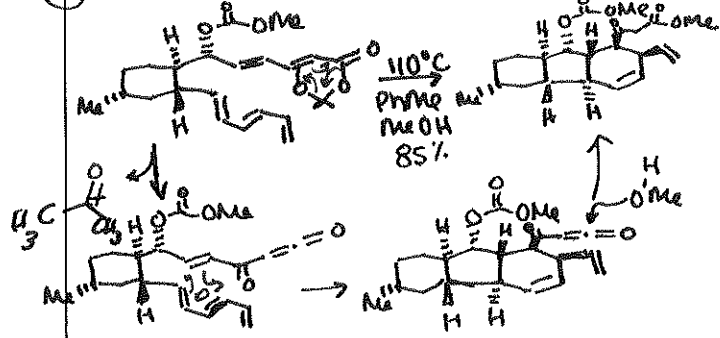


① Lecture 18

PERICYCLIC RXNS

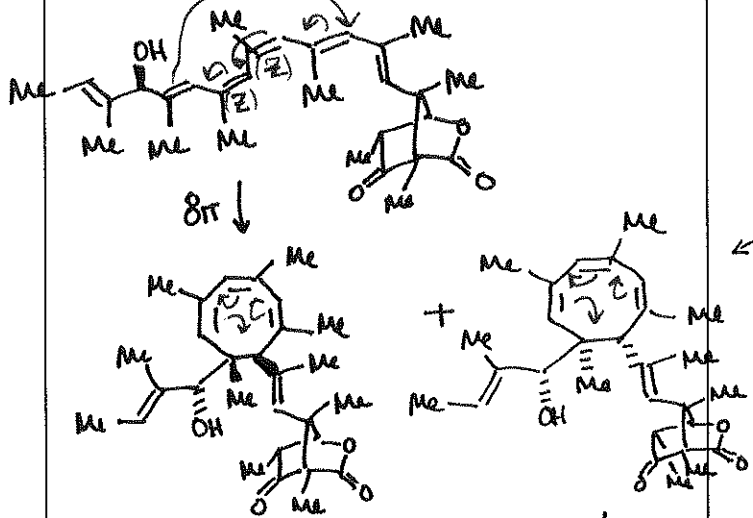
② Inspiration: Powerful Transformations

① Sorensen, OL 2009, 11, 701 (toward Hirustellone B)

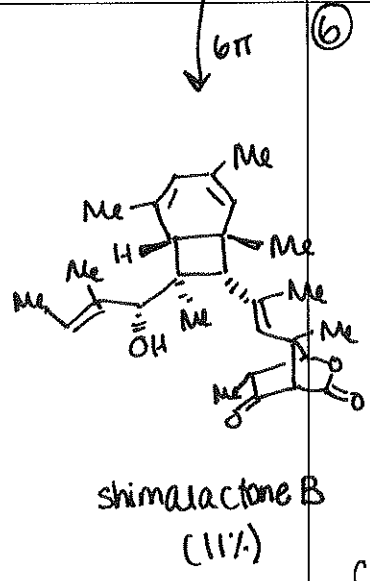
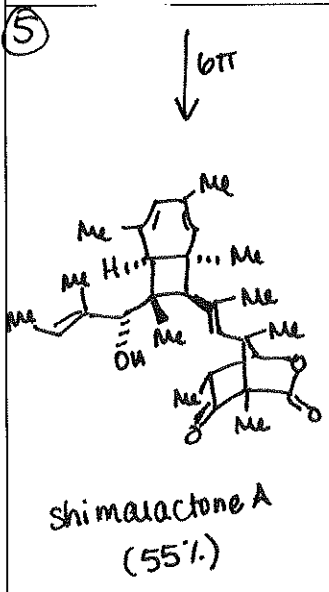


Stereospecific w/ respect to olefin & diene substituents

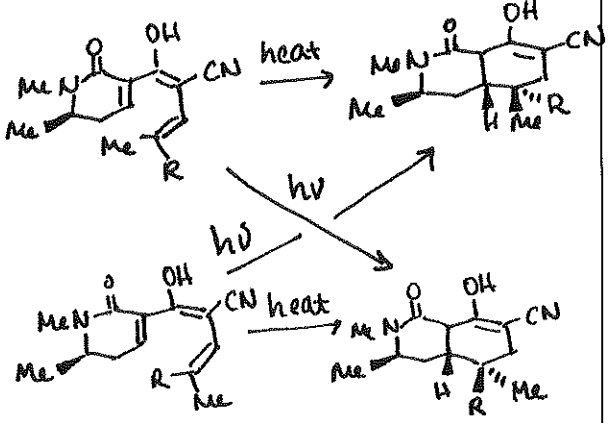
③ Trauner OL 2008, 10, 149



← stereospecific w/ respect to olefin substituents (both up or both down)
 stereoselective → either up or down.



Woodward



Conditions change rxn course.

⑦ How do we explain these rxns?

PERICYCLIC RXNS

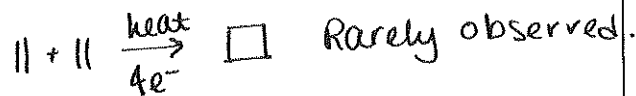
Continuous, concerted reorganization of electrons

Concerted = no intermediate / single TS

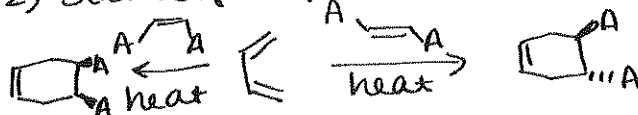
Continuous = cyclic TS.

⑧ Factors to consider:

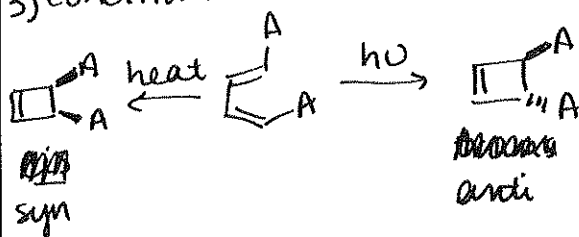
1) # of e⁻s affects reactivity:



2) Stereospecific



⑨ 3) Conditions



⑩ 3 Theories (all correct)

1) Woodward-Hoffmann: Conservation of orbital symmetry

- 1st historically
- correlation diagrams

2) Fukui: Frontier Molecular Orbital interactions

- Easier than WH
- Homo/LUMO interactions

3) Dewar-Zimmerman: Aromatic TS

- easiest to apply for all rxn types but not easy to understand why it's valid.

(more on these later)

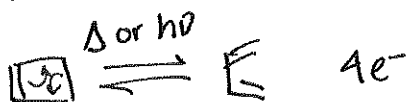
⑪ 5 Categories of Pericyclic Rxns

1) Electrocyclic Ring closure/Ring opening

Exchange π bond \rightarrow σ -bond (Thermodynamic)

Classify by # of e⁻s

ex:

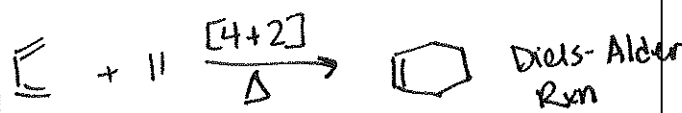
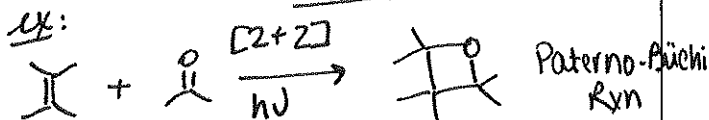


⑫ 2) Cycloaddn / Cycloreversion

Union of 2 π -systems exchange π -bonds for σ -bonds

Classified by [m+n]

of conjugated atoms of each π system.

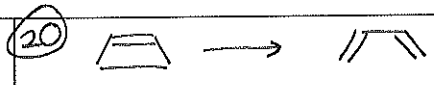


Note: [cyclohexene] >> C=C + C=C retro-[4+2]

19 Correlation Diagrams

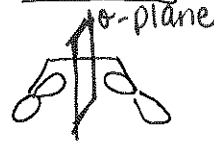
- Consider all MO's (or at least all the ones involved)
- Consider symmetry of MO's of SM & Product & IS!
- Orbitals of different symmetry can cross (orthogonal).
- Orbitals of same symmetry cannot cross (extreme energetic cost).

Woodward & Hoffmann ACIE 1969, 8, 781.



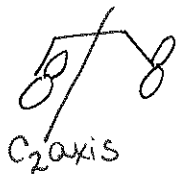
Transition States:

Disrotatory



Throughout rxn σ -plane of symmetry conserved.

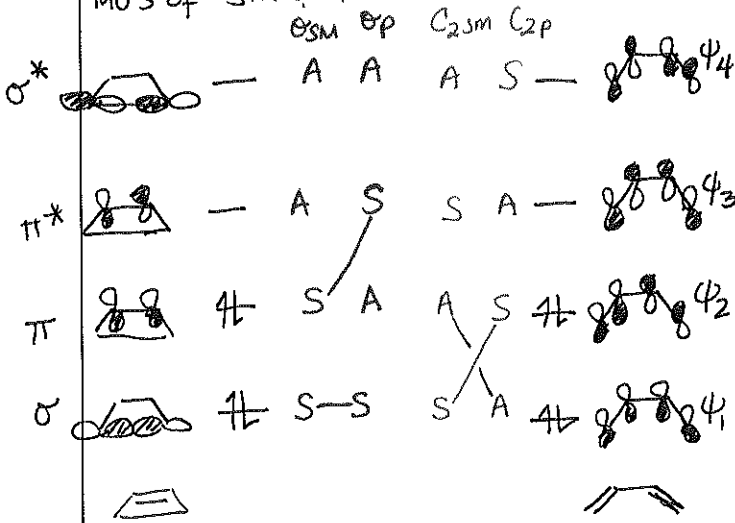
Conrotatory



Throughout rxn C_2 -axis of symmetry is conserved.

Each MO will be S (symmetric) or A (antisymmetric) w.r.t. σ & C_2 ...

21 MO's of SM & P...



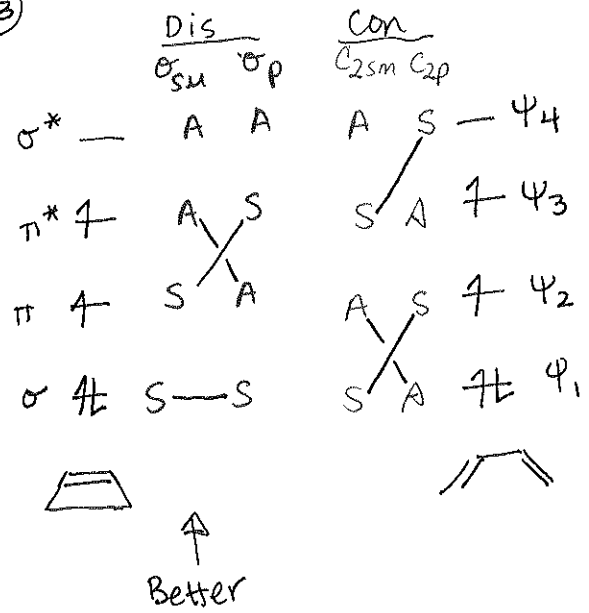
22

So disrotatory path \Rightarrow less stable electronic state (disfavored)

Conrotatory path \Rightarrow lowest energy state (favored) UNDER THERMAL CONDITIONS.

What about $h\nu$? \Rightarrow Excited states of molecules.

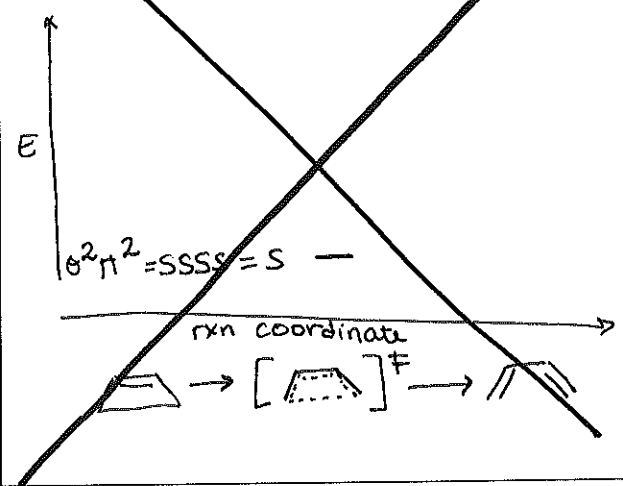
23



24

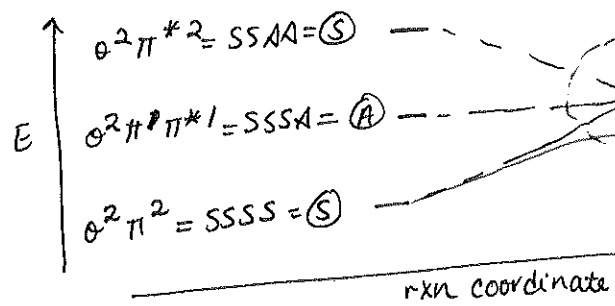
Electronic Configurations/State Diagrams:

Disrotatory



25

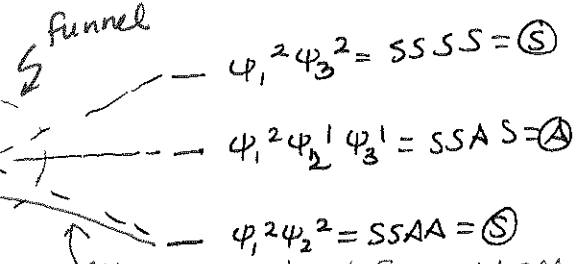
State Diagrams: Energy barriers
Disrotatory Pathway



Predicts high barrier to thermal rxn.
 " low barrier to ~~the~~ excited state rxn.

26

Note: $SS = S$
 $S \times A = A$
 $A \times A = S$



flip symmetries \Rightarrow Energetically costly but not as costly as crossing symmetry lines.

27

Can do similar analysis for all pericyclic rxns.

Drawback: Burdensome.

28

Next time:
 Other Models: Fukui FMO
 Dewar-Zimmerman

29

30