Diels-Alder Cycloaddition

A lab practice for the reaction between cyclopentadiene and maleic anhydride

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The Diels-Alder Cycloaddition

- Conjugated diene
- Dienophile
- Diels-Alder reaction:
  * Stereospecific
  * Prefer Endo product to Exo product

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The general Diels-Alder reaction forms a cyclohexene product. Two new $\sigma$ bonds are formed at the expense of two $\pi$ bonds. The conjugated diene is a 4$\pi$-electron system. The dienophile ("diene lover") is a 2$\pi$-electron system. The product is called an adduct.
Factors Favoring the DA Reaction

The simplest possible example of a Diels-Alder reaction goes at very low yield and requires high temperatures.

![Diagram of Diels-Alder reaction with 200°C and 20% yield.]

To proceed in good yield and at low temperature the dienophile should have electron-withdrawing groups.

- It also helps if the diene has electron-releasing groups.
- Dienes with electron-donating groups and dienophiles with electron-withdrawing group can also react well together.

![Chemical structures of diene, dienophile, and products.]

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Dienes

- The dienes must be in the s-cis conformation to react
- S- Trans conformation would lead to formation of a highly unstable trans bond in a 6-membered ring
- Cyclic dienes which must be in the s-cis conformation are highly reactive

\[
\text{Highly strained} \quad \text{Dr. Zerong Wang at UHCL}
\]

Conjugated diene

- Contain alternating double and single bond:

  \[
  \text{Conjugated diene} \quad \text{Dr. Zerong Wang at UHCL}
  \]

- Adopt S-cis conformation:

\[
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\]

- More stable than non-conjugated diens.
**S-cis conformation of diens**

Severe steric strain in s-cis form

\[ \text{Severe steric strain in s-cis form} \]
Cyclopentadiene is so reactive it spontaneously undergoes Diels-Alder reaction with itself at room temperature.

- This dimer can be “cracked” (undergo retro-Diels-Alder reaction) by heating and the cyclopentadiene product isolated by distillation.

Dienophile

- Has carbon carbon double or triple bond that is next to the positively polarized carbon of a electron-withdrawing substituent group
- Reactive and uncreative
Propenal (Acrolein)

Ethyl propenoate (Ethyl acrylate)
Maleic Anhydride

Benzoquinone
Propenenitrile (Acrylonitrile)

Methyl Propynoate
Unreactive

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Unreactive

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Heating 1,3-butadiene and maleic anhydride gives a 6-membered ring product in 100% yield.
**Stereochemistry**

The Diels-Alder reaction is **stereospecific**, *i.e.* the reaction is a *syn* addition, and the configuration of the dienophile is retained in the product.

![Stereospecificity Diagram](image)

**Stereospecificity**

- The stereochemistry of the starting dienophile is maintained during the reaction, and a single product stereoisomer results.
- Example:
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[Diagram showing a chemical reaction and molecular orbitals]

Highest Occupied Molecular Orbital

Lowest Unoccupied Molecular Orbital

Highest Occupied Molecular Orbital

1,3-butenone

164 kcal (171 nm)

215 nm

129 kcal (217 nm)
suprafacial

\[ \pi^4s + \pi^2s \]

\[ (\pi^2s + \pi^2s + \pi^2a + \pi^2s) \]

antarafacial

\[ \pi^4a + \pi^2s \]

\[ (\pi^2s + \pi^2a + \pi^2s) \]
Woodward-Hoffmann Rules

In any concerted process, the starting material orbitals must be transformed into product orbitals of the same symmetry.

Arrows on the diagram indicate avoided crossings, where orbitals of the same symmetry do not cross.

Legend:
- \( \psi_4A \)
- \( \psi_3S \)
- \( \psi_2A \)
- \( \psi_1S \)
- \( \pi_2A \)
- \( \pi_1S \)
- \( \sigma_4A \)
- \( \sigma_3S \)
- \( \sigma_2A \)
- \( \sigma_1S \)

Thermally allowed and photochemically forbidden orbitals.
• When the molecules approach each other there are favorable interactions between the LUMO of maleic anhydride and the HOMO of cyclopentadiene

• In the endo orientation favorable secondary orbital interactions between the LUMO of the carbonyl groups and the HOMO of the cyclopentadiene carbons at the C2 and C3 positions of the diene can also occur
Molecular Orbital Considerations that Favor an Endo Transition State

- When maleic anhydride and cyclopentadiene react, the major product is the endo product.
- The major product has the anhydride linkage endo.

Secondary orbital overlap favors the endo product formation.