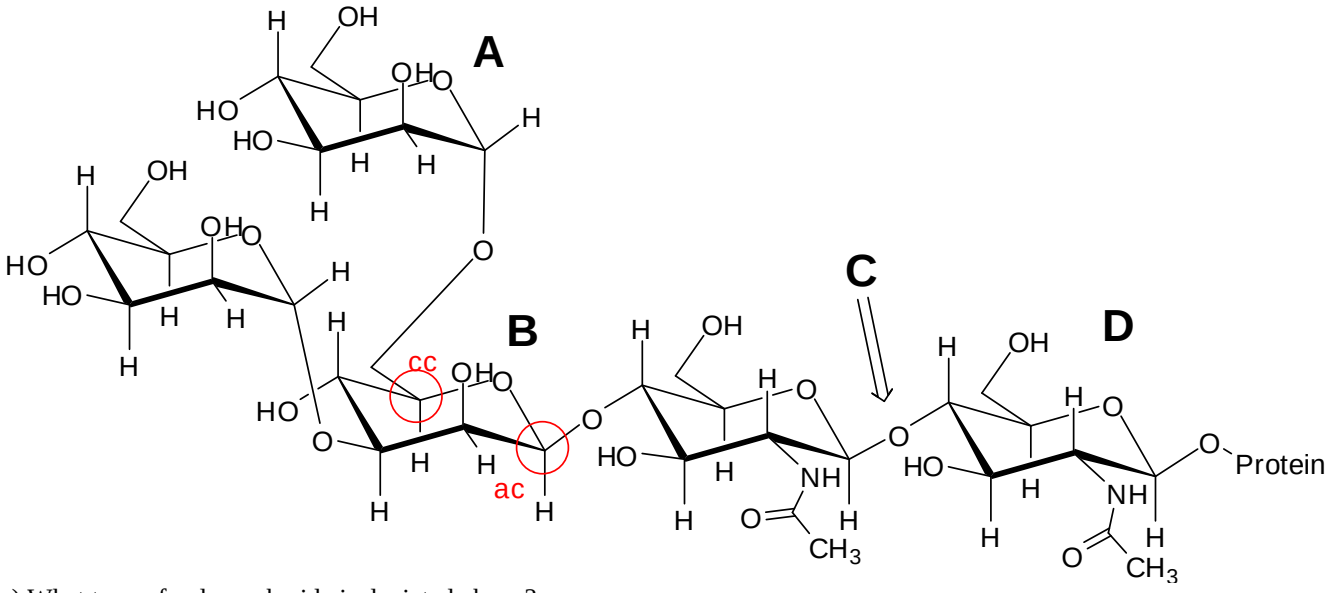
salicylic acid

most acidic __A__ > __B__ > __C__ least acidic

b) Show the acid dissociation equilibrium for <u>one</u> of these protons. (3 pts.)



8. The polysaccharide shown below is attached to many proteins and often becomes a key component of cell membranes where it controls cell adhesion processes. Answer the questions below based on your understanding of carbohydrates. (18 pts.)



a) What type of polysaccharide is depicted above?

(i) trisaccharide
(ii) tetrasaccharide
(iii) pentasaccharide
(iv) hexasaccharide
(v) heptasaccharide

b) What type of carbohydrate is **A**?

(i) α-D-mannopyranose
(ii) β-D-glucopyranose
(iii) α-D-altropyranose
(iv) β-D-gulopyranose
(v) α-D-galactopyranose

/14 pts.

c) Circle the configurational and anomeric carbon of carbohydrate **B** and label them with a 'cc' and 'ac', respectively.

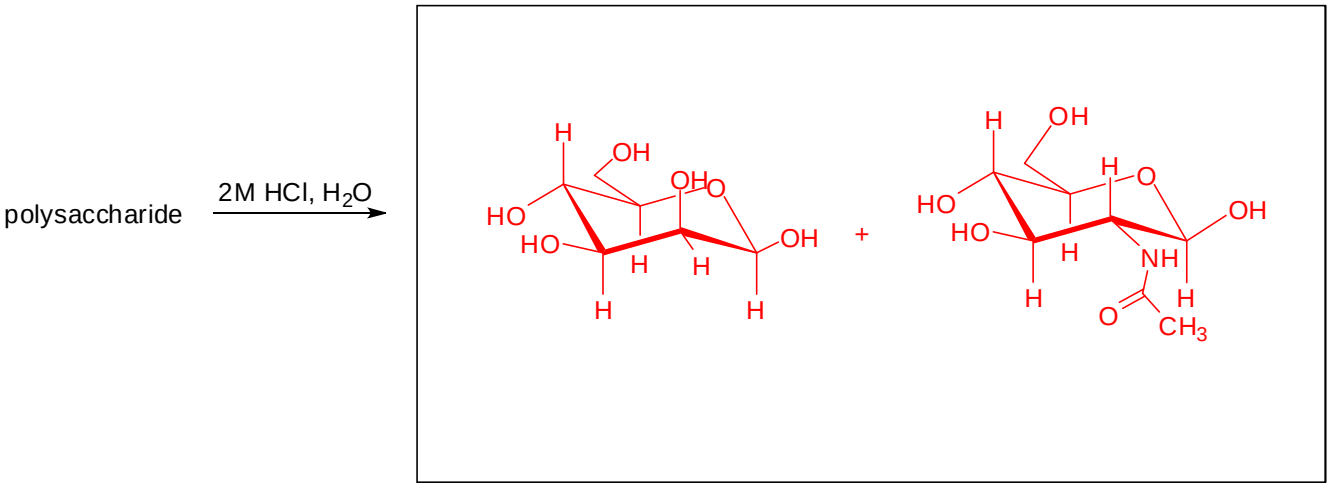
d) What glycosidic linkage is shown at **C**?

(i) α-1,6
(ii) α-1,5
(iii) β-1,2
(iv) β-1,3
(v) β-1,4

e) What type of carbohydrate is **D**?

(i) α-D-N-acetyl-mannosaminopyranose
(ii) β-D-N-acetyl-glucosaminopyranose
(iii) α-D-N-acetyl-iodosaminopyranose
(iv) α-D-N-acetyl-talosaminopyranose
(v) β-D-N-acetyl-galactosaminopyranose

f) Draw <u>one</u> carbohydrate product of the reaction of the polysaccharide with 2M HCl in H_2O.



/12 pts.