

Chapter 24

Carbohydrates

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 24. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

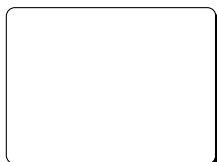
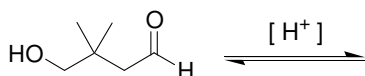
- **Carbohydrates** are polyhydroxy _____ or ketones.
- Simple sugars are called _____ and are generally classified as **aldoses** and _____.
- For all **D sugars**, the chirality center farthest from the carbonyl group has the ____ configuration.
- Aldohexoses can form cyclic hemi_____ that exhibit a **pyranose** ring.
- Cyclization produces two stereoisomeric hemiacetals, called _____. The newly created chirality center is called the _____ **carbon**.
- In the **α anomer**, the hydroxyl group at the anomeric position is _____ to the CH₂OH group, while in the **β anomer**, the hydroxyl group is _____ to the CH₂OH group.
- Anomers equilibrate by a process called _____, which is catalyzed by either _____ or _____.
- Some carbohydrates, such as D-fructose, can also form five-membered rings, called _____ rings.
- Monosaccharides are converted into their ester derivatives when treated with excess _____.
- Monosaccharides are converted into their ether derivatives when treated with excess _____ and silver oxide.
- When treated with an alcohol under acid-catalyzed conditions, monosaccharides are converted into acetals, called _____. Both anomers are formed.
- Upon treatment with sodium borohydride an aldose or ketose can be reduced to yield an _____.
- When treated with a suitable oxidizing agent, an aldose can be oxidized to yield an _____.
- When treated with HNO₃, an aldose is oxidized to give a dicarboxylic acid called an _____.
- D-Glucose and D-mannose are **epimers** and are interconverted under strongly _____ conditions.
- The **Kiliani-Fischer synthesis** can be used to lengthen the chain of an _____.
- The **Wohl degradation** can be used to shorten the chain of an _____.
- _____ are comprised of two monosaccharide units, joined together via a glycosidic linkage.
- **Polysaccharides** are polymers consisting of repeating monosaccharide units linked by _____ bonds.
- When treated with an _____ in the presence of an acid catalyst, monosaccharides are converted into their corresponding **N-glycosides**.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 24. The answers appear in the section entitled *SkillBuilder Review*.

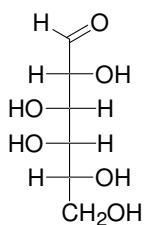
24.1 Drawing the Cyclic Hemiacetal of a Hydroxyaldehyde

DRAW THE CYCLIC HEMIACETAL THAT IS FORMED WHEN THE FOLLOWING HYDROXYALDEHYDE UNDERGOES CYCLIZATION UNDER ACIDIC CONDITIONS.

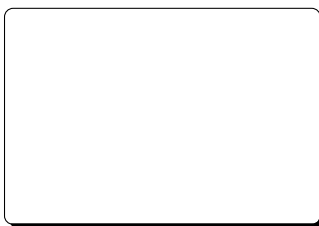
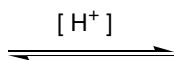


24.2: Drawing a Haworth Projection of an Aldohexose

DRAW A HAWORTH PROJECTION OF α -D-GALACTOPYRANOSE.

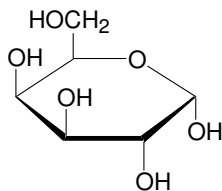


D-GALACTOSE



24.3: Drawing the More Stable Chair Conformation of a Pyranose Ring

DRAW THE MORE STABLE CHAIR CONFORMATION OF α -D-GALACTOPYRANOSE.



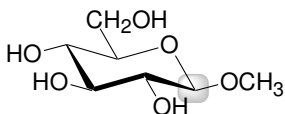
α -D-GALACTOPYRANOSE



MORE STABLE CHAIR CONFORMATION

24.4 Identifying a Reducing Sugar

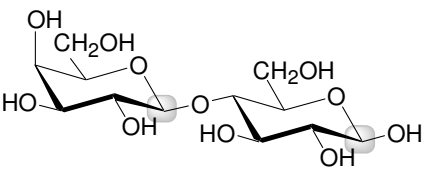
STEP 1 - IDENTIFY THE _____ POSITION.



STEP 2 - DETERMINE IF THE GROUP ATTACHED TO THE ANOMERIC POSITION IS A _____ GROUP OR _____ GROUP.

- IF _____ GROUP, THEN THE COMPOUND IS A REDUCING SUGAR
- IF _____ GROUP, THEN THE COMPOUND IS NOT A REDUCING SUGAR.

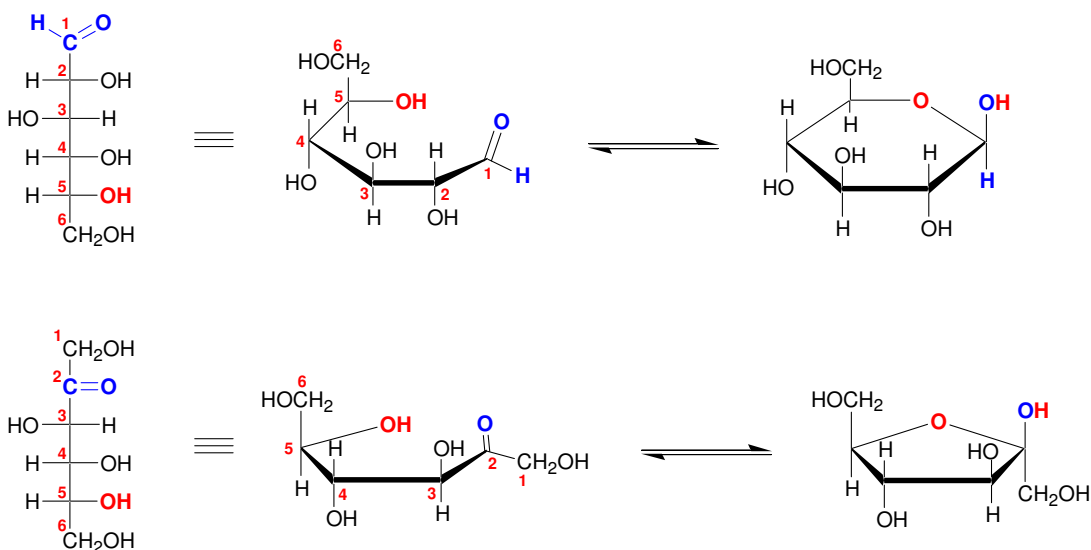
24.5 Determining Whether a Disaccharide Is a Reducing Sugar

<p>STEP 1 - IDENTIFY THE _____ POSITIONS.</p> 	<p>STEP 2 - DETERMINE IF THE GROUPS ATTACHED TO THE ANOMERIC POSITIONS ARE HYDROXY GROUPS OR ALKOXY GROUPS.</p> <p>- IF ONE IS A _____ GROUP, THEN THE COMPOUND IS A REDUCING SUGAR.</p> <p>- IF NEITHER ARE _____ GROUPS, THEN THE COMPOUND IS NOT A REDUCING SUGAR.</p>
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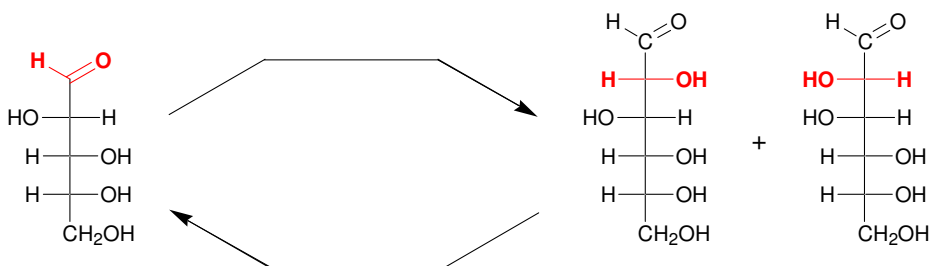
Review of Reactions

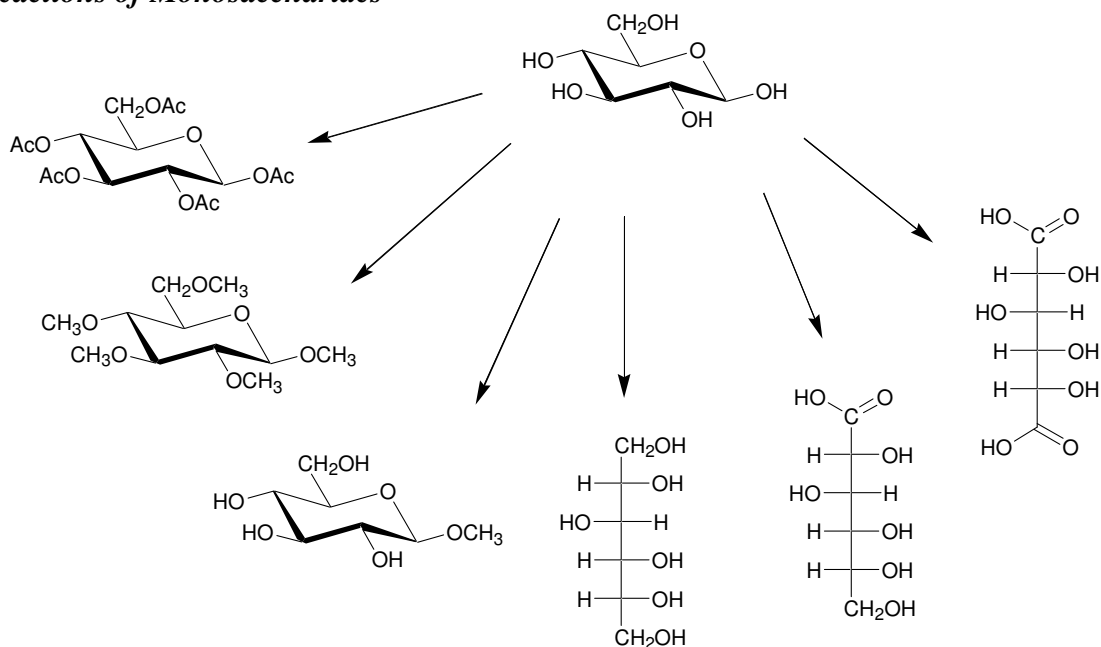
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 24. The answers appear in the section entitled *Review of Reactions*.

Hemiacetal Formation



Chain Lengthening and Chain Shortening



Reactions of Monosaccharides**Solutions****24.1.**a) an aldohexose
d) an aldotetroseb) an aldopentose
e) a ketohexose

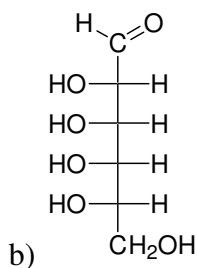
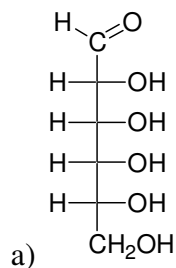
c) a ketopentose

24.2. Both are hexoses so both have molecular formula ($C_6H_{12}O_6$). Although they have the same molecular formula, they have different constitution – one is an aldehyde and the other is a ketone. Therefore, they are constitutional isomers.

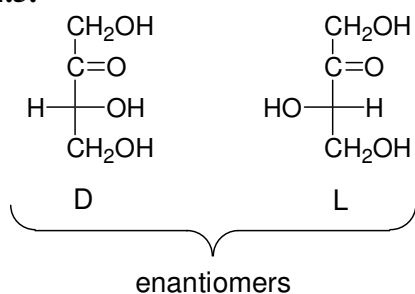
24.3. All are D sugars except for (b), which is an L sugar.

a) 2S, 3S, 4R, 5R b) 2R, 3S, 4S c) 3R, 4R d) 2S, 3R e) 3S, 4S, 5R

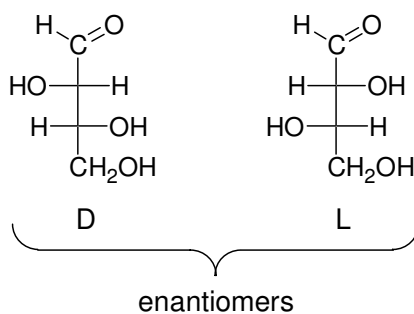
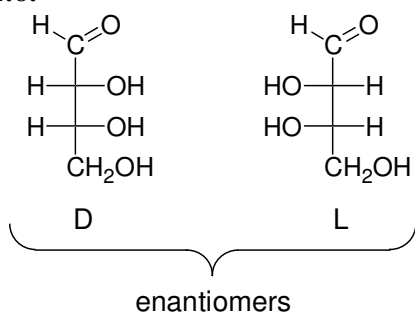
Pay special attention to the following trend: The configuration of each chirality center is *R* when the OH group is on the right side of the Fischer projection, and the configuration is *S* when the OH group is on the left side.

24.4.

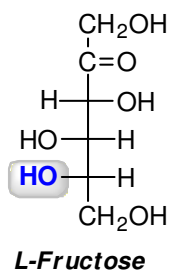
24.5.



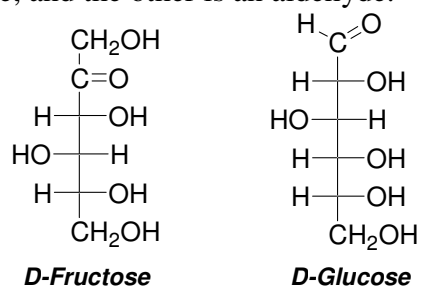
24.6.



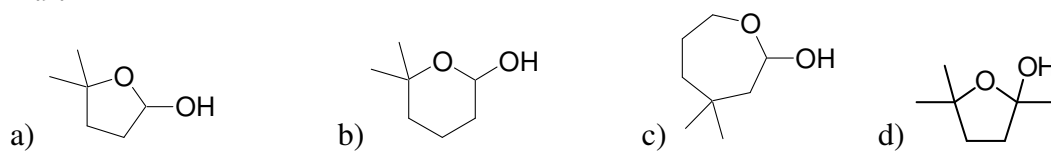
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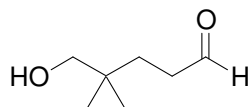
24.8. D-fructose and D-glucose are constitutional isomers. Both have molecular formula ($\text{C}_6\text{H}_{12}\text{O}_6$). Although they have the same molecular formula, they have different constitution – one is a ketone, and the other is an aldehyde.



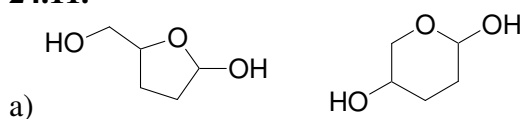
24.9.



24.10.

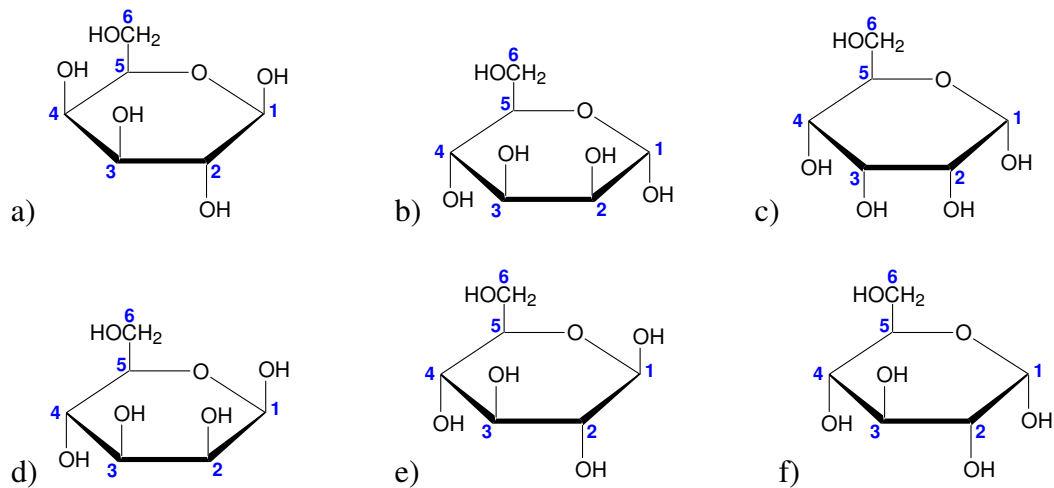


24.11.

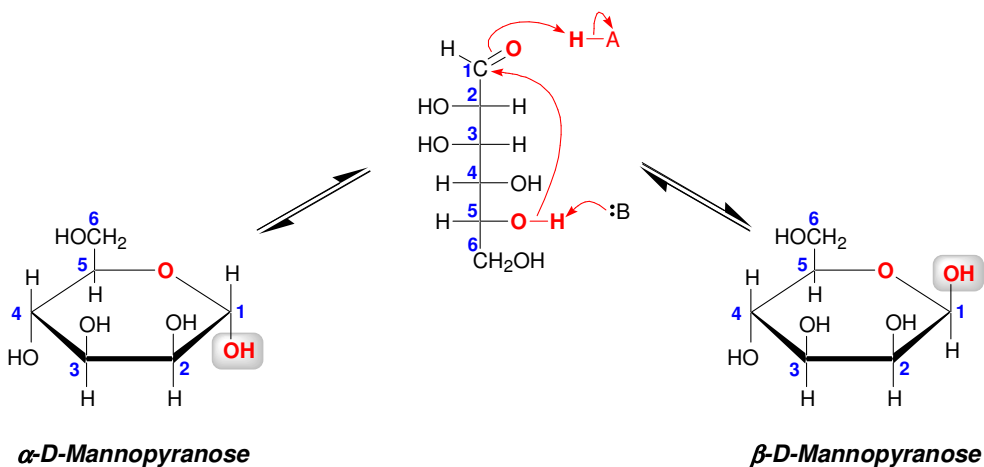


b) The six-membered ring is expected to predominate because it has less ring strain than a five-membered ring.

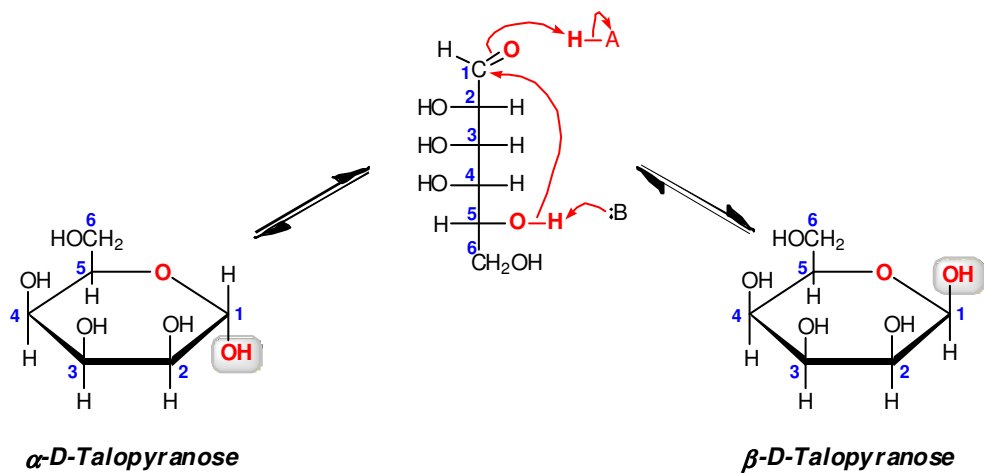
24.12.

24.13. β -D-galactopyranose

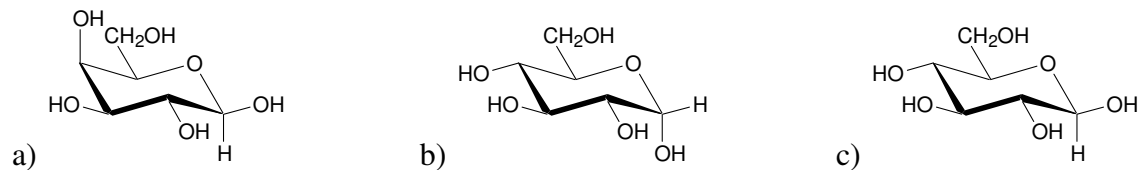
24.14.



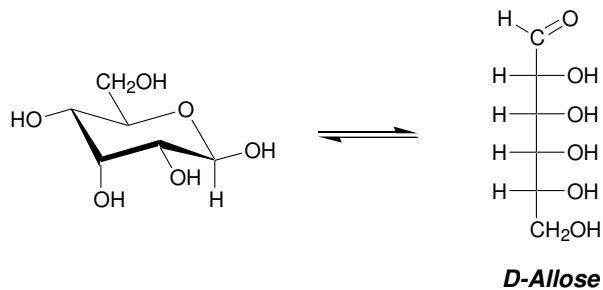
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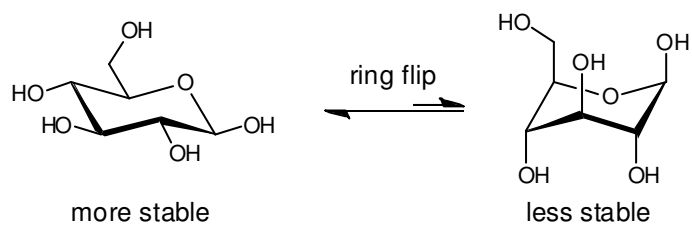
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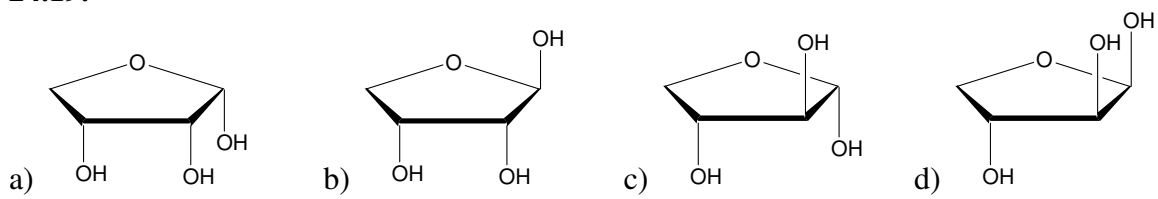
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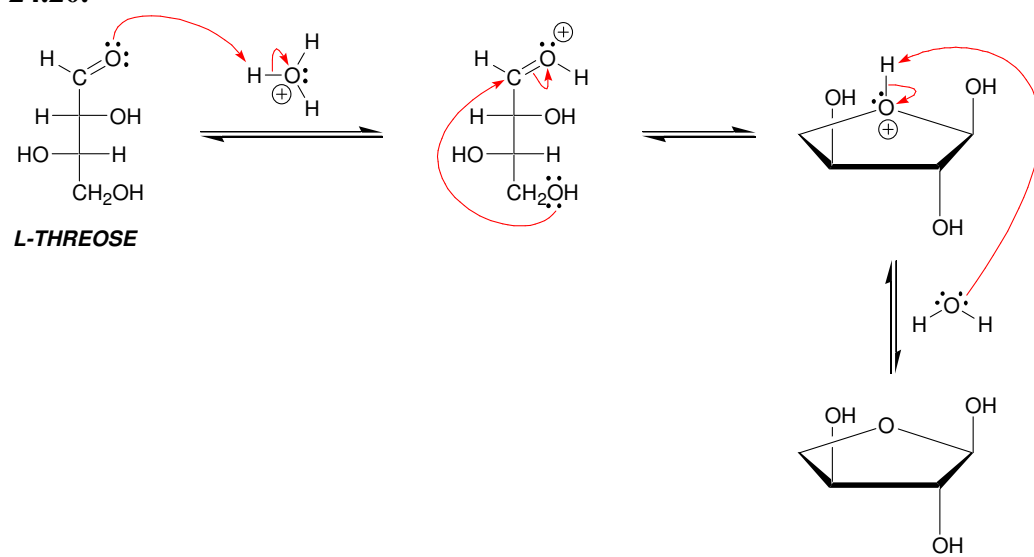
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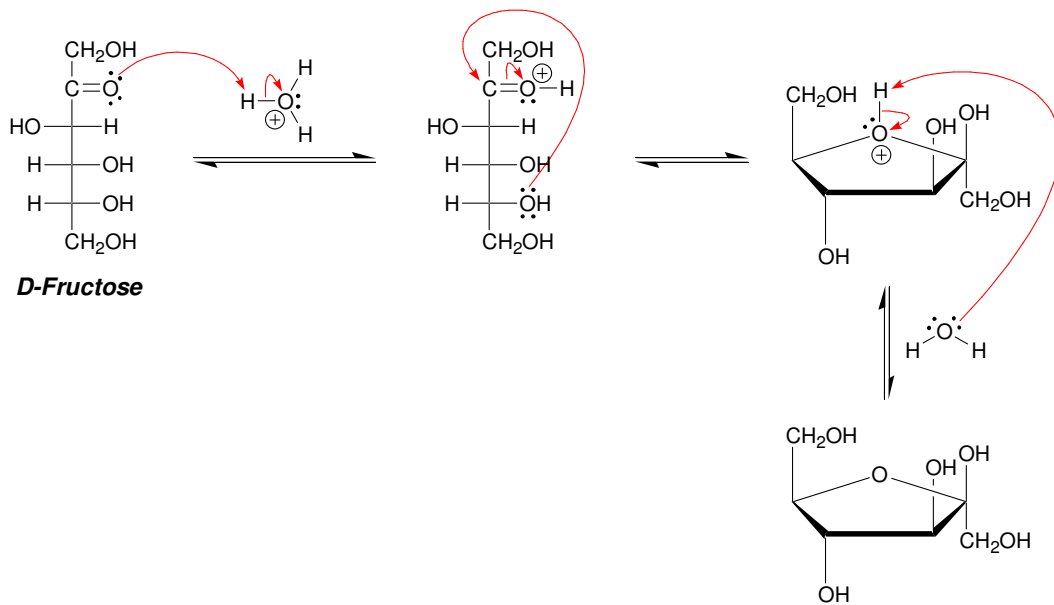
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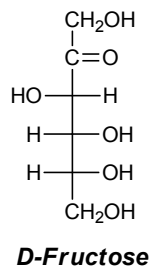
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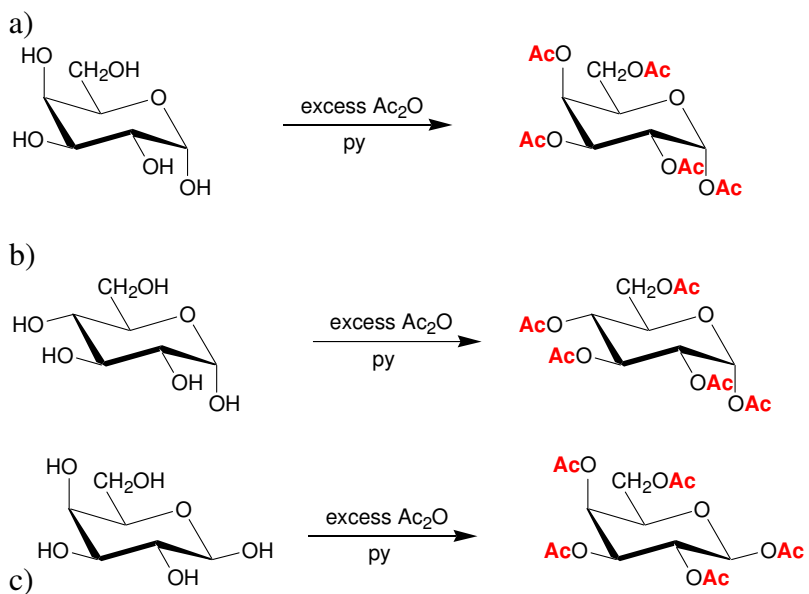
24.21.



24.22.

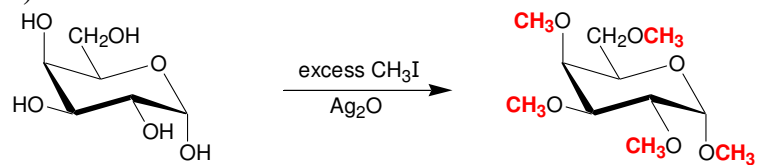


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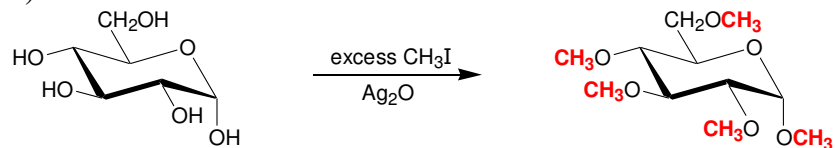


24.24.

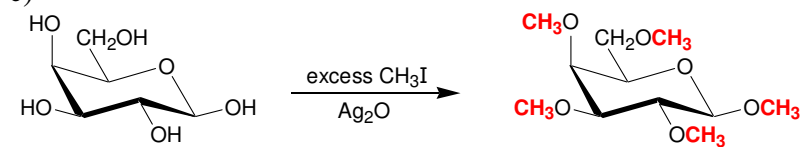
a)



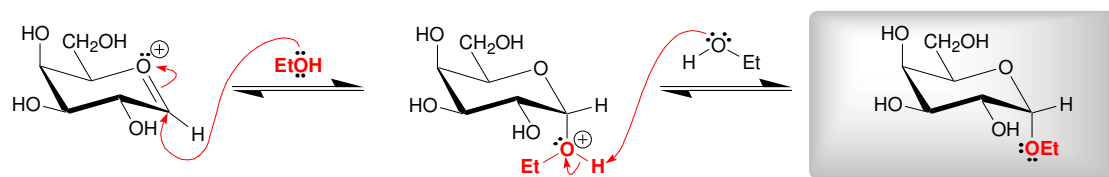
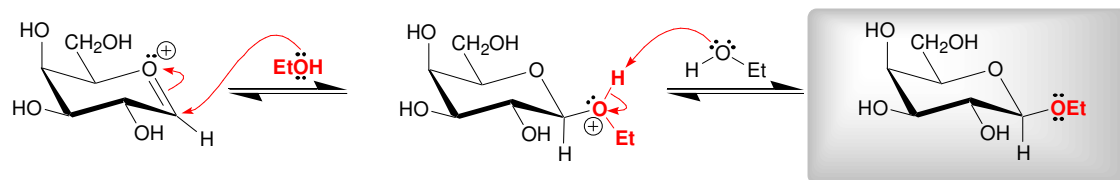
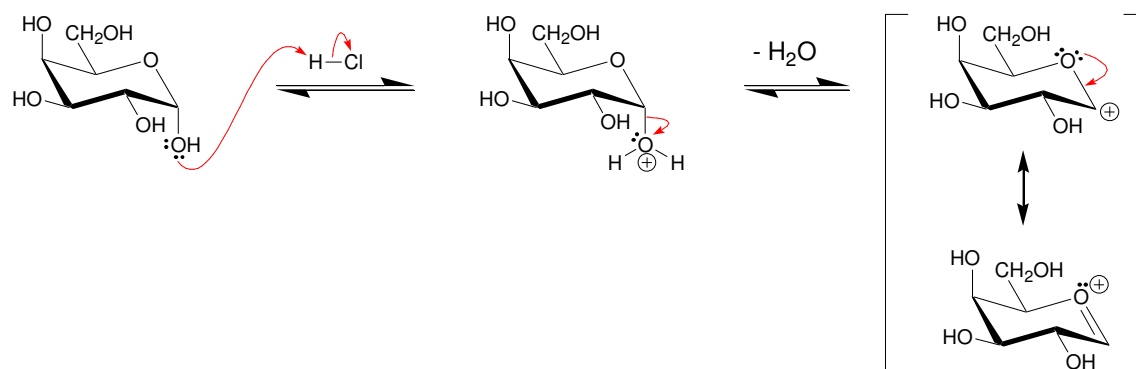
b)



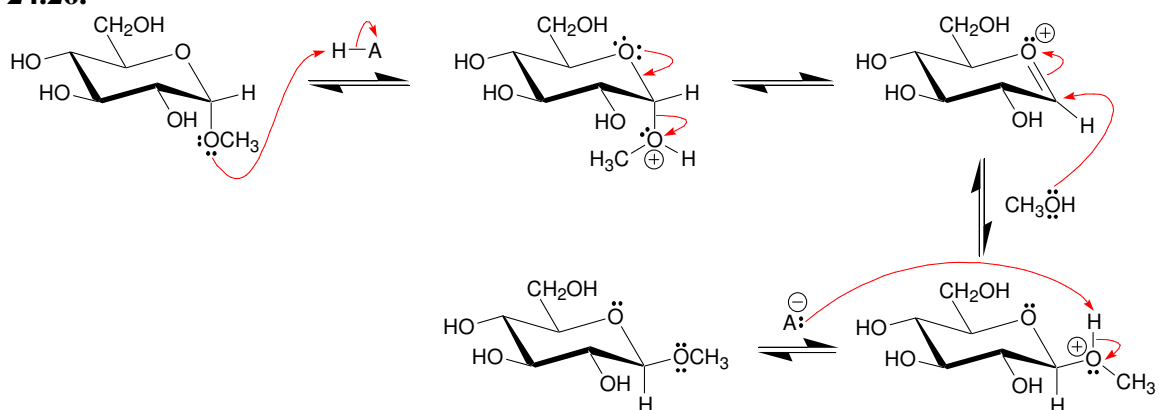
c)



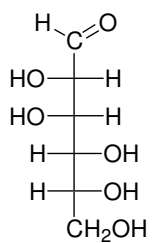
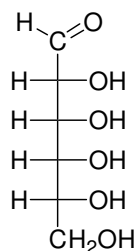
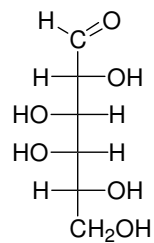
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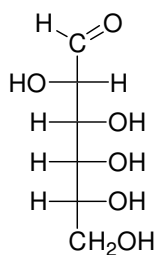
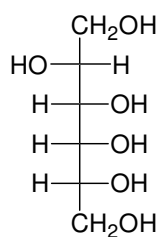
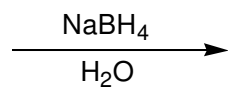
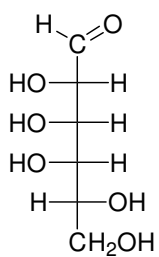
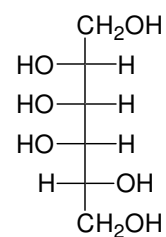
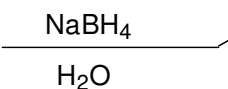
24.26.



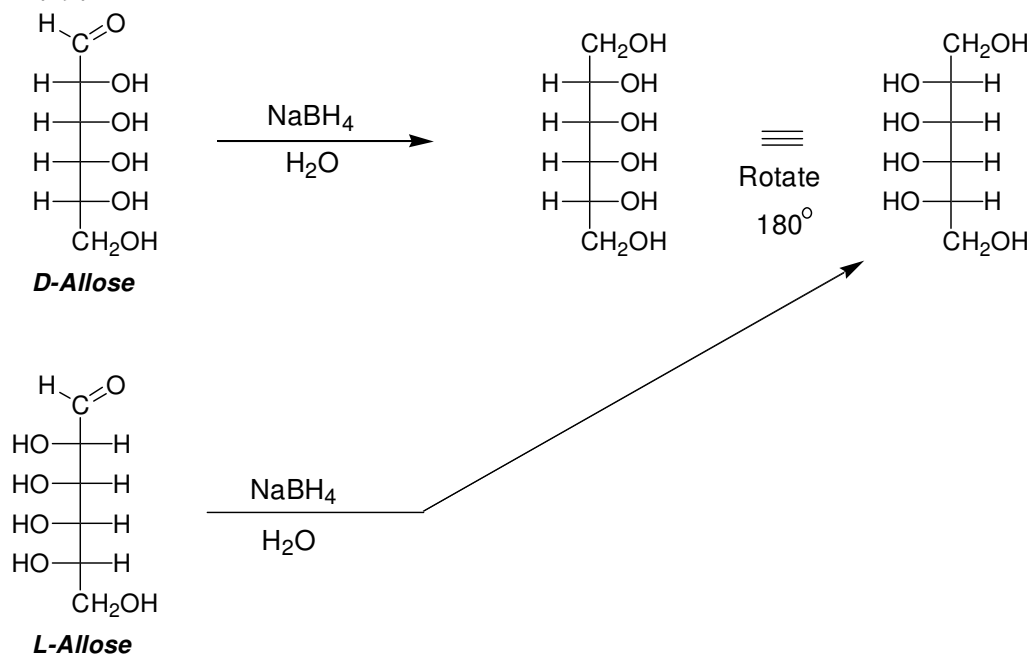
24.27.


 a) *D-Mannose*

 b) *D-Allose*

 c) *D-Galactose*

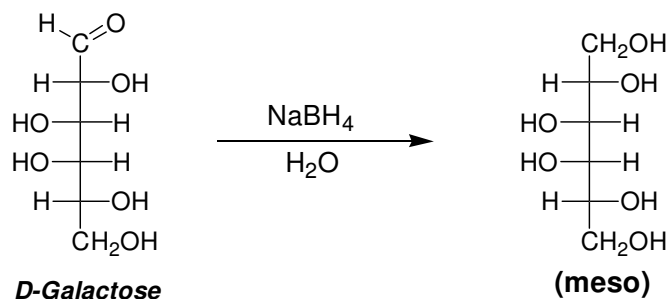
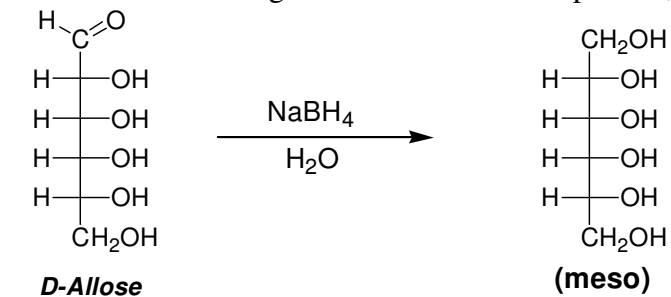
24.28.


D-Altose

 \equiv
 Rotate
 180°

D-Talose


24.29.



24.30. The following alditols are meso compounds, and are therefore optically inactive:



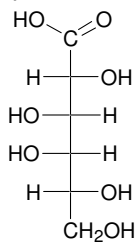
24.31.

a) No (an acetal)

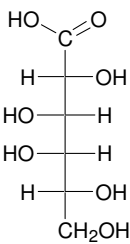
b) Yes

c) Yes

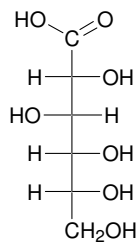
24.32.



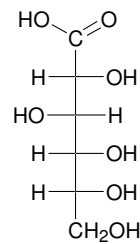
a) *D-Galactonic acid*



b) *D-Galactonic acid*

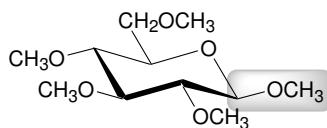


c) *D-Gluconic acid*



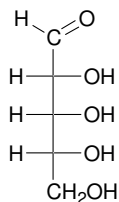
d) *D-Gluconic acid*

24.33. This compound will not be a reducing sugar because the anomeric position is an acetal group.



β-D-Glucopyranose pentamethyl ether

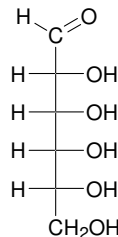
24.34.



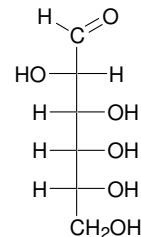
D-Ribose

a)

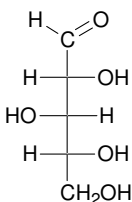
Fischer-Kiliani



D-Allose



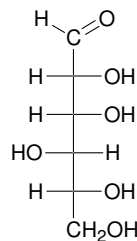
D-Altose



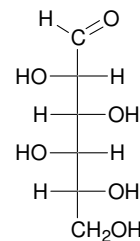
D-Xylose

b)

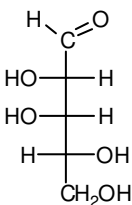
Fischer-Kiliani



D-Gulose



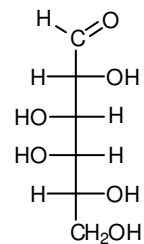
D-Idose



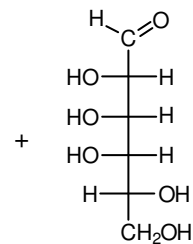
D-Lyxose

c)

Fischer-Kiliani

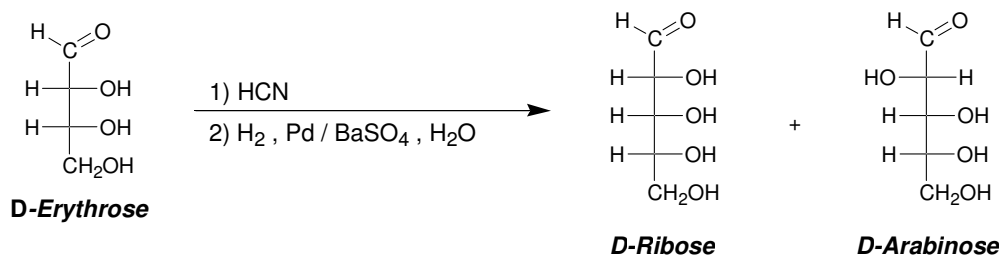


D-Galactose

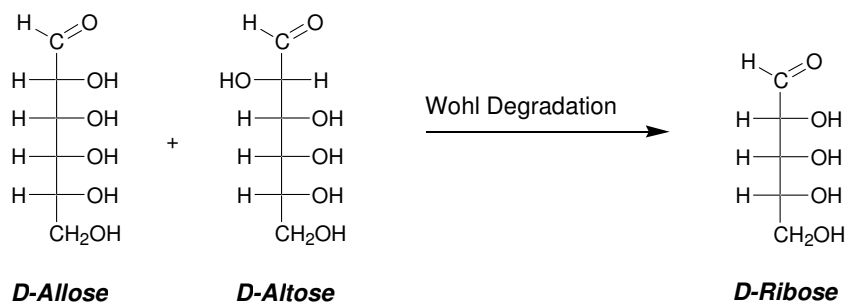


D-Talose

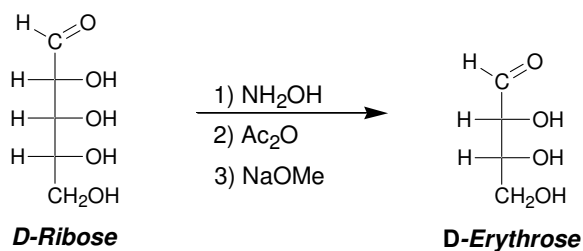
24.35.



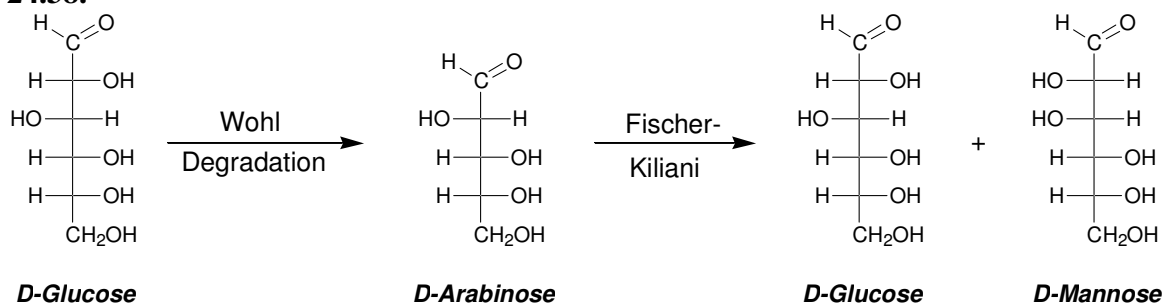
24.36.



24.37.



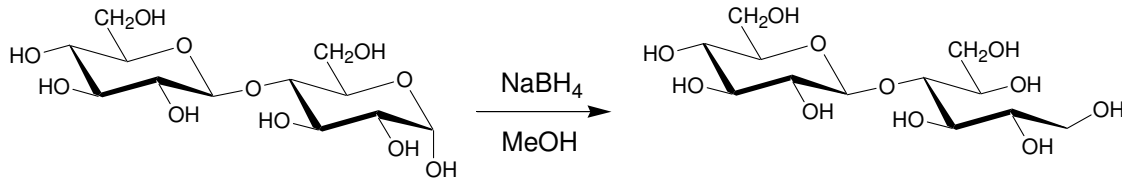
24.38.



24.39.

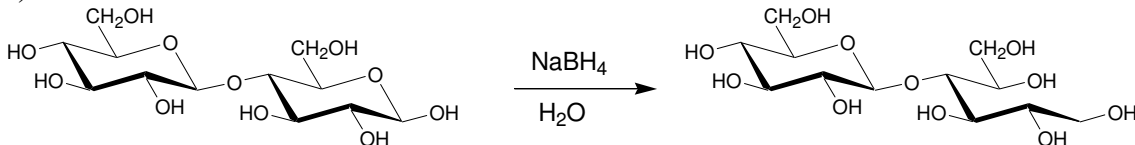
- Yes, one of the anomeric positions bears an OH group.
- No, both anomeric positions bear acetal groups.
- No, both anomeric positions bear acetal groups.

24.40.

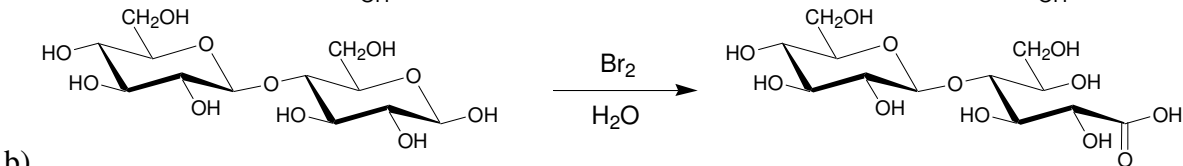


24.41.

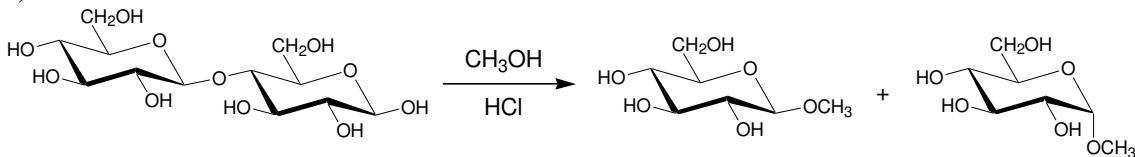
a)



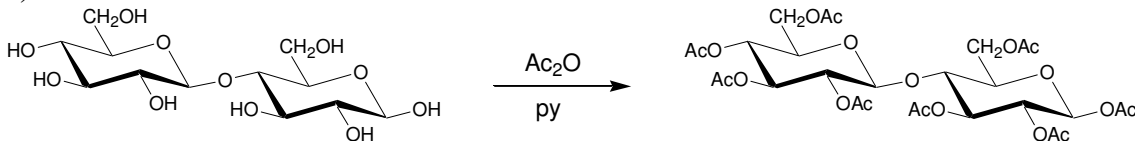
b)



c)



d)



24.42.

- a) a D-aldotetrose b) an L-aldopentose c) a D-aldopentose
 d) a D-aldohexose e) a D-ketopentose

24.43.

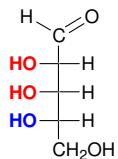
- a) D-glyceraldehyde b) L-glyceraldehyde c) D-glyceraldehyde d) L-glyceraldehyde

24.44.

- a) D-Glucose b) D-Mannose c) D- Galactose d) L-Glucose

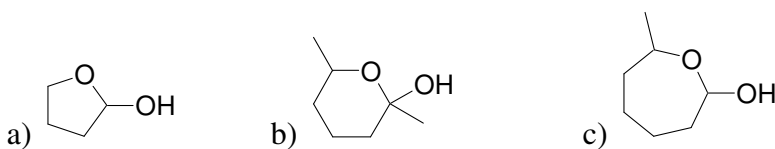
24.45.

- a) D-Ribose
b) D-Arabinose

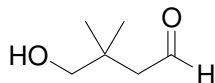


- c) *L-Ribose*
d) Same compound
e) Diastereomers

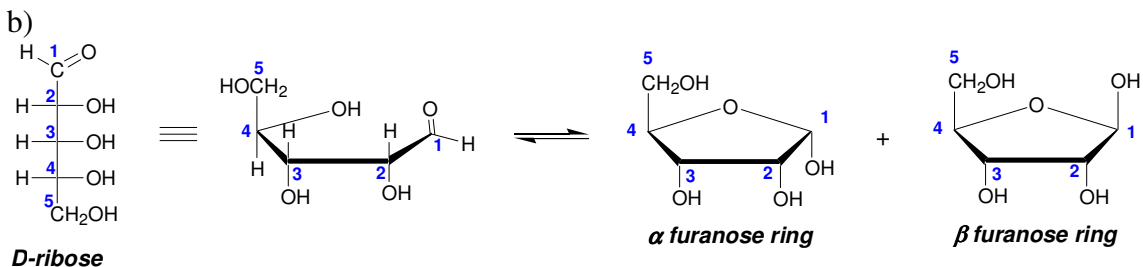
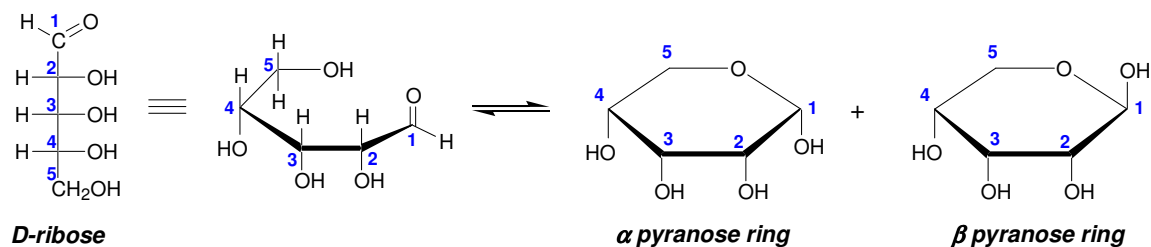
24.46.



24.47.



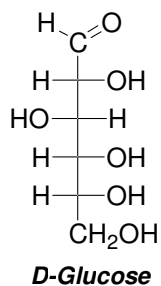
24.48.



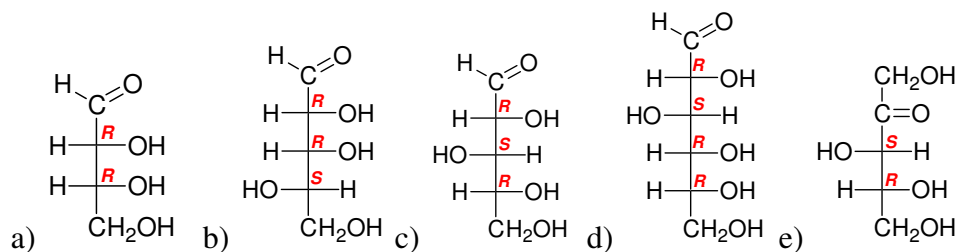
24.49.

- a) epimers b) diastereomers c) enantiomers d) identical compounds

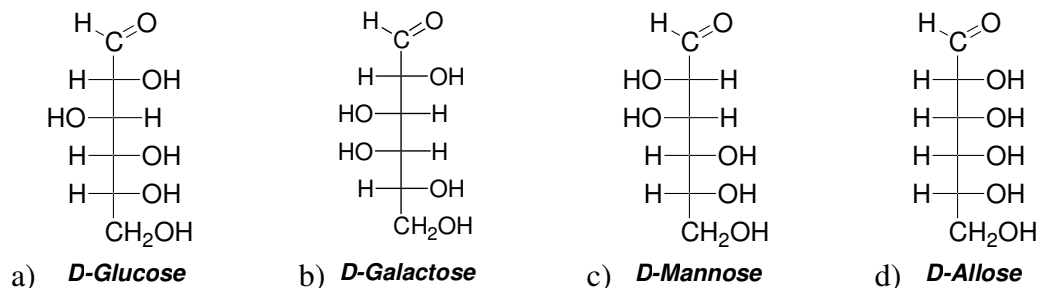
24.50.



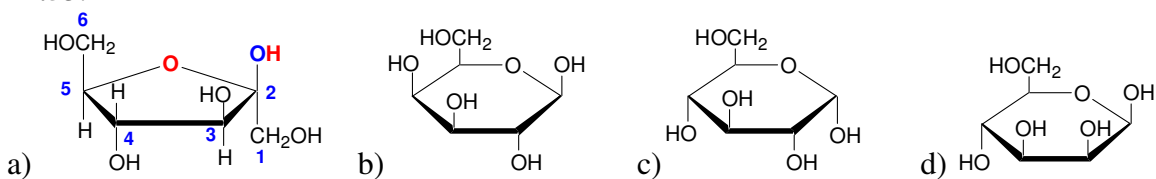
24.51.



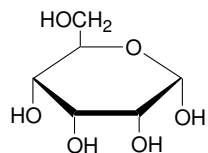
24.52.



24.53.



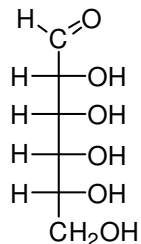
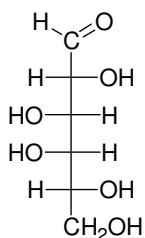
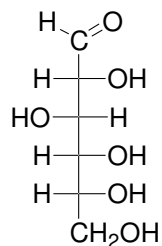
24.54.



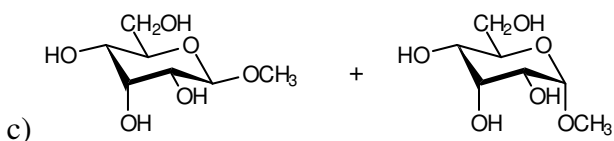
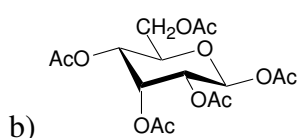
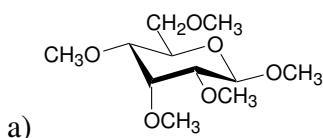
24.55.

- a) α -D-allopyranose
- b) β -D-galactopyranose
- c) methyl β -D-glucopyranoside

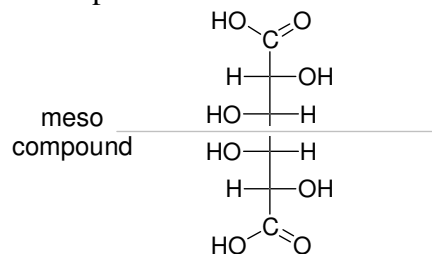
24.56.

a) ***D-Allose***b) ***D-Galactose***c) ***D-Glucose***

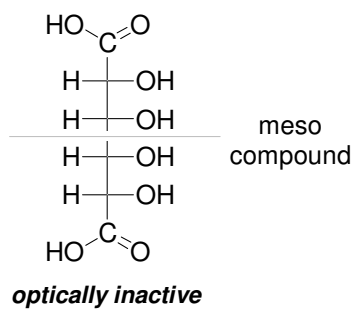
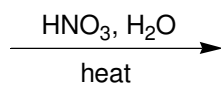
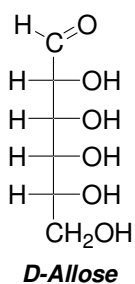
24.57.



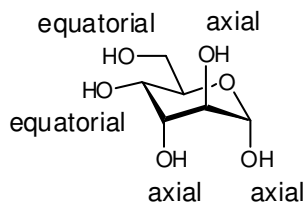
24.58. The product is a meso compound



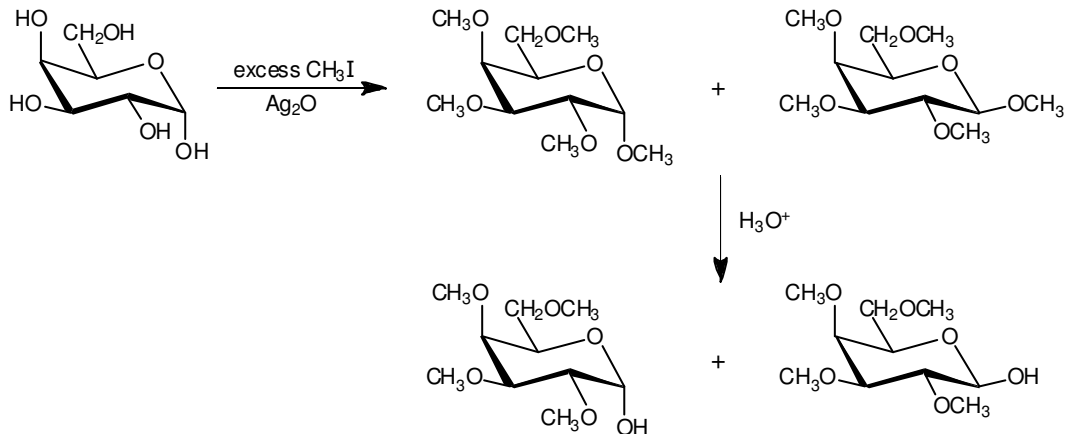
24.59.



24.60.



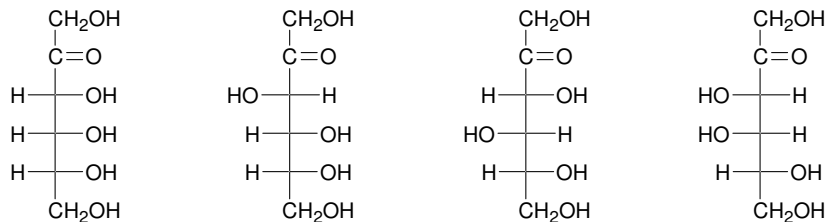
24.61.



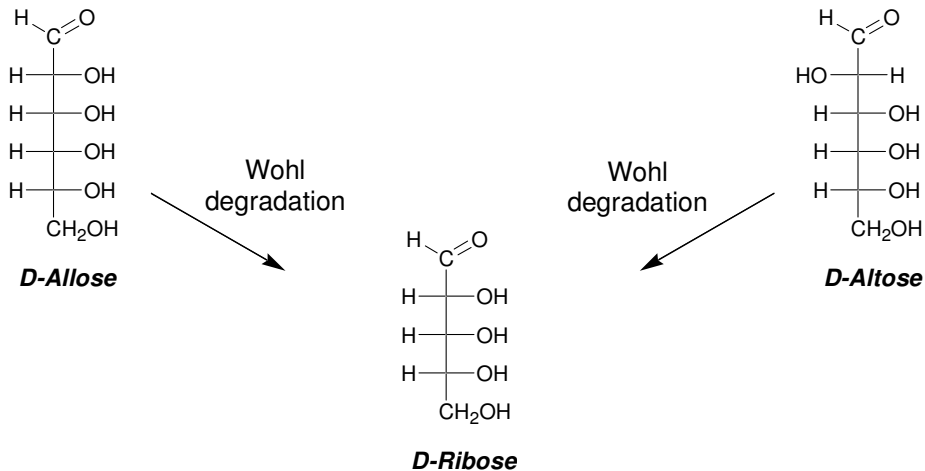
24.62.

- a) diastereomers
- b) same compound

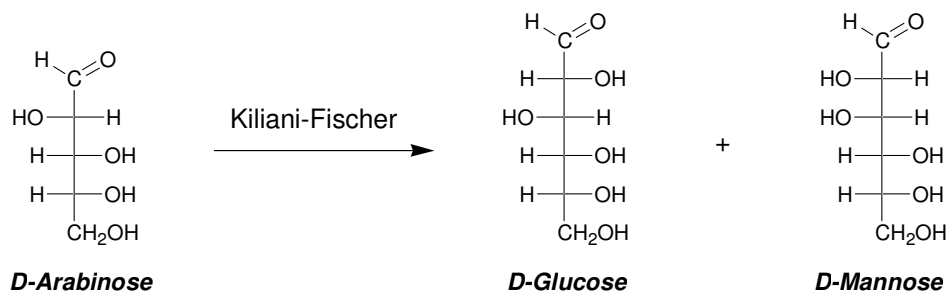
24.63.



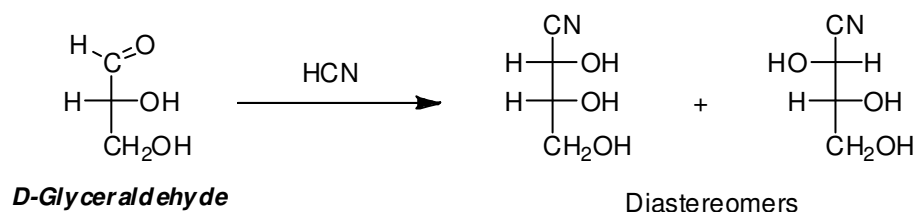
24.64.



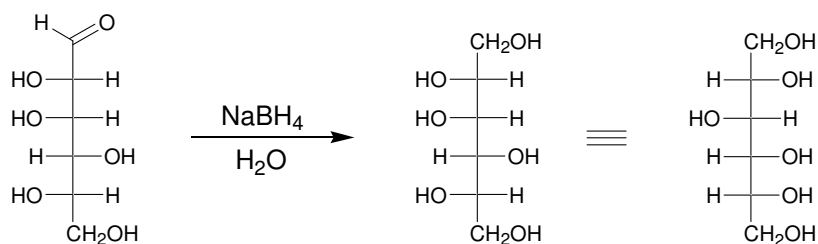
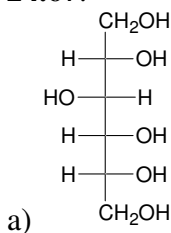
24.65.



24.66.



24.67.

b) *L-Gulose*

24.68. D-Allose and D-Galactose

24.69.

- a) This compound will not be a reducing sugar because the anomeric position is an acetal group.
- b) This compound will be a reducing sugar because the anomeric position bears an OH group.

24.70.

- a) CH_3OH , HCl
- b) CH_3OH , HCl
- c) HNO_3 , H_2O , heat
- d) excess CH_3I , Ag_2O followed by H_3O^+

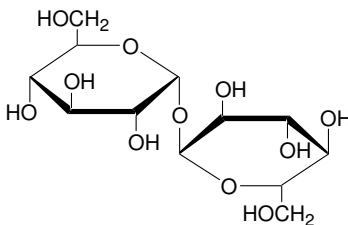
24.71.

- a) α -D-glucopyranose and β -D-glucopyranose
- b) α -D-galactopyranose and β -D-galactopyranose

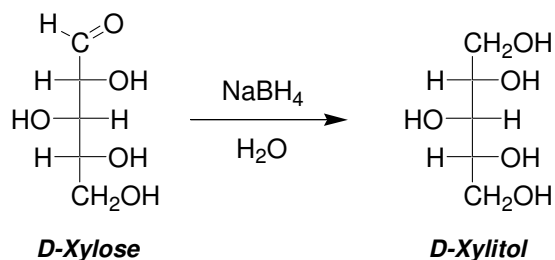
24.72.

- a) D-Arabinose
- b) D-Ribose and D-xylose
- c) D-xylose
- d) D-xylose

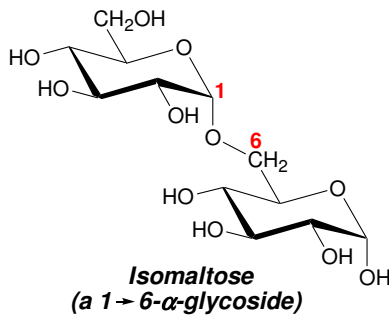
24.73.



24.74.

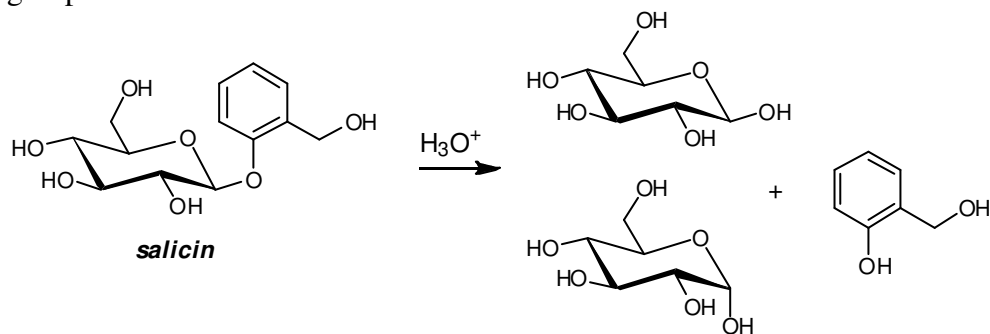


24.75.

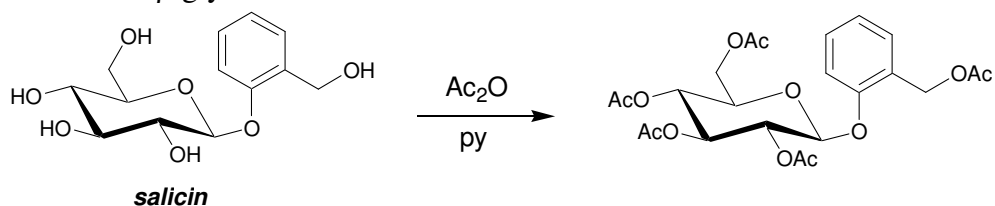


24.76.

- a) No, it is not a reducing sugar because the anomeric position has an acetal group.

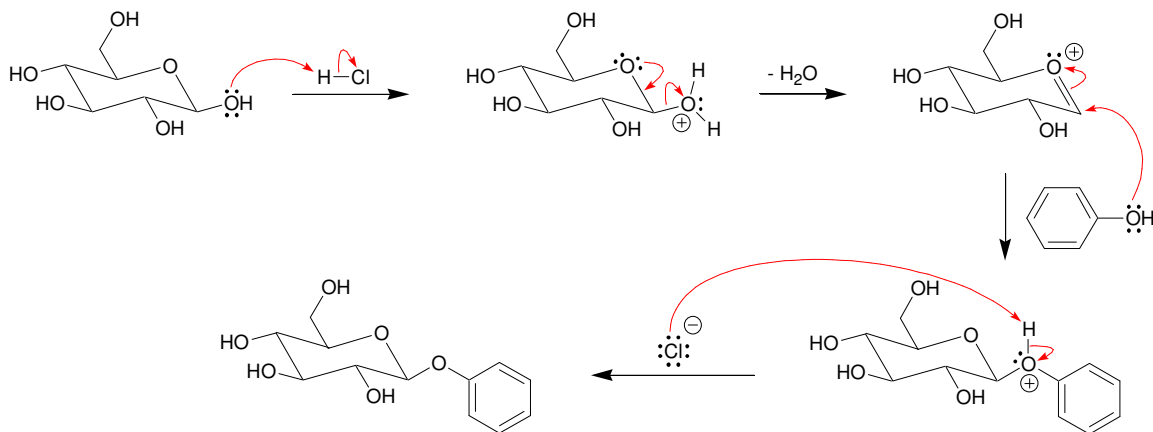


- b)
c) Salicin is a β -glycoside.

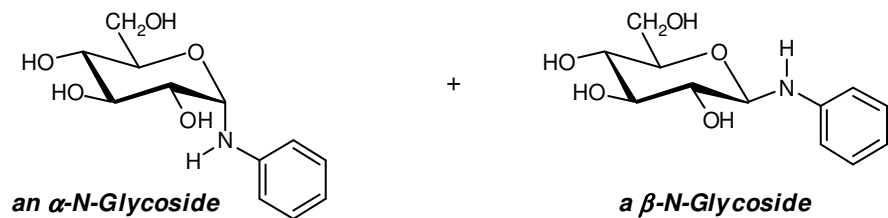


- d) **salicin**
e) No. In the absence of acid catalysis, the acetal group is not readily hydrolyzed.

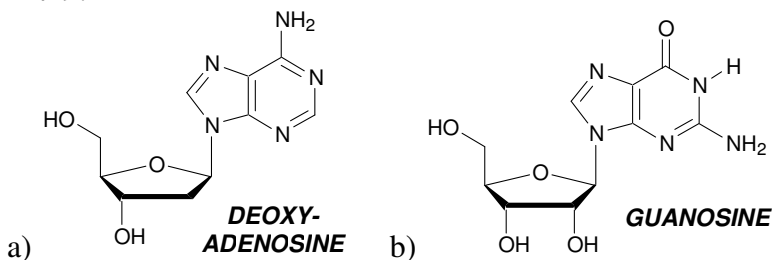
24.77.



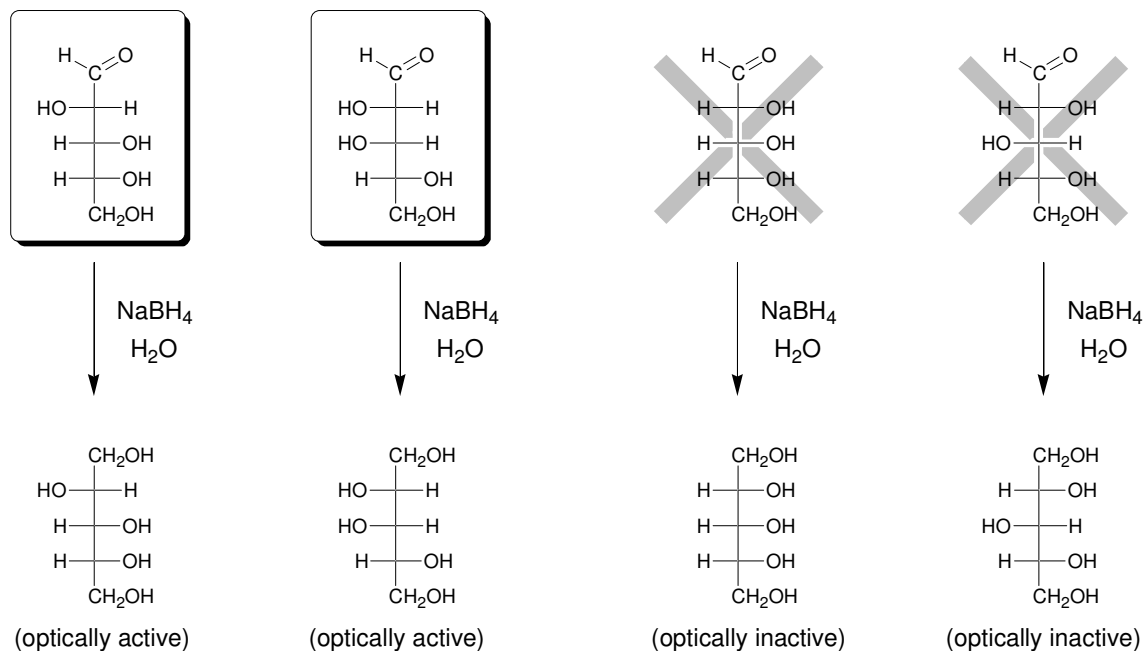
24.78.



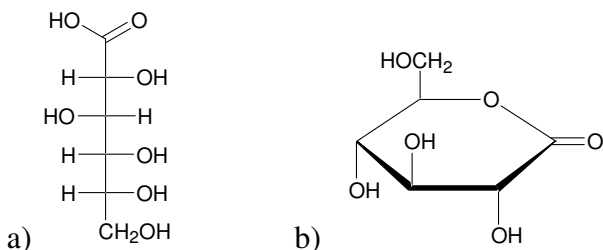
24.79.



24.80.



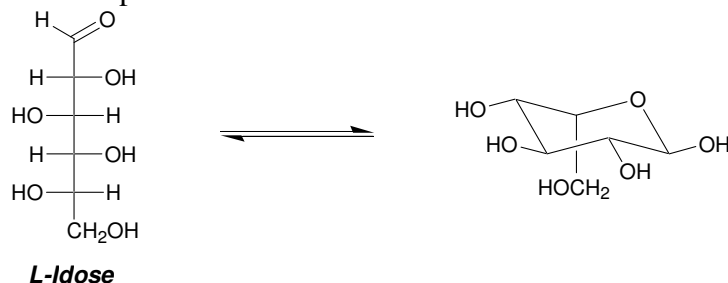
24.81.



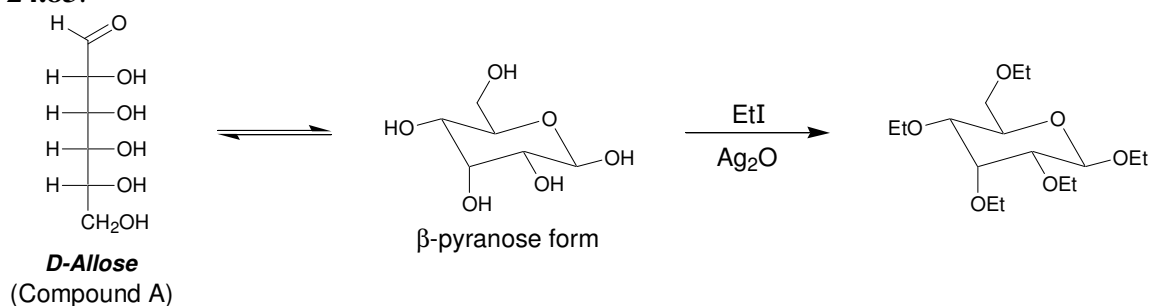
c) Yes. The compound has chirality centers, and it is not a meso compound. Therefore, it will be optically active.

d) The gluconic acid is a carboxylic acid and its IR spectrum is expected to have a broad signal between 2500 and 3600 cm⁻¹. The IR spectrum of the lactone will not have this broad signal.

24.82. In order for the CH₂OH group to occupy an equatorial position, all of the OH groups on the ring must occupy axial positions. The combined steric hindrance of all the OH groups is more than the steric hindrance associated with one CH₂OH group. Therefore, the equilibrium will favor the form in which the CH₂OH group occupies an axial position. The structure of L-idose is:

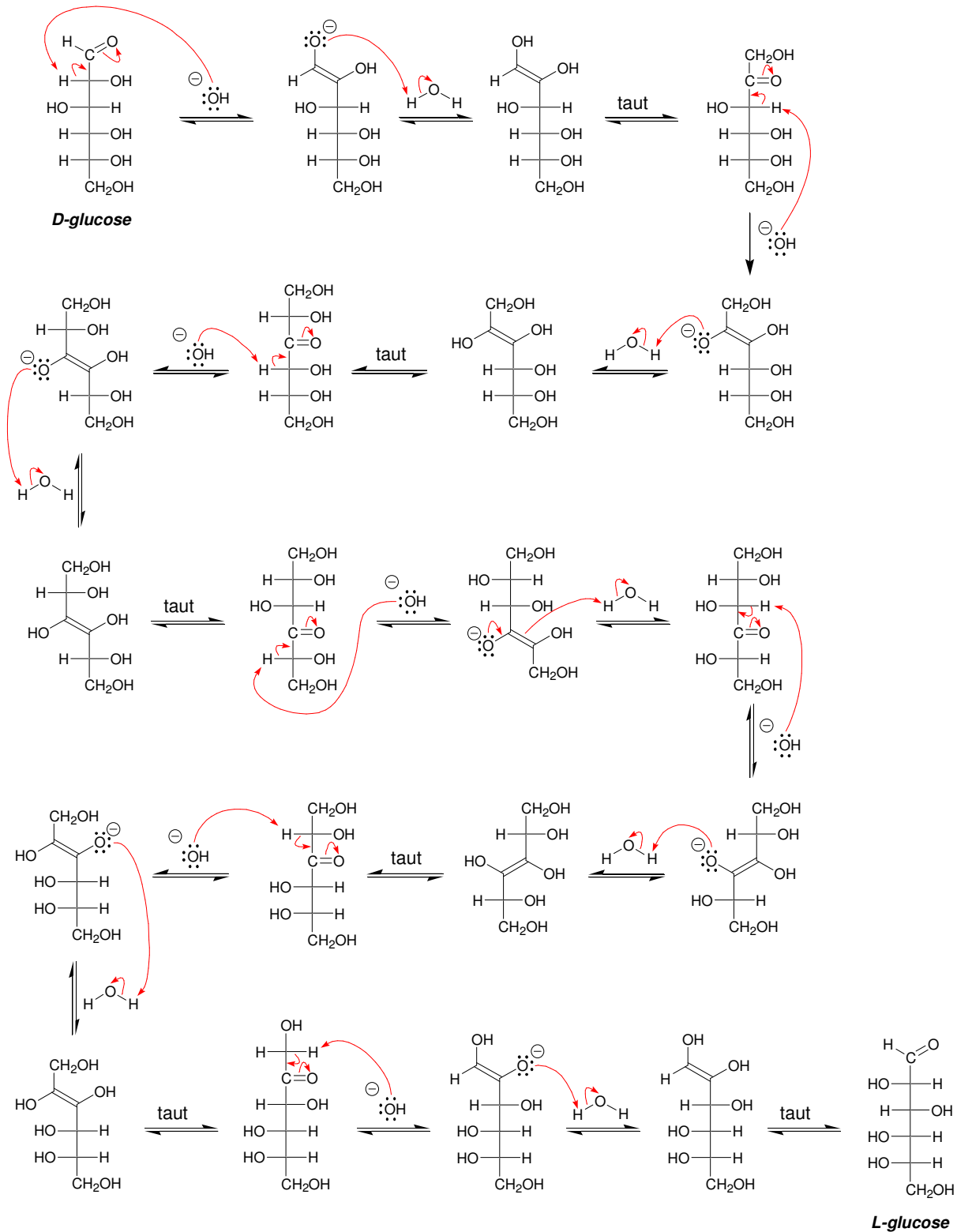


24.83.



24.84. Glucose can adopt a chair conformation in which all of the substituents on the ring occupy equatorial positions. Therefore, D-glucose can achieve a lower energy conformation than any of the other D-aldohexoses.

24.85.



24.86. Compound X is a D-aldohexose that can adopt a β -pyranose form with only one axial substituent. Recall that D-glucose has all substituents in equatorial positions, so compound X must be epimeric with D-glucose either at C2 (D-mannose), C3 (D-allose), or C4 (D-galactose).

Compound X undergoes a Wohl degradation to produce an aldopentose, which is converted into an optically active alditol when treated with sodium borohydride.

Therefore, compound X cannot be D-allose, because a Wohl degradation of D-allose followed by reduction produces an optically *inactive* alditol.

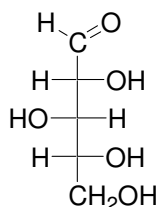
We conclude that compound X must be either D-mannose or D-galactose.

The identity of compound X can be determined by treating compound X with sodium borohydride. Reduction of D-mannose should give an optically active alditol, while reduction of D-galactose gives an optically inactive alditol.

24.87. Compound A is a D-aldopentose. Therefore, there are four possible structures to consider (Figure 24.4).

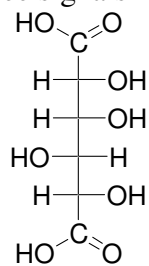
When treated with sodium borohydride, compound A is converted into an alditol that exhibits three signals in its ^{13}C NMR spectrum. Therefore, compound A must be D-ribose or D-xylose both of which are reduced to give symmetrical alditols (thus, three signals for five carbon atoms).

When compound A undergoes a Kiliani-Fischer synthesis, both products can be treated with nitric acid to give optically active aldaric acids. Therefore, compound A cannot be D-ribose, because when D-ribose undergoes a Kiliani-Fischer synthesis, one of the products is D-allose, which is oxidized to give an optically inactive aldaric acid. We conclude that the structure of compound A must be D-xylose.

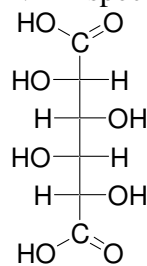


a) **D-Xylose**

b) Compound D is expected to have six signals in its ^{13}C NMR spectrum, while compound E is expected to have only three signals in its ^{13}C NMR spectrum.



Compound D



Compound E