

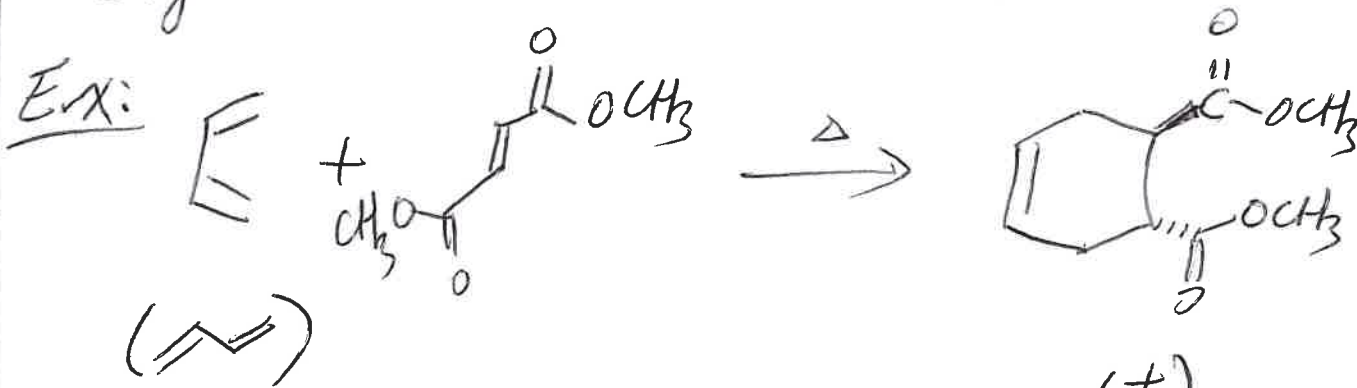
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Recall: Pericyclic Rxns (MO symmetry)

1) Electrocyclic Rxns

2) Cycloaddition Rxns

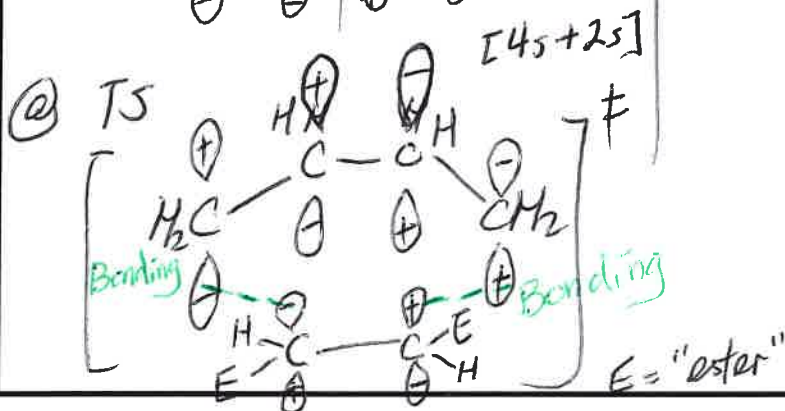
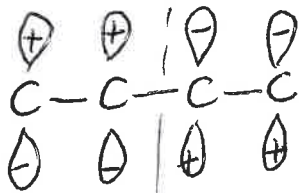
E.g. Diels-Alder, aka [4+2]



MO perspective — HOMO on one component, LUMO on the other

HOMO on diene =  $\pi_2$

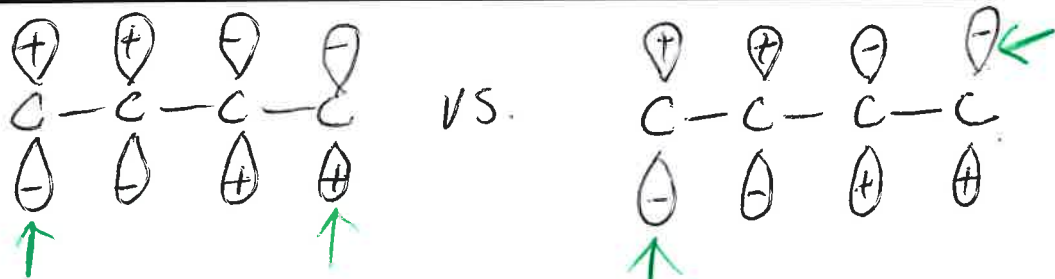
LUMO on dienophile =  $\pi^*$



Thus, [4+2] = allowed  
 New aspect to our analysis involving the "sidedness" of the  $\pi$  systems ...

Course Chem 345 Lecturer Gellman  
 Day Friday Date 4-29-16  
 Notes Taken By LL Total # of Pages 4

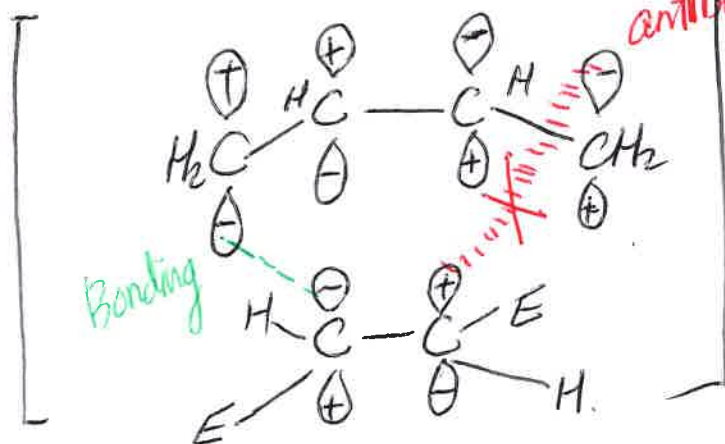
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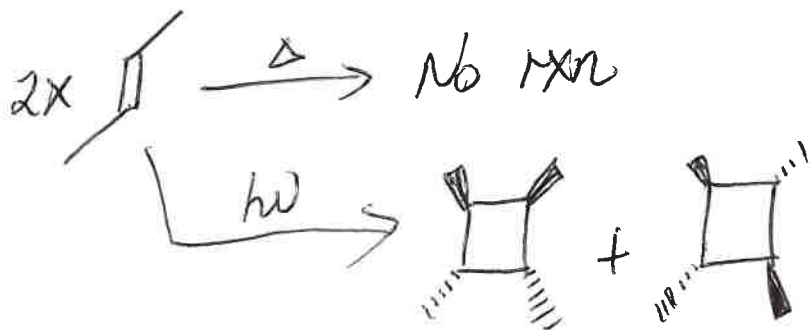
"suprafacial"

"antarafacial"

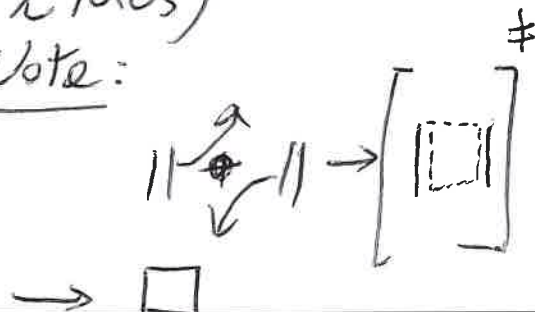
Considers  $[4a + 2s] \Rightarrow$  forbidden  $\neq$  antibonding



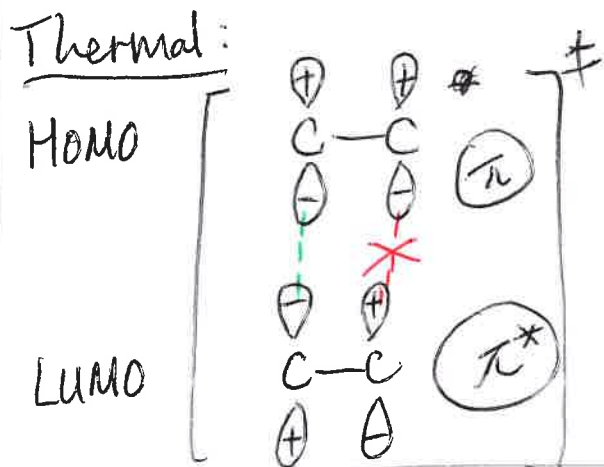
Consider  $[2+2]$



Why no thermal rxn?  
 (Recall: ground state  $\pi$  MOs)  
 Note:

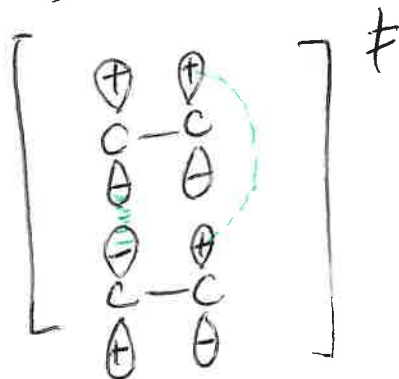


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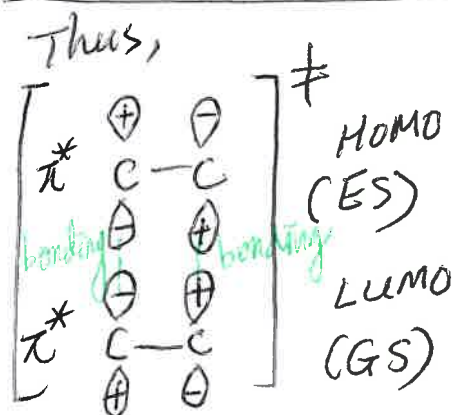
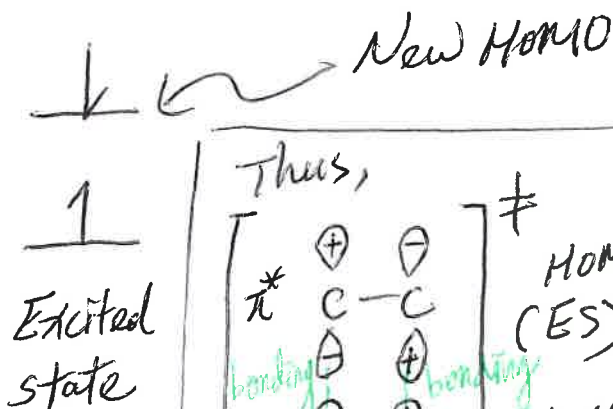
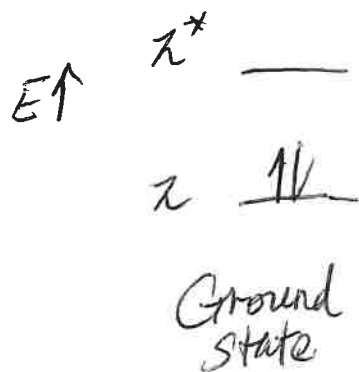
$\therefore [2s+2s]$  forbidden

$[2a+2s]$



Physically impossible

photochemical  $[2+2]$ , MOs...

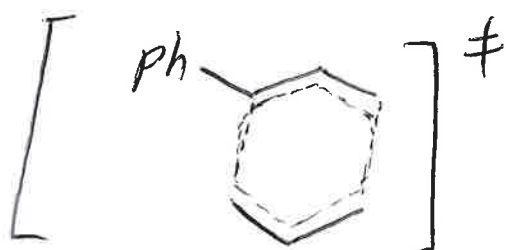


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Thus, expect photochemical  $[2s+2s]$  to be allowed  
(as observed.)

3) Sigmatropic Rearrangements (unimolecular)  
Observe - positions of  $\sigma$  &  $\pi$  bonds move w/in  
molecule.

Ex: ("cope rearrangement")



Easy to be fooled...

Note:

