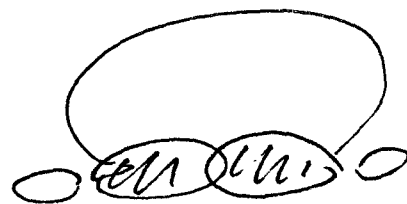
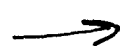
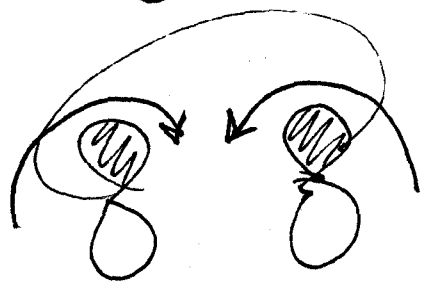
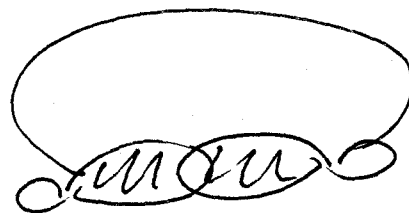
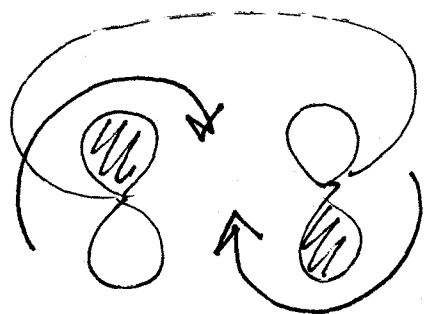


thermal rxn - use ground state orbitals
 photochemical rxn - use excited state orbitals



~~con~~ disrotatory



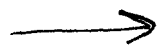
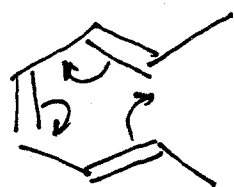
conrotatory

two modes of bond formation - which one happens is determined by the symmetry of the MO.
 * HOMO is the one that reacts.

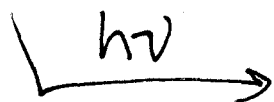
Electrocyclic Rxns

symmetric HOMO \rightarrow disrotatory ring closure
is symmetry-allowed (conrotatory
is symmetry-forbidden)

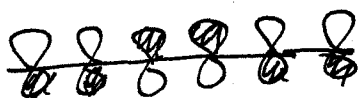
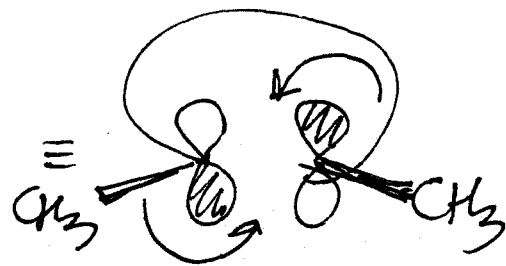
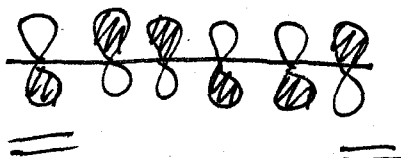
asymmetric HOMO \rightarrow conrotatory ring closure
is symmetry allowed



cis or trans?

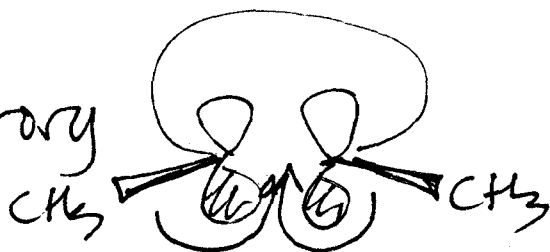


HOMO:

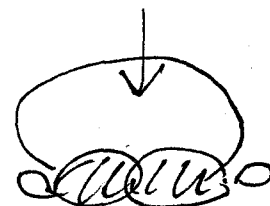


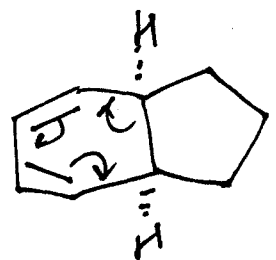
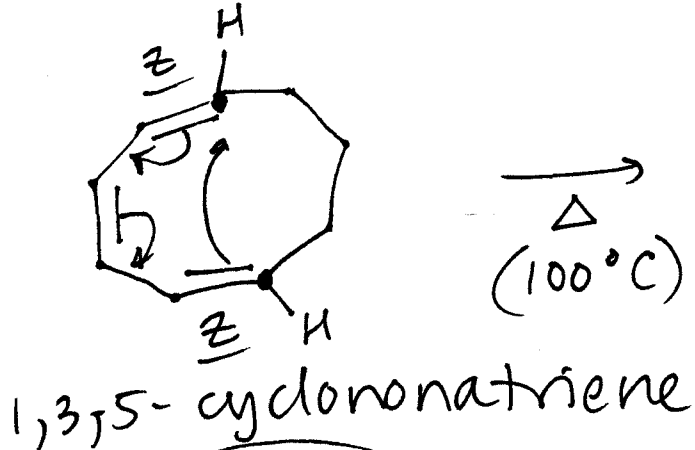
trans CH₃'s

disrotatory

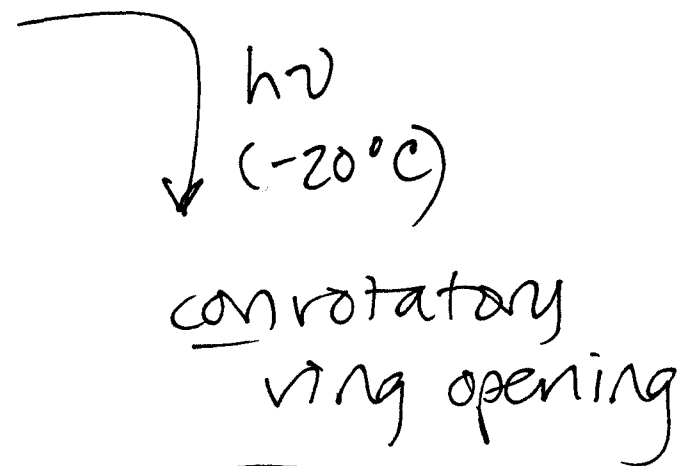


\rightarrow cis CH₃'s

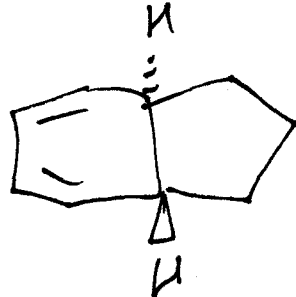
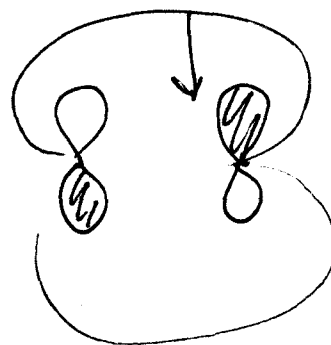
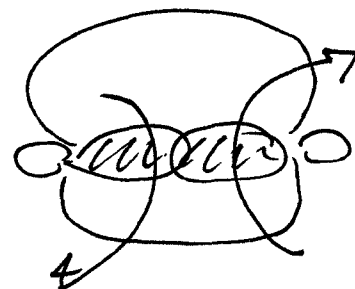
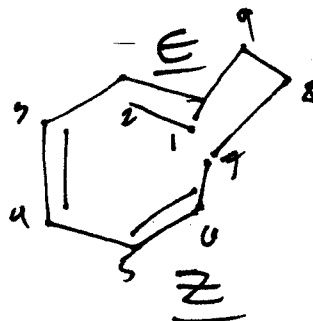




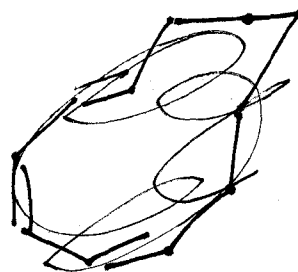
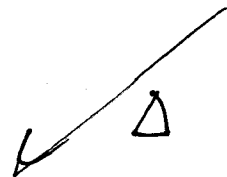
cis ring
fusion



disrotatory
ring closure



trans ring
fusion



cycloadditions $[A + B]$

count the π e's in the two reactive pieces

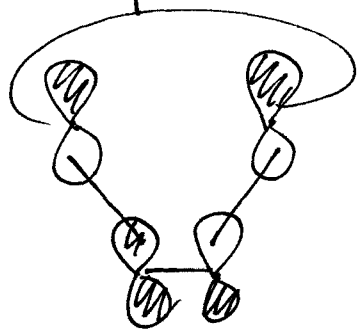


$[4+2]$

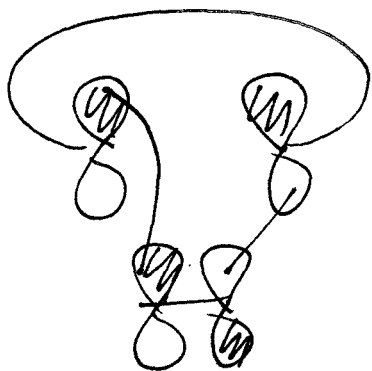
Diels-Alder

- the orbitals of one piece must overlap with the orbitals of the other piece in a constructive manner. $\text{HOMO}_A + \text{LUMO}_B$

- two ways to overlap

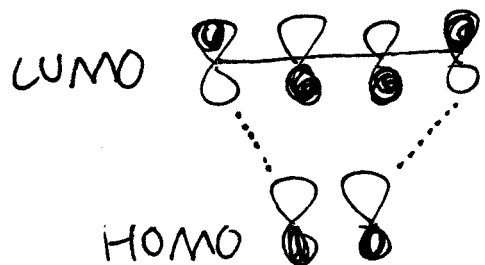


suprafacial overlap
(think syn addition)

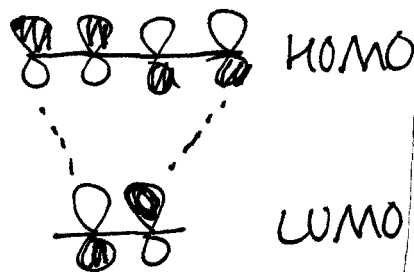


antarafacial overlap
(think anti addition)

most cycloadditions leading to "small" rings
(4,5,6-membered) must be suprafacial
because of geometrical constraints.

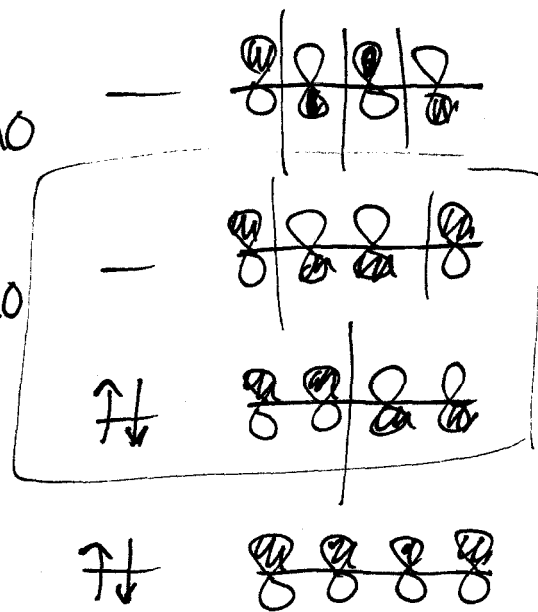


or



dienophile
MO

orbitals overlap
perfectly - using
ground state MO's
 \Rightarrow thermal



consider a $[2+2]$ - thermal or photochemical?

