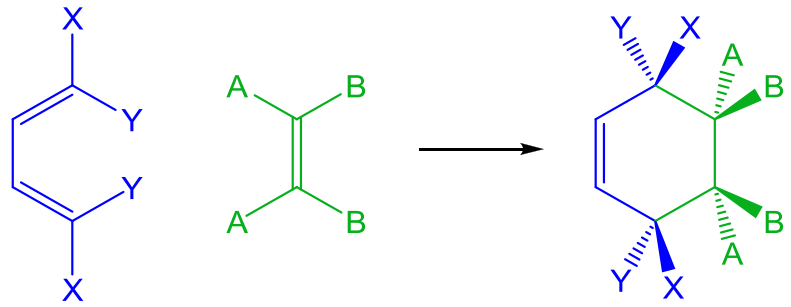
CHEM 342 – Lecture 7 29/01/15

Overheads: - Today's Outline

Quiz 2:

Recap Thursday: Diels-Alder Reaction

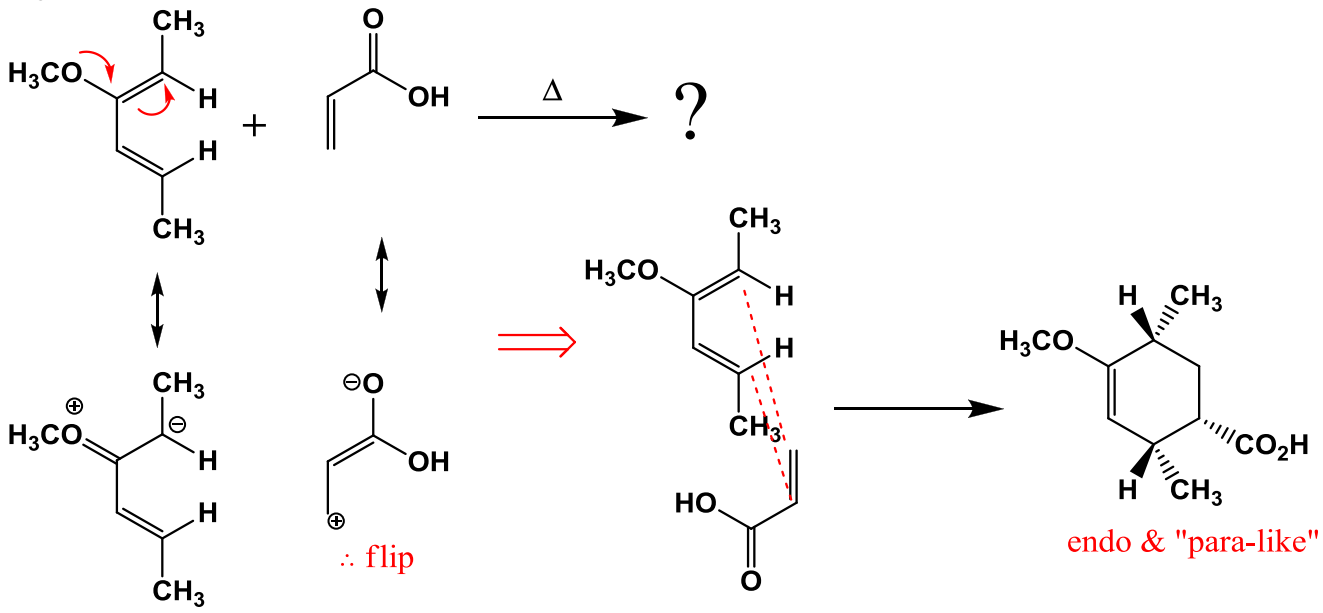


endo rule:
big groups go "under" the C=C

ins → cis cis → cis
outs → cis trans → trans

Regiochemistry: generally get "ortho/para-like" products.

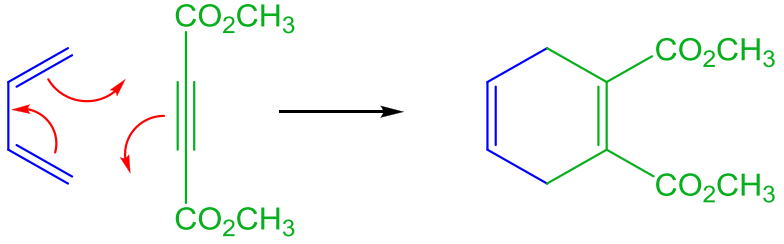
Try:



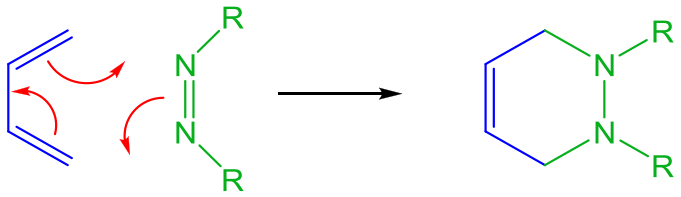
Other examples of cycloadditions [4+2]:

Dieneophiles:

- can be triple bonds:

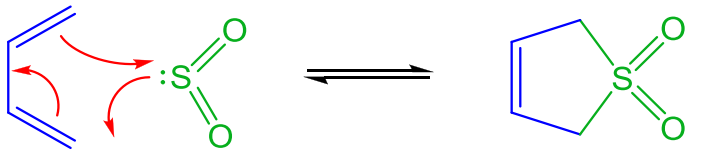


- can have other atoms:



Cheletropic Cycloaddition:

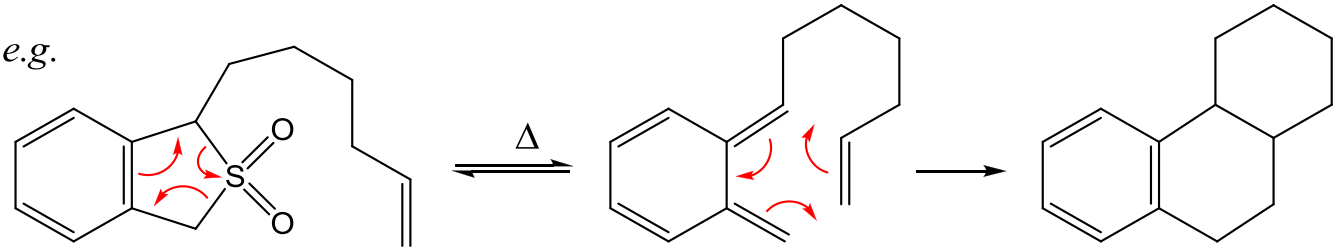
- both new π bonds formed to same atom



butadiene ⇓ flammable gas

butadiene sulfone ⇓ white solid - stable, easy to store, cheap!
- can be used to generate butadiene in reaction

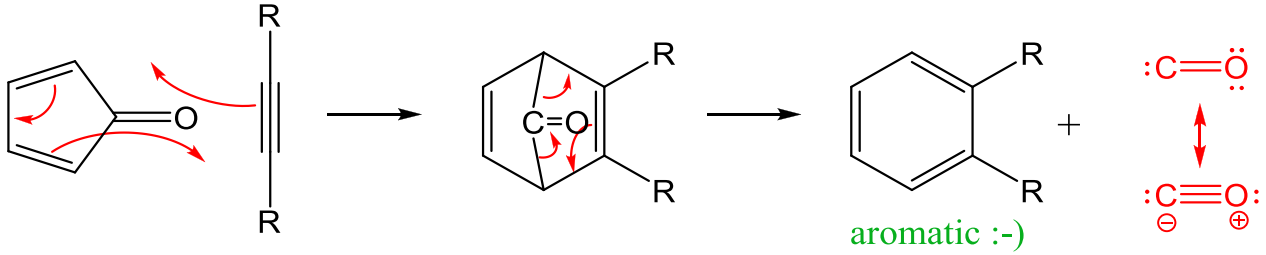
e.g.



intramolecular Diels-Alder

- makes 2 new rings!
- part of steroid skeleton

Another example: (similar to lab #8)



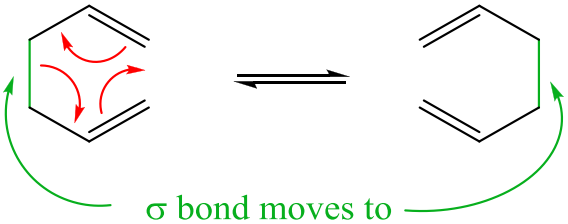
aromatic :-)

Recap Pericyclic Reactions so far: Woodward-Hoffman Rules

Electrocyclic:	4n / even	Δ	= con
		hν	= dis
	4n+2 / odd	Δ	= dis
		hν	= con
Cycloaddition:	4n / even	Δ	= antara
		hν	= supra
	4n+2 / odd	Δ	= supra
		hν	= antara

Sigmatropic Rearrangements:

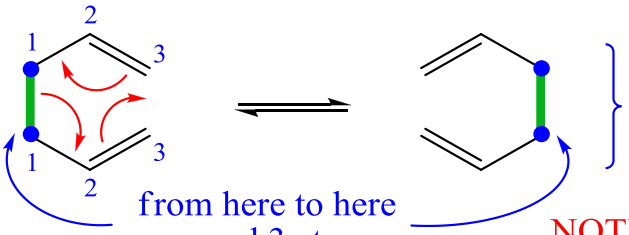
- σ bond changes position



- similar to electrocyclic, but not fully conjugated (db on ends only)

Numbering/naming system:

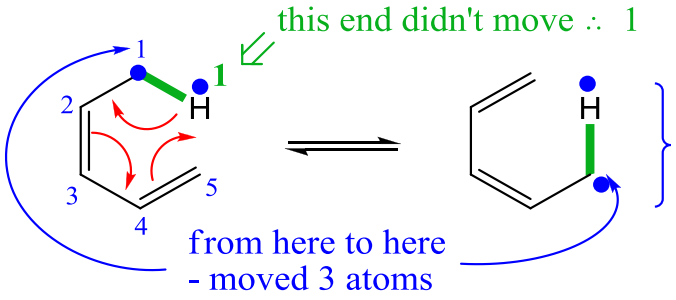
- Numbered according to how far σ bond has moved on each end



[3,3] sigmatropic rearrangement

NOTICE: 3+3 = 6; total 6 e^- moving (3 pairs)

Another example:



[1,5] sigmatropic rearrangement

(aka 1,5-hydride (H^-) shift)

smaller number first in name

** usually get product that looks similar, but R groups have moved

Woodward-Hoffman Rules

4n+2 / odd	Δ	= supra
	hν	= antara (if goes, is by different mechanism)
4n / even	Δ	= antara
	hν	= supra

***identical rule as for cycloaddition!