Course Chem 315 Lecturer Prof. Gellman

Day Monday Date 4/27/15

Notes Taken By Cassie Jarvis Total # of Pages 5

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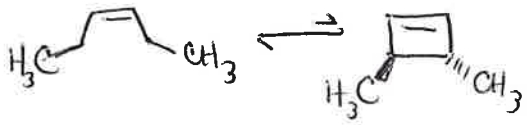
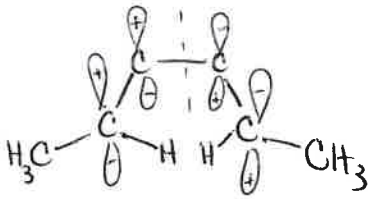
Recall:



Stereochem?

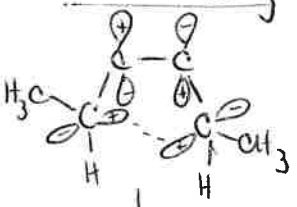
Draw HOMO on top of molecule:



"HOMO"

π_2

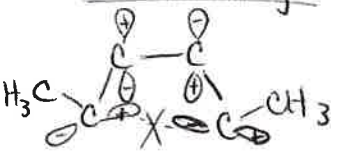
Conrotatory



* bonding

"ALLOWED"

Disrotatory



* antibonding

"FORBIDDEN"

= Not observed

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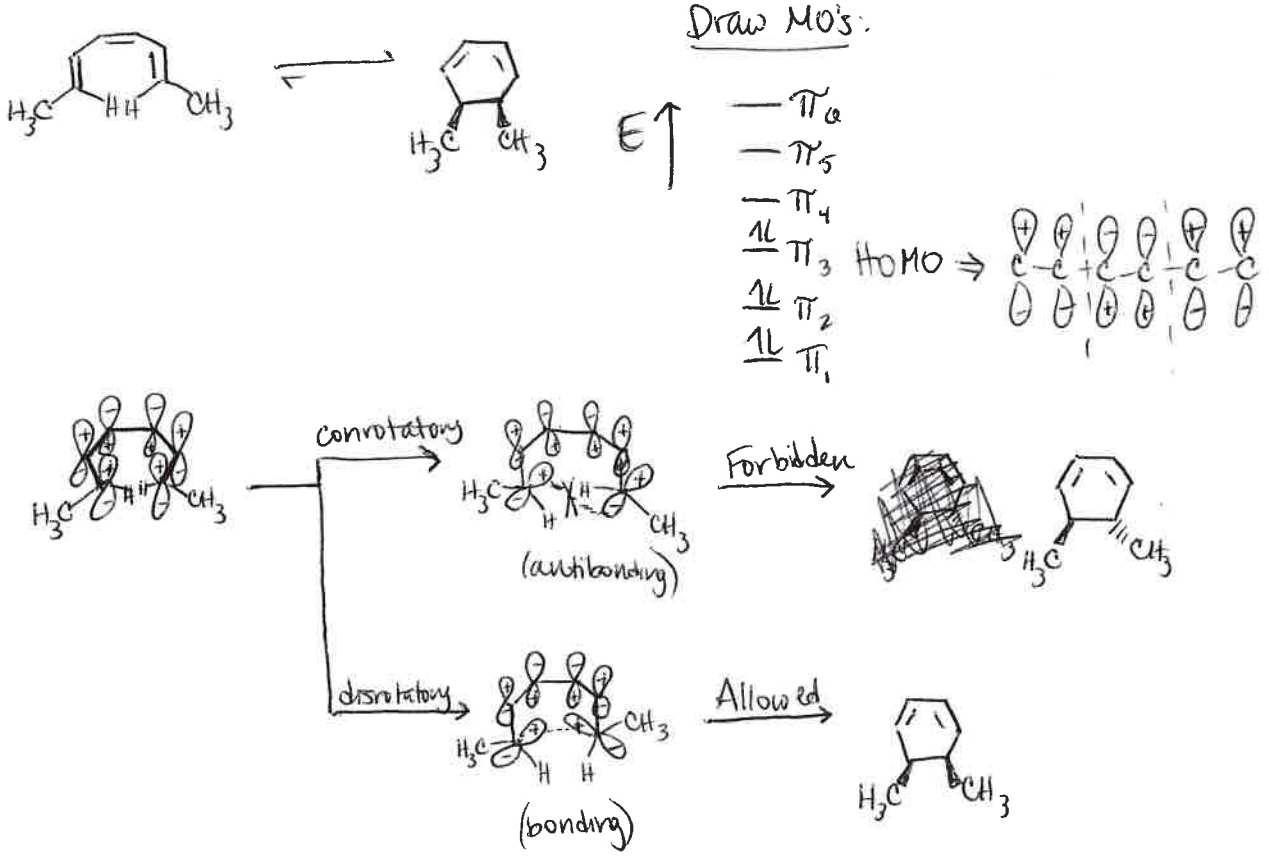
- MO symmetry explains the 2nd electrocyclic reaction we saw:



- So far, all reactions promoted by heat (ie. thermal)
  - * occur by way of ground state (ie most stable)
  - * can also be done by a "photochemical" pathway, which generates an excited state

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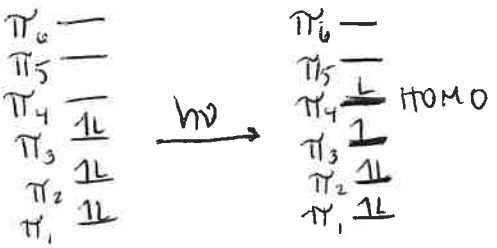
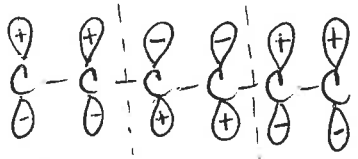
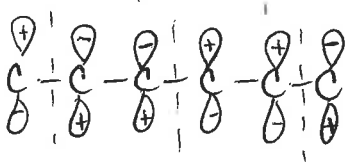
ie. triene



= promotes one electron up to π_4 = new HOMO

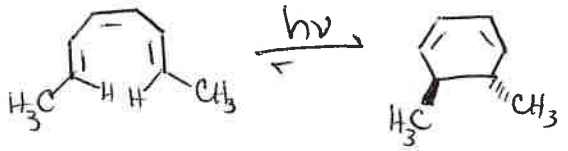
Recall:

π^3 =  overall = symmetric

π^4 =  overall = anti-symmetric

ie. Stereochem changes w/photochemical pathway:

= b/c π_4 is HOMO now instead of π_3



(you fill in π_4 conrotatory vs. disrotatory)

trans

- Generally, thermal/photochemical versions of electrocyclic reactions show divergent stereochemical outcomes

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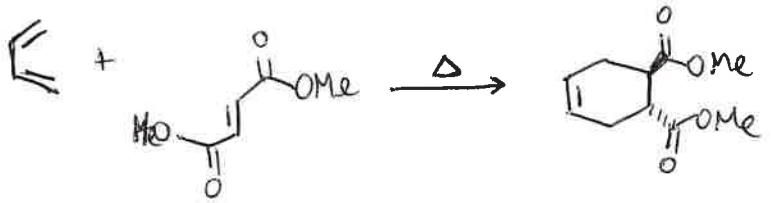
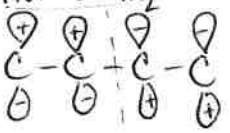
- Cycloadditions:

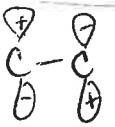
ie. Diels Alder [4+2]



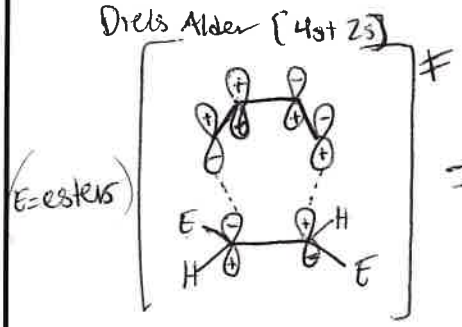
Diene: HOMO π_2



Dienophile: LUMO π^*



Diels Alder [4s+2s]



(E=esters)

⟹ both orbital contacts are allowed

* observe:

- At the TS, for each reactant the points of contact occur on the same side. This is said to be suprafacial (opposite = antarafacial)

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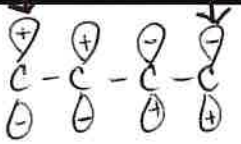
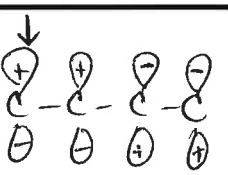


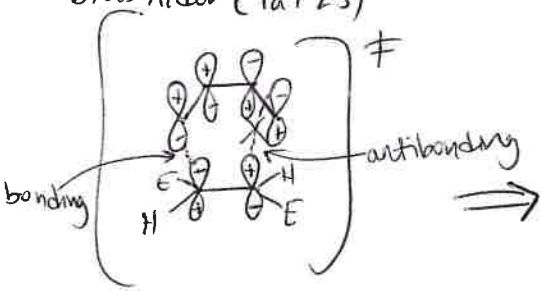
Suprafacial

vs.



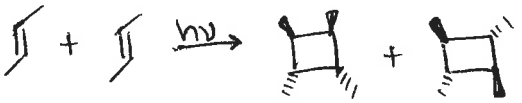
antarafacial

Diels Alder [4a+2s]



$\Rightarrow$ [4a+2s] is Forbidden

* consider [2+2]



Why?

Thermal version of this does not occur.