PROBLEM SET #5 SOLUTIONS

1. $A = H_2N-NH_2 \mid KOH$ (Wolff-Kishner reduction)
   $B = 1. BH_3$; 2. $H_2O_2$, $-OH$ (Hydroboration/oxidation)
   $C = TsCl$, pyridine
   $D = NaCN$, DMF ($SN_2$)

2. This mechanism involves a carbocation rearrangement —
   good practice in electron-pushing:

   $\text{[Diagram showing a sequence of chemical reactions]}$

3. Draw six $\pi$ orbitals:

   $\theta$ is $sp^2$: 2 $e^-$ in $sp^2$ orbital
   2 $e^-$ in $\pi$ orbital

   2 $\pi e^-$ from each double bond = $4\pi e^-$
   2 $\pi e^-$ from $\theta$ = $2\pi e^-$

   $\left\{ \text{Aromatic} \right\}$
Because the 2 protons in $\Theta$ resides in different "types" or orbitals, they are technically nonequivalent: one participates in the aromatic system, the other does not.

4. (a) There are two isomers of mono-substituted furan:

$$\begin{array}{cc}
\text{2-substituted furan} & \text{3-substituted furan} \\
\begin{array}{c}
\text{2-substituted: } \begin{array}{c}
\text{E} \\
\text{O} \\
\text{E} \\
\text{E} \\
\text{E}
\end{array} \\
\text{3-substituted: } \begin{array}{c}
\text{E} \\
\text{O} \\
\text{E}
\end{array}
\end{array}
\end{array}$$

(b) To decide which of the above is the major substitution product, we must examine the carbocation intermediates here:

2-substituted:

$$\text{E} \xrightarrow{\text{carbocation}} \text{E}$$

3-substituted:

$$\text{E} \xrightarrow{\text{carbocation}} \text{E}$$

There is more resonance stabilization in the carbon intermediate for the 2-substituted furan, so this product predominates over its 3-substituted counterpart.
5. Formation of the benzylic cation is key here. Any factors that stabilize the cation will increase the rate of reaction. Of the three substrates, 5 (with OCH₃) will react fastest; OCH₃ donates e⁻ to stabilize the carbocation. In contrast, the NO₂ group in 6 is a strong e⁻ withdrawer and will destabilize the carbocation.

[Diagram of molecular structures with reactions and annotations]

additional res. form helps to stabilize

this res. form VERY UNSTABLE
6. (a) \[ \text{CH}_3 \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \text{COOH} \xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4} \begin{array}{c} \text{NO}_2 \\ \text{COOH} \end{array} \]

(b) \[ \text{CH}_3 \xrightarrow{\text{AlCl}_3} \xrightarrow{\text{NBS} \Delta} \]

(c) \[ \begin{array}{c} \xrightarrow{\text{Cl}_2/\text{FeCl}_3} \xrightarrow{\text{CH}_3\text{CH}_2\text{Cl} \text{AlCl}_3} \xrightarrow{\text{NBS} \Delta} \end{array} \]

\[ \begin{array}{c} \text{KOH} \\ \text{(elimination)} \end{array} \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} \]

\[ \text{Br} \]

\[ \text{Br} \]