CHEM 241-Davis, Examination 2

YOUR NAME __________________________

(Last, First)

University Honor Code Acknowledgment
I have neither given nor received assistance in taking this examination.

__________________________ Signature

Notes

• This exam is worth 100 points

• There are 8 Problems on pages 3-11. Make sure your exam has all the pages.

• Nothing written on page 12 will be graded-this is for scratch work

• The exam period is for 75 minutes (9:30-10:45 am).

Points

Problem 1 _____ (10)
Problem 2 _____ (10)
Problem 3 ____ (10)
Problem 4 _____ (15)
Problem 5 _____ (15)
Problem 6 _____ (15)
Problem 7 _____ (10)
Problem 8 _____ (15)
Total _____ (100)
**Question 1 (10 pt).** Fischer esterification is an acid-catalyzed reaction, as shown below:

\[
\begin{align*}
\text{RO} \text{O} \text{H} & + \text{H} \text{O} \text{CH}_3 \quad \xrightleftharpoons{\text{H}^+ \text{(cat)}} \quad \text{RO} \text{O} \text{CH}_3 + \text{H}_2\text{O} \\
\text{RO} \text{O} \text{H} & + \text{H} \text{O} \text{CH}_3 \quad \xrightarrow{\text{OH}^- \text{(cat)}} \quad \text{RO} \text{O} \text{CH}_3 + \text{H}_2\text{O}
\end{align*}
\]

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

\[
\begin{align*}
\text{RO} \text{O} \text{H} & + \text{H} \text{O} \text{CH}_3 \quad \xrightarrow{\text{OH}^- \text{(cat)}} \quad \text{RO} \text{O} \text{CH}_3 + \text{H}_2\text{O} \\
\text{RO} \text{O} \text{H} & + \text{H} \text{O} \text{CH}_3
\end{align*}
\]

No Reaction

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.**

\[
\begin{align*}
\text{Intermediate A} & : & \quad \text{H}_3\text{C}^+\text{O}^-\text{S}^-\text{Cl}_- + \text{Cl}^- & \rightarrow & \text{H}_3\text{C}^-\text{O}^+\text{Cl}^- + \text{SO}_2 + \text{Cl}^- \\
\end{align*}
\]
Question 3. (10 pts) For each pair, circle the compound that is more electrophilic

A) R\textsubscript{O}O\textsubscript{H} or R\textsubscript{O}O\textsubscript{CH\textsubscript{3}}

B) R\textsubscript{O}O\textsubscript{CH\textsubscript{3}} or R\textsubscript{O}S\textsubscript{CH\textsubscript{3}}

C) R\textsubscript{O}O\textsubscript{CH\textsubscript{3}} or R\textsubscript{O}N\textsubscript{CH\textsubscript{3}}

D) R\textsubscript{O}Cl or R\textsubscript{O}O\textsubscript{O}

E) R\textsubscript{O}O\textsubscript{O} or R\textsubscript{O}CH\textsubscript{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.

```
O          O
H          H^+
+-+         +-+

1           2
```

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

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

```
R            R
O          O
H          \Delta
+-+         +--+

R            R
H            \ CO_2
```
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.

\[ \text{Br}_2 \quad \text{H}_2\text{O}, \text{H}_3\text{O}^+ \rightarrow \]

\[ \text{NaOH} \quad \text{H}_2\text{O} / \text{THF} \rightarrow \]

\[ \text{H}^+ \quad \text{remove water} \rightarrow \]

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

\[ \text{D}_2\text{O} \rightarrow \]

\[ \text{mol wt= 148} \rightarrow \]

\[ \text{mol wt= 150} \]
Question 7. Multiple Choice (10 pts)

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

\[
\begin{align*}
&\text{H}_3\text{C} - \text{O} - \text{SCoA} \\
&\text{H}_3\text{C} - \text{O} - \text{CH}_3 \\
&\text{H}_3\text{C} - \text{CH}_3 \\
&\text{H}_3\text{C} - \text{O} - \text{CH}_3
\end{align*}
\]

b) Circle the strongest base

\[
\begin{align*}
&\text{N} - \text{H} \\
&\text{CH}_2 - \text{O} \\
&\text{N} - \text{H} \\
&\text{H} - \text{O} \\
\end{align*}
\]

c) Circle the strongest acid

\[
\begin{align*}
&\text{O} - \text{CH}_3 \\
&\text{O} - \text{CH}_2 - \text{CH}_3 \\
&\text{O} - \text{CH}_2 - \text{CH}_3 \\
&\text{H} - \text{CH}_3
\end{align*}
\]

d) Circle the most stable anion

\[
\begin{align*}
&\text{N} - \text{H} \\
&\text{CH}_2 - \text{O} \\
&\text{H} - \text{O} \\
&\text{H} - \text{O}
\end{align*}
\]

e) Circle the strongest acid

\[
\begin{align*}
&\text{O} - \text{CH}_3 \\
&\text{O} - \text{CH}_2 \\
&\text{C} - \text{Br} \\
&\text{C} - \text{Br}
\end{align*}
\]
**Question 8** (Problem 22.69) (15 pts)

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

\[
\begin{align*}
&\text{H}_3\text{C} \quad \text{N} \quad \text{O} \\
&\text{H} \quad \text{C} \quad \text{H}_3 \\
\end{align*}
\]

2-nitropropane

\[
\begin{align*}
&\text{H}_3\text{C} \quad \text{N} \quad \text{O} \\
&\text{H} \quad \text{C} \quad \text{H}_3 \\
\end{align*}
\]

Conjugate Base

\[
\begin{align*}
&\text{EtO}^- + \quad \text{EtOH} \\
\end{align*}
\]

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.

\[
\begin{align*}
&\text{EtO}^- \\
\end{align*}
\]

3 (C$_8$H$_{15}$NO$_4$)

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.

\[
\begin{align*}
&\text{O}_2\text{N} \\
&\text{H}_3\text{C} \quad \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
&\text{O} \quad \text{Et} \\
&\text{EtO}^- \quad \text{EtOH} \\
\end{align*}
\]
BLANK PAGE FOR SCRATCH WORK-NOTHING WILL BE GRADED ON THIS PAGE