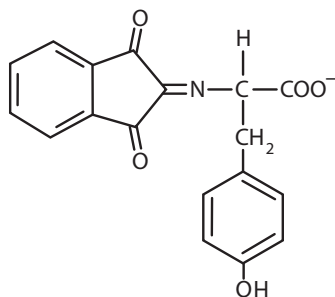


Aldehydes & Ketones Practice Items

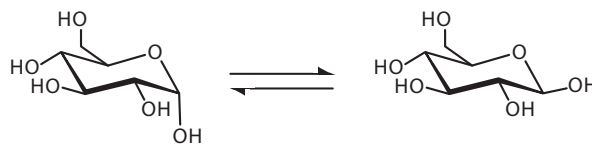
1. The substance ninhydrin is a tool of quantitative analysis. The reaction of two equivalents of ninhydrin with an α -amino acid produces both CO_2 and the intensely colored Ruheman's purple. Reaction with the first equivalent of ninhydrin produces a ketamine such as is depicted in the figure below.



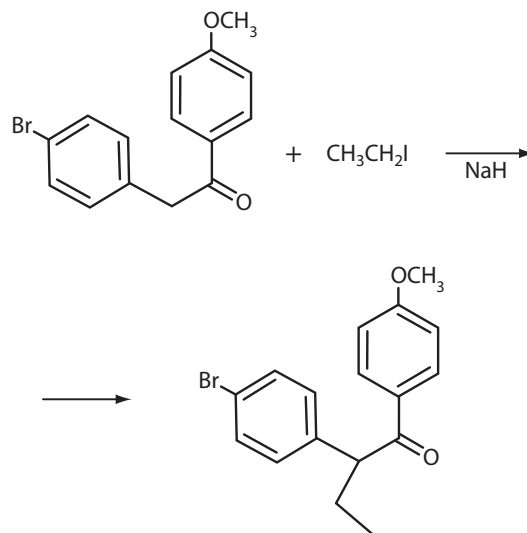
Which figure below represents the structure of ninhydrin?

- A.
- B.
- C.
- D.

2. Which of the following choices best describes the pathway of interconversion of α -glucopyranose and β -glucopyranose?

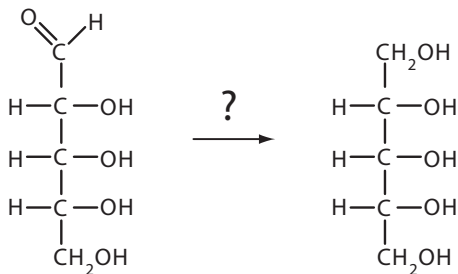


- A. tautomerization
 B. ring flipping
 C. hemiacetal formation
 D. aldol cleavage
3. The figure below shows a step in the benchtop synthesis of tamoxifen, a medication used to treat hormone-receptor positive early and metastatic breast cancers. What is the mechanism of this reaction?

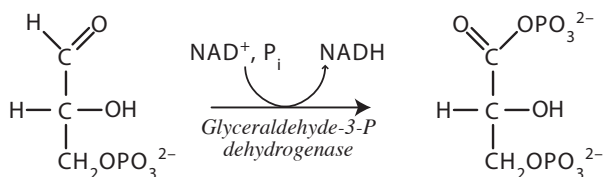


- A. $\text{S}_{\text{N}}2$ substitution
 B. cyanohydrin formation
 C. aldol addition
 D. nucleophilic acyl substitution

4. Which reagent could be used to carry out the conversion of D-ribose to D-ribitol?



- A. FAD
 B. NaBH_4
 C. KOH
 D. PCC
5. In one of the reactions of the glycolytic pathway, glyceraldehyde-3-phosphate is oxidized by NAD^+ to form 1,3-bisphosphoglycerate in a reaction catalyzed by the enzyme glyceraldehyde-3-phosphate dehydrogenase.

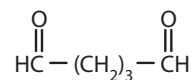


What change has occurred to the oxidation state of the aldehyde carbon of glyceraldehyde-3-phosphate as a result of this reaction?

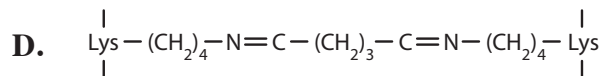
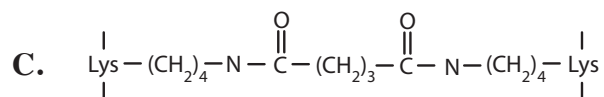
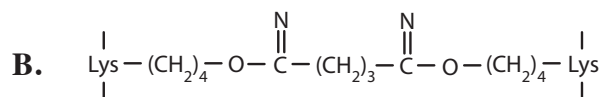
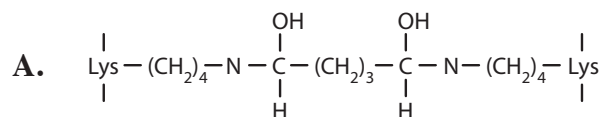
- A. $+1 \rightarrow +2$
 B. $+1 \rightarrow +3$
 C. $+2 \rightarrow +3$
 D. $+2 \rightarrow +4$

6. A method for quaternary structure analysis, which is especially useful for oligomeric proteins that decompose easily, employs cross-linking agents.

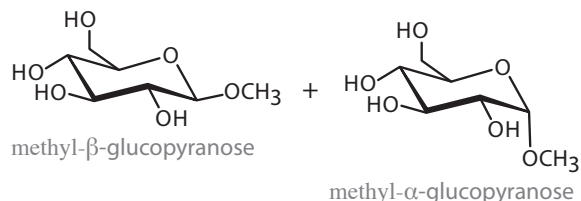
Glutaraldehyde is a bifunctional reagent that reacts to covalently crosslink two Lys residues.



Which of the following structures below represents the cross-links formed by treatment of a multi-subunit protein with glutaraldehyde?



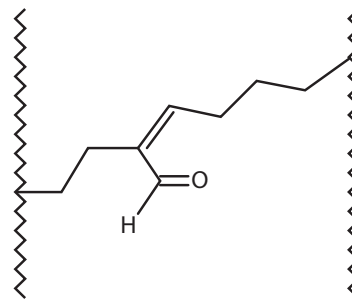
7. Under conditions of acid catalysis, glucose reacts with methanol to form a mixture of glucoside anomers.



Because normal glucose crystallizes as the α form, a solution of the pure α anomer of glucose can be obtained upon dissolving crystallized glucose in water. Excess methanol was introduced under acidic conditions to a pure solution of the α anomer of glucose and the reaction completed prior to any significant mutarotation having occurred. In other words, only the α form and not the β form of the glucose reagent was available to react. The rate of glucoside formation at normal temperatures is several orders of magnitude faster than mutarotation of glucose. The optical activity of the solution was measured upon completion of synthesis of the methyl glucoside. The optical activity measurement obtained was most likely consistent with which of the following solutions?

- A. pure methyl- α -glucopyranose
 B. pure methyl- β -glucopyranose
 C. a mixture of the α and β forms with a greater concentration of the β form
 D. a racemic mixture
8. To elongate the carbon chain of an aldose, the Kiliani-Fisher synthesis utilizes a particular reagent to form a new carbon-carbon bond. What is that reagent?
- A. sodium cyanide
 B. dihydroxyacetone
 C. sodium amalgum
 D. methyl amine

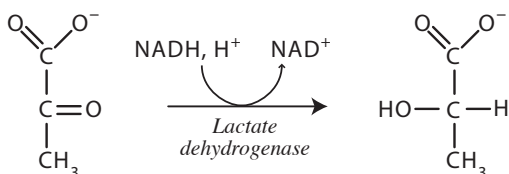
9. Subsequent to its export to the extracellular compartment by a fibroblast, tropocollagen is assembled into collagen fibrils via cross-linking. The figure below depicts a crosslink between two modified amino acid side chains in side-by-side tropocollagen helices.



Which of the following depictions represents one of the modified side chains prior to the formation of the cross-link?

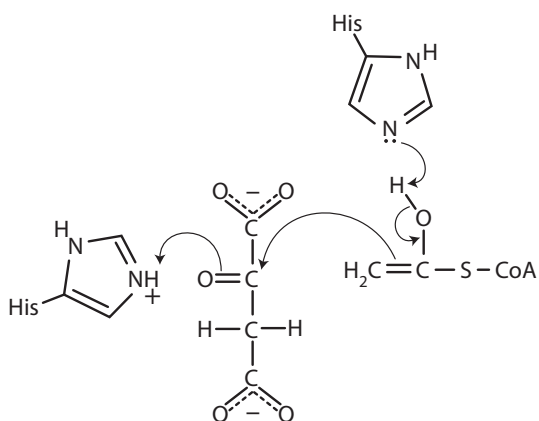
- A.
- B.
- C.
- D.

10. In the process of fermentation, pyruvate is reduced by NADH to form lactate in a reaction catalyzed by the enzyme lactate dehydrogenase.



What change has occurred to the oxidation state of the carbonyl carbon of pyruvate as a result of this reaction?

- A. $-2 \rightarrow 0$
 B. $-2 \rightarrow -1$
 C. $+2 \rightarrow +1$
 D. $+2 \rightarrow 0$
11. What reaction is occurring in this step of the citrate synthase mechanism?



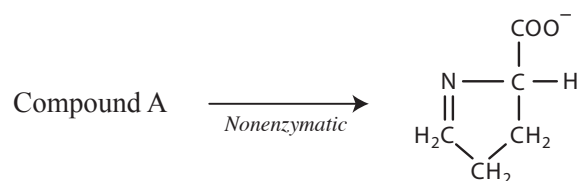
- A. Michael addition
 B. Claisen condensation
 C. Aldol addition
 D. Hydrolysis of a thioester

12. Fill in the blank to complete the following analogy:

An enol is to a ketone as an enamine is to a(n) _____.

- A. amine
 B. amide
 C. nitrile
 D. Schiff base

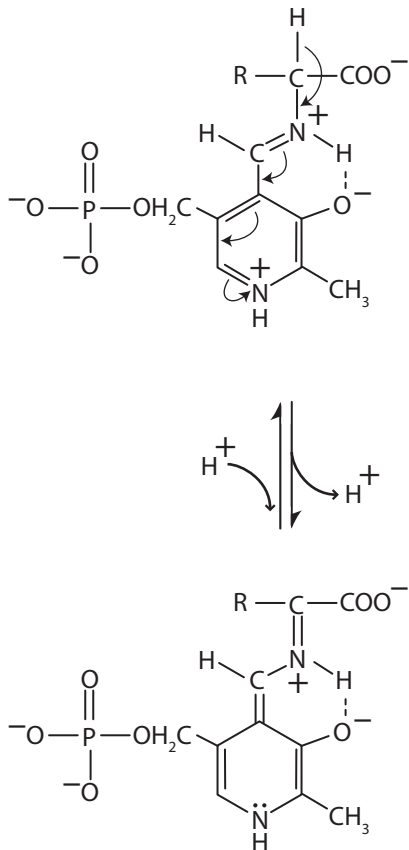
13. A step in the biosynthesis of proline involves the non-enzymatic conversion of Compound A into 1-pyrroline-5-carboxylic acid.



Which of the following is Compound A?

- A.
- B.
- C.
- D.

14. The figure below depicts a step in the transaminase mechanism. Loss of a proton occurs in this step from the PLP-amino acid Schiff base, leading to formation of a resonance stabilized ketimine intermediate.



The mechanism then proceeds with subsequent hydrolysis of the ketimine intermediate. Which of the following is a product of the subsequent hydrolysis of the ketimine intermediate?

- A. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{COO}^-$
- B. $\text{R}-\text{CH}_2-\text{COO}^-$
- C. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$
- D. $\text{R}-\text{C}\equiv\text{N}$

15. Which of the following reaction mechanisms involves an enolate or enol intermediate?

- I. decarboxylation of acetoacetate
 II. pyruvate kinase
 III. enoyl CoA hydratase
 IV. triose phosphate isomerase

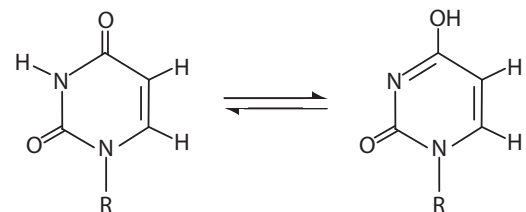
- A. I and II
 B. II and IV
 C. I, II, and III
 D. I, II, III and IV

16. The liberation of cyanide serves as a defense mechanism against herbivores and microbial attack in plants. The activity of which of the following enzymes corresponds to this phenotype?

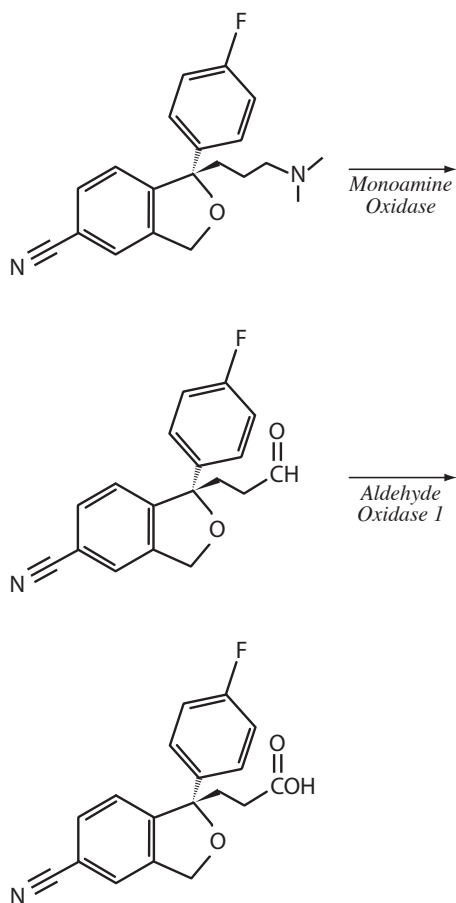
- A. hydroxynitrile lyase
 B. transaminase
 C. hydroxylamine oxidoreductase
 D. fatty acylamidase

17. The interconversion shown below between the lactam and lactim forms of uracil is a type of

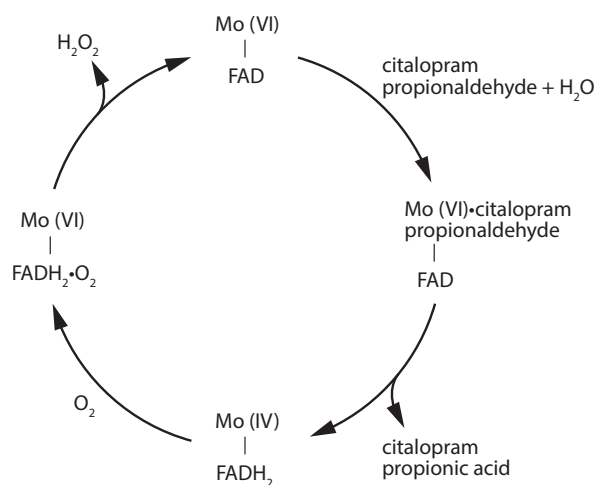
- A. mutarotation
 B. epimerization
 C. tautomerization
 D. resonance



18. One of the pathways in the liver for the metabolism of the drug citalopram involves the activity of the enzymes monoamine oxidase and aldehyde oxidase.



The figure below shows the catalytic cycle of aldehyde oxidase.



Which of the following is a true description of the net aldehyde oxidase reaction in the metabolism of citalopram?

- A. a transfer of two electrons from molecular oxygen to citalopram propionaldehyde
- B. a transfer of four electrons from citalopram propionaldehyde to molybdenum and FAD
- C. a transfer of two electrons from citalopram propionate to molecular oxygen
- D. a transfer of two electrons from citalopram propionaldehyde to molecular oxygen