I. Nomenclature

2. Explain why the C=O bond of conjugated esters have lower vibrational frequencies and lactones have higher frequencies than unconjugated acyclic esters.

The greater the C-O single bond contrib. the weaker the C=O bond & lower the ν.

3. Which would you expect to have a higher C=O bond frequency, an ester or a thioester? Explain.

Thioester

S does not form strong π bonds.

4. In considering the rate of hydrolysis of an ester and a thioester to carboxylic acids, which would proceed most rapidly?

Thioester - lacks resonance stabilization compared to ester.

III. Reactions

1. What might be a side reaction associated with the direct alkylation of an ester?

\[ \text{Claisen ester condensation} \]

\[ (\text{OE}) + (\text{RX}) \rightarrow \text{RX} \Rightarrow \text{OE} \]

\[ \text{2nd equivalent lost} \]
2. In the Claisen ester condensation reaction, why do only two molecules condense and not several to form a polymer?

\[ \text{H}_3\text{C}-\text{C(OEt)}_2 + \text{H}_2\text{C}-\text{C(OEt)}_2 \xrightarrow{1. \text{NaOEt}} \xrightarrow{2. \text{H}_2\text{O}^+} \text{H}_3\text{C}-\text{C(OEt)}_2 \]

Resonance and decrease electrophilicity of ketone + ester.

3. In nucleophilic addition to a conjugated ketone, explain the factors favoring 1,2 addition versus 1,4 addition. Draw out intermediates.

4. Provide the starting material, reagent, or product of the reactions on the last page.
IV. Mechanisms

1. Provide the mechanisms of the following reactions:

\[
\begin{align*}
\text{electrophile} & \quad \text{strong nucleophile} \\
\text{weak nucleophile} &
\end{align*}
\]

1) \( \text{NaOH, H}_2\text{O, heat} \)

\[
\begin{align*}
\text{weak} & \quad \text{electrophile} \\
\text{strong nucleophile} &
\end{align*}
\]

2) \( \text{H}_2\text{O}^+ \)

\[ \text{H}_3\text{C}-\text{OCH}_3 \rightarrow \text{H}_3\text{C}-\text{OH} + \text{OCH}_3 \quad \text{pK}_a = 5 \]

\[ \text{H}_3\text{C}-\text{OCH}_3 + \text{H}_3\text{C}-\text{OH} \quad \text{pK}_a = 5.2 \]

weak electrophile

\[ \text{EtOH, H}^+, \text{heat} \]

\[ \text{PhCO}_2\text{Et} \]

Activated

\[ \text{PhCO}_2\text{Et} \]

\[ \text{PhCO}_2\text{Et} \]

[Ph...H] → [Ph...H] → [Ph...H]
NaOH, \( \text{Ph} \) → \( \text{Ph} \) → \( \text{HO}^- \)

[aldol product]

1) NaOEt
2) allyl bromide
3) \( \text{H}_2\text{O}^+ \), heat

\[ \text{ET}_{2}\text{CHCO}_2\text{Et} \]

\[ \text{ET}_{2}\text{CHCO}_2\text{Et} \]

\( \text{CO}_2 \) (Decarboxylation)

\( \text{HO}^- \) (Not require showing saponification mech. portion here)