This exam has seven (7) questions, two cover pages, eight (8) exam pages, and three scratch pages.

Please check before beginning to make sure no questions or pages are missing.

65 minutes have been allotted for completion of the exam.

All scratch work should be done on the attached blank pages.

Please put your name on BOTH cover pages.

This exam is to be taken under the Dartmouth Honor Principle.

Make sure that your final answers are clearly indicated and that you clearly cross out any mistakes!!
Name: _________________________

1. _____ (10)

2. _____ (15)

3. _____ (30)

4. _____ (12)

5. _____ (33)

6. _____ (13)

7. _____ (27)     Total: __________ (140)

**TIPS:**

- Look over the entire exam first!
- If you get stuck someplace, draw out the structures and start moving electrons.
- If you really get stuck on a problem, move on and come back to it later.
1. **Multiple choice questions.** Circle the **best** answer for each question. (2 pts. each, 10 pts. total)

A. What would you expect the **major** product (carboxylic acid derivative) to be from reaction of an equimolar mixture of methanol, isopropanol, and **tert**-butanol (1 mole of each) with acetyl chloride (1 mole) in the presence of pyridine (1 mole)?
   a) methyl acetoacetate  
   b) methyl acetate  
   c) isopropyl acetate  
   d) **tert**-butyl acetate  
   e) ethyl methanoate

B. In which selection are the carboxylic acid derivatives arranged from most reactive to least reactive toward nucleophilic acyl substitution?
   a) acid anhydride, acid chloride, carboxylic amide, carboxylic ester  
   b) carboxylic amide, carboxylic ester, acid anhydride, acid chloride  
   c) acid anhydride, acid chloride, carboxylic ester, carboxylic amide  
   d) acid chloride, acid anhydride, carboxylic amide, carboxylic ester  
   e) acid chloride, acid anhydride, carboxylic ester, carboxylic amide

C. In which selection are the carbonyl compounds arranged from that with the most acidic α-hydrogen(s) to that with the least acidic α-hydrogen(s)? Consider only the most acidic hydrogens in each compound.
   a) diethyl malonate, ethyl acetoacetate, 2,4-pentanedione, ethyl acetate, diethyl ketone  
   b) ethyl acetate, diethyl ketone, diethyl malonate, ethyl acetoacetate, 2,4-pentanedione  
   c) 2,4-pentanedione, ethyl acetoacetate, diethyl malonate, diethyl ketone, ethyl acetate  
   d) 2,4-pentanedione, diethyl malonate, ethyl acetoacetate, ethyl acetate, diethyl ketone  
   e) diethyl malonate, 2,4-pentanedione, ethyl acetate, acetate, diethyl ketone, ethyl acetate

*Continued on Next Page*
D. Which of the following reaction sequences would provide the best synthetic route to \textit{tert}-butyl benzoate?

a) Reaction of \textit{tert}-butanol with benzoic acid with acid catalysis and removal of water

b) Reaction of sodium benzoate with \textit{tert}-butyl bromide

c) Conversion of \textit{tert}-butylcarboxylic acid to \textit{tert}-butylcarboxylic acid chloride followed by reaction with benzyl alcohol in the presence of pyridine

d) Conversion of benzoic acid to benzoyl chloride with thionyl chloride followed by reaction with \textit{tert}-butanol in the presence of pyridine

e) Reaction of benzaldehyde with potassium \textit{t}-butoxide followed by an acidic work-up

E. In which of the selections below will the two components of the Michael (or Michael-type) reaction listed not give a high yield of the conjugate addition product?

a) DONOR: ethyl acetate, ACCEPTOR: methyl vinyl ketone (3-butene-2-one)

b) DONOR: ethyl acetoacetate, ACCEPTOR: propenal

c) DONOR: diethyl malonate, ACCEPTOR: ethyl propenoate

d) DONOR: enamine from cyclohexanone and pyrrolidine, ACCEPTOR: propenenitrile

e) DONOR: nitromethane, ACCEPTOR: nitroethylene
2. Hydrolysis of vinyl acetate (1) gives a mixture of two products. Reduction of this product mixture with lithium aluminum hydride gives a single product. (15 pts. total)

(A) Draw a detailed mechanism with arrows showing the movement of electrons for the acid-catalyzed cleavage of vinyl acetate and clearly indicate the final products.

(B) What is the single product formed upon reduction of the organic product mixture with LiAlH₄?
3. Predict the major organic product for each set of reactions (six total) given below. For each reaction, show the intermediate product in the space provided and draw your final product in the box.
(5 pts. ea., 30 pts. total)

a) \[
\begin{align*}
\text{1) NaOEt/EtOH} & \rightarrow \\
\text{2) } & \rightarrow \\
\text{1) excess LiAlH}_4 & \rightarrow \\
\text{2) } & \rightarrow \\
\end{align*}
\]

b) \[
\begin{align*}
\text{PBr}_3, \text{Br}_2 & \rightarrow \\
\text{PhOH} & \rightarrow \\
\text{pyridine} & \rightarrow \\
\end{align*}
\]

c) \[
\begin{align*}
\text{1) SOCl}_2 & \rightarrow \\
\text{2) NH}_3 (\text{excess}) & \rightarrow \\
\text{SOCl}_2, \Delta & \rightarrow \\
\end{align*}
\]

d) \[
\begin{align*}
\text{-H}_2\text{O} & \rightarrow \\
\text{1) } & \rightarrow \\
\text{2) H}_3\text{O}^+, \Delta & \rightarrow \\
\end{align*}
\]

**Hint — IR:** bands at 1710, 1715 and 2500 – 3300 cm\(^{-1}\)
(nothing at 2230 cm\(^{-1}\))
4. Fill in the missing reagents (each box represents one step and may need more than one reagent) and the final product. (12 pts.)
5. Propose efficient syntheses from the starting materials shown for the two transformations shown below. Use any other reagents you need. Use of reactions discussed in the past three chapters should facilitate the transformations. (33 pts.)

(A)

(B)

Continued on Next Page
6. Consider the following reaction scheme:

\[ \text{1,3-diphenyl-1,3-propanedione} \xrightarrow{1} \text{I}_2, \text{NaOH, H}_2\text{O} \xrightarrow{2} \text{H}_3\text{O}^+ \]

Draw a detailed mechanism with arrows showing the movement of electrons for the formation of benzoic acid and iodoform from 1,3-diphenyl-1,3-propanedione (2). (13 pts.)
7. Each of the compounds shown below can be prepared by the reaction between compounds or parts of compounds containing carbonyl groups (*i.e.* by aldol, Claisen, Dieckmann, Michael, enamine, or Robinson-type reactions).

For each compound, draw the molecule(s) which can form the given product through a carbonyl condensation reaction. (27 pts.)

**EXAMPLE:**

\[ \text{HOH} \quad \text{H OH} \quad \text{H OH} \]

(a) \[ \text{O} \]

(b) \[ \text{O} \]

(c) \[ \text{O} \]

(d) \[ \text{O} \]

(e) \[ \text{O} \]

Last page.