CHEM60001:
Advanced Chemistry Topics 1 – Pericyclic Reactions

LECTURE 2
Introduction to Pericyclic Reactions & Orbital Symmetry

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Format & scope of lecture 2

- **The nature of pericyclic reactions**
  - *cf.* ionic and radical processes
- **Types of pericyclic reaction**
  - Cycloaddition reactions, group transfer reactions, sigmatropic rearrangements and electrocyclic reactions
- **Conservation of orbital symmetry**
  - Woodward & Hoffmann
  - Symmetry correlation diagrams
    - Diels-Alder reactions
    - [2+2]-cycloaddition reactions
    - Electrocyclic ring-opening of cyclobutenes
    - Electrocyclic ring-closure of hexatrienes


Key further reading:
- <u>BOOK</u>: Clayden, Greeves & Warren, <u>*Organic Chemistry*</u>, 2nd Ed.,
  - <u>*Chapter 34*</u> *– pericyclic reactions 1*

- <u>WEB</u>: Pericyclic Reactions - https://www.stereoelectronics.org/webPR/PR_home.html
 - <u>*Chapter 1*</u> *– introduction to pericyclic reactions*

The nature of pericyclic reactions
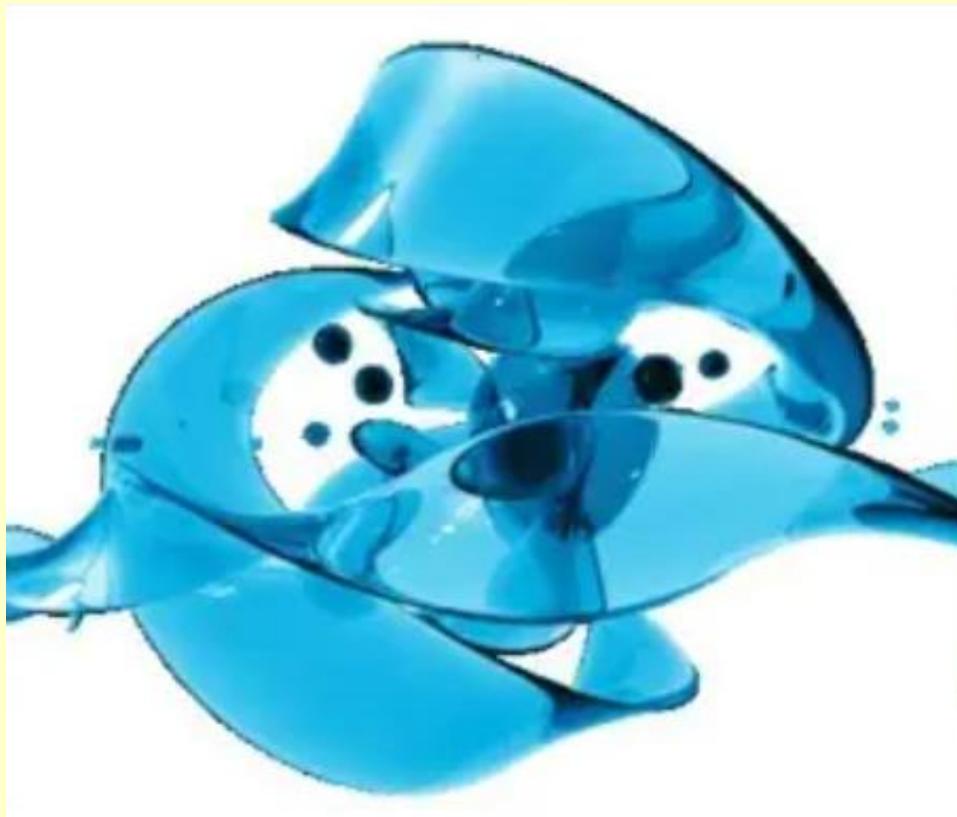
Ionic reactions

- *Ionic reactions (e.g. S_N1 and S_N2 reactions) may or may not have an intermediate*
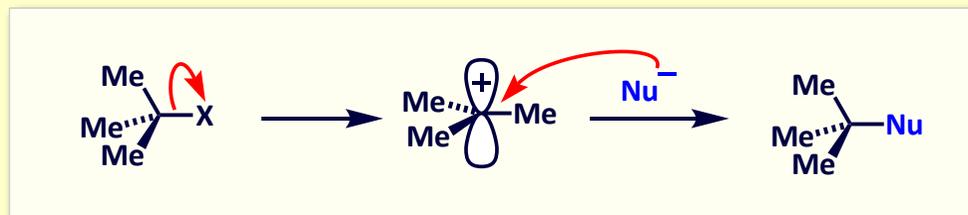
S_N1 reactions are stepwise
& have a defined intermediate
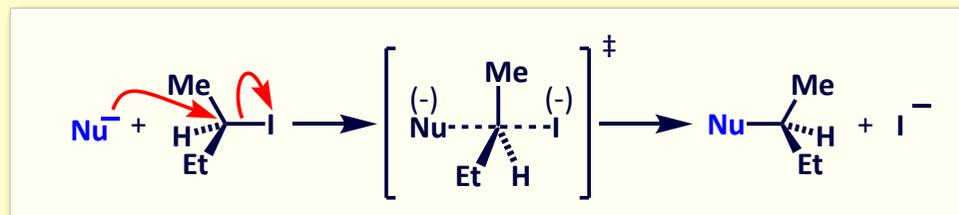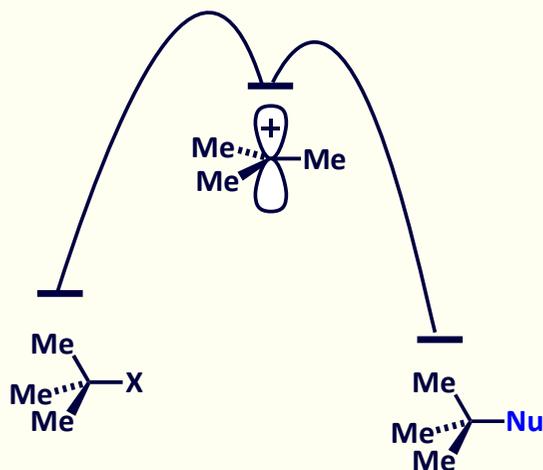
S_N2 reactions are *concerted*
& have no intermediate
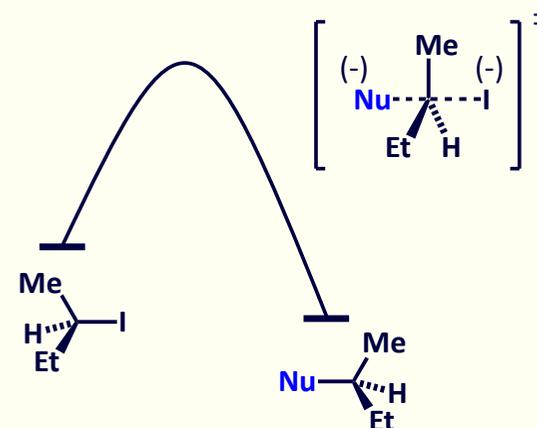
- *In ionic reactions the curly arrows identify where the electrons have come from and where they are going and which bonds have been made and which broken*

Radical reactions

- *Radical reactions involve the correlated movement of single electrons*
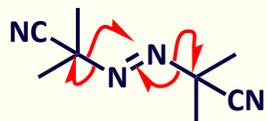

frequently shortened to
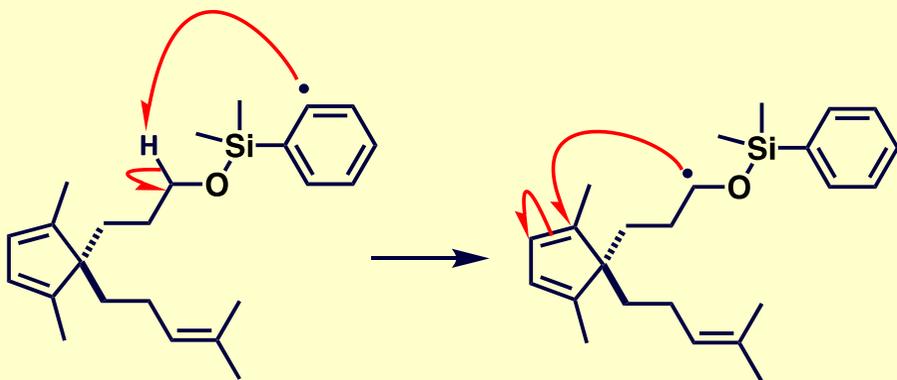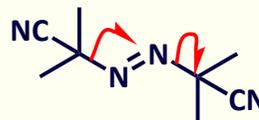
...as seen in radical cascades
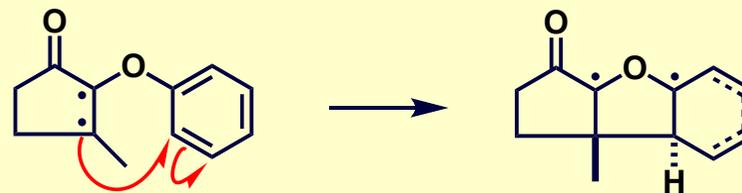
...and photochemical radical processes

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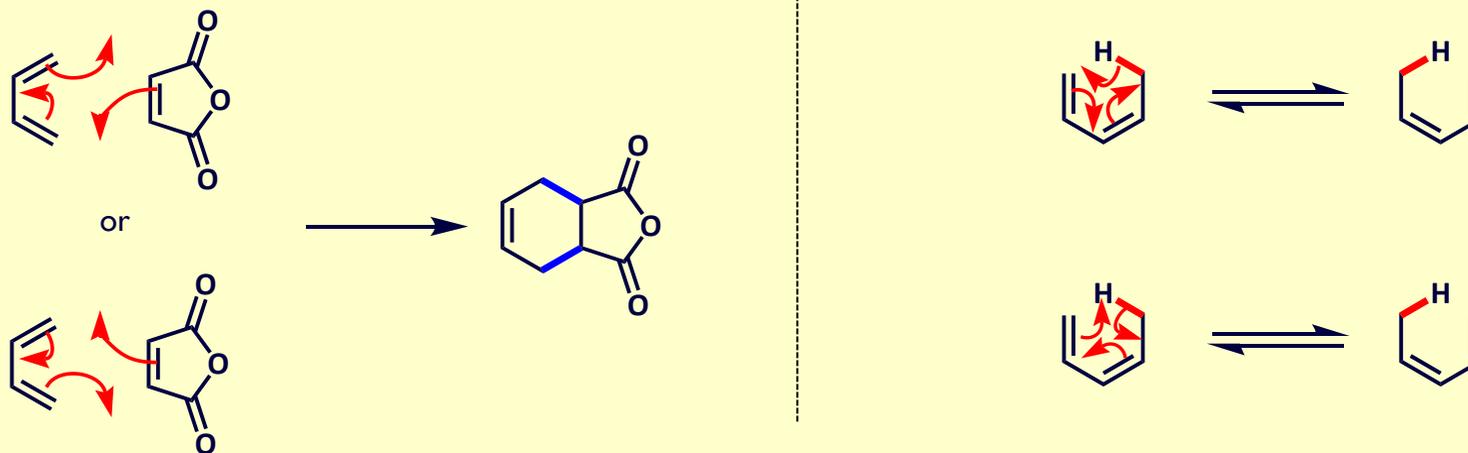
- *There is no absolute sense in which the electrons flow from one component to another (but it is sometimes more sensible to push the arrows in one direction than the other)*
- *This means that the arrows demonstrate which bonds are being broken and made rather than the 'flow' of electrons'*

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]-cycloaddition (Diels Alder) reaction occurs thermally, whereas the [2+2]-cycloaddition reaction does not**
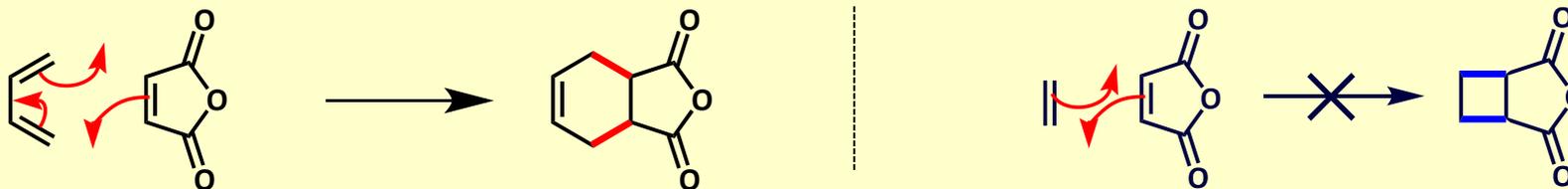
  – **Heating or irradiating hexatrienes leads to different stereochemistry**

Types of pericyclic reaction

IMAGE: https://www.thoughtco.com/definition-of-molecular-orbital-605367
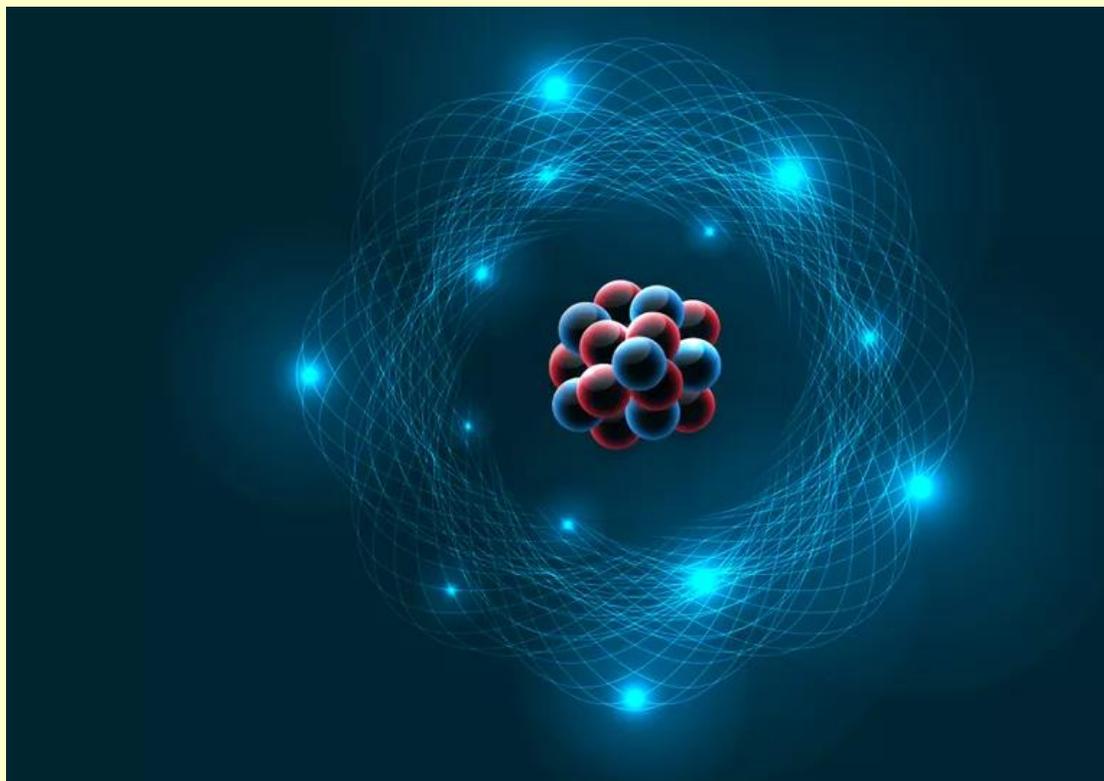
Four classes of pericyclic reactions

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
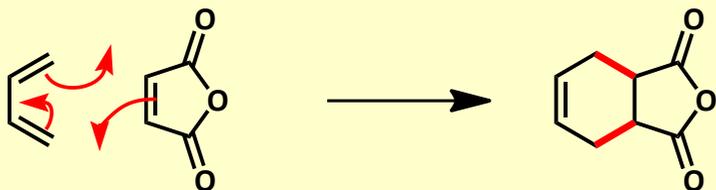
1,3-Dipolar cycloaddition
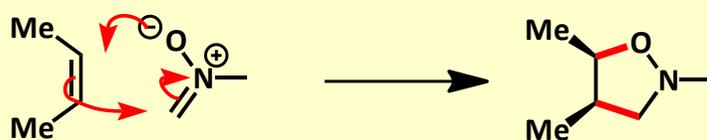
Cheletropic extrusion

Alder-ene reactions
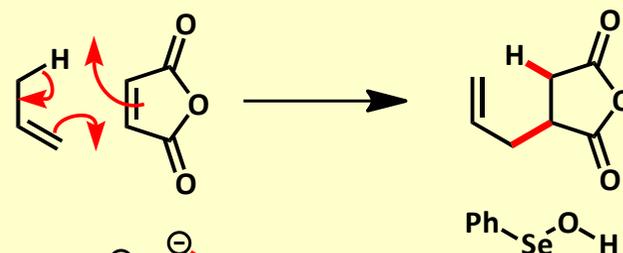
Diimide reduction
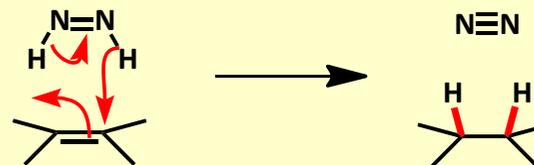
# Four classes of pericyclic reactions

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
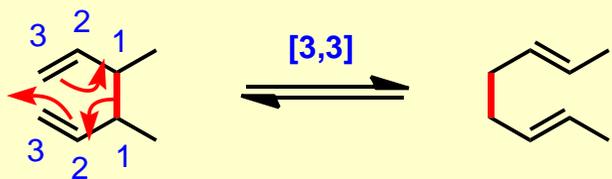
Claisen rearrangement

[1,5]-hydride shift

Hexatriene electrocyclic ring-closure
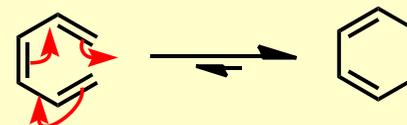
Cyclobutene electrocyclic ring-opening
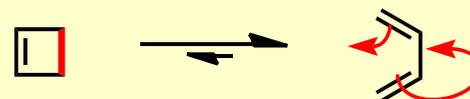
# Conservation of orbital symmetry
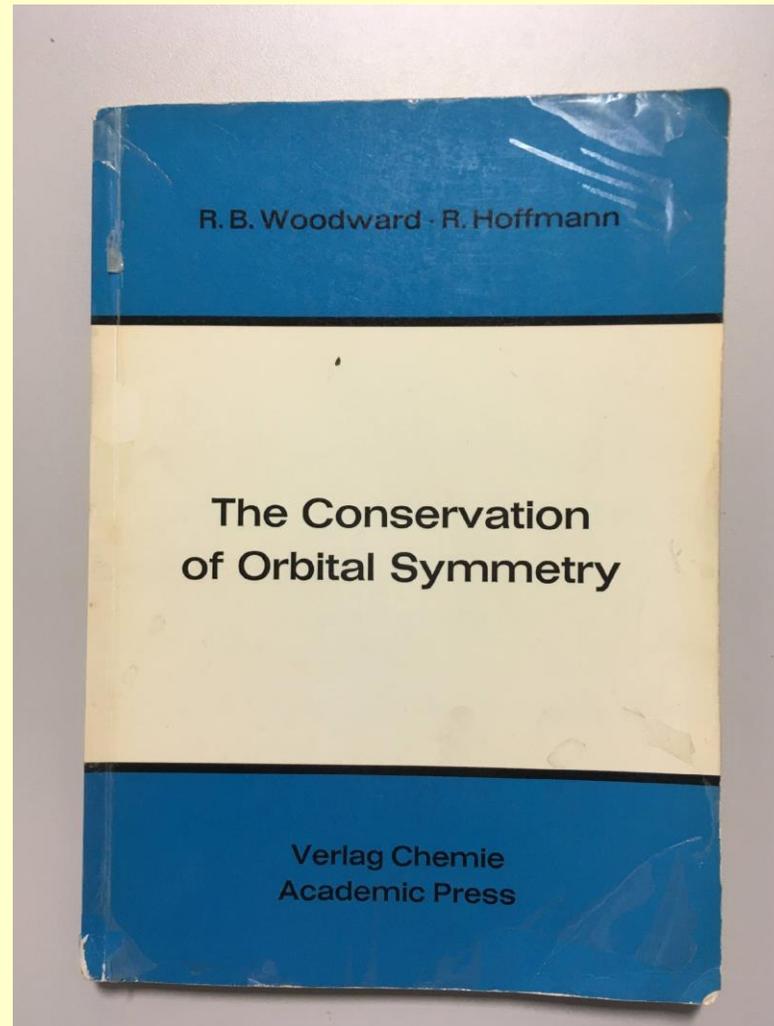
IMAGE: My copy of the classic text!

Conservation of orbital symmetry

During a pericyclic reaction the molecular orbitals of the starting material are smoothly converted into the molecular 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'
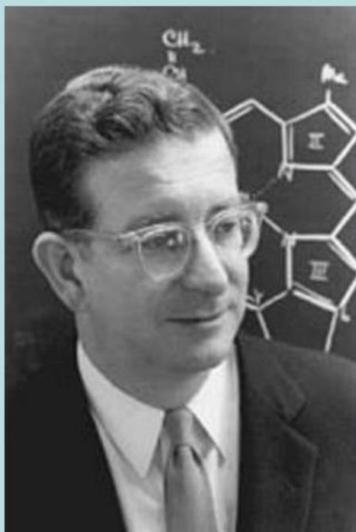
Robert Burns Woodward 1917-1979
American, Nobel 1965

Roald Hoffmann 1937
American, Nobel 1981

Conservation of orbital symmetry

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

• A *thermal* [4+2]-cycloaddition (Diels-Alder) reaction & a *photochemical* [2+2]-cycloaddition:
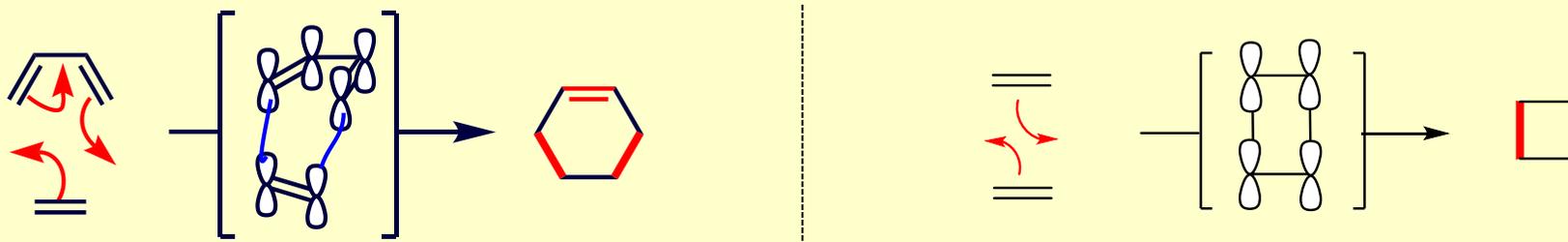

• An electrocyclic ring-opening reaction & an electrocyclic ring-closure reaction:

conrotatory

disrotatory

conrotatory
under C$_2$

disrotatory
under S
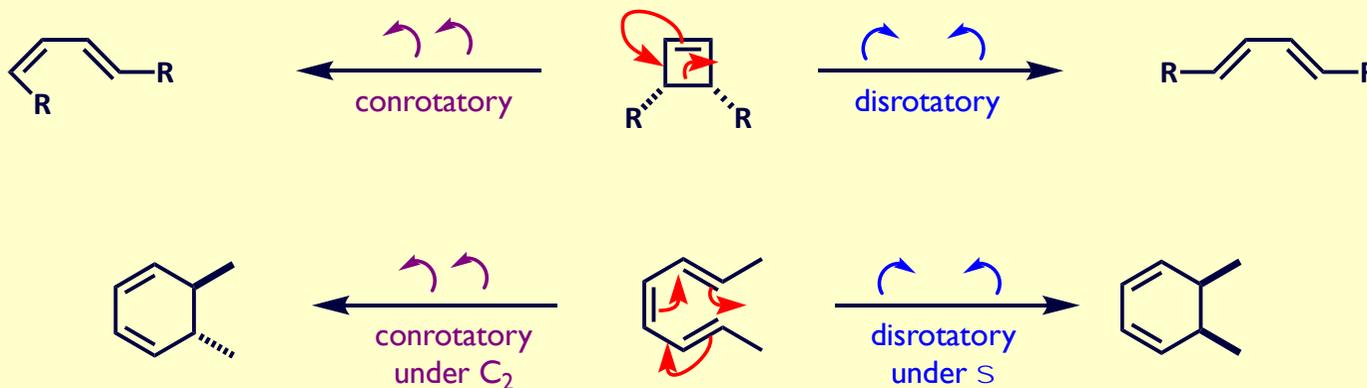
• *NB.* **I will NOT expect you to be able to construct orbital correlation diagrams in an exam.**

■ 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.

■ The 'reactant' ground state ($\psi_1^2\pi^2\psi_1^2$) correlates with the product ground state ($\sigma_1^2\sigma_2^2\pi^2$) so the reaction is *thermally allowed*.
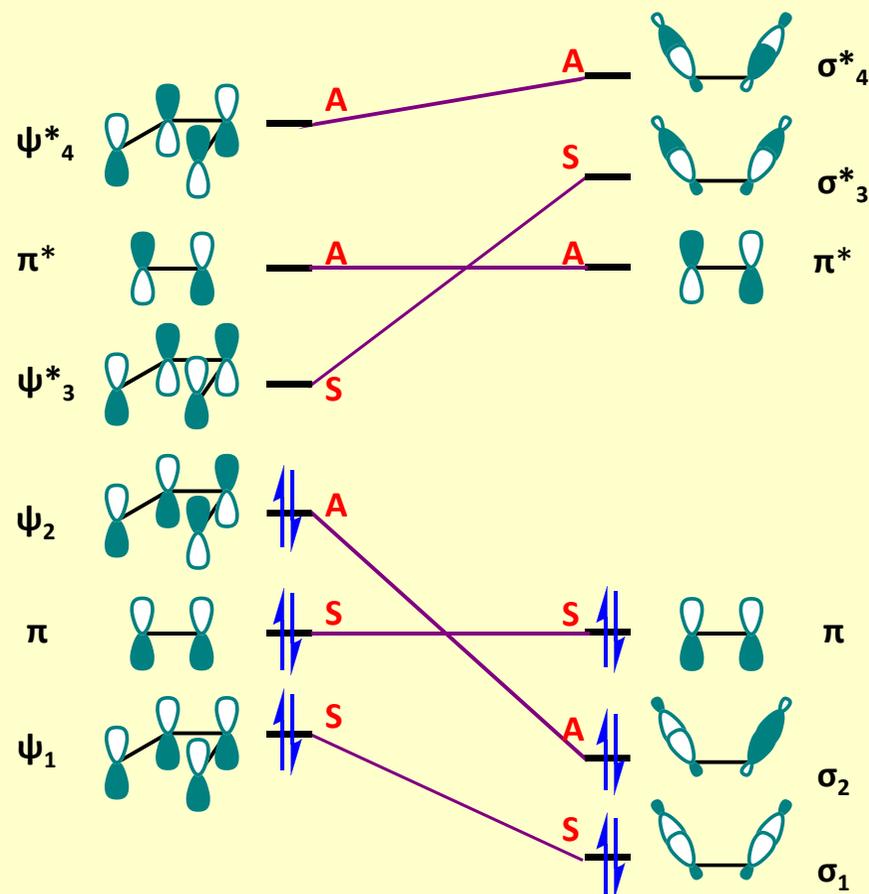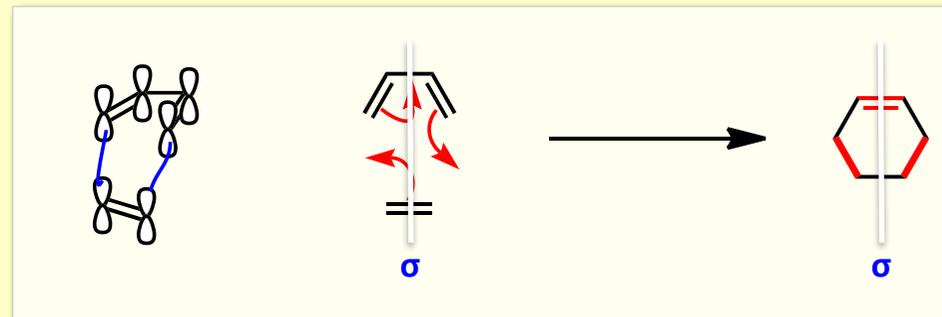
■ Identify orbitals undergoing change (curly arrows tell us which orbitals these are).

■ 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.

■ The 'reactant' ground state ($\pi_1^2\pi_2^2$) does *not* correlate with the product ground state ($\sigma_1^2\sigma_2^2$) but with a doubly excited state ($\sigma_1^2\sigma_3^2$) so the [2+2]-cycloaddition of alkenes is *thermally disallowed*.

■ However, photochemical excitation of the 'reactant' gives the 1st excited state ($\pi_1^2\pi_2^1\pi_3^1$, not shown), which correlates smoothly with the 1st excited state of the product ($\sigma_1^2\sigma_2^1\sigma_3^1$, not shown) so the [2+2]-cycloaddition of alkenes is *photochemically allowed*.
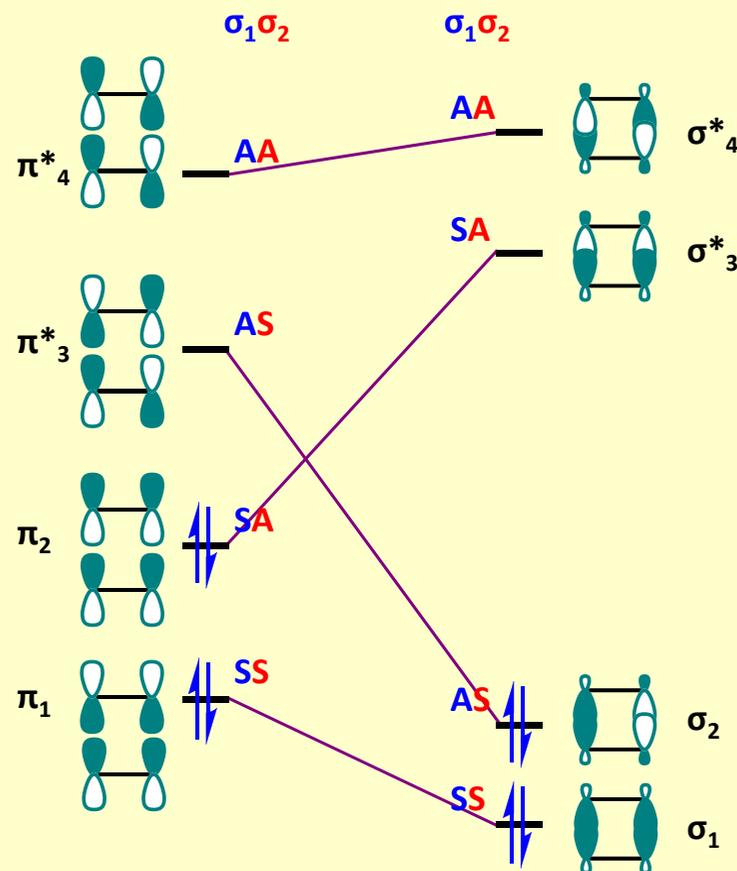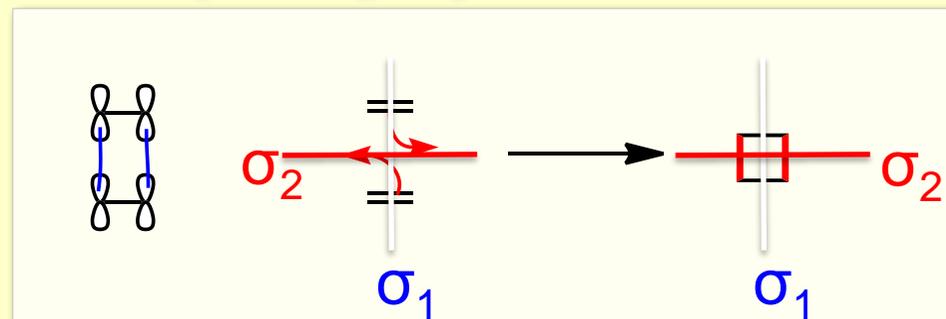
Orbital correlation diagram: electrocyclic ring-opening[16]

Z,E : E,E 20,000:1
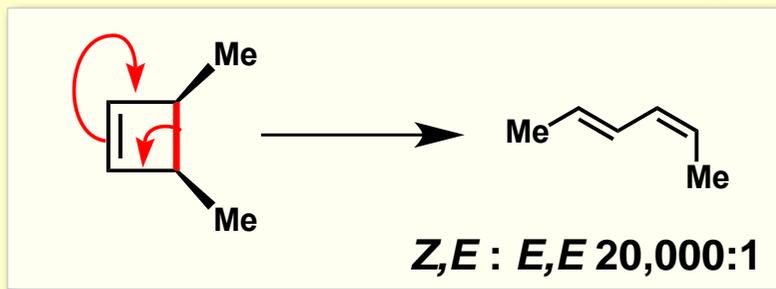
- There are two modes of opening – ***conrotatory*** or ***disrotatory***

- ***Conrotatory*** – *rotation around the axes of the σ-bonds (dotted lines) occurs in the same direction -* throughout this process the molecule retains a C_2-axis which passes through the plane of the molecule and the breaking σ bond.

C_2
plan view
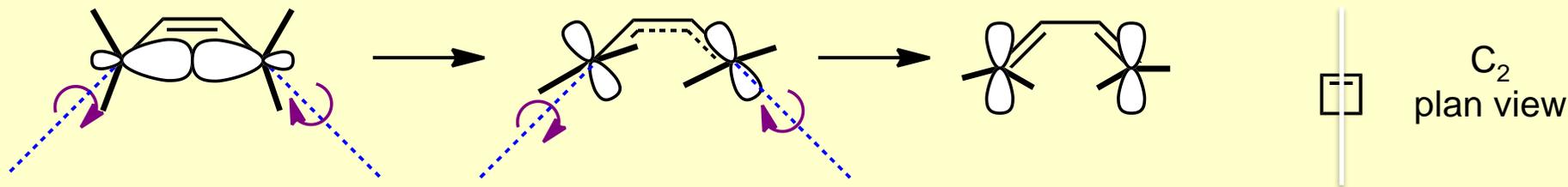
- ***Disrotatory*** – *rotation around the axes of the σ-bonds (dotted lines) occurs in opposite directions –* throughout this process the molecule retains a plane of symmetry which is perpendicular to the plane of the molecule and passes through the breaking σ-bond
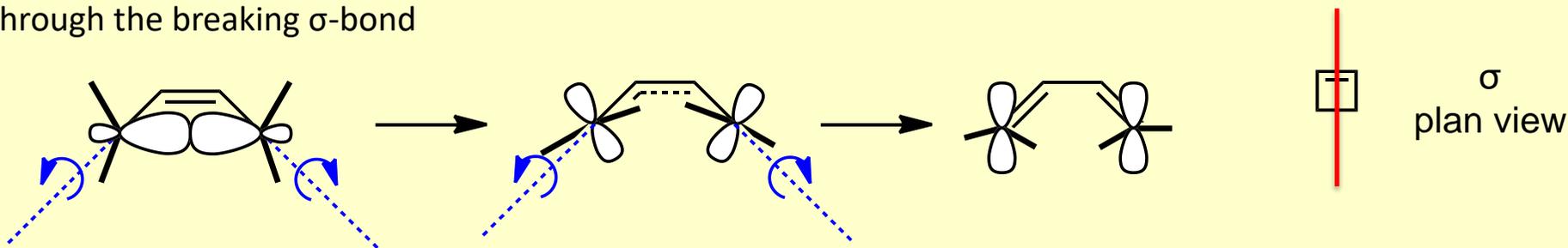
σ
plan view

- Identify orbitals undergoing change (curly arrows) – σ and π.
- The orbitals undergoing change are either symmetric or antisymmetric with respect to the symmetry elements preserved during the reaction.
- Rank orbitals approximately by energy.
- Label orbitals as 'S' or 'A'.
- Construct orbital correlation diagram connecting orbitals of starting materials with those closest in energy and of the same symmetry in the product.
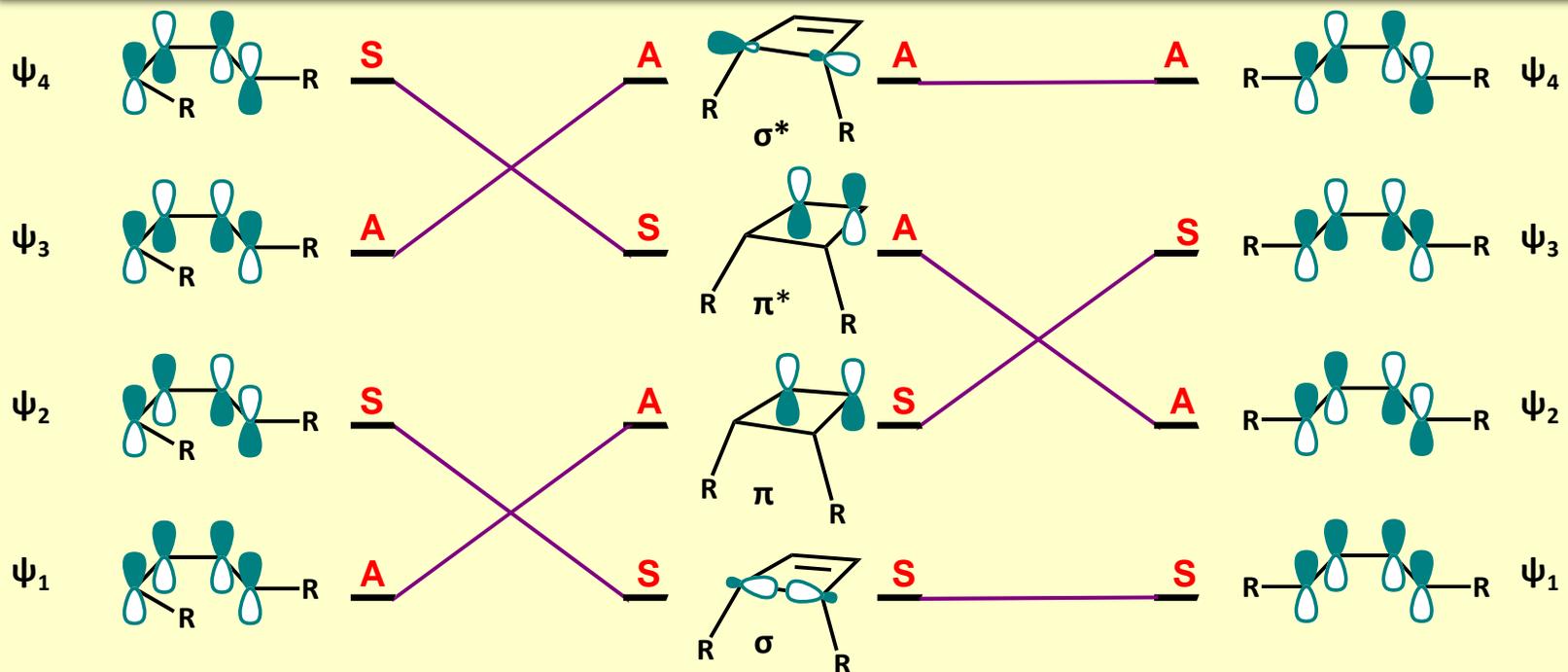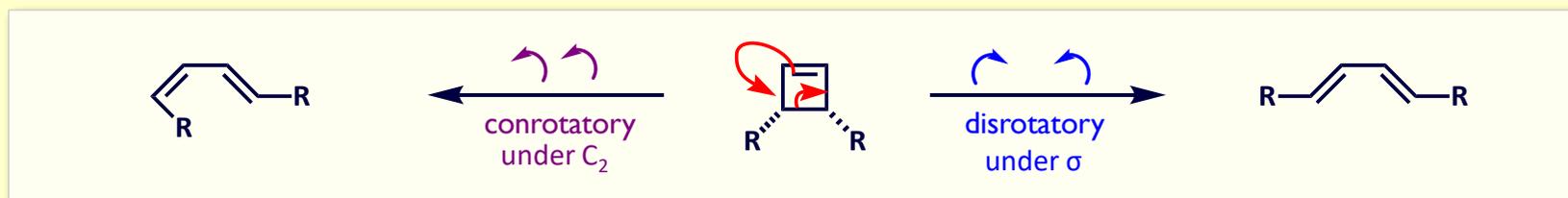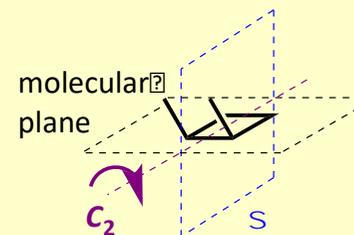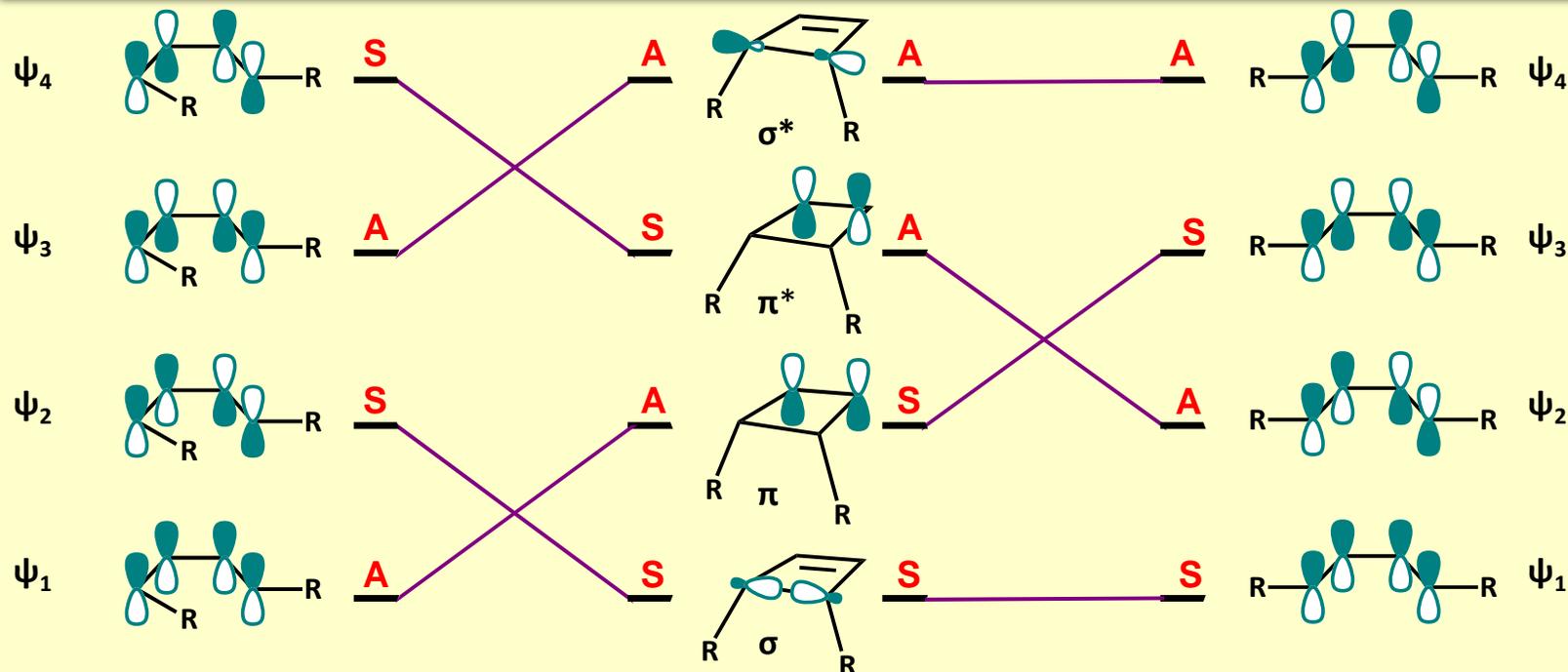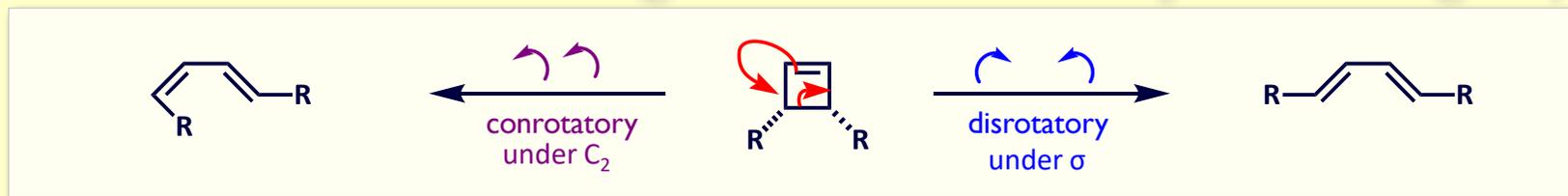
- In the conrotatory mode, all ground state bonding orbitals in cyclobutene ($\sigma^2\pi^2$) correlate with ground state bonding orbitals in butadiene ($\psi_1^2\psi_2^2$) – the **conrotatory opening of butadiene is thermally allowed** (favoured).

- In the disrotatory mode, the ground state bonding orbitals in cyclobutene ($\sigma^2\pi^2$) correlate with a doubly excited state of butadiene ($\psi_1^2\psi_3^2$) – the **disrotatory opening of butadiene is thermally forbidden** (disfavoured).

- The **photochemical ring closure of butadiene is disrotatory**.

The 1st excited state of butadiene is $\psi_1^2\psi_2^1\psi_3^1$ which correlates smoothly with the 1st excited state of cyclobutene ($\sigma^2\pi^1\pi^{*1}$); under conrotatory ring closure, $\psi_1^2\psi_2^1\psi_3^1$ correlates with a much high energy state in cyclobutene ($\sigma^1\pi^2\sigma^{*1}$).
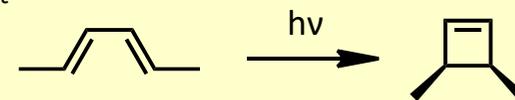
Orbital correlation diagram: electrocyclic ring-closure[19]

conrotatory under C_2 ← **HEXATRIENE** → *disrotatory under S*
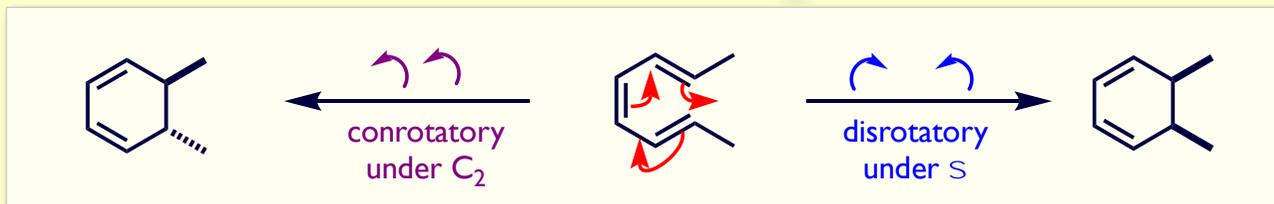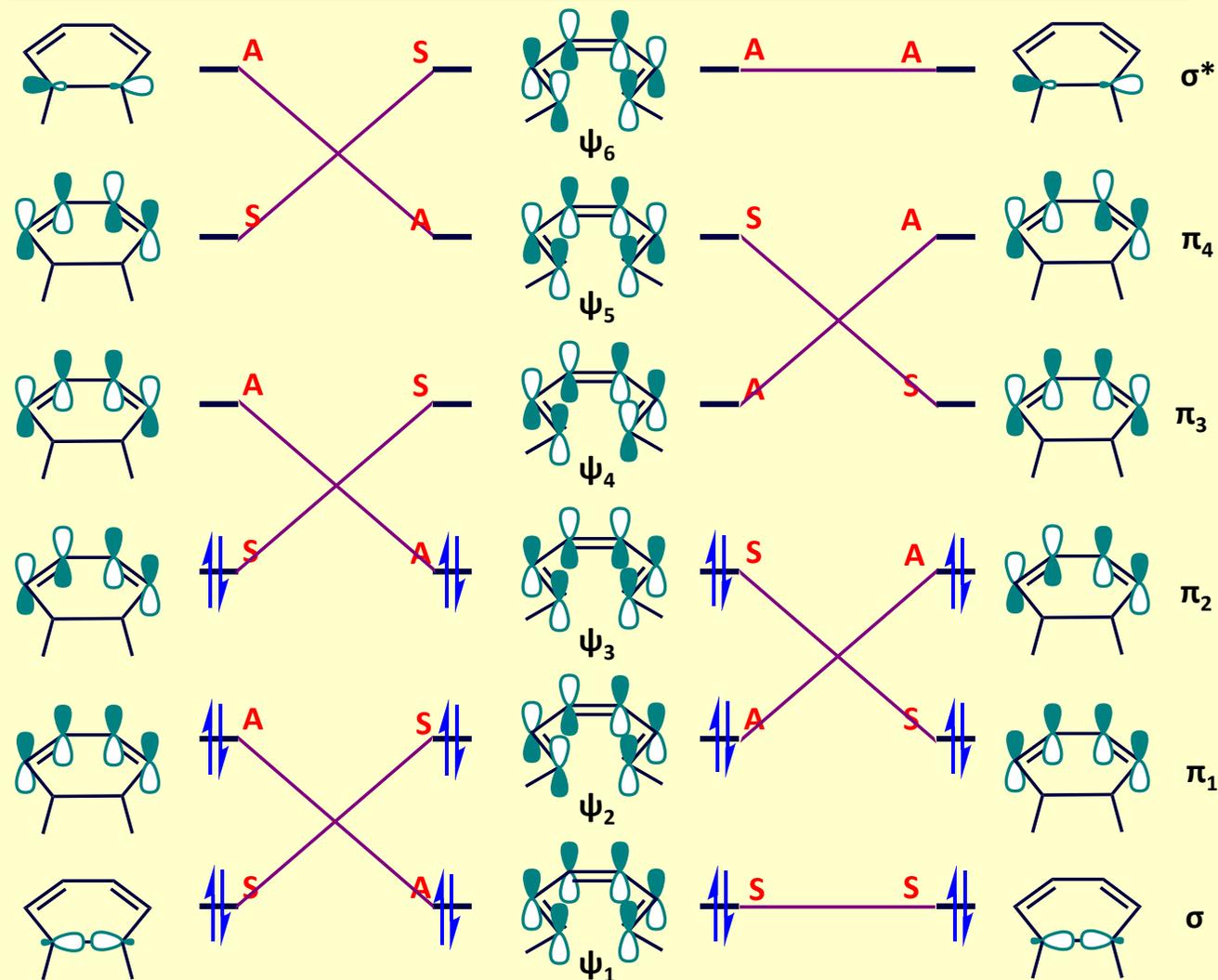
- In the disrotatory mode, all ground state bonding orbitals in hexatriene ($\psi_1^2\psi_2^2\psi_3^2$) correlate with ground state bonding orbitals in the ring closed product ($\sigma^2\pi_1^2\pi_2^2$) – the *disrotatory hexatriene ring closure is thermally allowed* (favoured).

- In the controtatory mode, cyclization leads to a high energy doubly excited state of the product – the *conrotatory hexatriene ring closure is thermally forbidden* (dis favoured).

- The *photochemical ring closure of hexatriene is controtatory* . The 1st excited state of hexatriene is $\psi_1^2\psi_2^2\psi_3^1\psi_4^1$ which correlates smoothly with the 1st excited state of cyclohexadiene ($\sigma^2\pi_1^2\pi_2^1\pi_3^1$)