1) Consider the molecule pentadienyl anion (1) shown below. The molecular orbitals and energy values for each MO are also shown for this system.

\[ \text{HOMO: } -1.732 \text{ eV} \]

\[ \text{LUMO: } -1 \text{ eV} \]

\[ \text{Other MOs: } 0 \text{ eV}, 1 \text{ eV}, 1.732 \text{ eV} \]

![Molecular orbital diagram](image)

a. How many nodes are in the HOMO for 1?

b. How many nodes are in the LUMO for 1?

c. On which carbons (C₁-C₅) is the negative charge located for a pentadienyl anion?

d. How much energy is required to excite an electron in a UV-Vis experiment for 1? (answer in electron volt units {eV} used in picture shown)

e. What would be the thermodynamic product if pentadienyl anion reacts with an H⁺ electrophile?
2) Rank by shift of $\lambda_{\text{max}}$ in a UV-Vis. The compound that absorbs with the highest $\lambda_{\text{max}}$ (largest number in nm units) is 1, while the compound that absorbs with the shortest $\lambda_{\text{max}}$ is 5.

3) Below are shown 5 isomers with molecular formula $\text{C}_7\text{H}_{12}$. Rank the isomers by stability. The most stable isomer is 1, while the least stable isomer is 5.

4) Rank the following compounds by the stability of the double bond. The compound with the most stable double bond is 1, while the compound with the least stable double bond is 5.
1) Consider the molecule pentadienyl anion (1) shown below. The molecular orbitals and energy values for each MO are also shown for this system.

![Diagram of pentadienyl anion](image)

<table>
<thead>
<tr>
<th>C1 C2 C3 C4 C5</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.732</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>-1.732</td>
</tr>
</tbody>
</table>

a. How many nodes are in the HOMO for 1?

There are 6 conjugated electrons, therefore the third MO is the HOMO. It has 2 nodes.

b. How many nodes are in the LUMO for 1?

The LUMO is the fourth MO. It has 3 nodes.

c. On which carbons (C1-C5) is the negative charge located for a pentadienyl anion?

The negative charge is located on C1, C3 and C5. By looking at the HOMO, these are the atoms that have a coefficient besides 0 on the atoms.

d. How much energy is required to excite an electron in a UV-Vis experiment for 1? (answer in electron volt units {eV} used in picture shown)

Would require 1 eV. This is the energy from the HOMO to the LUMO orbitals.

e. What would be the thermodynamic product if pentadienyl anion reacts with an H+ electrophile?

Want to keep the two double bonds in conjugation.
2) Rank by shift of $\lambda_{\text{max}}$ in a UV-Vis. The compound that absorbs with the highest $\lambda_{\text{max}}$ (largest number in nm units) is 1, while the compound that absorbs with the shortest $\lambda_{\text{max}}$ is 5.

3) Below are shown 5 isomers with molecular formula $\text{C}_7\text{H}_{12}$. Rank the isomers by stability. The most stable isomer is 1, while the least stable isomer is 5.

4) Rank the following compounds by the stability of the double bond. The compound with the most stable double bond is 1, while the compound with the least stable double bond is 5.
16.56 Intramolecular Diels–Alder reactions are possible when a substrate contains both a 1,3-diene and a dienophile, as shown in the following general reaction.

![Diels–Alder reaction diagram]

With this in mind, draw the product of each intramolecular Diels–Alder reaction.

a. \[ \text{1,3-diene} \xrightarrow{\Delta} \]

b. \[ \text{1,3-diene} \xrightarrow{\Delta} \]

General Reactions of Dienes

16.57 Draw the products of each reaction and indicate stereochemistry where appropriate.

a. \[ (\text{CH}_3)\text{C}=\text{CHCH}_2\text{CH}2\text{CH}=\text{CH}_2 \xrightarrow{\text{HCl}} (1 \text{ equiv}) \]

b. \[ \text{HCl} \]

(c). \[ \text{c. } \]

d. \[ \text{COOCH}_3 \xrightarrow{\Delta} \]

e. \[ \text{COOH} + \text{COOH} \xrightarrow{\Delta} \]

f. \[ \text{HBr} (1 \text{ equiv}) \]

Spectroscopy

16.58 The treatment of isoprene \([\text{CH}_2=\text{C(\text{CH}_3)\text{CH}2=\text{CH}_2}]\) with one equivalent of mCPBA forms A as the major product. A gives a molecular ion at 84 in its mass spectrum, and peaks at 2850–3150 cm\(^{-1}\) in its IR spectrum. The \(^1\text{H} \text{NMR} \) spectrum of A is given below. What is the structure of A?

![1H NMR of A graph]

- 1H
- 2H
- 3H
- 2H
  - two doublets
- ppm
16.59 The treatment of \((\text{CH}_2)_2\text{C}==\text{CHCH}_2\text{Br}\) with \(\text{H}_2\text{O}\) forms \(\text{B}\) (molecular formula \(\text{C}_3\text{H}_{10}\text{O}\)) as one of the products. Determine the structure of \(\text{B}\) from its \(^1\text{H}\) NMR and IR spectra.

**UV Absorption**

16.60 Rank the following compounds in the order of increasing \(\lambda_{\text{max}}\):

- \(\text{C}_2\text{H}_4\)
- \(\text{C}_4\text{H}_{10}\)
- \(\text{C}_6\text{H}_{12}\)
- \(\text{C}_8\text{H}_{14}\)
Problem 16.56 (intramolecular Diels - Alder)

a)

b)

Problem 16.57

a) \((\text{CH}_3)_2\text{C} = \text{CH}_2 \text{CH}_2 \text{CH} = \text{CH}_2\) 

\[4 + (\text{CH}_3)_2\text{C} \rightarrow \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} = \text{CH}_2\] 

major product

b)

minor product
c) \( \text{cyclopentadiene} + \text{maleic anhydride} \xrightarrow{\Delta} \text{endo} \)

d) \( \text{cyclopropene} + \text{acrylic acid} \)

\text{cis and trans are trans}

\( \text{cyclopropene} + \text{acrylic acid} \rightarrow \text{end products} \)

\text{encumbered}

\text{Rule to remember: The stereochemistry of dienophile is retained in the product.}

A \text{ cis dienophile forms a cis substituted cyclohexene}

A \text{ trans dienophile forms a trans substituted cyclohexene.}

A \text{ cyclic dienophile forms bicyclic product.}

Example: \( \text{cyclopropene} + \text{maleic anhydride} \xrightarrow{\Delta} \text{bicyclic product} \)

It in cis
Fused bicyclic system
One bond is shared by two rings

**Endo** ⇒ a substituent on one bridge is endo if it is closer to the longer bridge that joins the two carbons common to both rings.

**Exo** ⇒ a substituent is exo if it is closer to the shorter bridge that joins the carbons together.

\[ \text{Cl}_2 \quad \rightarrow \quad \text{H} \quad \rightarrow \quad \text{H} \quad \rightarrow \quad \text{H} \quad \rightarrow \quad \text{2 is endo} \]

\[ e) \quad \text{[Structure]} \quad + \quad \text{[Structure]} \quad \rightarrow \quad \text{[Product]} \]

\[ f) \quad \text{[Structure]} \quad \rightarrow \quad \text{[Structure]} \quad + \quad \text{[Structure]} \quad \text{1,4 product} \quad + \quad \text{1,2 product} \]
Problem 16.58

\[ \text{Isoprene} \xrightarrow{\text{MCPBA}} \text{epoxidation is selective \to will occur at the most substituted double bond} \]

Protons a, b \to two doublets at 2.7 - 2.9 ppm

Proton c \to doublet of doublets at 5.6 ppm

Protons d and e \to doublet of doublets at 5.2 - 5.4 ppm

Problem 16.59

\[ \text{Br} \xrightarrow{\text{H}_2\text{O}} \text{peak at 1.5 ppm} \]

Protons a \to 6H singlet at 1.3 ppm

Protons b and c \to doublet of doublets at 4.9 - 5.2 ppm

Proton d \to doublet of doublets at 6.0 ppm
Problem 15.29 (Wade)

a) Diels-Alder reaction: place the partial charges to align the $\delta^-$ of the diene with the $\delta^+$ of the dienophile

\[ \begin{array}{c}
\text{COOHCH}_3 \\
\text{COOHCH}_3
\end{array} + \begin{array}{c}
\delta^+
\end{array} \xrightarrow{\text{H}} \begin{array}{c}
\delta^-
\end{array} \xrightarrow{\text{CO}} \begin{array}{c}
\text{COOHCH}_3
\end{array} \]

b) Retro Diels-Alder reaction $\rightarrow$ electrocyclic rearrangement of electron which generates a stable aromatic compound.

\[ \begin{array}{c}
\text{COOHCH}_3 \\
\text{COOHCH}_3
\end{array} \xrightarrow{- \text{CO}_2} \begin{array}{c}
\text{COOHCH}_3
\end{array} \]