Chapter 25: Practice Problems: Introductory Level

19. Convert the sugars shown below to their cyclic forms (pyranoses/hemiacetals). Show proper stereochemistry and draw the anomeric carbons in α configurations.

\[
\begin{align*}
&\text{CHO} & & \text{CHO} \\
&\text{CHO} & & \text{CHO} \\
&\text{CHO} & & \text{CHO} \\
&\text{CHO} & & \text{CHO} \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
\end{align*}
\]

\(\text{D-glucose} \quad \text{D-allose}\)

b. Number the carbons on each ring from 1 to 6.

c. Draw a glucose-allose disaccharide with a 1,2-α-glycosidic bond between the anomeric carbon of glucose and the \(\text{C2}\) carbon of allose.

d. Draw a disaccharide with a 1,4-β-glycosidic bond between the anomeric carbon of allose and the \(\text{C4}\) carbon of glucose.

2. Draw the sugar molecule that upon oxidation with periodic acid (\(\text{H}_2\text{IO}_6\)) forms 3 molecules of formic acid (\(\text{H}_2\text{CO}_2\text{H}\)), 2 molecules of formaldehyde (\(\text{H}_2\text{COH}\)) and 1 molecule of \(\text{CO}_2\).
19. Convert the sugars shown below to their cyclic forms (pyranoses/hemiacetals).

Show proper stereochemistry & draw the anomeric carbons in α configurations. α anomeric OH opposite glucose.

\[
\begin{align*}
\text{CHO} & \quad \text{CHO} \\
2 \quad \text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{HO} \\
4 & \quad \text{OH} \\
5 & \quad \text{OH} \\
\text{CHOH} & \\
\text{D-glucose} & \quad \text{D-allose}
\end{align*}
\]

b. Number the carbons on each ring from 1 to 6.

c. Draw a glucose-allose disaccharide with a 1,2-α-glycosidic bond between the anomeric carbon of glucose and the C2 carbon of allose.

d. Draw a disaccharide with a 1,4-β-glycosidic bond between the anomeric carbon of allose and the C4 carbon of glucose.

2. Draw the sugar molecule that upon oxidation with periodic acid (HgIO₆) forms 3 molecules of formic acid (HCOH), 2 molecules of formaldehyde (H₂CO), and 1 molecule of CO₂.
25.35 Draw structural formulas for the products formed by hydrolysis at pH 7.4 (the pH of blood plasma) of all ester, thioester, amide, anhydride, and glycoside groups in acetyl coenzyme A. Name as many of the products as you can.

Disaccharides and Oligosaccharides

25.36 In making candy or sugar syrups, sucrose is boiled in water with a little acid, such as lemon juice. Why does the product mixture taste sweeter than the starting sucrose solution?

25.37 Trehalose is found in young mushrooms and is the chief carbohydrate in the blood of certain insects. Trehalose is a disaccharide consisting of two D-monoosaccharide units, each joined to the other by an α-1,1-glycosidic bond.

(a) Is trehalose a reducing sugar?
(b) Does trehalose undergo mutarotation?
(c) Name the two monosaccharide units of which trehalose is composed.

25.38 The trisaccharide raffinose occurs principally in cottonseed meal.

(a) Name the three monoosaccharide units in raffinose.
(b) Describe each glycosidic bond in this trisaccharide.
(c) Is raffinose a reducing sugar?
(d) With how many moles of periodic acid will raffinose react?
Chapter 26 Practice Problems

1. Compare and contrast the following 3 compounds (in terms of their structures and chemical properties):

   Fat

   Phospholipid

   Soap
Much of our understanding of conformational analysis has arisen from studies on the reactions of rigid steroid nuclei. For example, the concept of transaddition ring opening of epoxysteroids was proposed to explain the stereoselective reactions seen with steroidial epoxides. Predict the product when each of the following steroidial epoxides is treated with LiAlH₄.

(a) Propose a set of experimental conditions to bring about the alkylation in Step 1. Account for the regioslectivity of the alkylation, that is, that it takes place on the carbon between the two carbon groups rather than on the other side of the ketone carbonyl.

(b) Propose experimental conditions to bring about Steps 2 and 3.

(c) Propose experimental conditions for bromination of the ring in Step 4 and dehydrobromination in Step 5.

(d) Write equations to show that Step 6 can be brought about using either methanol or diazoethane (CH₂N₂) as a source of the CH₂⁻ in the methyl ester.

(e) Describe experimental conditions to bring about Step 7 and account for the fact that the trans isomer is formed in this step.

(f) Step 8 is done by a Wittig reaction. Suggest a structural formula for a Wittig reagent that gives the product shown.

(g) Name the type of reaction involved in Step 10.

(h) Step 11 can best be described as a Grignard reaction with methylmagnesium bromide under very carefully controlled conditions. In addition to the observed reaction, what other Grignard reactions might take place in Step 11?

(i) Assuming that the two side chains on the cyclopentanone ring are non-s, how many stereoisomers are possible from this synthetic sequence?
1. Compare and contrast the following 3 compounds (in terms of their structures and chemical properties):

- Fatt
- Phospholipid
- Soap

Soap is positive at blood pH. Phosphate is negative.
Chapter 26 cont

26.29 Much of our understanding of conformational analysis has arisen from studies on the reactions of rigid steroid nuclei. For example, the concept of s-cis/s-trans ring opening of epoxycyclohexane was proposed to explain the stereoselective reactions seen with steroidal epoxides. Predict the product when each of the following steroidal epoxides is treated with LiAlH₄.

26.19 Docusate, an orally active bronchodilator patterned after the natural prostaglandins (Section 26.5), is synthesized in the following series of reactions starting with ethyl 2-norcyclopentane-carboxylate. Except for the NaN₃ reaction in Step 8, we have seen examples of all other types of reactions involved in this synthesis.

(a) Propose a set of experimental conditions to bring about the alkylation in Step 1. Account for the regiospecificity of the alkylation, that is, that it takes place on the carbon between the two carbonyl groups rather than on the other side of the ketone carbonyl.
(b) Propose experimental conditions to bring about Steps 2 and 3.
(c) Propose experimental conditions for bromination of the ring in Step 5 and dehydrobromination in Step 6.
(d) Write equations to show that Step 6 can be brought about using either methanol or diisomethyl ether (CH₃)₂O as a source of the —CH₂⁻ ion in the methyl ester.
(e) Describe experimental conditions to bring about Step 7 and account for the fact that the trans isomer is formed in this step.

(f) Step 8 is done by a Wittig reaction. Suggest a structural formula for a Wittig reagent that gives the product shown.
(g) Name the type of reaction involved in Step 10.
(h) Step 11 can best be described as a Grignard reaction with methylmagnesium bromide under very carefully controlled conditions. In addition to the observed reaction, what other Grignard reactions might take place in Step 11?
(i) Assuming that the two side chains of the cyclopentane ring are trans, how many stereoisomers are possible from this synthetic sequence?
1. Draw the dipeptide Ala-Phε with proper stereochemistry.

![Diagram of Ala-Phε]

2. The dipeptide His-Asp is drawn below in the form it would adopt at a very low pH.

![Diagram of His-Asp with pKa values]

3. If the pH were increased gradually, which acidic H would be removed first? Second? Third? Last?

4. Draw the resulting dipeptide structures that would form if 1, 2, 3, or 4 H's were removed.

5. Calculate the overall charge for each dipeptide structure you drew in question 4 and circle the zwitterion (the structure which is neutral in charge).

6. What is the isoelectric point (pI) for the dipeptide? (Which 2 pKa's should you average to find the pI?)

7. Which dipeptide structure would predominate at pH 5? pH 7.5?
1. Draw the dipeptide Ala-phi with proper stereochemistry.

2. The dipeptide His-Asp is drawn below in the form it would adopt at a very low pH.

   a. If the pH were increased gradually, which acidic H would be removed first? Second? Third? Last?
   b. Draw the resulting dippeptide structures that would form if 1, 2, 3 or 4 H's were removed.
   c. Calculate the overall charge for each dippeptide structure you drew in question b. & circle the zwitterion (the structure which is neutral in charge).
   d. What is the isoelectric point (pI) for the dippeptide? (Which 2 pkas should you average to find the pI?)
   e. Which dippeptide structure would predominate at pH 5? pH 7.5?

\[
\left(\frac{\text{pk}a_2 + \text{pk}a_3}{2}\right) = 5.0
\]
1. Draw the cyclic/hemiacetal form of β-ribose and of β-α-deoxyribose. Number the carbons and show proper stereochemistry.

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
& \quad \text{CH}_2\text{OH} \\
\text{D-ribose}
\end{align*}
\]

2. Draw the structural formulas of the following two nucleotides:

a. 2′-Deoxythymidine 5′-monophosphate

\[
\begin{align*}
\text{thymine (T)} & \quad \text{guanine (G)} & \quad \text{phosphate} \\
\text{These nitrogens} & \quad \text{attach to position 1 of deoxyribose} \\
& \quad \text{via a β glycosidic bond}
\end{align*}
\]

b. 2′-Deoxyguanosine 5′-monophosphate

3. Attach the 2 nucleotides from question 2 via a phosphodiester bond between C3 of nucleotide a + C5 of nucleotide b.
1. Draw the cyclic/hemiacetal form of β-ribose and of β-2-deoxyribose. Number the carbons and show proper stereochemistry.

\[ \text{H}_2\text{O} \]
\[ \text{H} \]
\[ \text{H} \]
\[ \text{H} \]
\[ \text{O} \, \text{OH} \]
\[ \text{CH}_2\text{OH} \]

\( \text{D-ribose} \)

aromatic base + sugar = nucleoside

\( \text{OH} \) ribose + phosphate = nucleotide

\( \text{OH} \) deoxyribose nucleic acid = DNA or RNA Strand

2. Draw the structural formulas of the following two nucleotides:

a. 2'-Deoxythymidine 5'-monophosphate

b. 2'-Deoxyguanosine 5'-monophosphate

3. Attach the 2 nucleotides from question 2 via a phosphodiester bond between C3 of nucleotide a + C5 of nucleotide b.
Chapter 2.9 Practice Problems

1. Give the structures of the monomers used to form the following polymers:

   a. 
   
   b. 
   
   c. 
   
   d. 

2. Using the monomer shown, draw a polymer segment of 3 repeating monomer units, and show the mechanism for its formation. (Don’t worry about stereochemistry.)

   a. 
   
   b. 
   
   c. 
   
   d. 

   ROMP catalysis
Chapter 2.9 Practice Problems

1. Give the structures of the monomers used to form the following polymers:
   a. Diol + diacyl chloride = polyester
   b. Aminet acid = polyamide, NYLON
   c. (Polymer structure)
   d. (Polymer structure)

2. Using the monomer shown, draw a polymer segment of 3 repeating monomer units and show the mechanism for its formation. (Don’t worry about stereochemistry.)
   a. \[ \text{H}^+ \rightarrow \text{X} \rightarrow \text{X}_n \]
   b. \[ \text{CH}_2\text{CH} = \text{CH}_2 \rightarrow \text{AIBN} \rightarrow \text{Free radical initiator} \]
   c. (Polymerization mechanism)
   d. (Polymerization mechanism)