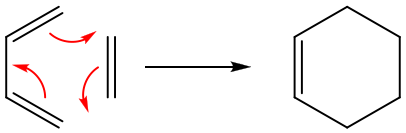
CHEM 342 – Lecture 3 13/01/15

Overheads: - Today's Outline

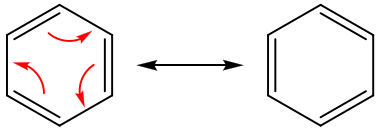
Recap: Reactions so far = ionic or radical (Nu^- / E^+)

Pericyclic Reactions: different type of reaction
- Cyclic reorganization of electrons
- Electrons in π and/or σ bonds move in ring to make new π and/or σ bonds

e.g. Diels-Alder Reaction:



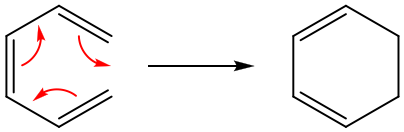
-notice how arrows resemble resonance in benzene:



→ referred to as "aromatic transition state"

4 kinds of pericyclic reactions:

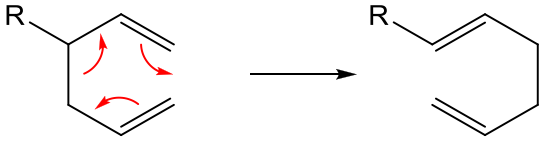
1) Electrocyclic Reactions
- conjugated diene/triene etc cyclizes to make ring



- get ring joined by new σ bond

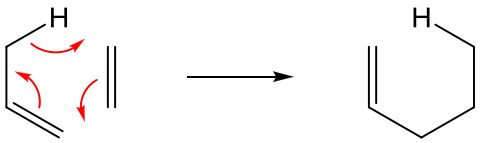
2) Cycloaddition Reactions
- two alkenes/dienes/trienes etc combine to form ring
- E.g. Diels-Alder

3) Sigmatropic Rearrangements
- bond "moves" within molecule
  – similar to electrocyclic but missing middle π bond



= Cope rearrangement

4) Group Transfer Reactions
- one atom or group gets transferred to other end



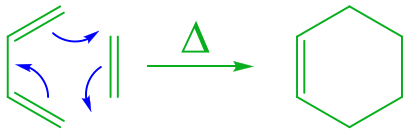
= "ene" reaction

Common Features of Pericyclic Reactions:

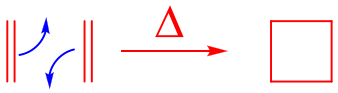
- All concerted (e move in one step)
- All highly stereoselective (will see why)
- Can occur by heating (thermal) or light (photochemical)
- Can include other atoms (eg O instead of C)

**Not all possible pericyclic reactions actually occur

e.g.



"allowed"

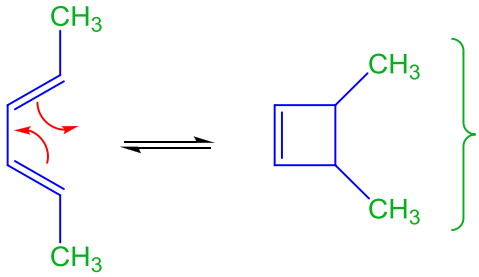


"forbidden"

→ based on symmetry of orbitals

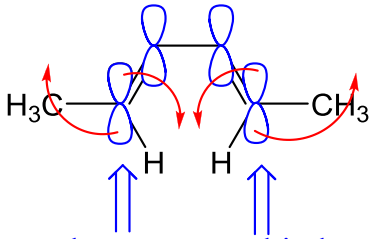
- In order for orbitals to overlap (*ie* make bond) they must have same sign (+/-)
- Depends on # of e pairs and Δ or hν

1) Electrocyclic Reactions

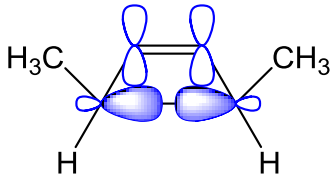


cis or trans?

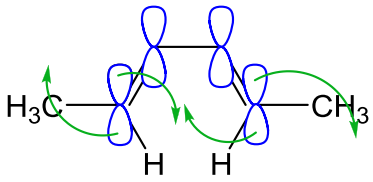
Look at orbitals:

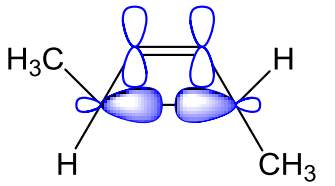


these two p orbitals spin sideways to make new σ bond



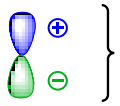
tops spin towards each other (opposite direction) = disrotary (dis=opposite)



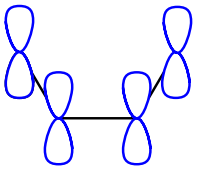


bottom spins up to meet top (same direction) = conrotary (con=same)

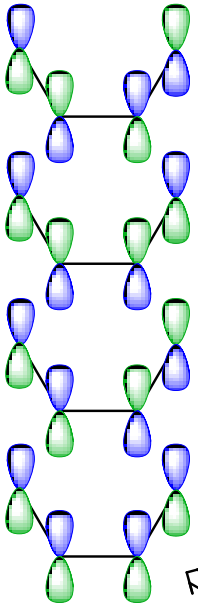
Which one happens depends on symmetry of orbitals:

p:  has + / - phase
- always must overlap with same sign/colour

How do we know signs? Look at molecular orbitals



4 p orbitals (with 4 e^-) ∴ 4 molecular orbitals



4 e^-

anti-bonding

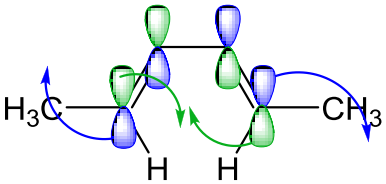
LUMO = lowest unoccupied molec. orbital

HOMO = highest occupied molecular orbital

bonding

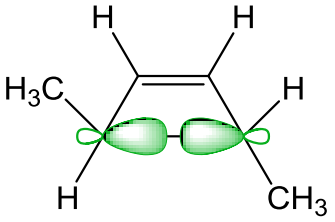
lowest E if all lined up (no nodes)

→ for an electrocyclic reaction it is the HOMO that reacts

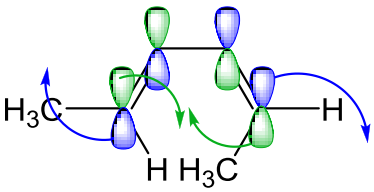


diene = trans,trans

conrotary

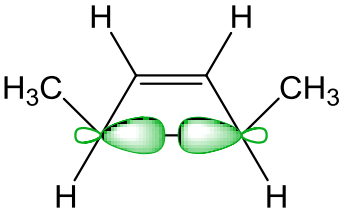


gives **only** trans product



diene = trans,cis

conrotary



gives **only** cis product

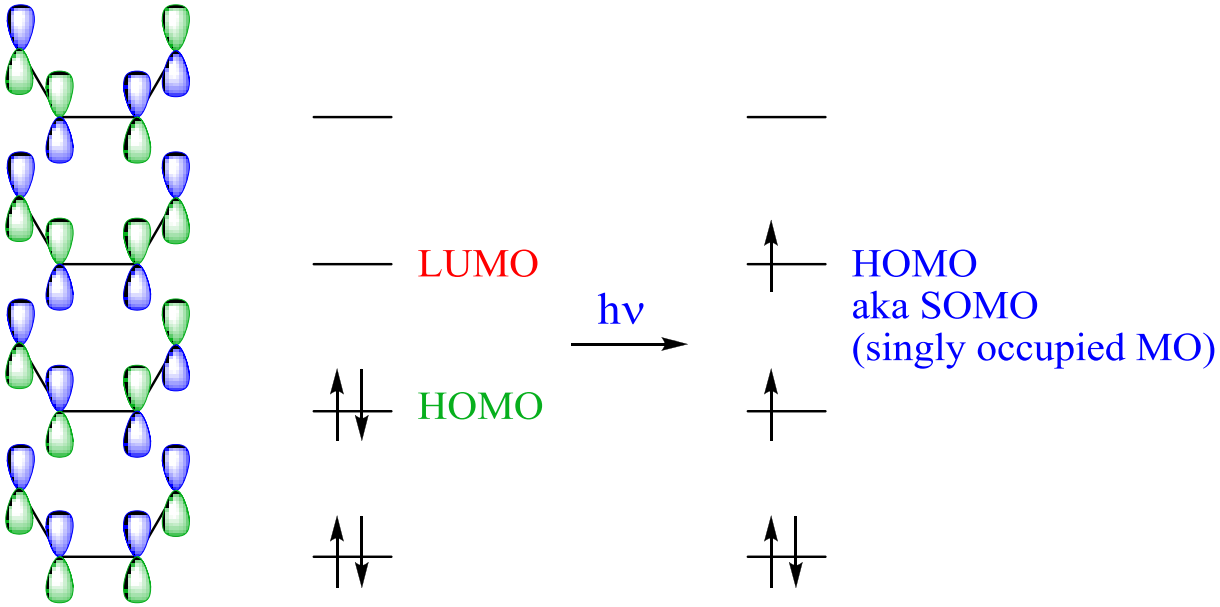
→ Reaction is stereospecific!

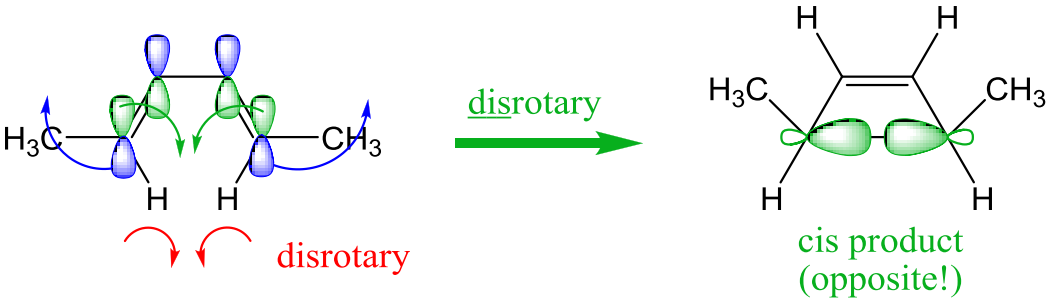
Trans-trans → trans

Trans-cis → cis

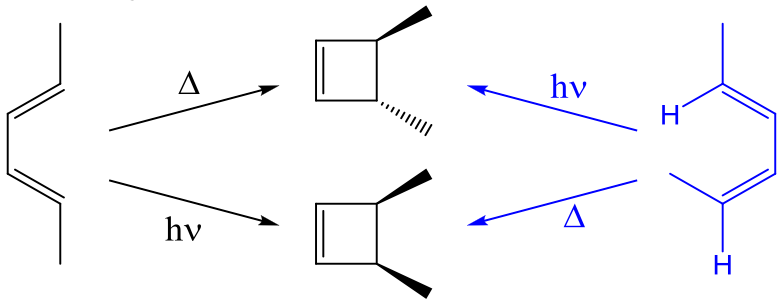
What about cis-cis? Gives trans (check it yourself!)

What if reaction is promoted by light instead of heat?

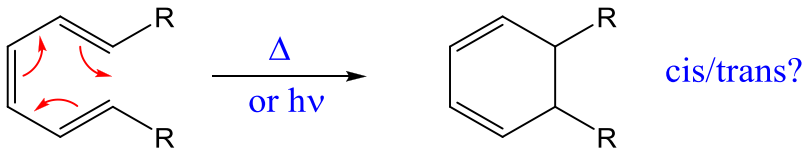




Summary:



Let's try:



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