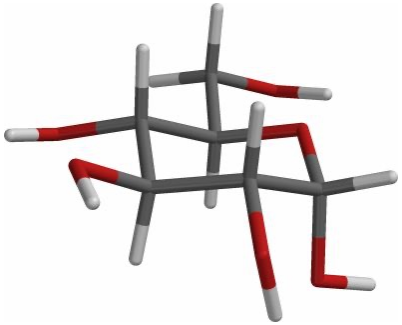

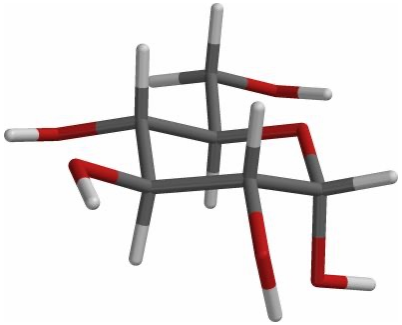

Chem 109 C

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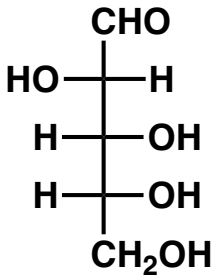
Chapter 21 Practice Problems set 1

http://web.chem.ucsb.edu/~zakariangroup/courses.html

Practice problem 1

A D-aldopentose is oxidized by nitric acid to an optically active aldaric acid. A Wohl degradation of the aldopentose leads to a monosaccharide that is oxidized by nitric acid to an optically inactive aldaric acid.

Identify the D-aldopentose



Practice problem 1.3

Starting with the D-pentose, identify the structure of all mentioned monosaccharides based on the following observations.

- a D-pentose does not react with Br_2 but gives a positive Tollens test (reacts with Ag^+/NH_3)
- after reaction with $NaOH/H_2O$ (ene-diol rearrangement), the D-pentose gives two new D-pentoses, which react with Br_2
- both of these new D-pentoses, after Wohl degradation followed by reduction with $NaBH_4$, give an optically inactive alditol

Answers: D-ribulose, D-arabinose, D-ribose, D-erythrose

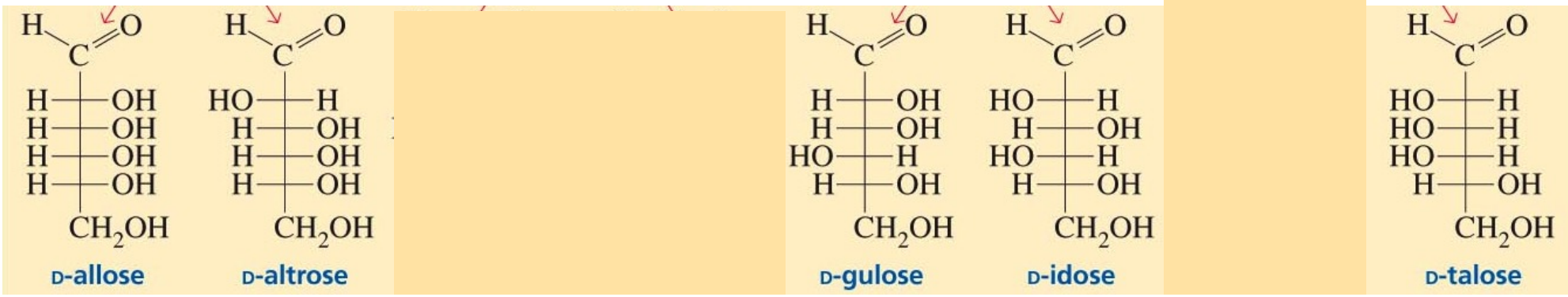
Practice problem 2

1a. What other monosaccharide is reduced only to the alditol obtained from

1. D-talose (D-altrose)
2. D-galactose (L-gal)

b. What monosaccharide is reduced to two alditols, one of which is the alditol obtained from the reduction of

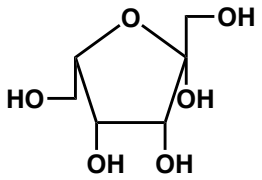
1. D-talose (D-tagatose)
2. D-allose (D-psicose)



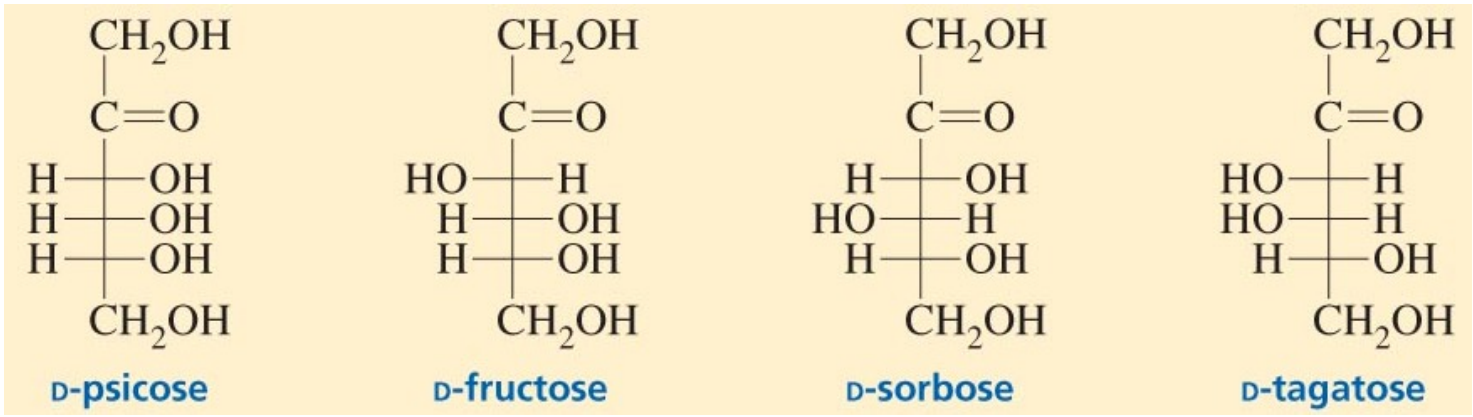
Practice problem 2a

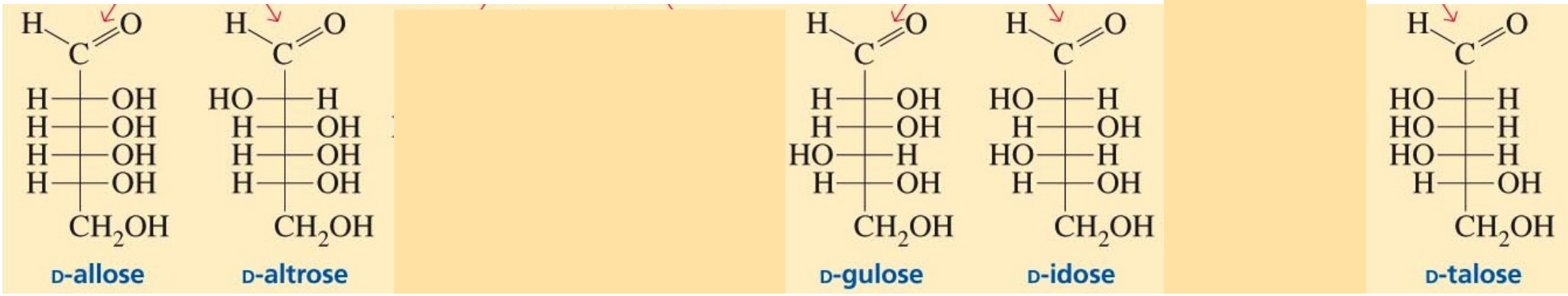
Draw

1. α-D-idopyranose
2. β-L-tagatofuranose
3. α-L-tagatopyranose



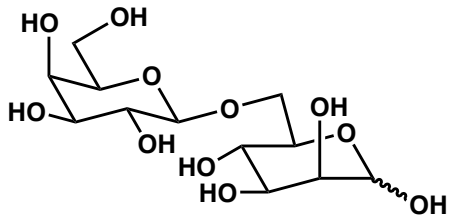
beta-L-tagatofuranose





Practice problem 3

An unknown disaccharide gives a positive Tollens test (reacts with Ag_2O, NaOH). A β-1,4’-glycosidase hydrolyzes it to D-galactose and D-mannose. When the disaccharide is treated with CH_3I and Ag_2O and then hydrolyzed with HCl, the products are 2,3,4,6-tetra-O-methylgalactose and 2,3,4-tri-O-methylmannose. Propose a structure for the disaccharide

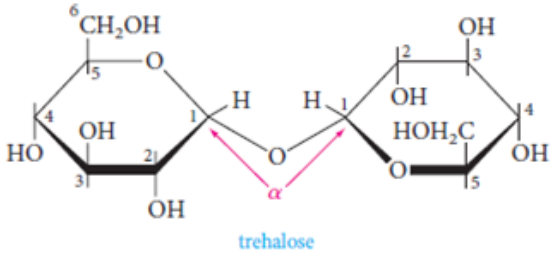


Practice problem 4

Trehalose, $C_{12}H_{22}O_{11}$, …when hydrolyzed by acid or enzyme maltase forms only D-glucose. When treated with MeI and Ag_2O and then hydrolyzed with water under acidic conditions, only 2,3,4,6-tetra-O-methyl-D-glucose is formed.

a. draw the structure of trehalose

b. what is the function of silver (I) oxide? Answer: silver oxide serves as a base and as a strong binder to idodide, making it a better leaving group

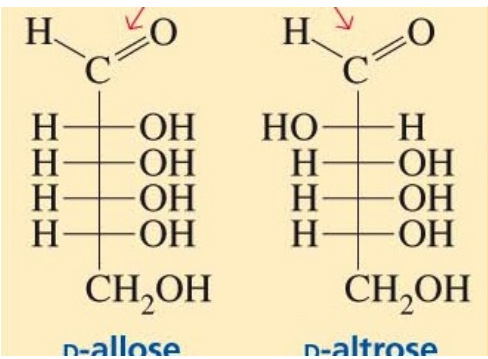


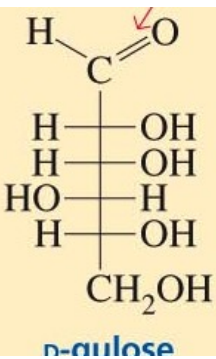
trehalose

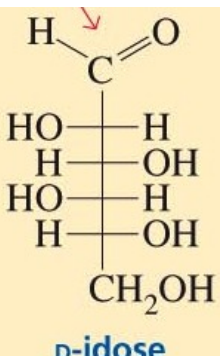
Practice problem 6

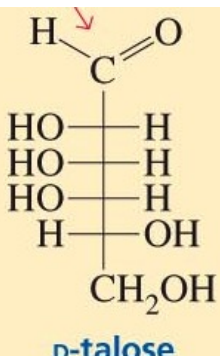
Compounds A, B, and C are three different D-aldohexoses. Compounds A and B are reduced to enantiomeric alditols, but form diastereomeric aldopentoses after Wohl degradation. Compounds B and C form the same aldopentoses after Wohl degradation, but reduced to different alditols. Give the structures of A, B, and C.

Answer: **A –**
B –
C –





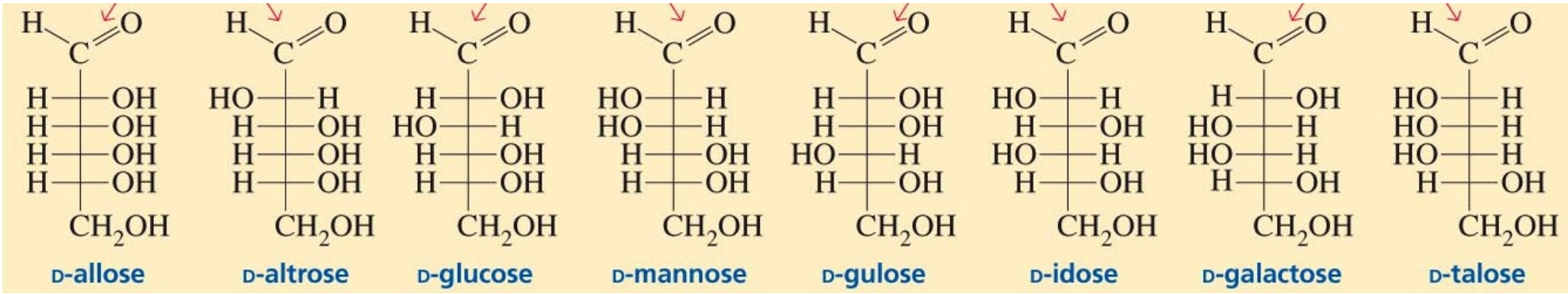




Practice problem 6 ("solution")

Solution: if A and B form *enantiomeric* alditols, they cannot be both derived from D-aldohexoses. In addition, if the alditols are enantiomeric, then aldopentoses after Wohl degradation **must** be enantiomeric as well. So the problem as stated does not have a solution.

However See next problem

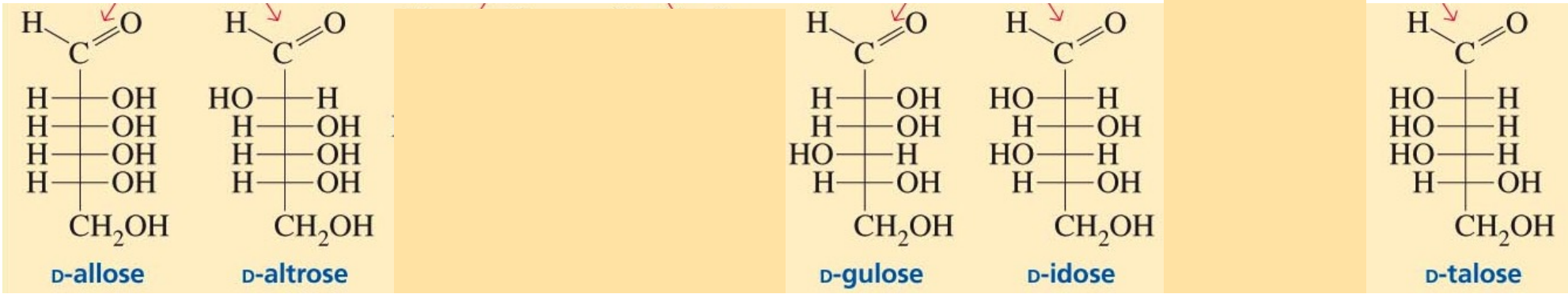


1 2 3 4 5 6 7 8

Practice problem 7

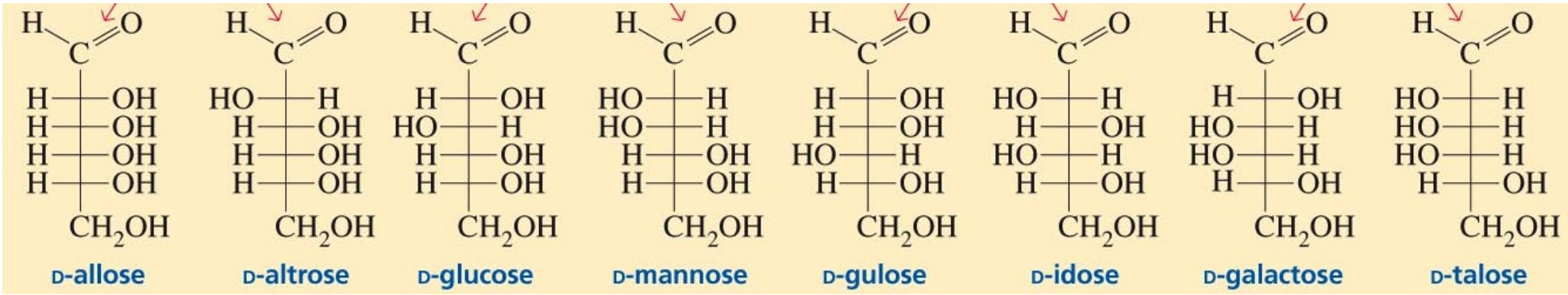
Compounds A, B, and C are three different aldohexoses. Compounds A and B are reduced to identical alditol, but form enantiomeric aldopentoses after Wohl degradation. Compounds B and C form the same aldopentose after Wohl degradation, but reduced to different alditols. Give the structures of A, B, and C.

Solution on the next slide



Practice problem 7

Solution: If A and B form enantiomeric aldopentoses after Wohl degradation, then it must be a D/L pair of aldohexoses (enantiomers). The only way enantiomeric aldohexoses can form the same alditol is that if the alditol is achiral. Only sugars 1 and 7 form achiral alditols. Therefore, there will be 4 correct answers. An example of one is:
A = D-galactose, B = L-galactose, C = L-talose



1 2 3 4 5 6 7 8