Note: (60%) was graded out of 3: everyone got it added to score.

1. (6 points) Which of the two nitrogens on imidazole (shown below) is more basic, and why?

![Imidazole structure]

- More: in sp², not needed for aromaticity.
- Less: in sp³, needed for aromaticity.

Can you show orbital drawing? As long as it's clear to you.

2. (8 points) Label each of the following molecules as being aromatic, antiaromatic, or neither:

a) ![Molecule A]

b) ![Molecule B]

c) ![Molecule C]

3. (6 points) The reaction below favours the formation of product B at lower temperatures, and product C at higher temperatures. Explain why.

![Butadiene reaction]

HBr

A → B + C

1,2
kinetic
low T

1,4
thermodynamic
high T
4. (8 points) Rank the following compounds in order of reactivity to electrophilic aromatic substitution (1 = most reactive, 5 = least reactive):

\[
\begin{array}{cccc}
& \text{NH} & \text{CN} & \text{NH}_2 & \text{Cl} \\
\text{2nd} & \text{most} & \text{least} & \text{most} & \text{2nd least}
\end{array}
\]

5. (8 points) Give Molecular Orbital (MO) diagrams (hint: you can use a Frost circle) for the cycloheptatrienyl cation and anion. Using them, show which is aromatic and which is antiaromatic. Also using the MO diagrams, explain why the aromatic electron configuration is more stable than the antiaromatic.

\[
\begin{array}{c}
\text{Cycloheptatrienyl cation} \\
\text{Cycloheptatrienyl anion}
\end{array}
\]

\[\text{6 \pi e}^-, \text{HOMO filled, aromatic, more stable}\]

\[\text{7 \pi e}^+, \text{HOMO unfilled, antiaromatic, less stable}\]
6. (24 points) Give the major organic product(s) for the following reactions:

a) \[
\begin{align*}
\text{\ce{C6H5CH2CH_3}} & \xrightarrow{\text{H}_2\text{NNH}_2 / \text{KOH} / \Delta} \text{Product} \\
\end{align*}
\]

b) \[
\begin{align*}
\text{\ce{CH2=CH2}} & \xrightarrow{\text{HBr / peroxides}} \text{Product} \\
\end{align*}
\]

Markovnikov 2
Allene bromination 2

c) \[
\begin{align*}
\text{\ce{CHCl(CH2)2C6H5}} & \xrightarrow{\text{AlCl}_3} \text{Product} \\
\end{align*}
\]

d) \[
\begin{align*}
\text{\ce{CH2=CH2}} & \xrightarrow{\text{MeO_2C-CO_2Me} / \Delta} \text{Product} \\
\end{align*}
\]

Wrong place 1
Wrong lone stereo 1

e) \[
\begin{align*}
\text{\ce{Cyclopentene}} & \xrightarrow{\text{KMnO}_4 / \Delta} \text{Product} \\
\end{align*}
\]

Wrong regio 2

f) \[
\begin{align*}
\text{\ce{CH_3OC6H_4}} & \xrightarrow{\text{H}_2\text{SO}_4 / \Delta} \text{Product} \\
\end{align*}
\]

Wrong regio 2
7. (12 points) Provide reagents for all the following transformations:

a)  
\[
\text{PhSO}_3\text{H} \xrightarrow{\text{H}_2\text{O}^+} \text{Ph}
\]
(any dil. aq. aqueous acid. ok)

b)  
\[
\text{Ph} \xrightarrow{\text{N}_2\text{Cl}^-} \text{PhI}
\]

(c)  
\[
\text{Ph} \xrightarrow{\text{MeO}^+\text{C}^-\text{CO}_2\text{Me}} \text{PhCO}_2\text{Me}
\]

(d)  
\[
\text{Ph} \xrightarrow{\text{Zn/Hg}} \text{Ph}
\]
(base sensitive)

\[
\text{Ph} \xrightarrow{\text{KOH}, \text{HCl}} \text{Ph}
\]
9. (12 points) Mechanisms: Choose ONE of the following TWO problems. If you work on more than one, CLEARLY indicate which you want to be graded for credit.

(a) Provide the major product or products for the chlorination of benzenenitrile, as well as a mechanism for the formation for one such product. The mechanism should include the generation of the electrophile as well as the addition of the electrophile to the aromatic ring. Use the mechanism to explain the predicted regioselectivity (o-/p- or m- substitution) for the reaction.

\[
\begin{align*}
\text{CN} & \quad \text{Cl}_2 \quad \text{FeCl}_3 \\
\text{C}_6\text{H}_5 & \quad \rightarrow \quad \text{Cl} \quad \text{Cl} \\
\end{align*}
\]

(b) Give a mechanism for the following reaction. Your mechanism should show how both products can be formed.

\[
\begin{align*}
\text{CH}_2\text{CH} & \quad \text{Br}_2 \\
\text{C}_6\text{H}_5 & \quad \rightarrow \quad \text{CH}_2\text{CH} & \quad \text{Br} \\
\end{align*}
\]

**TYPO**: Intended product was

\[
\begin{align*}
\text{CH}_2\text{CH} & \quad \text{Br} \\
\end{align*}
\]

But if you showed an anti-Hofmann-Keko mechanism, good! That would explain formation of this wrong product.
10. (12 points) Provide a synthesis for one of the following compounds from benzene. Retrosynthetic analysis may also be provided for partial credit. **If you show work on both, CLEARLY INDICATE WHICH SYNTHESIS YOU WANT GRADED.** Otherwise, the one first worked on will be graded.

- **CN**
- **SO₃H**

**CN**

1. **Br**

2. **HNO₃**

3. **H₂SO₄**

4. **FeCl₃**

5. **Br₂**

6. **CuCN**

7. **H₂NNO₂**

8. **HCl**

9. **Zn/Hg**

10. **H₂O**

**OR**

- **Br**

- **CN**

Technically, opposite order doesn’t work, but give full credit.