Diels-Alder Cycloaddition

A lab practice for the reaction between cyclopentadiene and maleic anhydride

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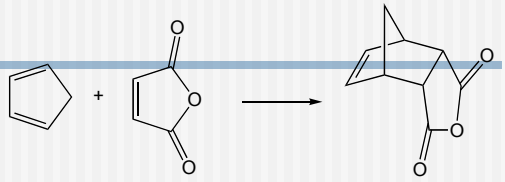
The Diels-Alder Cycloaddition



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

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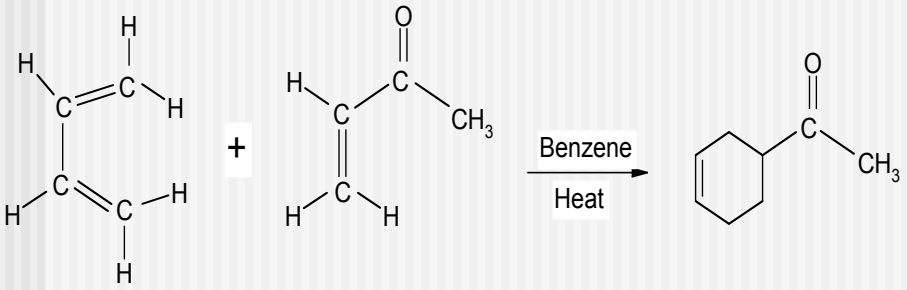
Diels-Alder reaction



Conjugated diene **Dienophile**

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- The general Diels-Alder reaction forms a cylohexene product
- Two new σ bonds are formed at the expense of two π bonds
- The conjugated diene is a 4π-electron system
- The dienophile ("diene lover") is a 2π-electron system
- The product is called an adduct

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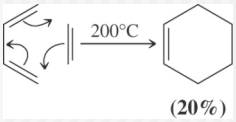
Factors Favoring the DA Reaction

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



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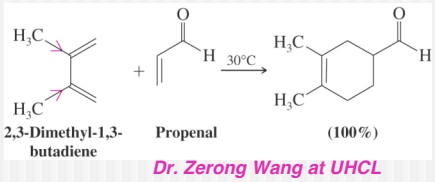
Factors Favoring the DA Reaction

- 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**



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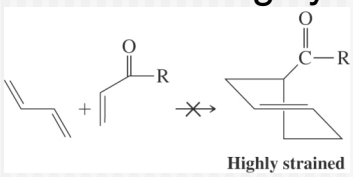
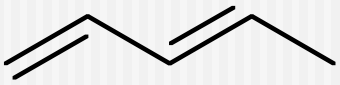
Dienes

- 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

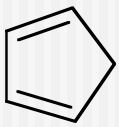


Conjugated diene

- **Contain alternating double and single bond:**

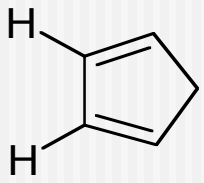


- **Adopt S-cis conformation :**

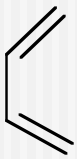


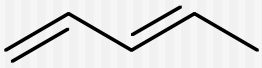
- **More stable than non-conjugated diens.**

S-*cis* conformation of diens

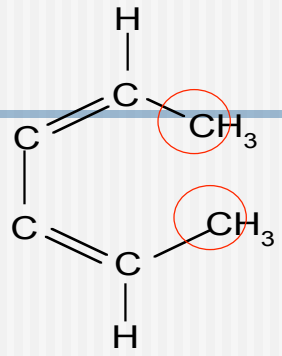


S-cis

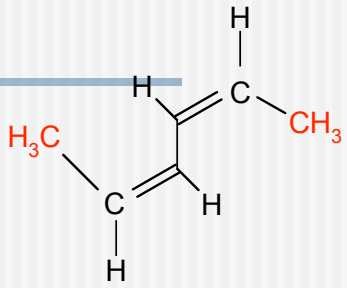




S-trans



Severe steric strain
in s-*cis* form

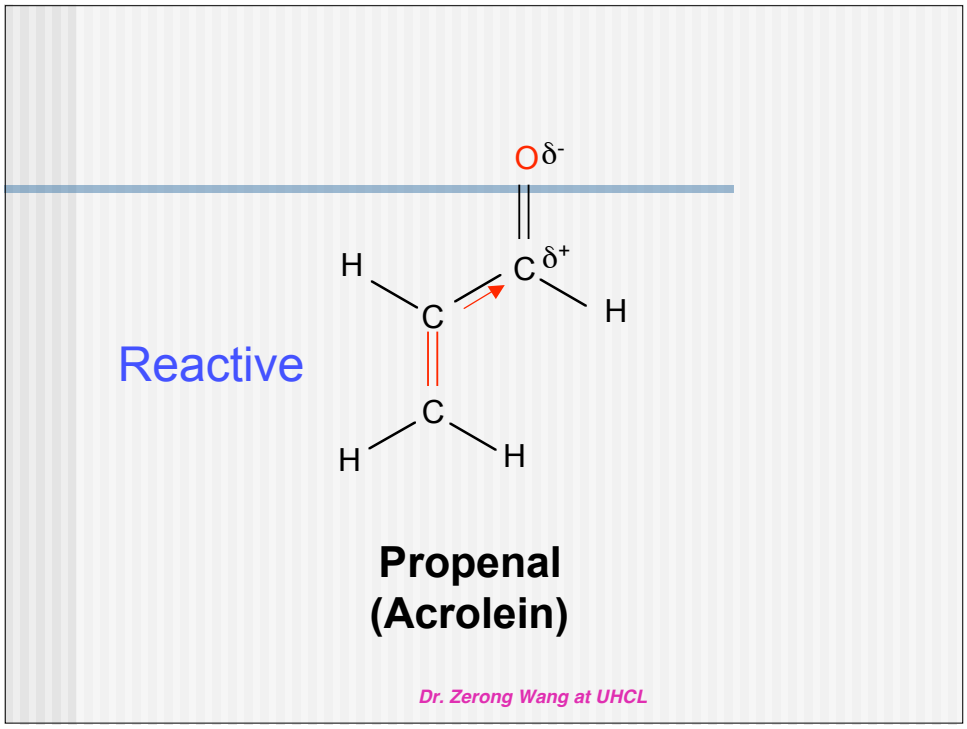


S-*trans*

- 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**


Reactive
Propenal
(Acrolein)
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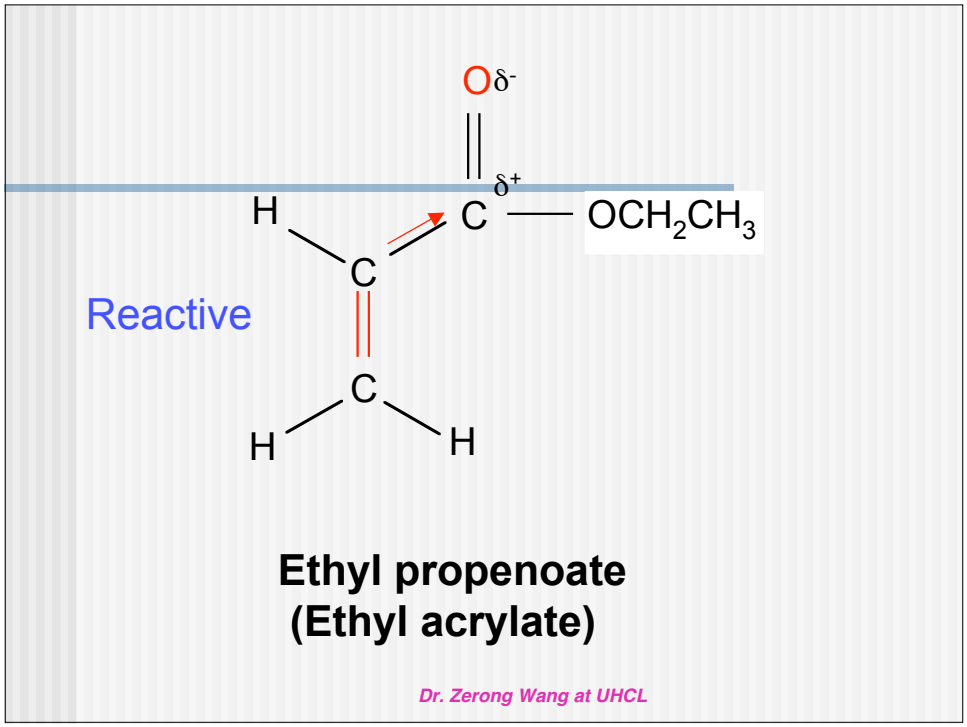
Reactive
Ethyl propenoate
(Ethyl acrylate)
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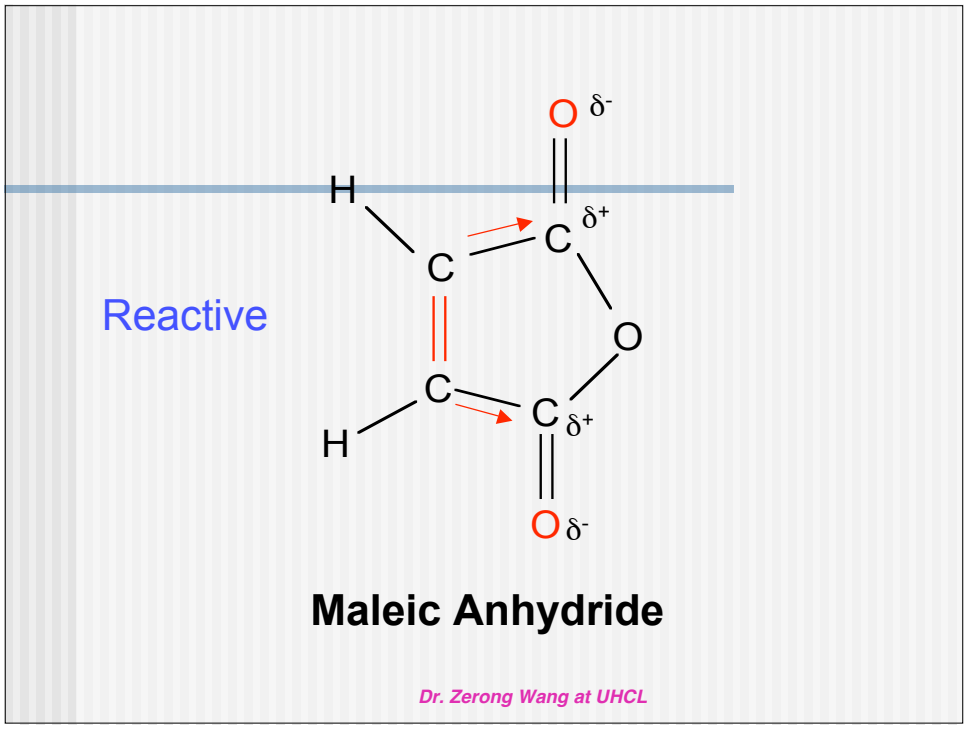
Reactive
O δ-
H
C
δ+
C
O
C
H
C
δ+
O δ-
Maleic Anhydride
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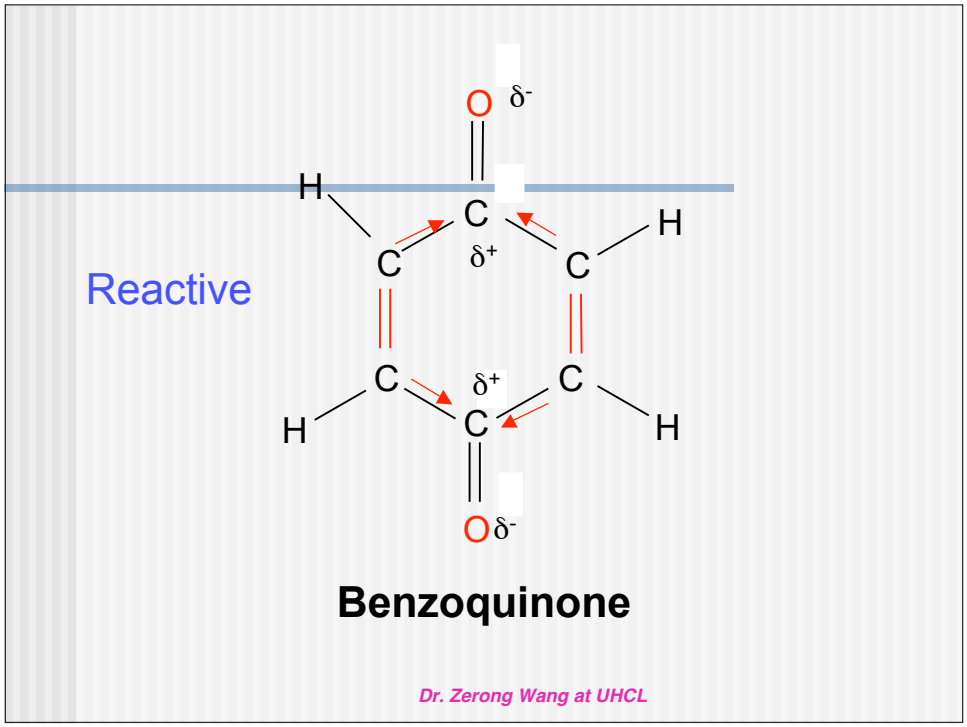
Reactive
O δ-
H
C
δ+
C
H
C
C
δ+
C
H
C
H
O δ-
Benzoquinone
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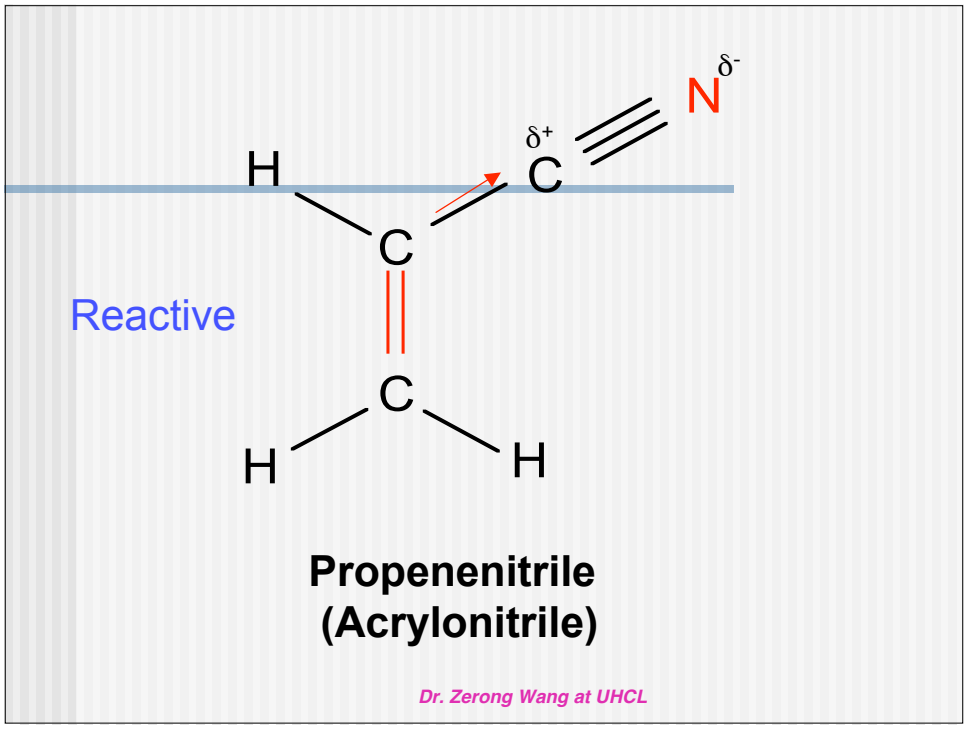

Propenenitrile
(Acrylonitrile)

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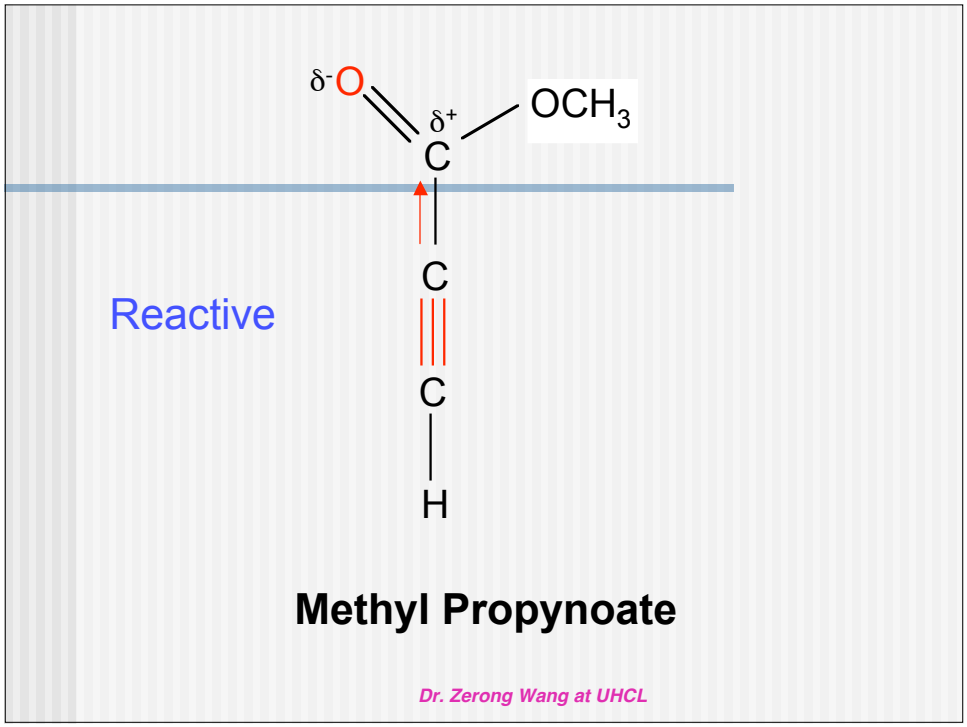

Methyl Propynoate

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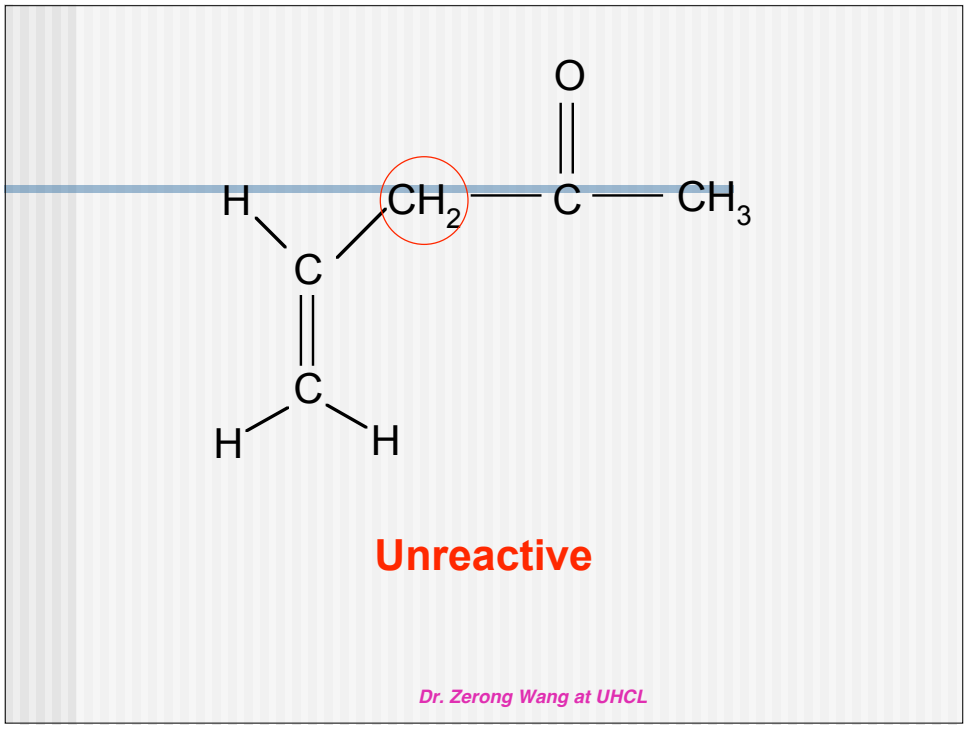

Unreactive

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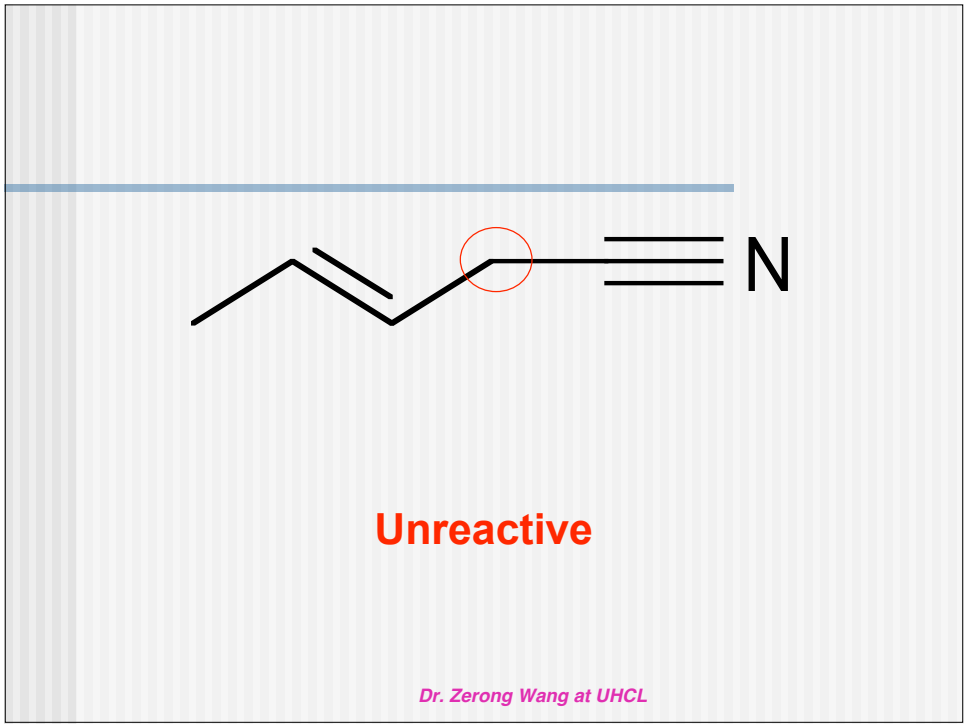

Unreactive

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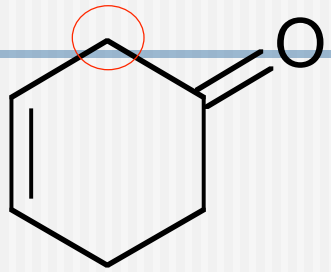
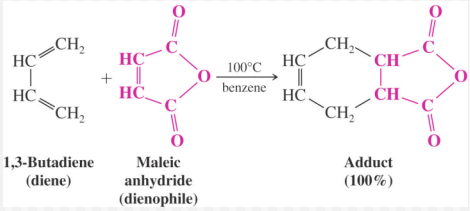


Unreactive

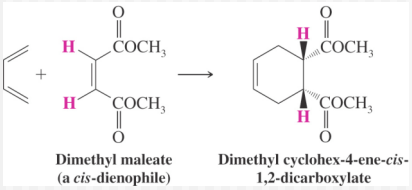
Heating 1,3-butadiene and maleic anhydride gives a 6-membered ring product in 100% yield



1,3-Butadiene (diene) + Maleic anhydride (dienophile) → Adduct (100%)

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



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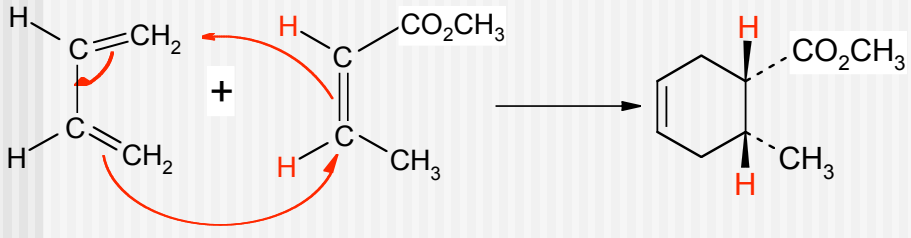
Stereospecificity

- The stereochemistry of the starting dienophile is maintained during the reaction, and a single product stereoisomer results.
- Example:



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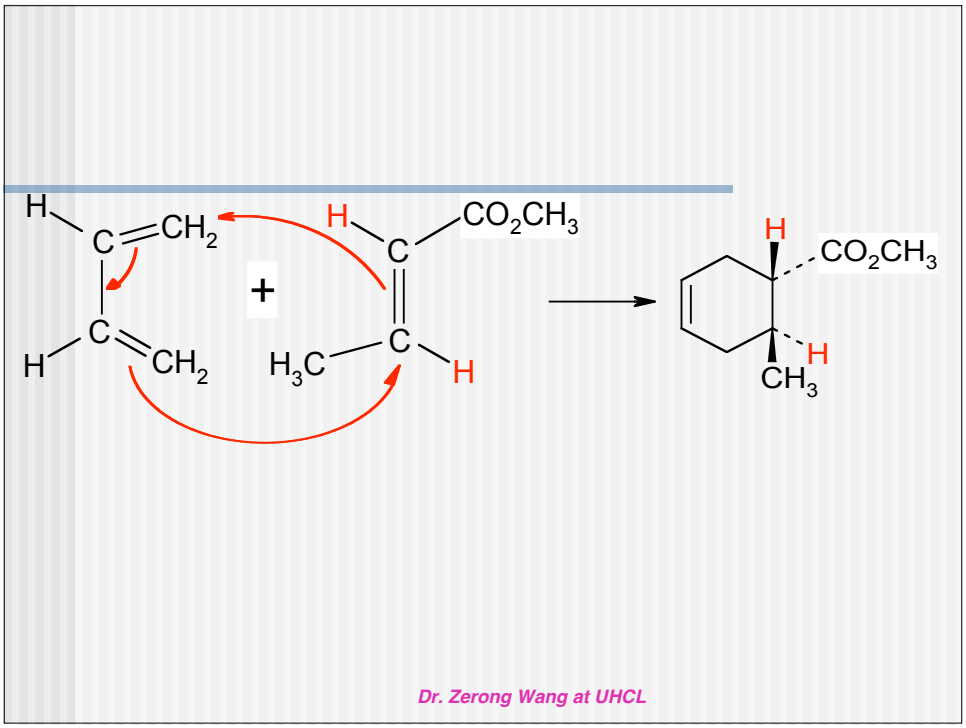

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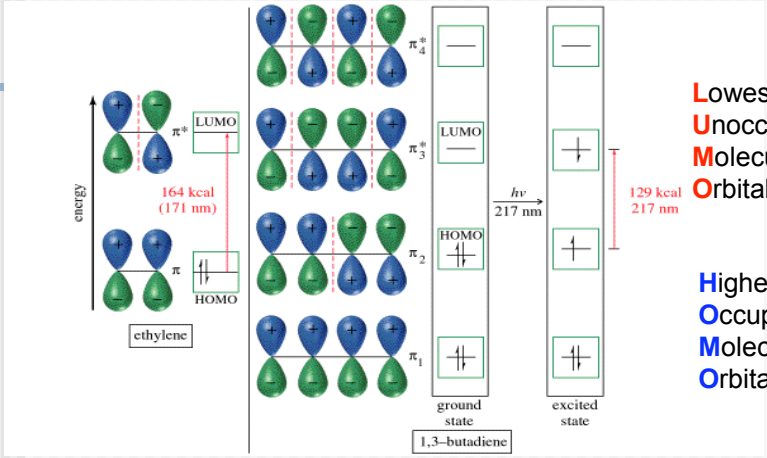

Lowest
Unoccupied
Molecular
Orbital

Highest
Occupied
Molecular
Orbital

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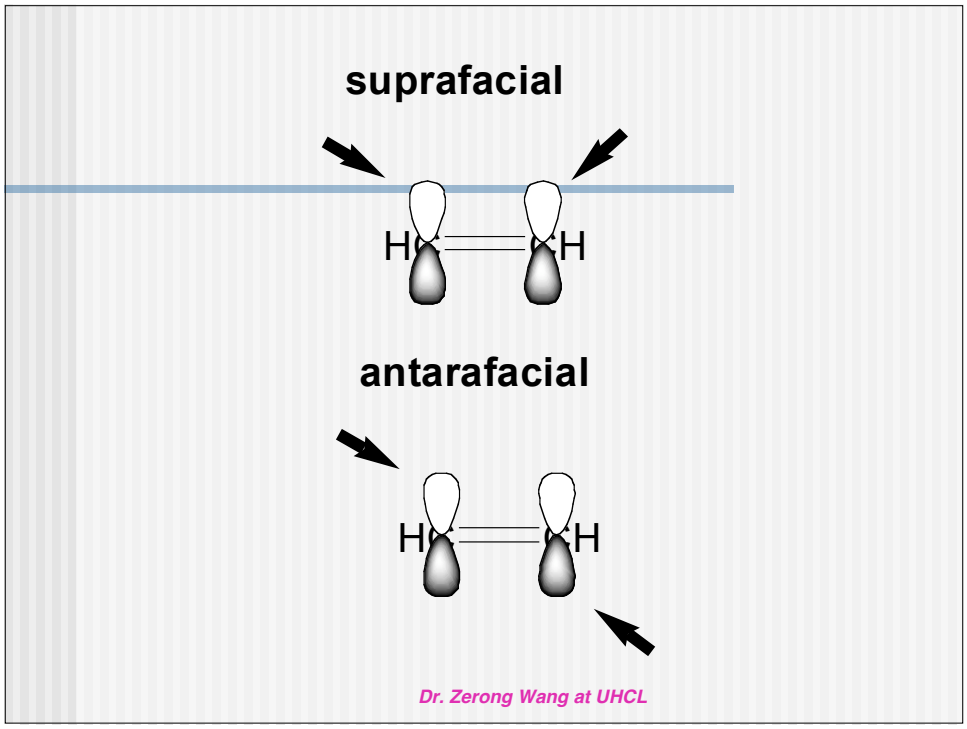
suprafacial
H
H
antarafacial
H
H
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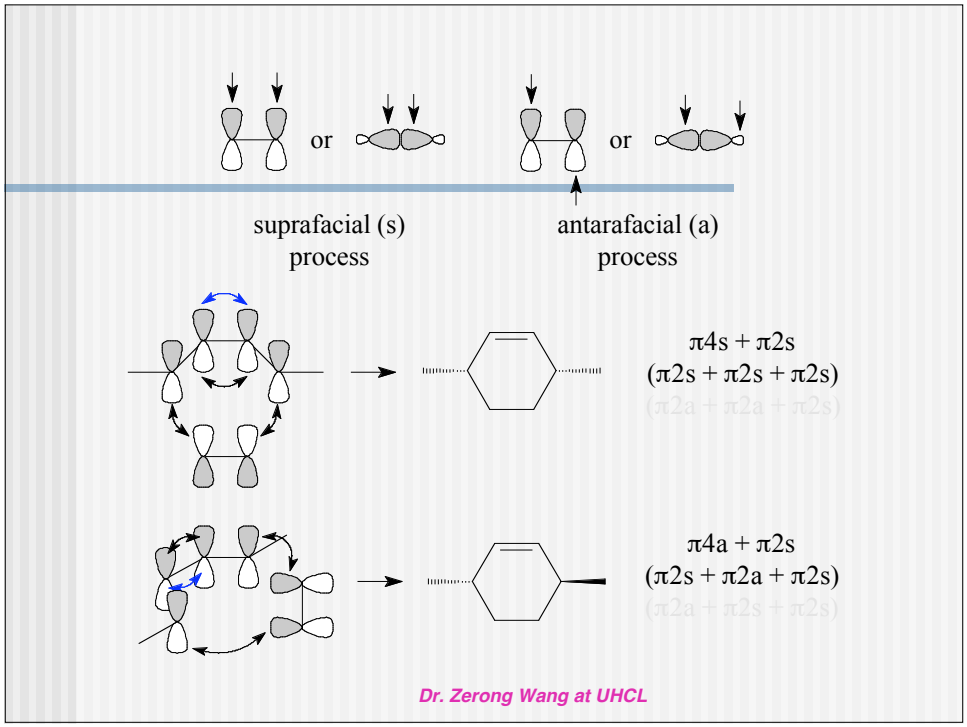
or
or
suprafacial (s)
process
antarafacial (a)
process
π4s + π2s
(π2s + π2s + π2s)
π4a + π2s
(π2s + π2a + π2s)
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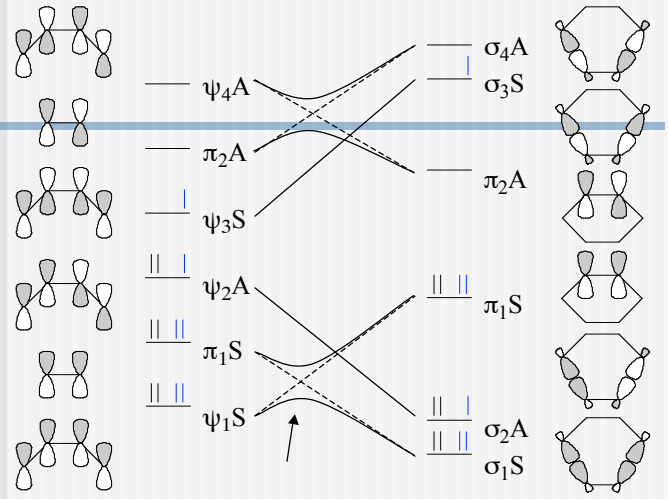
Woodward-Hoffmann Rules

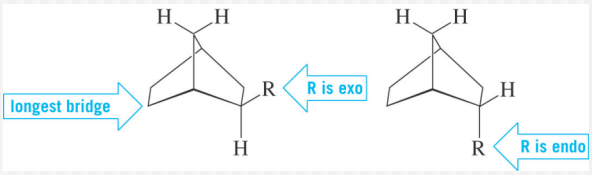
In any concerted process, the starting material orbitals must be transformed into product orbitals of the same symmetry.

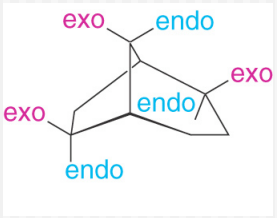


thermally allowed
photochemically forbidden

avoided crossings
-orbitals of the same symmetry do not cross

Endo & Exo product





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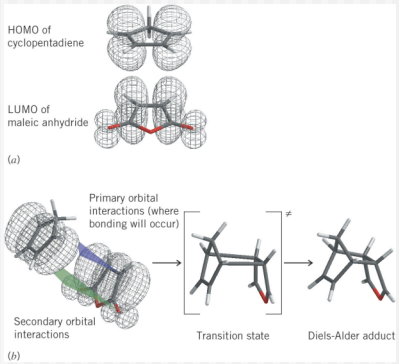
- When the molecules approach each other there are favorable interactions between the LUMO of maleic anhydride and the HOMO of cyclopentadiene
  - In the endo orientation favorable secondary oribtal interactions between the LUMO of the carbonyl groups and the HOMO of the cyclopentadiene carbons at the C2 and C3 positions of the diene can also occur



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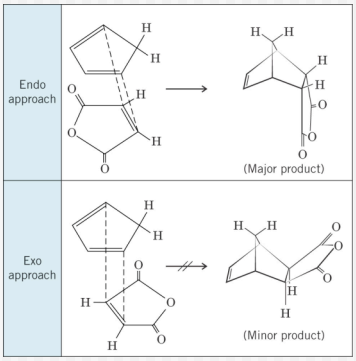
- Molecular Orbital Considerations that Favor an Endo Transition State
  - When maleic anhydride and cyclopentadiene react the major product is the endo product
    - The major product has the anhydride linkage endo



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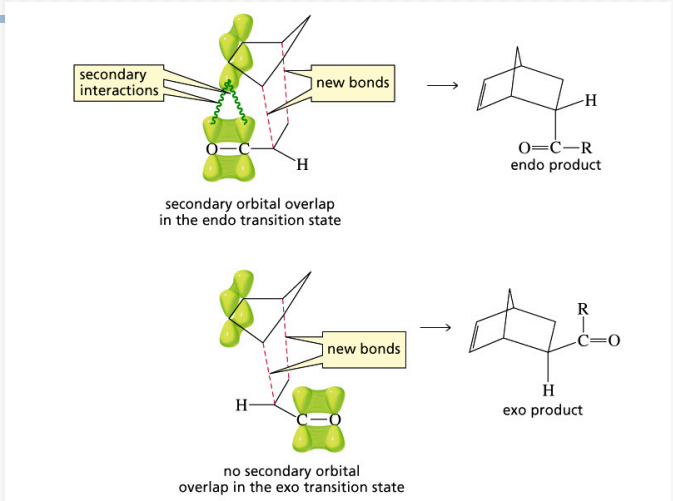
Secondary orbital overlap favors the endo product formation



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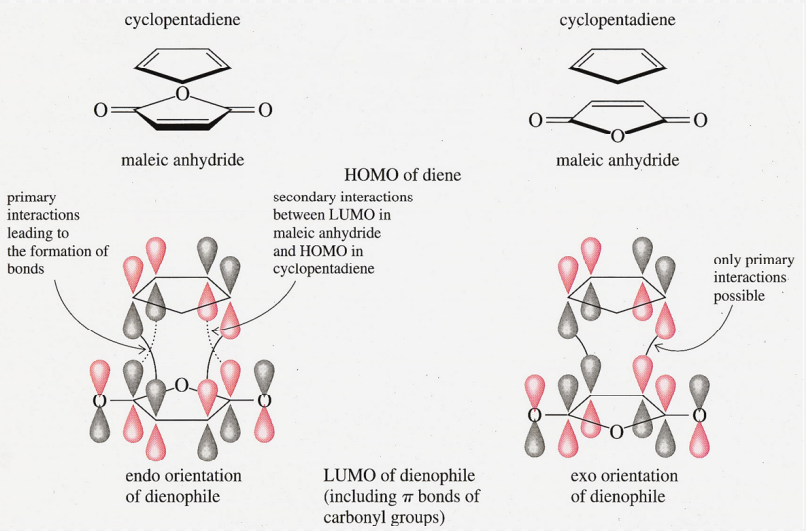

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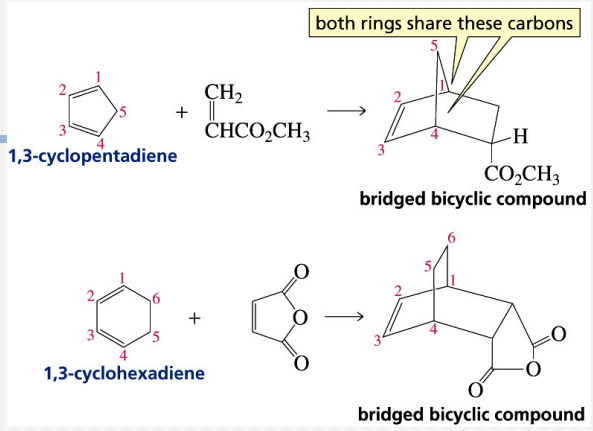

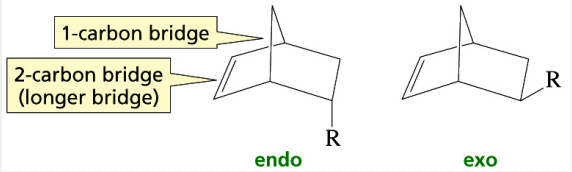

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