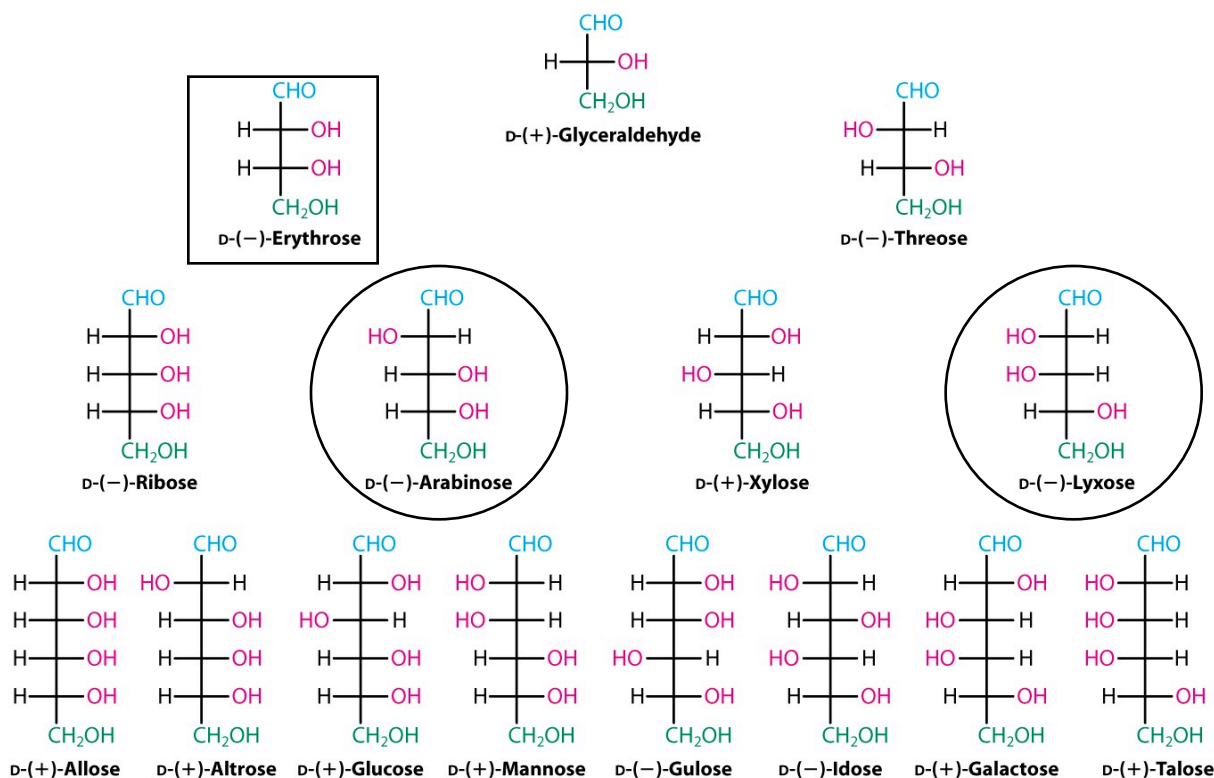


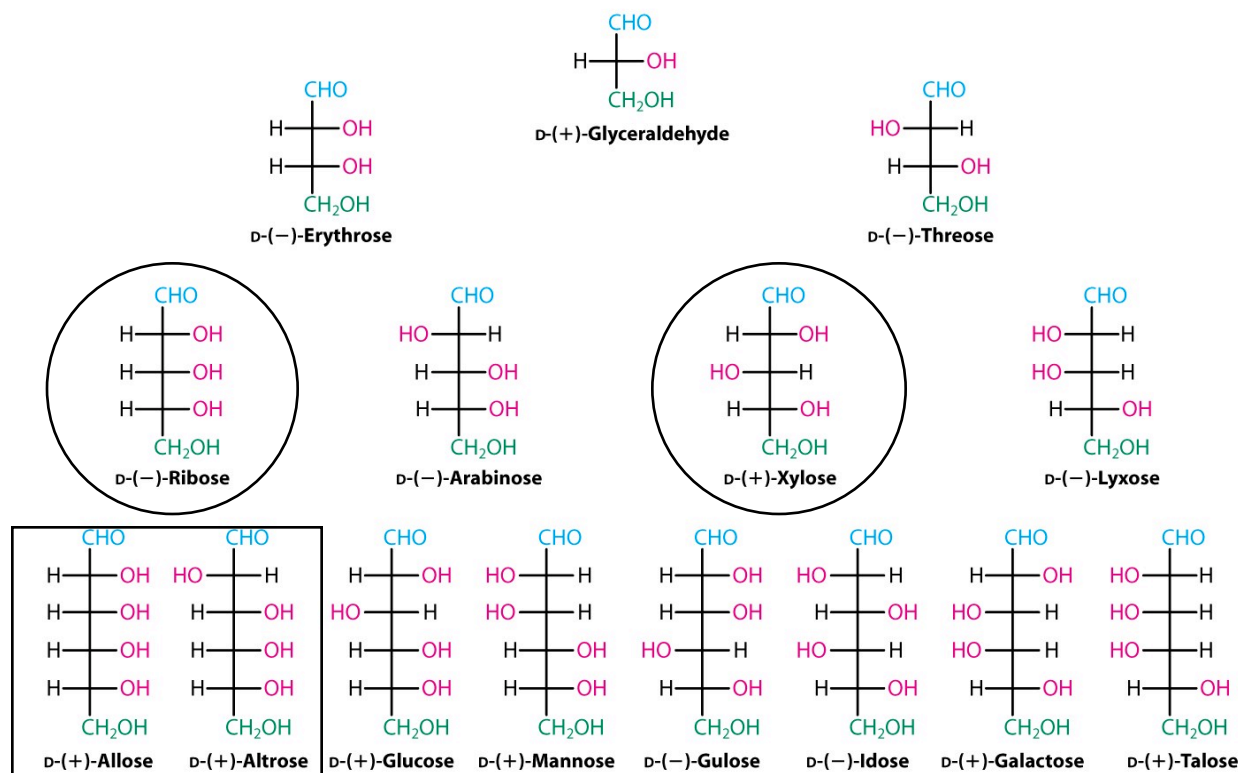
Use Table 24-2 of Vollhardt and Schore to answer questions 1 and 2.

1. An aldopentose is oxidized by HNO_3 to give an optically active diacid. Wohl degradation of that same aldopentose gives an aldotetrose. This aldotetrose provides an optically inactive diacid upon HNO_3 oxidation. Identify the aldopentose.



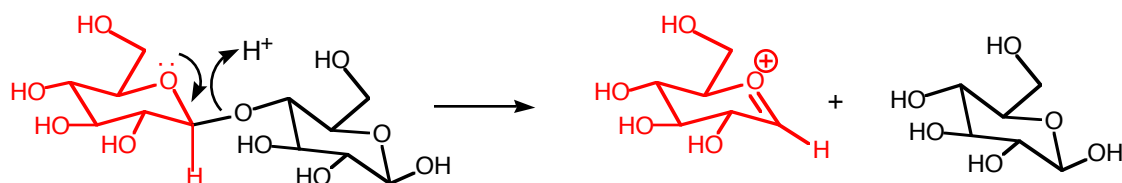
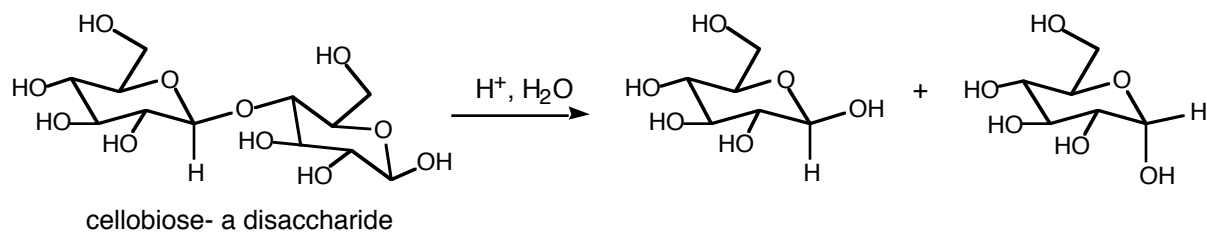
Answer: Of the four D-aldopentoses, only arabinose and lyxose give optically active diacids upon oxidation with nitric acid. Wohl degradation of lyxose gives threose, which gives an optically active diacid with HNO_3 . Wohl degradation of Arabinose gives erythrose, which gives a meso (optically inactive) diacid upon oxidation with HNO_3 . Thus, the correct aldopentose is Arabinose.

2. An aldopentose is oxidized by HNO_3 to give an optically inactive diacid. Kiliani-Fischer synthesis on that same aldopentose gives two aldohexoses. Oxidation of the aldohexoses with HNO_3 gives two diacids, only one of which is optically active. Identify the aldopentose.



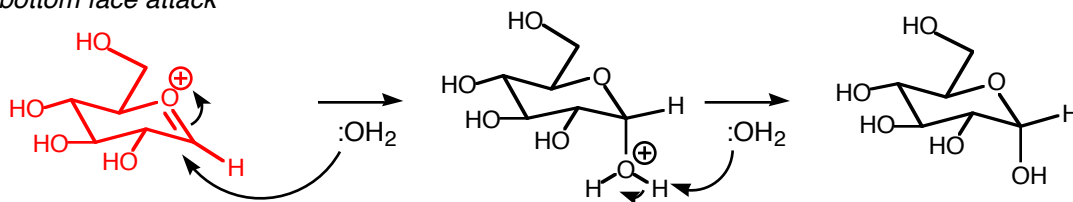
Answer: Of the four D-aldopentoses, only ribose and xylose give optically active diacids upon oxidation with nitric acid. Kiliani Fischer synthesis with Xylose gives Gulose and Idose, both of which provide optically active acids upon oxidation. Kiliani Fisher synthesis with Ribose gives Allose and Altrose. HNO_3 oxidation of Altrose gives an optically active diacid, but oxidation of allose gives a meso diacid. Therefore, the correct aldopentose is Ribose.

3. Provide a mechanism for the following transformation

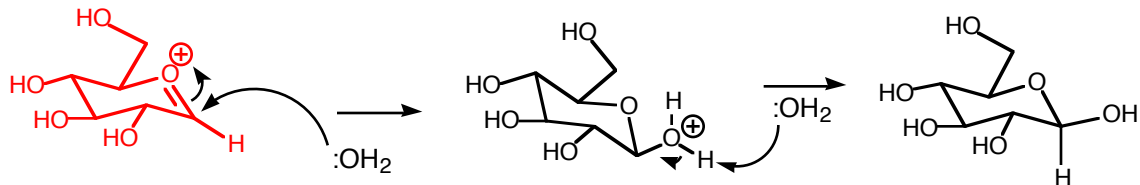


Attack on the oxonium ion can occur from either face

bottom face attack

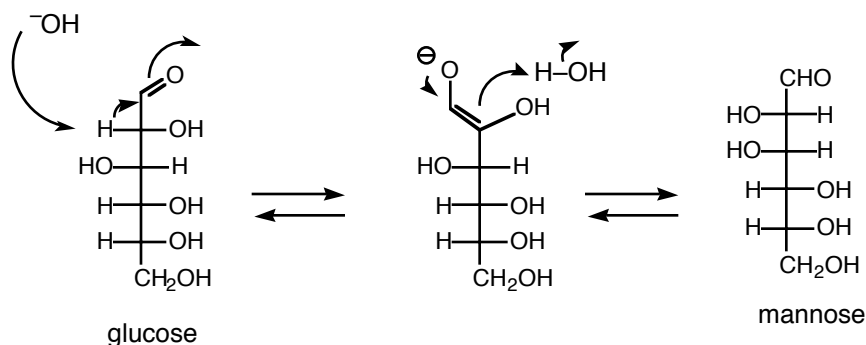


top face attack

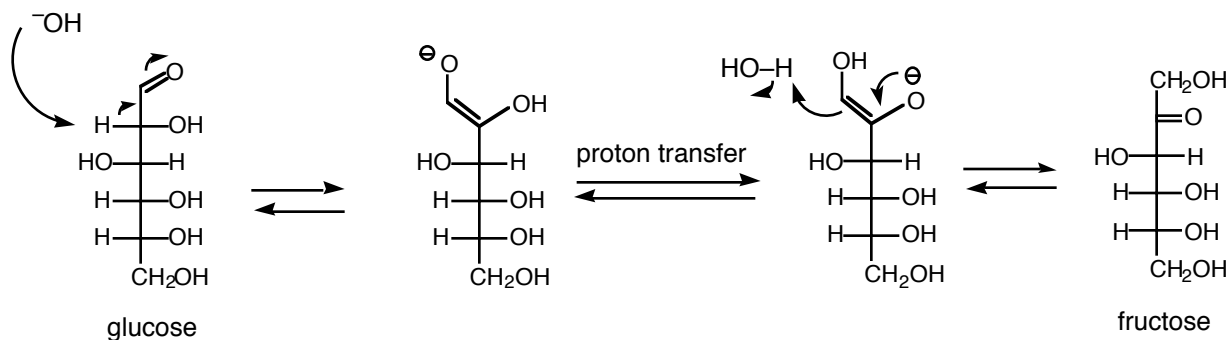


4. Provide a mechanism for interconversion of glucose with fructose and mannose.

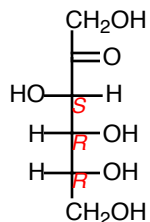
Glucose to mannose is a simple epimerization reaction of the aldehyde enolate.



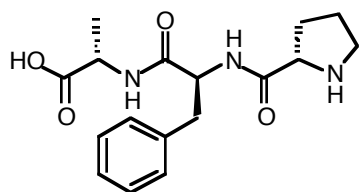
Glucose to fructose begins the same way, but is followed by proton transfer to give a ketone enolate before reprotonation



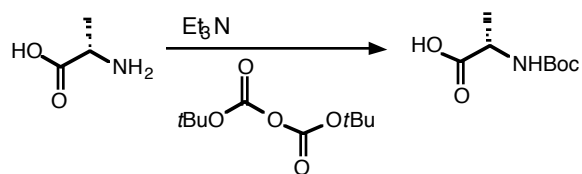
5. Identify each of the stereocenters of fructose as either (R) or (S)



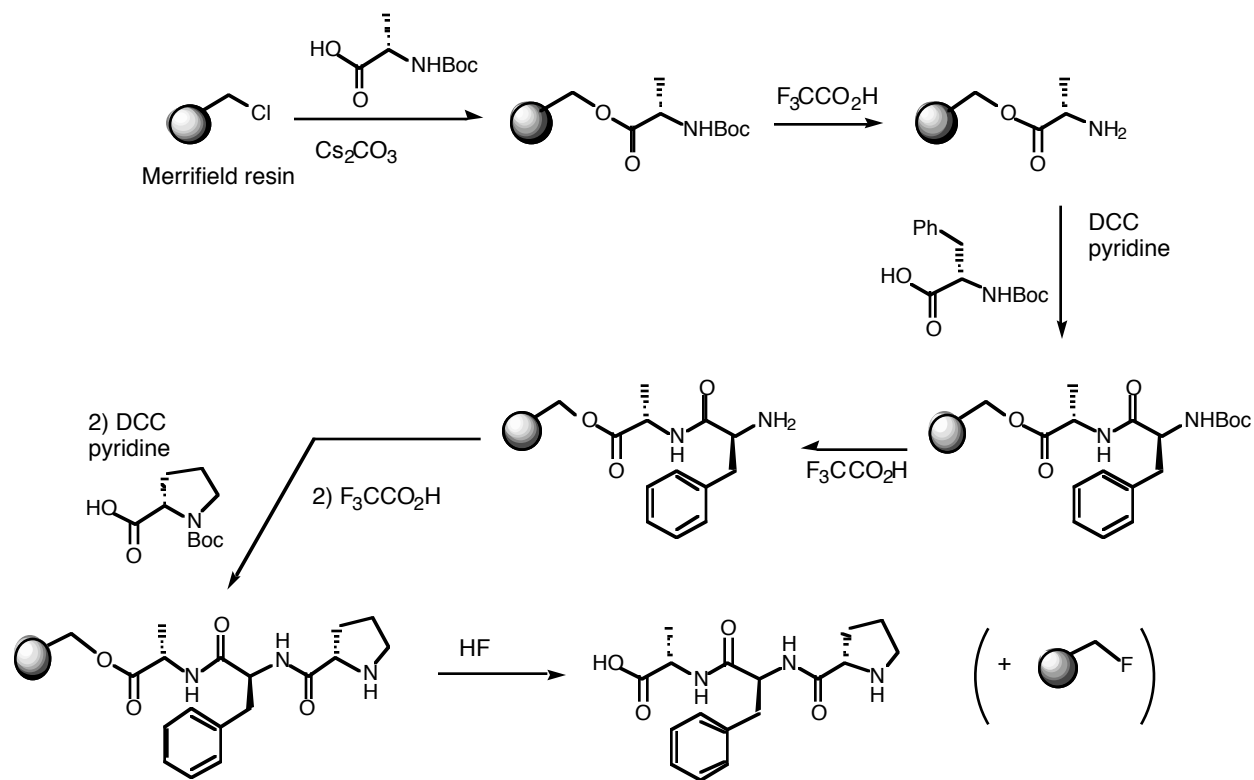
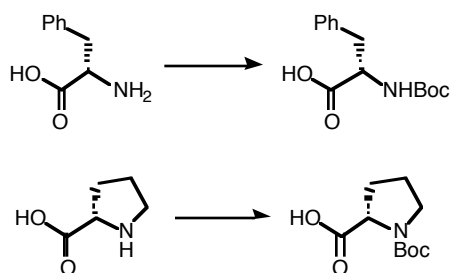
6. Provide a synthesis of the following tripeptide using Merrifield solid phase synthesis and BOC protecting group strategies.



Synthesis of BOC-protected amino acids:



similarly



7. Provide a mechanism for the formation of **B**, which occurs through the intermediacy of structure **A**.

