There are 7 pages and 250 pts on this exam. Please read each question carefully before answering. Be clear and concise in your explanations, and draw your structures carefully to depict any necessary stereochemistry.

1. (10 pts) Rank the following compounds (from 1 to 5) in order of increasing acidity (1 = least acidic):

   ![Chemical Structures]

   4  1  3  2  5

2. (9 pts) Rank the following compounds (from 1 to 3) in order of increasing value of the C-H stretch in their infrared spectra in cm⁻¹ (1 = smallest value of the IR stretch):

   ![Chemical Structures]

   3  2  1

3. (8 pts) Rank the following compounds (from 1 to 4) in order of increasing value of the C=O stretch in their infrared spectra (1 = smallest value of the IR stretch):

   ![Chemical Structures]

   3  2  1  4

4. (10 pts) Rank the following compounds (from 1 to 5) in order of increasing value of the proton NMR chemical shift (δ) in ppm for the H indicated in bold (1 = smallest value of δ):

   ![Chemical Structures]

   2  4  3  1  5
5. (15 pts) Each of three bottles (A, B, and C) is labeled only \textbf{"C}_6\textbf{H}_2\textbf{O}" and contains a colorless liquid. Identify each compound based on the spectroscopic and reactivity information provided below. And \textbf{explain your reasoning}.

(a) Compound A: \textbf{\textit{H}} NMR: \( \delta \) 1.66 (s); reacts with Br\(_2\) in CCl\(_4\); IR: no significant absorption in the range 1620 - 1700 cm\(^{-1}\)

\[
\text{C}_6\text{H}_2\rightarrow 1 \text{ degree of unsaturation} \quad \text{must have a double bond}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} = \text{C} \quad \text{CH}_3 \\
\text{each CH}_3 \quad \text{group is identical} \quad \text{may be a symmetrical double bond so stretch is not intense}
\end{align*}
\]

(b) Compound B: \textbf{\textit{H}} NMR: \( \delta \) 1.07 (6H, d, \( J = 7 \) Hz); \( \delta \) 1.70 (3H, d, \( J = 1.5 \) Hz); \( \delta \) 2.20 (1H, septet, \( J = 7 \) Hz); \( \delta \) 4.60 (2H, d, \( J = 1.5 \) Hz); IR: 1642, 891, 3080 cm\(^{-1}\)

\[
\delta 1.07 \rightarrow \quad \text{CH}_3 \quad \text{CH}_3
\]

\[
\delta 1.70 \rightarrow \quad \text{CH}_3 \quad \text{accidentally the same} \quad \text{\& in ppm} \quad (4.60)
\]

\[
\delta 2.20 
\]

(c) Compound C: \textbf{\textit{H}} NMR: \( \delta \) 1.40 (s); does NOT react with Br\(_2\) in CCl\(_4\)

\[
\text{cyclohexane} = \quad \text{no double bonds and all H's are the same}
\]

6. (15 pts) To which of the compounds below does the following \textbf{\textit{C}}-NMR spectral data belong. \textbf{Explain}.

\( \delta \) 15.5 (quartet), \( \delta \) 20.1 (quartet), \( \delta \) 60.7 (triplet), \( \delta \) 99.6 (doublet)

\[
\begin{align*}
\text{A} & & \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 \\
\text{would generate} & & \text{15.5} \quad \text{H}_3\text{C} \quad \text{CH}_3 \\
\text{3 different \textbf{\textit{C}}} & & \text{CH}_3\text{CH}_2\text{O} \quad \text{CH}_3 \quad \text{CH}_3\text{OCH}_2 \quad \text{CH}_3
\end{align*}
\]

\[
\text{B} & & \text{CH}_3\text{OCH}_2 \quad \text{CH}_3
\]

\[
\text{C} & & \text{both methyl groups}\]

\[
\text{on same would appear at large } \delta \text{ due to being next to oxygen}
\]
7. (36 pts) Provide the products of the following reactions. If there is more than one product, predict which will be major.

(a) \[
\begin{align*}
\text{H}_2\text{C} \quad \text{N} \quad \text{HC} \\
\end{align*}
\]
\[ \xrightarrow{1) \text{Br}} \]
\[ \xrightarrow{2) \text{H}_3\text{O}^+} \]

(b) \[
\begin{align*}
\text{C}_2\text{H}_5 & \xrightarrow{1) \text{LDA, } -78^\circ\text{C}} \\
\text{CO} & \xrightarrow{2) \text{H}_2\text{O}} \text{OCH}_3
\end{align*}
\]

(c) \[
\begin{align*}
\text{CH}_3\text{O} - \text{CH}_2 - \text{OCH}_3 & \xrightarrow{1) \text{NaOCH}_3} \\
\end{align*}
\]
\[ \xrightarrow{2) \text{H}_2\text{O}} \]

(d) \[
\begin{align*}
\text{C}_2\text{H}_5 & \xrightarrow{1) \text{CN}} \\
\end{align*}
\]
\[ \xrightarrow{2) \text{H}_2\text{O}} \]

(e) \[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{NaOH, excess Br}_2} \\
\end{align*}
\]

(f) \[
\begin{align*}
\text{C}_2\text{H}_5 & \xrightarrow{1) \text{NaOH}} \\
\text{C}_2\text{H}_5 & \xrightarrow{2) \text{H}_3\text{O}^+} \\
\end{align*}
\]

(g) \[
\begin{align*}
\text{CH}_3\text{O} \xrightarrow{1) \text{CH}_3\text{O}^+} \\
\end{align*}
\]

(h) \[
\begin{align*}
\text{C}_2\text{H}_5 & \xrightarrow{1) \text{NaOCH}_3} \\
\end{align*}
\]
\[ \xrightarrow{2) \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}} \\
\xrightarrow{3) \text{H}_3\text{O}^+, \text{heat}} \]

(i) \[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{Br}_2} \\
\end{align*}
\]
\[ \xrightarrow{\text{mixture}} \]
8. (25 pts) Provide all reagents for the following reactions. In some cases, more than one step may be required.

9. (30 pts) Provide the products you would obtain from reaction of β-D-galactose with the following reagents:
10. (45 pts) Provide syntheses for these compounds with reagents and conditions. Assume that you can separate isomers.

(a) Start with
\[
\text{CH}_3\text{O}_2\text{C} - \text{CH}_2\text{C} = \text{CO}_2\text{CH}_3
\]
and prepare
\[
\text{H}_3\text{C} - \text{C} - \text{O} - \text{CO}_2\text{CH}_3
\]
and heat
\[
\text{H}_3\text{C} - \text{O} - \text{CO}_2\text{CH}_3
\]
1) \(\text{NaOH}\)
2) \(\text{H}_2\text{O}^+\)
workup

(b) Start with
\[
\text{O} - \text{C} - \text{H}
\]
\[
\text{H} - \text{OH}\]
\[
\text{H} - \text{OH}\]
\[
\text{CH}_2\text{OH}
\]
and prepare
\[
\text{O} - \text{C} - \text{H}
\]
\[
\text{H} - \text{OH}\]
\[
\text{H} - \text{OH}\]
\[
\text{CH}_2\text{OH}
\]
\[
\text{Br}_2
\]
\[
\text{H}_2\text{O}
\]
\[
\text{CO}_2\text{H}
\]
\[
\text{H} - \text{OH}\]
\[
\text{H} - \text{OH}\]
\[
\text{CH}_2\text{OH}
\]
\[
\text{H}_2\text{O}_2
\]
\[
\text{Fe}_2\text{SO}_4\]

(c) Start with
\[
\text{O}
\]
\[
\text{CH}_2\text{OCH}_3
\]
and prepare
\[
\text{O}
\]
\[
\text{CH}_3\text{CH}_2\text{OCH}_3
\]
1) \(\text{NaOCH}_3\)
2) \(\text{CH}_3\text{I}\)
11. (12 pts) Sucrose is a disaccharide that is shown below.

(a) What sugar units make up sucrose? **glucopyranose and fructofuranose**

(b) What kind of glycosidic linkage is depicted above by the bond marked A? \(\alpha (1\rightarrow2')\)

(c) Is sucrose a reducing or non-reducing sugar? **non-reducing**

(d) What anomeric stereochemistry is depicted above by B? **\(\beta\)**

12. (15 pts) Suggest a structure for the \(m/z = 87\) ion in the electron impact mass spectrum of 2-methyl-2-pentanol, and provide a mechanism for its formation.

\[
\text{C}_6\text{H}_{14}\text{O} \quad \text{102 amu}
\]

One of these electrons is lost.

**Stable carbocation is generated by loss of \(\text{CH}_3\) radical from initially formed radical cation.**
13. (20 pts) Provide a mechanism for the following transformation.

\[ \text{H}_3\text{C}-\text{OCH}_3 + \text{C}_6\text{H}_5\text{COCH}_3 \rightarrow \text{C}_6\text{H}_5\text{C}-\text{CH}_2\text{COCH}_3 \text{ OCH}_3 \]

1) 1 eq \( \text{NaOCH}_3 \)
2) \( \text{H}_3\text{O}^+ \)
workup

\[ \text{CH}_2-\text{COCH}_3 \]

\[ \text{OCH}_3 \]

\[ \text{CH}_3\text{OH} \]

\[ \text{NaOCH}_3 \]

\[ \text{H}_3\text{O}^+ \text{ workup} \]

\[ \text{Equilibria for all steps} \]

This step is driven to completion by acid-base reaction to favor products.