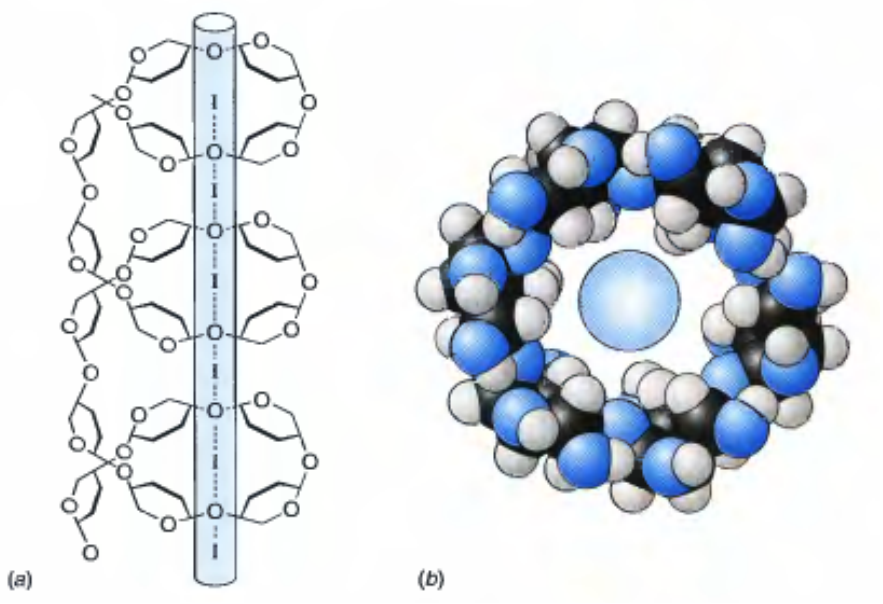
Chemistry 41c
FOURTH QUIZ KEY
May 31, 2013

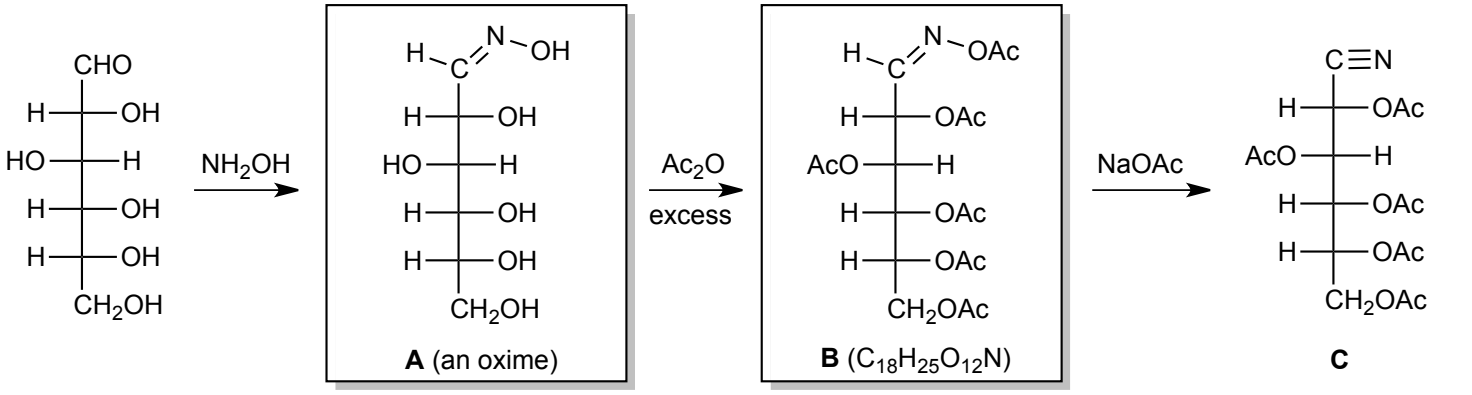
Name (print)_____Answer Key_____

Note: You have 55 minutes to take the quiz. This exercise is to be worked alone and is closed book and closed notes. No electronic devices are allowed. Molecular models are allowed. It is recommended to skim the entire exam and work more familiar problems first.

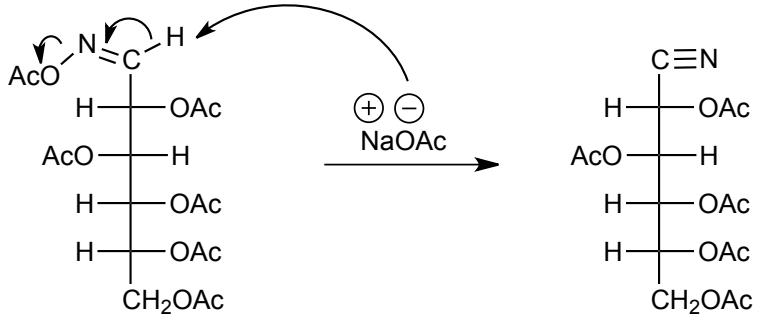


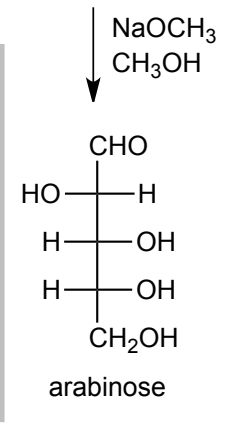
Hikers not packing their own water are encouraged to disinfect natural water sources with iodine tablets, which provide a solution of I_2, I^-, and the complex ion I_3^-. At meal time, trekkers are sometimes surprised by a brilliant blue solution that forms when treated water is used to cook pasta. Shown above are representations of the host-guest complex that is thought to form.

1. The Wohl degradation, shown below, can be used to convert an aldose into another aldose with one fewer carbon. Give the structure of the missing compounds as well as the curved-arrow mechanisms for the conversion of **B** to **C** and **C** to arabinose. (8 pts)

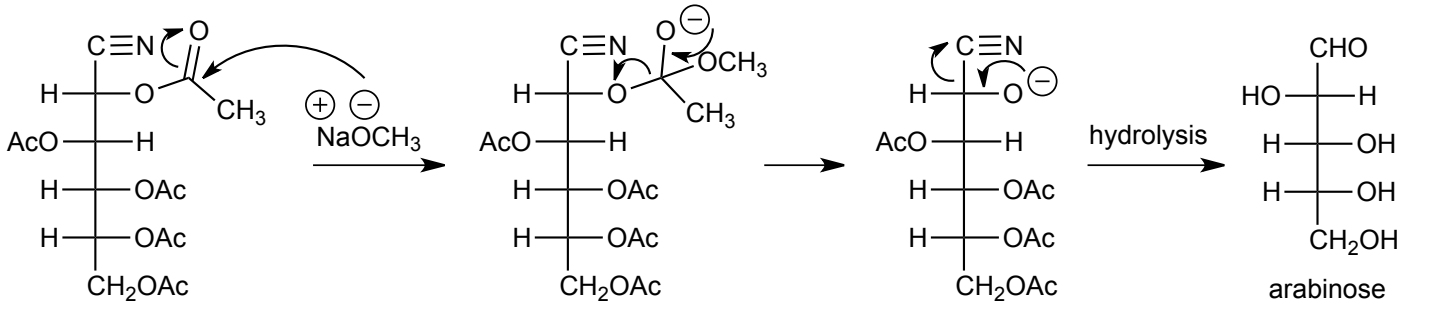


Mechanism for conversion of **B** to **C** (how the nitrile is formed):



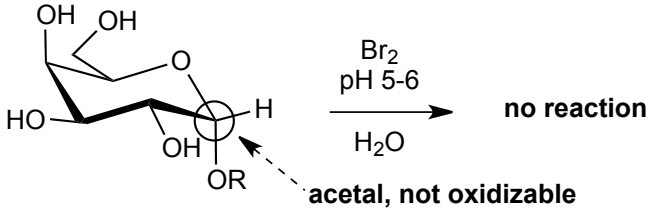


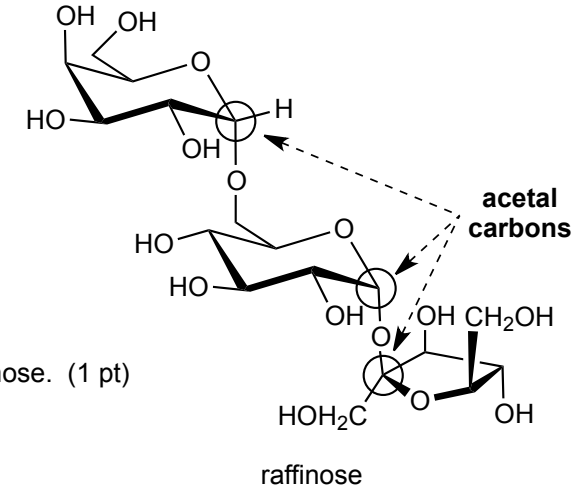
Mechanism for conversion of **C** to arabinose (focus on how the aldehyde is formed):



2. Consider the structure of raffinose, a trisaccharide found in sugar beets, beans, cabbage, and other plants. Classify raffinose as a reducing or nonreducing sugar, and use abbreviated structures to support your claim. (2 pts)

Raffinose is a non-reducing sugar, which is evidenced by its lack of hemiacetal carbons:

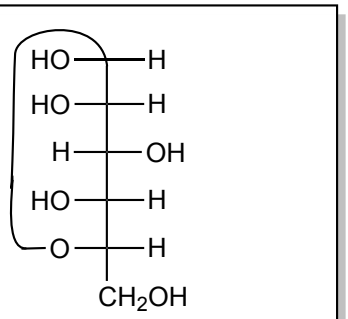




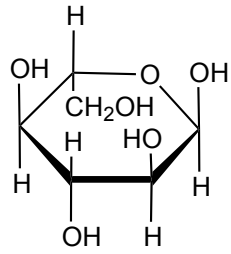
Bonus: Name one of the constituent monosaccharides found within raffinose. (1 pt)

D-glucose, D-galactose, or D-fructose

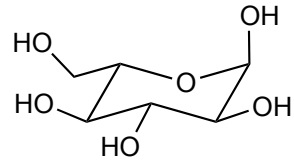
3. Draw a Fischer projection, a Haworth projection, and a chair structure for α-L-glucopyranose. (6 pts)



Fischer projection

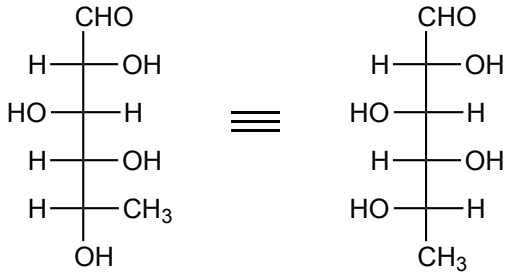


Haworth projection



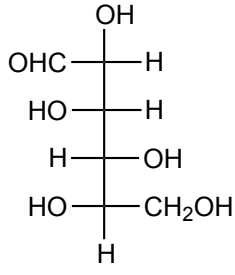
chair structure

4a. Classify the following aldose as D or L. (2 pts)

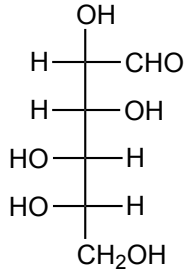


L

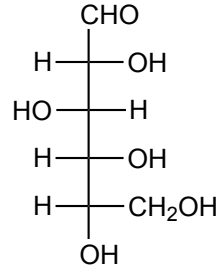
4b. Which pair of the following aldoses are epimers and which pair are enantiomers? (2 pts)



A



B



C

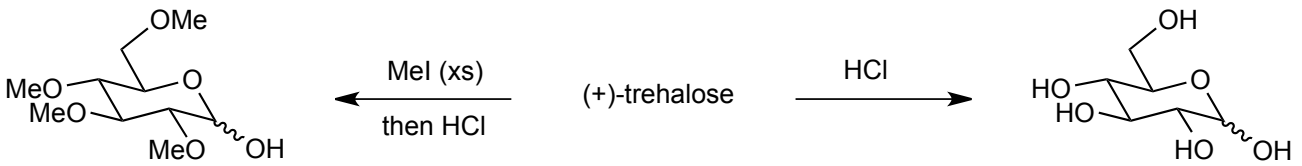
Compounds **A** and **C** are epimers.

Compounds **A** and **B** are enantiomers.

Bonus: Which pair of compounds are diastereomers? (1 pt) **B** and **C** or **A** and **C**

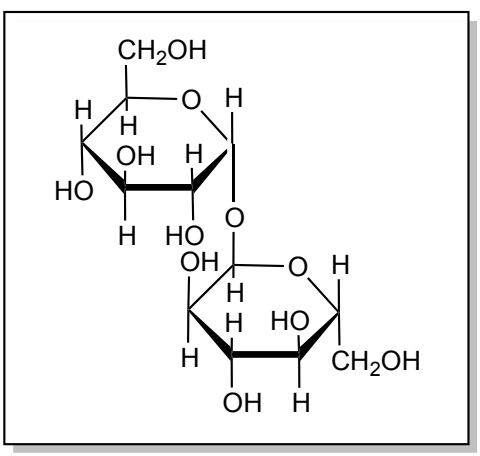
5. (+)-Trehalose, $C_{12}H_{22}O_{11}$, is a non-reducing sugar found in young mushrooms and is the energy source for certain flying insects. It gives only D-glucose when hydrolyzed by aqueous acid or by α-glucosidase. It is inert to β-glucosidase. Methylation with excess methyl iodide gives an octa-*O*-methyl derivative that, upon hydrolysis, yields only 2,3,4,6-tetra-*O*-methyl-D-glucose. Explain the exerimental data with annotated chemical structures. What is the structure of (+)-trehalose? Represent your answer using a Haworth representation. (6 pts)

Bonus: Provide a common name for the polysaccharide shown on the cover of the quiz. (1 pt) **starch**

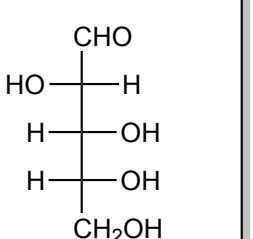


2,3,4,6-tetra-*O*-methyl-D-glucose D-glucose

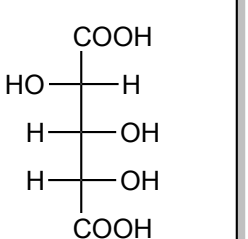
The chemical formula $C_{12}H_{22}O_{11}$ suggests that (+)-trehalose is a disaccharide. The observed inertness to β-glucosidase and classification as a non-reducing sugar indicate that the glycosidic bond is an α–1,1-linkage. Since acid-mediated hydrolysis produces only D-glucose, (+)-trehalose is likely composed of two D-glucose constituent monosaccharides:



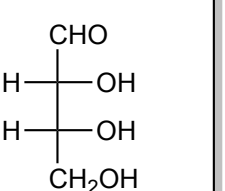
6. An aldopentose, **O**, is oxidized to a diacid, **P**, which is optically active. Compound **O** is also Ruff-degraded to an aldotetrose, **Q**, which undergoes oxidation to an optically inactive diacid, **R**. Assuming that **O** has the D-configuration, what are the structures of **O**, **P**, **Q**, and **R**? Represent your answers in each box by using Fischer projections displayed in the standard carbohydrate orientation. (4 pts)



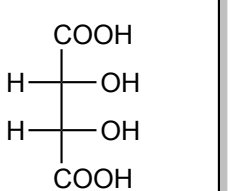
compound **O**



compound **P**



compound **Q**



compound **R**

Bonus: List the reagent(s) necessary to effect Ruff degradation of compound **O** to compound **Q**. (2 pts)

1. **Br_2, H_2O (can also include $Ca(OH)_2$ or $CaCO_3$)**
2. **H_2O_2, Fe_2SO_4 or H_2O_2, $Fe(OAc_3)$**