CHEM95002:
Orbitals in Organic Chemistry – Pericyclics

LECTURE 5 *Introduction to Pericyclic Reactivity I*

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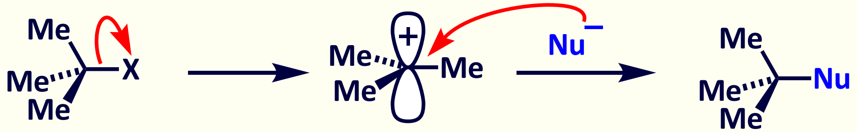
Format & scope of lecture 5

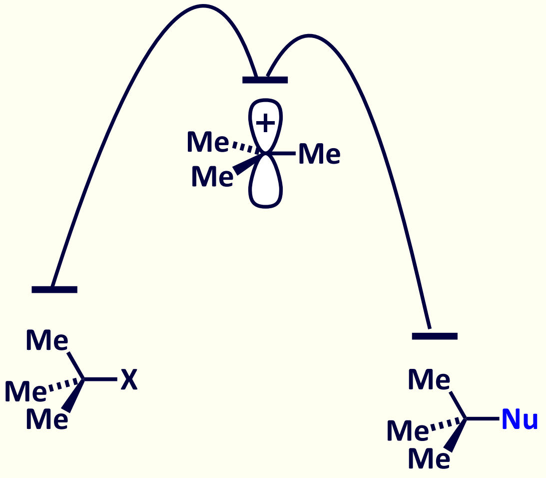
- ***The nature of pericyclic reactions***
- ***Types of pericyclic reactions***
  - Cycloadditions
  - Group Transfer reactions
  - Sigmatropic rearrangements
  - Electrocyclic reactions
- ***Drawing molecular orbitals for conjugated π-systems***
  - FMO approach
- ***Symmetry correlation diagrams***
  - Diels-Alder reaction (a thermal reaction)
  - [2+2]-cycloaddition (a photochemical reaction)

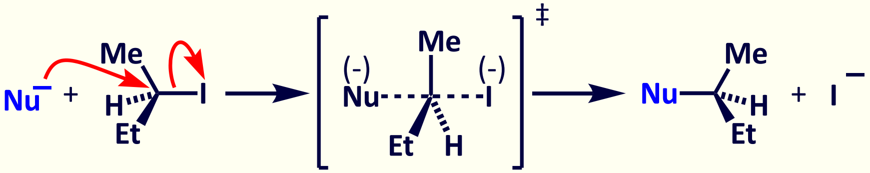
Ionic reactions

- ***Ionic reactions (e.g. S_N1 and S_N2 reactions) may or may not have an intermediate***

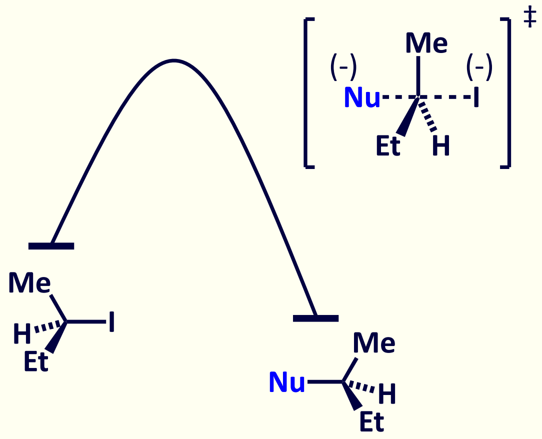


S_N1 reactions are stepwise
& have a defined intermediate





S_N2 reactions are *concerted*
& have no intermediate

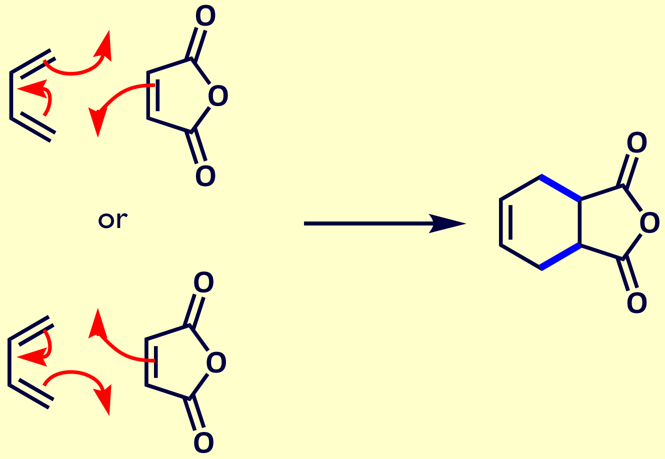


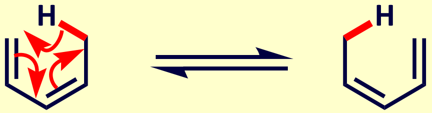
- ***In ionic reactions the curly arrows identify where the electrons have come from and where they are going and which bonds have been made and which broken***

Pericyclic reactions

- *Pericyclic reactions are those ‘in which all first-order changes in bonding relationships take place in concert on a closed curve’ (Woodward and Hoffmann, 1969)*

- *This means that the reactions have cyclic transition states in which all bond-forming and bond-breaking take place in a concerted manner without the formation of an intermediate*
- *Reactions involve a transition state with a cyclic array of interacting orbitals; a reorganisation of σ and π-bonds occurs within this cyclic array*



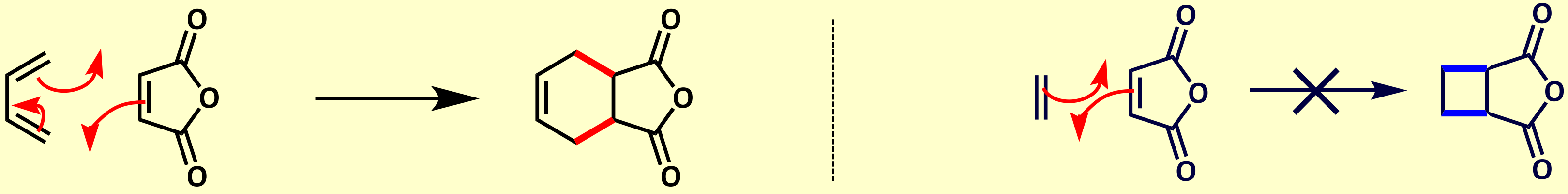


- *There is no absolute sense in which the electrons flow from one component to another (but it is sometimes more sensible to push the arrows in one direction than the other). This means that the arrows demonstrate which bonds are being broken and made rather than the ‘flow’ of electrons’*

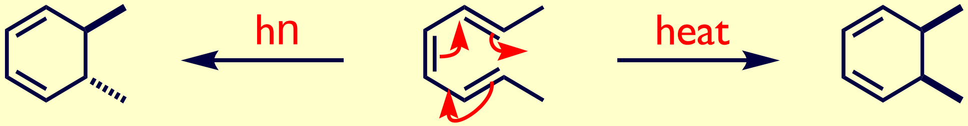
Pericyclic reactions

*"“No-mechanism” is the designation given, half in jest, half in desperation, to ‘thermo-reorganization’ reactions like the Diels-Alder and the Claisen and Cope rearrangements’**

- ***Observations that required an explanation, e.g.:***
  - **The [4+2] (Diels Alder) reaction occurs thermally, whereas the [2+2] reaction does not**



  - **Heating or irradiating hexatrienes leads to different stereochemistry**



*Doering, *Tetrahedron*, **1962**, *18*, 67 [DOI]

Four classes of pericyclic reactions

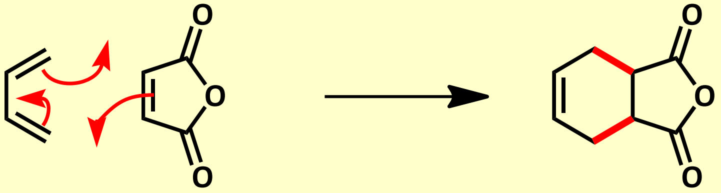
1. **Cycloaddition reactions**

Two components come together to form two new σ-bonds at the ends of both components and joining them together to form a ring.

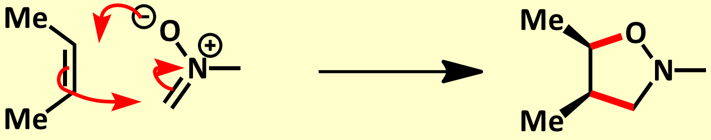
2. **Group transfer reactions**

A mix of a sigmatropic rearrangement and a cycloaddition. Bimolecular, so not sigmatropic rearrangements, and no ring is formed so they are not cycloadditions.

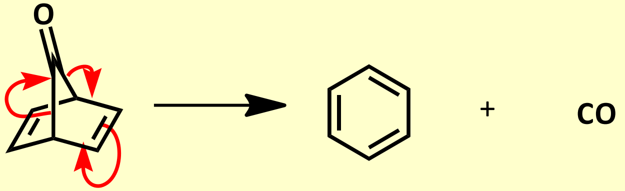
Diels-Alder reaction



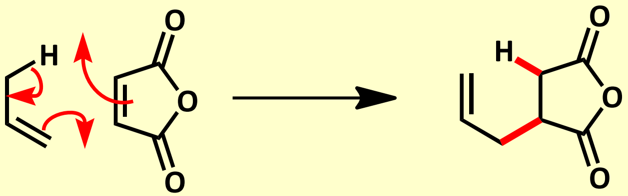
1,3-Dipolar cycloaddition



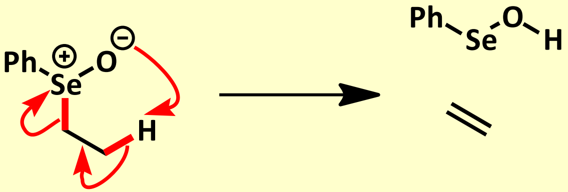
Cheletropic extrusion



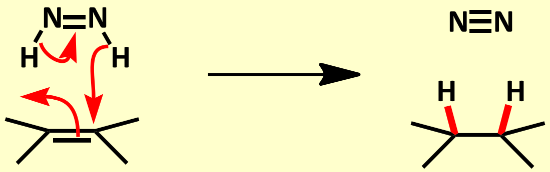
Alder-ene reaction



***Syn*-elimination reaction**



Diimide reduction



Four classes of pericyclic reactions

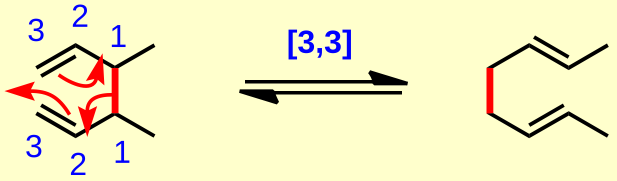
3. **Sigmatropic rearrangements**

Unimolecular isomerisations which formally involve the overall movement of a σ-bond from one position to another.

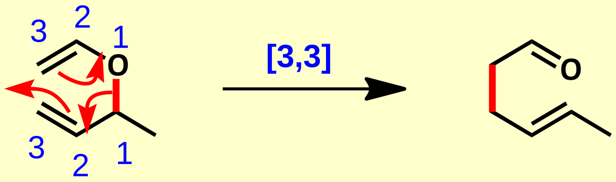
4. **Electrocyclic reactions**

Unimolecular reactions characterized by the formation of a ring from an open chain conjugated system with a σ-bond forming across the ends of the conjugated system.

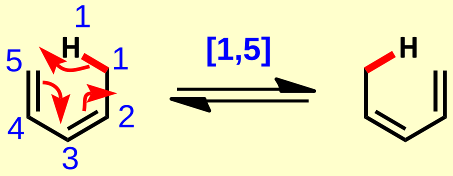
Cope rearrangement



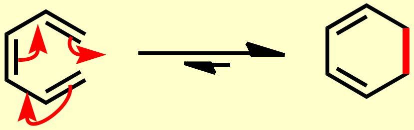
Claisen rearrangement



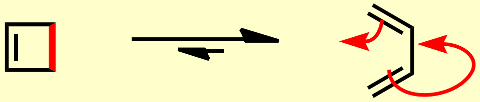
[1,5]-hydride shift



Hexatriene electrocyclic ring-closure



Cyclobutene electrocyclic ring-opening



Drawing MO diagrams and identifying FMOs

- To draw a molecular orbital diagram for a ***conjugated array of p-orbitals***:

i) count the number of p-orbitals: n

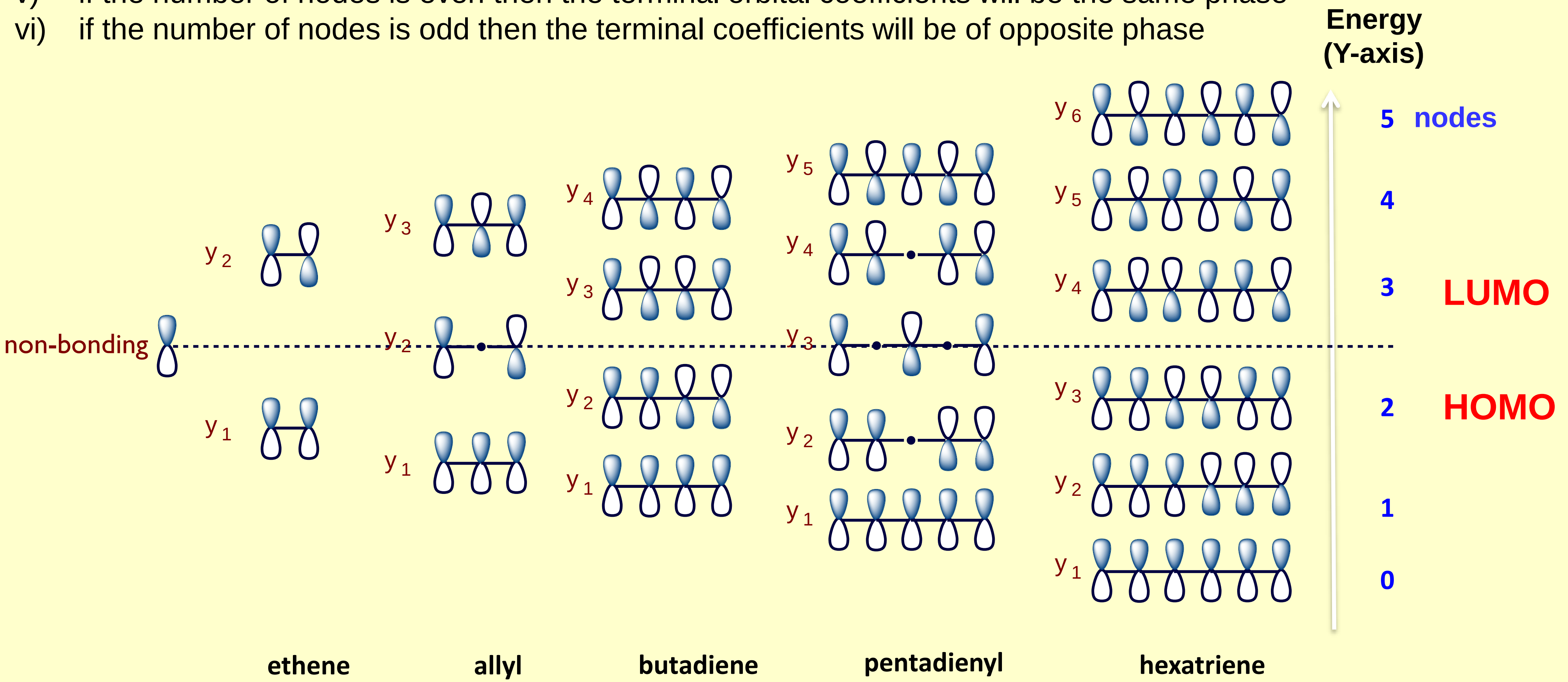
ii) count the number of electrons: π-bond = 2, unpaired electron = 1, carbanion = 2, carbocation = 0

iii) draw n horizontal lines stacked on top of one another to represent the MOs

iv) draw the MOs as the combination of p-orbitals with an increasing number of **nodes** from 0 for ψ_1 to n-1 for ψ_n such that *each MO is symmetric or antisymmetric with respect to any symmetry operation of the array.*

v) if the number of nodes is even then the terminal orbital coefficients will be the same phase

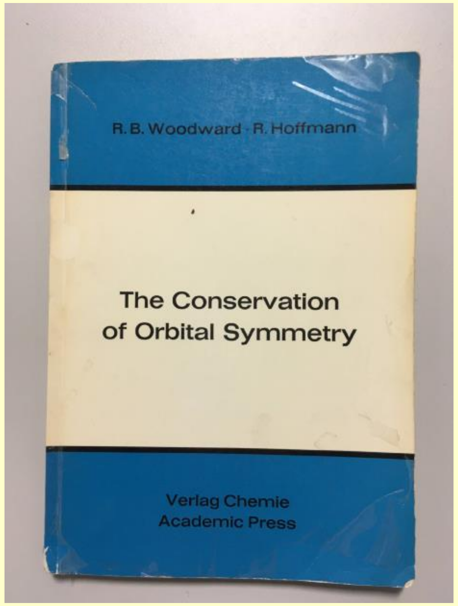
vi) if the number of nodes is odd then the terminal coefficients will be of opposite phase



Orbital correlation diagrams

During a pericyclic reaction the orbitals of the starting material are smoothly converted into the orbitals of the product.

This means that the symmetry of the orbitals with respect to any symmetry operations of the molecule must be conserved in moving from the starting material(s) to product.
This is the '***Conservation of Orbital Symmetry***', which is readily depicted in an 'orbital correlation diagram'



R. B. Woodward · R. Hoffmann

The Conservation
of Orbital Symmetry

Verlag Chemie
Academic Press

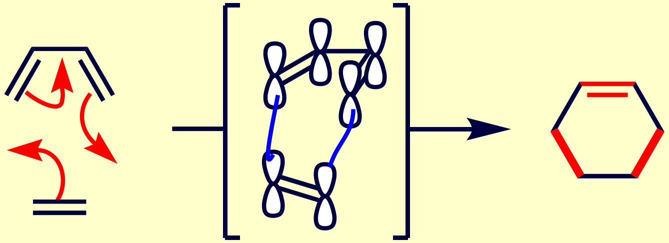
Robert Burns Woodward 1917-1979
American, Nobel 1965

Roald Hoffmann 1937
American, Nobel 1981

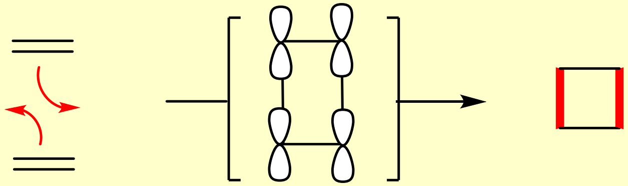
Conservation of orbital symmetry

- We will exemplify ***conservation of orbital symmetry*** by looking at orbital correlation diagrams for:

- the *thermal* Diels-Alder reaction between butadiene and ethene:



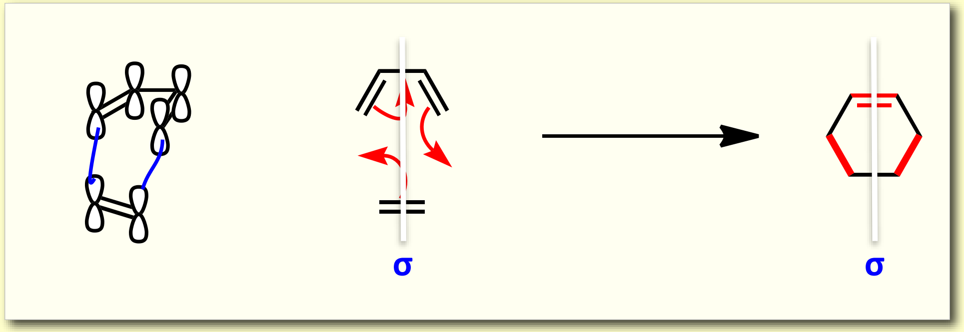
- the *photochemical* [2+2]-cycloaddition (dimerization) of ethene:

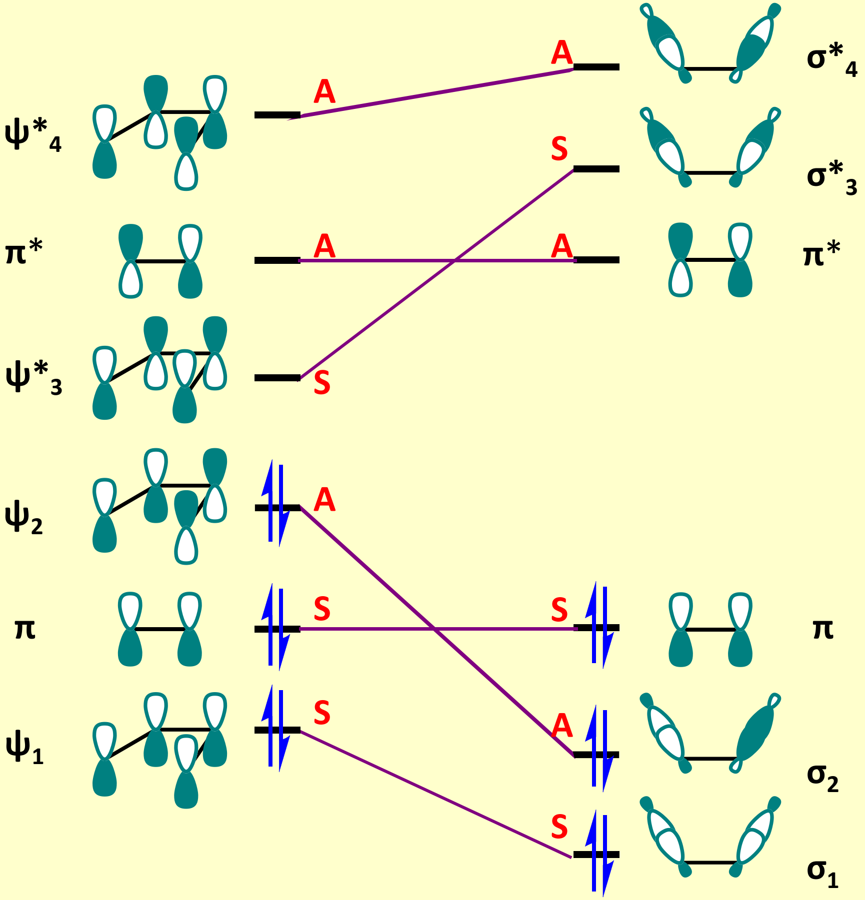


- ***NB*. I will NOT expect you to be able to construct orbital correlation diagrams in an exam.**

Orbital correlation diagram: the Diels-Alder reaction

- Identify orbitals undergoing change (curly arrows tell us which orbitals these are).
- Draw the approach of substrates for maximum orbital overlap.
- Identify symmetry elements maintained during reaction (*i.e*. present in both starting materials and product) – in this case a plane of symmetry (σ) perpendicular to the molecular planes of both the diene and dienophile and passing through the double bond of the dienophile and the central single bond of the diene.
- Rank orbitals approximately by energy.
- Classify each orbital as ***symmetric*** (S) or ***antisymmetric*** (A) with respect to the symmetry element conserved during the reaction.
- Construct orbital correlation diagram connecting orbitals of starting materials with those closest in energy and of the same symmetry in the product & add electrons according to the Aufbau principle.
- In the orbital correlation diagram of the Diels- Alder reaction all interacting bonding orbitals in the diene/dienophile are correlated with new *bonding* orbitals in the product. The reaction is ***thermally allowed***.





Orbital correlation diagram: [2+2] cycloaddition

- Identify orbitals undergoing change (curly arrows tell us which orbitals these are).
- Draw the approach of substrates for maximum orbital overlap – in this case face on approach of the two alkenes.
- Identify symmetry elements maintained during reaction (*i.e.* present in both starting materials and product) – in this case two planes of symmetry, σ_1 and σ_2.
- Rank orbitals approximately by energy.
- Classify each orbital as ***symmetric*** (S) or ***antisymmetric*** (A) with respect to the symmetry elements conserved during the reaction.
- Construct orbital correlation diagram connecting orbitals of starting materials with those closest in energy and of the same symmetry in the product & add electrons according to the Aufbau principle.
- Here the ground state $\pi_l{}^2\pi_2{}^2$ does not correlate with the ground state of the product ($\sigma_1{}^2\sigma_2{}^2$) but with a doubly excited state $\sigma_1{}^2\sigma_3{}^2$ – the thermal [2+2] cycloaddition of alkenes is thermally disallowed but ***photochemically allowed***.