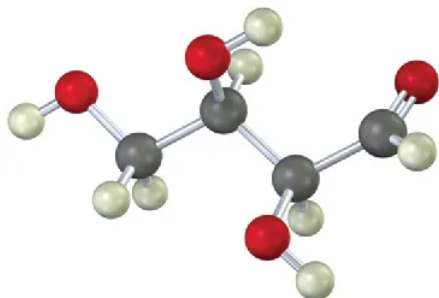


11.13: Additional Problems

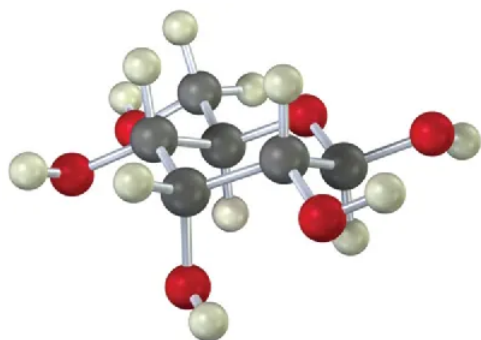
25 • Additional Problems 25 • Additional Problems

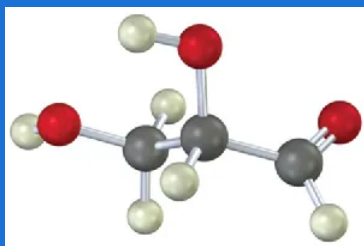
Visualizing Chemistry

Identify the following aldoses, and tell whether each is a D or L sugar: (a)

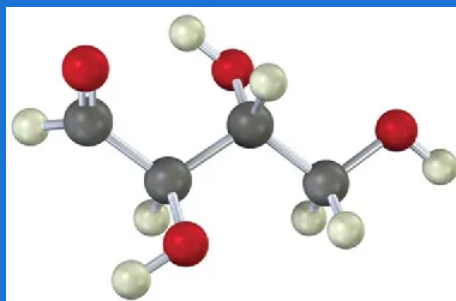


(b)



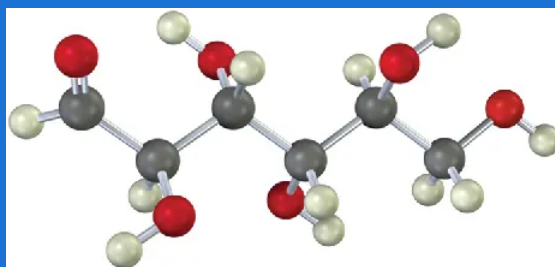
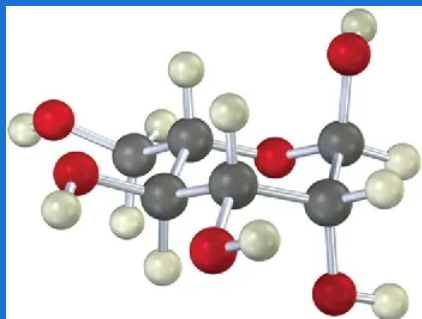


(b)



D or L sugar. (a)
Problem 25-28

The following structure is that of an L aldohexose in its pyranose form. Identify it, and tell whether it is an α or β anomer.



(a)

The following model is that of an aldohexose:

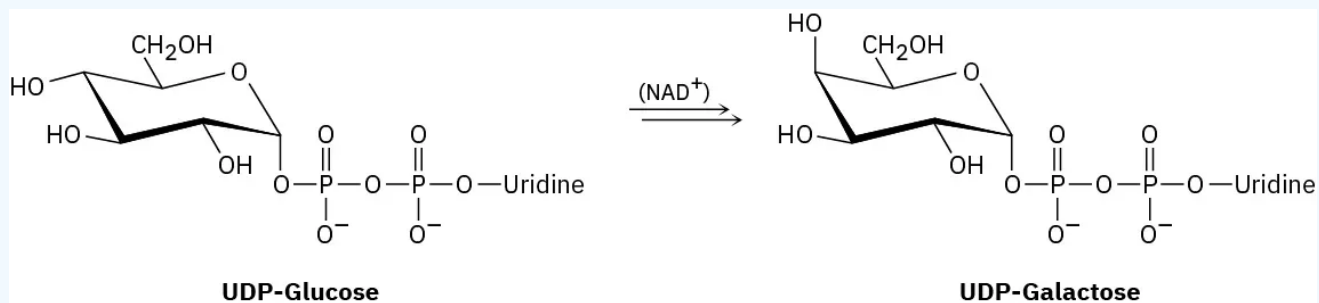
(b)

Is this a D sugar or an L sugar? Explain.

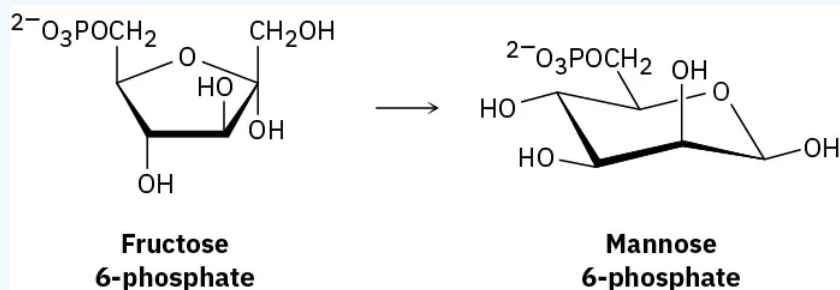
(c) Draw the β anomer of the sugar in its furanose form.

Mechanism Problems

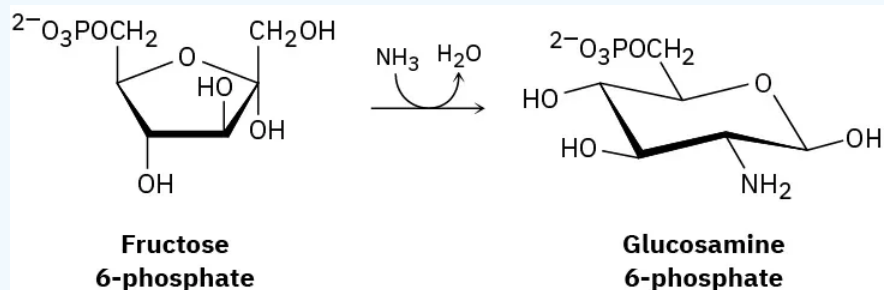
Galactose, one of the eight essential monosaccharides (Section 25.7), is biosynthesized from UDP-glucose by galactose 4-epimerase, where UDP = uridylyl diphosphate (a ribonucleotide diphosphate; Section 28.1). The enzyme requires NAD^+ for activity (Section 17.7), but it is not a stoichiometric reactant, and NADH is not a final reaction product. Propose a mechanism.



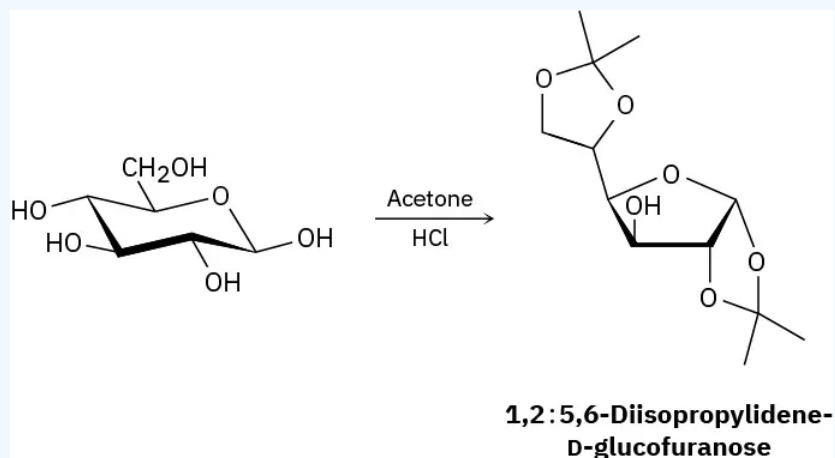
Mannose, one of the eight essential monosaccharides (Section 25.7), is biosynthesized as its 6-phosphate derivative from fructose 6-phosphate. No enzyme cofactor is required. Propose a mechanism.



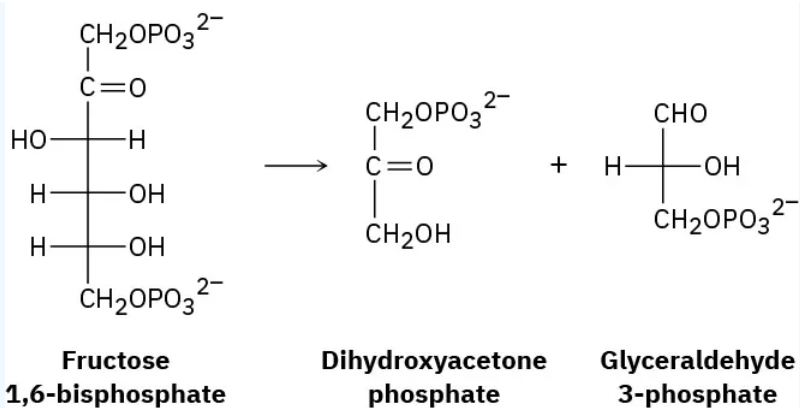
Glucosamine, one of the eight essential monosaccharides (Section 25.7), is biosynthesized as its 6-phosphate derivative from fructose 6-phosphate by reaction with ammonia. Propose a mechanism.



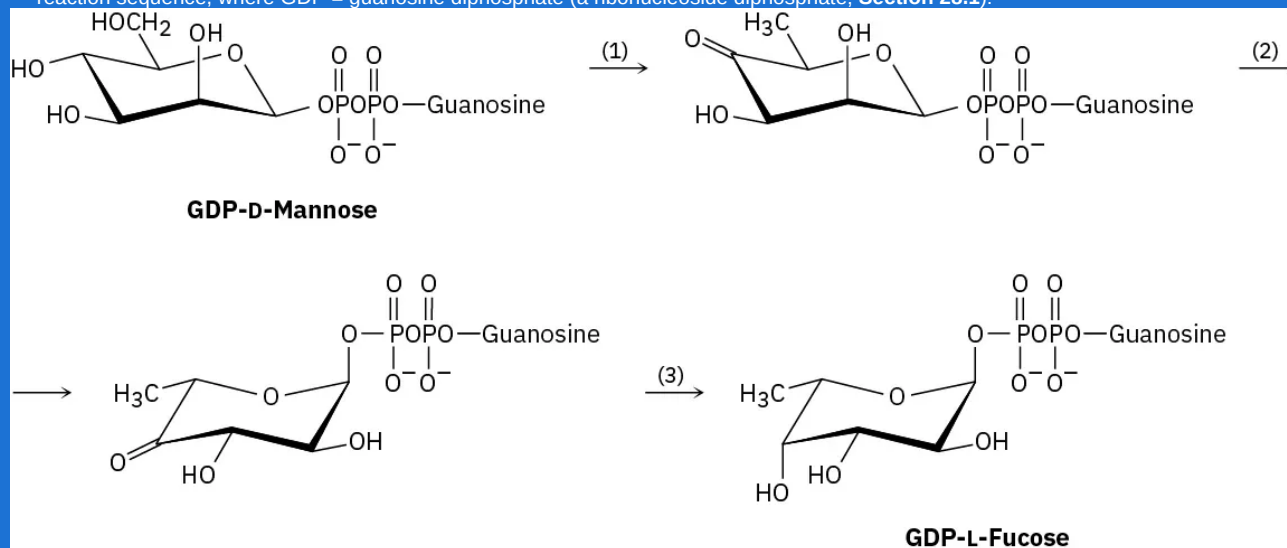
D-Glucose reacts with acetone in the presence of acid to yield the nonreducing 1,2 : 5,6-diisopropylidene-D-glucofuranose. Propose a mechanism.



One of the steps in the biological pathway for carbohydrate metabolism is the conversion of fructose 1,6-bisphosphate into dihydroxyacetone phosphate and glyceraldehyde 3-phosphate. Propose a mechanism for the transformation.



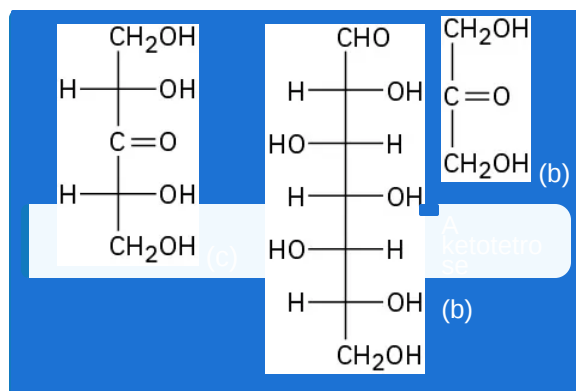
L-Fucose, one of the eight essential monosaccharides (Section 25.7), is biosynthesized from GDP-D-mannose by the following three-step reaction sequence, where GDP = guanosine diphosphate (a ribonucleoside diphosphate; Section 28.1):



(a) Step 1 involves an oxidation to a ketone, a dehydration to an enone, and a conjugate reduction. The step requires NADP^+ , but no NADPH is formed as a final reaction product. Propose a mechanism.

(b) Step 2 accomplishes two epimerizations and utilizes acidic and basic sites in the enzyme but does not require a coenzyme. Propose a mechanism. (c) Step 3 requires NADPH as coenzyme. Show the mechanism.

Carbohydrate Structures



A ketopentose

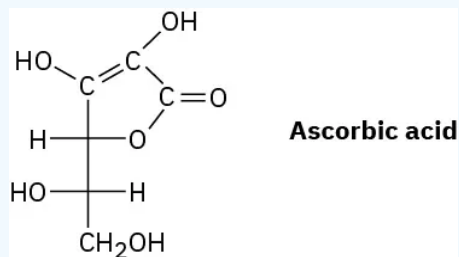
(c) A deoxyaldohexose (d) A five-carbon amino sugar

D-ribose to L-xylose? What generalizations can you make about the following properties of the two sugars? (a)

Melting point

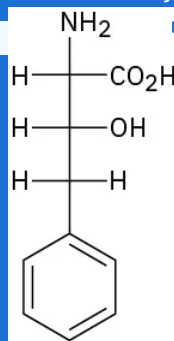
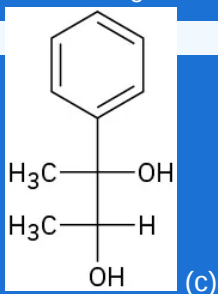
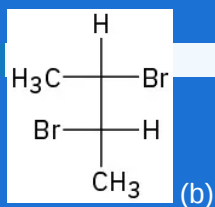
(b) Solubility in water (c) Specific rotation (d) Density

Does ascorbic acid (vitamin C) have a D or L configuration?



Draw the three-dimensional furanose form of ascorbic acid (Problem 25-39), and assign R or S stereochemistry to each chirality center.

R or S configuration to each chirality center in the following molecules: (a)



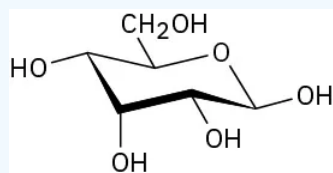
The S enantiomer of 2-bromobutane

The R enantiomer of alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$

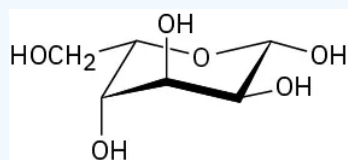
(c) The R enantiomer of 2-hydroxypropanoic acid (d) The S enantiomer of 3-methylhexane

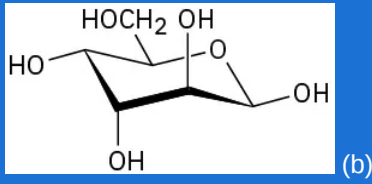
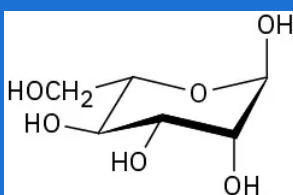
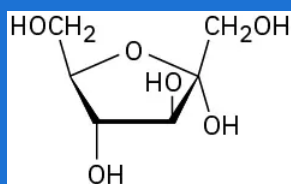
Draw Fischer projections for the two D aldohexoses whose stereochemistry at C3, C4, C5, and C6 is the same as that of D-glucose at C2, C3, C4, and C5.

The following cyclic structure is that of allose. Is this a furanose or pyranose form? Is it an α or a β anomer? Is it a D or an L sugar?

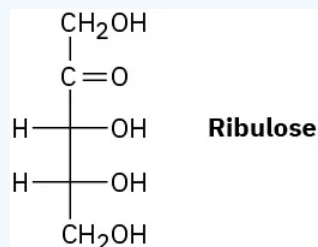


What is the complete name of the following sugar?





Draw D-ribulose in its five-membered cyclic β -hemiacetal form.



Look up the structure of D-talose in Figure 25.4, and draw the β anomer in its pyranose form. Identify the ring substituents as axial or equatorial.

Carbohydrate Reactions

β -D-talopyranose with each of the following reagents: (a)

NaBH_4 in H_2O

(b) Warm dilute HNO_3 (c) Br_2 , H_2O (d) $\text{CH}_3\text{CH}_2\text{OH}$, HCl (e) CH_3I , Ag_2O (f) $(\text{CH}_3\text{CO})_2\text{O}$, pyridine

How many D-2-ketohexoses are possible? Draw them.

One of the D-2-ketohexoses is called *sorbose*. On treatment with NaBH_4 , sorbose yields a mixture of gulitol and iditol. What is the structure of sorbose?

Another D-2-ketohexose, *psicose*, yields a mixture of allitol and altritol when reduced with NaBH_4 . What is the structure of psicose?

L-Gulose can be prepared from D-glucose by a route that begins with oxidation to D-glucaric acid, which cyclizes to form two six-membered-ring lactones. Separating the lactones and reducing them with sodium amalgam gives D-glucose and L-gulose. What are the structures of the two lactones, and which one is reduced to L-gulose?

Gentiobiose, a rare disaccharide found in saffron and gentian, is a reducing sugar and forms only D-glucose on hydrolysis with aqueous acid. Reaction of gentiobiose with iodomethane and Ag_2O yields an octamethyl derivative, which can be hydrolyzed with aqueous acid to give 1 equivalent of 2,3,4,6-tetra-O-methyl-D-glucopyranose and 1 equivalent of 2,3,4-tri-O-methyl-D-glucopyranose. If gentiobiose contains a β -glycoside link, what is its structure?

General Problems

All aldoses exhibit mutarotation. For example, α -D-galactopyranose has $[\alpha]_D = +150.7$, and β -D-galactopyranose has $[\alpha]_D = +52.8$. If either anomer is dissolved in water and allowed to reach equilibrium, the specific rotation of the solution is $+80.2$. What are the percentages of each anomer at equilibrium? Draw the pyranose forms of both anomers.

What other D aldohexose gives the same alditol as D-talose?

Which of the eight D aldohexoses give the same aldaric acids as their L enantiomers?

Which of the other three D aldopentoses gives the same aldaric acid as D-lyxose?

L-galactose, and then answer the following questions: (a)

Which other aldohexose gives the same aldaric acid as L-galactose on oxidation with warm HNO_3 ?

(b) Is this other aldohexose a D sugar or an L sugar? (c) Draw this other aldohexose in its most stable pyranose conformation.

Amygdalin, or laetrile, is a cyanogenic glycoside first isolated in 1830 from almond and apricot seeds. If acidic hydrolysis of amygdalin liberates HCN , along with benzaldehyde cyanohydrin with gentiobiose (Problem 25-54), what is its structure?

Trehalose is a nonreducing disaccharide that is hydrolyzed by aqueous acid to yield 2 equivalents of D-glucose. Methylation followed by hydrolysis yields 2 equivalents of 2,3,4,6-tetra-O-methylglucose. How many structures are possible for trehalose?

Trehalose (Problem 25-61) is cleaved by enzymes that hydrolyze α -glycosides but not by enzymes that hydrolyze β -glycosides. What is the structure and systematic name of trehalose?

Isotrehalose and neotrehalose are chemically similar to trehalose (Problems 25-61 and 25-62) except that neotrehalose is hydrolyzed only by β -glycosidase enzymes, whereas isotrehalose is hydrolyzed by both α - and β -glycosidase enzymes. What are the structures of isotrehalose and neotrehalose?

D-Mannose reacts with acetone to give a diisopropylidene derivative (Problem 25-33) that is still reducing toward Tollens' reagent. Propose a likely structure for this derivative.

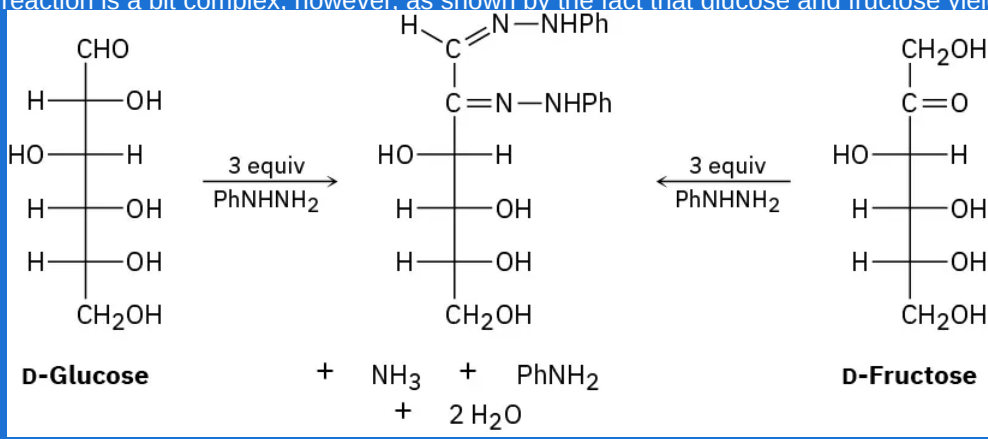
Glucose and mannose can be interconverted (in low yield) by treatment with dilute aqueous NaOH. Propose a mechanism.

Propose a mechanism to account for the fact that D-gluconic acid and D-mannonic acid are interconverted when either is heated in pyridine solvent.

The *cyclitols* are a group of carbocyclic sugar derivatives having the general formulation 1,2,3,4,5,6-cyclohexanehexol. How many stereoisomeric cyclitols are possible? Draw them in their chair forms.

Compound **A** is a D aldopentose that can be oxidized to an optically inactive aldaric acid **B**. On Kiliani-Fischer chain extension, **A** is converted into **C** and **D**; **C** can be oxidized to an optically active aldaric acid **E**, but **D** is oxidized to an optically inactive aldaric acid **F**. What are the structures of **A-F**?

Simple sugars undergo reaction with phenylhydrazine, PhNH-NH_2 , to yield crystalline derivatives called **osazones**. The reaction is a bit complex, however, as shown by the fact that glucose and fructose yield the



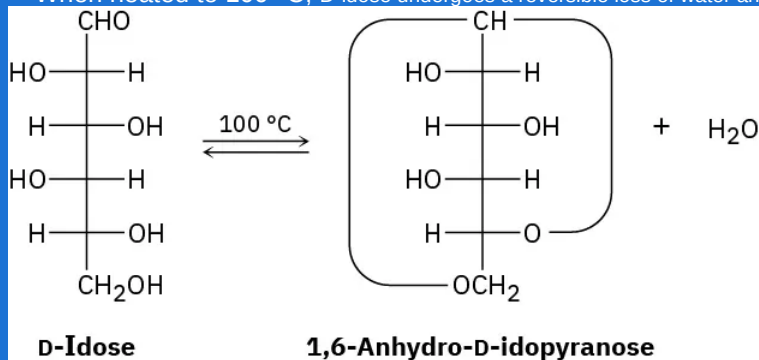
same osazone.

(a)

Draw the structure of a third sugar that yields the same osazone as glucose and fructose.

(b) Using glucose as the example, the first step in osazone formation is reaction of the sugar with phenylhydrazine to yield an imine called a *phenylhydrazone*. Draw the structure of the product. (c) The second and third steps in osazone formation are tautomerization of the phenylhydrazone to give an enol, followed by elimination of aniline to give a keto imine. Draw the structures of both the enol tautomer and the keto imine. (d) The final step is reaction of the keto imine with 2 equivalents of phenylhydrazine to yield the osazone plus ammonia. Propose a mechanism for this step.

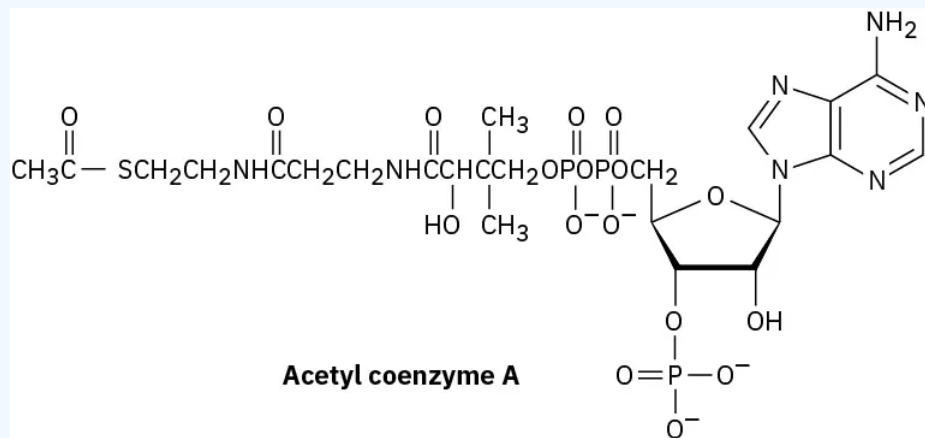
When heated to 100 °C, D-idose undergoes a reversible loss of water and exists primarily as 1,6-anhydro-D-idopyranose.



Draw D-idose in its pyranose form, showing the more stable chair conformation of the ring.

(b) Which is more stable, α -D-idopyranose or β -D-idopyranose? Explain. (c) Draw 1,6-anhydro-D-idopyranose in its most stable conformation. (d) When heated to 100 °C under the same conditions as those used for D-idose, D-glucose does not lose water and does not exist in a 1,6-anhydro form. Explain.

Acetyl coenzyme A (acetyl CoA) is the key intermediate in food metabolism. What sugar is present in acetyl CoA?



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