Problem Set  Chapter 23  Answer Key

1. (Actually, the toxic principal is the (S) enantiomer)

2. One way is:

\[
\begin{align*}
\text{Cyclopentyl-Br} & \xrightarrow{\text{Mg, Et}_2\text{O}} \text{Cyclopentyl-MgBr} \\
& \xrightarrow{\text{1. O}_3\text{C}} \text{Cyclopentyl-OH} \\
& \xrightarrow{\text{2. H}_3\text{O}^+} \\
& \xrightarrow{\text{Jones reagent}} \text{Cyclopentyl-Ketone} \\
& \xrightarrow{\text{H}_2\text{NCH}_3, \text{cat H}^+} \text{Cyclopentyl-Imine} \\
& \xrightarrow{\text{1. LiAlH}_4, \text{2. H}_2\text{O}} \text{Cyclopentyl-Amine}
\end{align*}
\]
3.

a. 

\[
\text{Br} \quad \text{C}_6\text{H}_5
\]

b. 

\[
\text{C}_5\text{H}_5\text{NCH}_3
\]

c. 

\[
\text{C}_6\text{H}_5\text{NCH}_3 + \quad \text{C}_6\text{H}_5\text{NCH}_3
\]

d. 

\[
\text{C}_6\text{H}_5\text{CH}_3\text{NCH}_3\text{NH}_2
\]

e. 

\[
\text{C}_8\text{H}_{18}
\]
4. In the noncyclic tertiary amine shown, the $\angle$ CNC is about 109.5°. For racemization to occur, inversion via an $sp^3 - sp^2 - sp^3$ pathway requires the $\angle$ CNC to open to a maximum of 120°. Thus, the energy required for racemization correlates to the $\Delta \angle$ CNC, which is about 10°.

5. In the aziridine case, the $\angle$ CNC is about 60°. Now, for racemization to occur, inversion via an $sp^3 - sp^2 - sp^3$ pathway still requires the $\angle$ CNC to open to a maximum of 120° and now corresponding to a $\Delta \angle$ CNC of about 60°. This is all but impossible—a three-membered ring cannot accommodate such a large bond angle. It follows, then, the racemization energy barrier for this case must be larger.