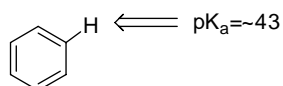
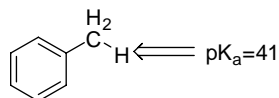
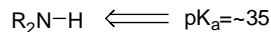
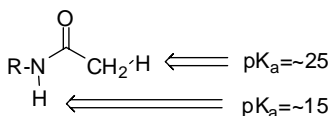
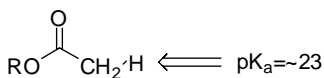
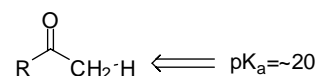
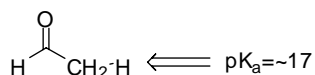
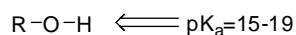
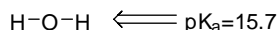
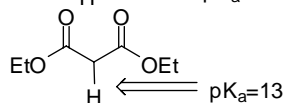
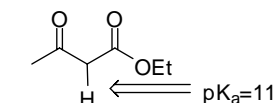
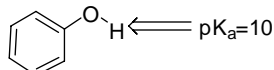
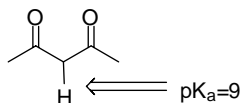
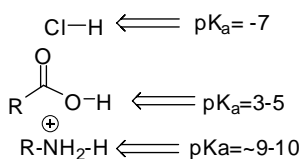


The examination has 8 questions on six pages. The point values for each question are found with the question. Partial credit where appropriate will be given.

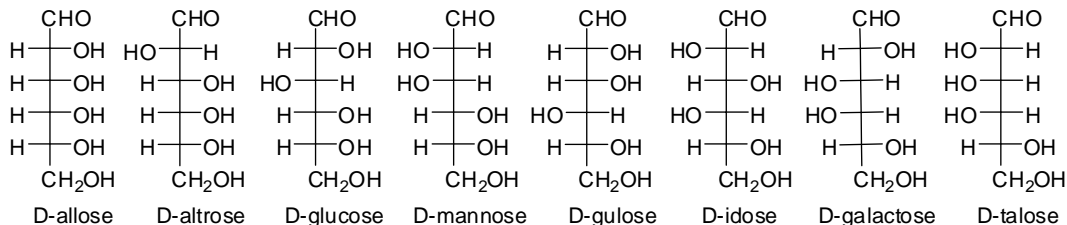
Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics.

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.

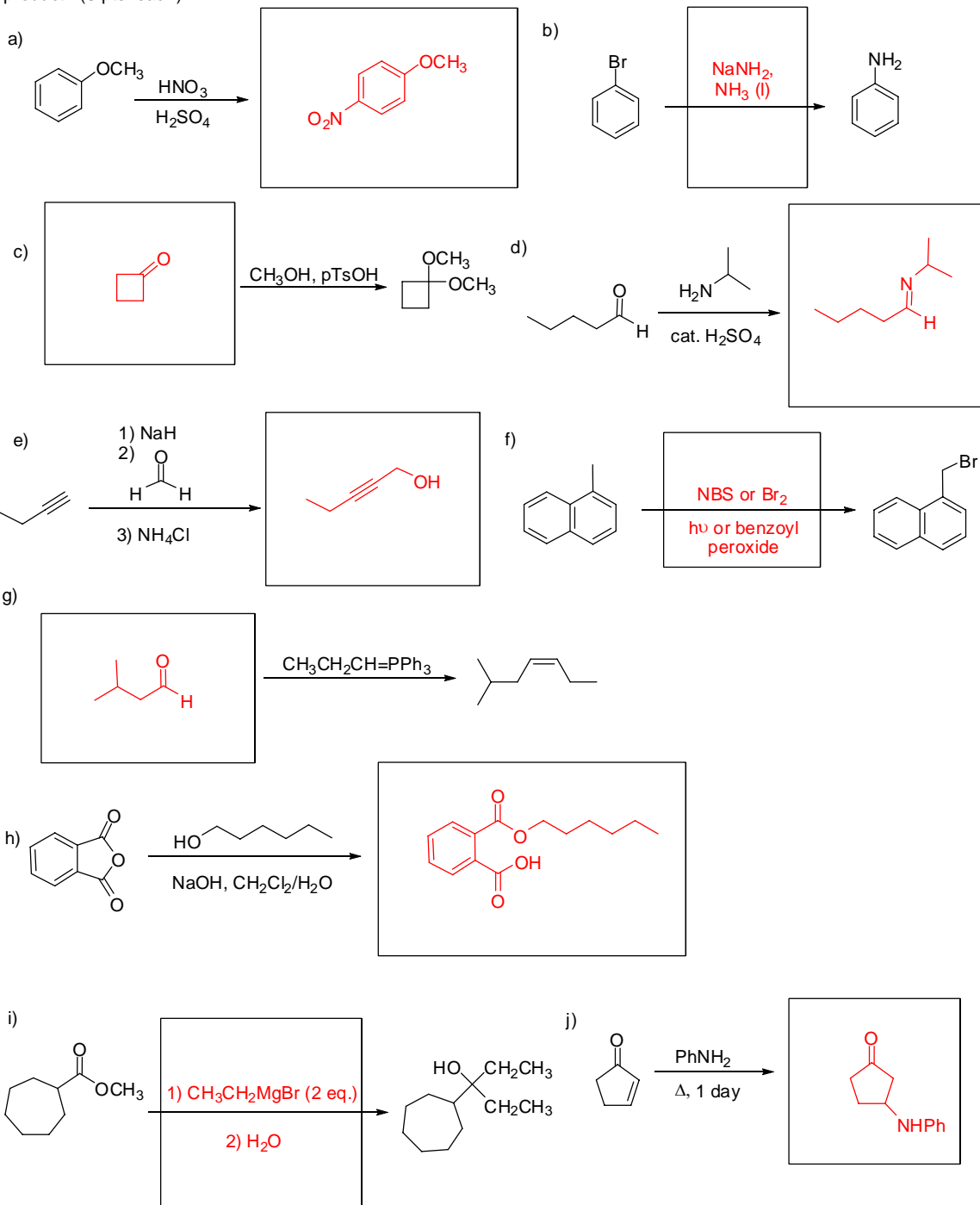
pK_a information:



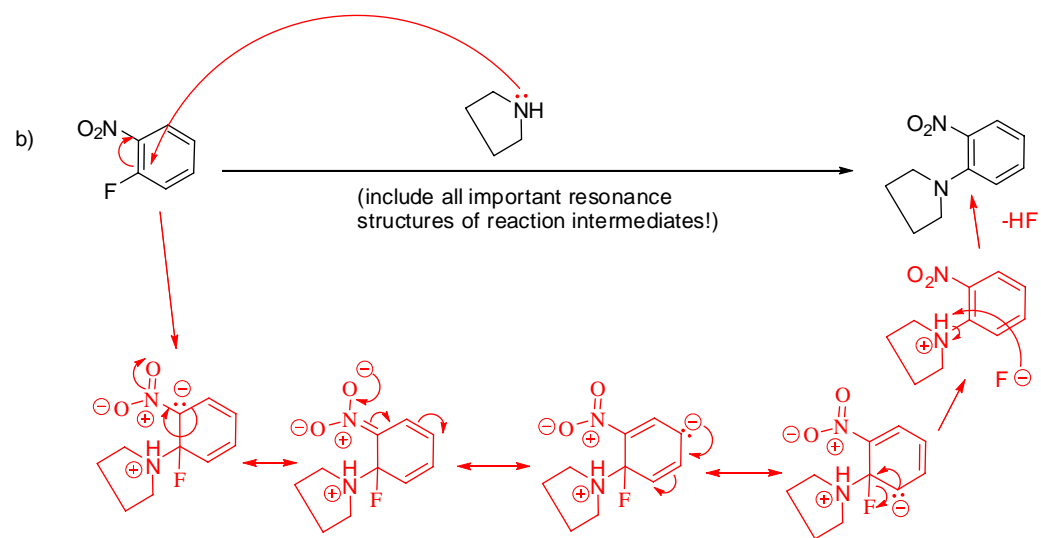
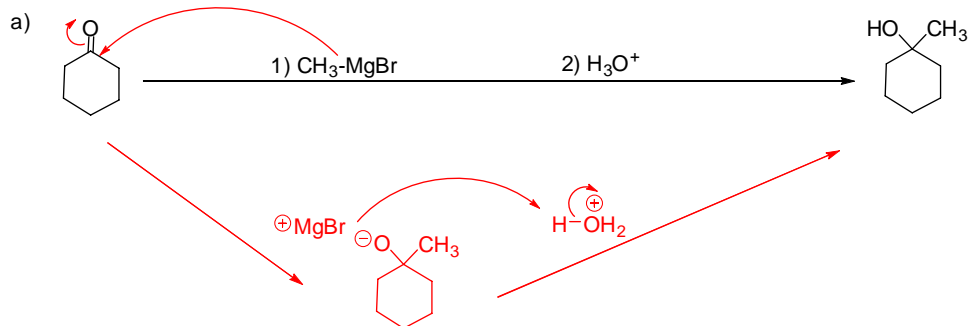
Note: R=alkyl



1. Complete the following reactions by providing the necessary information: starting material, reagent or major product. (3 pts. each)

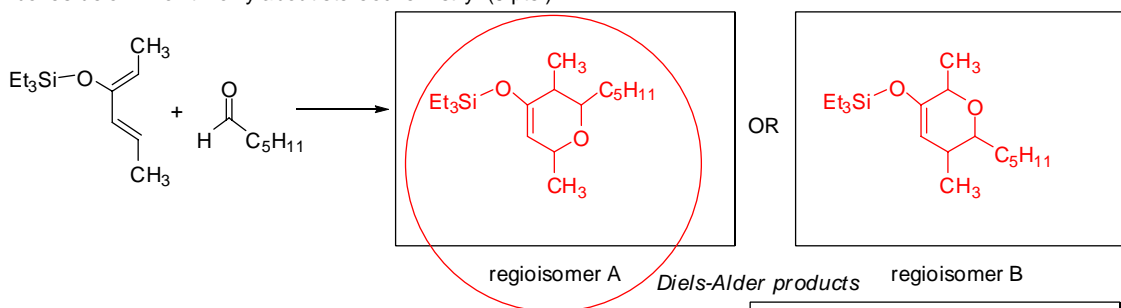


2. Draw the curved arrow electron flow mechanism for the following two reactions. Be sure to include formal charges and important resonance structures. (12 pts. each)

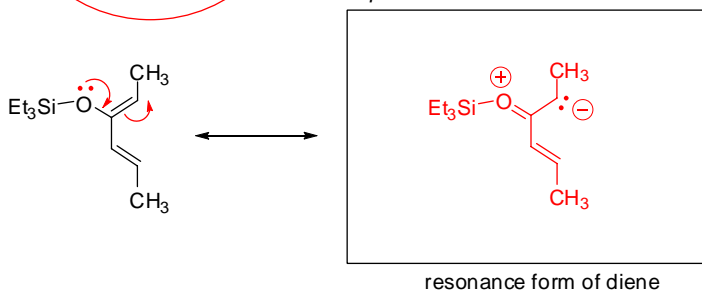


3. In class, we discussed Diels-Alder reactions between dienes and alkenes, but dienes can also react with other pi bonds, such as carbonyl groups. Based on your knowledge of resonance and Diels-Alder reactions answer the questions below about the following reaction that was reported by Harvard organic chemists.

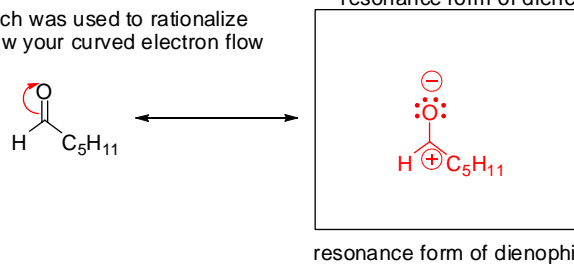
a) There are two possible regioisomer or structural isomer products in the boxes below. Draw the two possible regioisomer products in the boxes below. Don't worry about stereochemistry. (6 pts.)



b) Based on our discussions earlier in the semester, draw the important resonance contributor for the diene that would rationalize its reactivity and regioselectivity in a Diels-Alder reaction. Show your curved electron flow arrows that illustrate the transformation to the new resonance contributor. (5 pts.)

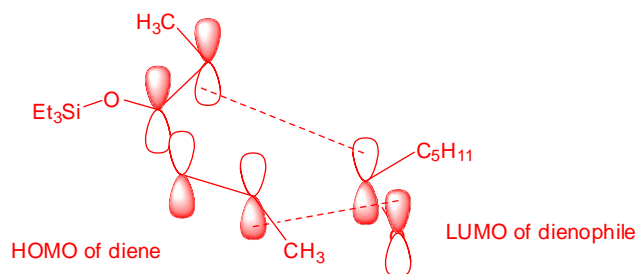


c) Draw a resonance structure of an aldehyde which was used to rationalize aldehyde reactivity in the course. Once again, show your curved electron flow arrows that illustrate the transformation. (4 pts.)

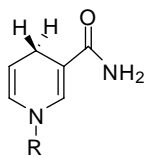


d) Finally, based on the resonance analysis in part b and c, which regioisomer do you predict is the major product? Circle the regioisomer in your answer to part a that you believe will be the major product. (4 pts.)

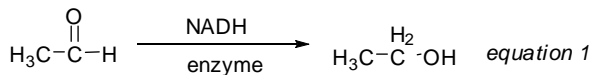
e) Draw the highest occupied molecular orbital (HOMO) of the diene pi system and the lowest unoccupied molecular orbital (LUMO) of the dienophile pi system in the Diels-Alder reaction. Label the HOMO and LUMO and show how the two orbitals would interact by drawing lines between the orbital lobes that would overlap to form the new bonds in the Diels-Alder reaction. (6 pts.)



4. Below is the structure of a coenzyme, NADH, used by enzymes in nature for important chemical transformations.



An example of a reaction that NADH would be involved in is shown below:



a) What type of chemical transformation is shown in *equation 1*? (3 pts.)

NADH

reduction or nucleophilic addition reaction

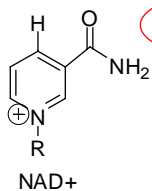
b) What reagent would an organic chemist use to effect the transformation shown in *equation 1*? (3 pts.)

NaBH_4 or LiAlH_4

c) Give the IUPAC or common name of the starting material. (3 pts.)

ethanal or acetaldehyde

d) NADH is transformed to NAD⁺ (structure below) in the process shown in *equation 1*. Circle the best reason why the transformation from NADH to NAD⁺ is thermodynamically favorable. (3 pts.)



(1) NAD⁺ is aromatic and NADH is not, therefore the NAD⁺ should be a more stable structure.

(2) NAD⁺ has a conjugated triene which is more stable than the conjugated diene of NADH.

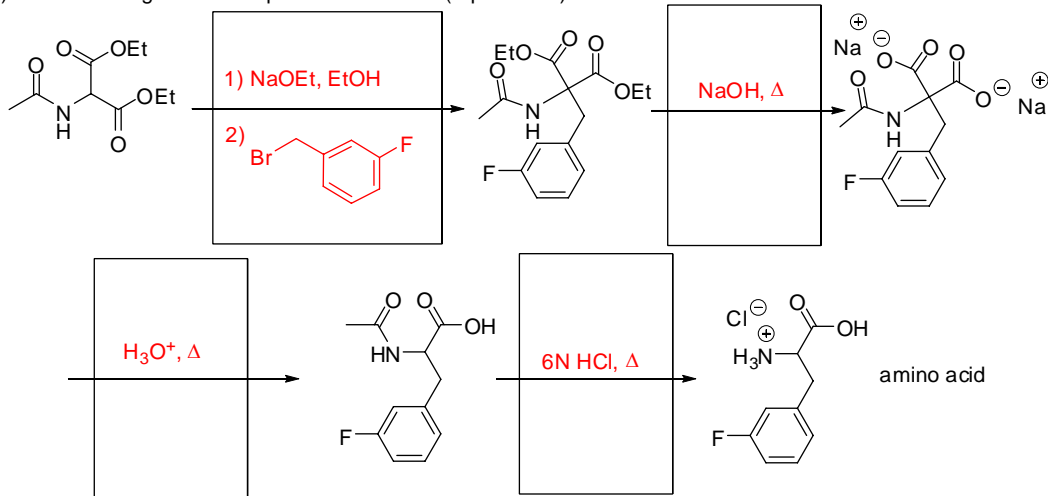
(3) NAD⁺ is 'RAD', need I say more.

(4) The loss of a C-H bond in NADH means there are fewer low energy C-H bonds present.

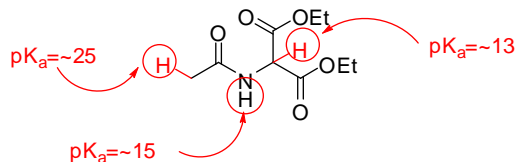
(5) With the cation on the nitrogen, NAD⁺ is a better electrophile and electrophiles are always lower in energy because they have fewer destabilizing electrons.

5. The classic method for amino acid synthesis is depicted in the following scheme.

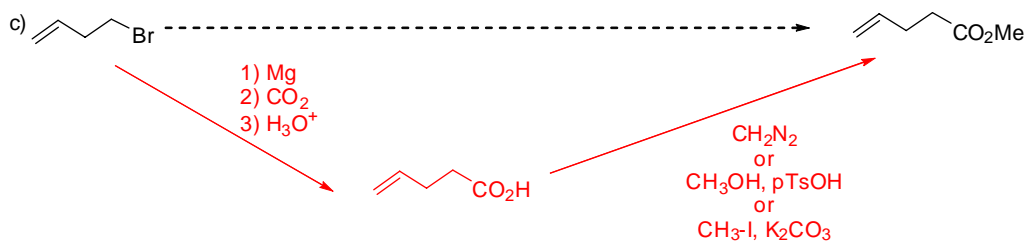
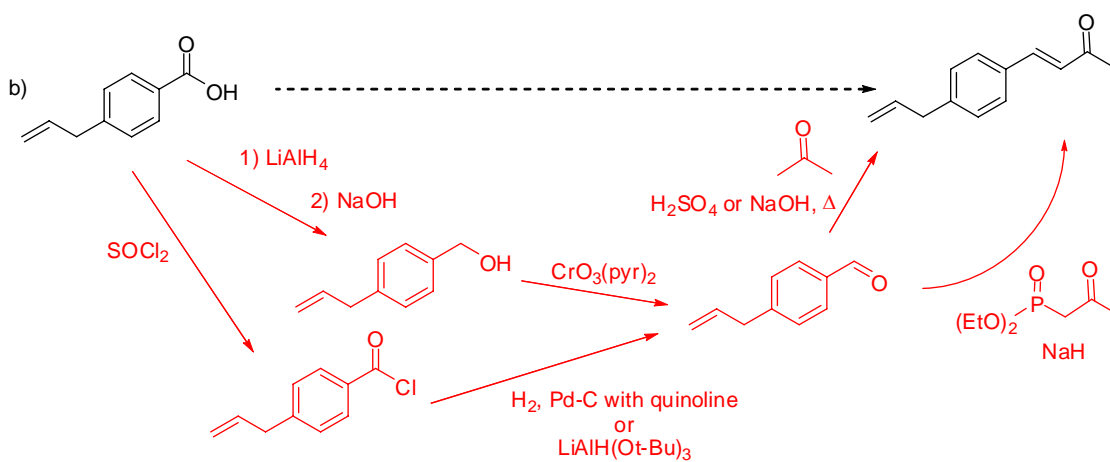
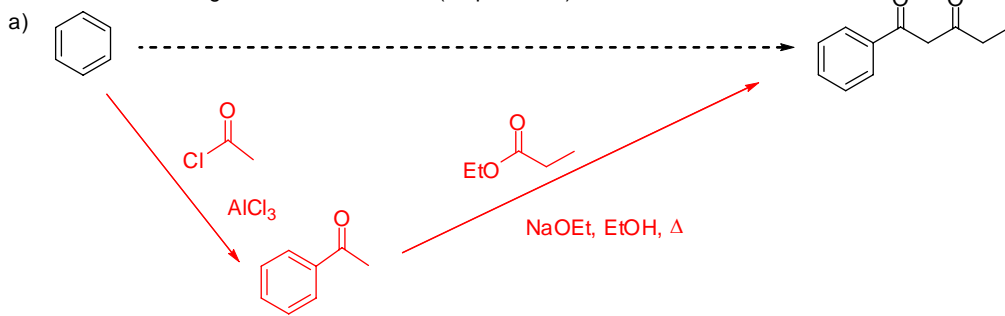
a) Fill in the reagents to complete the scheme. (3 pts. each)



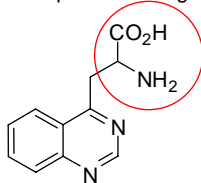
b) The starting material, diethyl acetamidomalonate, has three acidic protons. Identify all three by drawing them on the structure and/or circling them. Use the table on the exam cover page to determine the pK_a of each acidic proton and write that value next to the proton on the structure. (3 pts.)



6. Synthesize the molecule on the right from the starting material on the left. You may use any inorganic or organic materials with 4 contiguous carbons or less. (10 pts. each)

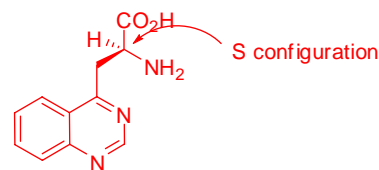


7. A student in my lab is currently working on making the previously unreported unnatural amino acid shown below as a potential drug for the treatment of cancer.

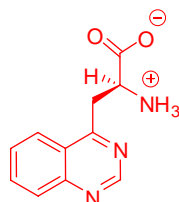


a) Circle the amino acid portion of this molecule. (2 pts.)

b) This molecule, like most amino acids, has a stereocenter. Redraw the essential parts of this molecule with the stereochemical configuration most commonly found for natural amino acids. (3 pts.)

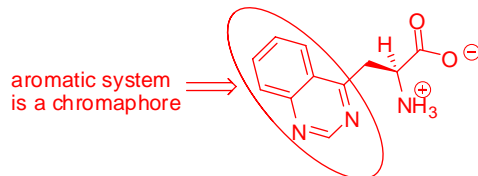


c) If this molecule were put in an aqueous solution of pH~7, it would be different than the structure drawn above. Draw the form of the molecule under these conditions. (3 pts.)



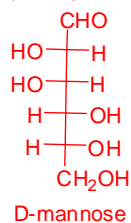
d) Would you expect this molecule to absorb UV or visible radiation? Briefly explain. (3 pts.)

The amino acid shown has a chromophore in the aromatic system (conjugated pi system) which will absorb UV radiation.



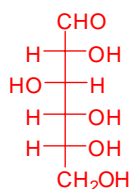
8. Draw the most stable pyranose chair form of the monosaccharide, β -D-mannose. (3 pts.)

1) Compare



D-mannose

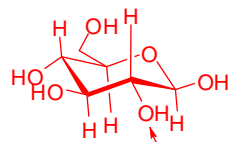
vs.



D-glucose

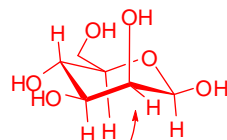
2) Analysis: D-mannose is the C-2 epimer of D-glucose

3) Draw D-glucose chair (all big groups equatorial)



D-glucose

4) Change stereochem at epimeric C's. β at anomeric C, so OH is cis to $-CH_2OH$ in C-5 position.



β -D-mannose

C-2 \Rightarrow epimer