ANSWER KEY
Question 8 (Problem 22.69) (15 pts)

a) The pKₐ of 2-nitropropane is 10. Give the structure of its conjugate base.

\[
\begin{align*}
\text{H}_3\text{C} & \text{N}^+ \text{O}^- \
\text{H} & \text{CH}_3 \\
\text{EtO}^- & \text{& EtOH} \\
\end{align*}
\]

2-nitropropane

Conjugate Base

b) Protonation of the conjugate base of 2-nitropropane can give a tautomer of 2-nitropropane. Draw the structure of the tautomer of 2-nitropropane that can be formed.

\[
\begin{align*}
\text{N}^+ & \text{O}^- \\
\leftrightarrow & \\
\text{O}^- & \text{H-0Et} \\
\end{align*}
\]

c) 2-nitropropane adds to ethyl acrylate under basic conditions to give predominantly the 1,4-addition product 3. Draw the structure of that product.

\[
\begin{align*}
\text{O}_2\text{N} & \text{H} \
\text{H}_3\text{C} & \text{CH}_3 \\
\text{EtO}^- & \text{EtOH} \\
\end{align*}
\]

3
\((\text{C}_8\text{H}_{15}\text{NO}_4)\)
Question 1 (10 pt). Fischer esterification is an acid-catalyzed reaction, as shown below:

\[ \text{R} \text{O} \text{H} + \text{H}_2\text{OCH}_3 \xrightleftharpoons{H^+ (\text{cat})} \text{R} \text{O} \text{CH}_3 + \text{H}_2\text{O} \]

a) Illustrate why there's not a base-catalyzed version of Fischer esterification (4 pts)

\[ \text{R} \text{O} \text{H} + \text{H}_2\text{OCH}_3 \xrightarrow{\text{OH}^- (\text{cat})} \text{R} \text{O} \text{CH}_3 + \text{H}_2\text{O} \]

No Reaction

\[ _{\text{pK}_a 4} \text{R} \text{O} \text{H} + \text{OH}^- \xrightarrow{} \text{R} \text{O}^- + \text{H}_2\text{O} \]

Hydroxylate deprotonates carboxylic acid and the resulting carboxylate is a very poor electrophile.

b) Fischer esterification involves different intermediates. Below are 3 pairs of structures. Circle the more stable structure in each pair (6 pts).

Pair 1

Pair 2

Pair 3
Question 2 (10 pts). Provide a stepwise mechanism for formation of an acid chloride and sulfur dioxide from reaction of A with chloride anion. **Show all intermediates, including electron pairs, formal charges and curved arrows in your mechanism.**
Question 3. (10 pts) For each pair, circle the compound that is more electrophilic.

A)\[\text{R O H} \quad \text{or} \quad \text{R O CH}_3\]

B)\[\text{R O CH}_3 \quad \text{or} \quad \text{R S CH}_3\]

C)\[\text{R O CH}_3 \quad \text{or} \quad \text{R N CH}_3\]

D)\[\text{R Cl} \quad \text{or} \quad \text{R O O R}\]

E)\[\text{R O O R} \quad \text{or} \quad \text{R C CH}_2\]
**Question 4 (15 pts).** The enol tautomer is usually less stable than the keto tautomer. However, in the case below the enol tautomer 2 is quite stable.

a) For 5 pts draw the structure of the enol tautomer 2 in the indicated box.

![Structure of enol tautomer 2](image)

b) Based on the structure in part a) provide 2 different reasons for the unusual stability of enol 2

1) Intramolecular hydrogen bonding

2) Formation of conjugated \(\alpha,\beta\)-unsaturated carbonyl system

c) Provide a reasonable mechanism for the decarboxylation shown below (5 pts).

![Mechanism of decarboxylation](image)
Question 5. (15 pts) Do only 1 of 2 synthesis problems on the next 2 pages. Cross out the problem that you do not want graded.

A) Propose a synthesis of 5 using any of the materials 1-4 (note that you may not need all of the materials for a successful synthesis). Show all inorganic reagents and conditions for each synthetic step and indicate all the intermediate compounds in the synthesis of compound 5.
B) Propose a synthesis of 6 using any of the materials 1-4 (note that you may not need all of the materials for a successful synthesis). Show all inorganic reagents and conditions for each synthetic step and indicate all the intermediate compounds in the synthesis of compound 6.
Question 6. (15 pts) Bromination of ketone 1 gives different products depending on the reaction conditions.

a) Draw the structures of 2, 3 in the empty boxes below.

\[
1 \quad \text{CH}_3 \quad \text{C} \quad \text{OH} \\
\text{Br}_2 \quad \text{H}_2\text{O}, \text{H}_3\text{O}^+ \quad \text{NaOH} \quad \text{H}_2\text{O} / \text{THF} \quad \text{H}^+ \quad \text{remove water} \quad \text{4} \quad \text{mol wt= 148} \\
\text{2} \\
\text{3} \quad \text{4} \quad \text{mol wt= 148} \\
\text{5} \quad \text{mol wt= 150}
\]

b) If compound 4 (mol. wt=148) is dissolved in a solution of D\text{2}O, a new compound 6 (mol. wt 150) is eventually formed. Draw the structure of compound 6 in the empty box below.

\[
\text{4} \quad \text{mol wt= 148} \\
\text{D}_2\text{O} \quad \text{6} \quad \text{mol wt= 150}
\]
Question 7. Multiple Choice (10 pts)

a) Circle the compound that is most likely to racemize under basic conditions

b) Circle the strongest base

c) Circle the strongest acid

d) Circle the most stable anion

e) Circle the strongest acid