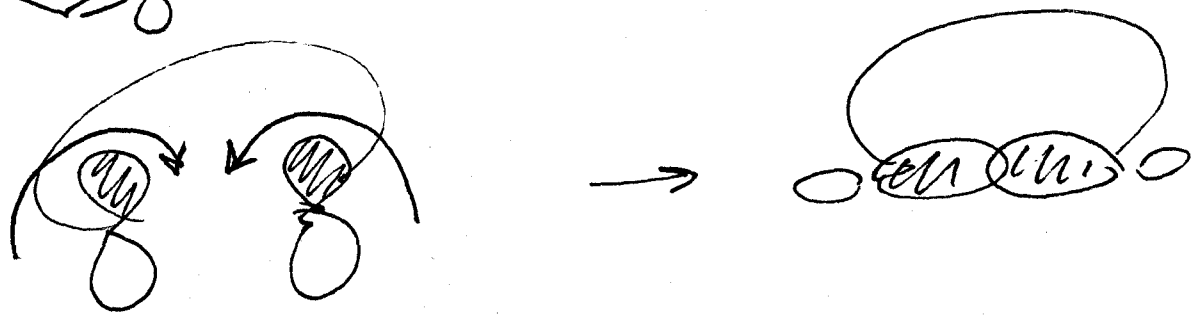
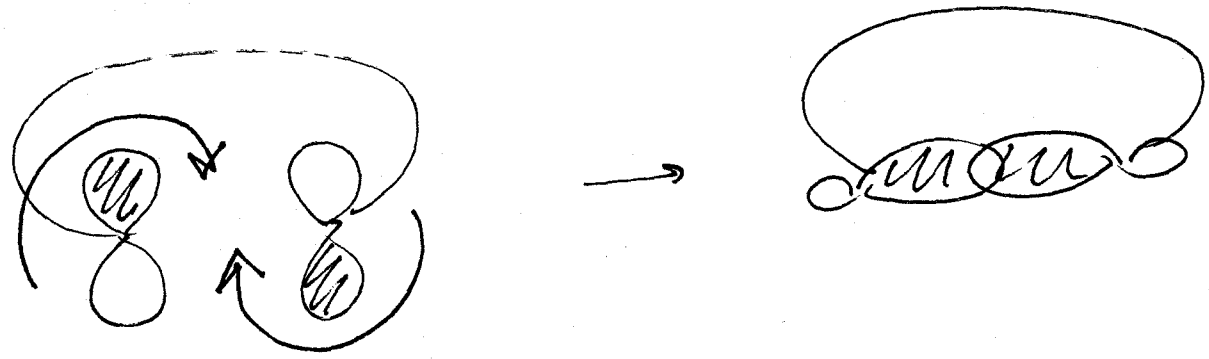
thermal rxn - use ground state orbitals
photochemical rxn - use excited state orbitals



disrotatory



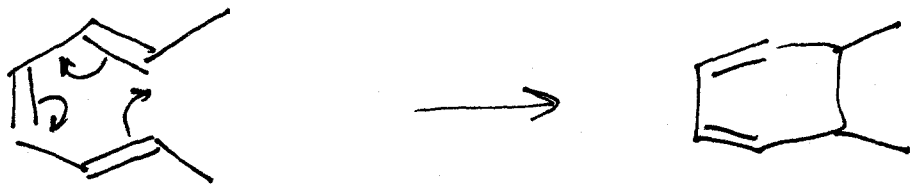
conrotatory

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

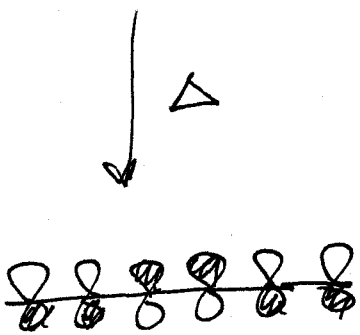
Electrocyclic Rxns

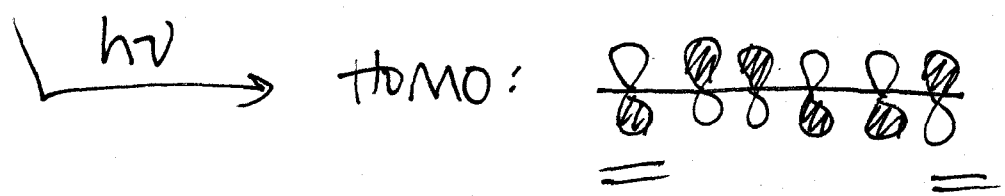
symmetric HOMO → disrotatory ring closure is symmetry-allowed (conrotatory is symmetry-forbidden)

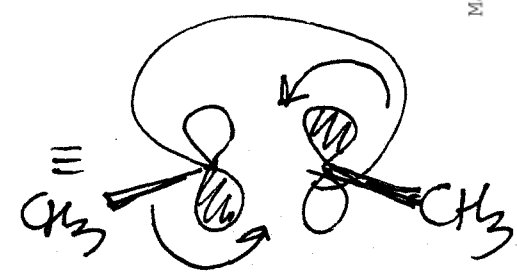
asymmetric HOMO → conrotatory ring closure is symmetry allowed

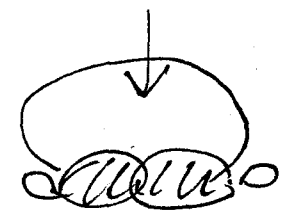


cis or trans?



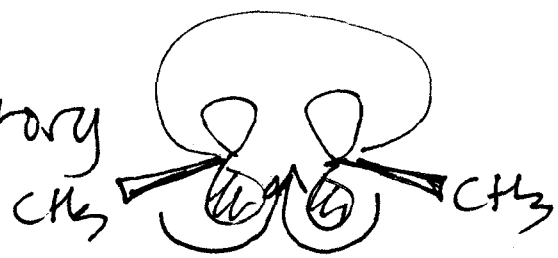






trans CH_3's

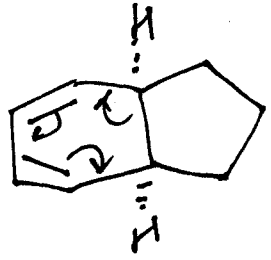
disrotatory



→ cis CH_3's

1,3,5-cyclononatriene

$\xrightarrow{\Delta}$ (100°C)

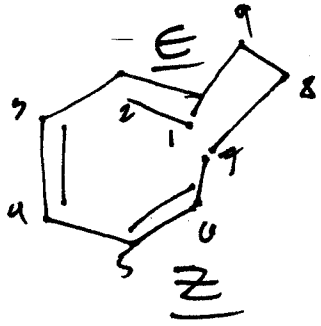


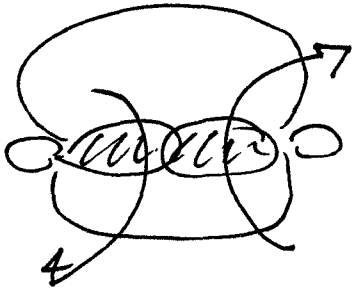
cis ring fusion

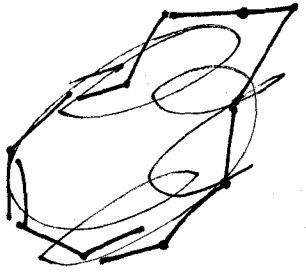
$h\nu$ (-20°C)

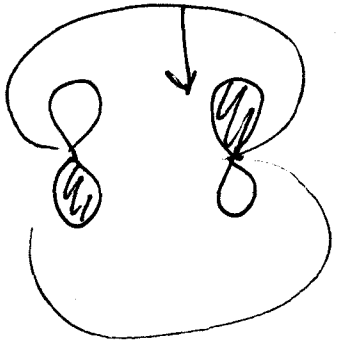
conrotatory ring opening

disrotatory ring closure

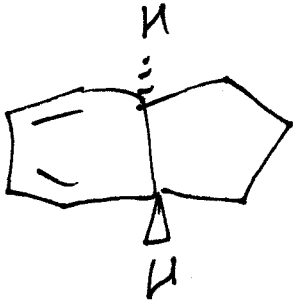








Δ



trans ring fusion

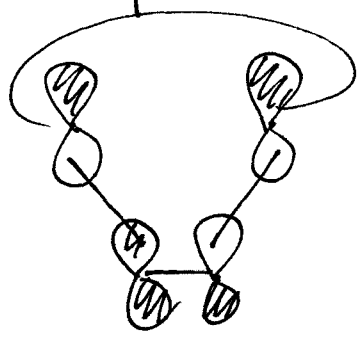
cycloadditions [A + B]

count the π e's in the two reactive pieces

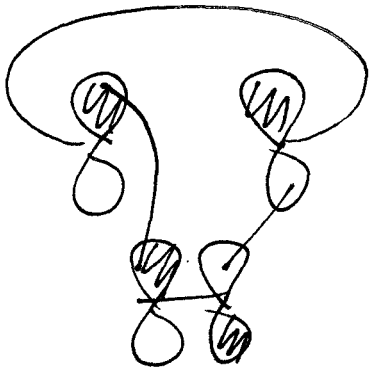
[4+2] Diels-Alder

- the orbitals of one piece must overlap with the orbitals of the other piece in a constructive manner. $HOMO_A + LUMO_B$

- two ways to overlap

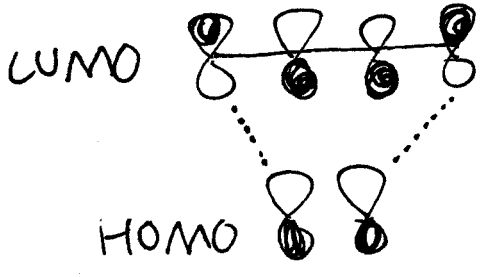


suprafacial overlap
(think syn addition)

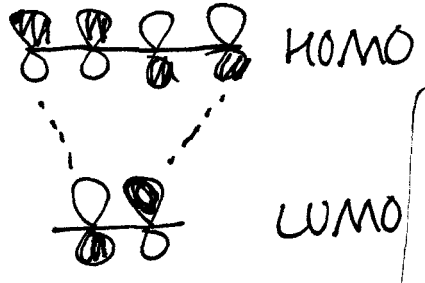


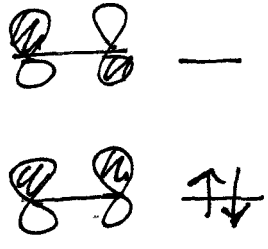
antarafacial overlap
(think <u>anti</u> addition)

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

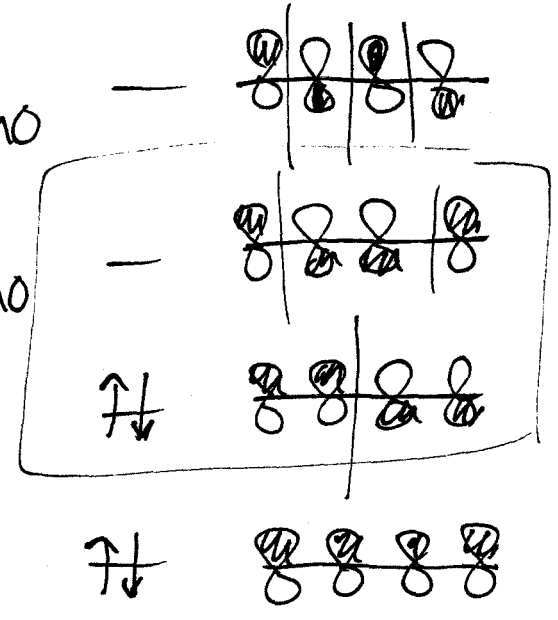


or





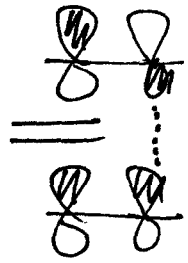
dienophile MO



orbitals overlap perfectly - using ground state MO's
⇒ thermal

consider a [2+2] — thermal or photochemical?

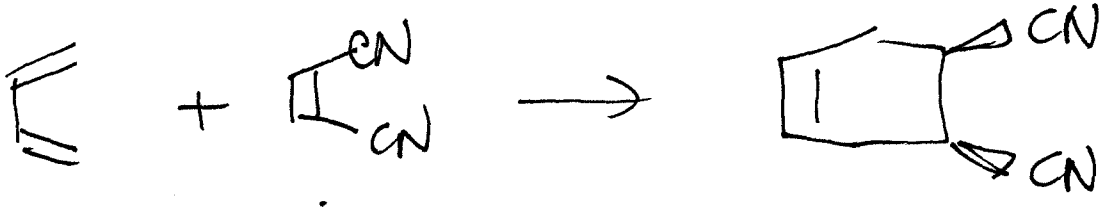
thermal:



doesn't work

photochemical:

works.



cis

cis