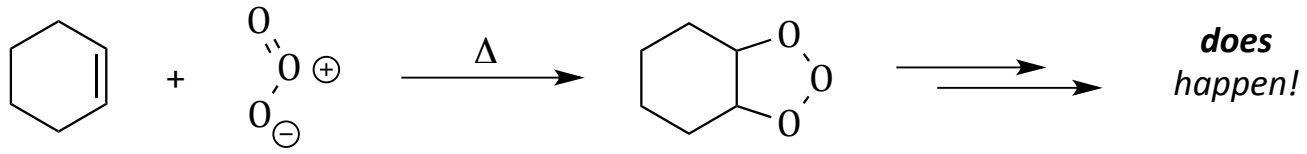
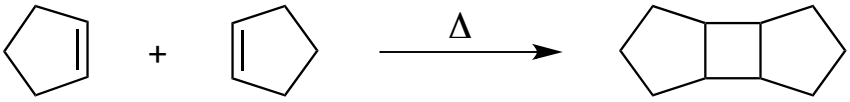
Pericyclic Reactions 1:
Cycloadditions

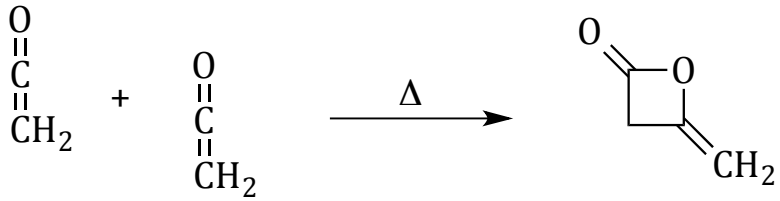
For each of the following "Diels-Alder-like" reactions, draw the curved-arrow mechanism.



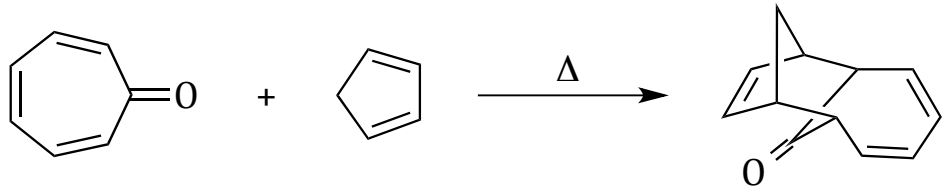
does *happen!*



does NOT *happen!*



does *happen!*



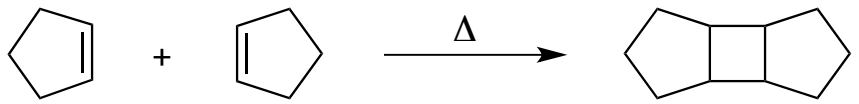
does *happen!*

Why do some reactions happen and others don't? Look at the ***frontier molecular orbitals…***

Reading: Section 27.3

Cycloadditions:
[2s + 2s]

Consider the following seemingly plausible reaction. Why doesn't it happen?



does NOT *happen!*

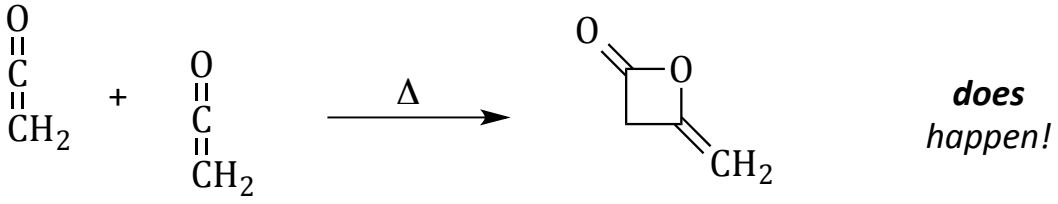
How can we *make* it happen? Change the frontier orbitals!

Thus, we observe that [2s + 2s] cycloadditions are **thermally forbidden** but **photochemically allowed.**

Reading: Section 27.3

Cycloadditions:
[2s + 2a]

Having said that [2s + 2s] cycloadditions are thermally forbidden, how can we explain the following *observed* reaction?



does *happen!*

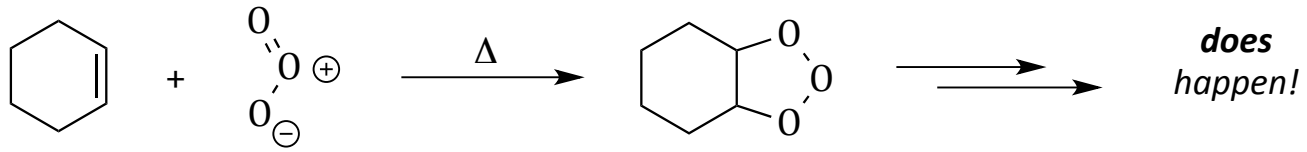
What are the requirements for **antarafacial** cycloadditions?

Reading: Section 27.3

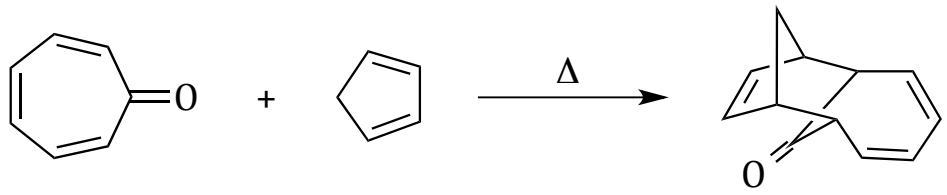
Cycloadditions:
Putting it Together

Summarize the *selection rules* for cycloadditions:

Now analyze the following cycloadditions:



does *happen!*

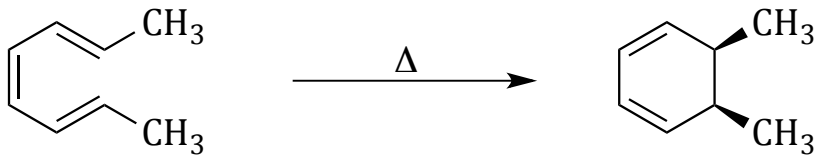


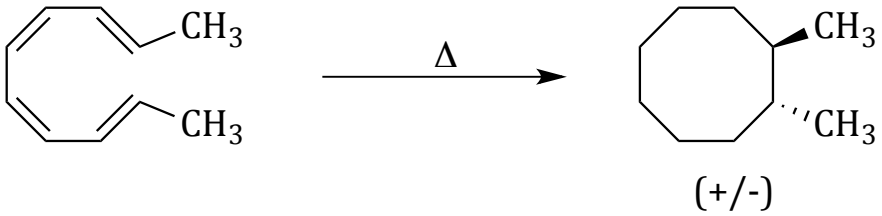
does *happen!*

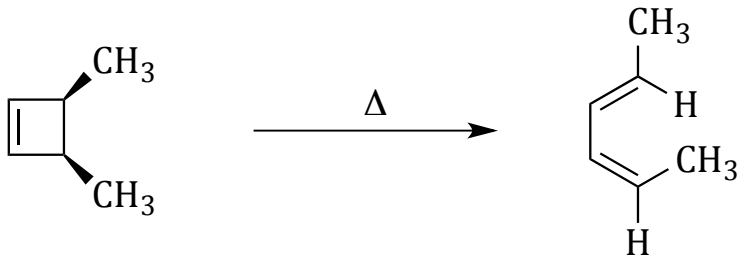
Reading: Section 27.3

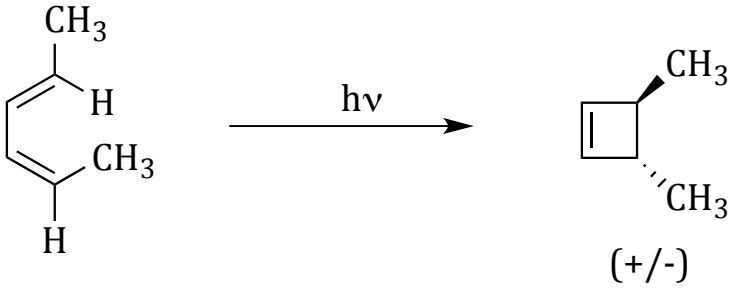
Pericyclic Reactions 2:
Electrocyclic Ring-Closing & Ring-Opening

Show the curved arrows for the following **electrocyclic reactions:**







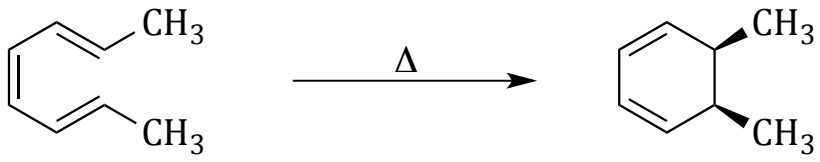


How can we explain the **stereochemistry**? Look at the **frontier molecular orbitals!**

Reading: Section 27.2

Electrocyclic Ring-Closing:
6 Electrons, Thermal

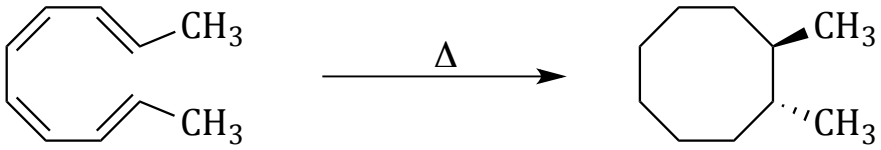
Explain the observed stereochemistry:



Reading: Section 27.2

Electrocyclic Ring-Closing:
8 Electrons, Thermal

Explain the observed stereochemistry:

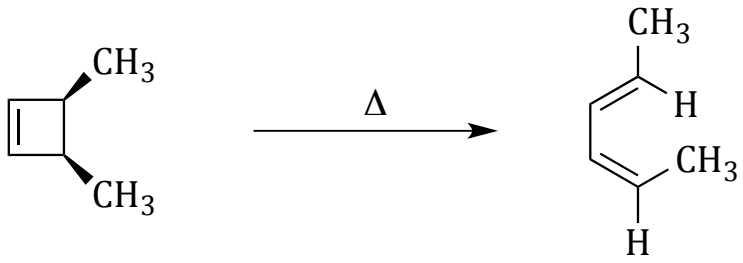


(+/-)

Reading: Section 27.2

Electrocyclic Ring-Opening:
4 Electrons, Thermal

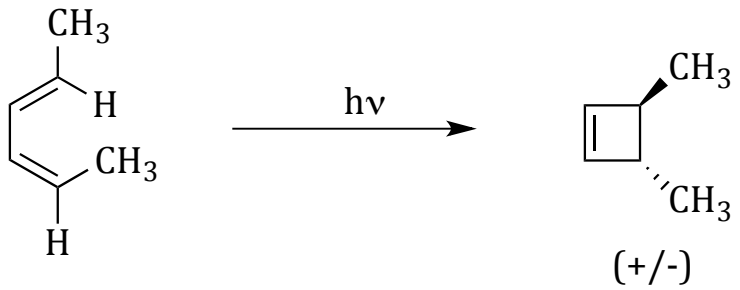
Explain the observed stereochemistry:



Reading: Section 27.2

Electrocyclic Ring-Closing:
4 Electrons, Photochemical

Explain the observed stereochemistry:



(+/-)

Reading: Section 27.2

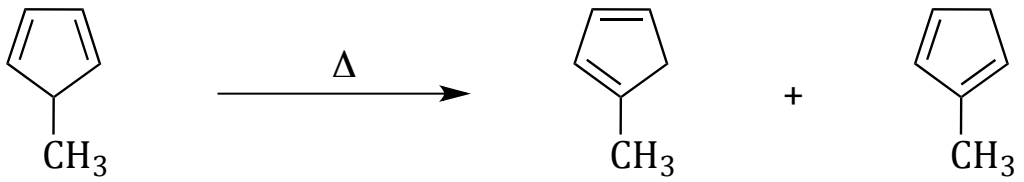
Electrocyclic Reactions:
Putting It Together

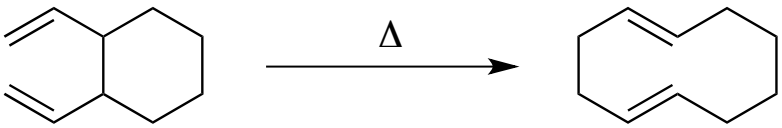
Summarize the *selection rules* for electrocyclic reactions:

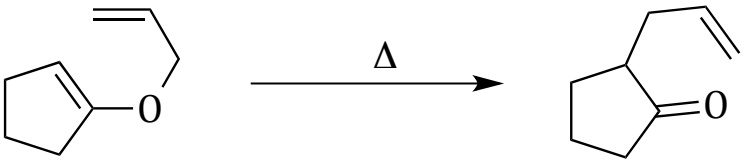
Reading: Section 27.2

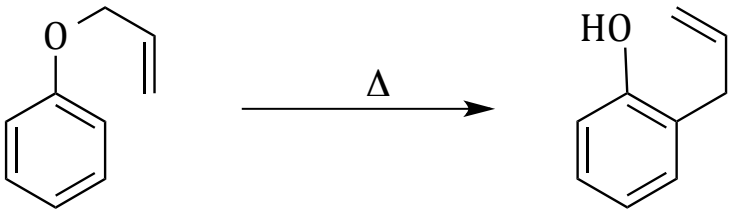
Pericyclic Reactions 3:
Sigmatropic Rearrangements

Show the curved arrows for the following reactions:





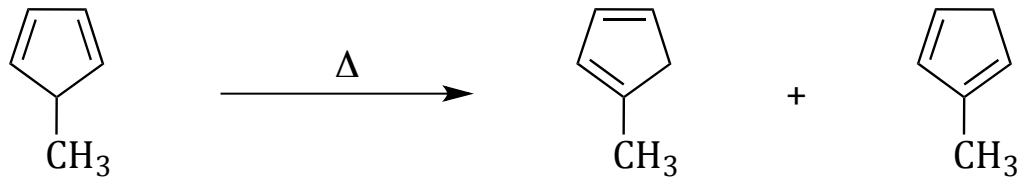




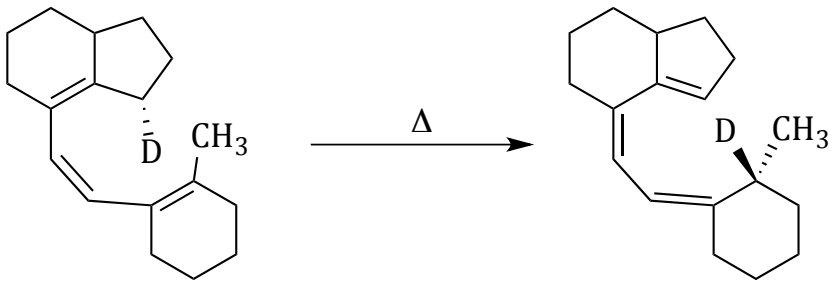
Reading: Section 27.4

Sigmatropic Rearrangements:
[1,n] & Stereochemistry

The following rearrangement is *suprafacial*. Why?



The following rearrangement is *antarafacial*. Why?

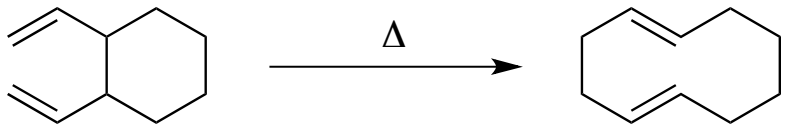


Reading: Section 27.4

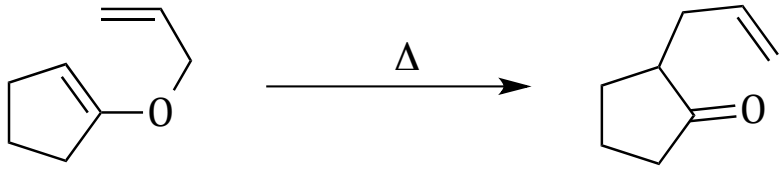
Sigmatropic Rearrangements:
MOs in [3,3] rearrangements

How can we understand the orbitals involved in the following rearrangements?

The *Cope Rearrangement:*



The *Claisen Rearrangement:*

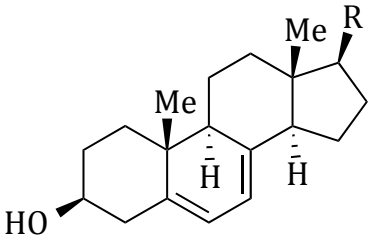


Reading: Section 27.4

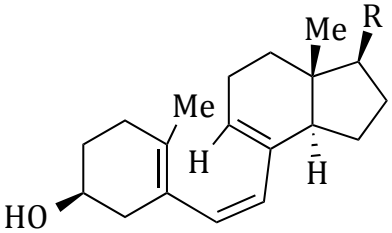
Sigmatropic Rearrangements:
Putting it Together

Summarize the *selection rules* for sigmatropic rearrangements:

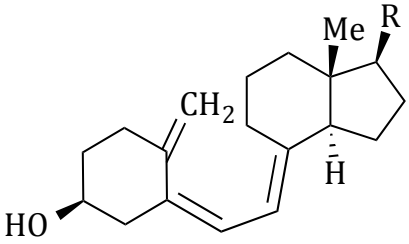
Let's examine the biosynthesis of Vitamin D. Why is sunlight required?



7-dehydrocholesterol



previtamin D_3



vitamin D_3

Reading: Section 27.7