MULTIPLE CHOICE (15 points)

1. \(^1\text{H}\) nuclei located near electronegative atoms tend to be _____ relative to \(^1\text{H}\) nuclei which are not.
   a) shielded  
   b) deshielded  
   c) resonanced  
   d) split  
   e) none of the above

2. How many signals would you expect to see in the \(^1\text{H}\) NMR spectrum of the following compound?

   ![Compound Diagram]

   a) 6  
   b) 3  
   c) 5  
   d) 4  
   e) 2

3. Which of the following protons gives an NMR signal with the lowest chemical shift value (farthest upfield)?

   ![Compound Diagram]

   a) 1  
   b) 2  
   c) 3  
   d) 4  
   e) 5

4. What splitting pattern is observed in the proton NMR spectrum for the underlined hydrogens?

   \(\text{CH}_3\text{-CH}_2\text{-O-CH}_3\)

   a) singlet  
   b) doublet  
   c) triplet  
   d) quartet  
   e) septet

Consider the following compounds and answer questions 1-4.

- a) \(\text{N}^+\text{NHCH}_3\)
- b) \(\text{HO-}\text{HO}\)
- c) \(\text{O-}\text{OCH}_3\)
- d) \(\text{H}_3\text{CO-}\text{OCH}_3\)
1. Which is a **hydrate**?
   - a) [ ]
   - b) [ ]
   - c) [ ]
   - d) [ ]

2. Which is a **hydrazone**?
   - a) [ ]
   - b) [ ]
   - c) [ ]
   - d) [ ]

3. Which would be converted to a **ketone** upon acid hydrolysis?
   - a) [ ]
   - b) [ ]
   - c) [ ]
   - d) [ ]

4. Which could be **saponified**?
   - a) [ ]
   - b) [ ]
   - c) [ ]
   - d) [ ]

4. An unknown compound, C₉H₁₂, gave the following NMR spectrum:
   - δ1.21, 3H, triplet
   - δ2.30, 3H, singlet
   - δ2.60, 2H, quartet
   - δ7.04, 4H

What is the structure of the compound?

- a) [ ]
- b) [ ]
- c) [ ]
- d) [ ]
- e) [ ]

  - only one with 4 H in 5 7 region.
  - only one with an ethyl group.

10. Which of the following alcohols is oxidized to a ketone by chromic acid?

- a) [ ]
- b) [ ]
- c) [ ]
- d) [ ]
- e) [ ]

**SHORT ANSWER**

14. (3 points) Ozonolysis of the following ketone gives formaldehyde plus another organic product. What is this product, and why you wouldn’t expect to see any evidence of a carbonyl group in its spectra (e.g. no C=O stretch visible in the IR spectrum)?

\[
\text{O}_3, -78 ^\circ C
\]

\[\rightarrow \]

\[
\text{formaldehyde} \rightarrow \text{product}
\]

\[
\text{hemiacetal}
\]
14. This question focuses on the conversion of compound I to compound II. Two types of reactions that you have learned are involved in this transformation. What are they? Show the structure of at least one of the reaction intermediates to show that you understand how I is converted to II. (Aside: Compound III is a key component in the aroma of baked goods. It has been synthesized by treating compound I with acid. In the presence of acid, I interconverts with compound II. Reference: Dake and Harrison, J. Org. Chem. 2005, 70, 10872.)

PROVIDE REAGENTS:

b)

\[ \text{phenyl OH} \xrightarrow{\text{MnO}_2 \text{ or } \text{CrO}_3 \text{, pyr} \text{ or } \text{Na}_2\text{Cr}_2\text{O}_7 \text{, } \text{H}_2\text{SO}_4 \text{, } \text{H}_2\text{O}\text{ (H}_2\text{CrO}_4\text{)}} \rightarrow \text{phenyl ketone} \]

a)

\[ \text{cyclohexane} \xrightarrow{\text{NO}_2 \text{, OH}^+ \text{, H}^+} \rightarrow \text{oxygenated product} \]

b)

\[ \text{phenyl ketone} \xrightarrow{\text{KCN}} \rightarrow \text{benzylic cyanohydrin} \]

c)

\[ \text{benzylmagnesium bromide} \xrightarrow{1) \text{H}_2\text{CH}_3 \text{, } 2) \text{H}_2\text{O}} \rightarrow \text{benzyl alcohol} \]

d)

\[ \text{acetate} \xrightarrow{\text{H}^+ \text{, H}_2\text{O}} \rightarrow \text{acetone} \]
COMPLETE THESE REACTIONS:

b)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{H}_3\text{O}^+} & \\
\text{C}_3\text{H}_7\text{CH}_2\text{COH} & + \text{C}_5\text{H}_9\text{N}
\end{align*}
\]

(c)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{1) \text{CH}_3\text{CH}_2\text{MgBr}} & \\
\xrightarrow{2) \text{H}^+} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]

(d)  \[
\begin{align*}
\text{C}_5\text{H}_{10} & \text{OH} \\
\xrightarrow{\text{NH}_2\text{OH} \quad \text{pH 4.5}} & \\
\text{C}_5\text{H}_{10} & \\
\end{align*}
\]

(i)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{H}_2\text{CrO}_4} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]

(j)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et}} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]

(h)  \[
\begin{align*}
\text{C}_5\text{H}_{10} & \text{OH} \\
\xrightarrow{\text{NH}_2\text{OH} \quad \text{pH 4.5}} & \\
\text{C}_5\text{H}_{10} & \\
\end{align*}
\]

(i)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{H}_2\text{CrO}_4} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]

(g)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{H}^+} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]

(h)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{H}^+} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]

(i)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{H}^+} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]

(j)  \[
\begin{align*}
\text{Ph}_3\text{P} = \text{C} = \text{C} & \text{Et} \\
\xrightarrow{\text{H}^+} & \\
\text{Ph}_3\text{C} & \text{C}_3\text{H}_7\text{CH}_2\text{COH}
\end{align*}
\]
21. (10 points) Analyze the following NMR spectrum for a molecule with the formula C₇H₇OBr. **SHOW YOUR ANALYSIS FOR CREDIT.** Correct usage of unsaturation number = extra credit.

\[
\text{C}_7\text{H}_7\text{OBr}:
\begin{array}{cccc}
\delta & \text{int} & \text{mult} & \text{assignment} \\
7.4 & 2H & d & \\
6.8 & 2H & d & \\
3.8 & 3H & s & \text{OCH}_3 \\
\end{array}
\]

\[
\text{C}_7\text{H}_7\text{O} \rightarrow \text{need } 16.5
\]

\[
\text{Br} - \text{O} - \text{OCH}_3
\]

22. (10 points) Analyze the following NMR spectrum for a molecule with the formula C₆H₁₂O. **SHOW YOUR ANALYSIS FOR CREDIT.** Correct usage of unsaturation number = extra credit.

\[
\text{C}_6\text{H}_12\text{O}:
\begin{array}{cccc}
\delta & \text{int} & \text{mult} & \text{assignment} \\
2.6 & 1H & \text{septet} & \\
2.4 & 2H & q & \\
1.1 & 6H & d & \\
1.0 & 3H & t & \\
\end{array}
\]

\[
\text{So: } x - \text{CH}_2\text{CH}_3
\]

- missing CO₁
- missing a double bond or ring

\[
\text{S}: x - \text{CH} - \text{CH}_3
\]

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

\[
\text{C}_5\text{H}_12
\]
18. (8 points) The $^1$H NMR spectrum for a compound with the molecular formula $C_{7}H_{14}O_{2}$, is shown below. Determine the structure of this compound. **Show your analysis.**

**MECHANISMS**

a) $\overset{\text{+}}{\text{CH}_3} \underset{\text{NH}}{\text{CH}_3} (\text{CH}_3)_2\text{NH}$

b) For this synthesis, all carbons must originate from 1-propanol.

b) Compound III was synthesized from compound IV (reference: Tamura, O. et al, *J. Org. Chem.* **2005**, **70**, 10720). Show how this could be done. Hint: Compound IV is a cyclic hemiacetal, which is in equilibrium with its open-chain aldehyde form. A 5-carbon chain present in both materials is in bold to aid your vision in tracking this segment between starting material and product.

$^1\text{H} \quad \text{mult} \quad \text{abs}^t \quad \text{t} \quad \text{d} \quad \text{t} \quad \text{t} \quad \text{t} \quad \text{t} \quad \text{t}$

**SYNTHESIS**

1) $^1\text{H} \\
2$