Solutions to Exercises, Chapter 18

18.1

\[
\begin{align*}
\text{Me}_2\text{NH} & \quad \text{Me}_2\text{NH} \\
\text{Me}_2\text{NH} & \quad \text{Me}_2\text{NH} \\
\end{align*}
\]

18.2

(a) \text{Et}_2\text{N} & \text{O} & \text{Et} \\
(b) \text{PhS} & \text{O} \\

18.3

18.4 The acid (AH) will protonate the CN\(^-\) to an extent determined by its strength (see Chapter 6): \(\text{AH} + \text{CN}^- \rightleftharpoons \text{A}^- + \text{HCN}\), then either HCN or AH will participate as the proton donor in the second steps of the following reactions.

Carbonyl addition:

\[
\begin{align*}
\end{align*}
\]

Conjugate addition:

\[
\begin{align*}
\end{align*}
\]
18.9

Michael addition:

Ester hydrolysis:

18.10

Ester hydrolysis:

18.11

Michael addition:

Ester hydrolysis:

Hydrolysis of the other ester occurs in the same way.
Decarboxylation:

\[
\begin{align*}
(B) & \quad \xrightarrow{-\text{CO}_2} \quad \xrightarrow{\text{ketonisation}} (C)
\end{align*}
\]

18.12

18.13

18.14 The intermediate carbanion (Meisenheimer complex) formed by addition of methoxide is resonance-stabilized by nitro groups in \( o \)- and \( p \)-positions, as shown in Scheme 18.12, and the effect is cumulative. In contrast, the \( m \)-nitro group cannot participate in the conjugative stabilization of the carbanion (see Sub-section 16.4.2 to compare the effects of substituents upon the stability of benzenium ions). Consequently, the order of reactivity is as shown.
A non-activated halobenzene can undergo nucleophilic substitution only by the benzyne mechanism, but this substrate cannot form a benzyne intermediate because both the ortho positions are blocked by methyl groups.