**P13.1:** Propose a mechanism for this early reaction in the biosynthesis of the isoprenoid building blocks:

\[
\text{enz} \quad \overset{\text{acetyl CoA}}{\underset{\text{H}_2\text{O}}{\longrightarrow}} \quad \overset{\text{CH}_3\text{O}}{\overset{\text{O}}{\text{HO}} \overset{\text{O}}{\text{CH}_3\text{O}}} \overset{\text{SCoA}}{\text{S}^\ominus} \]

**P13.2:** Given the intermediates shown for this biotin-dependent reaction in which acetyl-CoA is carboxylated (in the fatty acid biosynthesis pathway), propose a complete curved-arrow mechanism.

\[
\overset{\text{O}}{\overset{\text{O}}{\text{N}}} \overset{\text{N}}{\overset{\text{R}}{\text{S}}} \overset{\text{H}_2\text{C}}{\overset{\text{O}}{\text{O}^\ominus}} \overset{\text{SCoA}}{\text{CO}_2} \]

**P13.3:** Propose a likely mechanism for this final reaction in the degradation of cysteine in mammals.

\[
\overset{\text{O}}{\overset{\text{O}}{\text{S}}} \overset{\text{O}^\ominus}{\overset{\text{O}}{\text{O}}} \overset{\text{SO}_2}{\overset{\text{SO}_2}{\longrightarrow}} \overset{\text{H}_3\text{C}}{\overset{\text{O}^\ominus}{\overset{\text{O}}{\text{O}}}}
\]

**P13.4:** The following is a step in the degradation pathway for threonine. Propose a likely mechanism.

\[
\overset{\text{H}_3\text{N}}{\overset{\text{O}}{\overset{\text{O}^\ominus}{\text{CH}_3}}} \overset{\text{CoASH}}{\longrightarrow} \text{glycine + acetyl CoA}
\]

**P13.5:** Propose reasonable mechanisms for the following reactions:

- a)
**P13.6:** Propose a mechanism for the following carboxylation reaction. The complete reaction is dependent on the CO₂-carrying coenzyme biotin as well as ATP, but assume in your mechanism that the actual carboxylation step occurs with free CO₂ (you don’t need to account for the role played by biotin or ATP).

**P13.7:** The following step in the biosynthesis of lysine involves a condensation between aspartate semialdehyde (the reactant pictured below) and a common metabolic intermediate. Identify the intermediate, and propose a mechanism for the reaction.

**P13.8:** In the biosynthesis of leucine, acetyl CoA condenses with another metabolic intermediate ‘X’ to form 1-isopropylmalate. Give the structure for substrate X, and provide a mechanism for the reaction.
P13.9: 2-methyl-3-keto-butyryl CoA undergoes retro-Claisen cleavage (a step in isoleucine degradation). Predict the products.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{SCoA} & \quad \text{HSCoA}
\end{align*}
\]

P13.10: Propose a mechanism for the following reaction:

\[
\begin{align*}
\text{O}_2C & \quad \text{CO}_2^- \\
\text{GTP} & \quad \text{CO}_2 \quad \text{GDP} \quad \text{OP} \\
\end{align*}
\]

P13.11: Propose a mechanism for the following transformation (part of the degradation pathway for the uridine nucleotide).

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

P13.12: Provide a likely mechanism the reaction below, from tryptophan biosynthesis:

\[
\begin{align*}
\text{CO}_2 \quad \text{HO}^- & \quad \text{OP} \\
\text{N} & \quad \text{H} \\
\text{C} & \quad \text{N} \\
\text{H} & \quad \text{OH} \\
\end{align*}
\]

P13.13: Suggest a likely mechanism for the following reaction in the biosynthesis of morphine, being sure to identify the structure of species X, which is released in the reaction.

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

P13.14: Predict the product of the following reaction:
P13.15: Predict the major organic product of each of the following reactions:

a)

\[
\begin{align*}
\text{\textbf{C}} & \xrightarrow{1) \text{NaOCH}_2\text{CH}_3} \text{\textbf{D}} \\
\text{\textbf{D}} & \xrightarrow{2) \text{Br}} \text{\textbf{E}} \\
\text{\textbf{E}} & \xrightarrow{1) \text{NaOCH}_2\text{CH}_3} \text{\textbf{F}} \\
\text{\textbf{F}} & \xrightarrow{2) \text{HCl (aq)}} \text{\textbf{G}} \\
\end{align*}
\]

b)

c)

P13.16: Draw the structures of compounds designated by A – G in the reactions below.

a)  

\[
\begin{align*}
\text{A} & \xrightarrow{1) \text{NaOCH}_2\text{CH}_3} \text{B} \\
\text{B} & \xrightarrow{2) \text{HCl (aq)}} \\
\end{align*}
\]

b)  

c)  

P13.17: Predict the major organic product of the following laboratory synthesis reactions:

a)
b) 

\[\text{H}_3\text{C} \equiv \text{C} \equiv \text{H}\] 

THF 

\[\xrightarrow{\text{Mg, diethyl ether}} \] 

\[\xrightarrow{\text{H}_3\text{O}^+} \] 

c) 

\[\xrightarrow{1) \text{Li}} \] 

\[\xrightarrow{2) \text{Cl-SO}_2\text{-CH}_3} \] 

d) \text{(also predict the structure of species A)} 

\[\xrightarrow{\text{H}_3\text{O}^+} \] 

\[\xrightarrow{1) \text{NaNH}_2} \] 

\[\xrightarrow{2) \text{Br}} \] 

e) 

\[\xrightarrow{\text{NaOH (aq)}} \] 

\[\xrightarrow{\text{H}_3\text{O}^+} \] 

f) 

\[\xrightarrow{\text{Cl}_2 (\text{excess})} \] 

\[\xrightarrow{\text{SOCl}_2} \] 

\[\xrightarrow{\text{CH}_3\text{NH}_2} \] 

g)
P13.18: Propose routes for the following multistep syntheses. You may use any lab synthesis reagent covered so far in this text, plus the starting compound(s) given.

a) 

b) 

c) 

Challenge problems

C13.1: Suggest a mechanism for the following transformation. (Hint – only two mechanistic steps are required.)