Answer Key

1. (25.5) Show the first complete step of the arrow-pushing mechanism for each of the following. Additionally, show the consequence of your arrows for parts a) through d) only.

a) 
\[
\text{\begin{align*}
\text{\text{PhCO}_2^-Na^+} & \rightarrow \text{PhCO}_2^- + \text{NaBr} \\
\text{PhCO}_2^- \text{PhCH}_2\text{Br} & \rightarrow \text{PhCO}_2^- + \text{NaBr}
\end{align*}}
\]

b) 
\[
\text{\begin{align*}
\text{PhCO}_2^- \text{H}^- & \rightarrow \text{PhCO}_2^- \text{Li}^+ \\
\text{PhCO}_2^- \text{H}^- & \rightarrow \text{PhCO}_2^- \text{Li}^+ + \text{H}_2\text{O}
\end{align*}}
\]

c) 
\[
\text{\begin{align*}
\text{C}_5\text{H}_8\text{NH}_2 \text{Li}^+ & \rightarrow \text{C}_5\text{H}_8\text{NH}_2 \text{Li}^+ + \text{H}_2\text{O}
\end{align*}}
\]

d) 
\[
\text{\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_2^- \text{NHMe}_2 & \rightarrow \text{C}_6\text{H}_{12}\text{O}_2^- \text{NHMe}_2 + \text{H}_2\text{O}
\end{align*}}
\]

e) 
\[
\text{\begin{align*}
\text{CF}_3\text{CO}_2^- \text{H}^- & \rightarrow \text{CF}_3\text{CO}_2^- \text{H}^-
\end{align*}}
\]

f) 
\[
\text{\begin{align*}
\text{\text{PhCH}_3} & \rightarrow \text{\text{PhCH}_3} \\
\text{\text{PhCH}_3} & \rightarrow \text{\text{PhCH}_3}
\end{align*}}
\]

g) 
\[
\text{\begin{align*}
\text{\text{PhCO}_2^-Me} & \rightarrow \text{\text{PhCO}_2^-Me} \\
\text{\text{PhCO}_2^-Me} & \rightarrow \text{\text{PhCO}_2^-Me}
\end{align*}}
\]
*2. (7.5) Draw in the missing charges (if any) on the appropriate atoms in each of the following.

a) ![N≡C=CH₂ with charges]
b) ![N≡C—CH₃ with charges]
c) ![S=S with charges]

*3. (17.5) Complete each of the following acid-base reactions and, using your knowledge of pKa values, indicate which side of the reaction will be favored.

a) \[ \text{OK} + \text{CH₃CO₂H} \rightarrow \text{CH₃CO₂OH} + \text{CH₃CO₂K} \]
   favored

b) \[ \text{BO}_3^- + \text{Li}^+ \rightarrow \text{BO}_3^- + \text{H}_3\text{N} \]
   favored

c) \[ \text{BuLi} + \text{C₆H₅} \rightarrow \text{C₆H₅}^- + \text{BuH} \]
   favored

d) \[ \text{O=C=O} + \text{KO}^\text{tBu} \rightarrow \text{O=C=O} + \text{HO}^\text{tBu} \]
   favored

d) \[ \text{O=C=O} + \text{KO}^\text{tBu} \rightarrow \text{O=C=O} + \text{HO}^\text{tBu} \]
   favored

*4. (9) Circle the better nucleophile and put a square around the better leaving group in each of the following pairs. You do not need to explain your answers.

a) ![O=N=O with charges] and ![O=O with charges]

b) ![N(CH₃)₂ with charges] and ![N≡C(CH₃)₂ with charges]
c) \( \text{MeOCHOMe} \) and \( \text{MeO}_2\text{CCHOMe} \)

*5. (10) Draw all significant resonance forms for each of the following species.

a) 

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

b) 

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

*6. (12.5) For each reaction shown below, explain briefly but clearly why the reaction occurs as shown. You need not show arrow-pushing.

a) 

If the reaction with bromine occurs at any other double bond, the remaining aromatic system is, at best, naphthalene-like. As shown, the remaining system has two conjugated benzene rings. Accordingly, reaction as shown retains more aromaticity and, therefore, greater stability.

b) 

Nucleophiles attack the site indicated by the arrow even though the greatest \( \delta^+ \) is at the site marked by the *. Explain.

The main driving force for reaction with a nucleophile at the site marked with an arrow is leaving group stability. Attack at the \( \text{C}^* \) would yield an acetate ion leaving group whereas attack at the \( \text{C} \) marked by the arrow would yield a trifluoroacetate ion leaving group. Due to the strong electron-withdrawing effect of the F atoms, trifluoroacetate ion is much more stable and, therefore, is a much better leaving group. Steric hindrance at \( \text{C}^* \) may also play a minor role.
In the first example shown, the Bu anion attacks the most electron deficient site (the C of the C=O) to displace methoxide ion. A second nucleophilic attack is then possible at the C of the C=O of the resultant ketone. In the second example, attack at the C=O is prevented by the extreme steric bulk of the ester-attached C group. However, since the system is α,β-unsaturated, there is a δ+ at the β-carbon, allowing nucleophilic attack there.

*7. (6) In each of the following molecules, circle the hydrogen atom that will be most acidic. *Note: you may have to draw in the hydrogen.

a)  

b)  

c)  

*8. (6) In each of the following, circle the atom which is the most likely source of electrons.

a)  

b)  

c)  

*9. (6) In each of the following, circle the atom which is the most likely acceptor of electrons.

a)  

b)  

c)  