Conjugated Systems
Diels Alder Reactions

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Diels-Alder Reaction

- Otto Diels, Kurt Alder; Nobel prize, 1950
- Conjugate dienes can combine with alkenes to form six-membered cyclic compounds
- The formation of the ring involves no intermediate (concerted formation of two bonds)
- Diene + dienophile will give an adduct/product

![Diagram of Diels-Alder reaction](image)
Examples of Diels-Alder Reactions

No ring in diene or dienophile:
One cyclohexene ring in product.

One ring in diene:
One cyclohexene ring in product
+ one more ring
Bicyclic product.
Mechanism - Concerted

There is no clear nucleophile or electrophile.
Dienes and Dienophiles

- The diene component.
- Is more effective when it is electron rich.
- It can be made more electron rich by adding more electron donating groups.

<table>
<thead>
<tr>
<th>Diene</th>
<th>Dienophile</th>
</tr>
</thead>
<tbody>
<tr>
<td>• The diene component.</td>
<td>• The alkene component.</td>
</tr>
<tr>
<td>• Is more effective when it is electron rich.</td>
<td>• Is more effective if it electron poor.</td>
</tr>
<tr>
<td>• It can be made more electron rich by adding more electron donating groups.</td>
<td>• It can be made more electron poor by adding groups that are electron withdrawing.</td>
</tr>
</tbody>
</table>
# Groups on Dienes and Dienophile

<table>
<thead>
<tr>
<th>For Dienes</th>
<th>For Dienophiles</th>
<th>Some effective Dienophiles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electron-Releasing Groups</strong></td>
<td><strong>Electron-Withdrawing Groups</strong></td>
<td></td>
</tr>
<tr>
<td>−CH₃</td>
<td>O</td>
<td>Ethylene: unreactive</td>
</tr>
<tr>
<td>−CH₂CH₃</td>
<td>−CH (aldehyde)</td>
<td>Propenal (acrolein)</td>
</tr>
<tr>
<td>−CH(CH₃)₂</td>
<td>O</td>
<td>Ethyl propenoate (ethyl acrylate)</td>
</tr>
<tr>
<td>−C(CH₃)₃</td>
<td>−CR (ketone)</td>
<td></td>
</tr>
<tr>
<td>−R (other alkyl groups)</td>
<td>−COH (carboxyl)</td>
<td></td>
</tr>
<tr>
<td>−OR (ether)</td>
<td>−COR (ester)</td>
<td>Maleic anhydride</td>
</tr>
<tr>
<td>O</td>
<td>−NO₂ (nitro)</td>
<td>Benzoquinone</td>
</tr>
<tr>
<td>−OCR (ester)</td>
<td>−C≡N (cyano)</td>
<td>Propenenitrile (acrylonitrile)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methyl propynoate</td>
</tr>
</tbody>
</table>
Stereospecificity in Diels-Alder Reaction

1,3-Butadiene + Methyl (Z)-2-butenoate → Cis product

1,3-Butadiene + Methyl (E)-2-butenoate → Trans product

Trans dienophile give a trans product

Cis dienophile give a cis product
Regioselectivity of Diels-Alder Reaction

Reactants align to produce *endo* (rather than *exo*) product. *Endo* and *exo* indicate relative stereochemistry in bicyclic structures.

![Diagram showing the reaction between maleic anhydride and an unknown reactant, resulting in an endo product that is not formed.](Image)
Conformation of the Diene

• The relative positions of the two double bonds in the diene are “cis” or “trans” to each other about the single bond (being in a plane maximizes overlap)

• These conformations are called s-cis and s-trans (“s” stands for “single bond”)

• Dienes react in the s-cis conformation in the Diels-Alder reaction
Key Concepts

• Diene – Dienophile
• Electron withdrawing and donating groups.
• Stereoselectivity
• Regioselectivity
• Conformation of the diene