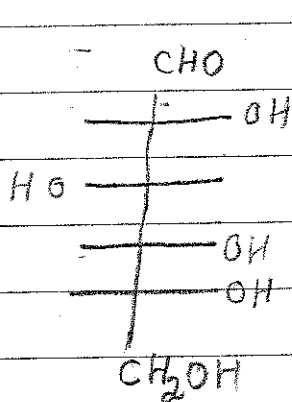
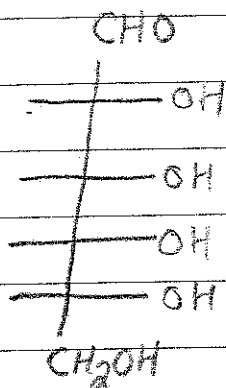


Chapter 25. Practice Problems: Introductory Level

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



D-glucose



D-allose

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

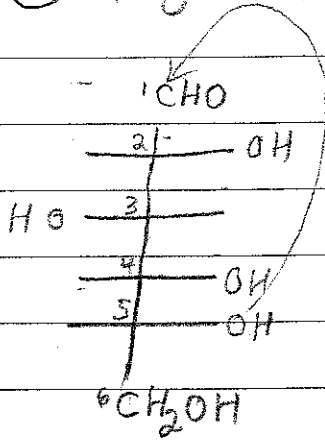
c. Draw a glucose-allose disaccharide with a 1,2- α -glycosidic bond btwn the anomeric carbon of glucose & the C2 carbon of allose.

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

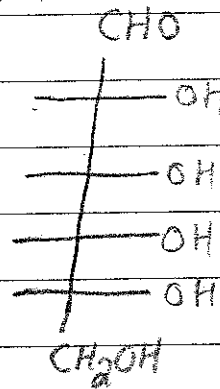
2. Draw the sugar molecule that upon oxidation with periodic acid (H_5IO_6) forms 3 molecules of formic acid ($HCOH$), a molecules of formaldehyde ($HCHO$) & 1 molecule of CO_2 .

Key

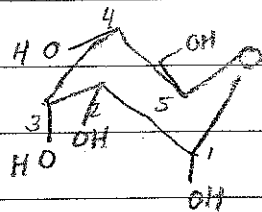
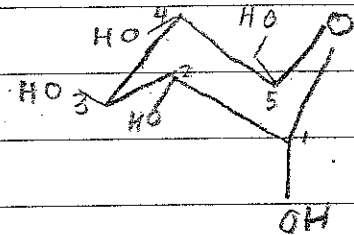
19. Convert the sugars shown below to their cyclic forms (pyranoses/hemiacetals). Show proper stereochemistry & draw the anomeric carbons in α configurations, & anomeric OH opposite glucose CH_2OH



D-glucose



D-allose



allose

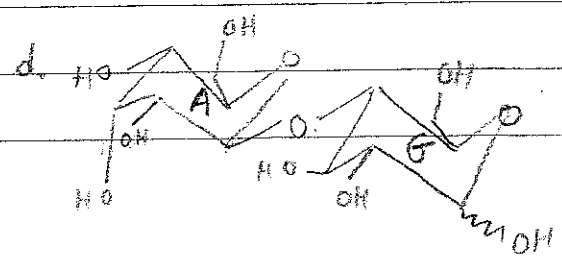
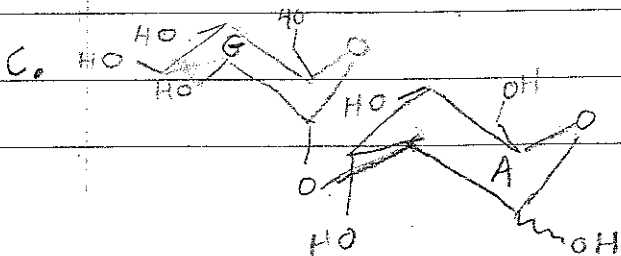
b. Number the carbons on each ring from 1 to 6.

c. Draw a glucose-allose disaccharide with a 1,2- α -glycosidic bond btwn the anomeric carbon of glucose & the C2 carbon of allose.
glycosidic bond - acetal involving anomeric C

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

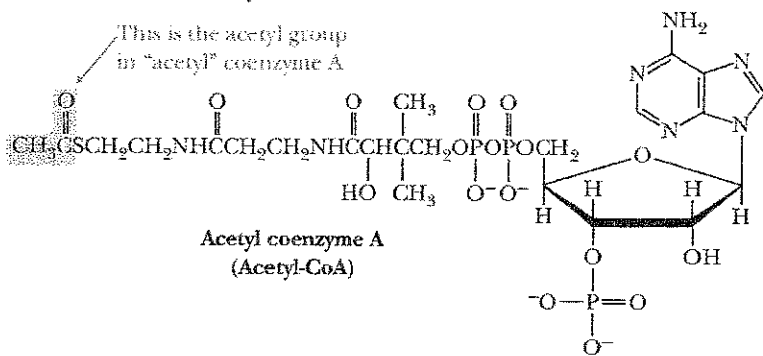
ketone, 2 terminal HOH's, 3 non terminal alcohols $\text{H}-\text{C}(\text{OH})_2-\text{C}(=\text{O})-\text{CH}_2\text{OH}$

2. Draw the sugar molecule that upon oxidation with periodic acid (H_5IO_6) forms 3 molecules of formic acid (HCOOH), 2 molecules of formaldehyde (HCHO) & 1 molecule of CO_2 .
non-terminal ROH, aldehyde \rightarrow formic acid; terminal ROH \rightarrow formaldehyde; ketone \rightarrow CO_2



KEYS

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.

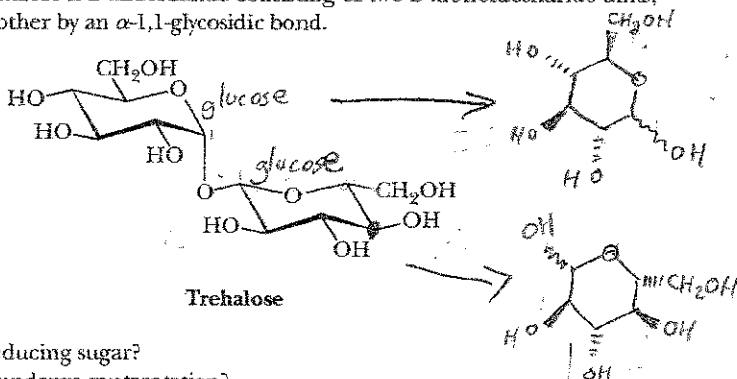


Disaccharides and Oligosaccharides

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?

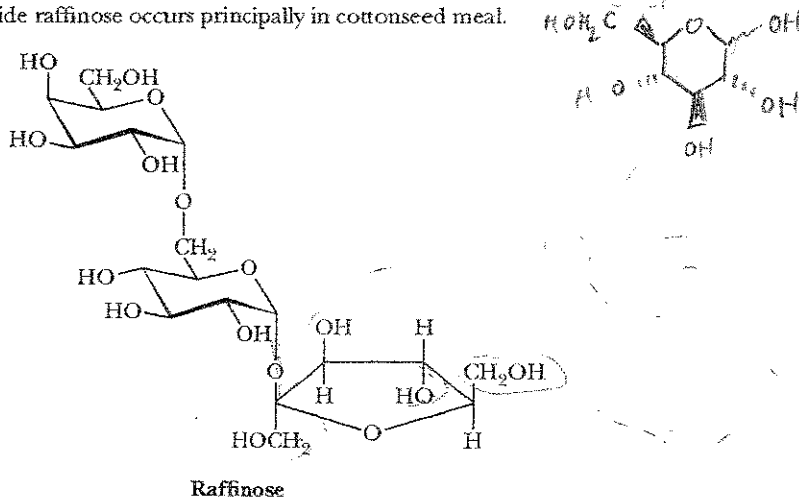
25.37 Trehalose is found in young mushrooms and is the chief carbohydrate in the blood of certain insects. Trehalose is a disaccharide consisting of two D-monosaccharide units, each joined to the other by an α -1,1-glycosidic bond.

number the carbons
identify anomeric C
isolate simple sugars
convert back to fisher



- (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.



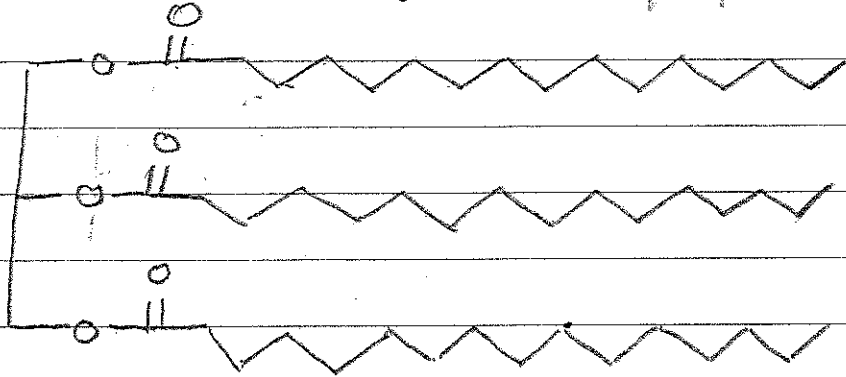
- (a) Name the three monosaccharide units in raffinose.
- (b) Describe each glycosidic bond in this trisaccharide.
- (c) Is raffinose a reducing sugar?
- (d) With how many moles of periodic acid will raffinose react?

diaxial OH's can ring flip

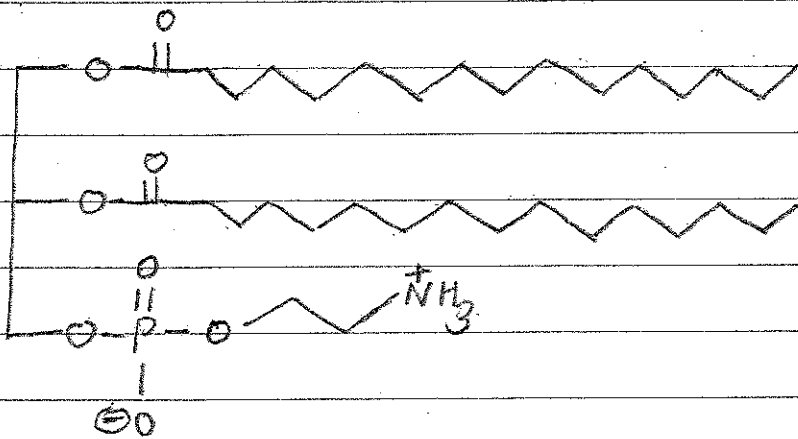
Chapter 26 Practice Problems

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

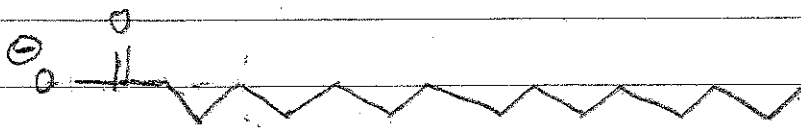
Fat



Phospholipid

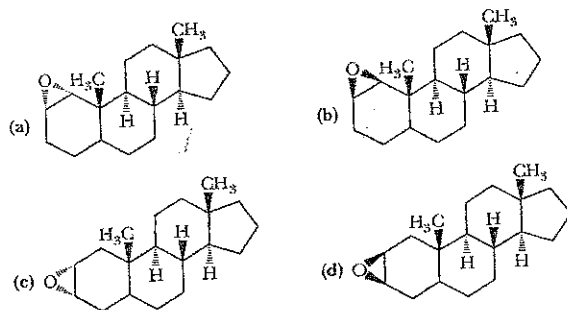


Soap

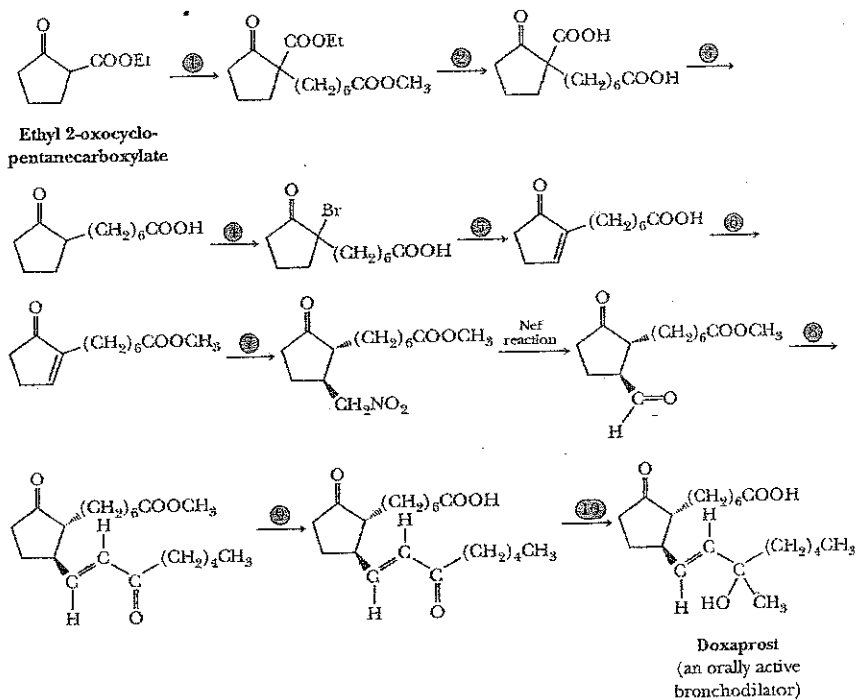


Chapter 26 cont

26.25 Much of our understanding of conformational analysis has arisen from studies on the reactions of rigid steroid nuclei. For example, the concept of *trans*-diaxial ring opening of epoxycyclohexanes was proposed to explain the stereoselective reactions seen with steroidal epoxides. Predict the product when each of the following steroidal epoxides is treated with LiAlH_4 .



26.19 Doxaprost, an orally active bronchodilator patterned after the natural prostaglandins (Section 26.3), is synthesized in the following series of reactions starting with ethyl 2-oxocyclopentanecarboxylate. Except for the Nef reaction in Step 8, we have seen examples of all other types of reactions involved in this synthesis.



- Propose a set of experimental conditions to bring about the alkylation in Step 1. Account for the regioselectivity 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.
- Propose experimental conditions to bring about Steps 2 and 3.
- Propose experimental conditions for bromination of the ring in Step 4 and dehydrobromination in Step 5.
- Write equations to show that Step 6 can be brought about using either methanol or diazomethane (CH_2N_2) as a source of the $-\text{CH}_3$ in the methyl ester.
- Describe experimental conditions to bring about Step 7 and account for the fact that the *trans* isomer is formed in this step.
- Step 9 is done by a Wittig reaction. Suggest a structural formula for a Wittig reagent that gives the product shown.
- Name the type of reaction involved in Step 10.
- 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?
- Assuming that the two side chains on the cyclopentanone ring are *trans*, how many stereoisomers are possible from this synthetic sequence?

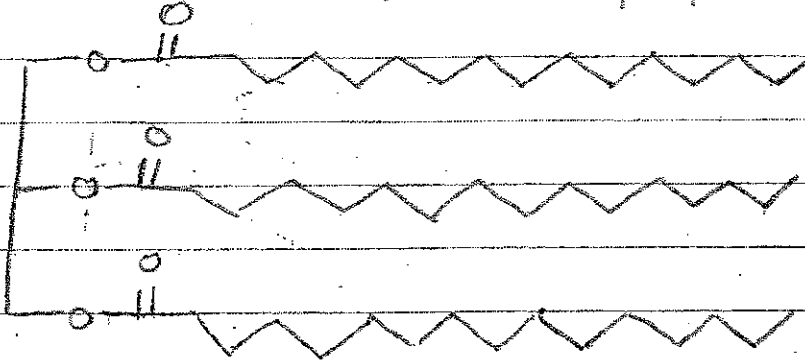
Chapter 26: Practice Problems

key

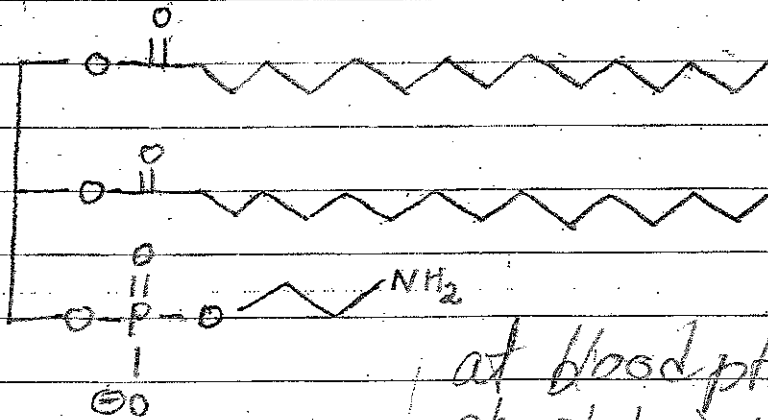
fats

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

Fat

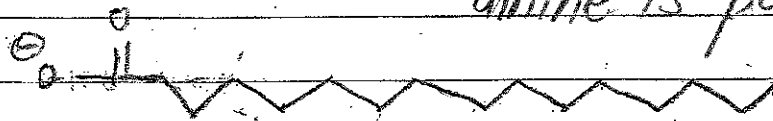


Phospholipid



Soap

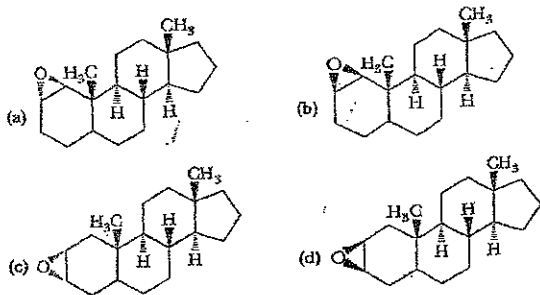
Soap



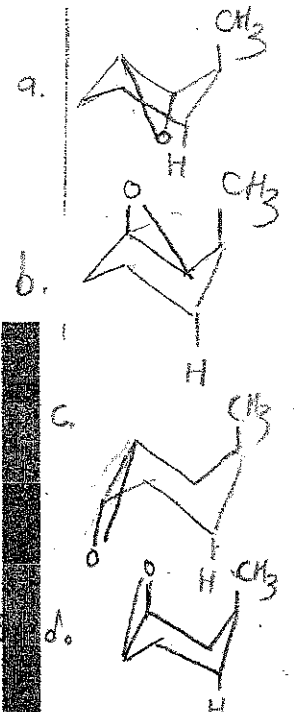
at blood pH:
phosphate is neg
amine is positive

Chapter 26 cont

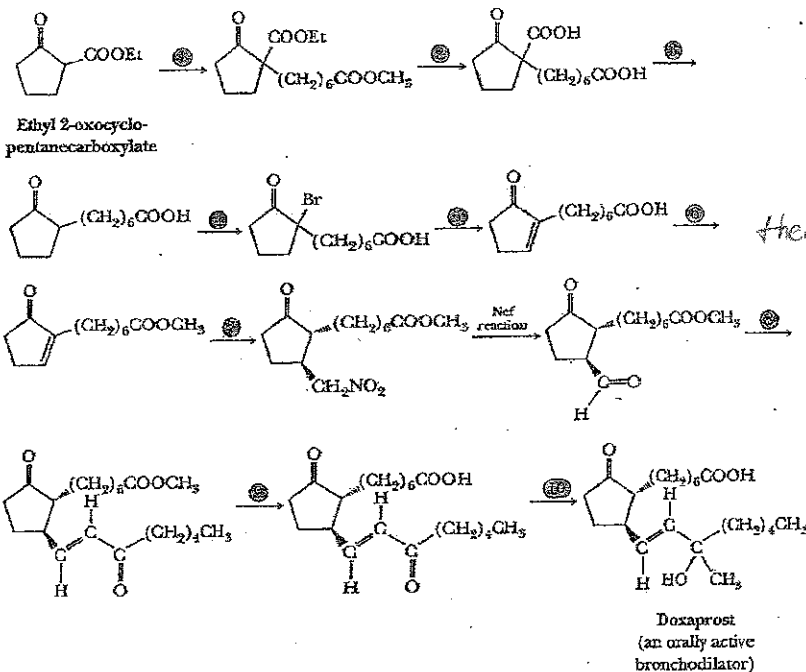
26.25 Much of our understanding of conformational analysis has arisen from studies on the reactions of rigid steroid nuclei. For example, the concept of *trans*-diaxial ring opening of epoxycyclohexanes was proposed to explain the stereoselective reactions seen with steroidal epoxides. Predict the product when each of the following steroidal epoxides is treated with LiAlH_4 .



steroids
all fusions are trans



26.19 Doxaprost, an orally active bronchodilator patterned after the natural prostaglandins (Section 26.3), is synthesized in the following series of reactions starting with ethyl 2-oxocyclopentanecarboxylate. Except for the Nef reaction in Step 8, we have seen examples of all other types of reactions involved in this synthesis.



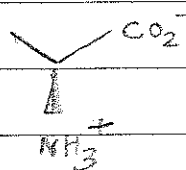
prostaglandins

1. $\text{LG}-(\text{CH}_2)_6\text{CO}_2\text{Me}$
base
2. H_3O^+
3. Δ
4. Br_2, H^+
5. KOH, Δ
6. $\text{CH}_3\text{OH}, \text{H}^+$
7. $\ominus\text{CH}_2\text{NO}_2$
9. $\text{Ph}_3\text{P}-\text{CH}(\text{CH}_2)_4\text{CH}_3$
10. alkylation

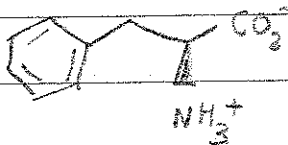
- (a) Propose a set of experimental conditions to bring about the alkylation in Step 1. Account for the regioselectivity of the alkylation, that is, that it takes place on the carbon between the two carbonyl groups rather than on the other side of the ketone carbonyl.
- (b) Propose experimental conditions to bring about Steps 2 and 3.
- (c) Propose experimental conditions for bromination of the ring in Step 4 and dehydrobromination in Step 5.
- (d) Write equations to show that Step 6 can be brought about using either methanol or diazomethane (CH_2N_2) as a source of the $-\text{CH}_3$ 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 9 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 *trans*, how many stereoisomers are possible from this synthetic sequence?

Chapter 27, Practice Problems: Introductory Level

1. Draw the dipeptide Ala-Phe with proper stereochemistry.

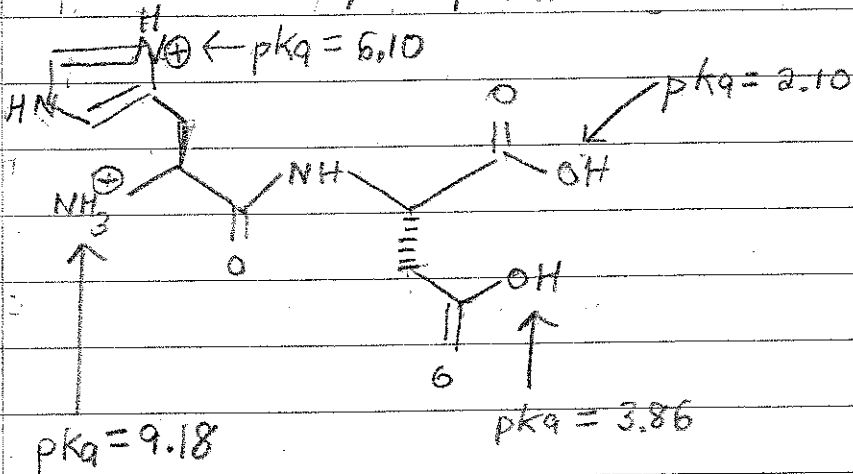


Alanine



Phenylalanine

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?

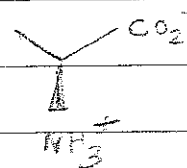
b. Draw the resulting dipeptide structures that would form if 1, 2, 3 or 4 H's were removed.

c. Calculate the overall charge for each dipeptide 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 dipeptide? (Which 2 pKa's should you average to find the pI?)

e. Which dipeptide structure would predominate at pH 5? pH 7.5?

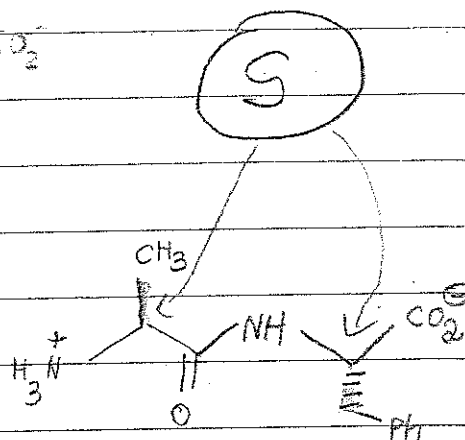
1. Draw the dipeptide Ala-Phe with proper stereochemistry.



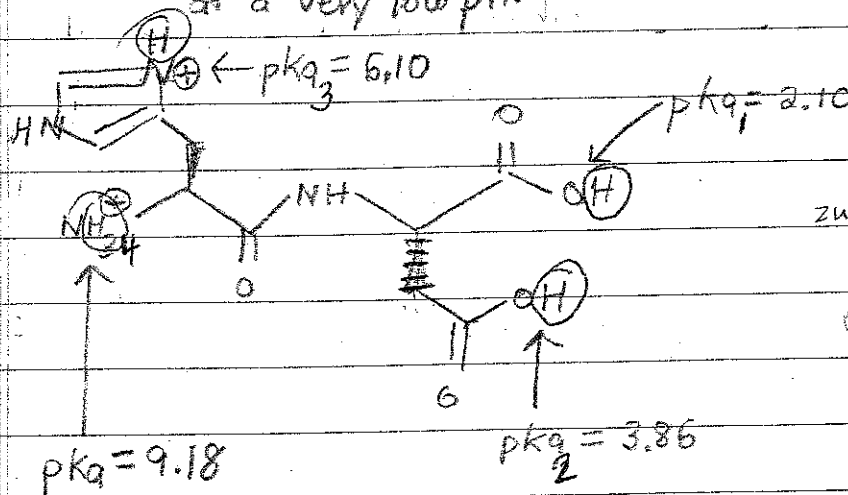
Alanine



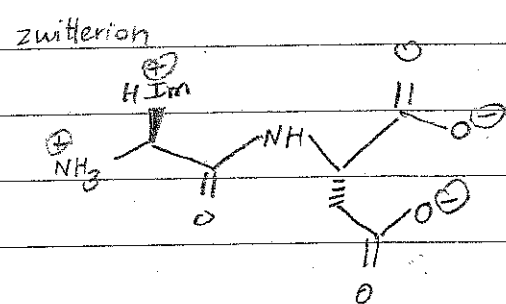
Phenylalanine



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



aspartic acid



a. If the pH were increased gradually, which acidic H would be removed first? second? third? Last?

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

c. Calculate the overall charge for each dipeptide structure you drew in question b & circle the zwitterion (the structure which is neutral in charge).

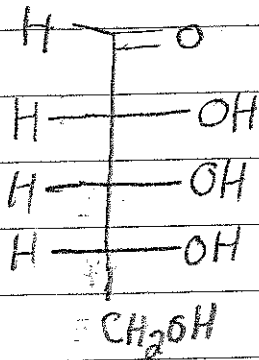
d. What is the isoelectric point (pI) for the dipeptide? (Which 2 pKa's should you average to find the pI?)

e. Which dipeptide structure would predominate at pH 5? pH 7.5?

$$(pKa_2 + pKa_3) / 2 = 5.0$$

Chapter 28 Practice Problems

1. Draw the cyclic/hemiacetal form of β -ribose and of β -2-deoxyribose. Number the carbons + show proper stereochemistry.

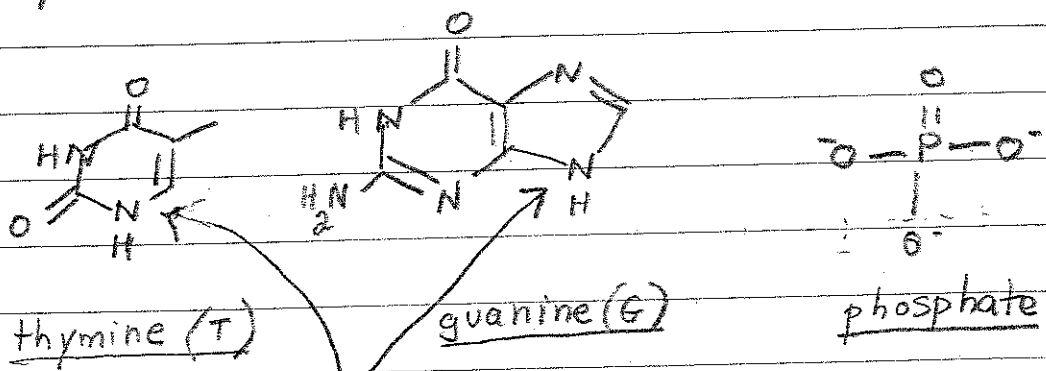


D-ribose

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

a. 2'-Deoxythymidine 5'-monophosphate

b. 2'-Deoxyguanosine 5'-monophosphate



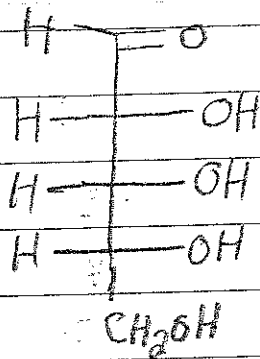
These nitrogens attach to position 1 of deoxyribose via a β glycosidic bond

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

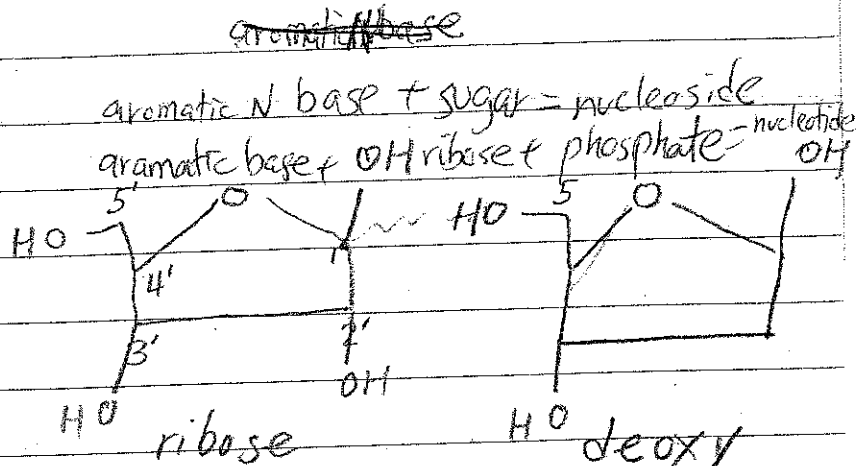
Chapter 28 Practice Problems

Key

1. Draw the cyclic/hemiacetal form of β -ribose and of β -2-deoxyribose. Number the carbons + show proper stereochemistry.



D-ribose

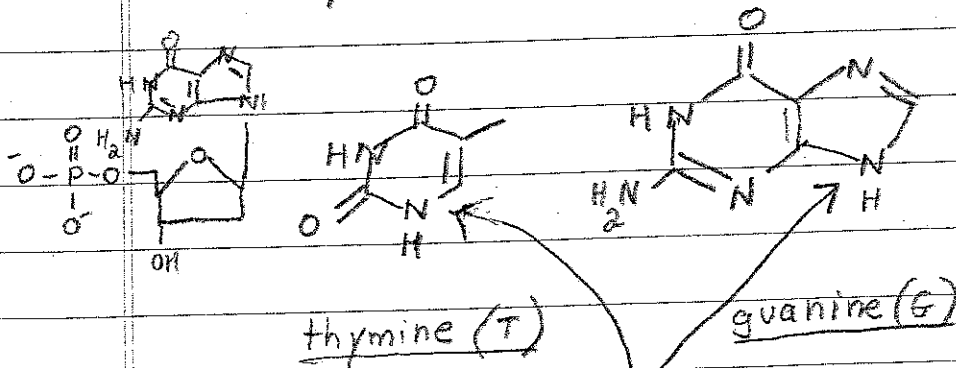
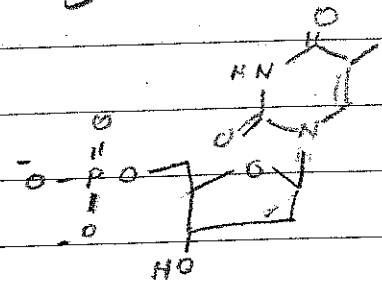


aromatic N base + sugar = nucleoside
 aromatic base + OH ribose + phosphate = nucleotide
 nucleic acid = DNA or RNA strand

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

a. 2'-Deoxythymidine 5'-monophosphate

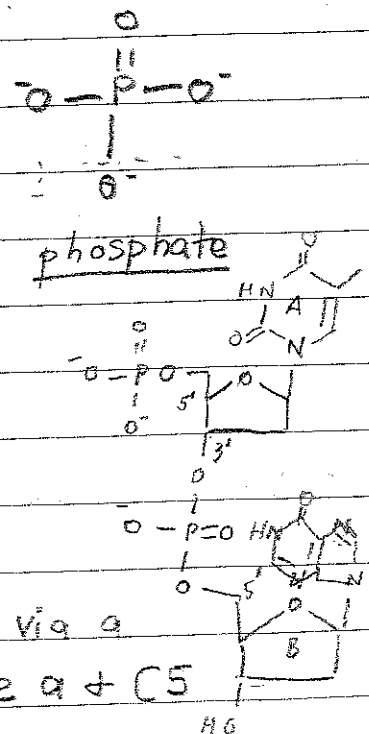
b. 2'-Deoxyguanosine 5'-monophosphate



thymine (T)

guanine (G)

These nitrogens attach to position 1 of deoxyribose via a β glycosidic bond

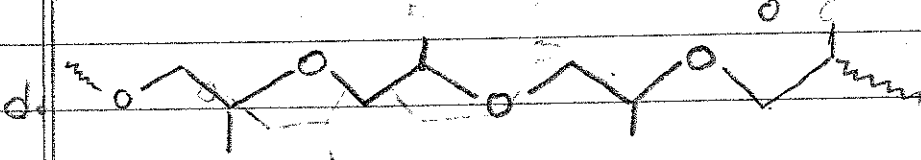
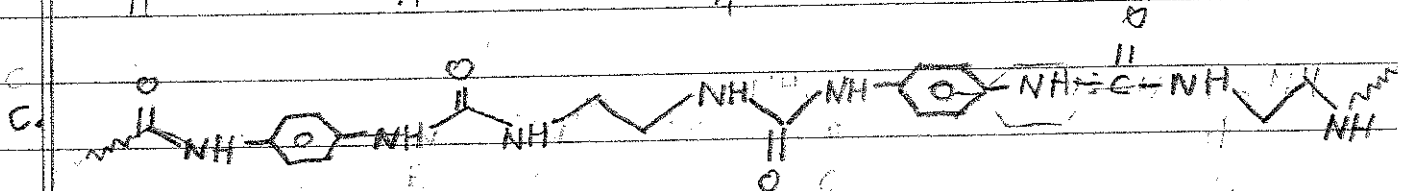
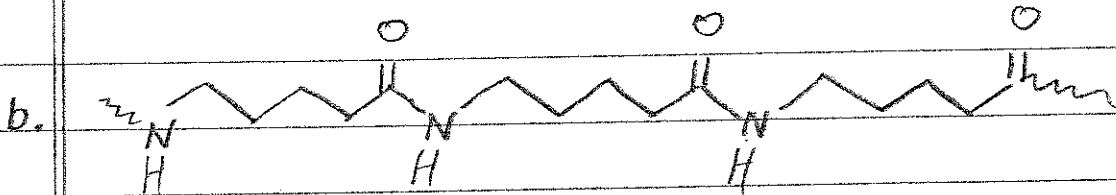
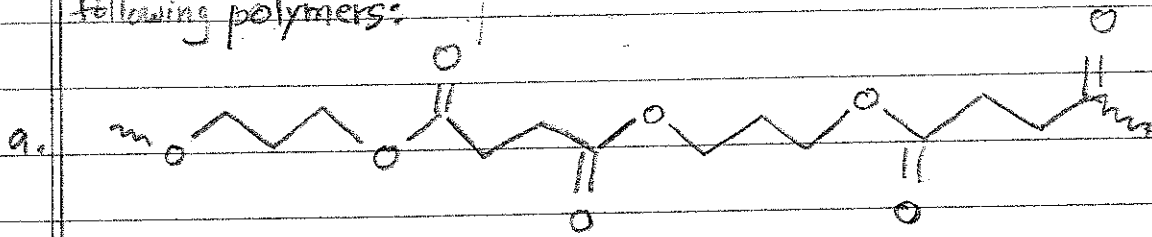


phosphate

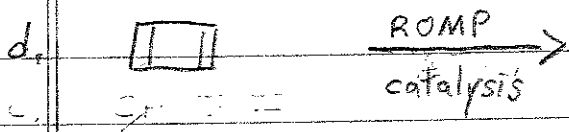
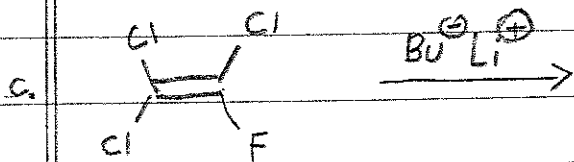
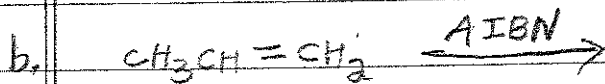
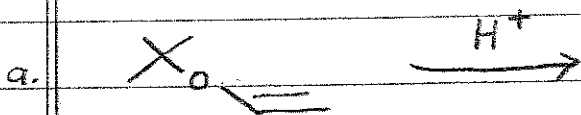
3. Attach the 2 nucleotides from question 2 via a phosphodiester bond between C3 of nucleotide a + C5 of nucleotide b.

Chapter 2.9 Practice Problems

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

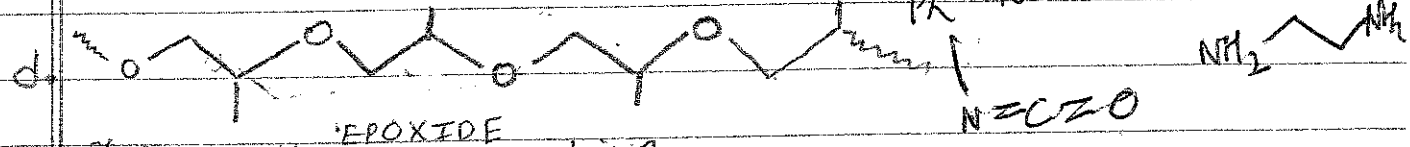
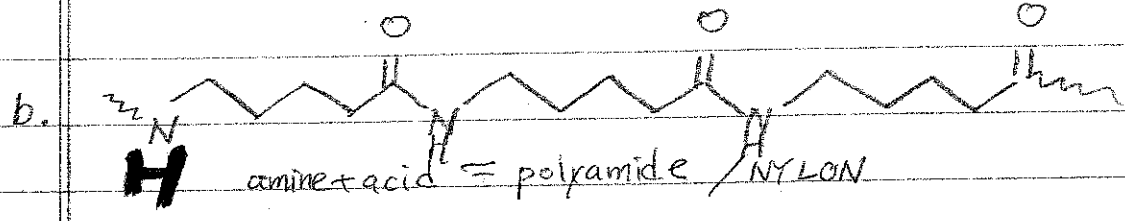
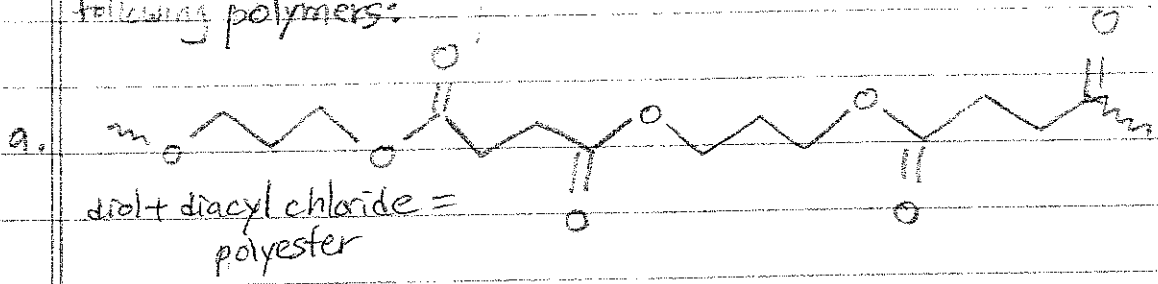


2. Using the monomer shown, draw a polymer segment of 3 repeating monomer units + show the mechanism for its formation. (Don't worry about stereochemistry.)



Chapter 29 Practice Problems key
 Condensation polymers (see more on back)

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



2. Chain growth polymerization
 Using the monomer shown, draw a polymer segment of 3 repeating monomer units + show the mechanism for its formation. (Don't worry about stereochemistry)

