This exam has six (6) questions, two cover pages, six exam pages, and three scratch pages.

Please check before beginning to make sure no questions 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. _____ (12)

2. _____ (12)

3. _____ (25)

4. _____ (30)

5. _____ (15)

6. _____ (16)

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.

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Periodic Table of the Elements
1. **Multiple choice questions.** Circle the *best* answer for each question. (2 pts. each, 12 pts. total)

A. In which selection are the carboxylic acids arranged from most acidic to least acidic?
   a) propanoic acid, acetic acid, trichloroacetic acid, trifluoroacetic acid
   b) trichloroacetic acid, trifluoroacetic acid, acetic acid, propanoic acid
   c) trichloroacetic acid, trifluoroacetic acid, propanoic acid, acetic acid
   d) trifluoroacetic acid, trichloroacetic acid, acetic acid, propanoic acid
   e) trifluoroacetic acid, trichloroacetic acid, propanoic acid, acetic acid

B. Which selection are the benzoic acids arranged from most acidic to least acidic?
   a) $p$-cyanobenzoic acid, $p$-chlorobenzoic acid, benzoic acid, $p$-methoxybenzoic acid
   b) $p$-cyanobenzoic acid, $p$-chlorobenzoic acid, $p$-methoxybenzoic acid, benzoic acid
   c) benzoic acid, $p$-methoxybenzoic acid, $p$-cyanobenzoic acid, $p$-chlorobenzoic acid
   d) $p$-chlorobenzoic acid, $p$-cyanobenzoic acid, benzoic acid, $p$-methoxybenzoic acid
   e) $p$-chlorobenzoic acid, $p$-cyanobenzoic acid, $p$-methoxybenzoic acid, benzoic acid

C. Which of the following synthetic pathways would have the best likelihood of giving a high yield of $m$-hydroxybenzoic acid?
   a) PCC oxidation of $m$-hydroxybenzaldehyde
   b) Acylation of phenol with acetyl chloride/AlCl$_3$ followed by CrO$_3$/H$_3$O$^+$ oxidation
   c) acidic hydrolysis of $m$-cyanophenol
   d) treatment of $m$-bromophenol with magnesium then carbon dioxide with subsequent acidic work-up
   e) S$_2$N$_2$ attack of hydroxide on $m$-bromobenzoic acid

D. Which derivative of a carbonyl compound can NOT necessarily be prepared from the set of precursors listed:
   a) Acetal: any aldehyde + 2 equivalents of alcohol (acid-catalyzed)
   b) Ketal: any ketone + 2 equivalents of alcohol (acid-catalyzed)
   c) Enamine: secondary amine + any aldehyde or ketone (acid-catalyzed)
   d) Imine: primary amine + any aldehyde or ketone (acid-catalyzed)
   e) Cyanohydrin: HCN + any aldehyde or ketone (base-catalyzed)
E. Which of the following methods would provide the best synthetic route to tert-butyl n-propyl ether:
   a) alkoxymercuration of propene with t-butanol
   b) ring-opening of 1,2-epoxypropane with sodium t-butoxide
   c) acid-catalyzed reaction of t-butanol with propanal (propionaldehyde)
   d) reaction of sodium n-propoxide with t-butyl bromide
   e) reaction of sodium t-butoxide and 1-bromopropane

F. Which of the following statements is NOT generally true of carboxylic acids:
   a) less acidic than mineral acids (HCl, HBr, etc.)
   b) more acidic than alcohols
   c) insoluble in dilute aqueous sodium bicarbonate
   d) susceptible to reduction with LiAlH₄
   e) show IR absorptions between 1710 – 1760 cm⁻¹ and 2500 – 3300 cm⁻¹

2. Draw a detailed mechanism with arrows to show the flow of electrons for the acid-catalyzed transformation of 2-phenyl-1,3-dioxane (A) to benzaldehyde and 1,3-propanediol. (12 pts.)

\[
\begin{align*}
\text{A} & \quad \xrightarrow{\text{H}_2\text{O}^+} \quad \text{PhCHO} + \text{HOCH}_2\text{CH}_2\text{OH}
\end{align*}
\]
3. Predict the major organic product for each set of reactions (seven total) given below. **Show each intermediate product in the space provided** and draw your final product in the box. Please show all relevant stereochemistry.
(5 pts. ea., 25 pts. total)

a) ![Reaction a Diagram]

b) ![Reaction b Diagram]

IR: 1715, 3300 – 3400 cm⁻¹.

c) ![Reaction c Diagram]

d) ![Reaction d Diagram]

3) H₂NNH₂/KOH/heat

 Partial₁H NMR data: multiplet at 5.8, doublets at 5.0 and 4.9 ppm.

e) ![Reaction e Diagram]

1) Dibal, toluene -78 °C

2) H₂O⁺
4. Propose *efficient* synthetic routes for the two transformations shown below. Use any *inorganic* reagents you need and any of the organic compounds listed below. Assume that different isomers can be separated. 

*Clearly indicate* your final synthetic route. Partial credit will be awarded if you remember that you can make a transformation but can’t remember the reagent, so keep going. (30 pts.)

**Additional permissible organic reagents:** NBS, peroxides, ethylene oxide, methyl bromide, formaldehyde, pyridine, methanol, ethanol. *(You won’t need all of these.)*

a) \[ \text{?} \rightarrow \text{H}_5\text{CO} \text{CO}_2\text{H} \]

b) \[ \text{CH}_3 \text{C}_6\text{H}_4 \text{?} \rightarrow \text{H}_3\text{CO} \text{OCH}_3 \text{OCH}_3 \text{C}_6\text{H}_4 \]
5. Boron tribromide (BBr₃) is a Lewis acid used for cleavage of ethers. Treatment of 2,3-dihydrobenzofuran (1) with BBr₃ leads to the formation of o-(2-bromoethyl)phenol (3) upon acidic work-up.

A. Draw a detailed mechanism with arrows clearly indicating the flow of electrons for the transformation of 1 to intermediate 2. (10 pts.)

B. Explain briefly why the phenol product (i.e., 3) is formed and not the aryl bromide product. (5 pts.)
6. Fill in the missing reagents and the final product. (15 pts.)

\[
\begin{align*}
&\begin{array}{c}
\text{OCl} \\
\text{OOCCH}_3
\end{array} \\
\rightarrow &\begin{array}{c}
\text{OCH}_3 \\
\text{OOCCH}_3
\end{array} \quad 1) \\
\rightarrow &\begin{array}{c}
\text{OCH}_3 \\
\text{OOCCH}_3
\end{array} \\
\rightarrow &\begin{array}{c}
\text{OCH}_3 \\
\text{OOCCH}_3
\end{array} \quad 2) \\
\rightarrow &\begin{array}{c}
\text{OCH}_3 \\
\text{OOCCH}_3
\end{array} \quad 3) \\
\rightarrow &\begin{array}{c}
\text{OCH}_3 \\
\text{OOCCH}_3
\end{array} \quad 4) \\
\rightarrow &\begin{array}{c}
\text{OCH}_3 \\
\text{OOCCH}_3
\end{array} \quad 5) \\
\end{align*}
\]

Predict the Major Product!
(Formula: C\text{\textsubscript{13}}H\text{\textsubscript{19}}ClO)