Chemistry 2030
"Introduction to Organic Chemistry"
Fall Semester 2013
Dr. Rainer Glaser

Examination #5: The Final
"Amines, Lipids, Carbohydrates, and Nucleobases"

Wednesday, December 11, 2013, 7:30 – 9:30 am.

Name: Answer Key

Question 1. Amines and Diazonium Ions.	20	
Question 2. Lipids and Detergents.	20	
Question 3. Carbohydrates.	20	
Question 4. Nucleobases, Nucleosides and Nucleotides.	28	
Question 5. Base Pairing.	12	
Total	100	

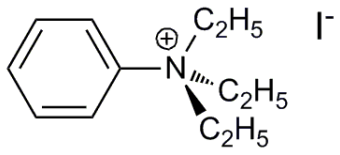
The final is written for 100 points and counts twice toward the course grade.

ALLOWED: Periodic System of the Elements (printed, w/o handwriting on it). Molecular models (you can bring pre-made models). Simple, non-programmable calculator (not really needed).

NOT ALLOWED: Books. Notes. Electronic devices of any kind (other than a simple calculator).

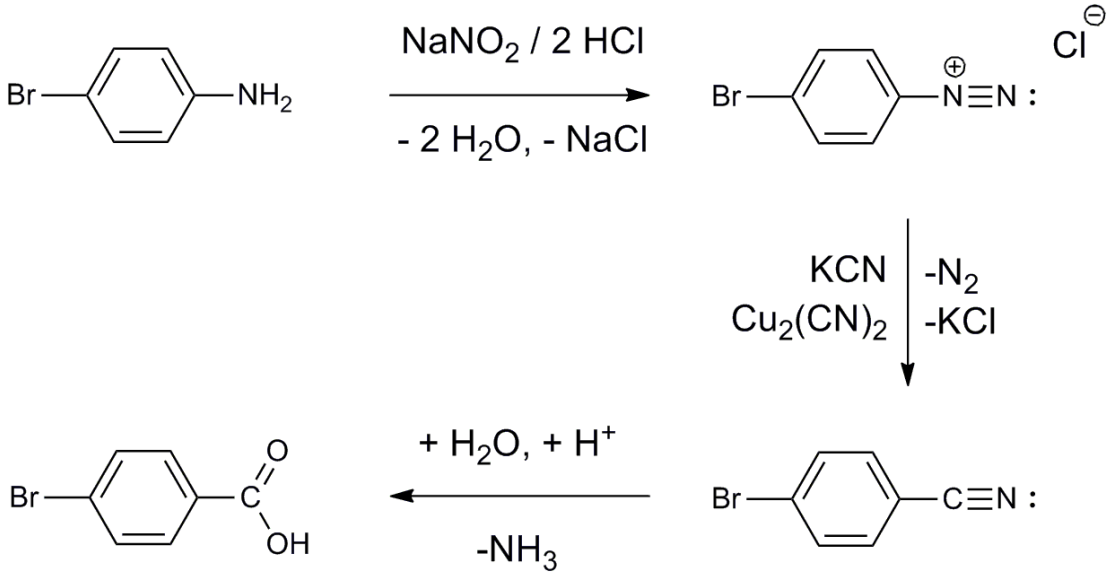
Question 1. Amines and Diazonium Ions. (20 points)

(a) Draw the structure of the product obtained by the reaction of **aniline with three molecules of ethyl iodide** and provide its name. (4 points)



N,*N*,*N*-triethylanilinium iodide or
Phenyltriethylammonium iodide

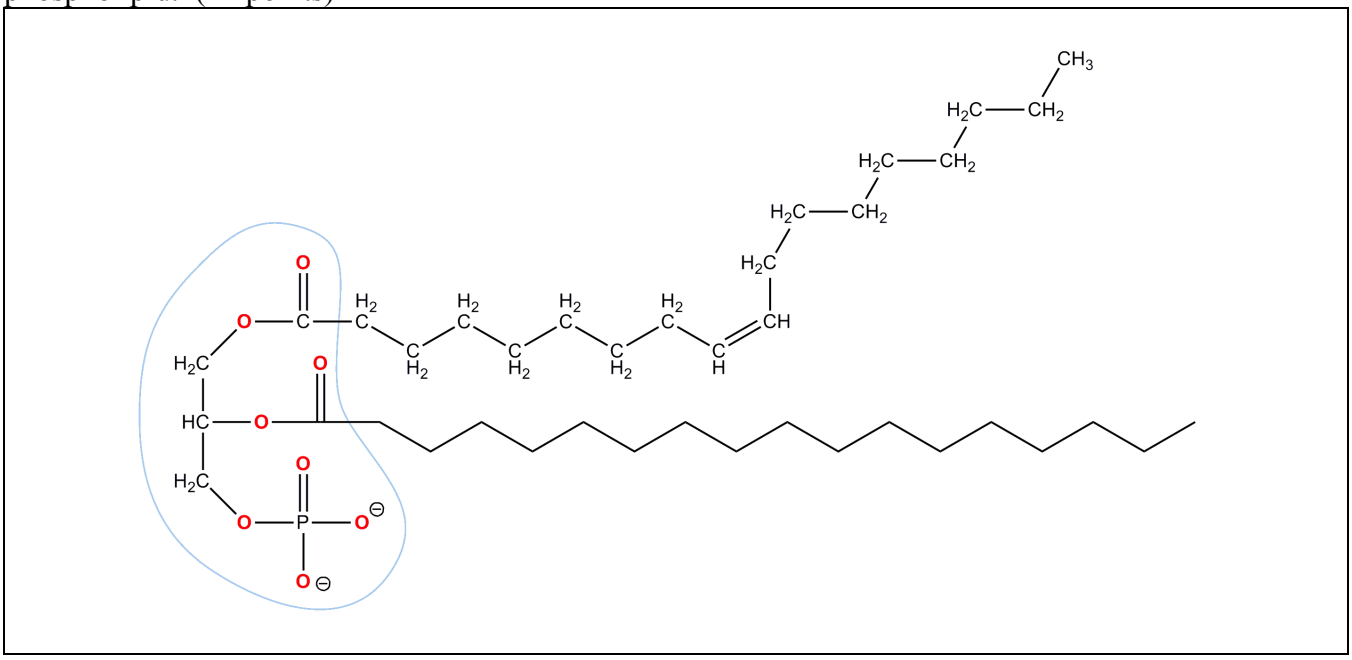
(b) Devise a synthesis of **para-bromobenzoic acid from para-bromoaniline**. For each of three reaction steps, specify substrate, reagent(s), catalyst(s) and product formed. The key step is the _____ (**electrophilic**, nucleophilic, radical) aromatic substitution reaction of the para-bromobenzenediazonium ion! (12 points)



(c) Consider the **bromination of benzonitrile** by electrophilic aromatic substitution. Draw the structure of the substrate, specify the reagent(s) and the catalyst(s), and draw the structure of the major product. (4 points)

Question 2. Lipids and Detergents. (20 points)

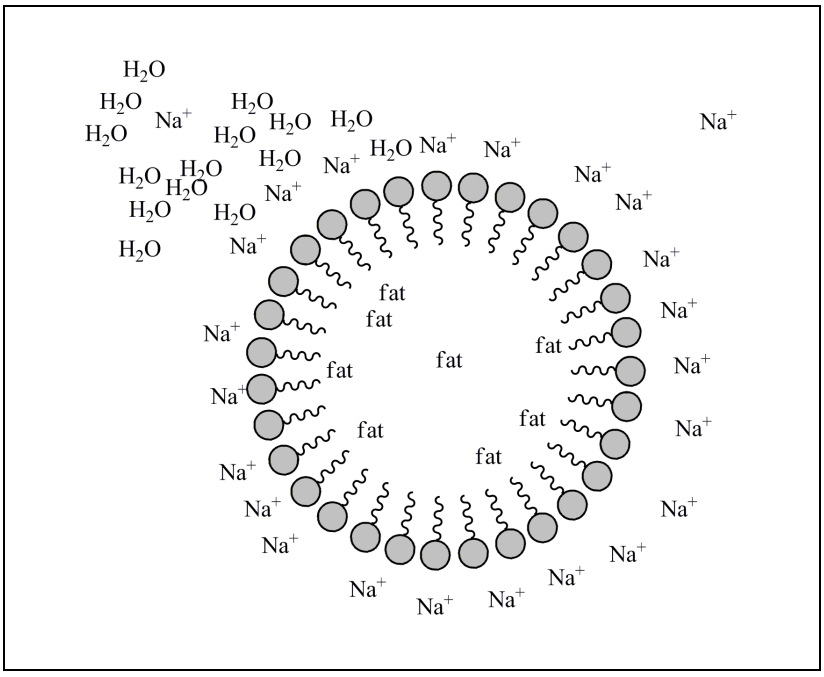
(a) Phosphatidic acids (PA) are very simple **phospholipids**. A phosphatidic acid is a derivative of glycerol that contains an inorganic ester formed with one of the primary alcohol and phosphoric acid and two organic esters formed with the remaining alcohol groups. Draw the complete structure of the phosphatidic acid formed with one stearic acid, $H_3C–(CH_2)_{16}–COOH$ and one molecule of the unsaturated fatty acid oleic acid, $H_3C–(CH_2)_7–CH=CH–(CH_2)_7–COOH$. In your drawing, attach the oleic acid to one of the primary alcohols of glycerol, clearly indicate whether the alkene in oleic acid is cis or trans, and show the phosphate fully deprotonated. Finally, circle the polar region of the phospholipid. (12 points)



(b) A simple micelle is shown schematically on the right. Each circle signifies a _____ (**polar**, nonpolar) head-group, and each wiggly line signifies a _____ (polar, **nonpolar**) alkyl chain.

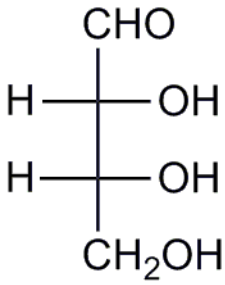
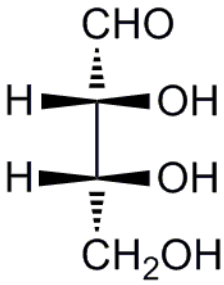
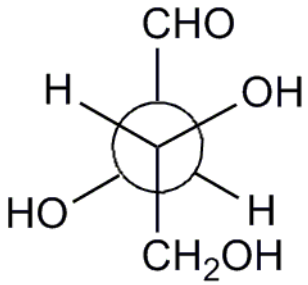
In the case of "normal" soap, the head-group is a __**carboxylate**__ anion. Indicate where we would find the associated cations (i.e., sodium cations; draw as many as needed in the scheme).

Water is on the _____ (inside, **outside**) of this micelle and fats will accumulate on the _____ (**inside**, outside) of this micelle. (8 points)



Question 3. Carbohydrates. (20 points)

(a) The structure is shown of **D-erythrose**. Draw a perspective drawing of D-erythrose in the conformation used in the Fischer Projection. Draw a Newman projection of a reasonable conformation of D-erythrose. Assign priorities and determine the configurations a C2 and C3. (14 points)

Fischer Projection of D-erythrose	Convert Fischer Projection into Perspective Drawing	Newman Projection of a Reasonable Conformation
		

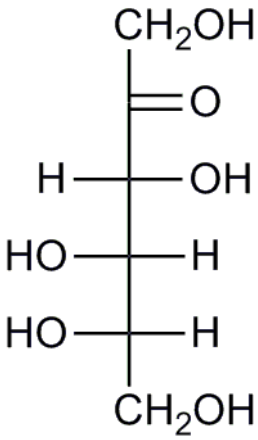
The **C2 carbon** in D-erythrose ____ (*S*, ***R***).

Highest priority substituent: __**O**__
Lowest priority substituent: ___**H**___
"List" of the carbonyl-C: C(**O O H**) Prio.: _**2**_
"List" of the other C: C(**O C H**) Prio.: _**3**_

The **C3 carbon** in D-erythrose ____ (*S*, ***R***).

Highest priority substituent: ___**O**__
Lowest priority substituent: __**H**__
"List" of the CH_2OH-C: C(**O H H**) Prio.: _**3**_
"List" of the other C: C(**O C H**) Prio.: _**2**_

(b) Draw the Fischer projection of **L-fructose**. The molecular formula of fructose is $C_6H_{12}O_6$. Fructose is a _____ (aldose, **ketose**). (6 points)

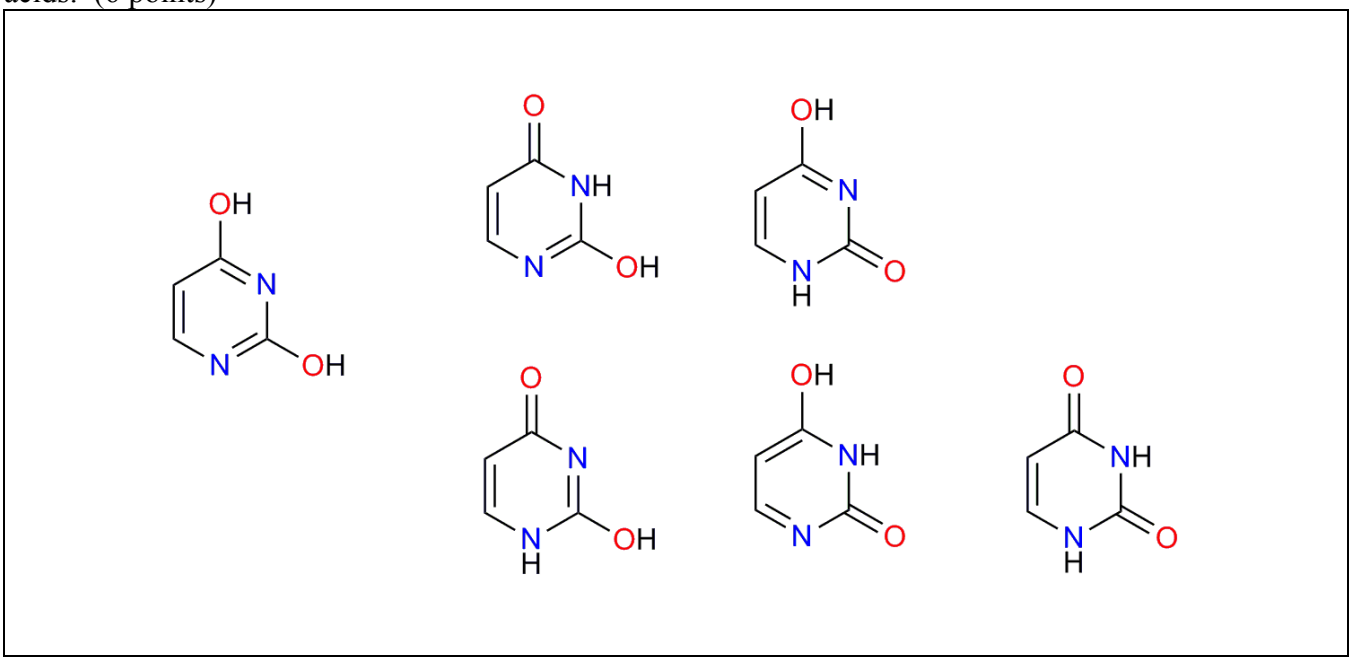


Question 4. Nucleobases, Nucleosides and Nucleotides. (28 points)

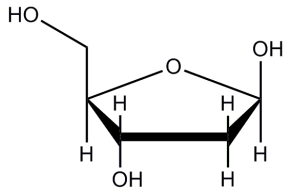
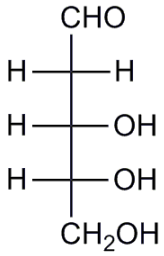
(a) Nucleobases. Mark each box in rows 2 – 4 with "yes" or "no", for the first row answer "DNA" or "RNA", and for the last row provide the single-letter abbreviation of the complementary base in the Watson-Crick base-pair. (12 points, 1 point deduction for each error)

	Adenine	**Cytosine**	**Guanine**	**Thymine**	**Uracil**
Occurs in (write DNA or RNA):	**DNA & RNA**	**DNA & RNA**	**DNA & RNA**	**DNA**	**RNA**
Contains an Imidazole:	**Yes**	**No**	**Yes**	**No**	**No**
Contains an Exocyclic Amine:	**Yes**	**Yes**	**Yes**	**No**	**No**
Contains a Carbonyl Group:	**No**	**Yes**	**Yes**	**Yes**	**Yes**
Base-Pairs with:	**T / U**	**G**	**C**	**A**	**A**

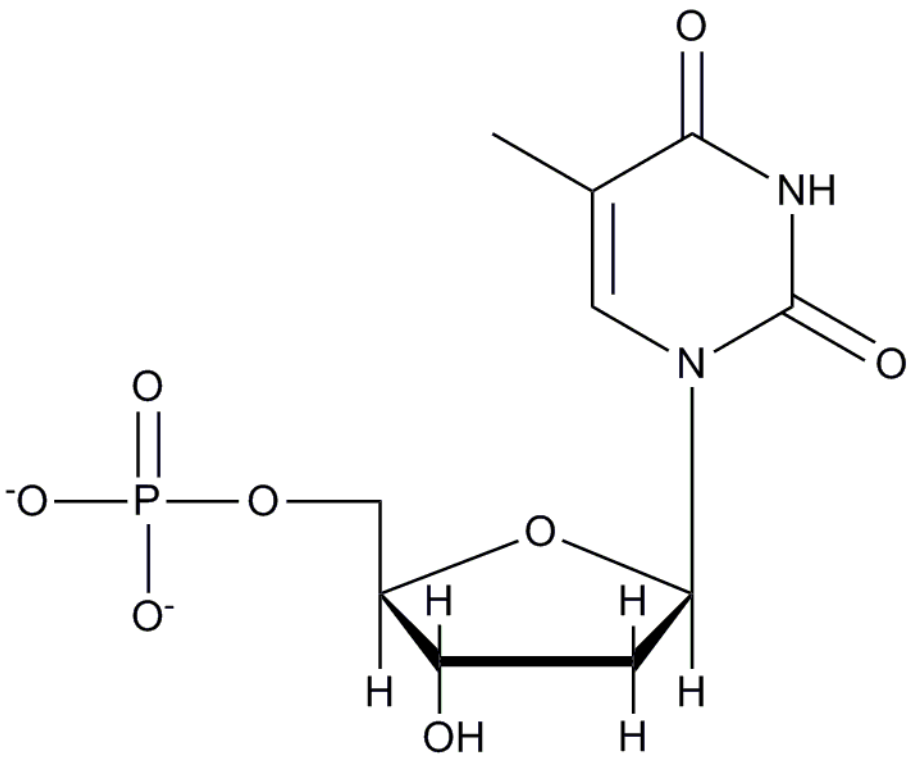
(b) Tautomers of Nucleobases. **Uracil** is a tautomer of 2,4-dihydroxypyrimidine, and the structure of 2,4-dihydroxypyrimidine itself is shown on the left below. Draw four more possible tautomers that contain one carbonyl group and one hydroxyl group, and draw one more tautomer with two carbonyl groups. The skeletons are provided; you need to add the H-atom(s) to the appropriate N-atom(s) and complete the structures by adding all missing double bonds. Indicate which tautomer occurs in nucleic acids. (6 points)



(c) The Haworth projection is shown of **D-2-deoxyribose**. This deoxyribose is _____ (*alpha*, ***beta***, *gamma*) at the _**anomeric**__ carbon. 2-Deoxyribose is a _____ (**aldose**, ketose). Deoxyribose is a _____ (triose, tetrose, **pentose**, hexose). (6 points)

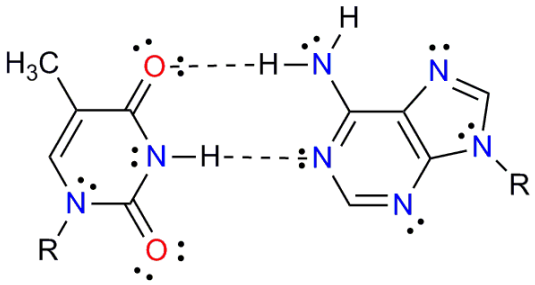
Cyclic D-2-deoxyribose	Fischer Projection of Acyclic D-2-deoxyribose
	

(d) Draw the Haworth projection of the 5'-monophosphate **nucleotide of 2'-deoxythymidine**. (4 points)



Question 5. Base Pairing. (12 points)

(a) The rough skeleton of the **TA base pair** is shown. Complete the structures of **T** and **A**: add all heteroatoms and all hydrogen atoms, add two R-groups to show where the sugar moieties are attached, and add double bonds, lone pairs, formal charges, etc. Indicate hydrogen bonds as dashed lines. (6 pts.)



(b) Crown ethers can complex K^+ ions as shown below. Oxygen lone pairs directed toward the central K^+ ion form strong dative bonds between the O-donors and the K^+ ion. Quadruplexes of guanosine, that is, H-bonded guanosine tetramers, also can complex K^+ ions effectively. (1) Indicate all H-bonds of the G quadruplex as dashed lines. (b) Add the K^+ ion at the appropriate location. (c) Draw dashed lines to indicate dative bonds to the K^+ ion. (6 pts.)