Summer 2014  Org II Exam 1  Chapters 14-17  

(50 points)

Name: 

(1-10) are True/False. (10pts)

1) Benzene undergoes electrophilic aromatic substitution (EAS) reactions with strong electrophiles.

2) During an EAS reaction, the aromatic compound loses its aromaticity in the first step, but then regains it in the last step of the reaction.

3) Kinetic products are always formed more quickly than thermodynamic products.

4) The rate determining step in an EAS reaction is the exothermic removal of a proton from the sp\(^3\) carbon.

5) Propylbenzene undergoes EAS reactions faster than Fluorobenzene.

6) [4+2] Cycloaddition reactions are also known as Birch-Koch-Gatterman reactions.

7) LUMO means highest occupied molecular orbital.

8) The amino group (-\(\text{NH}_2\)) is a deactivating, meta directing substituent for EAS reactions.

9) Dioxanes are 6 membered rings with 2 Nitrogens.

10) Oxetanes are 5 membered rings with 1 Oxygen.

11) Provide one good scientific reason why you are taught about Molecular Orbital Theory. (1pt)
12) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (8pts)

13) Using the polygon rule, draw out and decide whether the following charged species is aromatic or anti-aromatic. (3pts)
14) Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. (16pts)
15) (2+4 = 6pts) The addition of (1 equiv. of) Br₂ to cyclopenta-1,3-diene generates a mixture of products.

\[ \text{cyclopenta-1,3-diene} + \text{Br}_2 \rightarrow \text{product} \]

\[ \text{and} \]

\[ \text{product} \]

a) Identify the 1,2- and the 1,4-addition products.

b) Draw the mechanism showing how both products are formed.

16) Draw in the curly arrows that interconvert one resonance form into the next (from left to right). (3pts)

\[ \text{resonance forms} \]
17) Devise a synthetic scheme for either (a) or (b) to generate the products from the starting material; bearing in mind more than one step is obviously required. (3pts)

**BONUS Points (up to 3 points)**

Show how the carbon p orbitals overlap to form the LUMO of the allyl anion.
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(1-10) are True/False. (10pts)

1) Benzene undergoes electrophilic aromatic substitution (EAS) reactions with strong electrophiles.  
   - True (T)

2) During an EAS reaction, the aromatic compound loses its aromaticity in the first step, but then regains it in the last step of the reaction.  
   - True (T)

3) Kinetic products are always formed more quickly than thermodynamic products.  
   - False (F)

4) The rate determining step in an EAS reaction is the exothermic removal of a proton from the sp^3 carbon.  
   - False (F)

5) Propylbenzene undergoes EAS reactions faster than Fluorobenzene.  
   - True (T)

6) [4+2] Cycloaddition reactions are also known as Birch-Koch-Gatterman reactions.  
   - False (F)

7) LUMO means highest occupied molecular orbital.  
   - False (F)

8) The amino group (-NH_2) is a deactivating, meta directing substituent for EAS reactions.  
   - False (F)

9) Dioxanes are 6 membered rings with 2 Nitrogens.  
   - False (F)

10) Oxetanes are 5 membered rings with 1 Oxygen.  
    - False (F)

11) Provide one good scientific reason why you are taught about Molecular Orbital Theory. (1pt)
    - Accurately describes delocalized π systems; pericyclic "allowed" and "forbidden" reactions; aromatic; etc.
12) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (8pts)

Aromatic  Non-A  Aromatic  Anti-Aromatic

Aromatic  Non-A  Anti-aromatic  Aromatic

13) Using the **polygon rule**, draw out and decide whether the following charged species is *aromatic* or *anti-aromatic*. (3pts)

(cyclopentadienyl anion)

\[ 6 \pi \text{ electrons} \]

\[ \text{"Closed bonding shell"} \]

= AROMATIC
14) Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. (16pts)
15) \((2+4 = 6\text{pts})\) The addition of (1 equivalent of) \(\text{Br}_2\) to 1,3-cyclopentadiene generates a mixture of products.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

a) Identify the \(1,2\)- and the \(1,4\)-addition products.

b) Draw the mechanism showing how both products are formed.

16) Draw in the curly arrows that interconvert one resonance form into the next \((\text{from left to right})\). \((3\text{pts})\)

\[
\begin{align*}
\text{OH} & \quad \text{H} \\
\text{H} & \quad \text{Br} \\
\text{OH} & \quad \text{H} \\
\text{H} & \quad \text{Br}
\end{align*}
\]
17) Devise a synthetic scheme for either (a) or (b) to generate the products from the starting material; bearing in mind more than one step is obviously required. (3pts)

a) \[ \text{CH}_3 \rightarrow \text{NO}_2 \text{CO}_2\text{H} \]

b) \[ \text{CH}_2\text{CH}_3 \rightarrow \text{Br} \]

OR

\[ \text{NO}_2 \]

\[ \text{Br} \]

\[ \text{Br} \text{CO}_2\text{H} \]

\[ \text{CH}_2\text{CH}_3 \]

\[ \text{Br} \]

\[ \text{KNO}_3, \text{H}_2\text{SO}_4 \]

\[ \text{Br}_2, \text{FeBr}_3 \]

\[ \text{KNO}_3, \text{NaOH}, \text{then} \text{H}_2\text{O}^+ \]

\[ \text{CH}_3\text{CCl}_3, \text{HCl} \]

\[ \text{Br}_2, \text{FeBr}_3 \]

\[ \text{Zn} \text{(H}_2\text{)}, \text{HCl} \]

BONUS Points (up to 3 points)

Show how the carbon p orbitals overlap to form the LUMO of the allyl anion.

\[ \begin{array}{c}
\text{\( \Pi^* \)} \\
\text{\( \Pi_2 \)} \\
\text{\( \Pi_1 \)}
\end{array} \]

This is the LUMO.