*CHEM 342 – Lecture 3 13/01/15*

Overheads: - Today’s Outline

Recap: Reactions so far = ionic or radical (Nu- / E+)

Pericyclic Reactions: different type of reaction

* Cyclic reorganization of electrons
* Electrons in  and/or  bonds move in ring to make new  and/or  bonds



e.g. Diels-Alder Reaction:

-notice how arrows resemble

resonance in benzene:

→ referred to as “aromatic transition state”

4 kinds of pericyclic reactions:

1) Electrocyclic Reactions

- conjugated diene/triene etc cyclizes to make ring



2) Cycloaddition Reactions

- two alkenes/dienes/trienes etc combine to form ring

* E.g. Diels-Alder

3) Sigmatropic Rearrangements

- bond “moves” within molecule

– similar to electrocyclic but missing middle  bond



4) Group Transfer Reactions

- one atom or group gets transferred to other end



Common Features of Pericyclic Reactions:

* All concerted (e­ move in one step)
* All highly stereoselective (will see why)
* Can occur by heating (thermal) or light (photochemical)
* Can include other atoms (eg O instead of C)

\*\*Not all possible pericyclic reactions actually occur



→ based on symmetry of orbitals

* In order for orbitals to overlap (*ie* make bond) they must have same sign (+/-)
* Depends on # of e­ pairs and  or h

1) Electrocyclic Reactions



Look at orbitals:



Which one happens depends on symmetry of orbitals:



How do we know signs? Look at molecular orbitals





→ for an electrocyclic reaction it is the HOMO that reacts





→ Reaction is stereospecific!

Trans-trans → trans

Trans-cis → cis

What about cis-cis? Gives trans (check it yourself!)

What if reaction is promoted by light instead of heat?





Summary:



Let’s try:



MO’s for 1,3,5-hexatriene: 6 p orbitals 6 MO’s



