Organic Chemistry II Drill (CHEM2220D). Module 5. Aromatic Reactions

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REACTIONS OF AROMATIC COMPOUNDS

A STUDENT SHOULD BE ABLE TO:

1. Predict the product(s) of
   Electrophilic aromatic substitution (EAS): halogenation, sulfonation, nitration, Friedel-Crafts alkylation and acylation.
   Nucleophilic Aromatic Substitution ($S_{N}Ar$): Aromatic ring contains a leaving group and ortho and/or para NO$_2$ groups, with a good nucleophile.
   Elimination-Addition: Aromatic ring contains a leaving group and $\sim\text{NH}_2$ is used as a base.
   Side-chain reactions: Clemmensen reduction, reduction of nitro groups, and synthesis of diazonium salts. Also, all reactions from previous sections including free radical halogenation, oxidation, addition, and elimination reactions.
   Other Reactions: Desulfonation, Substitution of a Diazonium Salt, Birch Reduction

2. Predict the relative reactivity of compounds toward EAS.
   Important effects of EAS include:
   The substituent already on the ring directs the location of the incoming group.
   When two or more groups are present, the strongest activating group on the ring controls the location of the incoming group. If the only groups present are deactivating, the weakest deactivating group controls the location of the incoming group.
   Strong and moderate activators possess a lone pair of electrons adjacent to the aromatic ring; however, halogens are weakly deactivating. Weak activators are typically alkyl groups. Deactivators are electron-withdrawing groups.
   All activating groups are ortho, para directors. Moderate and strong deactivating groups are meta directors. Halogens are weak deactivators and ortho, para directors.
   Substitution does not occur between groups meta to one another if there are any other possibilities.
   Keep in mind the limitations of Friedel-Crafts reactions: No reaction occurs with aromatic rings only containing m-directing groups or amino groups ($\sim\text{-NH}_2$, $\sim\text{-NHR}$, $\sim\text{-NR}_2$), and rearrangement of side chains may occur with Friedel-Crafts alkylation.

3. Determine whether a substitution reaction will proceed by an electrophilic aromatic substitution (EAS, nucleophilic aromatic substitution ($S_{N}Ar$), or an Elimination-Addition mechanism.

4. Using the reactions of Objective 1, propose syntheses of substituted aromatic derivatives. The order in which reactions are performed is often important.

5. Understand and be able to draw the mechanism of an Electrophilic Aromatic Substitution (EAS) reaction, Nucleophilic Aromatic Substitution ($S_{N}Ar$), and Elimination-Addition. The mechanisms should include all intermediates and proper mechanistic arrows. Understand the chemistry dictating the observed regiochemistry.

6. Predict NMR signals of a given compound and be able to identify unknowns from the given $^1\text{H}$ NMR and/or infrared spectroscopic information. Also, predict substitution patterns based on $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectral data.
To best prepare for this module, please work appropriate Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Predict the product or products of the reactions shown (if any):

a) $\text{HNO}_3, \text{H}_2\text{SO}_4$

b) $\text{Cl}, \text{AlCl}_3$

c) $\text{Br}_2, \text{FeBr}_3$

d) 1. $\text{HNO}_3, \text{H}_2\text{SO}_4$
   2. $\text{Fe, H}_3\text{O}^{+}$
   3. $\text{NaNO}_2, \text{HCl}$
   4. $\text{CuCN}$

e) $\text{Br}, \text{SO}_3\text{H}, \text{dil. H}_2\text{SO}_4$

f) $\text{AlCl}_3$

g) $\text{Zn[Ag]}, \text{HCl, heat}$

h) $\text{Cl}_2, \text{FeCl}_3$
1. Rank the following compounds from fastest to slowest as they react in an EAS with Br$_2$/FeBr$_3$.

i) HO-CH$_2$-C$_6$H$_4$-NO$_2$ $\xrightarrow{\text{SO$_3$/H$_2$SO$_4$}}$

j) HO-C$_6$H$_4$-Br $\xrightarrow{\text{CH$_3$Cl/AlCl$_3$}}$

k) Cl-C$_6$H$_4$-NO$_2$ $\xrightarrow{\text{KOC$_3$/heat}}$

l) Cl-C$_6$H$_4$ $\xrightarrow{1. \text{NaNH$_2$/NH$_3$, 2. H$_2$O}}$

2. Rank the following compounds from fastest to slowest as they react in an EAS with Br$_2$/FeBr$_3$.

a) I  II  III  IV  V  VI

fastest ---> ---> ---> ---> ---> ---> slowest

b) I  II  III

IV  V  VI

fastest ---> ---> ---> ---> ---> ---> slowest
3. Under each reaction, circle the correct mechanism.
   
   a) \( \text{Br} \xrightarrow{\text{NaNH}_2, \text{NH}_3} \text{NH}_2 \)  
      EAS  \hspace{1cm} S_{\text{NAr}} \hspace{1cm} \text{Elimination-Addition} 
   
   b) \( \text{Br} \xrightarrow{\text{FeBr}_3} \text{Br} \)  
      EAS  \hspace{1cm} S_{\text{NAr}} \hspace{1cm} \text{Elimination-Addition} 
   
   c) \( \text{Br} \xrightarrow{1. \text{NaOH}, 70^\circ\text{C}} \text{OH} \)  
      EAS  \hspace{1cm} S_{\text{NAr}} \hspace{1cm} \text{Elimination-Addition} 

4. Propose a synthesis of each of the following compounds, from the given starting material and any other needed reagents.
   
   a) \( \text{Br} \xrightarrow{\text{NO}_2} \)  
      \( \text{from} \)  
      \( \text{Br} \)  
   
   b) \( \text{Cl} \xrightarrow{\text{OH}} \)  
      \( \text{from} \)  
      \( \text{Cl} \)  
   
   c) \( \text{Cl} \xrightarrow{\text{OH}} \)  
      \( \text{from} \)  
      \( \text{Cl} \)
4. d) 

\[
\begin{array}{c}
\text{from} \\
\text{from}
\end{array}
\]

\[
\text{NO}_2
\]

5.1 Draw the complete mechanism, using proper curved arrow notation, and include all resonance forms of all intermediates, for both the \textit{para} and \textit{meta} bromination of nitrobenzene in the presence of ferric bromide. Two complete mechanisms will have to be drawn. Identify any particularly unstable structure with an asterisk (*). Based on this, which regiochemistry is preferred?
5.2 Electrophilic aromatic substitution of a substrate could give *para* or *meta* products. Below are two reaction coordinates comparing the energies for chlorination of one aromatic substrate.

Which one of the two molecules below would give these graphs? Explain.

![Reaction Coordinate](image)

5.3 Propose a complete mechanism for the following reaction. Be sure to use correct curved arrow notation, add lone pairs, and show all intermediates.

![Mechanism](image)

6.1 Identify the following unknowns from the given $^1$H NMR and/or infrared spectroscopic information.

a) $\text{C}_{10}\text{H}_{15}\text{N}$
   - An aniline derivative
   - IR: 3400 cm$^{-1}$
   - $^1$H NMR:
     - Triplet, $\delta$ 1.2, 6H
     - Quartet, $\delta$ 2.7, 4H
     - Broad singlet, $\delta$ 5.3, 2H
     - Singlet, $\delta$ 6.6, 1H
     - Singlet, $\delta$ 6.8, 2H

b) $\text{C}_{12}\text{H}_{18}$
   - $^{13}$C NMR: $\delta$ 23, 34, 119, 123, 128, 148
   - $^1$H NMR:
     - Doublet, $\delta$ 1.2, 12H
     - Multiplet, $\delta$ 2.9, 2H
     - Doublet, $\delta$ 7.2, 2H
     - Singlet, $\delta$ 7.4, 1H
     - Triplet, $\delta$ 7.5, 1H
6.1 c) C₁₂H₁₅O

\(^{13}\text{C NMR:} \quad \delta 27, 31, 34, 125, 128, 134, 156, 197
\(^{1}\text{H NMR:} \quad \text{singlet, } \delta 1.3, 9\text{H}
\quad \text{singlet, } \delta 2.5, 3\text{H}
\quad \text{doublet, } \delta 7.2, 2\text{H}
\quad \text{doublet, } \delta 7.4, 2\text{H}

6.2 Xylenes are a mixture of the ortho, meta, and para isomers, and each isomer has a distinct \(^1\text{H NMR} \) and \(^{13}\text{C NMR} \) pattern. Draw the correct xylene isomer from the following data.

\(^{13}\text{C NMR:} \quad \delta 19, 126, 130, 137
\(^{1}\text{H NMR:} \quad 2.23 \text{ ppm, singlet, } 6\text{H}
\quad 7.05 \text{ ppm, doublet, } 2\text{H}
\quad 7.34 \text{ ppm, doublet, } 2\text{H}

SOLUTIONS TO SAMPLE PROBLEMS:
1.1 Predict the product or products of the reactions shown (if any)

a) \[
\begin{align*}
\text{HNO}_3 & \quad \text{H}_2\text{SO}_4 \quad \text{O}_2\text{N} & \quad \text{O}_2\text{N} \\
\text{O}_2\text{N} & \quad \text{H}_2\text{SO}_4 \\
\text{O}_2\text{N} & \quad \text{H}_2\text{SO}_4 \\
\end{align*}
\]

b) \[
\begin{align*}
\text{NO}_2 & \quad \text{Cl} & \quad \text{no reaction}
\end{align*}
\]

c) \[
\begin{align*}
\text{OH} & \quad \text{Br}_2 & \quad \text{Br}
\end{align*}
\]

d) \[
\begin{align*}
\text{NC} & \quad \text{H}_2\text{SO}_4 \\
\text{NC} & \quad \text{H}_2\text{SO}_4 \\
\text{NC} & \quad \text{H}_2\text{SO}_4 \\
\text{NC} & \quad \text{H}_2\text{SO}_4 \\
\text{NC} & \quad \text{H}_2\text{SO}_4 \\
\end{align*}
\]

(e) \[
\begin{align*}
\text{Br} & \quad \text{dil. } \text{H}_2\text{SO}_4 \\
\text{Br} & \quad \text{dil. } \text{H}_2\text{SO}_4 \\
\text{Br} & \quad \text{dil. } \text{H}_2\text{SO}_4 \\
\text{Br} & \quad \text{dil. } \text{H}_2\text{SO}_4 \\
\text{Br} & \quad \text{dil. } \text{H}_2\text{SO}_4 \\
\end{align*}
\]
1.1

f) \[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{AlCl}_3 \\
\text{CH}_3\text{Cl} & \quad \text{AlCl}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{AlCl}_3 \\
\text{CH}_3\text{Cl} & \quad \text{AlCl}_3 \\
\end{align*}
\]

g) \[
\begin{align*}
\text{Cl} & \quad \text{AlCl}_3 \\
\text{Zn}[\text{Hg}] & \quad \text{HCl, heat} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{AlCl}_3 \\
\text{Zn}[\text{Hg}] & \quad \text{HCl, heat} \\
\end{align*}
\]

h) \[
\begin{align*}
\text{Cl} & \quad \text{FeCl}_3 \\
\text{Cl} & \quad \text{FeCl}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{FeCl}_3 \\
\text{Cl} & \quad \text{FeCl}_3 \\
\end{align*}
\]

i) \[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

j) \[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

k) \[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

l) \[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\text{HO}_3\text{S} & \quad \text{SO}_3 \\
\end{align*}
\]

2. a) fastest  IV > III > I > V > VI > II  slowest
b) fastest  I > VI > V > IV > III > II  slowest

3. a) Elimination-Addition
b) Electrophilic Aromatic Substitution (EAS)
c) Nucleophilic Aromatic Substitution (S\text{N}Ar)
When *para* substitution occurs on nitrobenzene, a very high energy intermediate results in which two formal positive charges are adjacent (***) in one of the contributing resonance forms. The *meta* substitution has no particularly high energy intermediate. Based on the intermediates, the *meta* substitution product will preferentially form.
5.2 The two reaction coordinates show that the activation energy for the *meta* substitution is greater than for the *para* substitution. In addition, the energy of the intermediate of the *para* sigma complex is lower than that of the *meta* sigma complex. This shows that the substituent must be ortho/para directing, so either an activating group or a halogen. Of the two choices the nitro is a very strong electron withdrawing group and a deactivator. The correct choice is aniline.

5.3 Propose a complete mechanism for the following.

![Mechanism Diagram]

The primary carbocation complex rearranges to a more stable tertiary carbocation.

1,2 Hydride shift

6.1

![Structures](a) NH₂  (b)  (c) ![Structure Image]

6.2 The spectral data given is represents *ortho*-xylene. While two- 2H aromatic doublets are typical of *para* substitution, the $^{13}$C NMR is the distinguishing factor. The *para*-xylene has two planes of symmetry; therefore only 3 carbon peaks would be present in the $^{13}$C NMR spectrum.
1. Rank the following from fastest to slowest in a reaction with Cl\textsubscript{2}/FeCl\textsubscript{3}.

\begin{align*}
\text{phenyl-Cl} & \quad \text{phenyl-CH(CH\textsubscript{3})\textsubscript{2}} & \quad \text{phenyl-O-COCH\textsubscript{3}} & \quad \text{phenyl-N(CH\textsubscript{3})\textsubscript{2}}
\end{align*}

2. Predict the product of each of the following reactions.

a) \begin{align*}
\text{phenyl} & \quad \text{Cl} \\
& \quad \text{ClCH\textsubscript{2}CH(CH\textsubscript{3})\textsubscript{2}} \quad \text{AlCl\textsubscript{3}}
\end{align*}

b) \begin{align*}
\text{phenyl-NO\textsubscript{2}} & \quad \text{ClCH\textsubscript{2}CH(CH\textsubscript{3})\textsubscript{2}} \\
& \quad \text{AlCl\textsubscript{3}}
\end{align*}

c) \begin{align*}
\text{Br-phenyl-N(CH\textsubscript{3})\textsubscript{2}} & \quad 1. \text{NaNH\textsubscript{2}, NH\textsubscript{3}} \quad 2. \text{H\textsubscript{2}O} \\
& \quad \text{H\textsubscript{3}CO}
\end{align*}

d) \begin{align*}
\text{phenyl-H\textsubscript{3}CO} & \quad \text{CH\textsubscript{3}CH\textsubscript{2}Cl} \quad \text{AlCl\textsubscript{3}}
\end{align*}

e) \begin{align*}
\text{benzene} & \quad \text{HBr} \quad \text{no peroxides}
\end{align*}

f) \begin{align*}
\text{phenyl-OCH\textsubscript{3}} & \quad \text{HNO\textsubscript{3}} \\
& \quad \text{H\textsubscript{2}SO\textsubscript{4}}
\end{align*}

g) \begin{align*}
\text{Br-phenyl-NO\textsubscript{2}} & \quad 1. \text{Fe, H\textsubscript{3}O\textsuperscript{+}} \quad 2. \text{NaNO\textsubscript{2}, HCl} \quad 3. \text{H\textsubscript{2}O}
\end{align*}
3. Propose a synthesis of each of the following compounds from benzene and any other needed reagents.

a) \[ \text{Br} \quad \text{NH}_2 \]

b) \[ \text{OH} \]

c) \[ \text{NO}_2 \quad \text{CO}_2\text{H} \]

4. Provide a complete mechanism showing proper curved arrows, lone pairs, and all intermediates for the reaction shown. Show the formation of the electrophile.

5. Identify the following unknown from the given \(^1\text{H}\) NMR and infrared spectroscopic information.

\[ \text{C}_{12}\text{H}_{16}\text{O} \]

IR: 1650 cm\(^{-1}\)

\(^1\text{H}\) NMR:
- doublet, \(\delta \ 0.9, 6\text{H}\)
- multiplet, \(\delta \ 1.5, 1\text{H}\)
- singlet, \(\delta \ 2.4, 3\text{H}\)
- doublet, \(\delta \ 2.9, 2\text{H}\)
- doublet, \(\delta \ 6.8, 2\text{H}\)
- doublet, \(\delta \ 7.4, 2\text{H}\)
1. Circle the letter which correctly ranks the following compounds from fastest to slowest as they react in an EAS reaction with HNO₃ and H₂SO₄.

I

II

III

IV

a) I > II > III > IV
b) IV > III > II > I
c) III > IV > II > I
d) III > II > I > IV

2. Draw the structures of all of the major organic products of each of the following reactions. If no reaction occurs, write “NR”.

a) \[
\begin{align*}
&\text{F}_3\text{C} - \text{C}_6\text{H}_4 - \text{HNO}_3 \\
&\text{H}_2\text{SO}_4
\end{align*}
\]

b) \[
\begin{align*}
&\text{HO} - \text{C}_6\text{H}_4 - \text{Cl}_2 \\
&\text{FeCl}_3
\end{align*}
\]

c) \[
\begin{align*}
&\text{Br} - \text{C}_6\text{H}_4 - \text{NO}_2 \\
&1. \text{NaOCH}_2\text{CH}_3 \\
&2. \text{H}_3\text{O}^+
\end{align*}
\]

d) \[
\begin{align*}
&\text{HO} - \text{C}_6\text{H}_4 - \text{Br} \\
&\text{HNO}_3 \\
&\text{H}_2\text{SO}_4
\end{align*}
\]

e) \[
\begin{align*}
&\text{C}_6\text{H}_4 - \text{CO}_2\text{CH}_3 \\
&\text{ClCH}_2\text{CH}-(\text{CH}_3)_2 \\
&\text{AlCl}_3
\end{align*}
\]

f) \[
\begin{align*}
&\text{C}_6\text{H}_4 - \text{CH}_2\text{CH}_2\text{CH}_3 \\
&1. \text{KMnO}_4, \cdot\text{OH}, \text{heat} \\
&2. \text{H}_3\text{O}^+
\end{align*}
\]

g) \[
\begin{align*}
&\text{C}_6\text{H}_4 \\
&1. \text{CH}_3\text{CH}_2\text{Cl}, \text{AlCl}_3 \\
&2. \text{NBS}, \text{hv} \\
&3. \text{KOH}
\end{align*}
\]
3. Propose a synthesis of each of the following compounds from the indicated starting materials and any other needed reagents.

a) ![Chemical Structure]

b) ![Chemical Structure]

4. Provide a complete mechanism showing proper curved arrows, lone pairs, and all intermediates for the reaction shown.

![Chemical Reaction]

5. Identify the following unknown from the given $^1$H NMR and $^{13}$C NMR spectroscopic information.

$^{13}$C NMR: \( \delta \) 21, 22, 76, 110, 123, 141, 157

$^1$H NMR:
- Doublet, \( \delta \) 1.3, 6H
- Singlet, \( \delta \) 2.3, 6H
- Multiplet, \( \delta \) 4.7, 1H
- Singlet, \( \delta \) 6.7, 2H
- Singlet, \( \delta \) 7.1, 1H