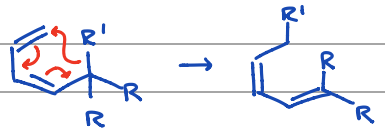
Pericyclic Reaction = a concerted reaction with a cyclic transition state.

↳ Single step rxn with no intermediates

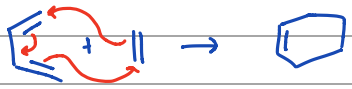
Examples:

1. Electrocyclization

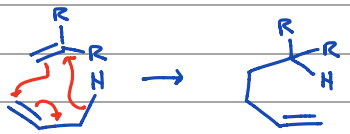
2. Sigmatropic Rearrangement



3. Cycloaddition

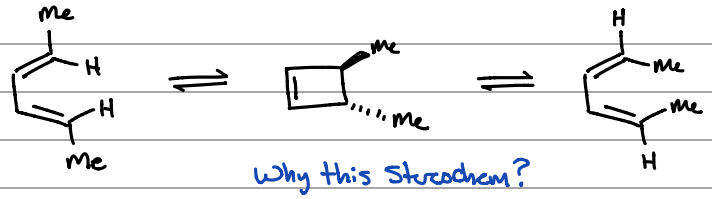


4. Ene Reaction



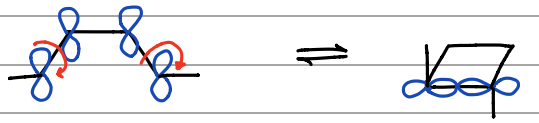
Electrocyclization

- Ring opening / closing
- Classified by # of e-



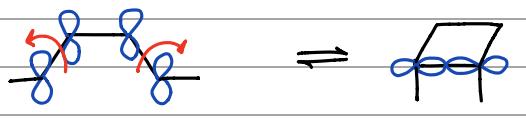
Why this Stereochem?

4e- electrocyclization



Conrotatory ↷↷ or ↶↶

molecule maintains C_2 Axis



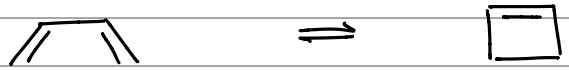
disrotatory ↷↶ or ↶↷

molecule maintains σ (mirror plane) Symmetry

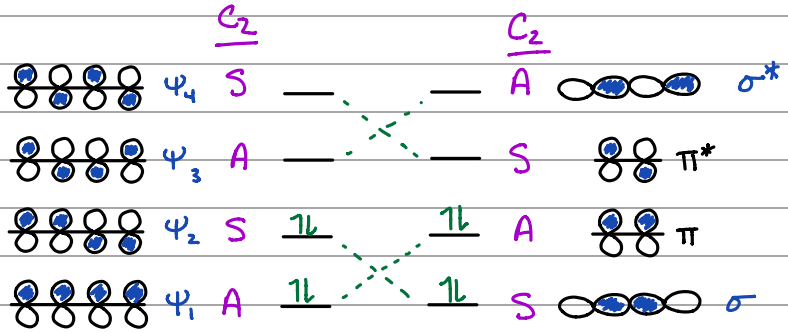
4e- electrocyclization found experimentally to be Conrotatory

3 Theories:

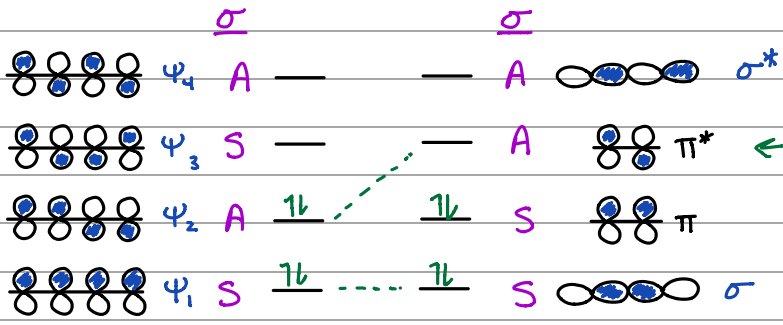
1. Woodward-Hoffmann Conservation of orbital Symmetry "Correlation diagrams"



Breaking 2 π bonds ⇌ Making 1 π bond + 1 σ bond



Conrotatory ✓

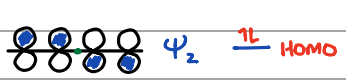


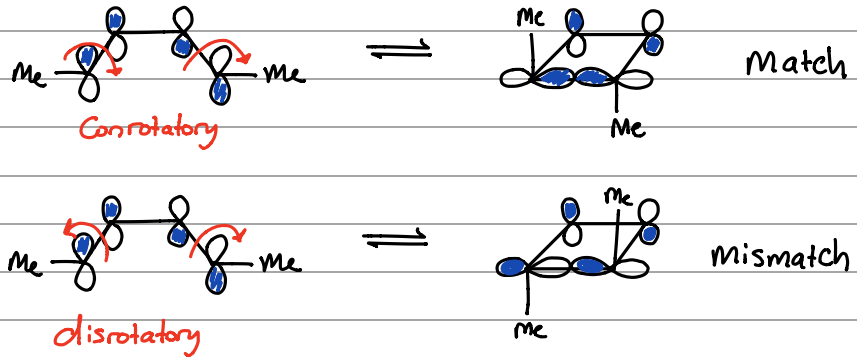
disrotatory

← Homo Correlates with an antibonding orbital

2. Frontier Molecular Orbital Theory

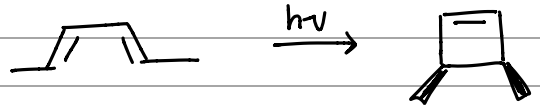
The unimolecular cyclization proceeds via the Homo.

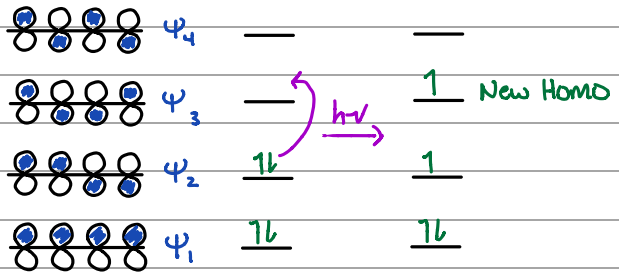


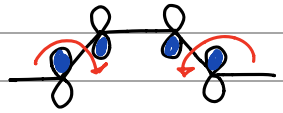


What is light is used?

↳ an electron is promoted







disrotatory Closure

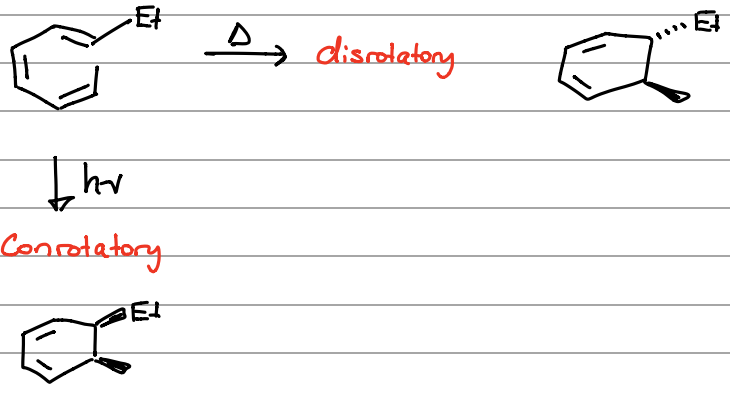
3. Huckel Theory

#e⁻ = 4n Δ Con
hν dis

4n+2 Δ dis
hν Con

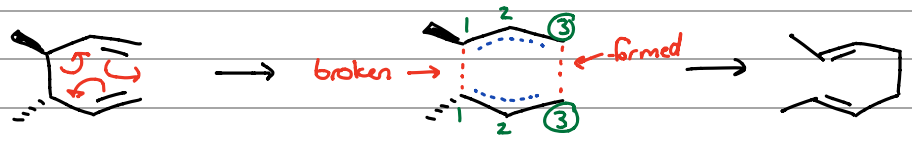
Thermal Disrotatory 6 e⁻
Touchdown = 6

Example:



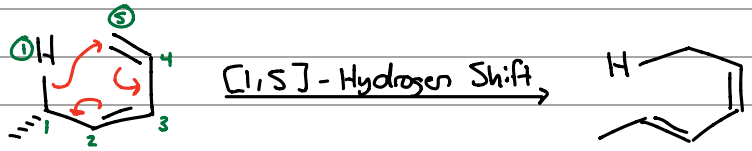
Sigmatropic Rearrangements

- Always involve the relocation of π-bonds as well as σ-bonds.
  - always one formed and one broken



[3,3]-Sigmatropic rearrangement
specify where new σ-bonds are formed.

from σ-bond breaking to σ-bond formed



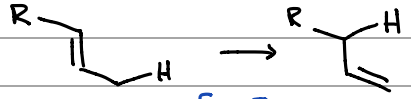
Stereochemistry

- migration on same side of the plane = suprafacial

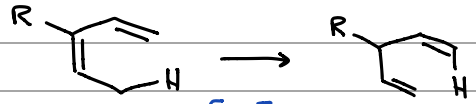
- migration on opposide side of the plane = antarafacial

Simple Approach: divide into a cation + conjugated anion

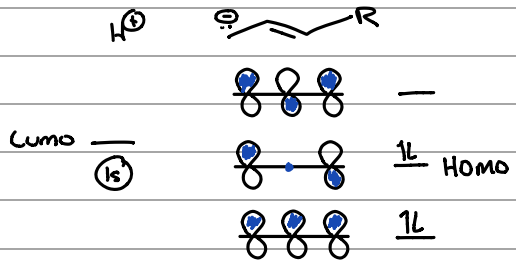
Use proton LUMO + conjugated anion HOMO to predict Stereochemistry

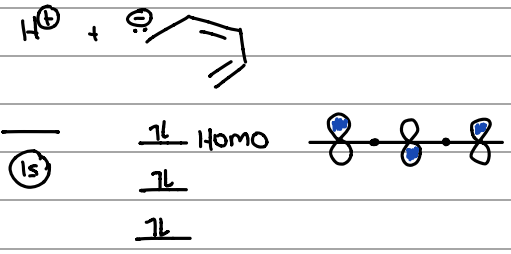


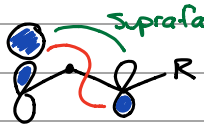
[1,3]



[1,5]



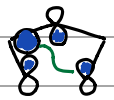




Suprafacial = Symmetry forbidden

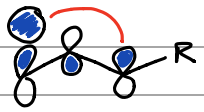
Antarafacial = Symmetry allowed

↳ but, geometrical constraints prevent this migration.



Suprafacial = Symmetry allowed

Using hν:



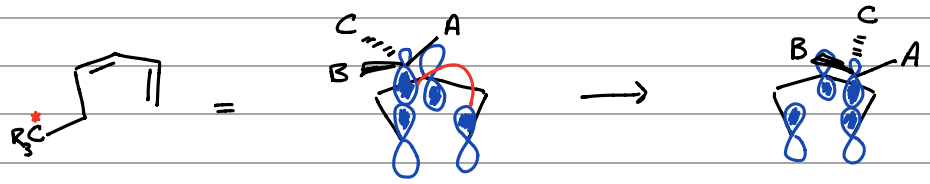
Now the HOMO → Suprafacial is allowed

Sigmatropic Rearrangements of C

May react using an sp^3 hybrid orbital or a 2p orbital

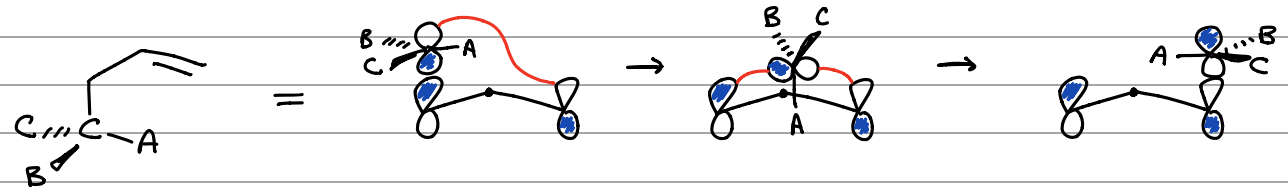
(Suprafacial rxns) (Antarafacial rxns)

[1,5] - C Shift

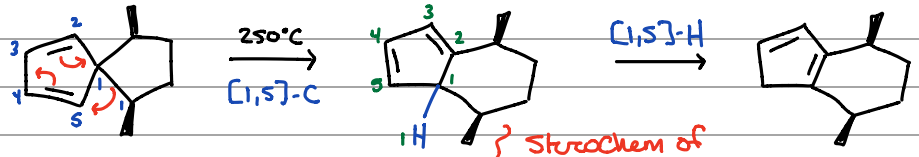


* Suprafacial
* Stereochem retained

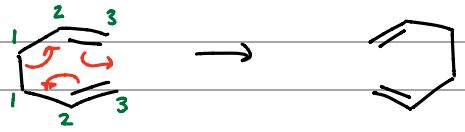
[1,3] - C Shift:



Example:



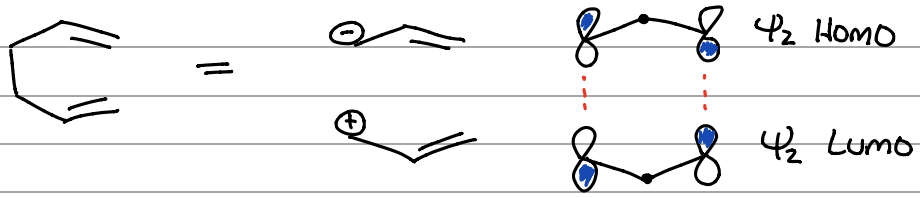
[3,3] - Sigmatropic Rearrangements



Cope Rearrangement

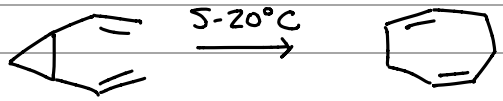
Retron: Spot two double bonds separated by 3 single bonds.

For analysis: treat as two allyl fragments



Suprafacial

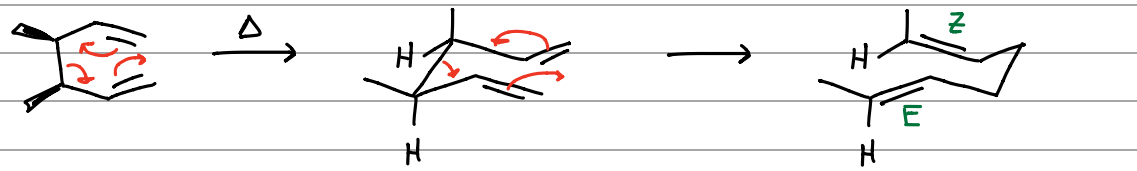
Rxn can be sped up with ring strain

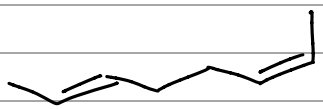


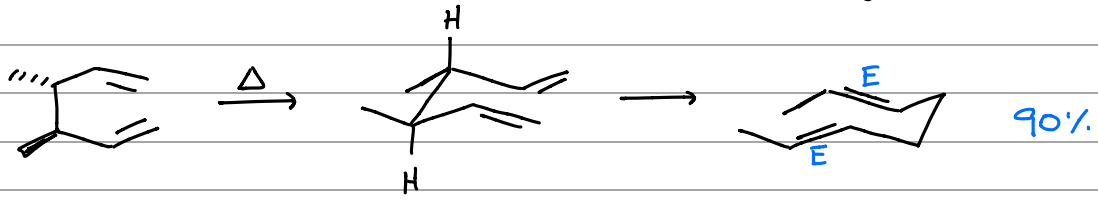
vs. 150°C for regular Cope

Stereochemistry:

In general, the rxn proceeds through a Chair-like transition State.

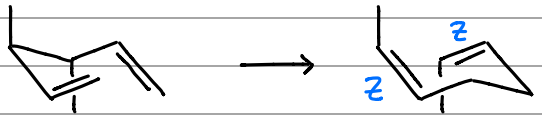






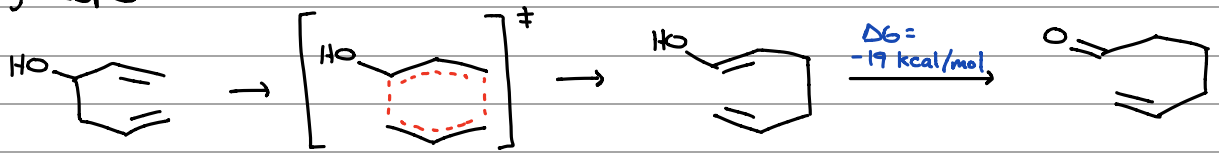
90%.

or

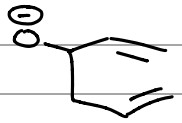


10%.

Oxy-Cope



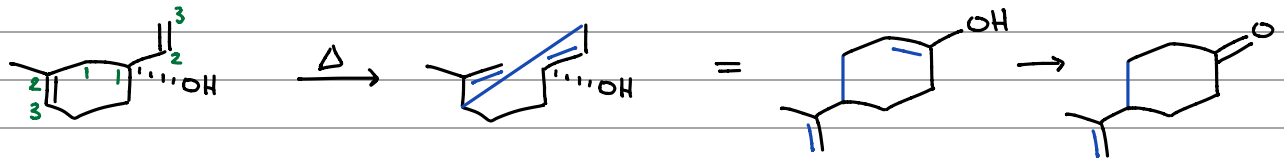
↓ Base



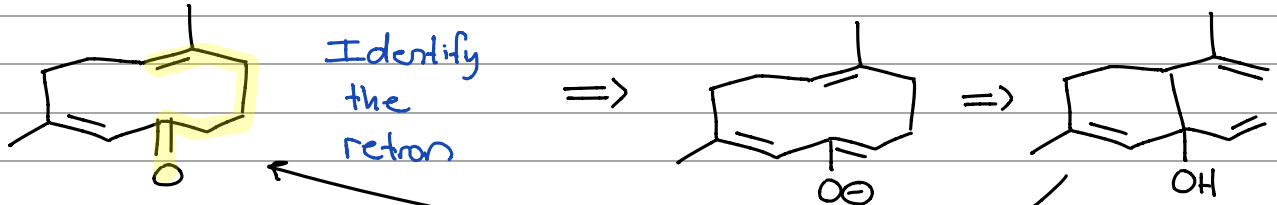
Anionic Oxy-Cope = Even Faster
- Less stable starting material
- Stabilized transition state

} Smaller ΔG‡

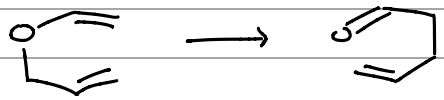
Ex:

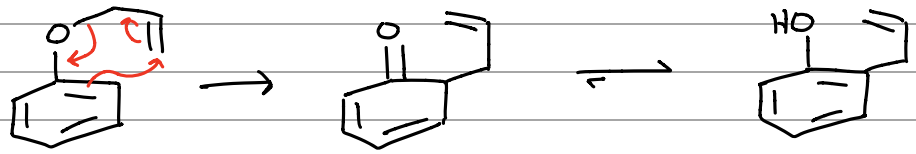


Ex:

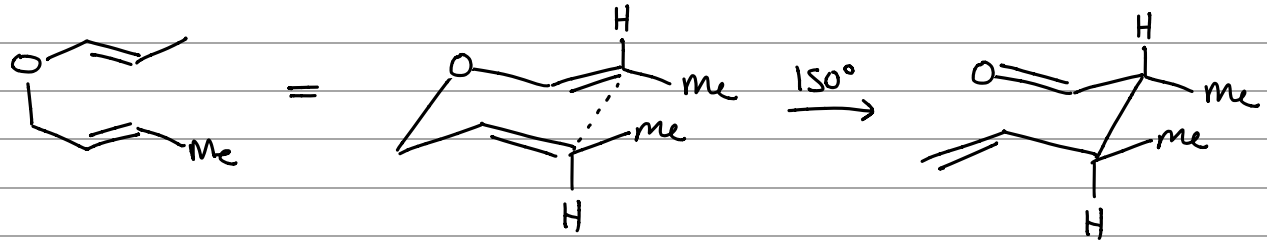


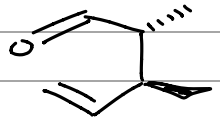
Claisen Rearrangement





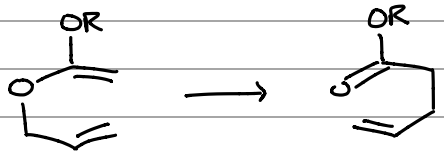
In the Claisen, equilibrium almost always favors the carbonyl products.



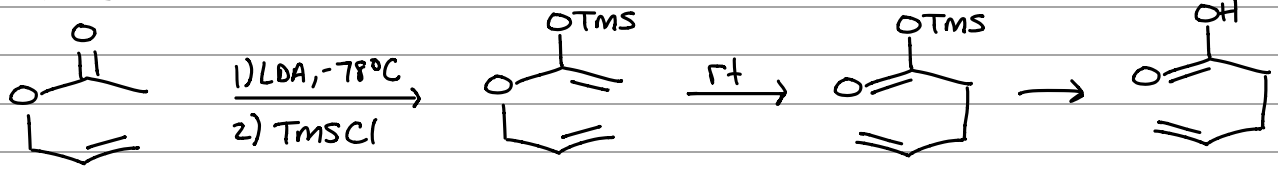


>95:5 dr

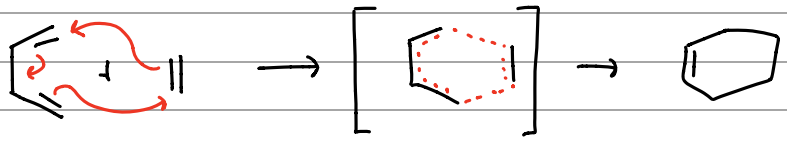
Johnson Claisen



Ireland Claisen



Cycloaddition Reactions

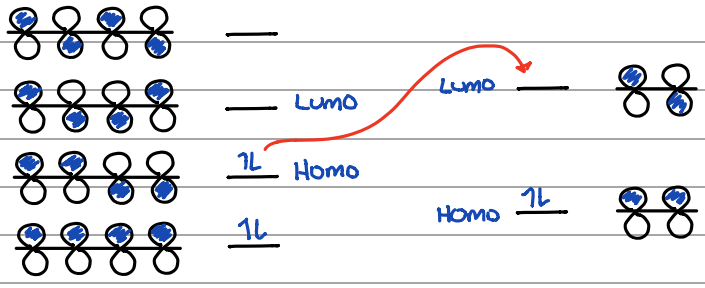


"Diels-Alder Reaction"

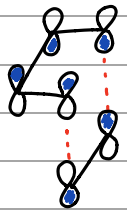
Concerted Rxn that is both regioselective + stereoselective

[4+2] Cycloaddition 4+2 refer to # of atoms, not e⁻

To achieve effective HOMO-LUMO overlap, the lobes at the ends of the diene must overlap with the lobes at the end of the dienophile.



Normal D-A



Diene HOMO Dienophile LUMO or Dienophile HOMO Diene LUMO

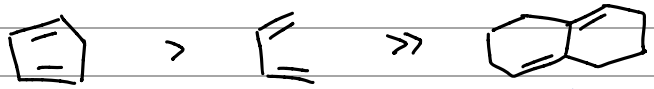
Normal D-A Rxn Inverse e⁻ demand D-A

EDG ↑ E of the HOMO EWG ↓ E of the LUMO

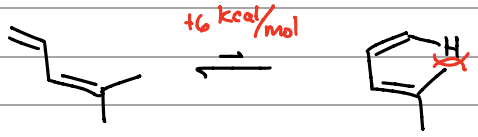
EWG on diene EDG on dienophile

Closes the HOMO-LUMO Gap
↑ accelerates the Rxn

The Diene: D-A Rxns must occur through the S-cis conformer of the diene



locked S-cis locked S-trans (unreactive)

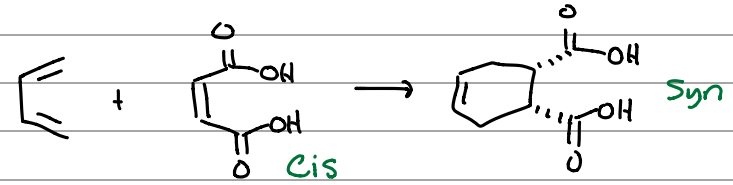


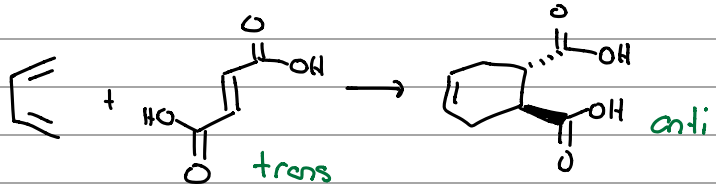
Difficult to attain the S-cis Conformation

This diene reacts very slowly + poorly in DA rxns

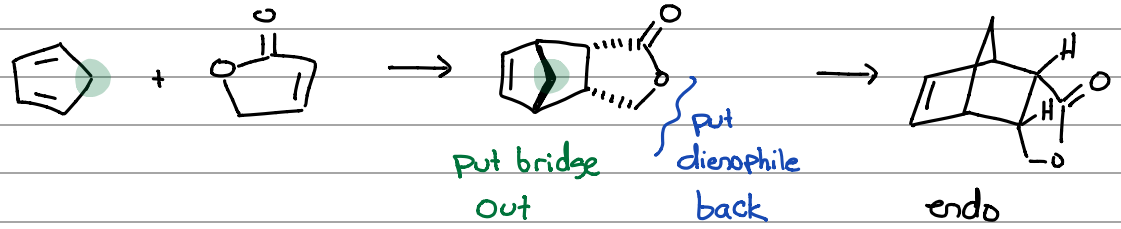
Stereochemistry:

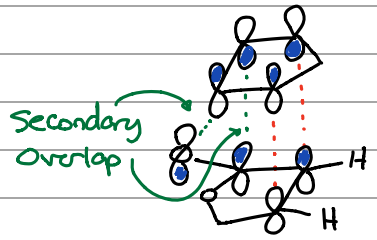
- Rxn is stereospecific





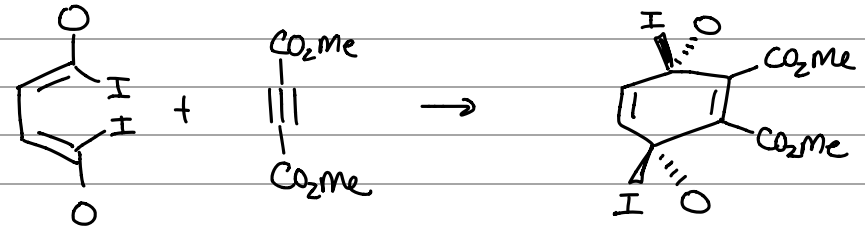
Conjugating substituents on the dienophile tend to become endo substituents in the cycloadduct. This is thought to be due to secondary orbital interactions.



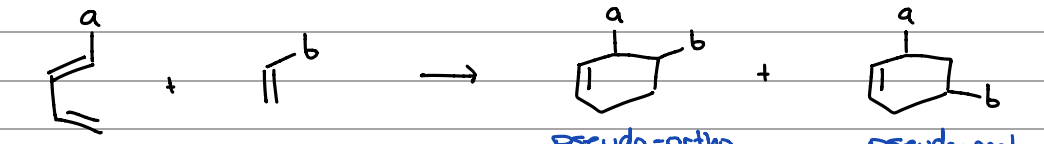


Diene Substituents

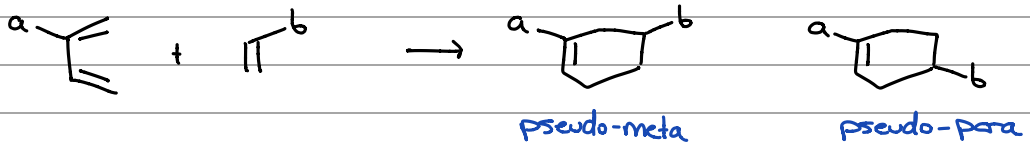
- Put inside (I) substituents "out" in the product
- Put outside (O) substituents "back" in the product



Diels-Alder Regiochemistry

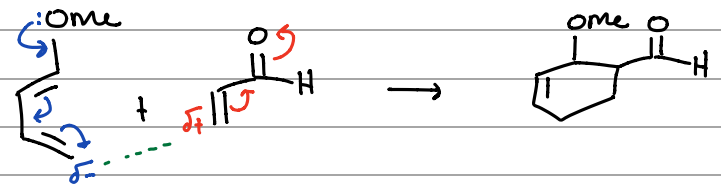


or

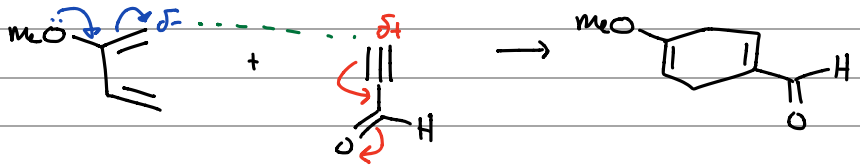


Ortho, para rule - When one reactant has an EDG & the other has an EWG, the major product will be ortho or para.

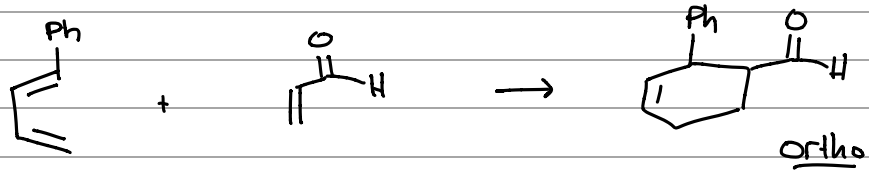
Ex 1:



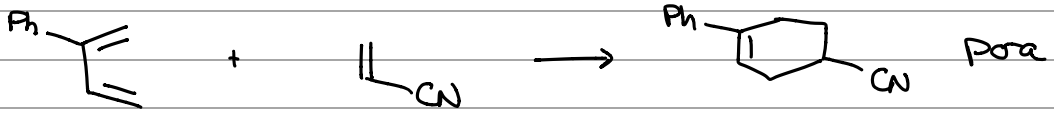
Ex 2:



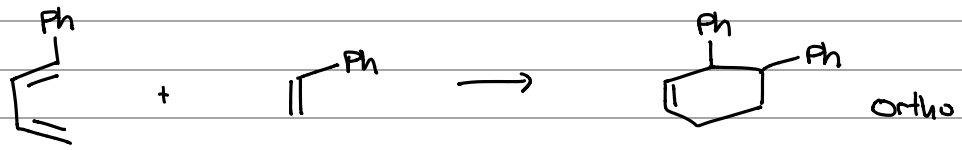
Ex 3:



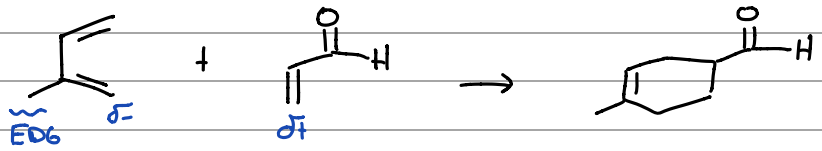
Ex 4:



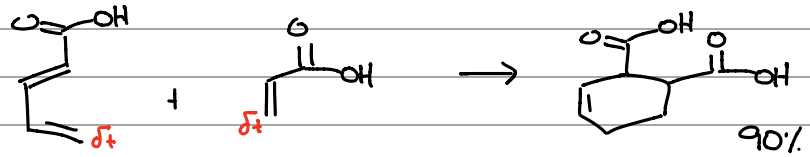
Ex 5:



Ex 6:



Ex 7: Exception



Despite the ⊕ Charges seemingly repelling, the ortho product dominates.

Ex 8: meta- Exception

EDG on Diene & Dienophile

↳ CH_3, OR, NR_2