*CHEM 342 – Lecture 5 20/01/15*

Overheads: - Today’s Outline

Quiz #1

Recap Thursday: Woodward-Hoffman Rule for Electrocyclic Reactions

4n / even  con

h dis

4n+2 / odd  dis

h con

Cool example: “Dewar Benzene”





\*\*Note that WH rule is same for reverse reaction (*ie* electrocyclic ring opening)



→ electrocyclic ring opening of dewar benzene to give benzene is symmetry-forbidden, so dewar benzene is unexpectedly stable

→ however, heating above RT gives benzene (by another mechanism)

2) Cycloaddition Reactions

- two components add to make ring



e.g. [2+2] cycloaddition (each component has two  e‑):



What about photochemical reaction?

→ HOMO of excited state reacts with LUMO of ground state molecule.





Diels-Alder Reaction





Combine HOMO of one with LUMO of the other:



* Works either way!

Summary:



Are the other reactions really “forbidden”?



Suprafacial: → both new bonds form from same side of  system

→ “straight-on” overlap

Antarafacial: → two new bonds are formed on opposite sides

(uses top of one end of orbital and bottom of other end)

→ “twisted” overlap

→ much more difficult (only works for big rings; > 6 C’s)

Woodward-Hoffman Rule for cycloadditions

4n  e­ (even pairs)  = antarafacial

h = suprafacial

4n+2  e­ (odd pairs)  = suprafacial = Diels-Alder!

h = antarafacial

→ remember any one, change one part get opposite