1. (a) (12 points) Write Lewis dot structures for the two different ions obtained by protonation of two different nitrogen atoms of imidazole (shown below). Clearly indicate all appropriate π-bonds, lone pairs of electrons, and formal charges.

Protonation will occur preferentially at \( \text{NA} \) and \( \text{NB} \). Why?

Protonation at \( \text{NA} \) preserves aromaticity and gives a delocalized cation. Protonation at \( \text{NB} \) destroys aromaticity.

(b) (4 points) Write a resonance structure for cytosine to explain its aromatic character. Clearly indicate all π-bonds, lone pairs of electrons, and formal charges.

(c) (6 points) \( p \)-Nitrophenol (\( \text{pK}_a = 7.2 \)) is much more acidic than phenol (\( \text{pK}_a = 10.0 \)). Draw one of the two most stable resonance structures of \( p \)-nitrophenoxide anion. Draw the key resonance structure of \( p \)-nitrophenoxide anion (not available for phenoxide anion) that is used in explaining the greater acidity of \( p \)-nitrophenol. Clearly indicate all appropriate π-bonds, lone pairs of electrons, and formal charges.
2. Nomenclature.

(a) (4 points) Complete the drawing of \((R)-2\)-ethyl-1-hexanol. Explicitly show all carbons and hydrogens.

![Ethyl Alcohol Structure](image)

(b) (4 points) Draw the structure of pentyl acetate (flavor and fragrance of bananas). Explicitly show all carbons and hydrogens.

![Pentyl Acetate Structure](image)

(c) (6 points) Draw the most stable CHAIR form of \(cis-3\)-chloro-1-methylcyclohexane. Explicitly show all ring hydrogens and CIRCLE an equatorial hydrogen.

![cis-3-Chloro-1-Methylcyclohexane Structure](image)

(d) (4 points) \(\beta\)-D-2-deoxyribofuranose (the sugar of DNA). Complete the drawing by writing all the substituents on the ring drawn below.

![Beta-D-2-Deoxyribofuranose Structure](image)

(a) (4 points) CIRCLE the compound with the highest water solubility. Draw a BOX around the compound with the lowest water solubility.

(b) (4 points) Suggest a structure for a hydrogen bonded dimer of 2-aminopyridine.

4. (a) (5 points) CIRCLE the aromatic compounds:

(b) (4 points) Draw a Fischer projection of an epimer of D-ribose.
5. Acid-Base Chemistry

(a) (4 points) **CIRCLE** the compound most soluble in water under **acidic conditions** (pH = 3).

(b) (4 points) **CIRCLE** the most acidic compound. Draw a **BOX** around the least acidic compound.

(c) (8 points) Aspartame is a dipeptide ester used as an artificial sweetener. The two pKa values of aspartame are 3.9 and 10.0. Draw the major form of aspartame present in the stomach at pH = 2.0. Draw the major form of aspartame present in the blood at pH = 7.0.

Aspartame

Stomach (pH = 2.0)    Blood (pH = 7.0)
6. (12 points) The structure of maltose is shown below.

CIRCLE the anomeric carbon atoms.

Draw an ARROW to the glycosidic linkage.

Maltose has 10 stereogenic centers (= asymmetric carbons),
2 aldose units, 0 ketose units,
0 furanose units, 2 pyranose units.

7. Write the expected products of the following reactions.

(a) (6 points)

\[ \text{HBr} \rightarrow \]

(b) (6 points)

\[ \text{HNO}_3 \text{H}_2\text{SO}_4 \rightarrow \]
(c) (8 points)

\[
\text{H} \quad \text{N} \quad \text{H} \quad \text{CH}_3 \\
\text{O} \quad \text{O} \\
\text{HCl} \quad \text{H}_2\text{O} \quad 100 \degree \text{C} \\
\text{CH}_2\text{OH}
\]

\[
\text{CH}_2\text{OH}
\]

(d) (6 Points)

\[
\text{CH}_3 \\
\text{H}_2\text{C} \quad \text{Br} \quad \text{I} \quad \text{H}_3\text{C} \\
\text{CH}_3 \\
\text{K}^+ \cdot \text{OC(CH}_3)_3
\]

\[
\text{HOC(CH}_3)_3 \\
3 \text{ isomers of C}_6\text{H}_{12}
\]

(e) (6 points)

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{Br} \quad \text{H} \\
\text{H}_2\text{C} \quad \text{C} \quad \text{CH}_3 \\
+ \text{CH}_3\text{S}^- \cdot \text{Na}^+ \\
\text{SCH}_2
\]

Show Stereochemistry of Product

(f) (6 points) Draw the product of the following aldol condensation

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{C} \quad \text{OH}^- \rightarrow \text{C}_6\text{H}_{12}\text{O}_2 \\
\text{CH}_3\text{CH}_2
\]

\[
\text{CH}_3\text{CH}_2
\]
8. (a) (8 points) Complete the following reaction by providing the required starting materials.

(b) (6 points) Complete the following reaction by providing the required reagents.

(c) (8 points) Show how the alcohol shown below can be made from compounds with 6 carbons or less (hint, one route involves a Grignard reagent).

(d) (8 points) Dacron is a polyester that is spun into fibers for use in textiles. Draw the structures of the two components used in the synthesis of Dacron.
9. (a) (8 points) Write a mechanism for the following reaction. Show all intermediates and use "electron pushing arrows" to show how each intermediate is converted to the next.

(b) (8 points) Write a mechanism for the following reaction. Show all intermediates and use "electron pushing arrows" to show how each intermediate is converted to the next.
10. (12 points) **Structure Determination.** Tables for IR and NMR are attached at the end of this exam. The mass spectrum of A indicates the molecular formula C₄H₇ClO₂. How many (π-bonds + rings) does C₄H₇ClO₂ have? __1__

The infrared spectrum of A (C₄H₇ClO₂) has a very intense band at 1740 cm⁻¹. This provides evidence for the presence of (circle all that apply):

- OH     C=C     C=O     ether     amine     hemiacetal

The ¹H NMR spectrum of A (C₄H₇ClO₂) is shown below. Integrations of peak areas are written over the peaks.

**Circle** the part structure(s) that are present in A (C₄H₇ClO₂):

- [ ] CH₂-Cl
- [ ] CH₃-O
- [ ] CH₃CH₂-C
- [ ] CH₃CH₂-O

The structure of A (C₄H₇ClO₂) is:

\[
\begin{align*}
\text{CH}_2\text{C} & \quad \text{O} \\
\text{CH}_2 & \quad \text{C} \\
\text{Cl} & \quad \text{CH}_3
\end{align*}
\]
11. (20 points) Indicate the RELATIONSHIP between the following structures.

(a) Check all that apply:
☐ enantiomers
☐ diastereomers
☒ conformers
☐ same
☐ structural isomers

(b) Check all that apply:
☐ enantiomers
☒ diastereomers
☐ conformers
☐ same
☐ structural isomers

(c) Check all that apply:
☒ tautomers
☐ diastereomers
☐ conformers
☐ same
☒ structural isomers

(d) Check all that apply:
☐ enantiomers
☒ diastereomers
☒ epimers
☐ anomers
☐ structural isomers

(e) Check all that apply:
☐ enantiomers
☒ diastereomers
☒ epimers
☒ anomers
☐ structural isomers
Extra Credit (do these only if you have plenty of time)

Explosives. (4 points) Dr. Allen Clauss gave a lecture on explosives. Write the structure of an organic compound that is an explosive.

\[
\begin{align*}
\text{Nitroglycerin} & \quad \text{TNT} \\
\text{Trinitrotoluene} & \quad \text{RDX} \\
\end{align*}
\]

Olefin Metathesis (4 points) was recognized this year with the 2005 Nobel Prize in Chemistry to Richard Schrock, Robert Grubbs, and Yves Chauvin. “Olefin” is an older word for an alkene. Olefin metathesis is truly an amazing reaction in which the strongest bond in an alkene, the C=C double bond, is broken and remade. The Grubbs ruthenium metathesis catalyst shown below catalyzes the reaction of 1,7-octadiene to produce ethylene and another product. What is the other product?

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Ru} & \quad \text{H} \\
\text{PPh}_3 & \quad \text{Ph} \\
\rightarrow & \\
\text{H}_2\text{C}=\text{CH}_2 & + \\
\end{align*}
\]

Circle the name of your discussion TA

- Chris Paradise
- Megan Jacobson
- Maren Buck
- Matt Windsor
- Tamas Benkovics

1____
2____
3____
4____
5____
6____
7____
8____
9____
10____
11____
TOTAL_____