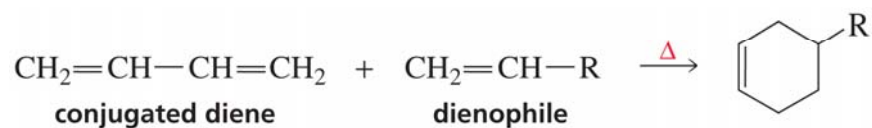


The Diels-Alder Reaction

The mechanism
The MO picture
Regio- and Stereochemistry
Kinetic and Thermodynamic control

The Diels-Alder Reaction

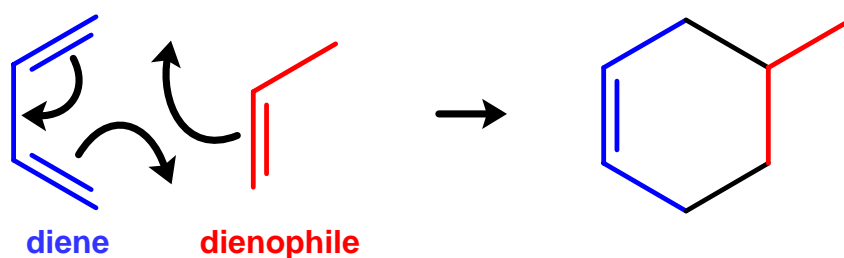
- Our first “name” reaction
 - Named after chemist(s) instead of the chemistry!
- A conjugated **diene** reacts with a double-bonded **dienophile**



Otto Diels, Kurt Alder
[Nobel Prize, Chemistry, 1950](#)

The Mechanism of the Diels-Alder Reaction

- Our first “name” reaction
 - Named after chemist(s) instead of the chemistry!
- A conjugated **diene** reacts with a double-bonded **dienophile**

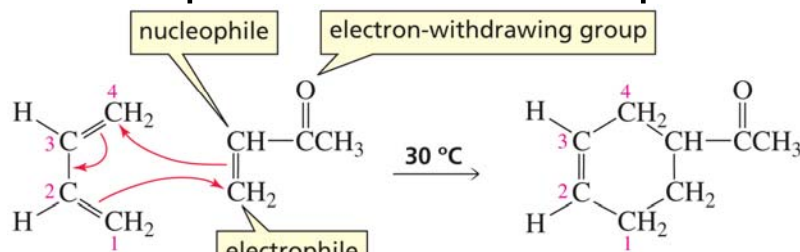


The Diels-Alder reaction is a six-electron cyclic reaction (think Hückel's rule!

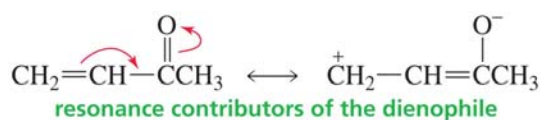
- The dienophile can be considered as simultaneously a nucleophile and electrophile
- The driving force is the conversion of two π bonds into two σ bonds
- The reaction will not happen without a Hückel number of electrons!



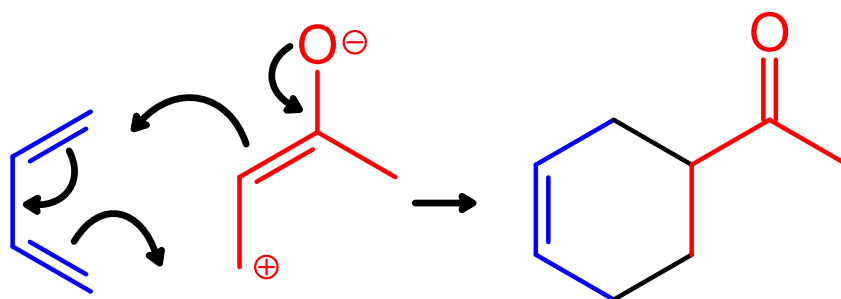
Normally, dienes are electron-rich;
dienophiles are electron-poor



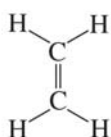
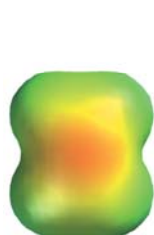
a 1,4-addition reaction to 1,3-butadiene



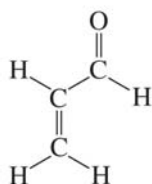
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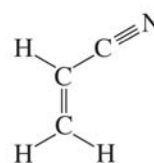
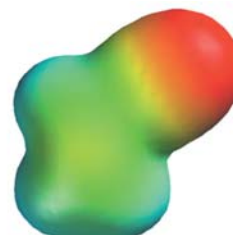
Typical dienophiles have
electron-poor double bonds



a poor
dienophile

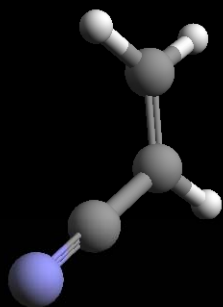


a good
dienophile

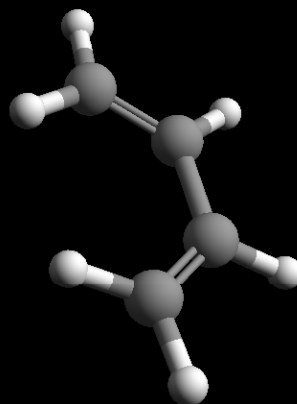


a good
dienophile

The Diels-Alder reaction as a
HOMO-LUMO interaction



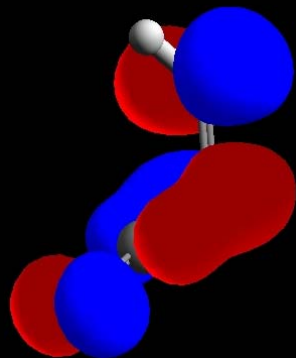
dienophile



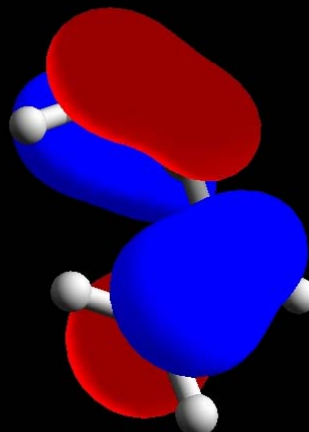
diene

The Diels-Alder reaction as a HOMO-LUMO interaction

HOMO and LUMO must have the same symmetry

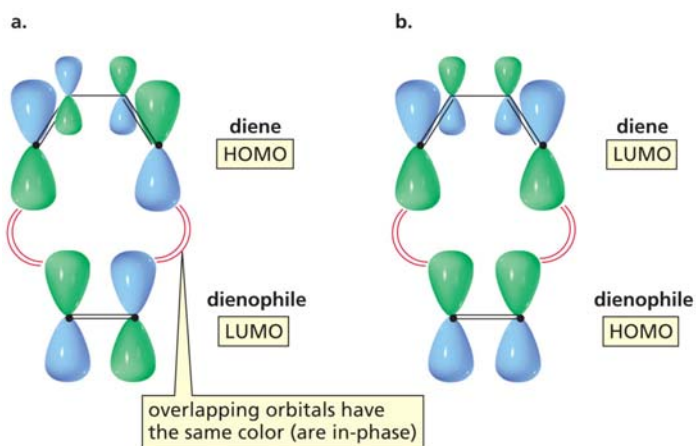


dienophile LUMO



diene HOMO

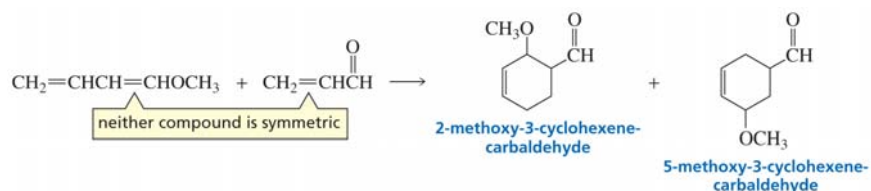
The HOMO-LUMO interaction works in either direction



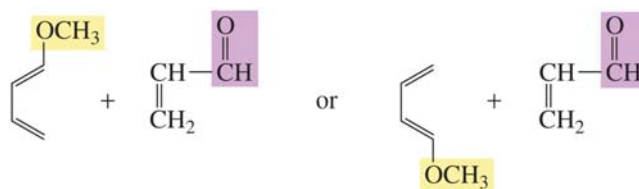
diene HOMO + dienophile LUMO

dienophile HOMO + diene LUMO

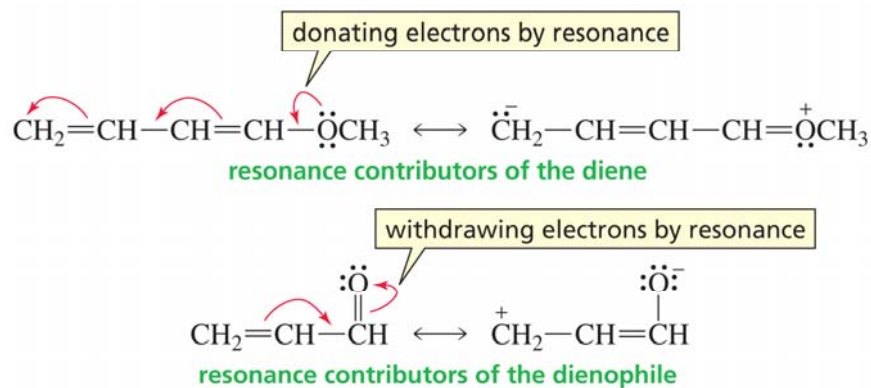
Regiochemistry of the Diels-Alder Reaction



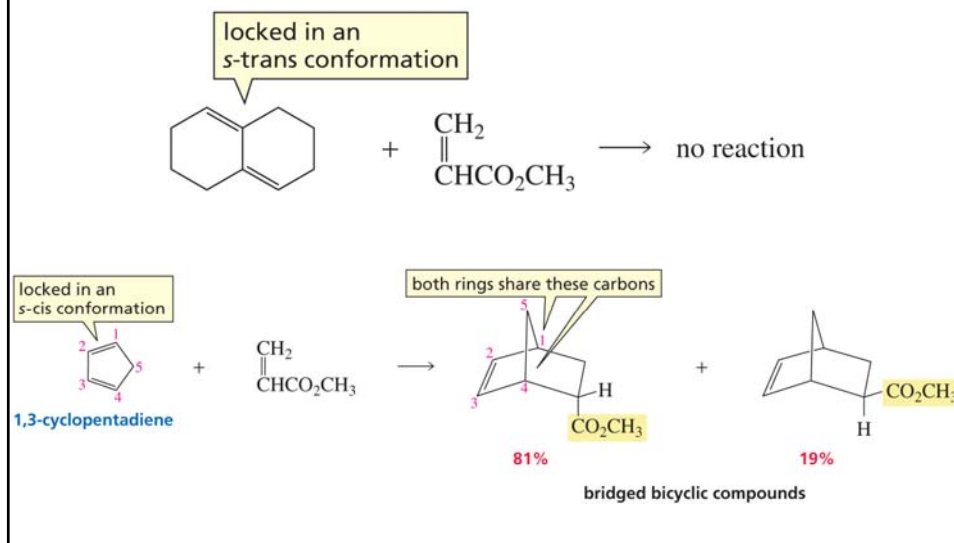
- With asymmetric diene and dienophile, there are two possible regiochemical orientations



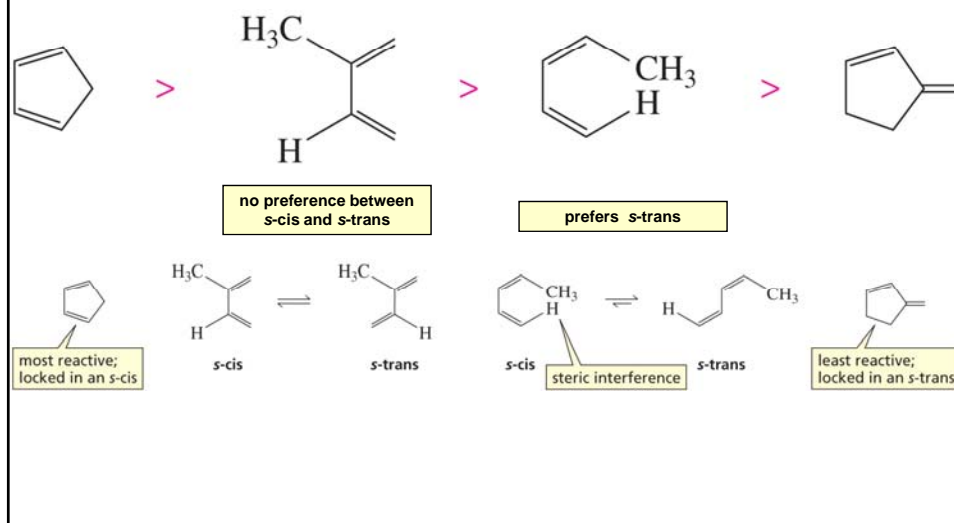
Examine the resonance contributors of the diene and dienophile



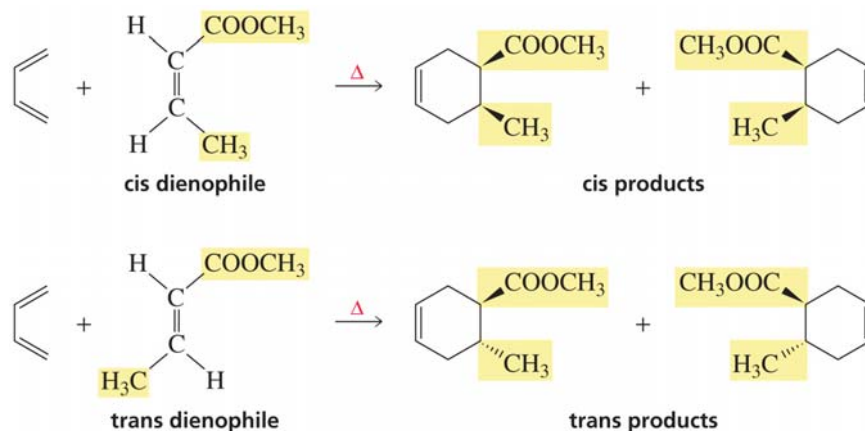
Conformational locking can make the difference in reactivity



Conformational locking can make the difference in reactivity

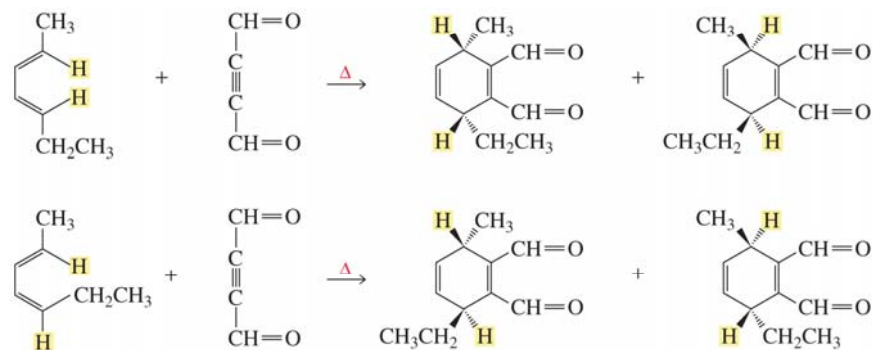


The Diels-Alder reaction is stereospecific in the dienophile



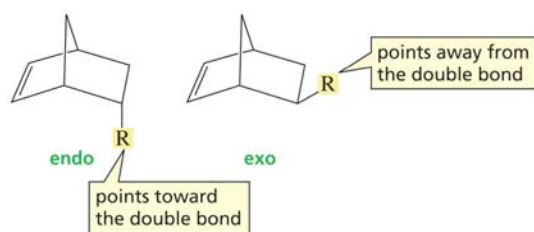
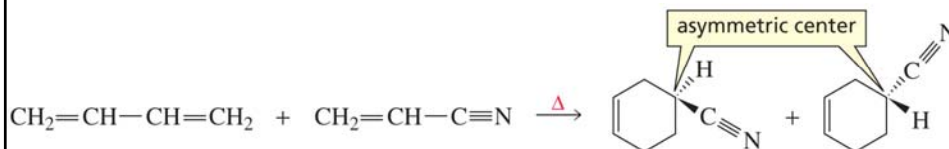
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The Diels-Alder reaction is stereospecific in the diene



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The Diels-Alder reaction can form asymmetric carbon atoms

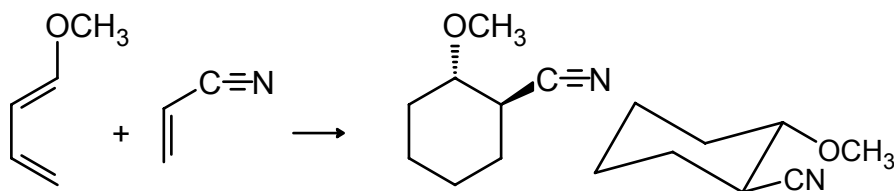


Endo orientation forms product faster

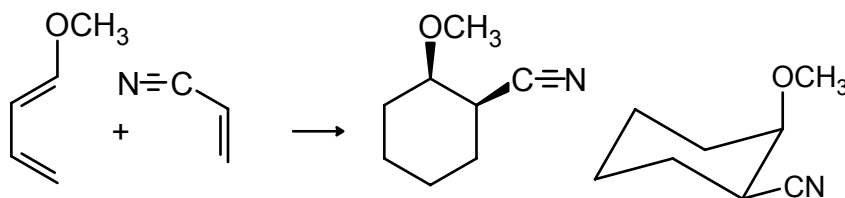
Exo orientation forms the more stable product

Endo vs Exo

Stereochemistry in cycloaddition of 1-methoxybutadiene and cyanoethylene

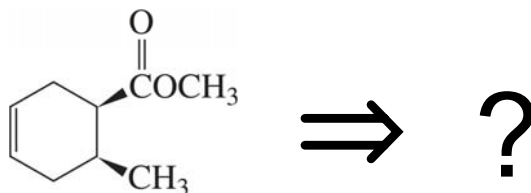


EXO addition is slower but gives the more stable product



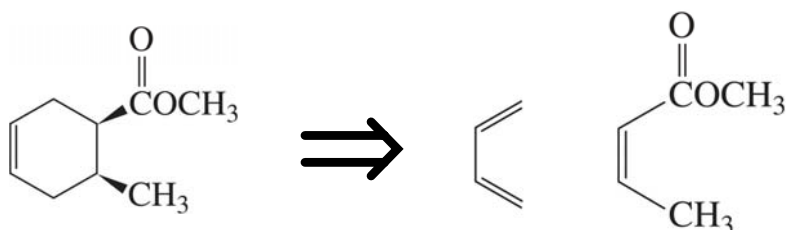
ENDO addition is faster but gives the less stable product

Retrosynthetic analysis using the Diels-Alder reaction



- In the product, the diene still has the central double bond
- In the product, the dienophile may have electron-withdrawing groups

Retrosynthetic analysis using the Diels-Alder reaction



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