1. Predict the major organic product for each set of reactions (six total) given below. Show intermediate products in the spaces provided and draw your final product in the box.
(5 pts. ea., 30 pts. total)

a) \( \text{CO}_2\text{Et} \xrightarrow{1)} \text{NaOEt/EtOH} \xrightarrow{2)} \text{Br} \rightarrow \xrightarrow{\Delta, \text{H}_2\text{O}^+} \text{CO}_2\text{Et} \rightarrow \xrightarrow{\text{EtOH}} \text{O} \xrightarrow{\Delta, \text{H}_2\text{O}^+} \text{EtOH} \)

b) \( \text{CH}_2\text{OH} \rightarrow \xrightarrow{\text{PBr}_3, \text{Br}_2} \text{Br} \rightarrow \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} \text{O} \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} \text{O} \)

c) \( \text{NHCH}_3 \rightarrow \xrightarrow{1)} \text{excess CH}_3\text{I} \rightarrow \xrightarrow{2)} \text{Ag}_2\text{O, } \Delta \)

d) \( \text{H}_2\text{O} \rightarrow \xrightarrow{1)} \text{H}_3\text{C} \rightarrow \xrightarrow{2)} \text{H}_3\text{O}^+ \)

e) \( \text{NH}_2 \rightarrow \xrightarrow{1)} \text{HNO}_2/\text{H}_2\text{SO}_4 \rightarrow \xrightarrow{2)} \text{KCN, CuCN} \rightarrow \xrightarrow{1)} \text{LiAlH}_4 \rightarrow \xrightarrow{2)} \text{H}_2\text{O} \rightarrow \)

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2. Fill in the missing reagents (each box represents one step and may need more than one reagent) and the final product. (15 pts.)
3. Propose efficient syntheses for the two transformations shown below. Use any other reagents you need. Assume that \( \alpha \)- and \( \beta \)-isomers can be separated. Use of reactions discussed in the past three chapters should facilitate the transformations.

(30 pts.)
4. Consider the reaction scheme drawn below.

\[
\text{Br-CH-CH-Br + EtO-CH-CH-CH-CH-CH-CH-CH-CH-Br} \xrightarrow{1) \text{NaOEt, EtOH}} \text{A} \xrightarrow{2) H_3O^+, \text{heat}} \text{pentanal} + \text{CO}_2 + \text{EtOH}
\]

(A) Draw a detailed mechanism with arrows showing the movement of electrons for the formation of ester A from the starting materials shown. (10 pts.)

(B) Hydrolysis of ester A under acidic conditions gives ethanol and a carboxylic acid which can be decarboxylated upon heating.

Draw a detailed mechanism with arrows showing the movement of electrons for the decarboxylation of this acid to give the products shown (not including ethanol). (5 pts)
5. Rank the following compounds according to their ability to act as bases from strongest on the left to weakest on the right. (10 pts.)

\[
\begin{array}{cccc}
\text{NH}_2 & \text{NH}_2 & \text{NH}_2 & \text{H}_3\text{CO} \text{NH}_2 \\
\text{LDA} & \text{NaOEt} & \text{Ethylamine} & p\text{-methoxy-aniline} \\
\text{STRONGEST Base} & & & (p\text{-anisidine}) \\
\end{array}
\]

\text{4'}-\text{amino-acetophenone ("p-acetyl-aniline")}

WEAKEST Base

6. Consider the following Claisen condensation:

\[
\text{H}_3\text{C} = \text{C} = \text{OEt} \xrightarrow{\text{NaOEt/EtOH}} \text{H}_3\text{C} - \text{CH}_3
\]

Why does the equilibrium lie to the left (starting ester) in this particular case? Give a detailed explanation with illustrative mechanisms.

(10 pts.)

Steric hindrance is likely to play some role in the equilibrium, but more importantly, the product has no particularly acidic \(\alpha\)-hydrogens, thus there is no thermodynamic driving force for its formation.

In high-yielding Claisen condensations, the product is deprotonated (see scheme below) at the carbon adjacent to both carbonyl groups and the equilibrium is driven to the right.

\[
\text{Continued on Next Page}
\]
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, Michael, enamine, or Robinson-type reactions).

For each compound, draw the molecule(s) which can form the given product through a carbonyl condensation reaction. (30 pts.)

EXAMPLE:

(a) $\text{HOCH_2COCH_3} \xrightleftharpoons{} \text{HOCOC_2H_5}$

(b) $\text{HOCH_2CH(CH_3)_2} \xrightleftharpoons{} 2\text{HOC_2H_5}$

(c) $\text{HOCH_2CH_2OCH_3} \xrightleftharpoons{} \text{EtOEt_2}$ or $\text{HOCH_2CH_2OCH_3}$

(d) $\text{CNCH(CN)CH}_3 \xrightleftharpoons{} \text{CNCH}_3, \text{HCN}$

(e) $\text{CO_2C_2H_5CH_3} \xrightleftharpoons{} \text{HOEt_2C_2H_5}$

Last page.