Overheads: - Today's Outline

Quiz feedback:

Recap Tuesday:

Woodward-Hoffman Rule for cycloadditions

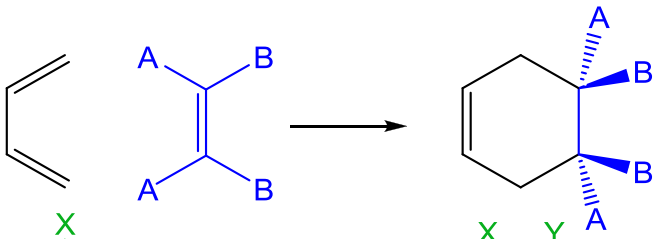
4n π e (even pairs)	Δ	= antarafacial
	hν	= suprafacial
4n+2 π e (odd pairs)	Δ	= suprafacial = Diels-Alder!
	hν	= antarafacial

Stereochemistry of Cycloaddition Reactions:

1) Reaction is concerted – so stereochemistry of reactants is retained

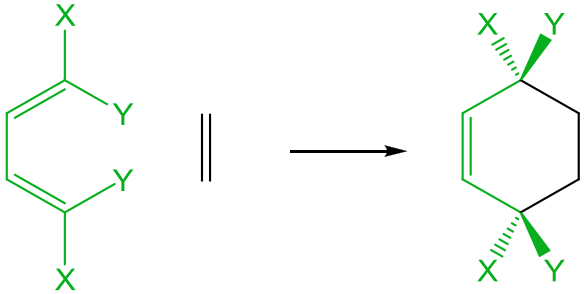
e.g. Diels-Alder

Dienophile:



cis → cis
trans → trans

Diene:

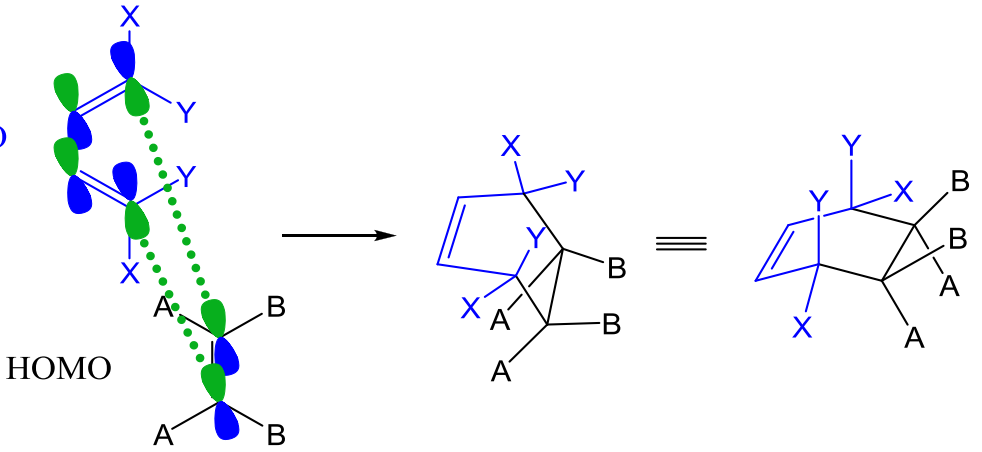


"outs" = x → cis
"ins" = y → cis

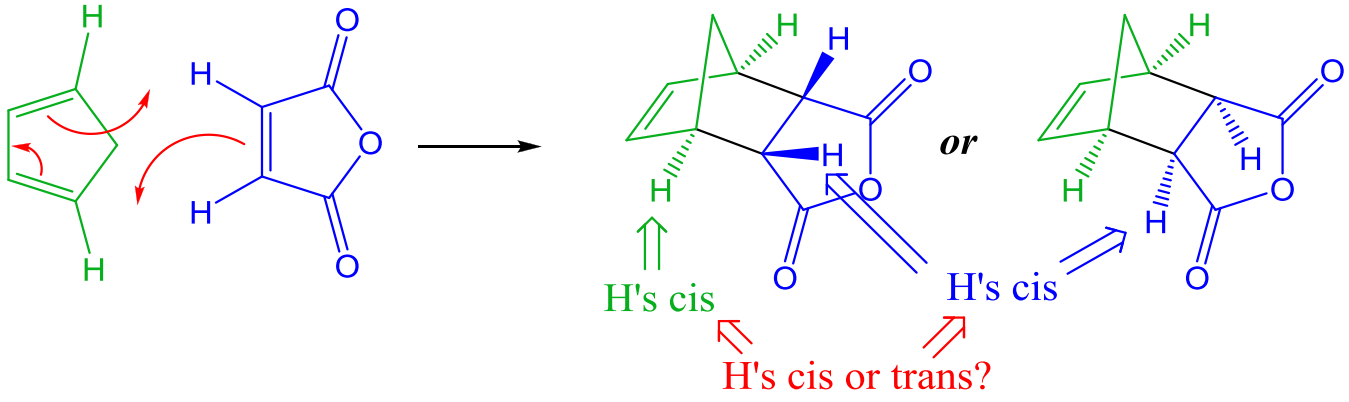
- Product is initially formed in "boat" conformation:

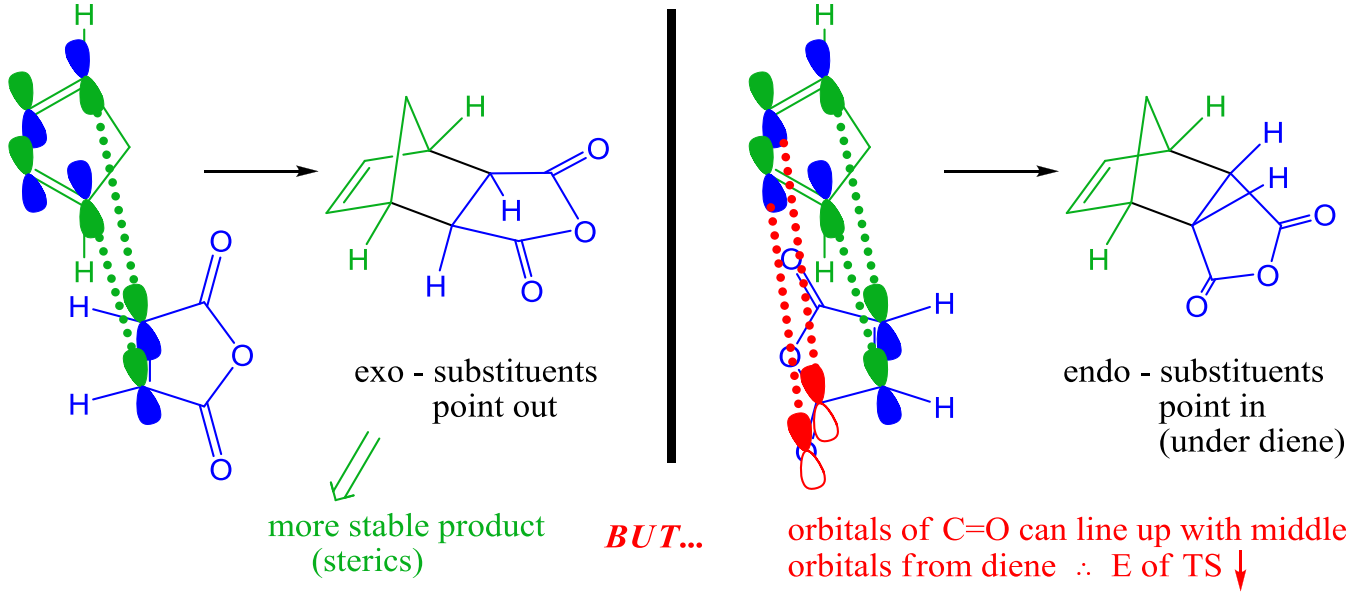
LUMO

HOMO



2) Relative stereochemistry between X/Y and A/B?



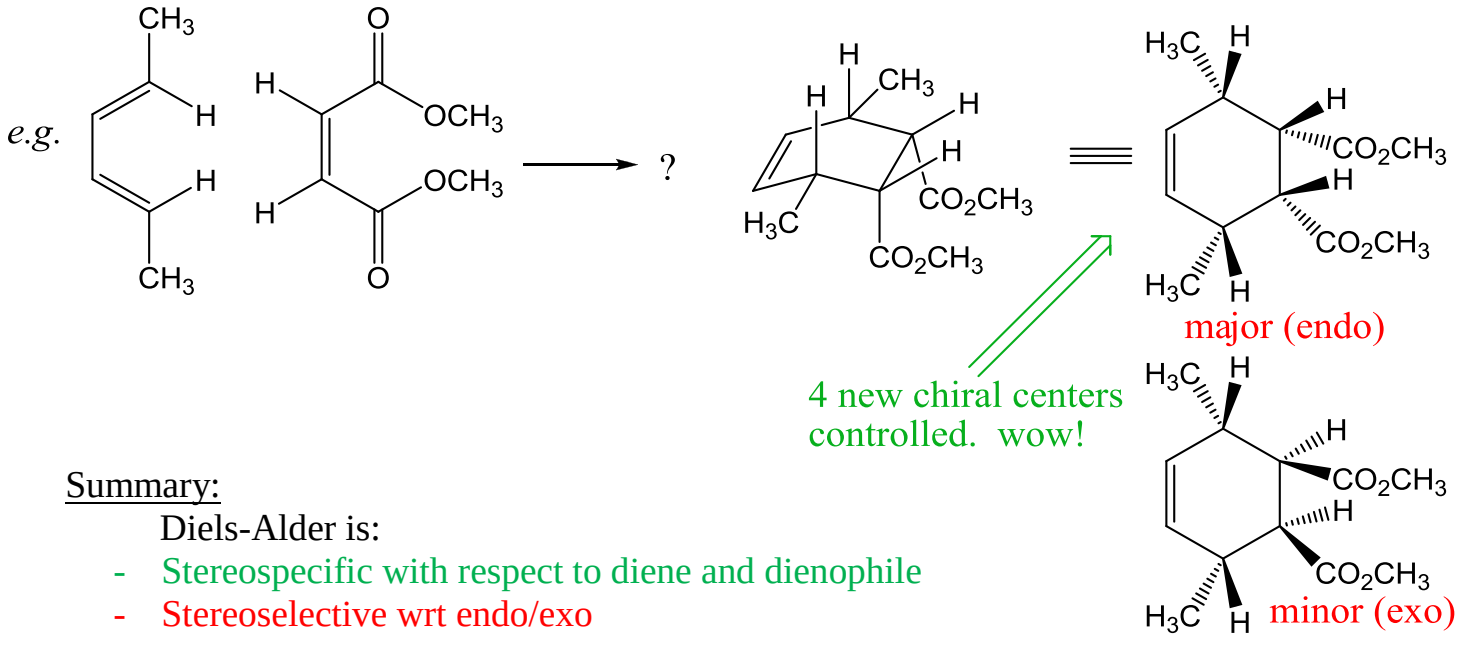


more stable product (sterics)

BUT...

orbitals of C=O can line up with middle orbitals from diene ∴ E of TS ↓

Alder's "endo rule": endo product usually favoured

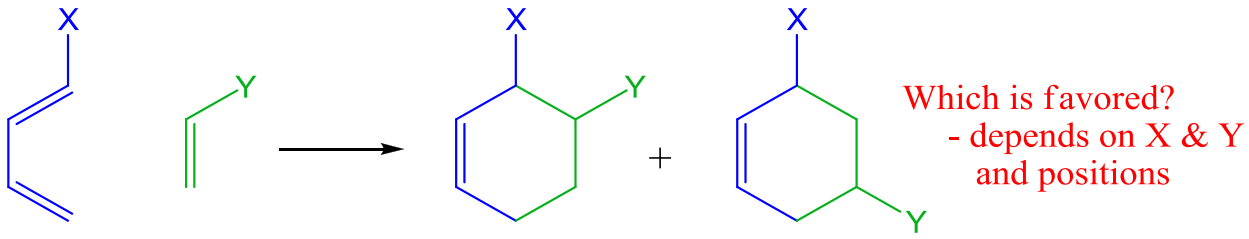


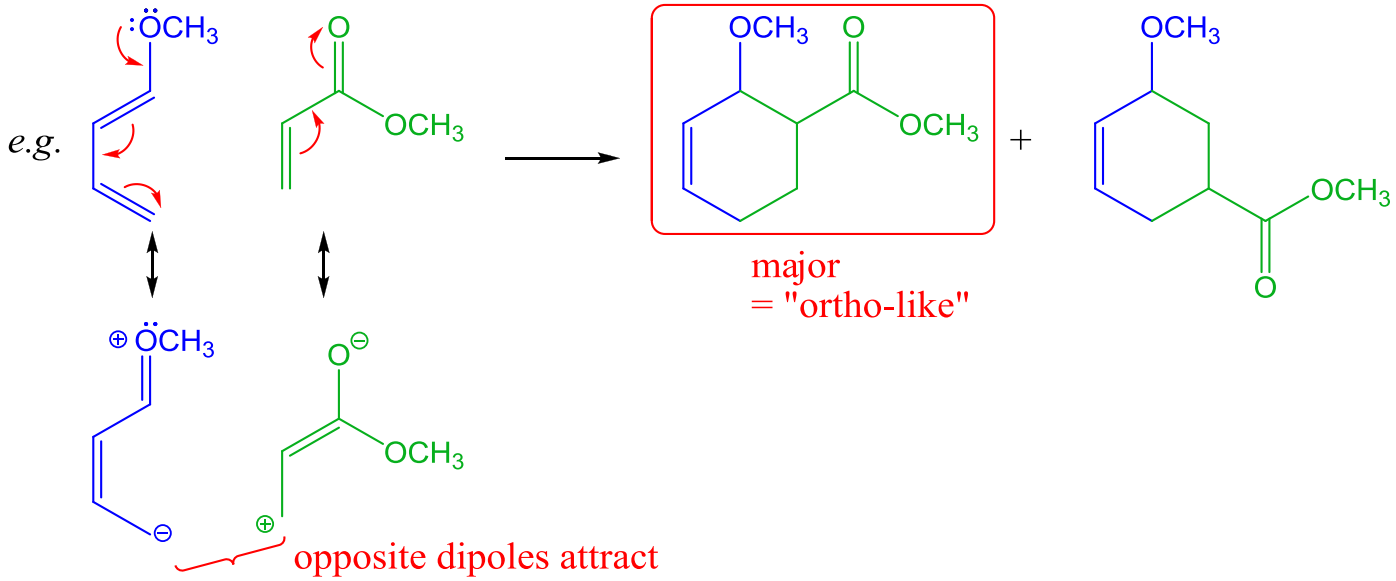
Summary:

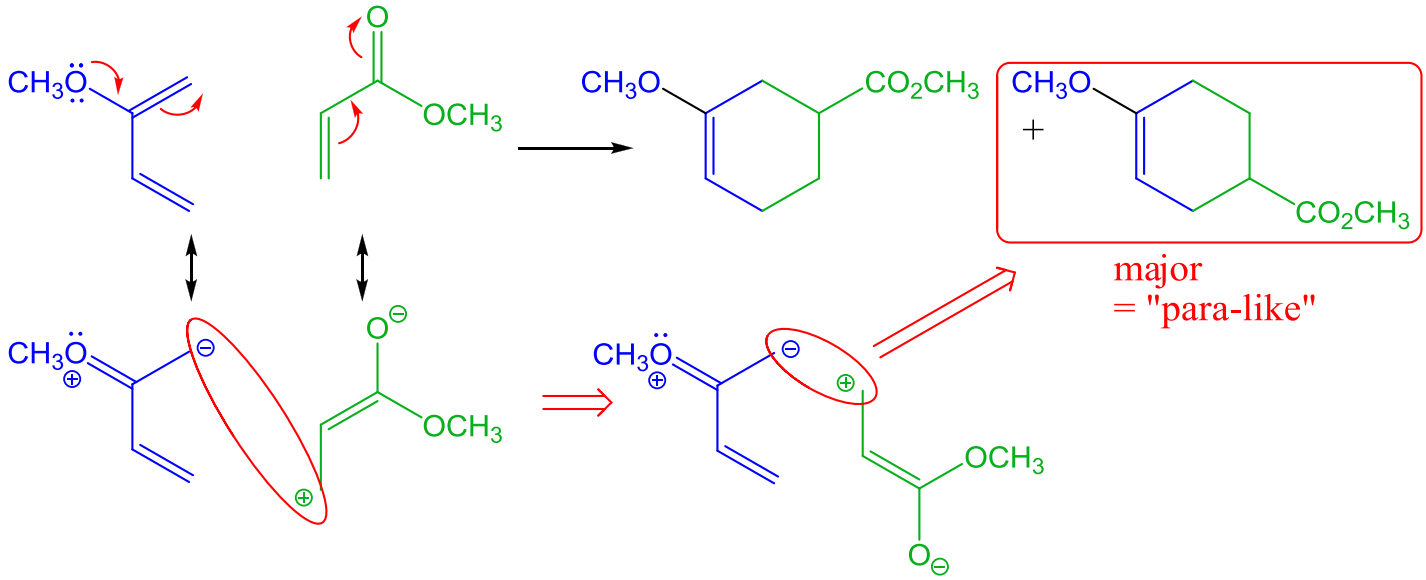
Diels-Alder is:

- Stereospecific with respect to diene and dienophile
- Stereoselective wrt endo/exo

Regiochemistry: what happens when diene and dienophile are not symmetrical?

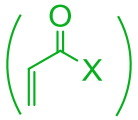






→ generally get "ortho/para-like" products if have electron-donating group matched with electron-withdrawing group.

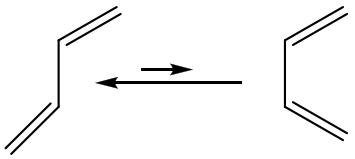
What makes a "good" Diels-Alder?:

(1) Electronwithdrawing group on dienophile 

synergy: δ+ / δ-

(2) Electron-donating group on diene (OR, Ar, R)

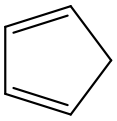
(3) Diene Conformation:***



⟸ only this conformation is pointed right way for Diels-Alder

s-trans ⇑ s-cis ("s" refers to single bond in the middle)

usually major @ equ'm

e.g.  great diene - locked in s-cis