Lecture 26 agenda...
Electrocyclizations (30.2-30.4)
Sigmatropic Rearrangements (30.7-30.8)
Claisen Rearrangement (18.4)
Group Question 12

Suggested Problems
Ch 30: 30.2 – 30.4, 30.7 – 30.9, 30.13 – 30.19, 30.23 – 30.40
Ch 18: 18.10, 18.61

Make-up Exam on Tuesday, July 15 during lecture. Sign-up now ‘til Friday.
Electrocyclization reactions involve a single starting material. They involve the rearrangement of $\pi$ bonds to form one new $\sigma$ bond.

Example of an electrocyclization:

A conjugated triene $\xrightarrow{\text{Heat}}$ A cyclohexadiene
There are minimal structural criteria for electrocyclizations:

A. To work, a \( \pi \) system must be conjugated without interruption.

B. Conjugated system must be able to achieve planarity.

C. Conjugated system must have a chromophore (molecular antenna that absorbs light) for photochemistry.
Consider the following example.

Using the same starting material, can get a different stereo-isomer depending on the reaction conditions.
What is the basis for stereochemical control?

Stereochemistry: Thermal vs. Photochemistry: only need to consider the HOMO and LUMO to predict.

The model that uses these orbitals has the following rules:

1. **Thermal** reactions utilize the HOMO of the conjugated system. **Photochemical** reactions utilize the LUMO of the conjugated system (the excited state of the system).

2. The lobes rotate (which leads to the stereochemistry of the product) in such a way as to maintain maximal overlap (bonding). Lobes can rotate either disrotatory or conrotatory.
Approaching electrocyclization reactions:
1. Consider the reaction conditions: heat or light
2. Next, draw out the HOMO or LUMO of the starting material. You’ll get one of the following depictions:

- Like lobes on same side
- Like lobes on opposite side
3. Rotate the lobes, disrotatory to achieve bond formation. This rotation will give a specific stereoisomer.

**Depiction #1**

- Clockwise
- Counterclockwise

Disrotatory = opposite direction
3. Rotate the lobes, conrotatory to achieve bond formation. This rotation will give a specific stereoisomer.

Conrotatory = same direction
Two electrocyclization examples. Note the difference in stereochemistry between the products; compare the starting materials as well.

(2E,4Z,6E)-2,4,6-Octatriene

(cis)-5,6-Dimethyl-1,3-cyclohexadiene

(2E,4Z,6Z)-2,4,6-Octatriene

(trans)-5,6-Dimethyl-1,3-cyclohexadiene
Stereochemistry summary of electrocyclizations...

<table>
<thead>
<tr>
<th>Table 30.1</th>
<th>Stereochemical Rules for Electrocyclic Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron pairs (double bonds)</td>
<td>Thermal reaction</td>
</tr>
<tr>
<td>Even number</td>
<td>Conrotatory</td>
</tr>
<tr>
<td>Odd number</td>
<td>Disrotatory</td>
</tr>
</tbody>
</table>

**Note:**
Thermal and photochemical conditions have opposite direction of rotation of lobes.

Odd and even # of π bonds have opposite direction of rotation of lobes.
**Sigmatropic rearrangements** involve a shift of a sigma-bonded atom or group across a pi system. The sigma bond breaks, pi bonds move, a new sigma bond forms.

Example of a sigmatropic rearrangement:

A [3,3] sigmatropic rearrangement

An allylic vinylic ether $\xrightarrow{\sigma$ bond broken}$ Cyclic transition state $\xleftarrow{\sigma$ bond formed}$ An unsaturated ketone

© 2007 Thomson Higher Education
Practice Problem. Classify each of the following sigmatropic reactions by order \([x,y]\) & draw the electron pushing arrows to indicate mechanism.