Chemistry 218, Problem Set 4


Recommended problems from the text: 12.18, 12.20-12.21, 12.25, 12.35 (f, i), 12.41 (a, b, c, f), 12.42-12.45, 12.47-12.48, 12.60, 16.1-16.2, 16.3-16.7 (review), 16.8, 16.16-16.22, 16.26, 16.30-16.31, 16.43-16.54.

1. Fill in the products which form when the reactants (vertical row) are treated with the reagents (horizontal row). Indicate relevant stereochemistry in the product. Draw the mechanism for each reaction.

<table>
<thead>
<tr>
<th></th>
<th>OsO₄</th>
<th>O₃; Me₂S</th>
<th>9-BBN; H₂O₂, NaOH</th>
<th>mCPBA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image1.png" alt="Product 1" /></td>
<td><img src="image2.png" alt="Product 2" /></td>
<td><img src="image3.png" alt="Product 3" /></td>
<td><img src="image4.png" alt="Product 4" /></td>
</tr>
<tr>
<td></td>
<td><img src="image5.png" alt="Product 5" /></td>
<td><img src="image6.png" alt="Product 6" /></td>
<td><img src="image7.png" alt="Product 7" /></td>
<td><img src="image8.png" alt="Product 8" /></td>
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<tr>
<td></td>
<td><img src="image9.png" alt="Product 9" /></td>
<td><img src="image10.png" alt="Product 10" /></td>
<td><img src="image11.png" alt="Product 11" /></td>
<td><img src="image12.png" alt="Product 12" /></td>
</tr>
</tbody>
</table>

2. Show how you can make the following compounds from any alkene that only contains carbons and hydrogens. All reactions can be performed in a single step.

(a)
9-BBN (or BH₃); NaOH, H₂O₂

H₃O⁺ (would give a cation shift)

Cl⁻ → Cl⁻ + EtI

Cl₂, H₂O → Cl⁻ → Cl⁻ + EtI

NaH;

EtI

Cl

Om

Me₂S

O₃; Me₂S
3. Draw the molecular orbitals and fill in the electrons for the following molecule:

\[
\begin{array}{c}
\text{HOMO} \\
\text{LUMO}
\end{array}
\]

4. Determine which of the following compounds are conjugated. If a compound is conjugated, sketch the \( \pi \)-molecular orbitals and fill in the orbitals with the appropriate number of electrons.

The following compounds are not conjugated:

(a) \[
\begin{array}{c}
- \\
- \\
- \\
- \\
- \\
\end{array}
\]

(b) \[
\begin{array}{c}
\text{HOMO} \\
\text{LUMO}
\end{array}
\]

The following compounds are conjugated:

(c) \[
\begin{array}{c}
- \\
- \\
- \\
- \\
- \\
\end{array}
\]

(d) \[
\begin{array}{c}
- \\
- \\
- \\
- \\
- \\
\end{array}
\]

(e) \[
\begin{array}{c}
- \\
- \\
- \\
- \\
- \\
\end{array}
\]

(f) \[
\begin{array}{c}
- \\
- \\
- \\
- \\
- \\
\end{array}
\]
(g) 

\[
\begin{align*}
H_2C\equiv C\equiv C & \quad \overset{\text{b}}{\rightarrow} \overset{\text{i}}{\rightarrow} \overset{\text{n}}{\rightarrow} \overset{\text{t}}{\rightarrow} \overset{\text{i}}{\rightarrow} \overset{\text{b}}{\rightarrow} \overset{\text{i}}{\rightarrow} \overset{\text{n}}{\rightarrow} \\
\end{align*}
\]
5. Give the Diels-Alder product(s) of the following reactions. Keep in mind you may have to do a bond rotation first.

(a) 

(b) 

(c) 

(d) 

(e) 

(f)
6. Choose the appropriate diene and dienophile to prepare the following compounds:

(a) 

\[
\begin{array}{c}
\text{Br} \\
\text{Br} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{C} \\
\text{Br} \\
\end{array}
\] 

(b) 

\[
\text{H} \\
\text{H}
\rightarrow
\begin{array}{c}
\text{C} \\
\end{array}
\]

(c) 

\[
\begin{array}{c}
\text{SO}_2\text{Ph} \\
\text{SO}_2\text{Ph}
\end{array}
\rightarrow
\begin{array}{c}
\text{C} \\
\text{SO}_2\text{Ph} \\
\text{SO}_2\text{Ph}
\end{array}
\]

7. The following are Diels-Alder reactions which have appeared in the literature. Predict the products for each one.

(a) A hetero-Diels-Alder reaction, where an aldehyde is the dienophile:

\[
\begin{array}{c}
\text{TBSO} \\
\text{OR} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{O} \\
\text{Me} \\
\text{TBSO} \\
\text{OR}
\end{array}
\]

(This one is not endo selective because the methyl does not have p-orbitals to interact with the p-orbitals on the diene)

(b) An intramolecular Diels-Alder reaction, where the diene and dienophile are attached:

(c) An intramolecular hetero-Diels-Alder reaction:
(d) A Diels-Alder reaction using an alkyne as the dienophile:

\[
\text{CO}_2\text{Et} + \text{CO}_2\text{Et} \rightarrow \text{Reaction Product}
\]