CHEM95002:
Orbitals in Organic Chemistry - Pericyclics

LECTURE 6 *Introduction to Pericyclic Reactivity II*

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Format & scope of lecture 6

- ***The Woodward-Hoffmann Rules***
  - Diels-Alder reactions
  - Sigmatropic rearrangements
  - Thermal & photochemical electrocyclic ring-opening
- ***Frontier Molecular Orbital Theory Treatment***
  - Diels-Alder reactions
  - Sigmatropic rearrangements
  - Thermal electrocyclic ring-opening
  - Photochemical electrocyclic ring-closure

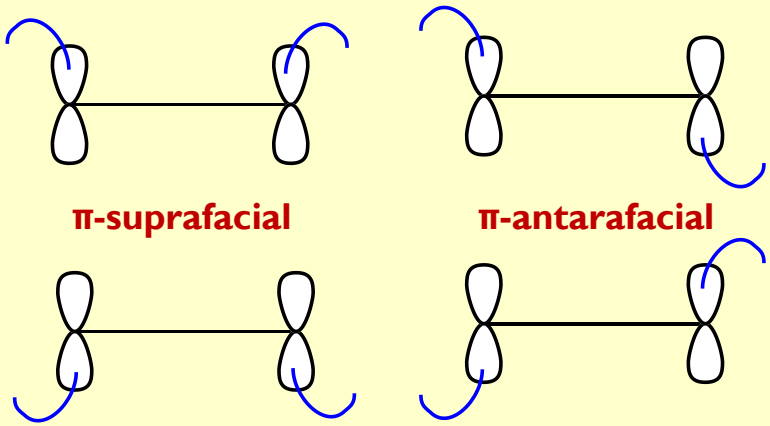
The Woodward-Hoffmann Rules

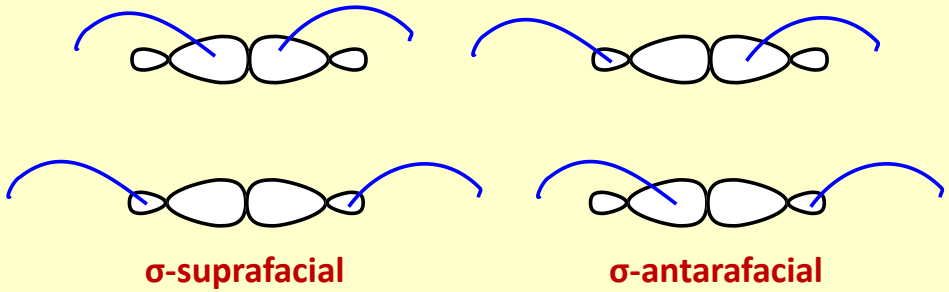
Correlation diagrams are useful for predicting which pericyclic reactions are allowed, but are not easy to construct. Happily, they can be distilled into a simple rule:

A ground state (*i.e.* **thermal**) pericyclic reaction is symmetry allowed when the total number of $(4q + 2)_s$ and $(4r)_a$ components is **odd** (where q and r must be integers).

A first electronically excited state (*i.e.* **photochemical**) pericyclic reaction is symmetry allowed when the total number of $(4q + 2)_s$ and $(4r)_a$ components is **even**.

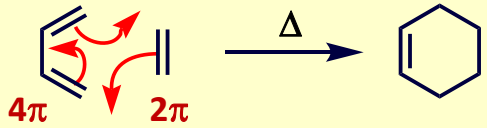
's' = **suprafacial** [bond formation on the 'same' faces of a molecular 'component']
'a' = **antarafacial** [bond formation on the 'opposite' faces of a molecular 'component']



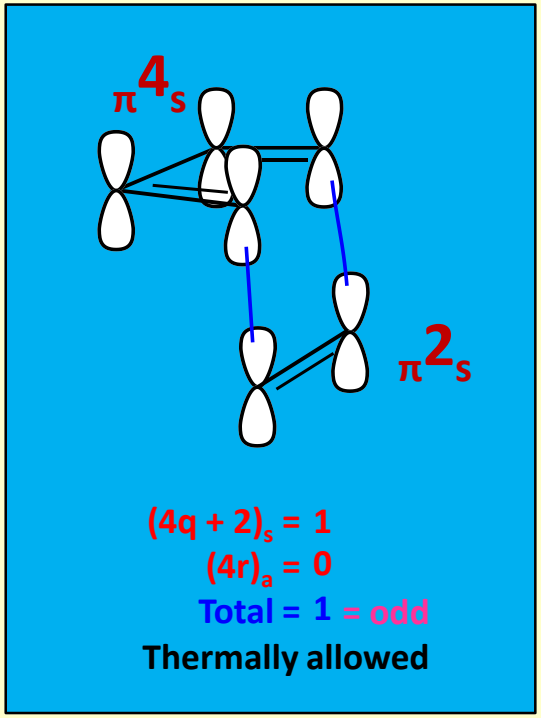


The W-H Rules: *a Diels-Alder reaction*

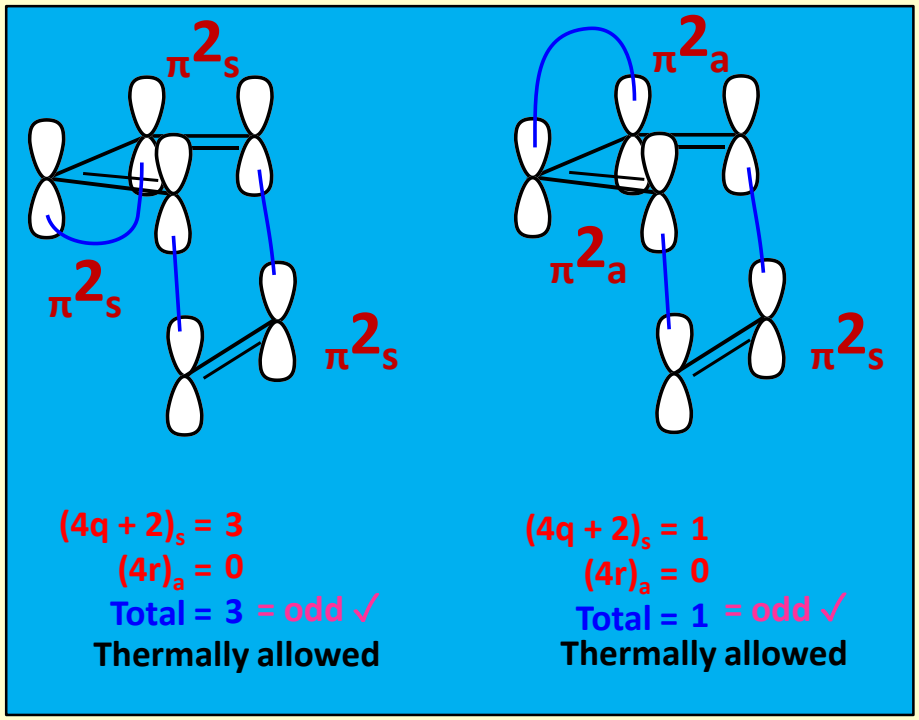
- 1. draw a ‘curly arrow’ mechanism
- 2. identify ‘components’ (how many p/s electrons in each component)
- 3. draw 3D orbital diagram to show approach and overlap of components
- 4. label **components** as suprafacial or antarafacial
- 5. sum components according to W-H rule and decide whether thermally or photochemically allowed



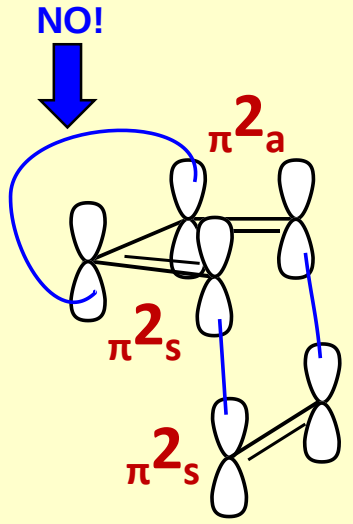
Diels-Alder [$_{\pi}4_{s}+_{\pi}2_{s}$] cycloaddition



Recommended method



Alternative valid methods

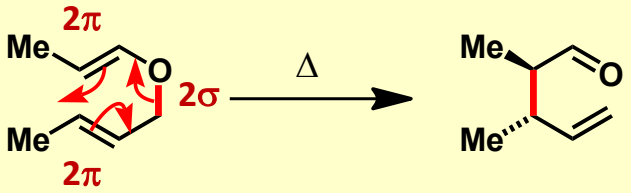


Blue line representing impossible developing orbital overlap

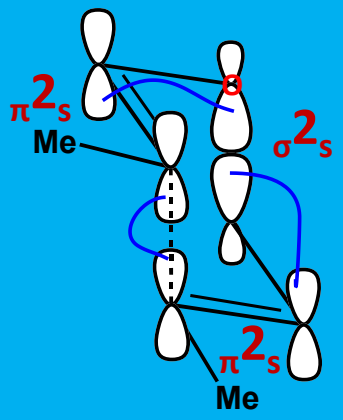
Invalid method

The W-H Rules: *a sigmatropic rearrangement*

- 1. draw 'curly arrow' mechanism and identify 'components'
- 2. draw 3D orbital diagram to show approach and overlap of components
- 3. label **components** as suprafacial or antarafacial
- 4. sum components according to W-H rule and decide whether thermally or photochemically allowed

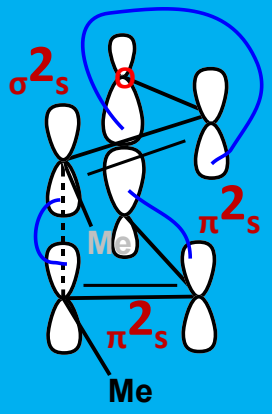


Claisen [3,3] rearrangement



$(4q + 2)_s = 3$
$(4r)_a = 0$
Total = 3 = odd
Thermally allowed

Claisen rearrangement *via* ***chair*** TS is allowed.



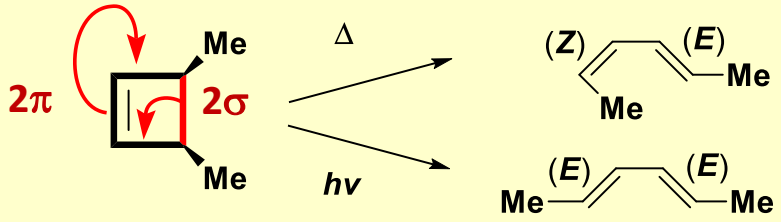
$(4q + 2)_s = 3$
$(4r)_a = 0$
Total = 3 = odd
Thermally allowed

Claisen rearrangement *via* ***boat*** TS is allowed.

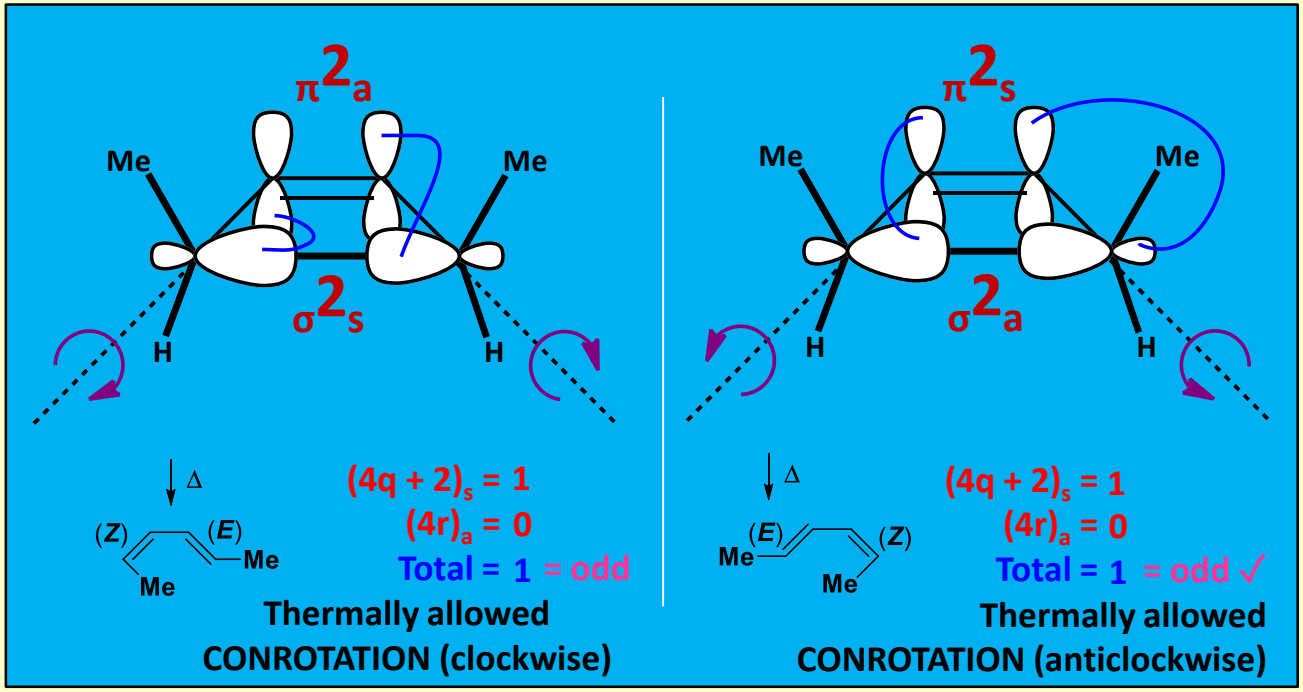
The Woodward-Hoffmann rule does **not** tell us that the chair TS is lower in energy than the boat TS - you need to use your knowledge/intuition to decide this.

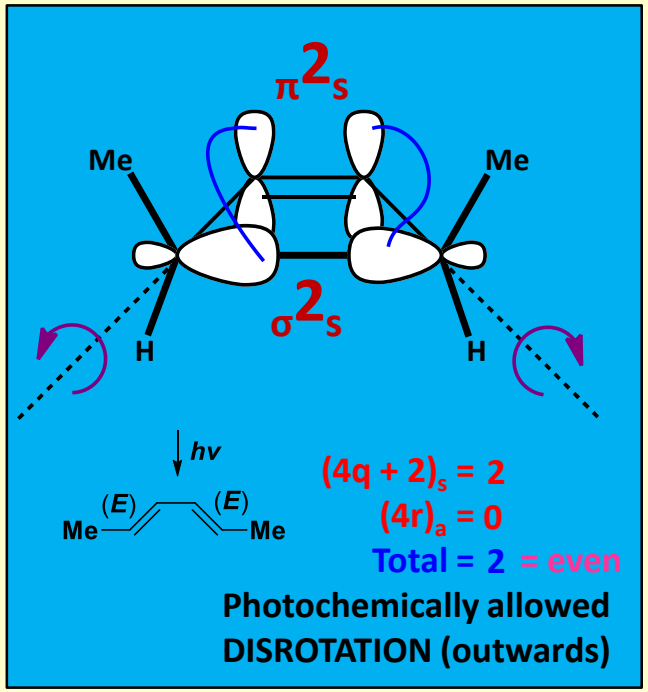
The W-H Rules: *electrocyclic ring-opening*

- 1. draw ‘curly arrow’ mechanism and identify ‘components’
- 2. draw 3D orbital diagram to show approach and overlap of components
- 3. label **components** as suprafacial or antarafacial
- 4. sum components according to W-H rule and decide whether thermally or photochemically allowed



Cyclobutene ring-opening



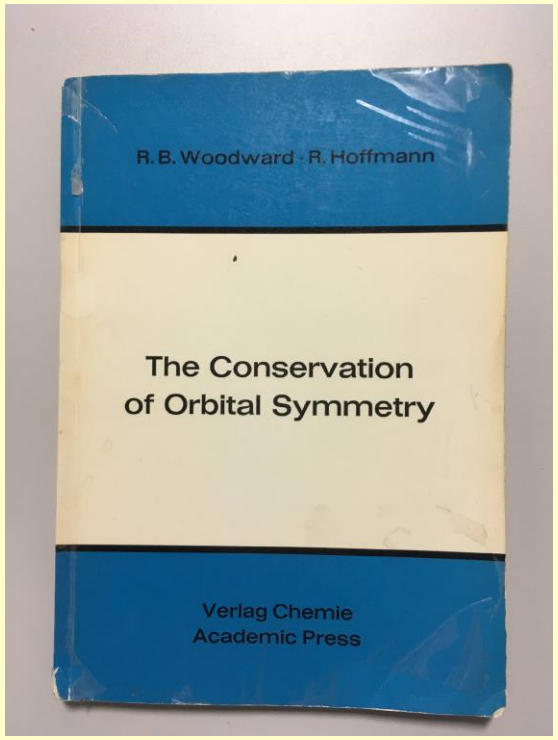


Both equally valid methods for this *thermal* case (products identical)
cf. slide 11

Thermal ring-opening is ***conrotatory***; ***Photochemical*** ring-opening is ***disrotatory***.

“Violations”

- There is an entire chapter in “The Conservation of Orbital Symmetry” given over to violations of the Woodward-Hoffmann rules



12. Violations

There are none!

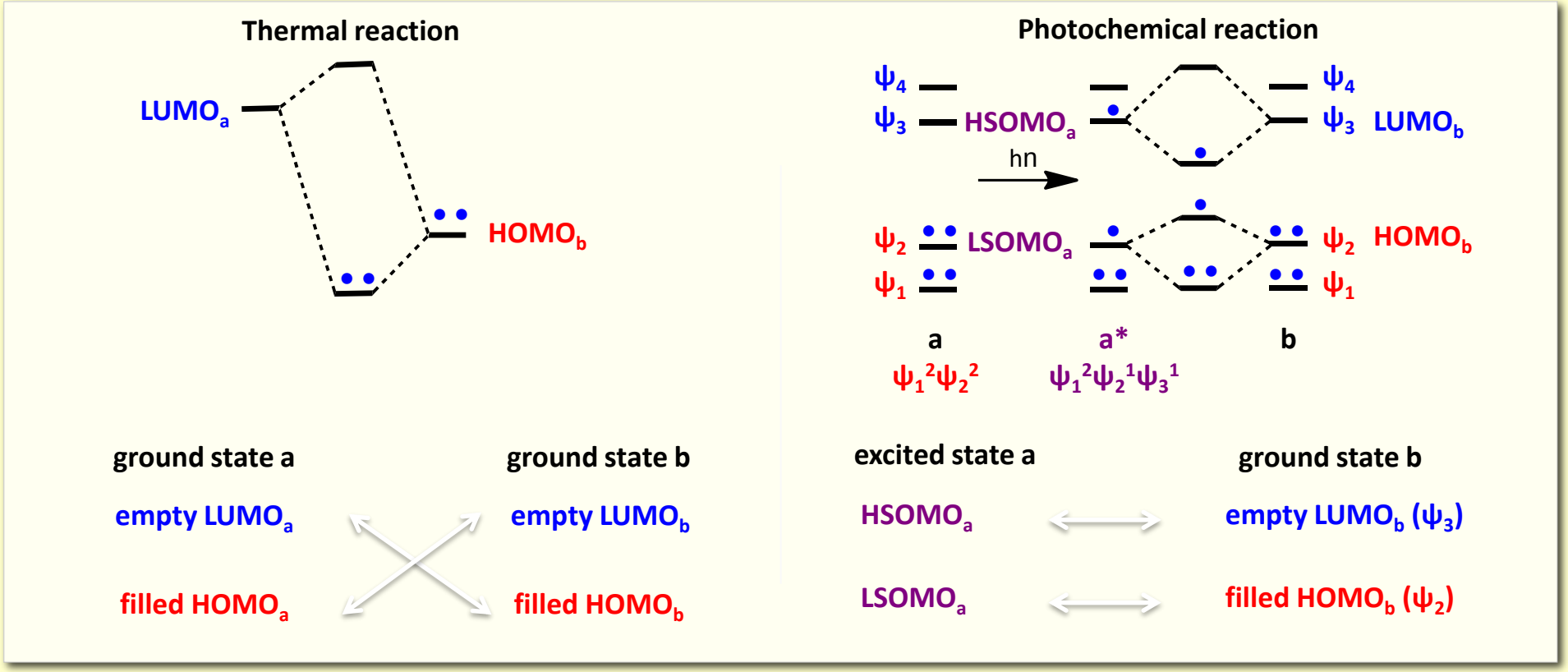
Nor can violations be expected of so fundamental a principle of maximum bonding. All the more is it then important to give consideration to some reactions which might appear on casual inspection to contravene orbital symmetry conservation.

- It’s great to be able to be so confident – but remember the rules only tell us whether there is a symmetry imposed barrier to a reaction – not what the mechanism actually is.

Frontier molecular orbital (FMO) approach

- FMO theory can also be applied to pericyclic reactions to predict whether reactions are thermally or photochemically allowed – it is a complementary approach to the W-H rules.

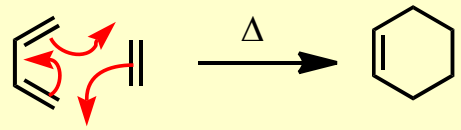
- For an excellent resource on applying FMO analysis to Pericyclic reactions see Tim Wallace's web pages at: ***https://www.stereoelectronics.org/webPR/PR_home.html***.



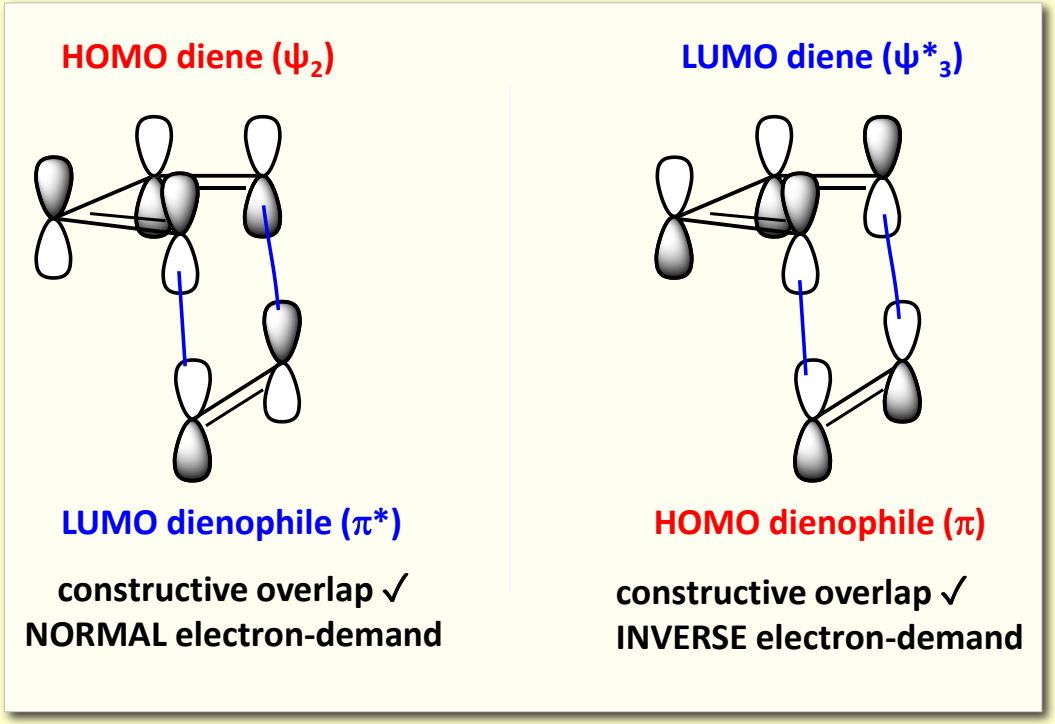
- FMO Analysis using *either* of the indicated H(S)OMO ↔ L(S)UMO pairings will give the same result, but the pair that are closest in energy are the ones that will in reality dominate reactivity.

FMO approach: *a Diels-Alder reaction*

- 1. assign single HOMO and single LUMO to the reaction
- 2. draw 3D orbital diagram to show approach and overlap of components
- 3. check for constructive overlap between the orbitals

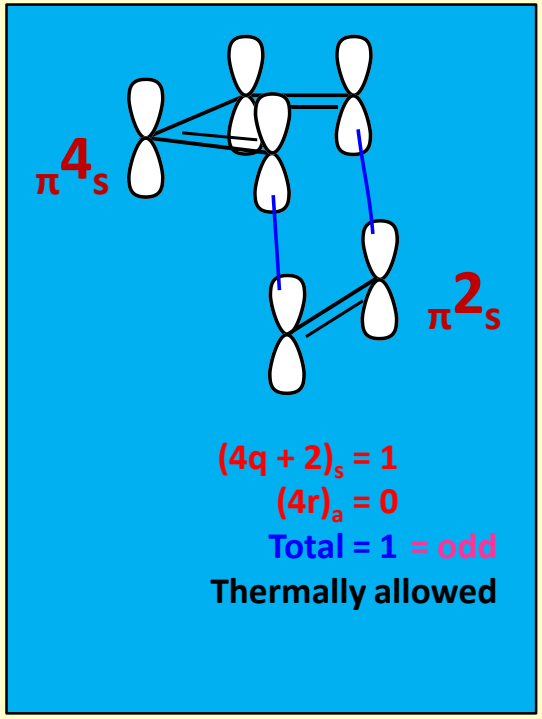


Diels-Alder [$_{\pi}4_s$+$_{\pi}2_s$] cycloaddition



FMO approach

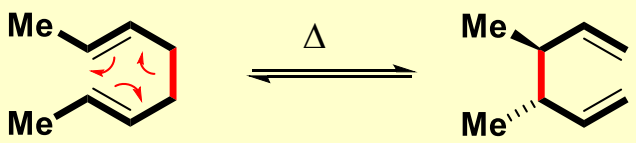
cf.



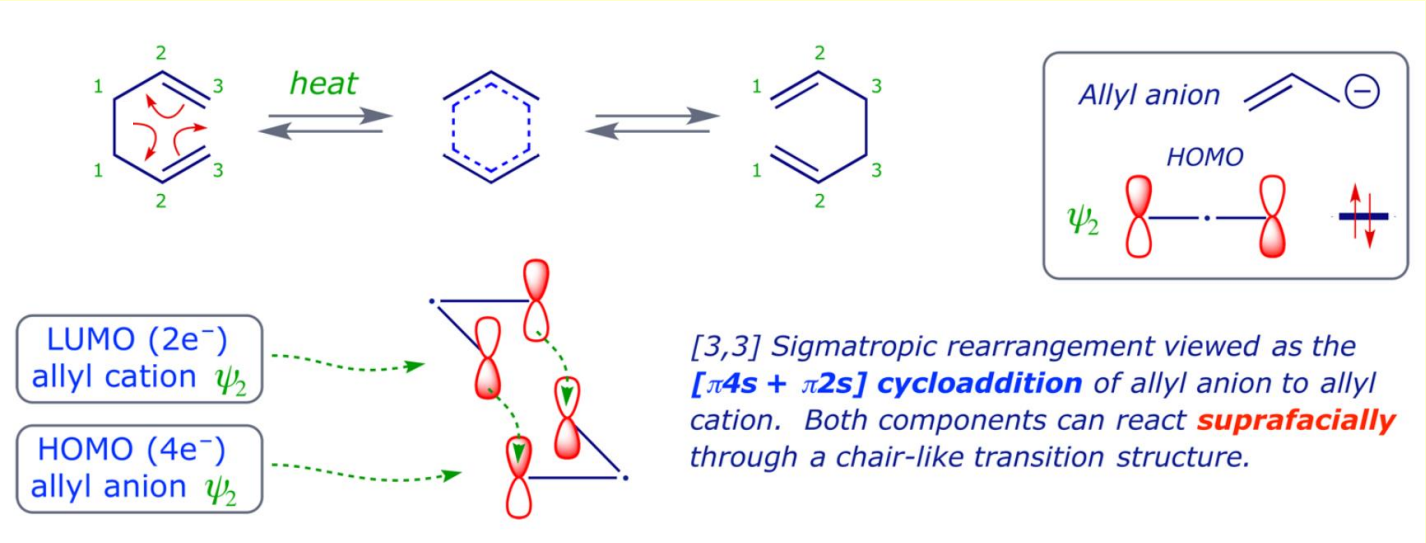
W-H approach (slide 4)

FMO approach: *a sigmatropic rearrangement*

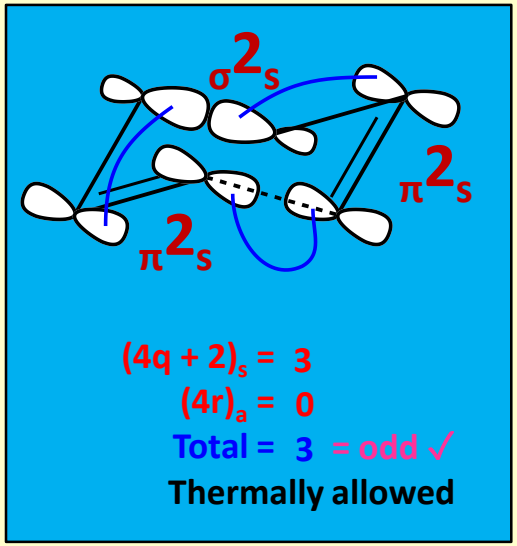
- 1. assign single HOMO and single LUMO to the reaction
- 2. draw 3D orbital diagram to show approach and overlap of components
- 3. check for constructive overlap between the orbitals



Cope [3,3] rearrangement



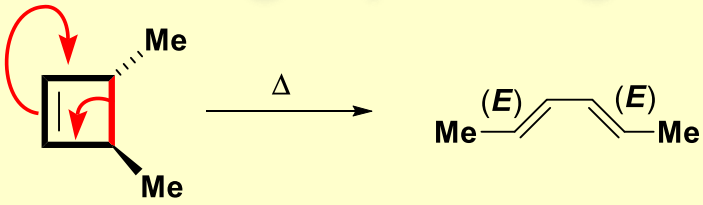
cf.



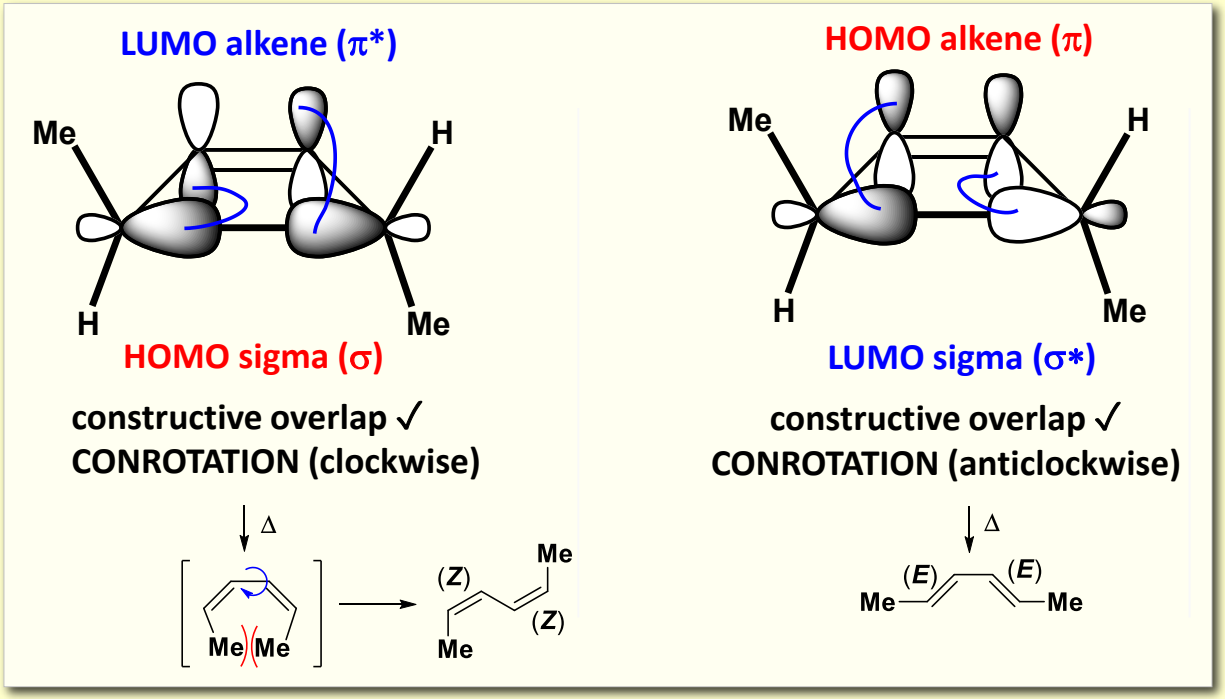
FMO approach ***W-H approach***

FMO approach: *thermal electrocyclic ring-opening*

- 1. assign single HOMO and single LUMO to the reaction
- 2. draw 3D orbital diagram to show approach and overlap of components
- 3. check for constructive overlap between the orbitals

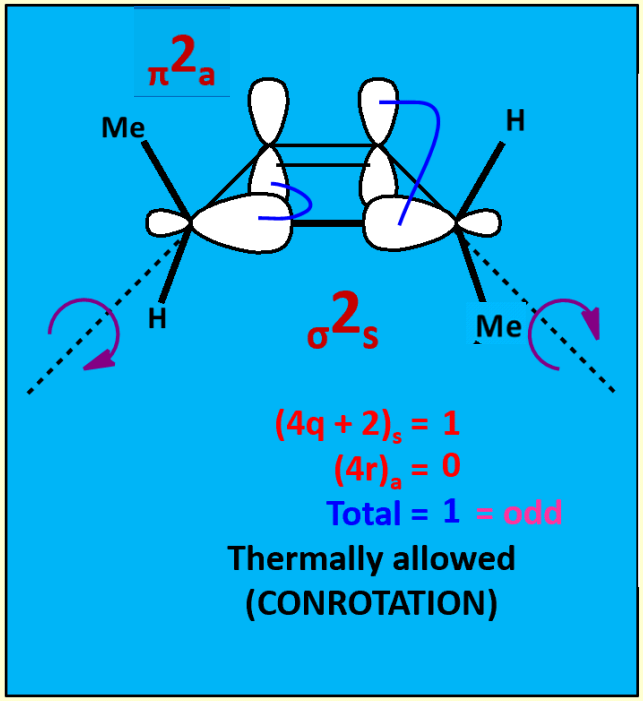


Cyclobutene ring-opening



FMO approach

cf.



W-H approach (cf. slide 6)

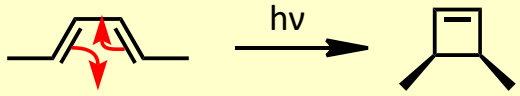
- The preference of one <u>conrotatory</u> mode (*i.e*. clockwise *vs*. anticlockwise) is termed ***torqueoselectivity***.
- Similarly for <u>disrotatory</u> modes – *i.e*. both 'inwards' *vs*. both 'outwards' is also ***torquoselectivity***.

FMO approach: *photochemical electrocyclic ring-closure*

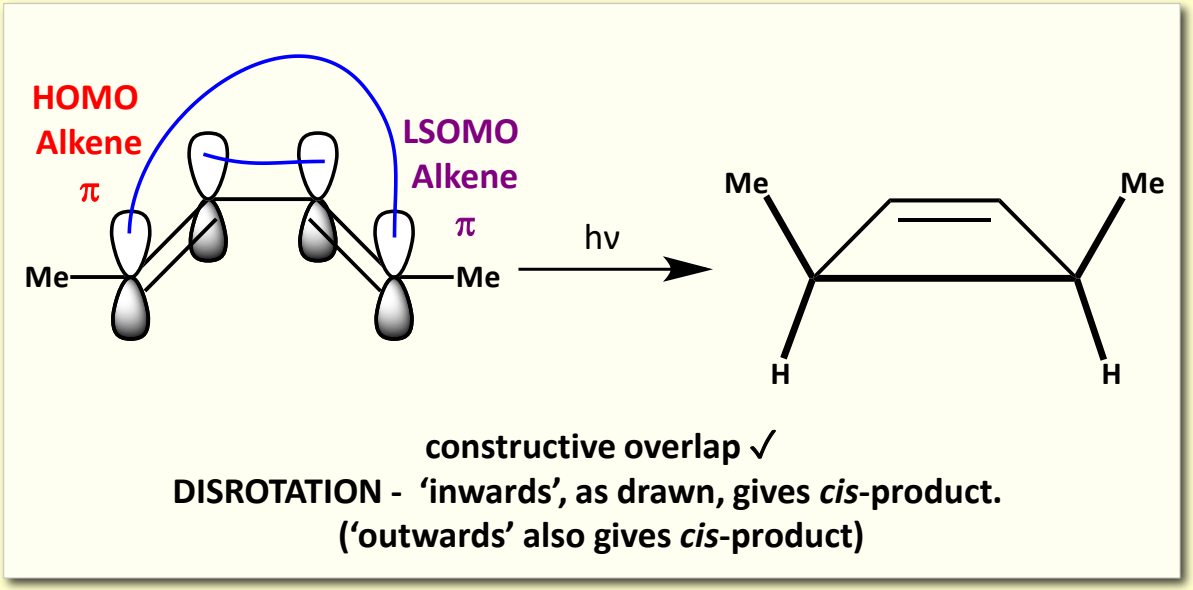
- 1. assign single HSOMO and single LUMO to the reaction (or LSOMO and HOMO). HSOMO has same phases as LUMO; LSOMO same phases as HOMO

- 2. draw 3D orbital diagram to show approach and overlap of components

- 3. check for constructive overlap between the orbitals

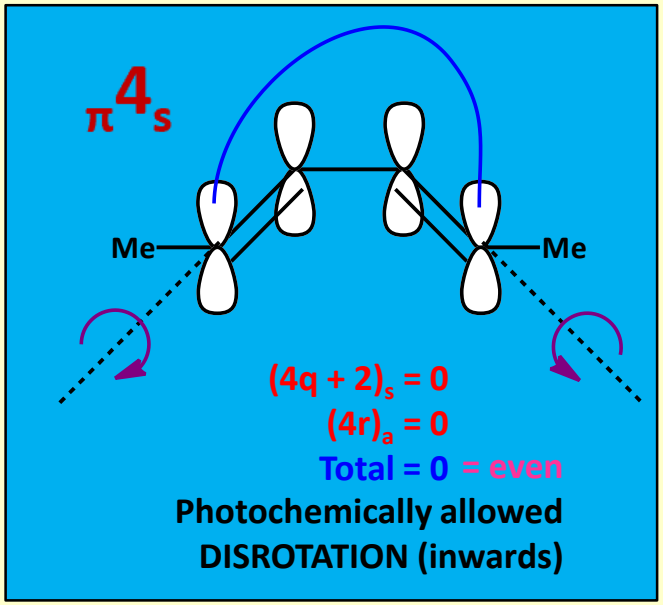


Cyclobutene ring-closure



FMO approach

cf.



W-H approach

Drawing MO diagrams and identifying FMOs