Hey guys! Hope all of your O-Chem Exams went well! If you have any questions or need study tips, please do not hesitate to reach out to me at Megan_Hudson2@baylor.edu!

In-person group tutoring sessions will take place every Thursday from 5:15 - 6:15 pm in Sid Rich Rm. 74! In these sessions I will provide practice problems and be available for specific questions. To reserve a spot, go to https://baylor.edu/tutoring. I hope to see you there!

**Key Words:** Conjugated vs. Isolated, Pericyclic, Molecular Orbital Diagrams, NMR

**TOPIC OF THE WEEK:**

**CONJUGATED PI SYSTEMS**

What is a conjugated system?

To be considered a conjugated system, a molecule must have pi-bonds that interact with each other. Having conjugated pi bonds increases the stability of a molecule.

**Constructing Polyene Molecular Orbitals:**

Step 1: There are 4 Carbon's involved in the conjugated system, so a dot is drawn for each carbon and 4 levels of MO's are labeled \( \pi_1 - \pi_4 \)

Step 2: Symmetric Nodes are drawn in red. If an odd number of Carbons are in the conjugated system, a node can be drawn through a carbon

Step 3: Phases are represented with +/-.
Start with a + from the left of each row and the nodes separate/break the phases

Step 4: Determine number of electrons; there is a maximum of 2 electrons per pi bond

Step 5: Assign Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).
**E lectrophilic Additions with Conjugated Systems:**

<table>
<thead>
<tr>
<th>Type of Addition:</th>
<th>Location of H</th>
<th>Location of Nucleophile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2- Addition</td>
<td>Attached to Carbon 1</td>
<td>Attached to Carbon 2</td>
</tr>
<tr>
<td>1,4- Addition</td>
<td>Attached to Carbon 1</td>
<td>Attached to Carbon 4</td>
</tr>
</tbody>
</table>

**Allylic Bromination:**

![Image of allylic bromination reaction]

**Pericyclic Reactions:**

<table>
<thead>
<tr>
<th>Type of Reaction:</th>
<th>Change in the number of sigma bonds</th>
<th>Change in the number of pi bonds</th>
<th>Illustration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycloaddition</td>
<td>+2</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>Electroyclic reaction</td>
<td>+1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>Sigmatropic rearrangement</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
1. **Cycloaddition: Diels-Alder Reaction**
   - Break 3 pi bonds, form 2 sigma bonds and 1 pi bond
   - Diene (electron rich) + Dienophile (electron poor) = cyclic ring
   - Retain stereochemistry

   ![Diels-Alder Reaction Diagram](image)

2. **Electrocyclic Reaction**: 1 pi bond forms sigma bond

   ![Electrocyclic Reaction Diagram](image)

   **NOTE:** Refer to HOMO to determine stereochem. Here 1C and 4C have different phases so they are on opposite sides.
3. Sigmatropic Rearrangements: sigmatropic bonds rearrange; one sigma bond is made, and one is lost

![Claisen Rearrangement](image1)

![Cope Rearrangement](image2)

HIGHLIGHT #1: Nuclear Magnetic Resonance

What is NMR? It is Nuclear Magnetic Resonance spectroscopy and it is a very useful analytical technique to give us info about a molecule’s structure.

Within an atom, if the nucleus has an odd atomic number or has an odd mass number, it has a nuclear spin. This spinning motion creates a magnetic moment. Within the magnetic field, the nucleus will either align with or against the direction of the field.

The $\alpha$-spin state possesses lower energy than $\beta$-spin state.

The electrons within the atom create an opposing magnetic field; if there is more electron density, the nucleus is said to be shielded, if there is less electron density, the nucleus is said to be deshielded.

In an NMR, we are measuring the $\Delta E$ (energy difference between $\alpha$-spin state and $\beta$-spin state).

What are patterns are you looking for in an NMR?
1. Number of signals/ resonances (groups of lines)
2. Chemical Shift (Location on y-axis): further downfield indicates a more electronegative environment
3. Integration: area under the curve; divide each signal’s value by the smallest signal to get ratios of the number of protons
4. Multiplicity: number of peaks (lines) in each resonance; $N + 1$ Rule
5. Degree of Unsaturation: distinguishes double/triple bonds and rings; 
\[ DU = 0.5 (2 (\#C) + 2 - \#H) \]

Try to refer to the 'H NMR for C₉H₁₀O and solve for its structure! Explanation will be at the end of the document but try to solve before referring to the answer.

**THINGS YOU MAY STRUGGLE WITH:**

1. Do not disregard the importance of drawing out molecular orbital diagrams! These take LOTS OF PRACTICE! You should’ve learned these in O-Chem I, but be sure to walk through the steps I listed above with some practice problems until you feel confident to do it independently (with no notes).

2. LOOK FOR PATTERNS! With the Pericyclic Reactions, it’s easy to get overwhelmed with the bonds changing and moving around. Diels- Alder is an important cycloaddition reaction in O-Chem II, so first identify your diene and the dienophile and try to piece together where the sigma bond will form.

**ANSWERS TO NMR PROBLEM:**

1. Number of Signals: there are 4 groups of signals, therefore, 4 types of H’s

2. Chemical Shift (Location): The 10.2 signal far downfield is in an electronegative environment, therefore, is likely near an electronegative atom like Oxygen. The 54.1 signal is at 7 ppm which often indicates aromatic rings. The 21.1 and the 22.3 signals are upfield, therefore, are most likely surrounded by Carbons

3. Integration: 10.2 is the lowest signal and will be used to find the remaining ratios

<table>
<thead>
<tr>
<th>Signal Ratio</th>
<th>Integration</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.2/10.2</td>
<td>1 H</td>
</tr>
<tr>
<td>54.1/10.2</td>
<td>5 H</td>
</tr>
<tr>
<td>21.1/10.2</td>
<td>2 H</td>
</tr>
<tr>
<td>22.3/10.2</td>
<td>2 H</td>
</tr>
</tbody>
</table>

4. Multiplicity

10.2 signal is a singlet; 21.1 and 22.3 signals are triplets
5. Degrees of Unsaturation

\[ DU = 0.5 \left( \left( 9 \text{ Carbons} \times 2 \right) + 2 - 10 \text{ Hydrogens} \right) = 5 \]

This means there are 5 constituents that are either rings, double bonds, or triple bonds. From Chemical Shift we know there is 1 aromatic ring, 3 double bonds within the ring, so one double/triple bond remains

Using the info you found above, put it all together!

All diagrams, tables, and external information is property of Organic Chemistry by David Klein, unless otherwise specified.