University of Illinois
at Chicago UIC

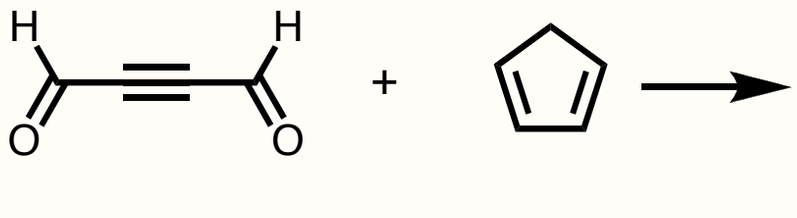
Lecture 23
Organic Chemistry 1

Professor Duncan Wardrop

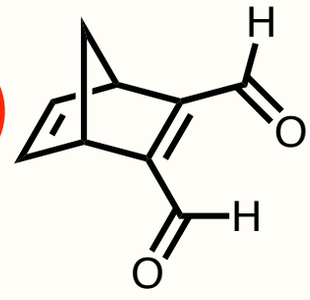
April 6, 2010

Self Test Question

Predict the product for the Diels-Alder reaction below.



A



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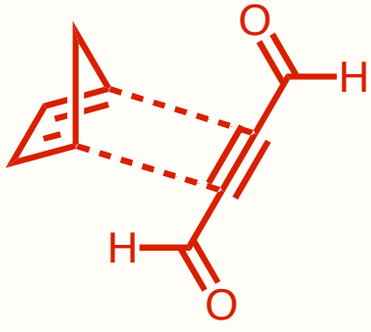
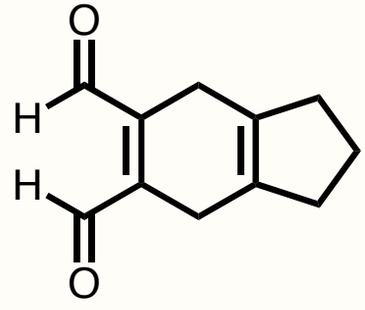
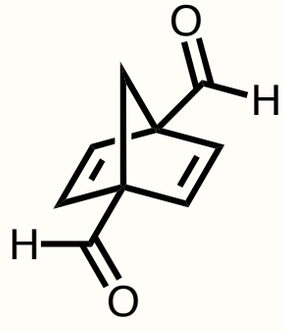


C

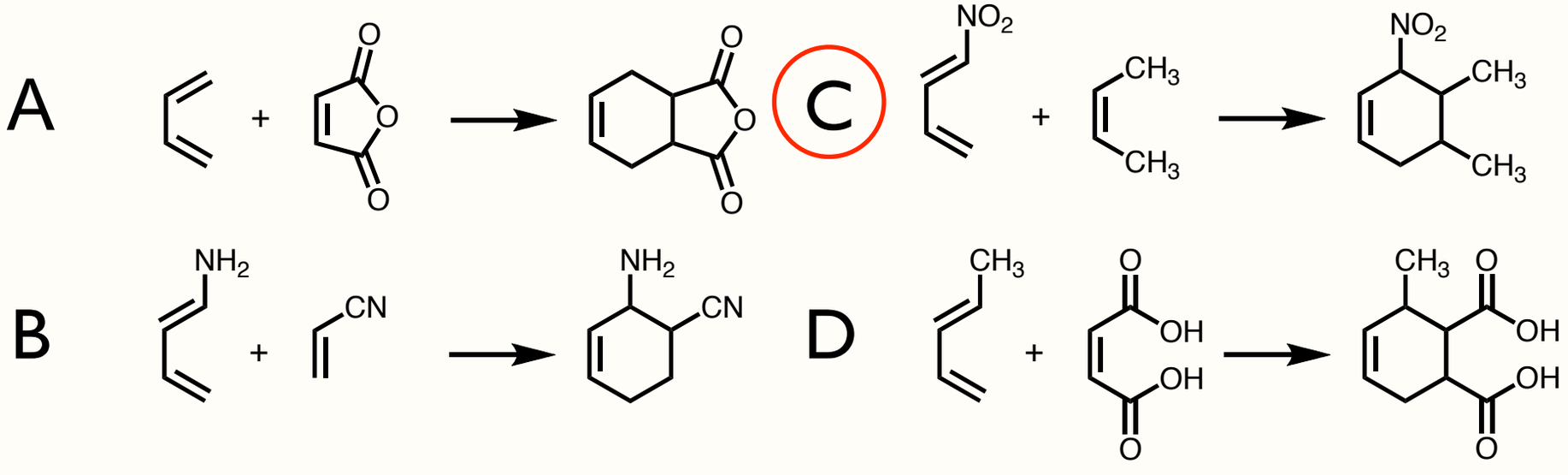


D

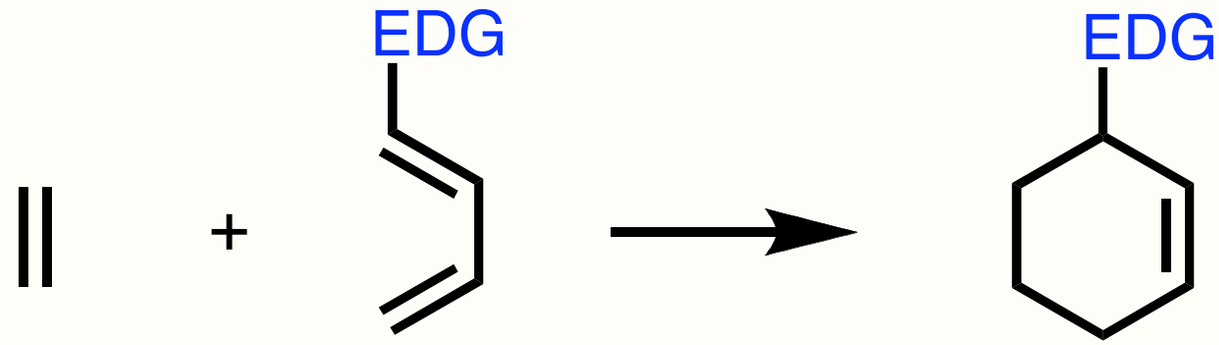


Self Test Question

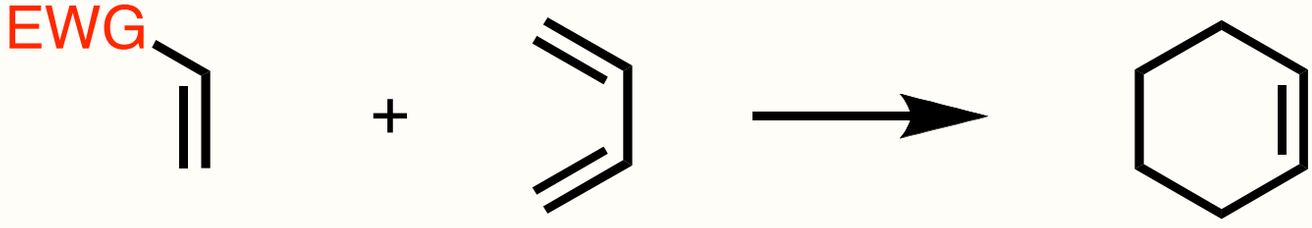
Diels-Alder reactions are accelerated by EWGs on the dienophile and EDG on the diene. Which reaction below does not meet these electronic demands?



Reactivity of Diels-Alder

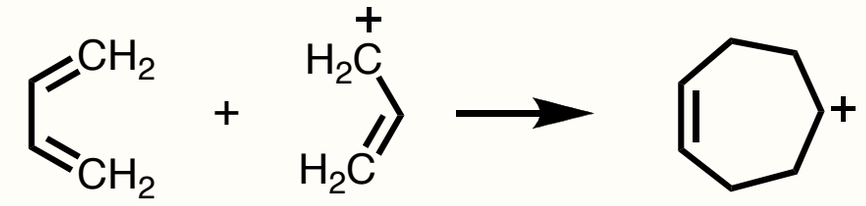


Electron donating groups (EDG) increase the reactivity of the diene = faster reaction

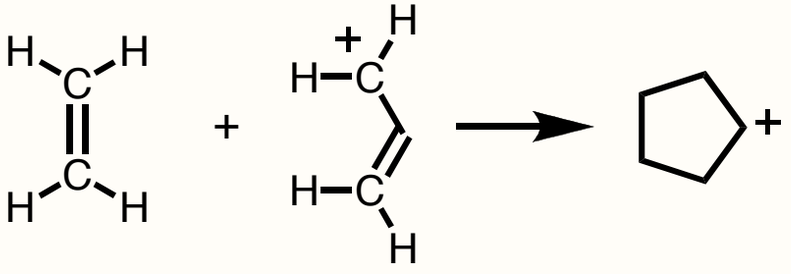


Electron withdrawing groups (EWG) increase the reactivity of the dienophile = faster reaction

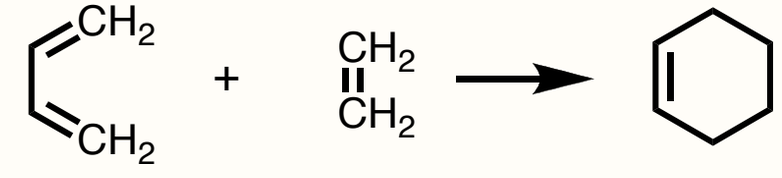
Pericyclic Reactions Raise Tough Questions



√ allowed



X forbidden

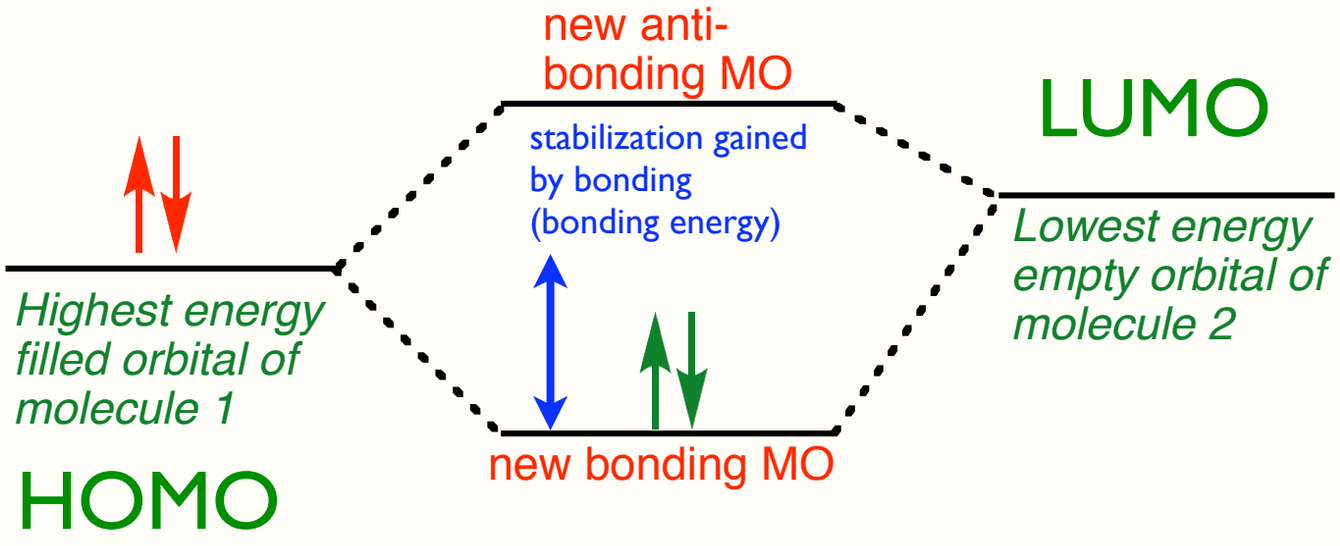


√ allowed

How do we rationalize these observations. . . .?

Frontier Molecular Orbitals (FMOs)

A complex molecule (many atoms) will have many molecular orbitals. However, only those orbitals highest in energy are involved in reactions (bond making/breaking).



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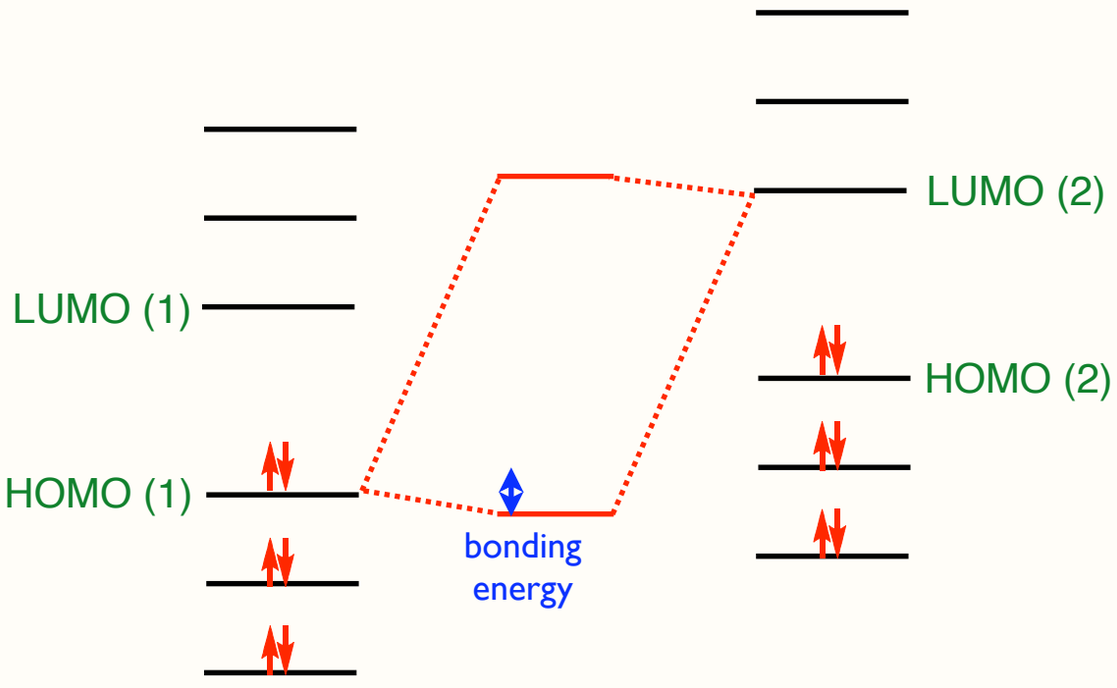

When MO energies for two molecules are different, the biggest energy drop (perturbation) occurs when the HOMO/LUMO energies are closest in energy

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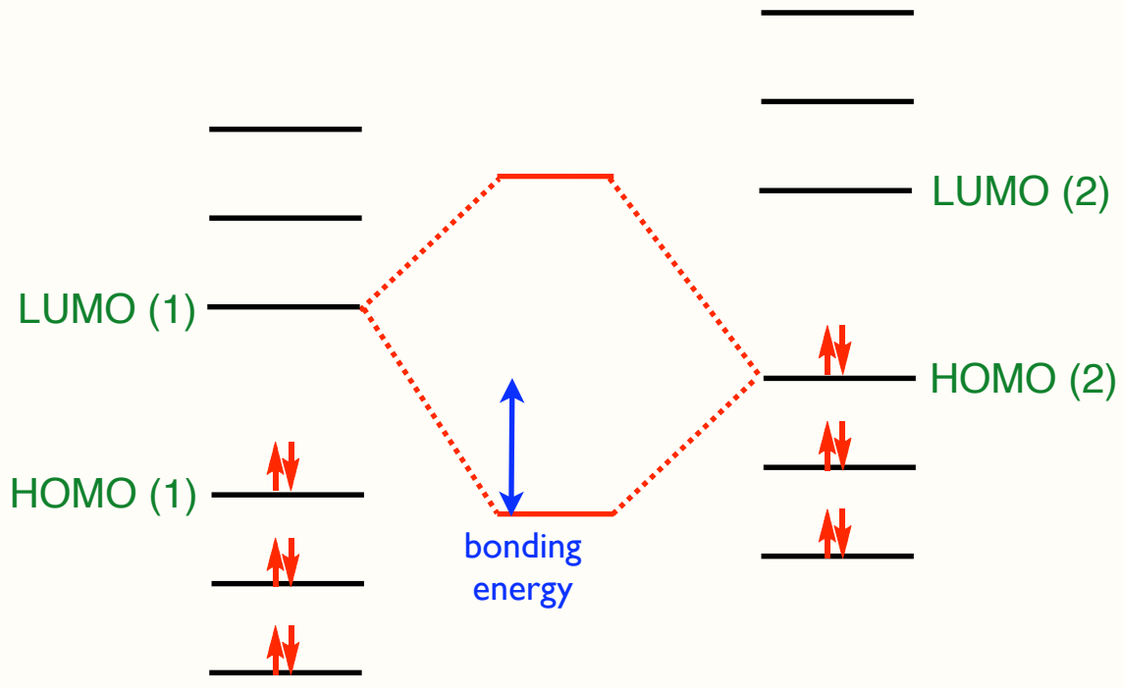

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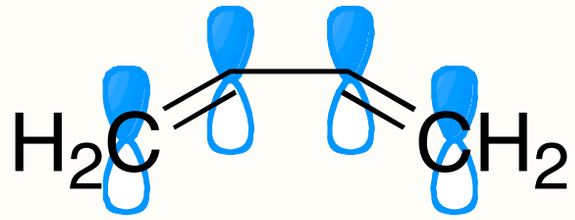
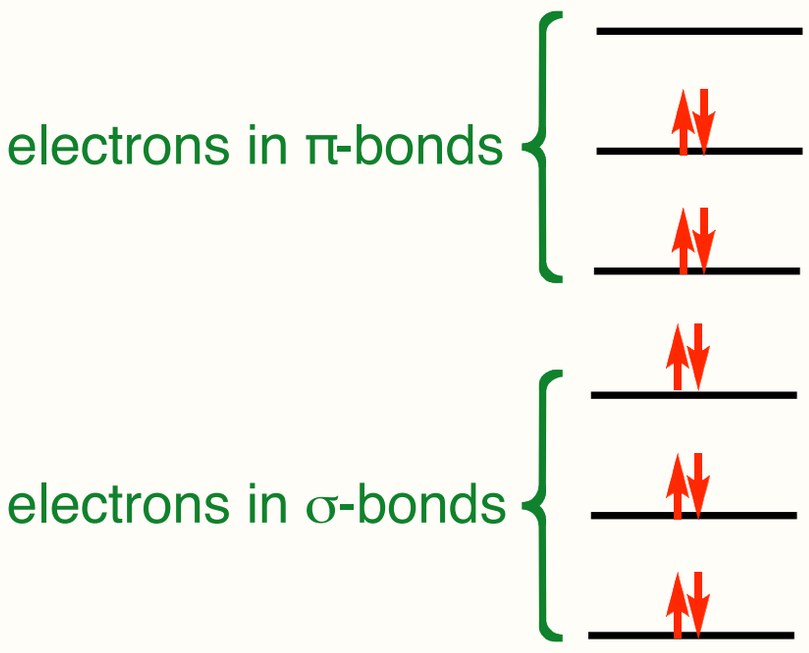


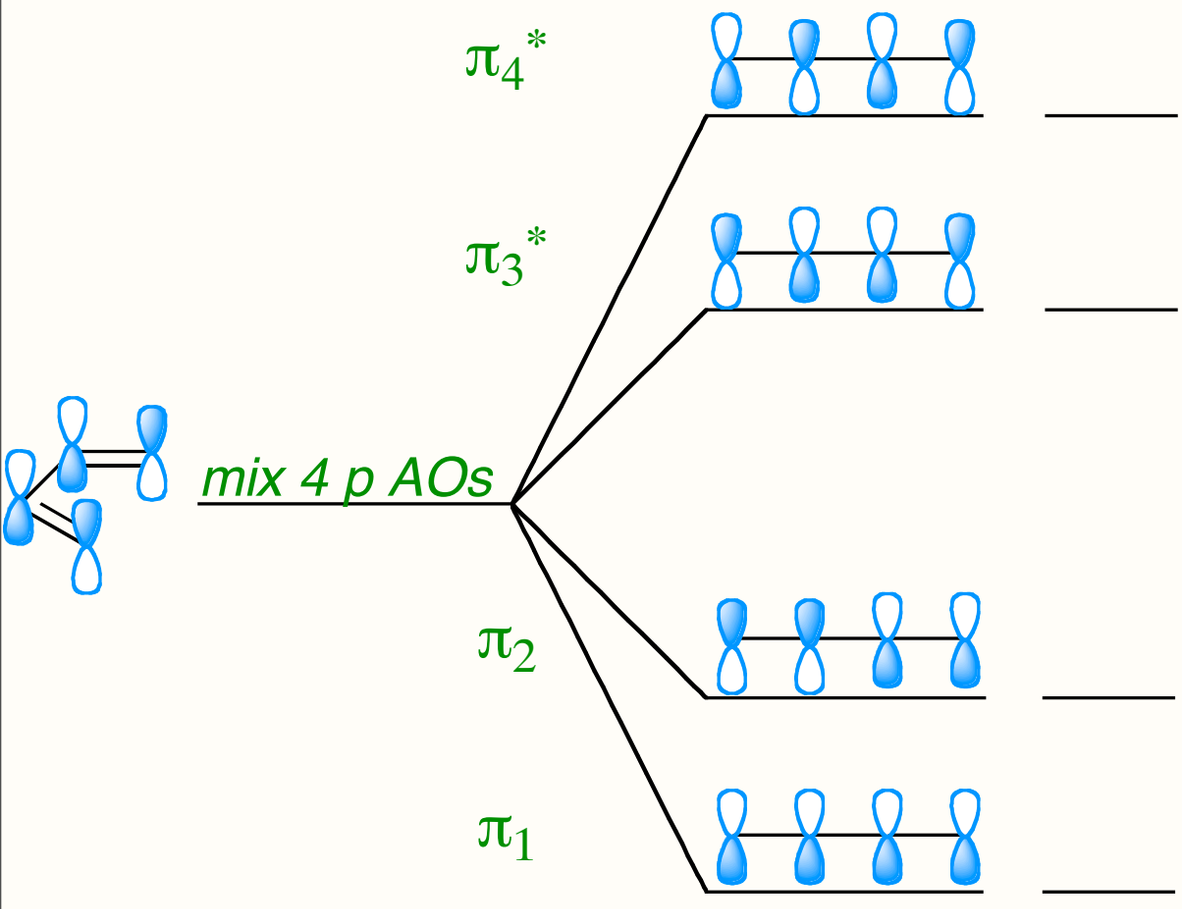


- electrons in p-orbitals are higher in energy than electrons in σ-orbitals =
- FMOs (HOMO/LUMO) of π-systems are formed by combining only the p-orbitals in the π-system
- We can ignore all other lower energy AOs.

FMO Picture of Diels-Alder Rxn (Diene)

4 p AO in = 4 MOs out

The diene contains 2 π-bonds = 4 π-electrons

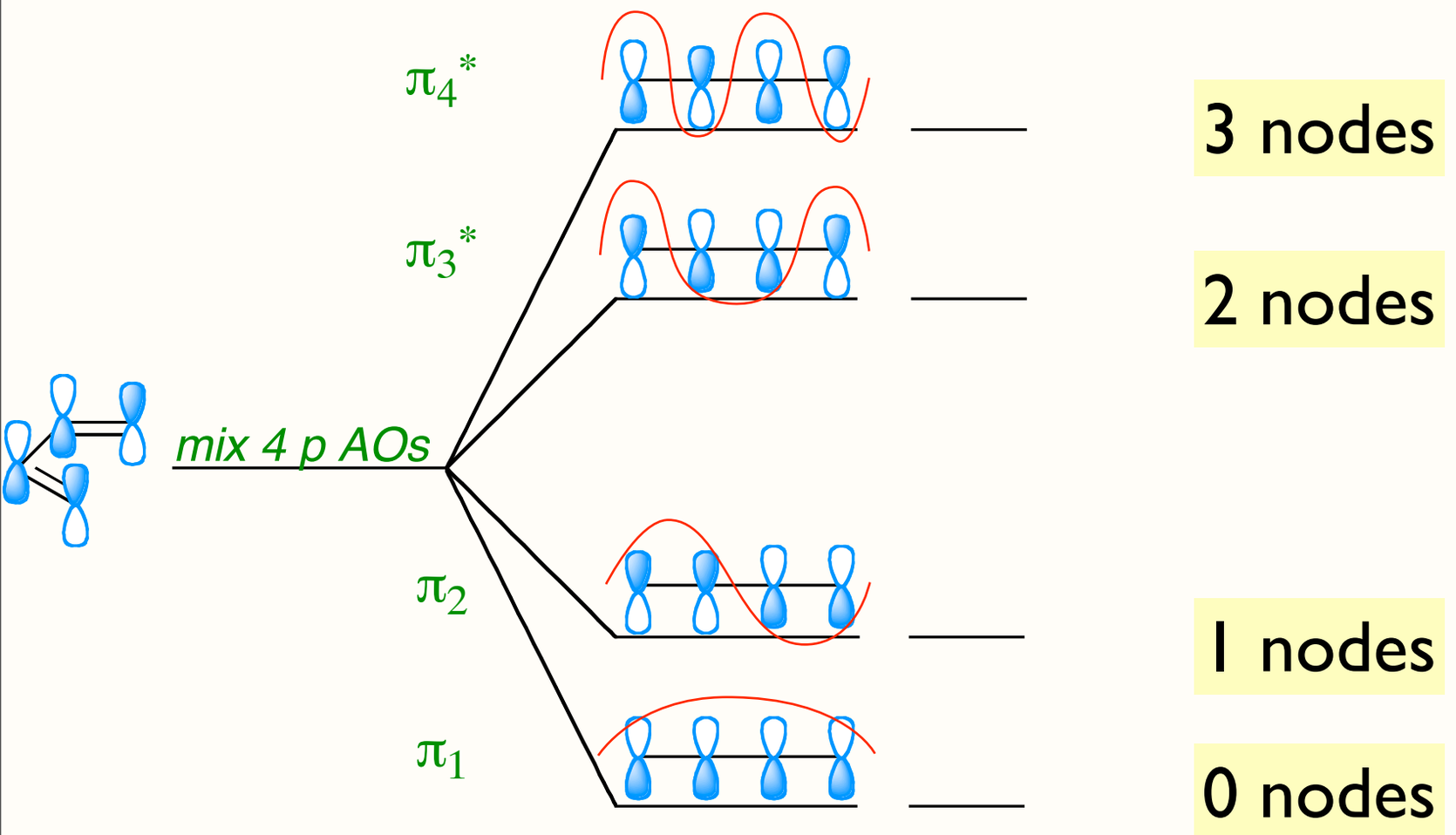


Antibonding orbitals

Bonding orbitals

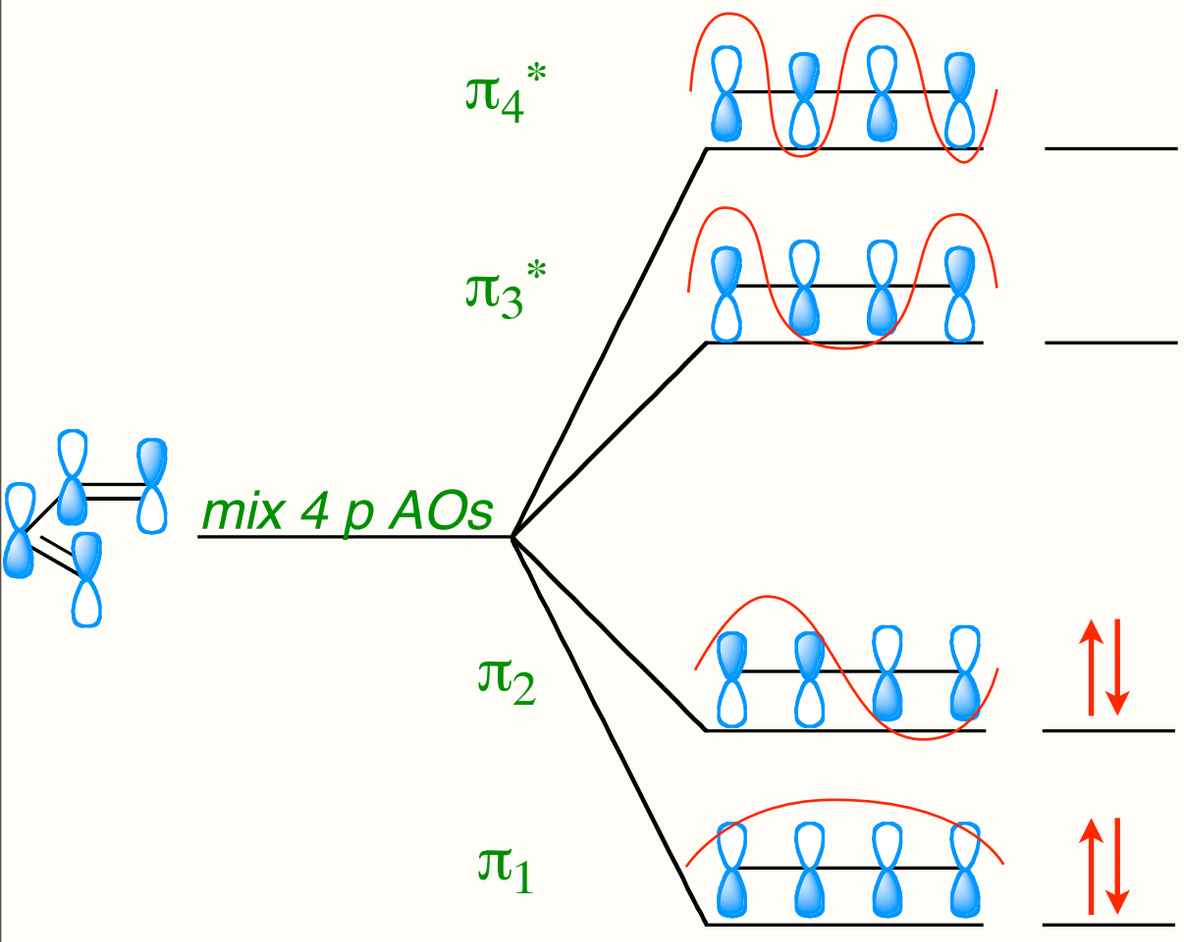
FMO Picture of Diels-Alder Rxn (Diene)

Node = area of zero electron density
More nodes = higher in energy



FMO Picture of Diels-Alder Rxn (Diene)

HOMO = highest occupied molecular orbital
LUMO = lowest unoccupied molecular orbital



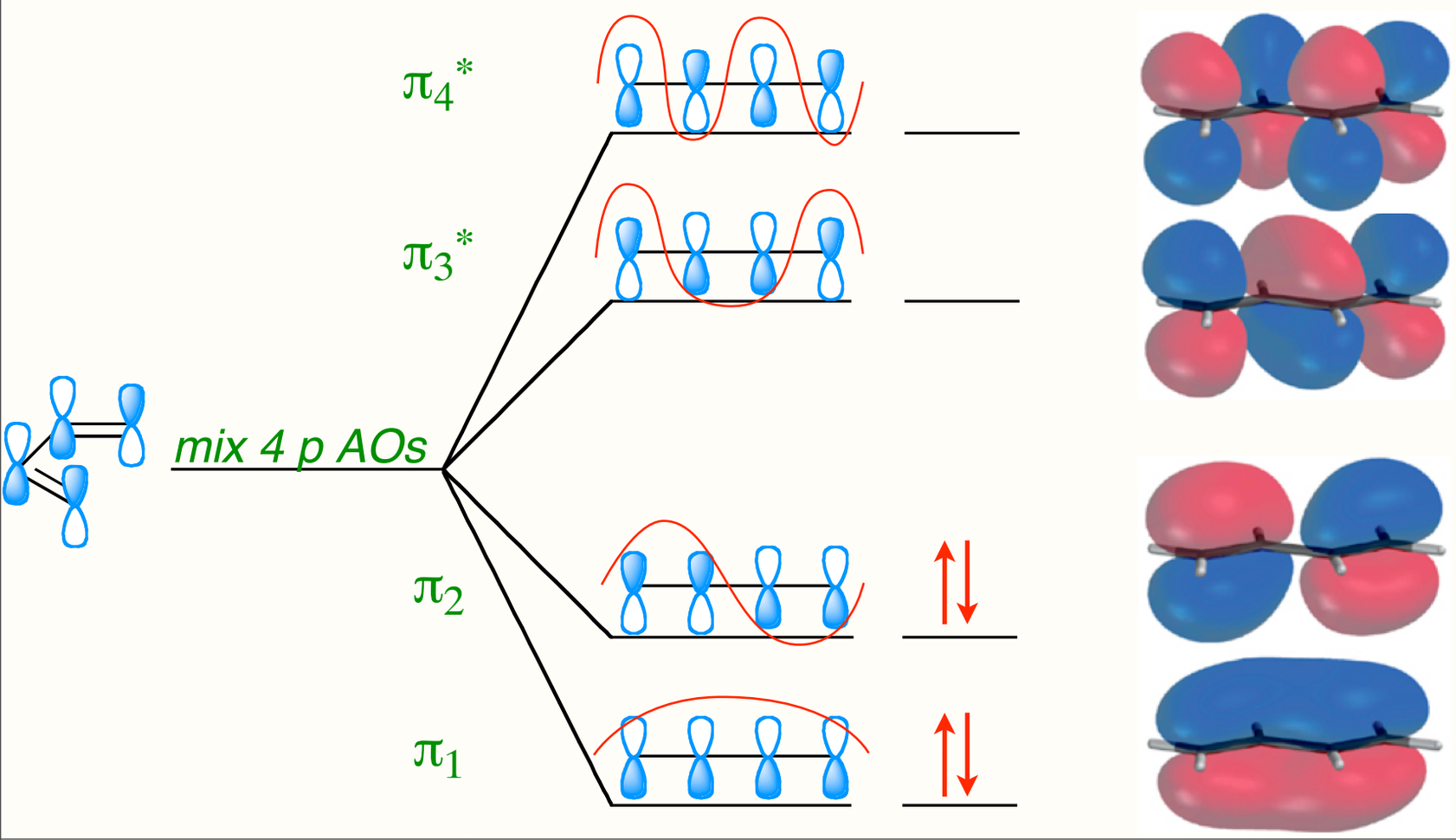
LUMO

Diene contains 2 Π-bonds:
Diene contains 4 Π-electrons

HOMO

FMO Picture of Diels-Alder Rxn (Diene)

True boundary surfaces for molecular orbitals of 1,3-butadiene



FMO Picture of Diels-Alder Rxn (Dienophile)

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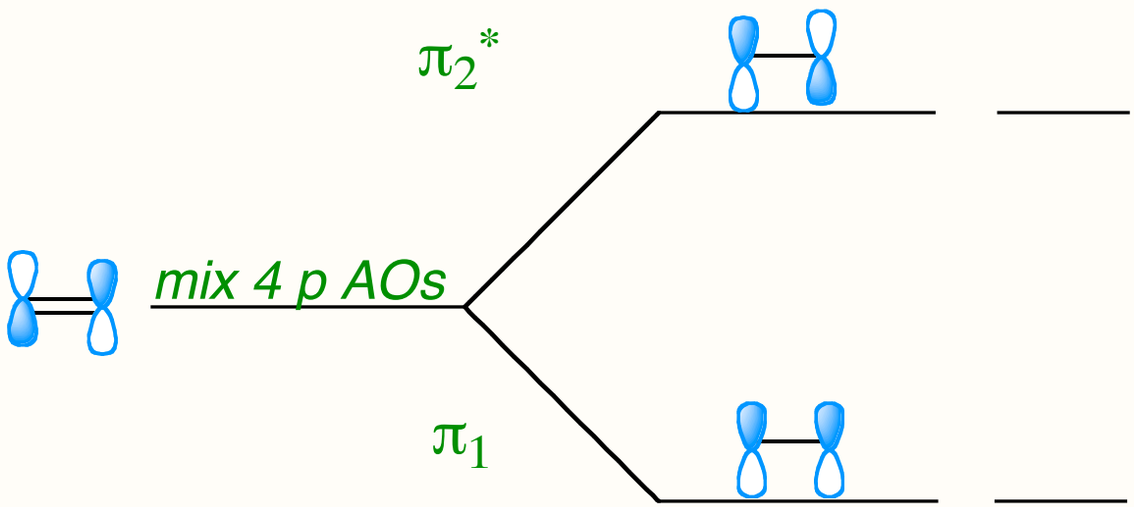

Antibonding orbital

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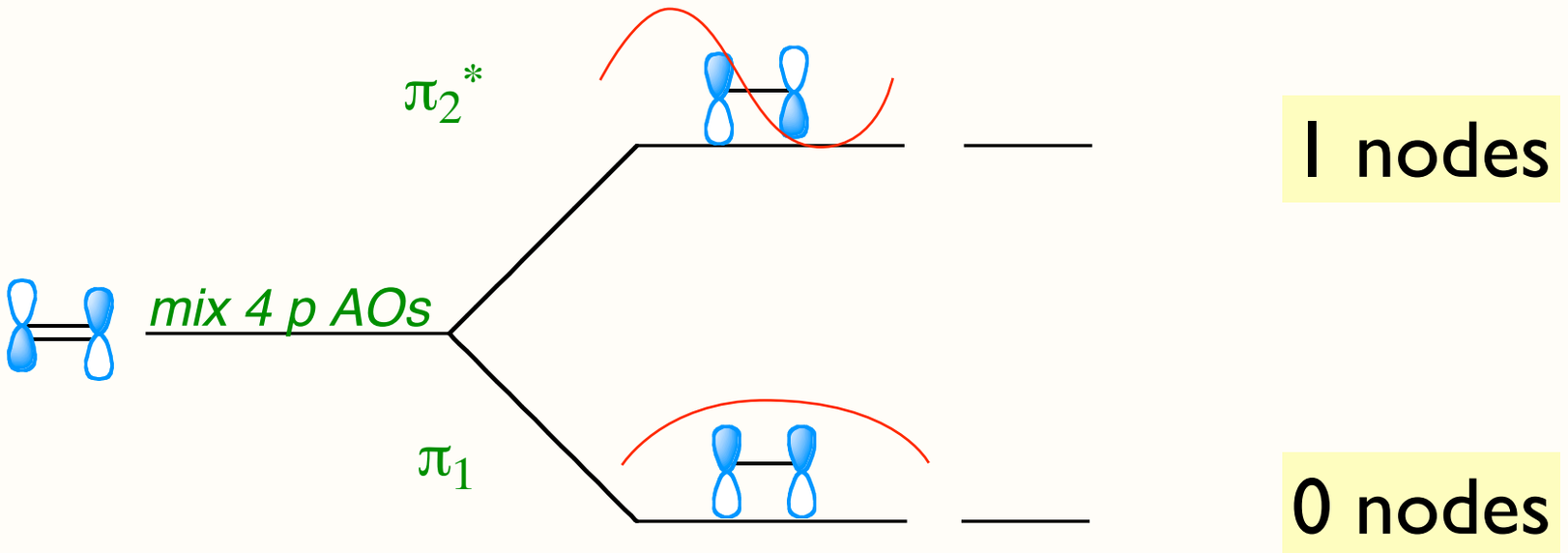

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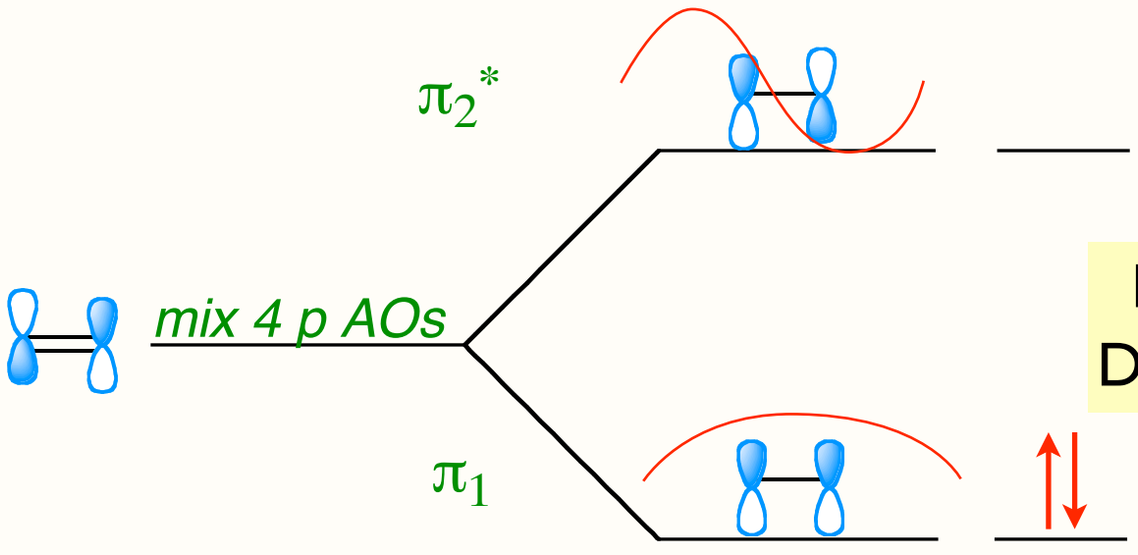

LUMO

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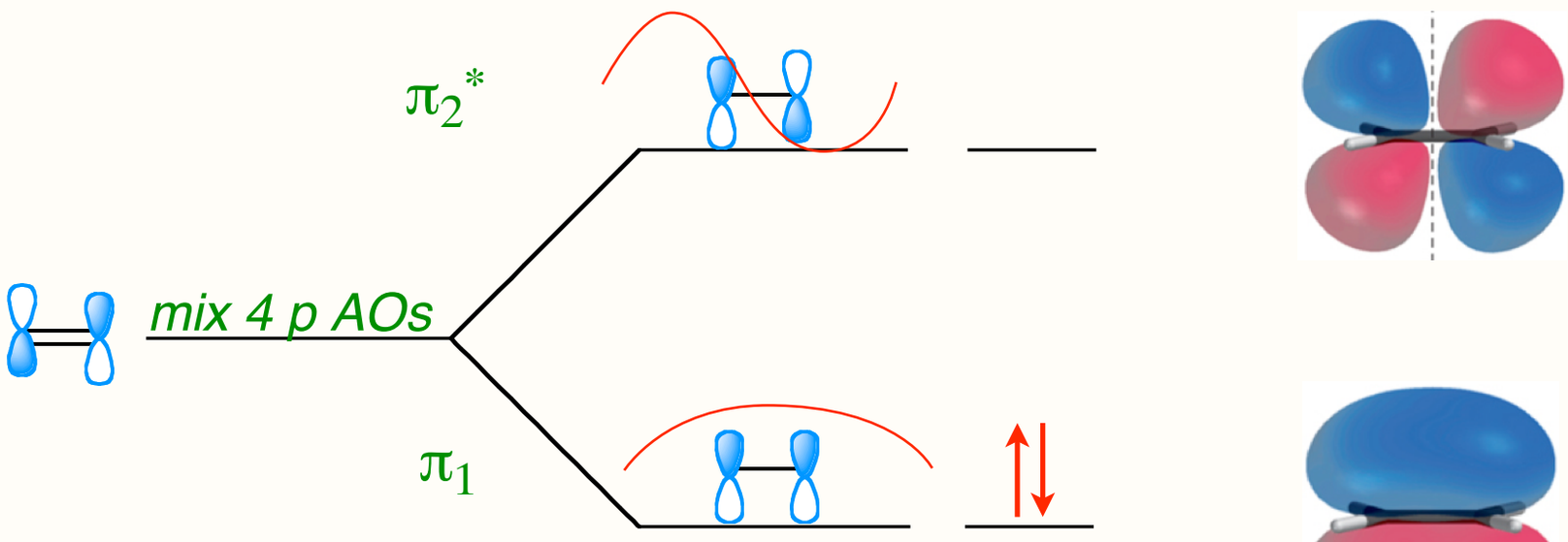
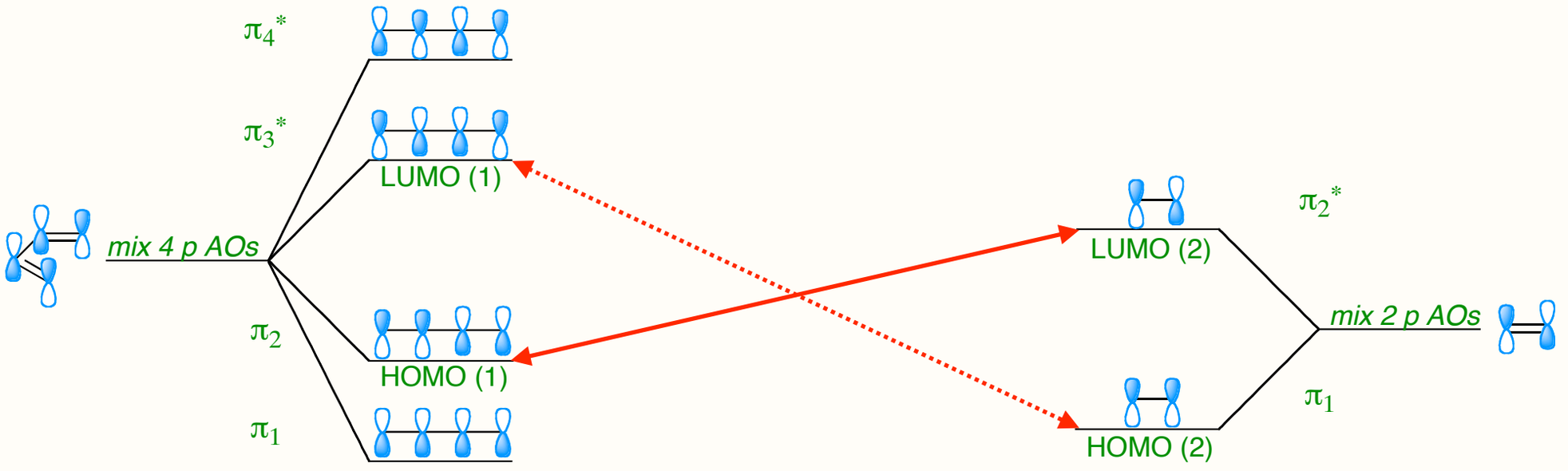
FMO Picture of Diels-Alder Rxn (Dienophile)

True boundary surfaces for molecular orbitals of ethylene



FMOs in Diels-Alder Reaction

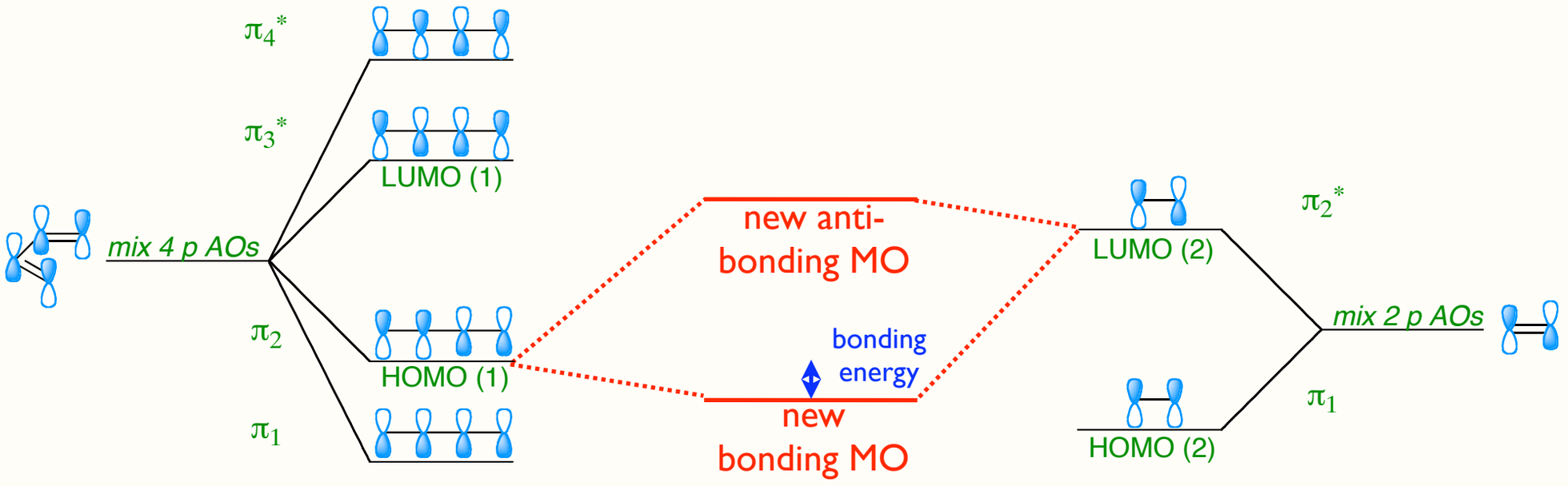


Energy of HOMO & LUMO of diene are usually **higher** in energy than dienophile

Orbital overlap occurs between HOMO & LUMO closest in energy

Energy of HOMO & LUMO of dienophile are usually **lower** in energy than diene

FMOs in Diels-Alder Reaction



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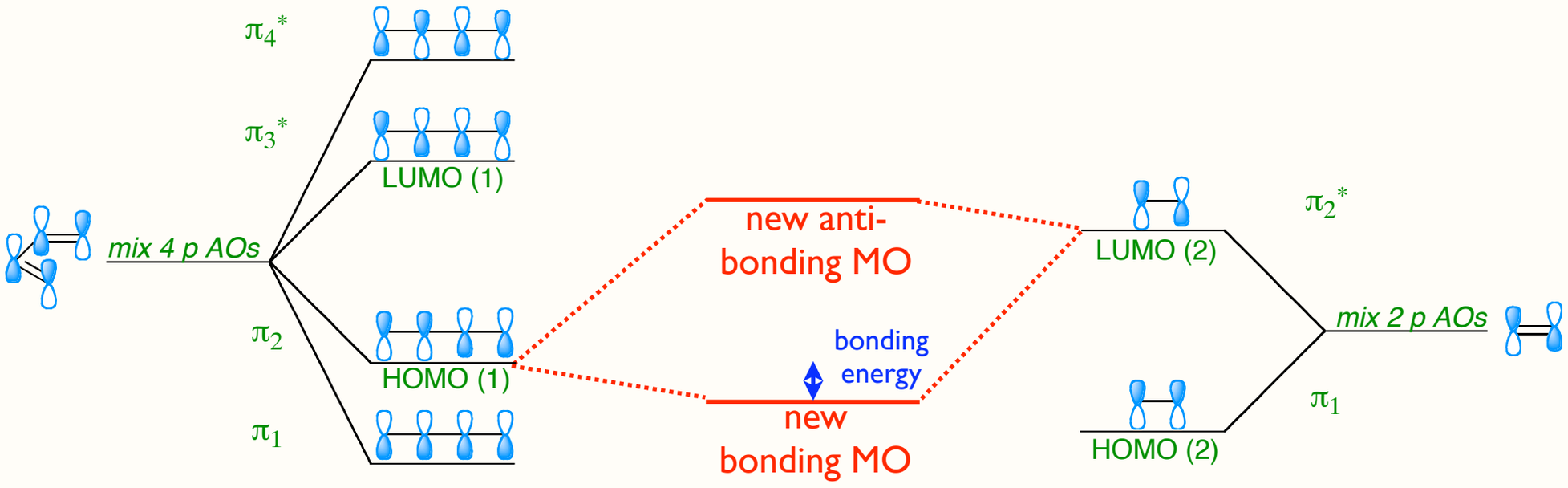
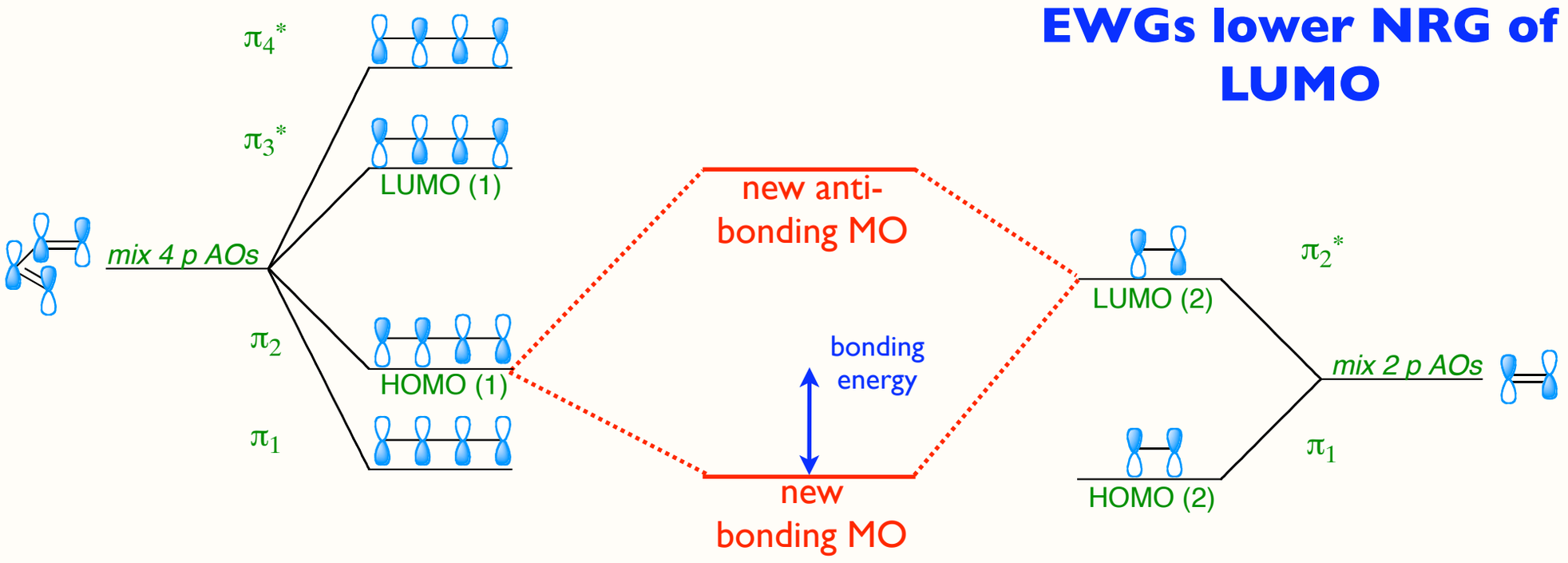


- As LUMO and HOMO become closer in energy, the overlap between orbitals becomes stronger =
- better/stronger bonding =
- Lower energy transition state =
- Faster Reaction

FMOs in Diels-Alder Reaction



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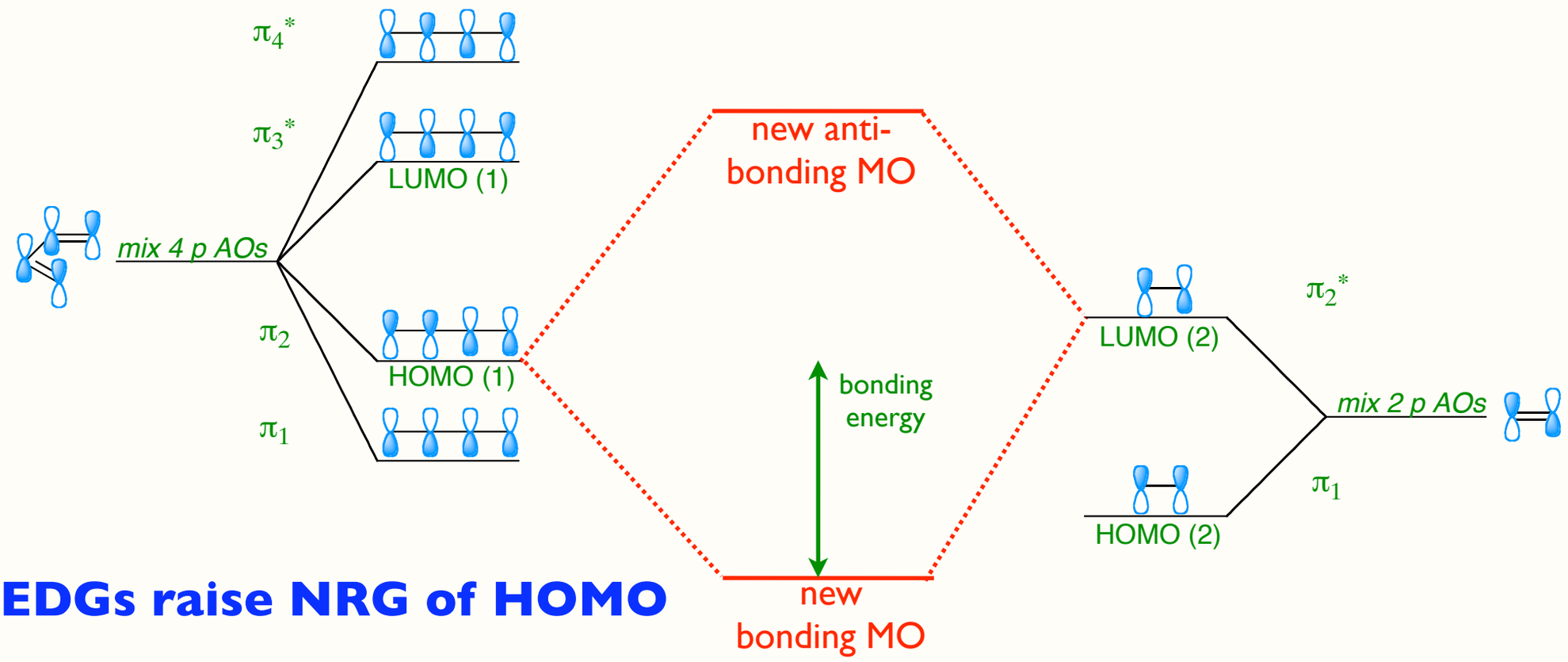

EDGs raise NRG of HOMO

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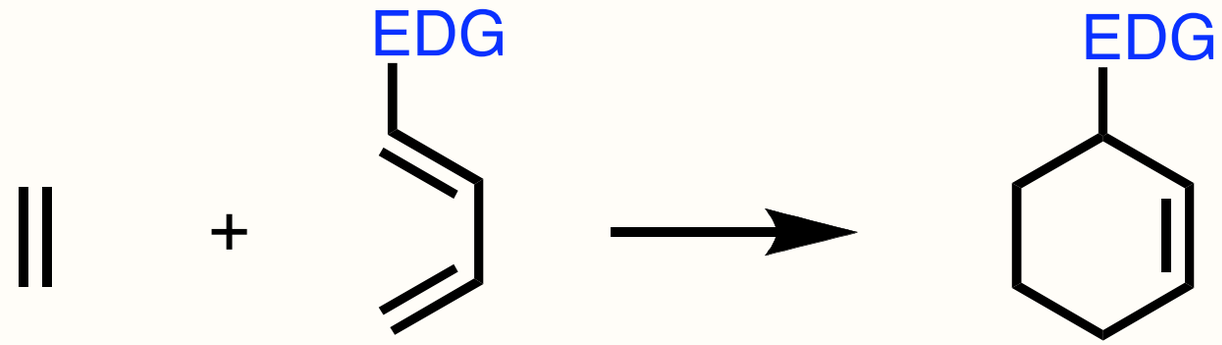
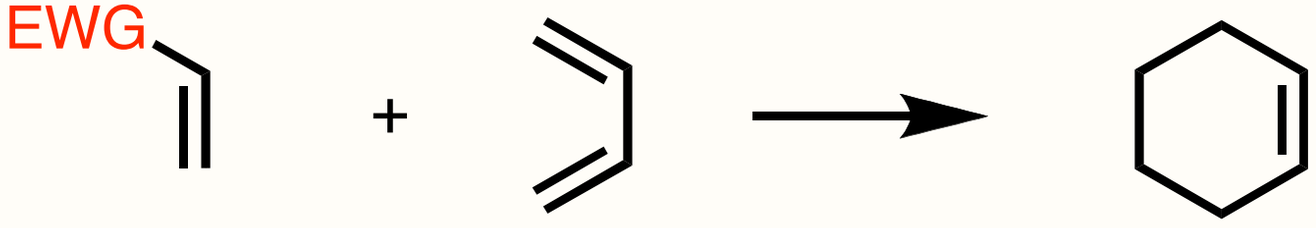
Substituent Effects on HOMO & LUMO



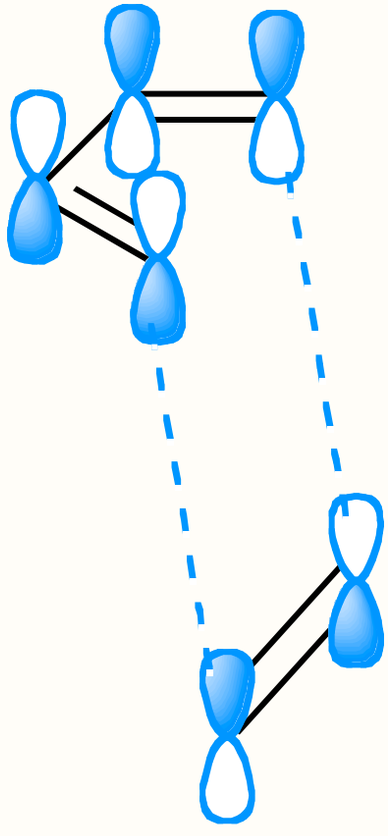
Electron donating groups (EDG) increase the energy of diene's HOMO



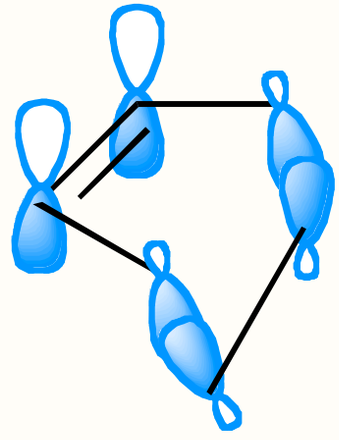
Electron withdrawing groups (EWG) decrease the energy of dienophile's LUMO

FMO Overlap in a Diels-Alder Reaction

HOMO of 1,3-butadiene (π_2)



symmetry allowed reaction



LUMO of ethylene (π^*)

orbitals must have identical symmetry for constructive interference (bonding overlap)

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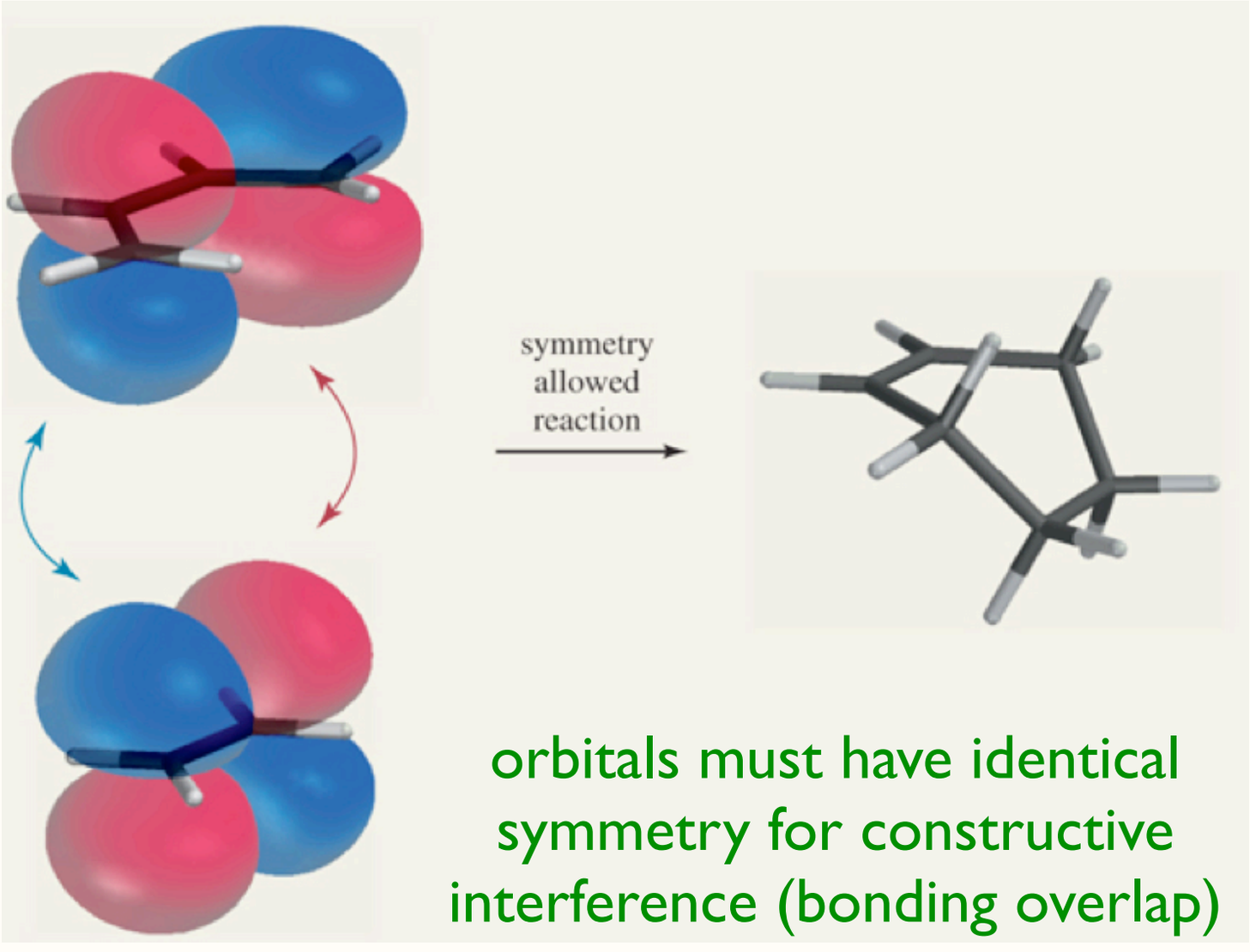

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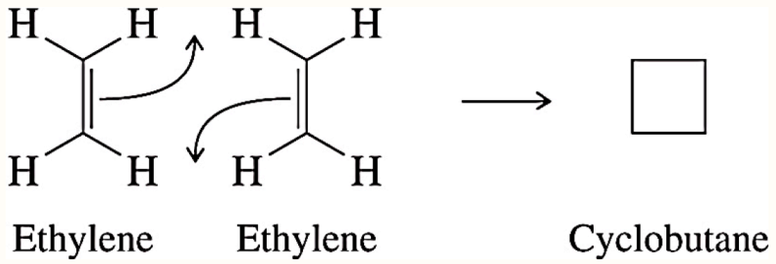
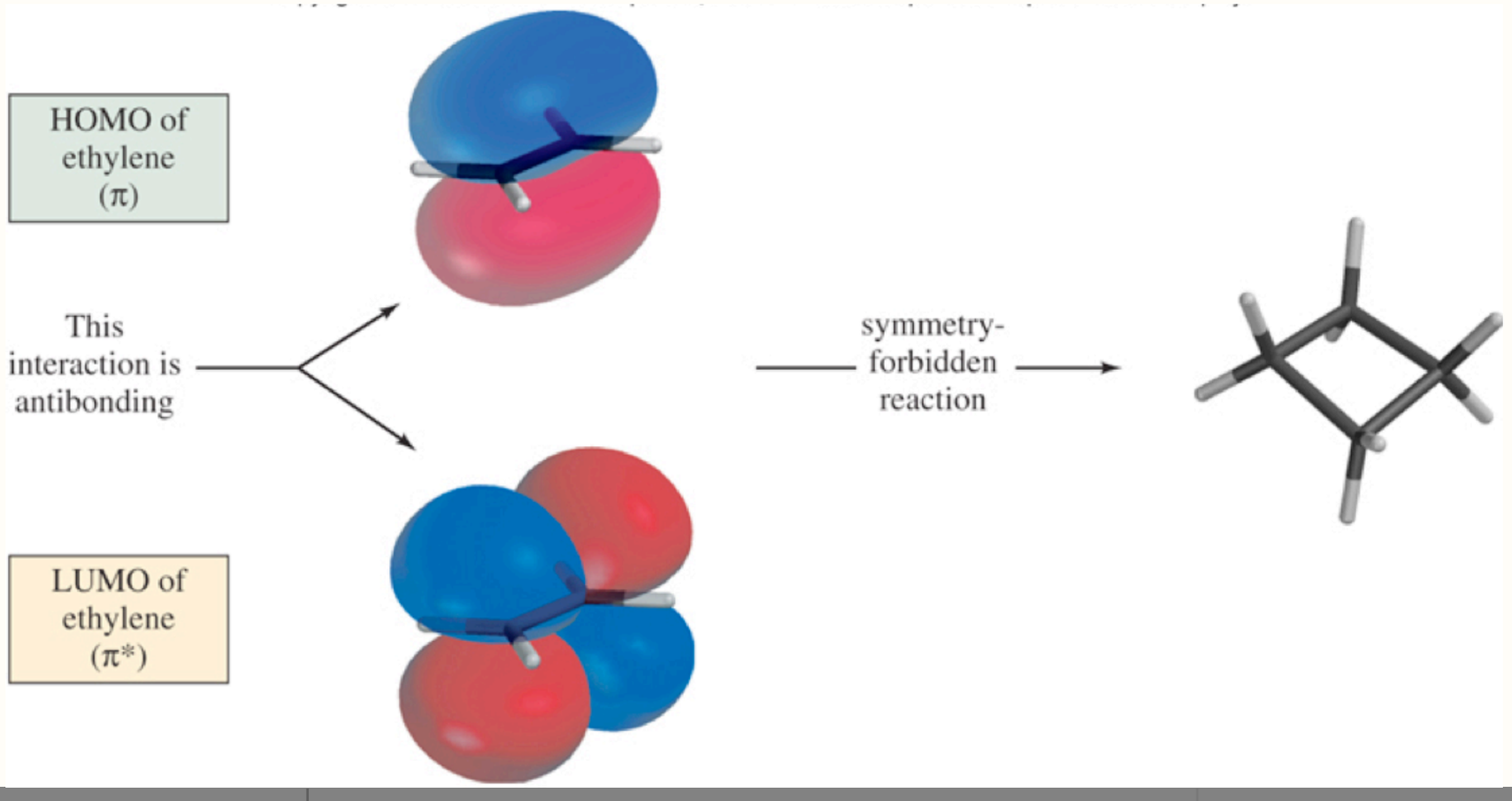
Not All Cycloadditions are Symmetry-Allowed

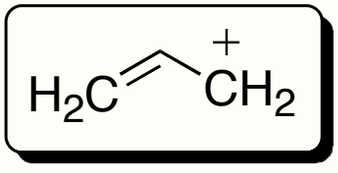


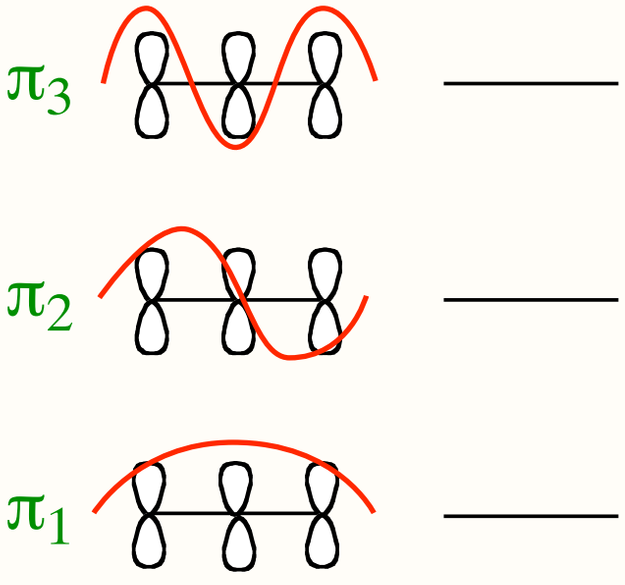


Self Test Question

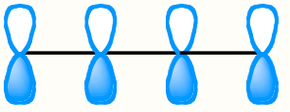
Which figure best represents the LUMO of an allylic carbocation?

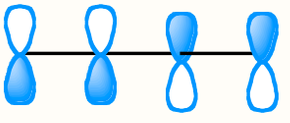
1. Step one: determine the number of p AOs in the π-system.
2. Step two: draw the same number of unshaded molecular orbitals as p AOs.
3. Assign nodes to MOs. Lowest = 0. Each higher MO has one more node.
4. Shade MOs to reflect node assignment in step 3.
5. Determine # of electrons in π-system. Place those electrons into MO according to Hund, Pauli & Aufbau principles.

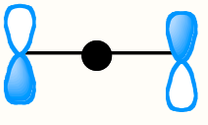


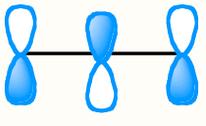


A. 

B. 

C. 

D. 

E. 

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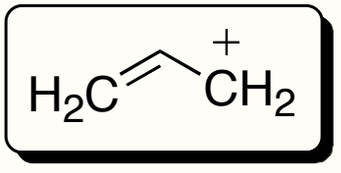
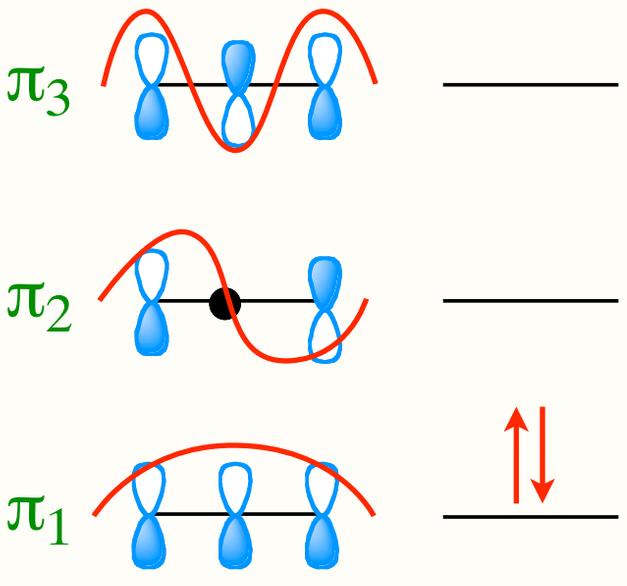
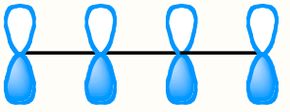
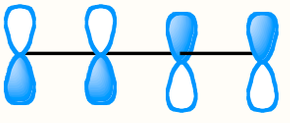
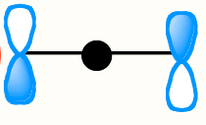


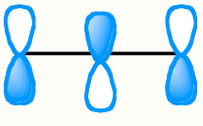


A. 

B. 

C. 

D. 

E. 

Self Test Question

Which figure best represents the HOMO of 1,3-butadiene?

1. Step one: determine the number of p AOs in the π-system.
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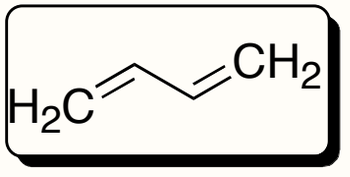
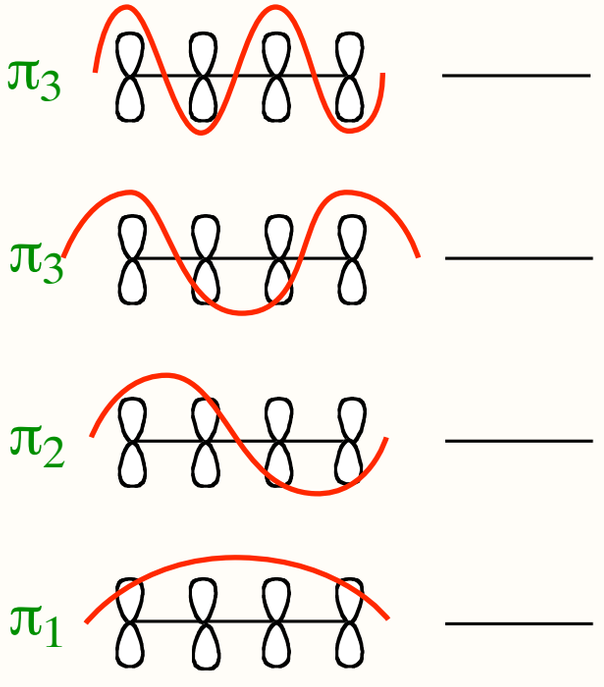
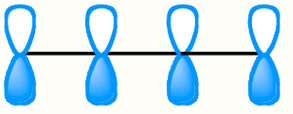
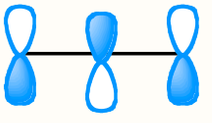
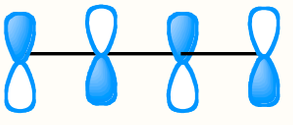
4. Shade MOs to reflect node assignment in step 3.
5. Determine # of electrons in π-system. Place those electrons into MO according to Hund, Pauli & Aufbau principles.

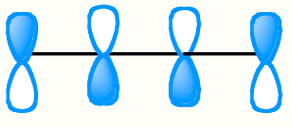


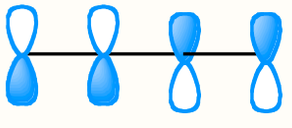


A. 

B. 

C. 

D. 

E. 

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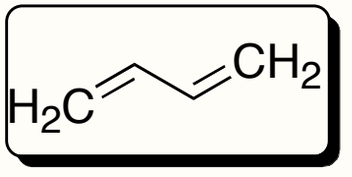
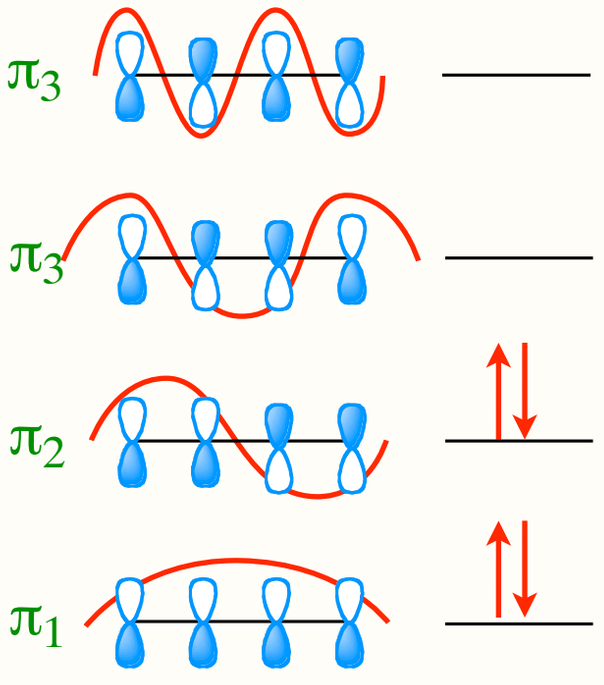
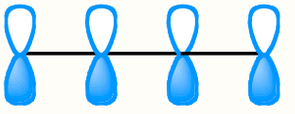
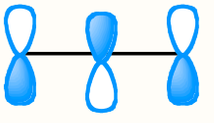
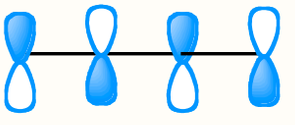
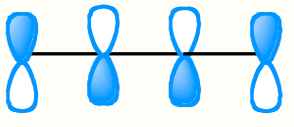


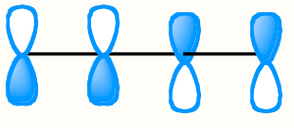


A. 

B. 

C. 

D. 

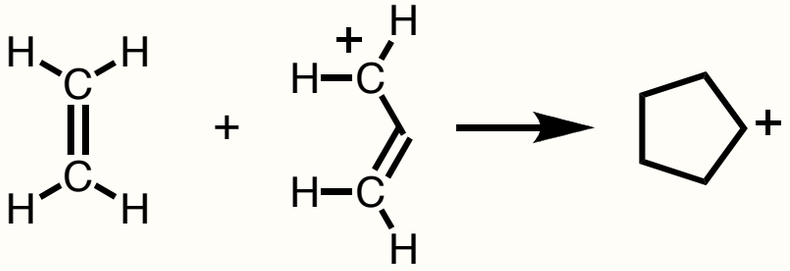
E. 

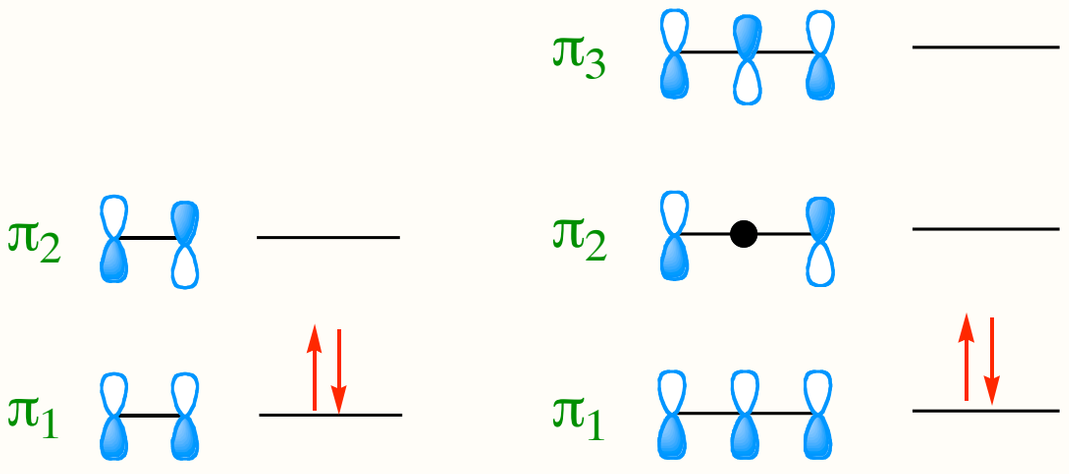
Self Test Question

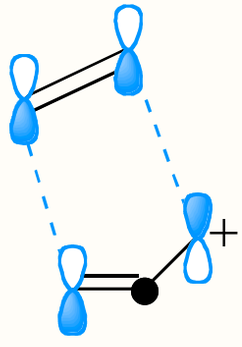
Using FMO theory, determine whether the cycloaddition drawn is symmetry-allowed or symmetry-forbidden? *Hint: draw the LUMO of the allylic carbocation and the HOMO of ethylene.*

A. symmetry-allowed

B. symmetry-forbidden

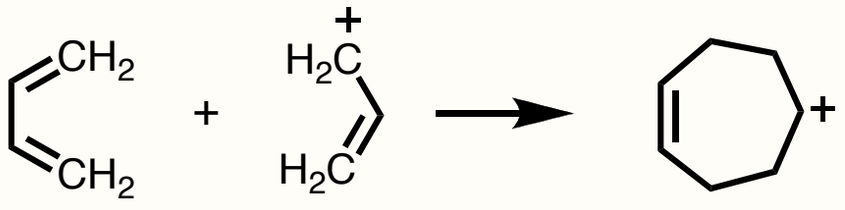






Self Test Question

Using FMO theory, determine whether the cycloaddition drawn is symmetrically-allowed or symmetry-forbidden. *Hint: draw the LUMO of the allylic carbocation and the HOMO of 1,3-butadiene.*



A. symmetry-allowed
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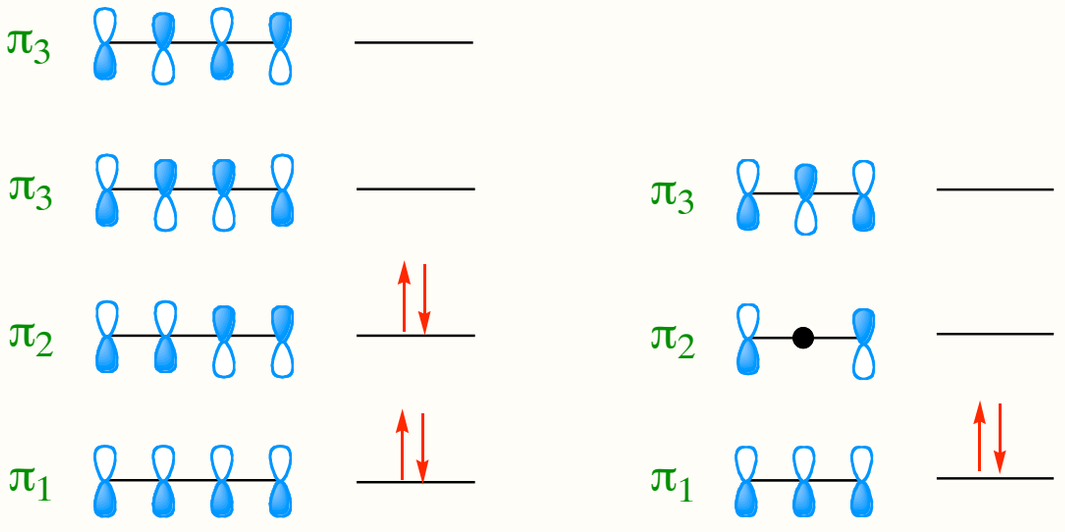
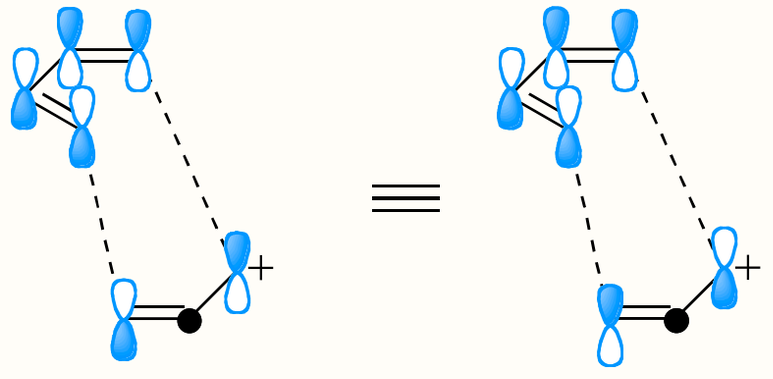
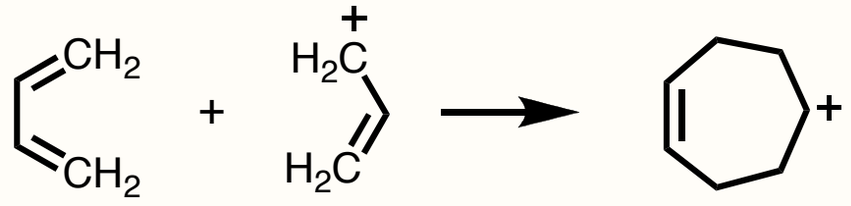




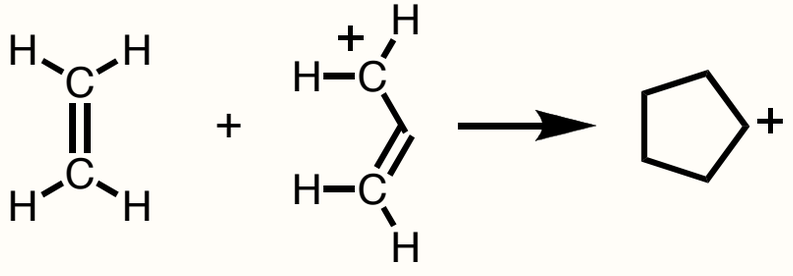
Thermally Allowed Cycloadditions

Cycloadditions are allowed under thermal conditions (no light) if the total number of π-electrons = 4n+2 (n = integer)



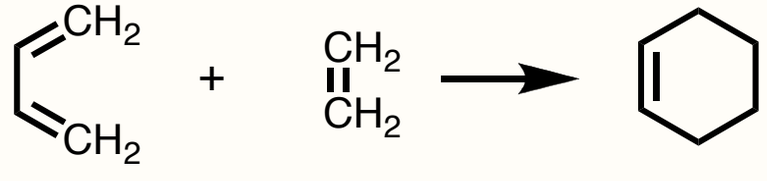
6 Π-electrons

√ allowed



4 Π-electrons

X forbidden

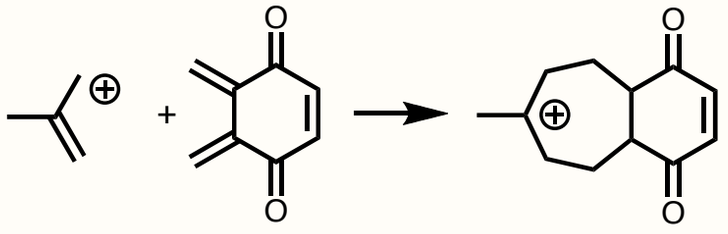


6 Π-electrons

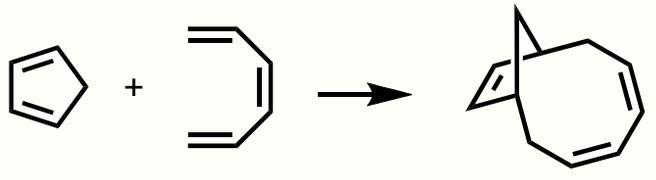
√ allowed

Self Test Question

Which of the following cycloadditions is *not* symmetry-allowed?

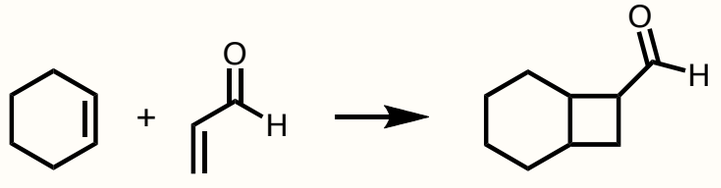
A 

6 Π-electrons

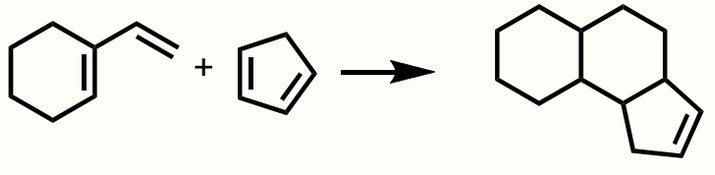
B 

10 Π-electrons

Only consider the π-electrons that are involved in the reaction!

C 

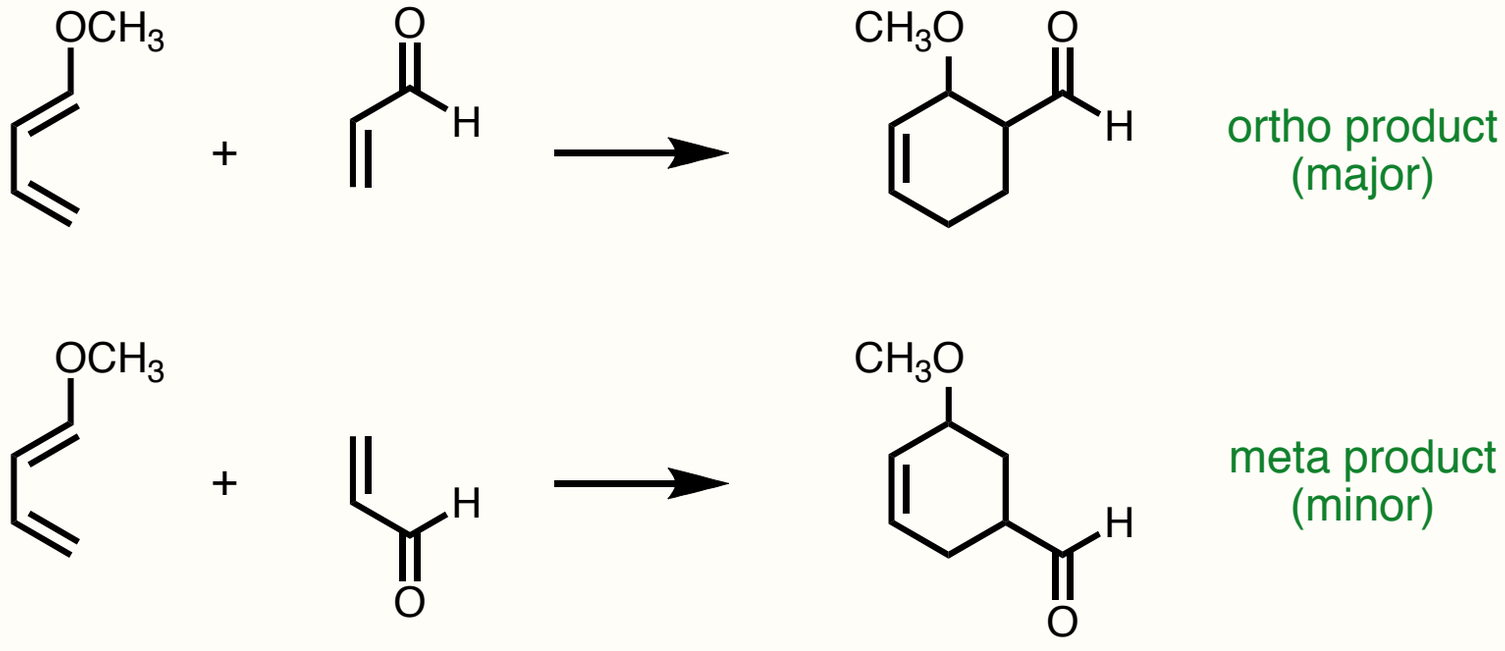
4 Π-electrons

D 

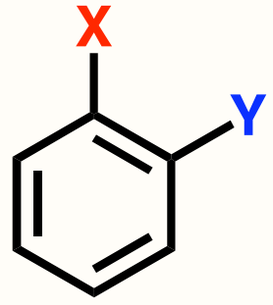
6 Π-electrons

Diels-Alder Reaction is Regioselective

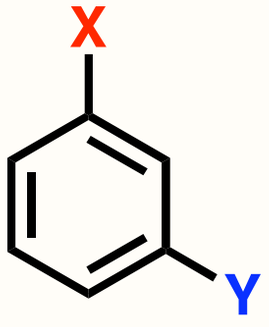
For 1-substituted dienes and monosubstituted dienophiles, the major products are *ortho*



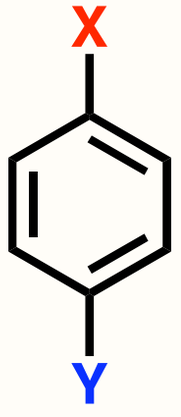
Ortho, Meta & Para ?



Ortho
(1,2-relationship)



Meta
(1,3-relationship)

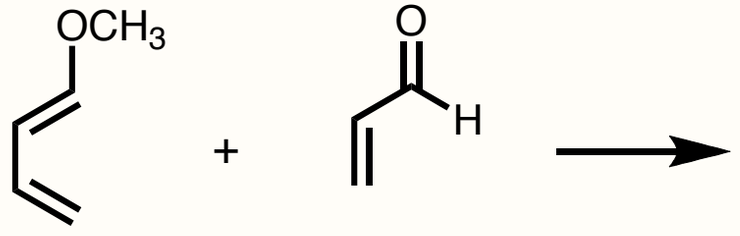


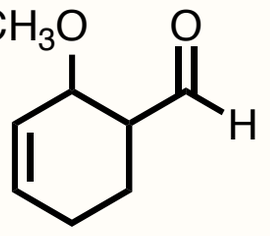
Para
(1,4-relationship)

ortho: 1,2-substituted groups on a six-membered ring (adjacent)
meta: 1,3-substituted groups on a six-membered ring
para: 1,4-substituted groups on a six-membered ring (opposite)

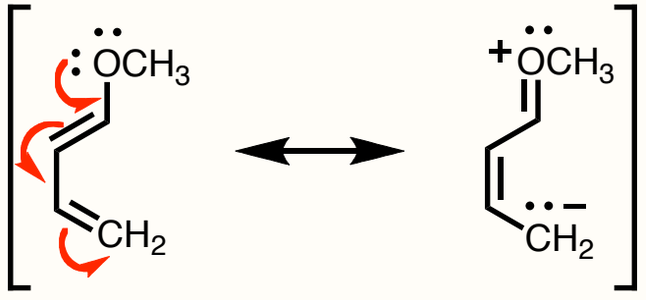
Diels-Alder Reaction is Regioselective

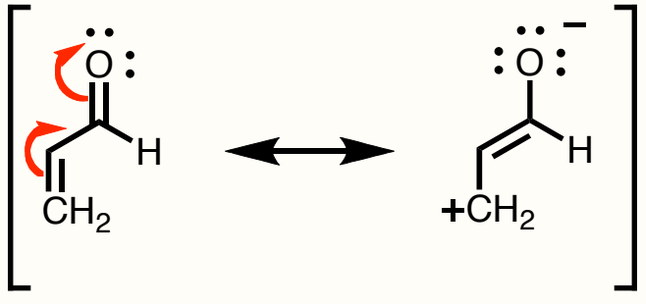
For 1-substituted dienes and monosubstituted dienophiles, the major products are *ortho*

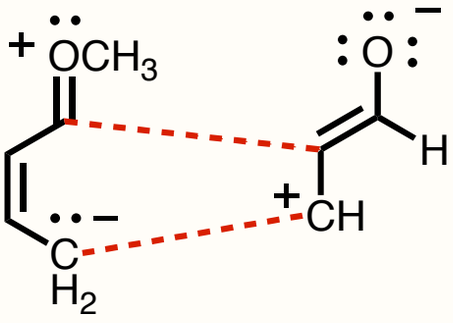




ortho product (major)



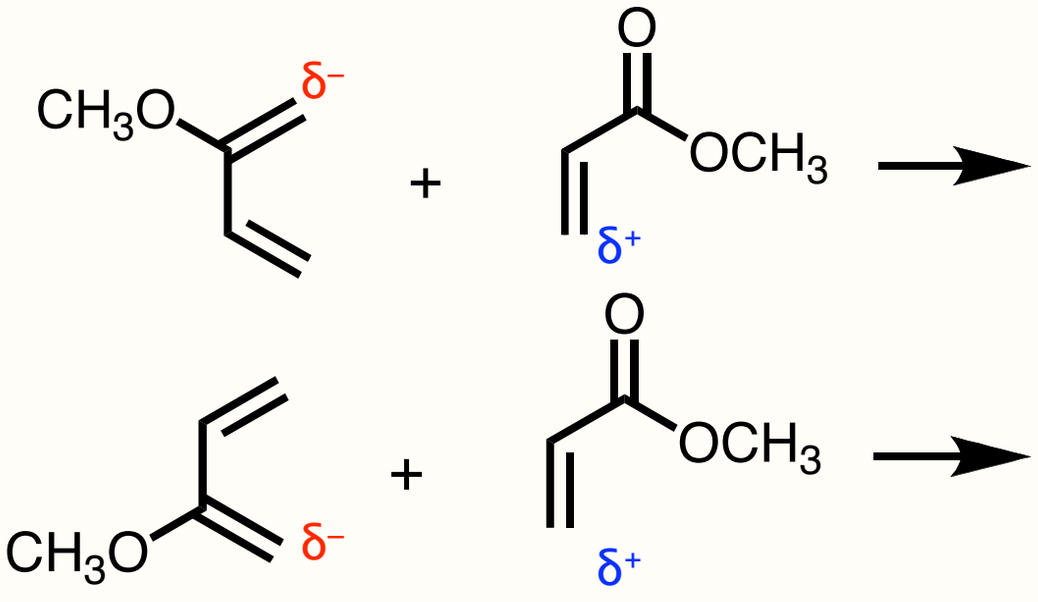




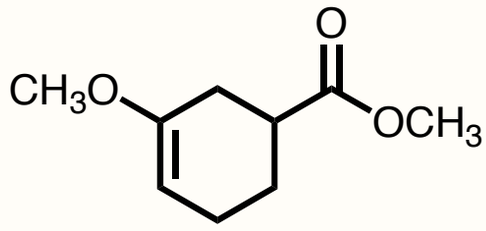
strongest interactions are between partially positively charged B-carbon on dienophile and partially negatively charged C-4 carbon on diene.

Self Test Question

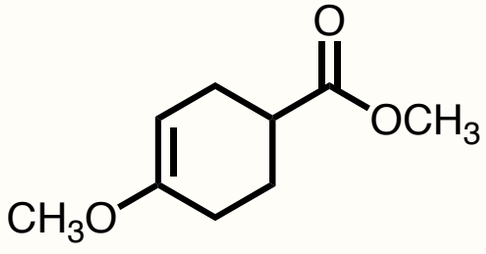
A different pattern is evident with 2-substituted dienes. Predict the product.



A



B



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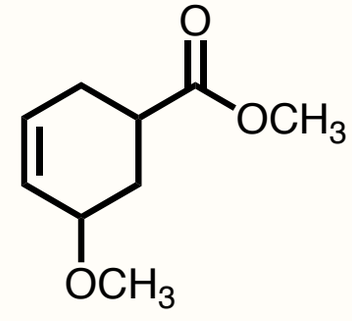
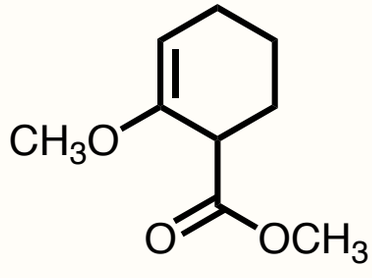
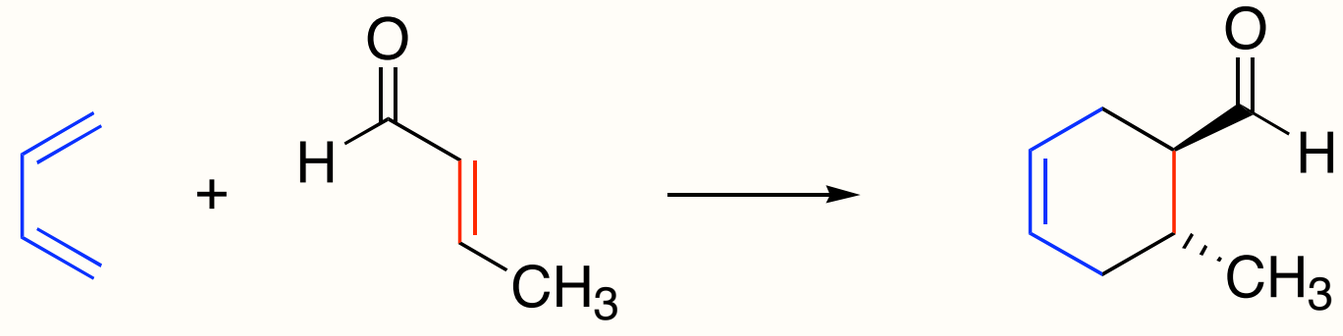


D



Diels-Alder Reaction is Stereospecific

Diels-Alder reaction is **stereospecific** (the stereoisomeric product formed depends on the stereoisomer of the reactant).



diene dienophile Diels-Alder adduct

Substituents that are *trans* on the dienophile are also *trans* in the Diels-Alder adduct.

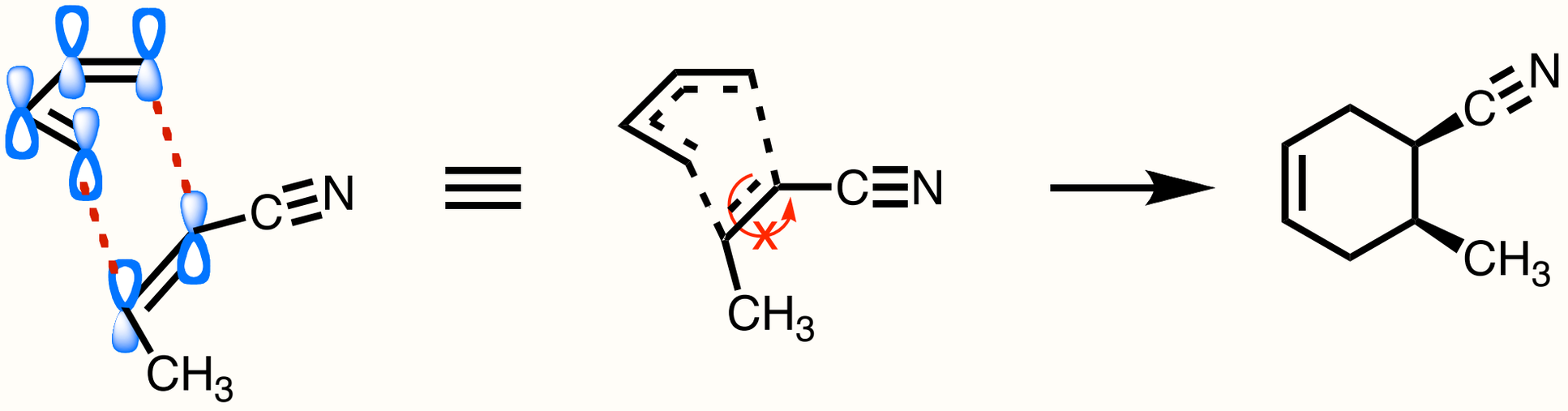
Diels-Alder Reaction is Stereospecific

Diels-Alder reaction is **stereospecific** (the stereoisomeric product formed depends on the stereoisomer of the reactant).

diene dienophile Diels-Alder adduct

Substituents that are *cis* on the dienophile are also *cis* in the Diels-Alder adduct.

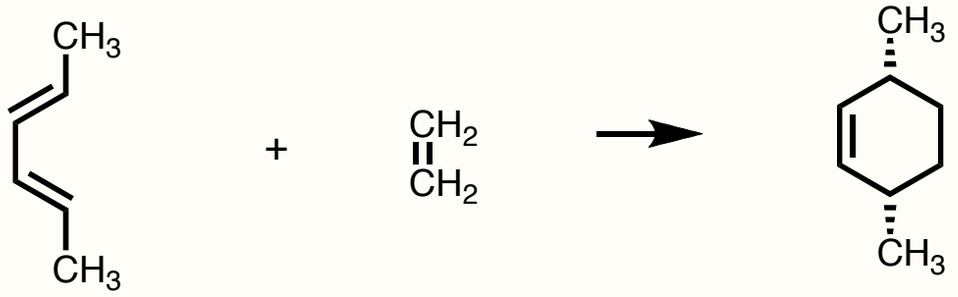
Diels-Alder Reaction is Stereospecific

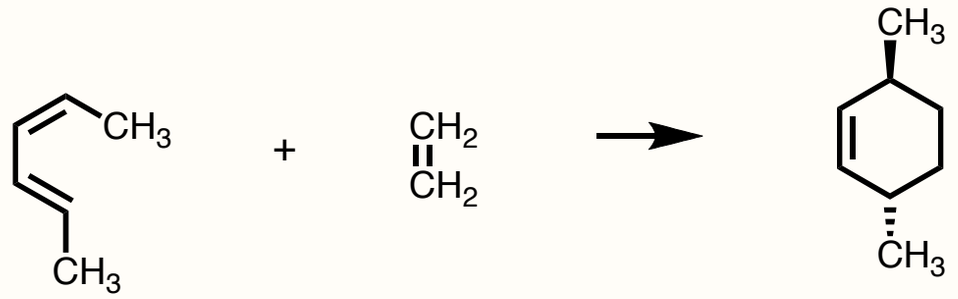


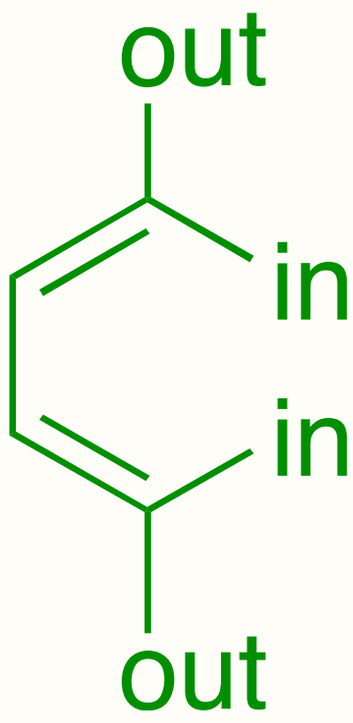
- to form new bonds, p-orbitals of diene overlap with p-orbitals of dienophile
- both bonds are being formed at the same time
- cannot rotate around dienophile bond =
- relationships of groups don't change

Diels-Alder Reaction is Stereospecific

A similar stereospecificity is observed for the diene. *Out* groups are *cis* to each other in the product; likewise *In* groups are *cis* to each other in the prodcut. *Out* & *In* = *trans*.

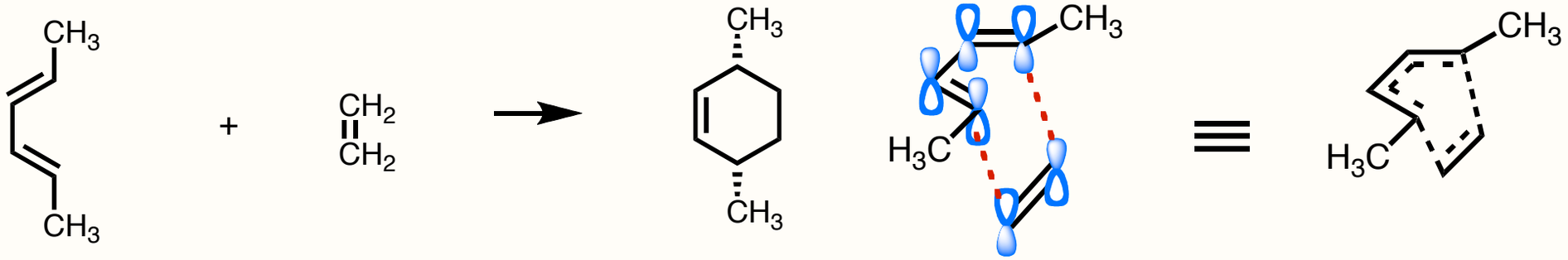


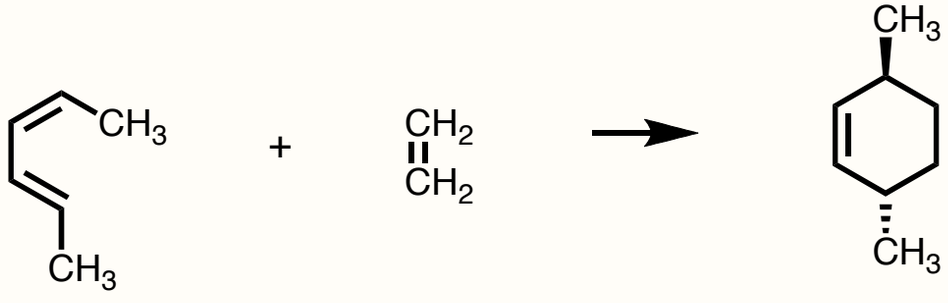




Diels-Alder Reaction is Stereospecific

A similar stereospecificity is observed for the diene. *Out* groups are *cis* to each other in the product; likewise *In* groups are *cis* to each other in the prodcut. *Out* & *In* = *trans*.

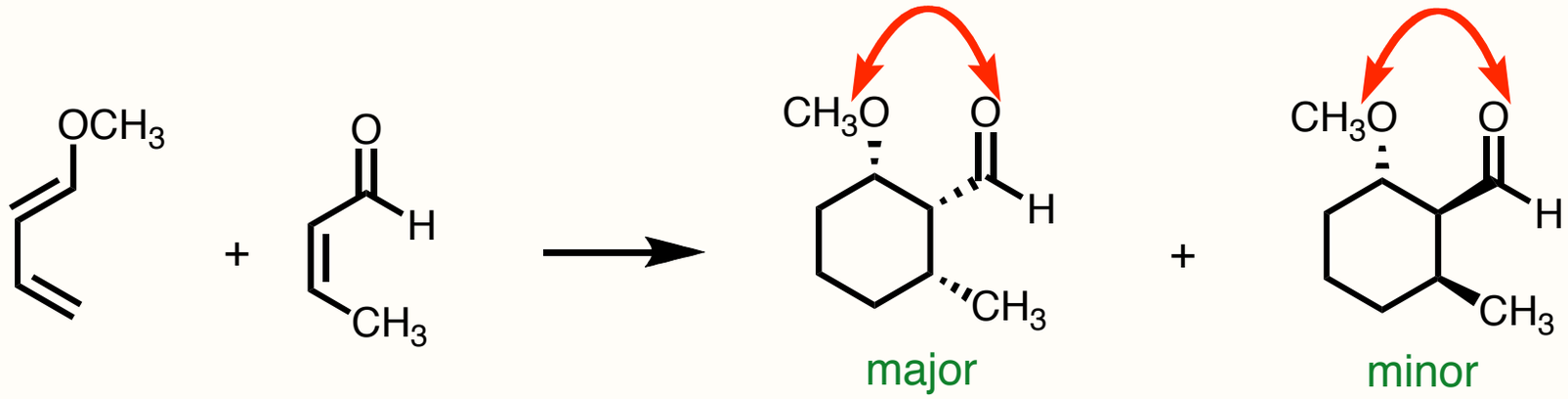




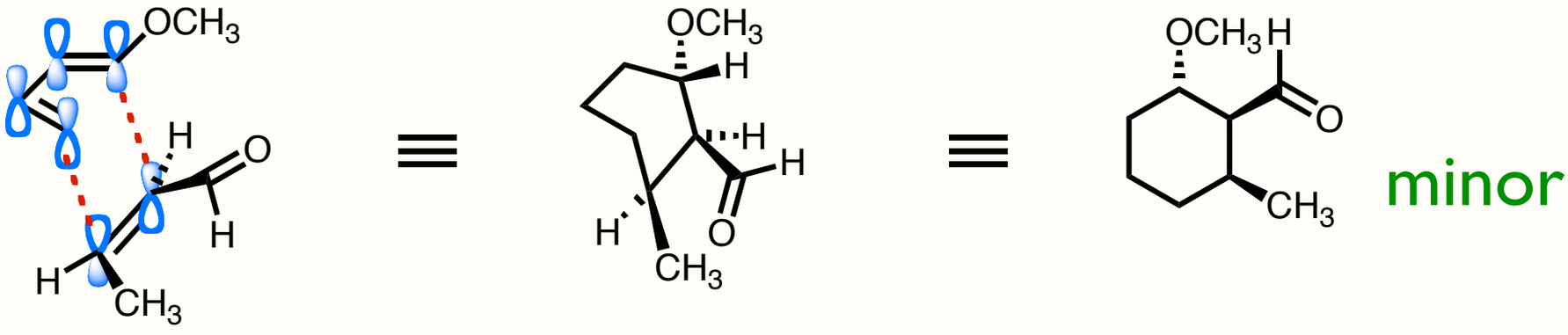
Because all bonding forming/ breaking is concerted, there is no opportunity to rotate around single bonds to change relative positions.

Endo Selectivity

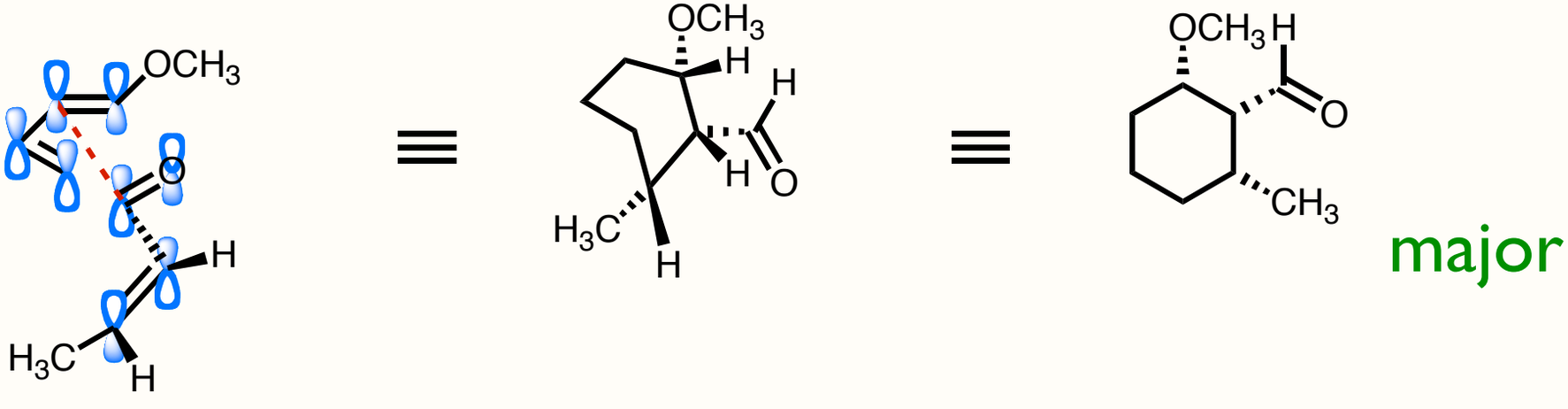
How do we explain the preference for relative stereochemistry between groups on the diene and groups on the dienophile?



Endo Selectivity

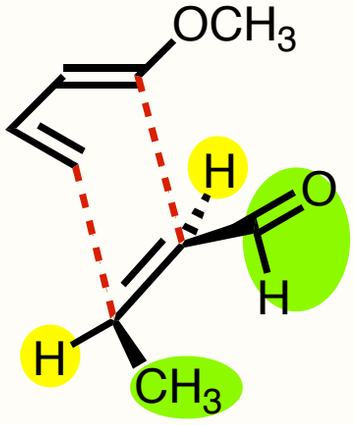


minor



major

Endo Selectivity



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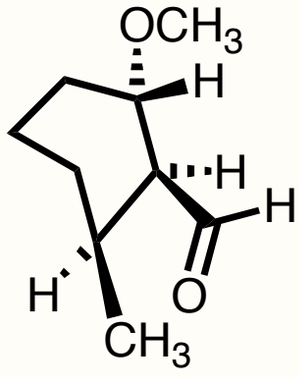

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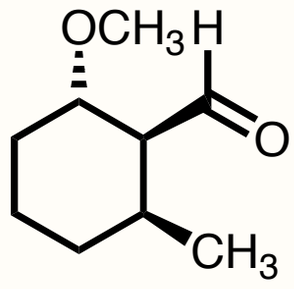

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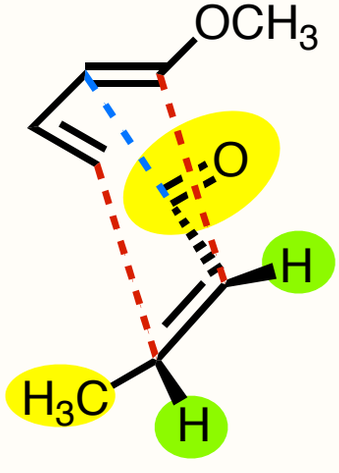

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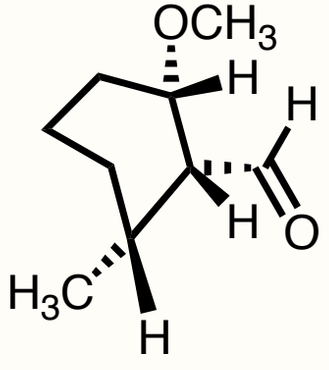

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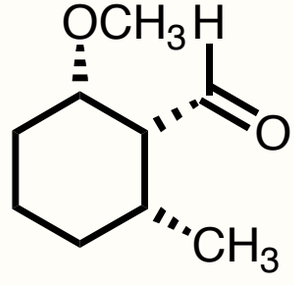
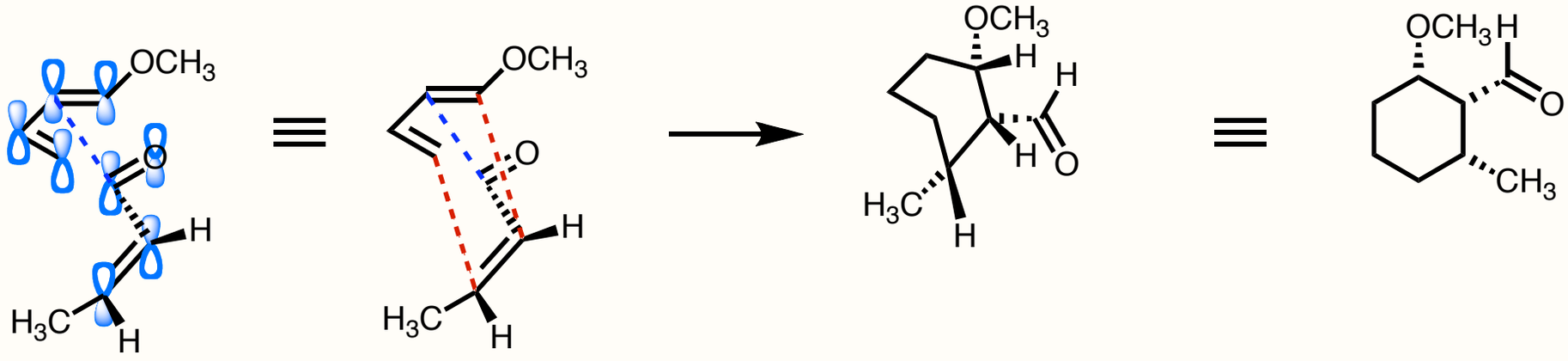


major

endo: inside (underneath diene)

exo: outside (outside of diene)

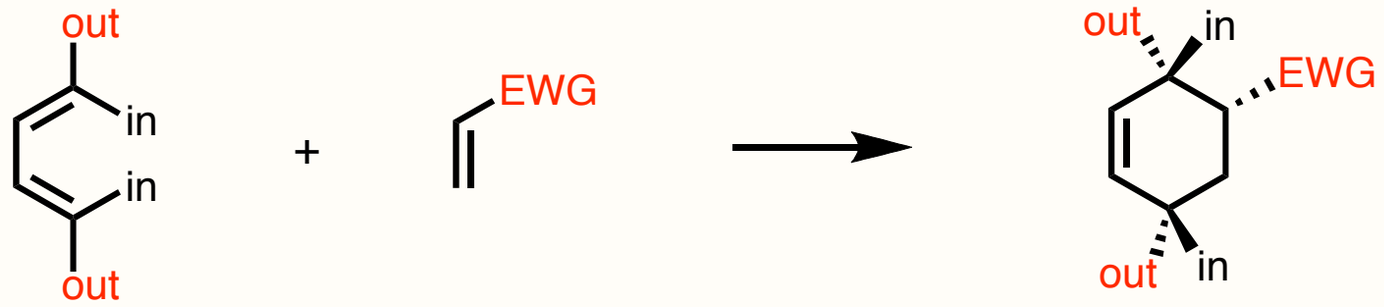
Endo Selectivity



- There is a preference (lower energy TS) for an *endo* relationship between EWGs with pi-systems and the diene
- The p-orbitals of the *endo* EWG interact favorably (stabilize TS) with the p-orbitals of the diene

Out-Endo-Cis Rule

Out-Endo-Cis Rule: the *out* groups on the diene and *endo* EWG are *cis* in the product.



All other stereochemical relationships already discussed remain the same (i.e. groups that are *cis* in the dienophile are *cis* in the product).

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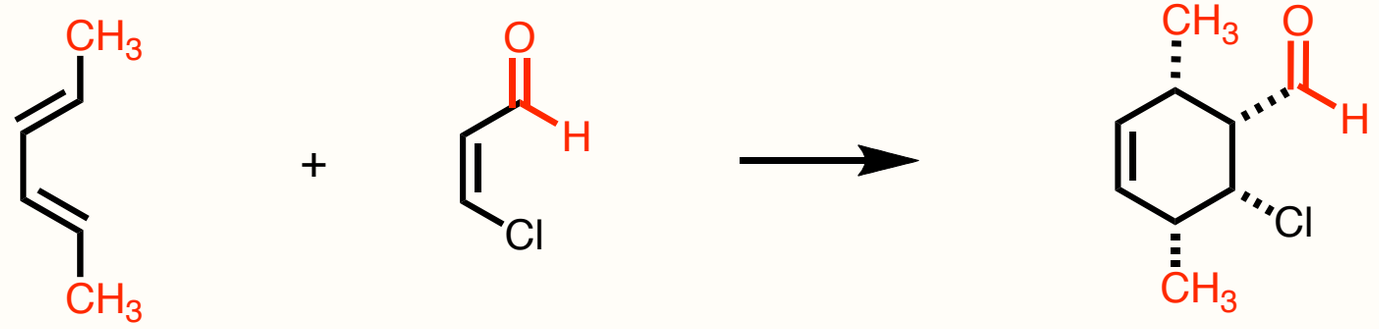

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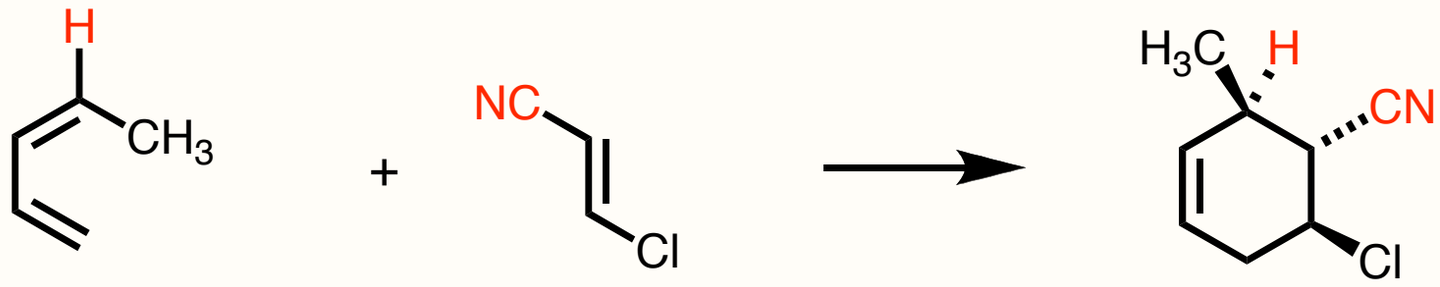
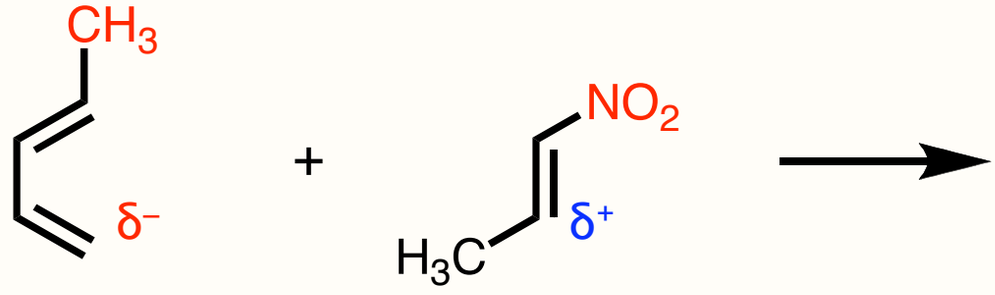
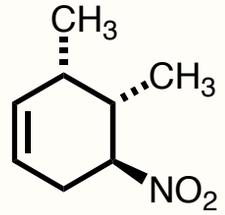


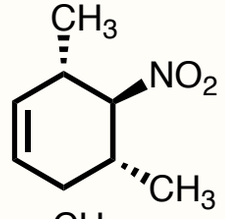
All other stereochemical relationships already discussed remain the same (i.e. groups that are *cis* in the dienophile are *cis* in the product).

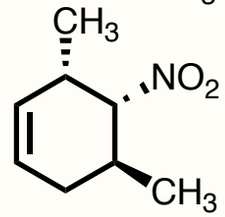
Self Test Question

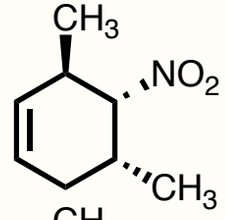
Predict the Diels-Alder adduct when *trans*-1,3-pentadiene reacts with *trans*-1-nitropropene.

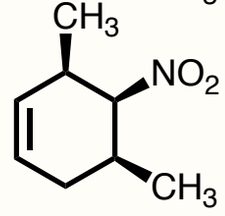


A 

B 

C 

D 

E 

Next Lecture...

Chapter 11: Sections 11.1-11.9

Quiz This Week. . .

1a. Predict the Diels-Alder adduct, including correct regiochemistry & stereochemistry (10 pts)

1b. Synthesis problem involving Diels-Alder reaction (10 pts)

2. Draw the MO diagram for 1,3-butadiene (shown on Slide 12) (5 pts)