

CHEM60001:
Advanced Chemistry Topics 1 – Pericyclic
Reactions

LECTURE 8
Electrocyclic Reactions

Alan C. Spivey
a.c.spivey@imperial.ac.uk

Imperial College
London

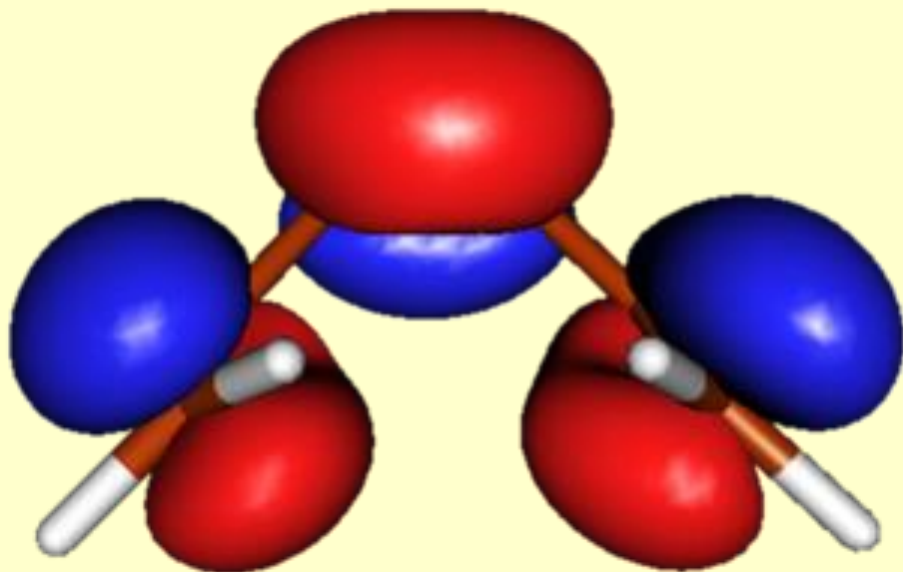
Format & scope of lecture 8

- ***Electrocyclic reactions***
 - Thermal reactions
 - Hexatriene – cyclohexadiene
 - Butadiene – cyclobutene
 - Allyl cation – cyclopropyl cation
 - Nazarov cyclisation
 - Photochemical reactions
 - Hexatriene – cyclohexadiene
 - Butadiene – cyclobutene

Key further reading:

- **BOOK:** Clayden, Greeves & Warren, *Organic Chemistry*, 2nd Ed.,
 - [Chapter 35](#) – *pericyclic reactions 2 – sigmatropic and electrocyclic reactions*
- **WEB:** Pericyclic Reactions - https://www.stereoelectronics.org/webPR/PR_home.html
 - [Chapter 5](#) – *Electrocyclic reactions*

Thermal electrocyclic reactions

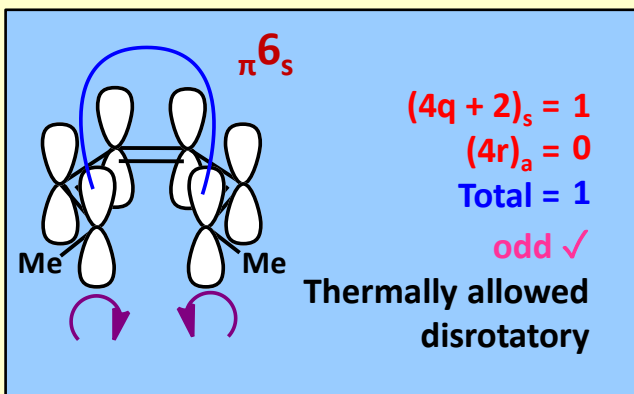
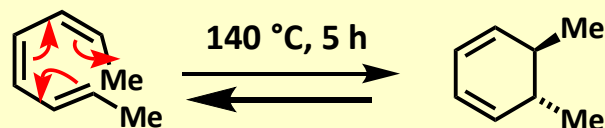
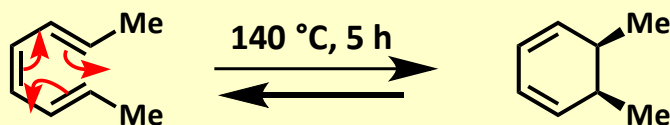


The HOMO of hexatriene. This orbital is important in the *thermal* electrocyclic ring-closure reaction. Disrotatory movement of the terminal =CH₂ groups brings the two red lobes together and allows favorable orbital overlap such that a new Sigma orbital can form.

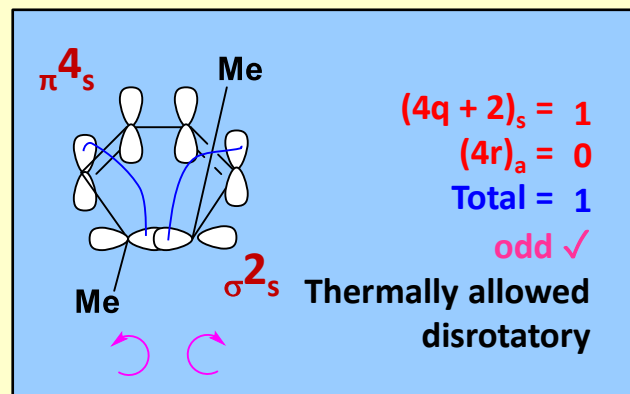
Electrocyclic reactions - *thermal*

Thermal electrocyclic processes are *conrotatory* if the total number of electrons is $4r$ and *disrotatory* if the total number of electrons is $(4q + 2)$.
This is reversed for photochemical reactions.

- **Thermal electrocyclic hexatriene ring-closure & cyclohexadiene ring-opening [$4q+2 = 6 (q = 1)$]**
 - Position of equilibrium depends on substituents
 - cf. Lecture 2 – symmetry allowed for disrotatory processes:



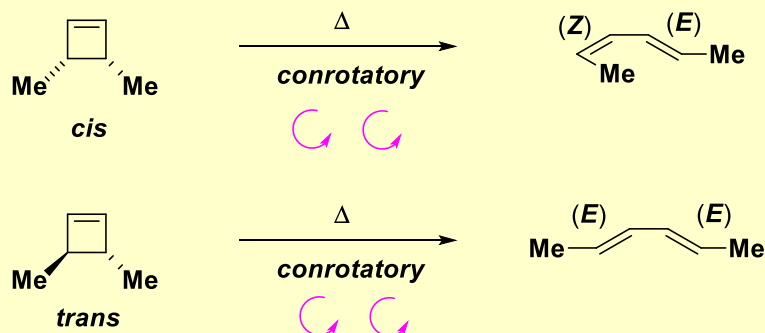
W-H approach (ring-closure)



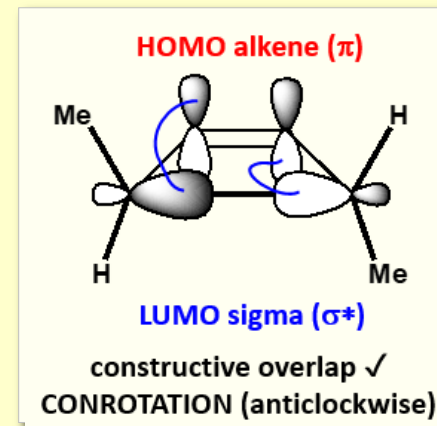
W-H approach (ring-opening)

Electrocyclic reactions - *thermal*

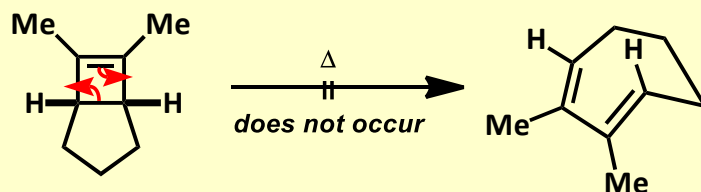
- **Thermal electrocyclic cyclobutene ring-opening** [$4r = 4$ ($r = 1$)]
 - cf. Lectures 2,3 and 4 – symmetry allowed for conrotatory processes:



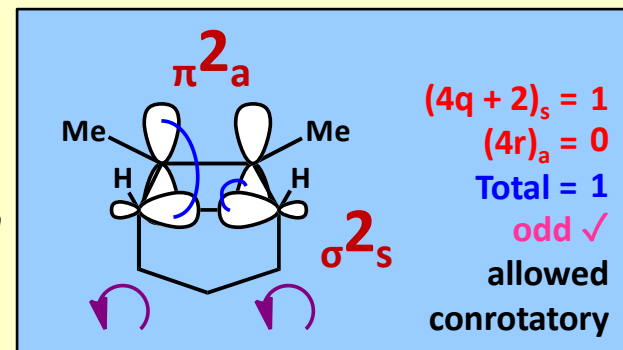
FMO approach



- However, geometrical constraints can prevent reaction, e.g.:

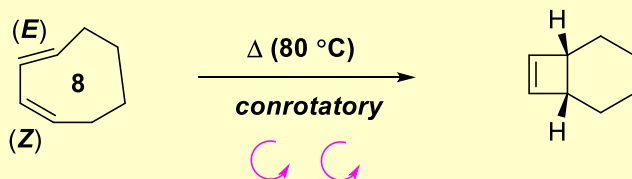


W-H approach



- **Thermal electrocyclic butadiene ring-closure** [$4r = 4$ ($r = 1$)]

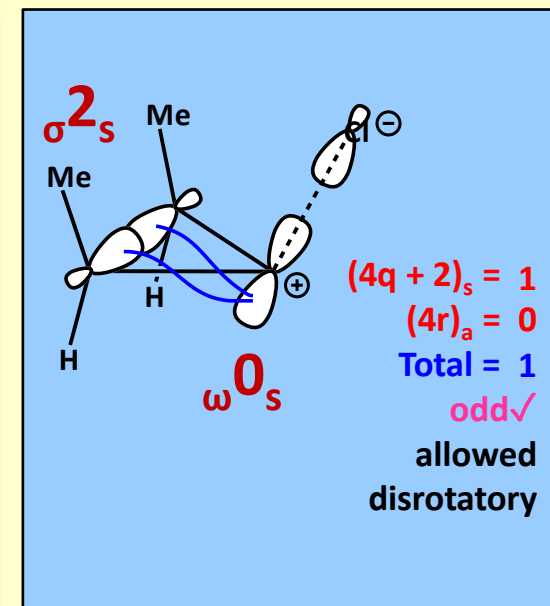
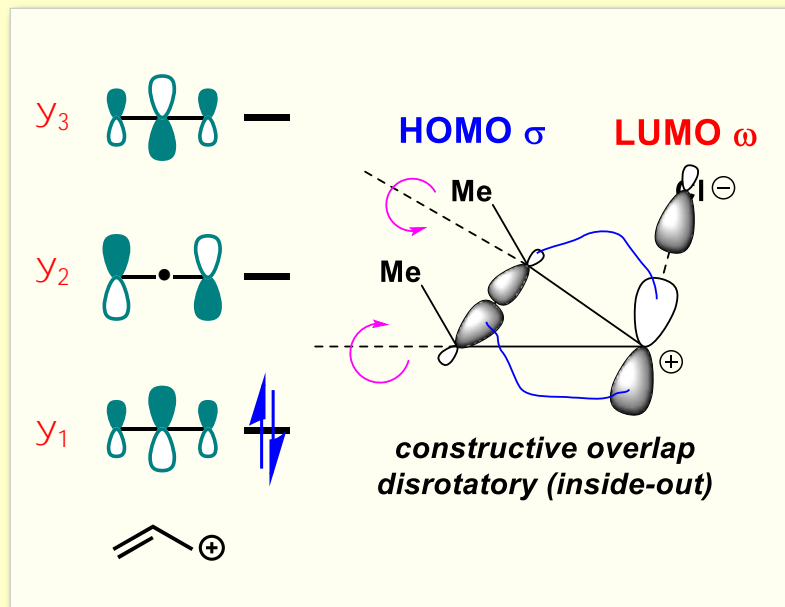
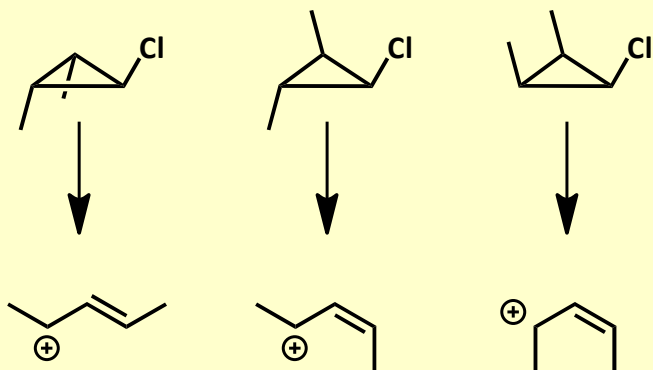
- also symmetry allowed for conrotatory processes
- **BUT** generally thermodynamically disfavoured unless build-up of 4-membered ring-strain can be compensated for
- e.g.:



relief of strain from *trans*-alkene in cyclooctadiene outweighs strain in bicyclobutene-containing product so ring-closure proceeds in good yield.

Electrocyclic reactions - *thermal*

- **Thermal electrocyclic cyclopropyl cation ring-opening to give allyl cation** [$4q+2 = 2$ ($q = 0$)]
 - symmetry allowed for disrotatory processes:



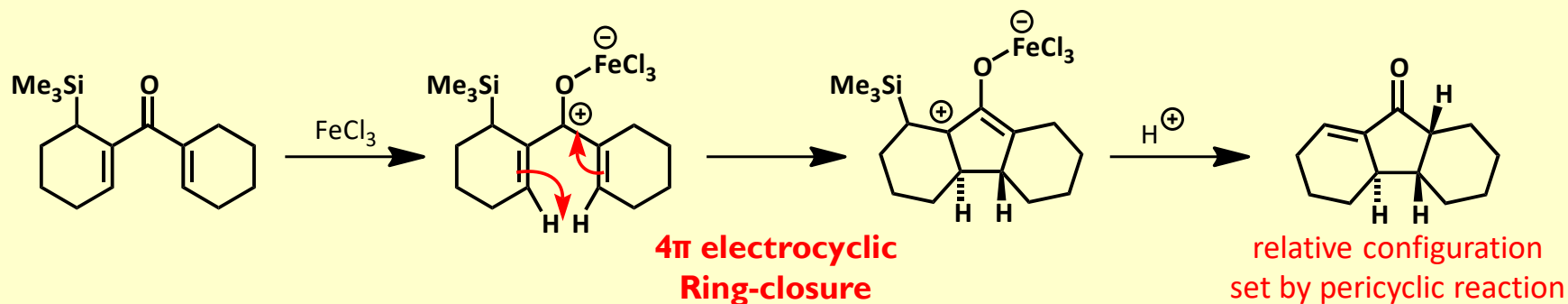
FMO approach

W-H approach

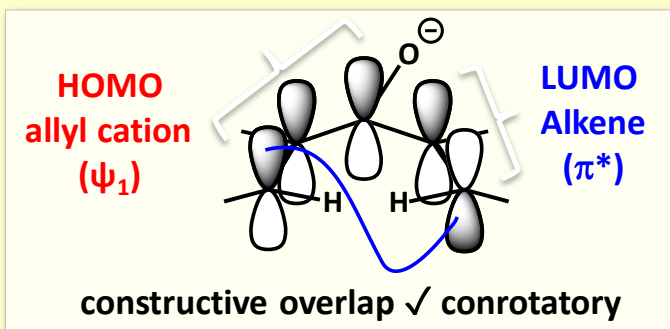
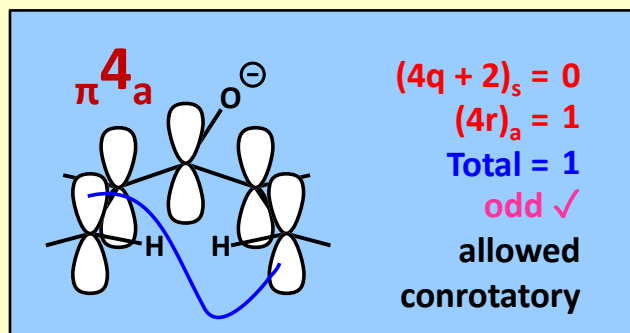
Electrocyclic reactions - *thermal*

- **Nazarov cyclisation [thermal electrocyclic, $4r = 4$ ($r = 1$)]**

- symmetry allowed for conrotatory processes:



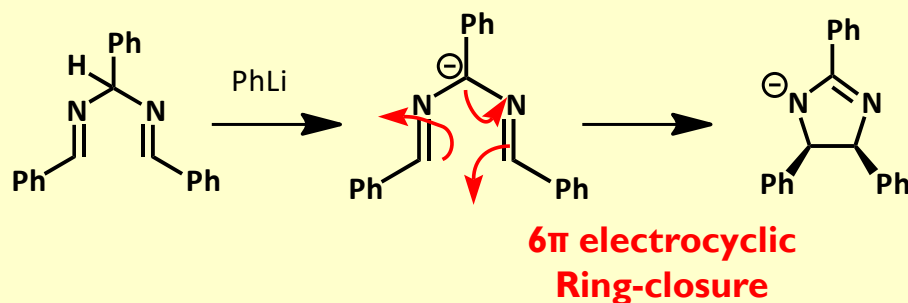
W-H approach



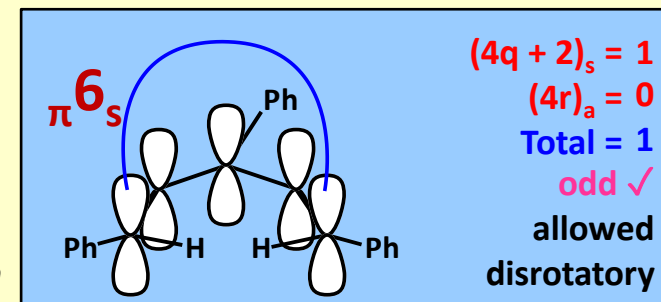
FMO approach

- **The analogous thermal pentadienyl anion cyclization is also electrocyclic [$4q+2 = 6$ ($q = 1$)]**

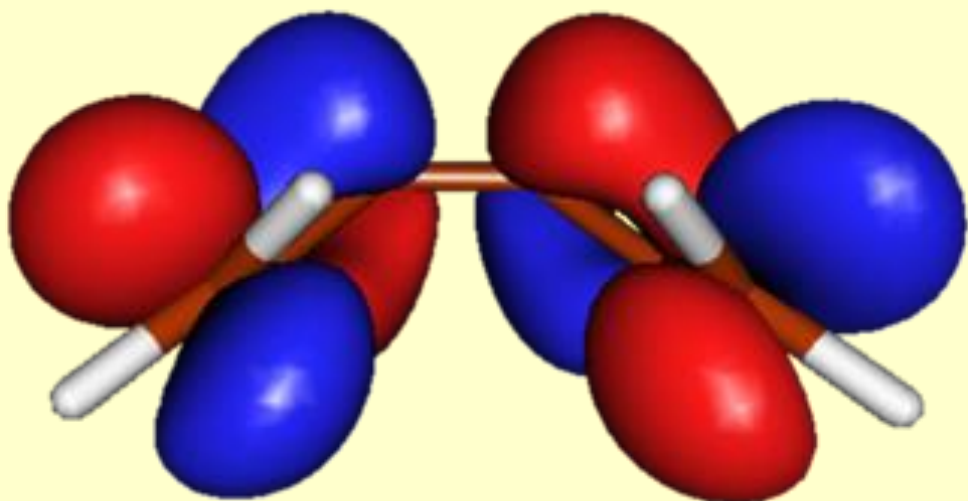
- Symmetry allowed for disrotatory processes:



W-H approach



Photochemical electrocyclic reactions



The LUMO of hexatriene. This orbital is important in the **photochemical** electrocyclic ring-closure reaction. Conrotatory movement of the terminal $=\text{CH}_2$ groups brings the two red lobes together and allows favorable orbital overlap such that a new Sigma orbital can form.

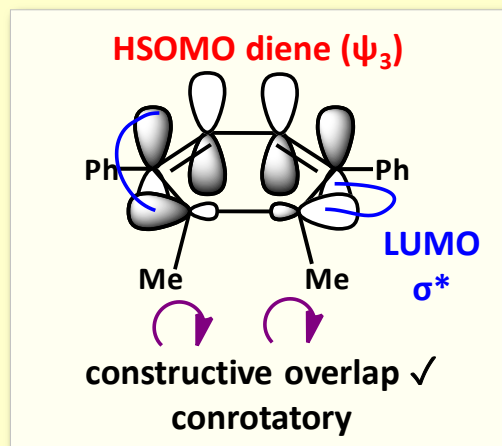
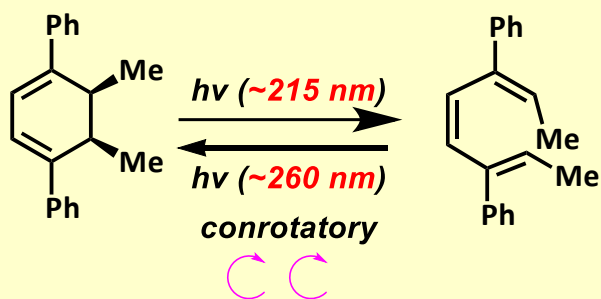
Electrocyclic reactions - *photochemical*

Photochemical electrocyclic processes are *disrotatory* if the total number of electrons is $4n$ and *conrotatory* if the total number of electrons is $(4n + 2)$.

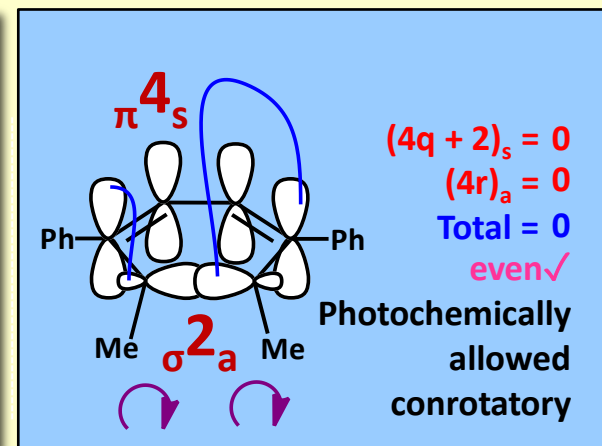
This is reversed for thermal reactions.

- **Photochemical electrocyclic hexatriene ring-closure & cyclohexadiene ring-opening [$4n+2 = 6$ ($n = 1$)]**

- Ring-closure vs. ring-opening dependent on wavelength of UV light
- cf. Lecture 2 – symmetry allowed for conrotatory processes:

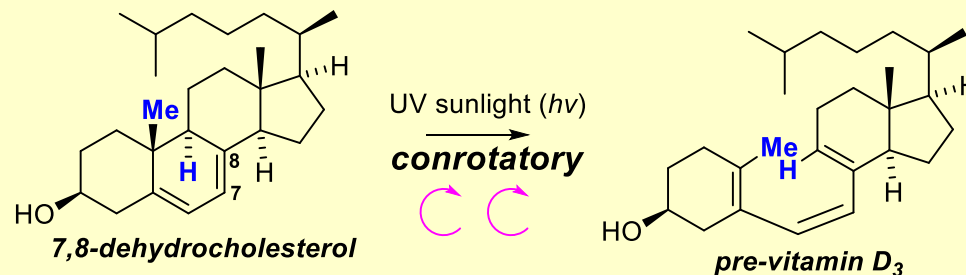


FMO approach



W-H approach

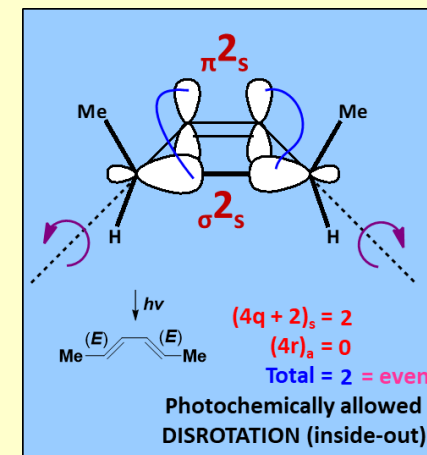
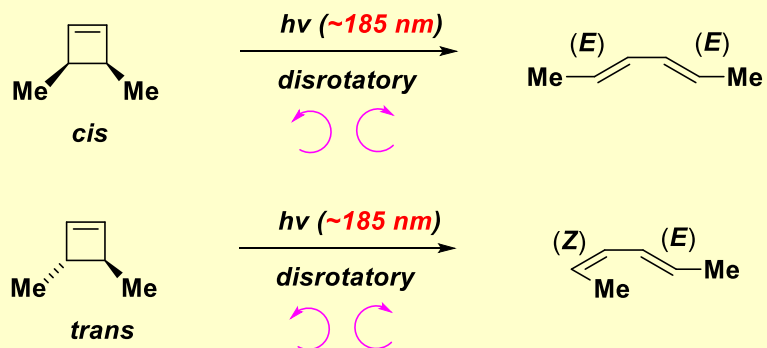
- e.g. natural synthesis of vitamin D from cholesterol:



Electrocyclic reactions - *photochemical*

- **Photochemical electrocyclic cyclobutene ring-opening [$4n = 4$ ($n = 1$)]**

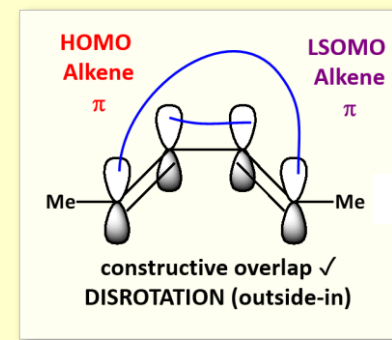
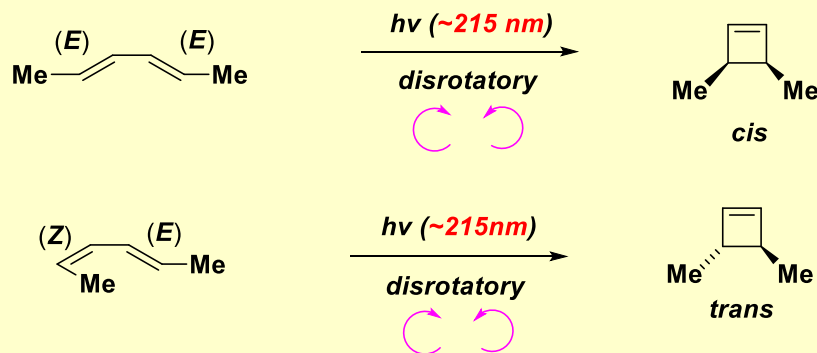
- cf. Lectures 2 and 3 – symmetry allowed for disrotatory processes:



W-H approach

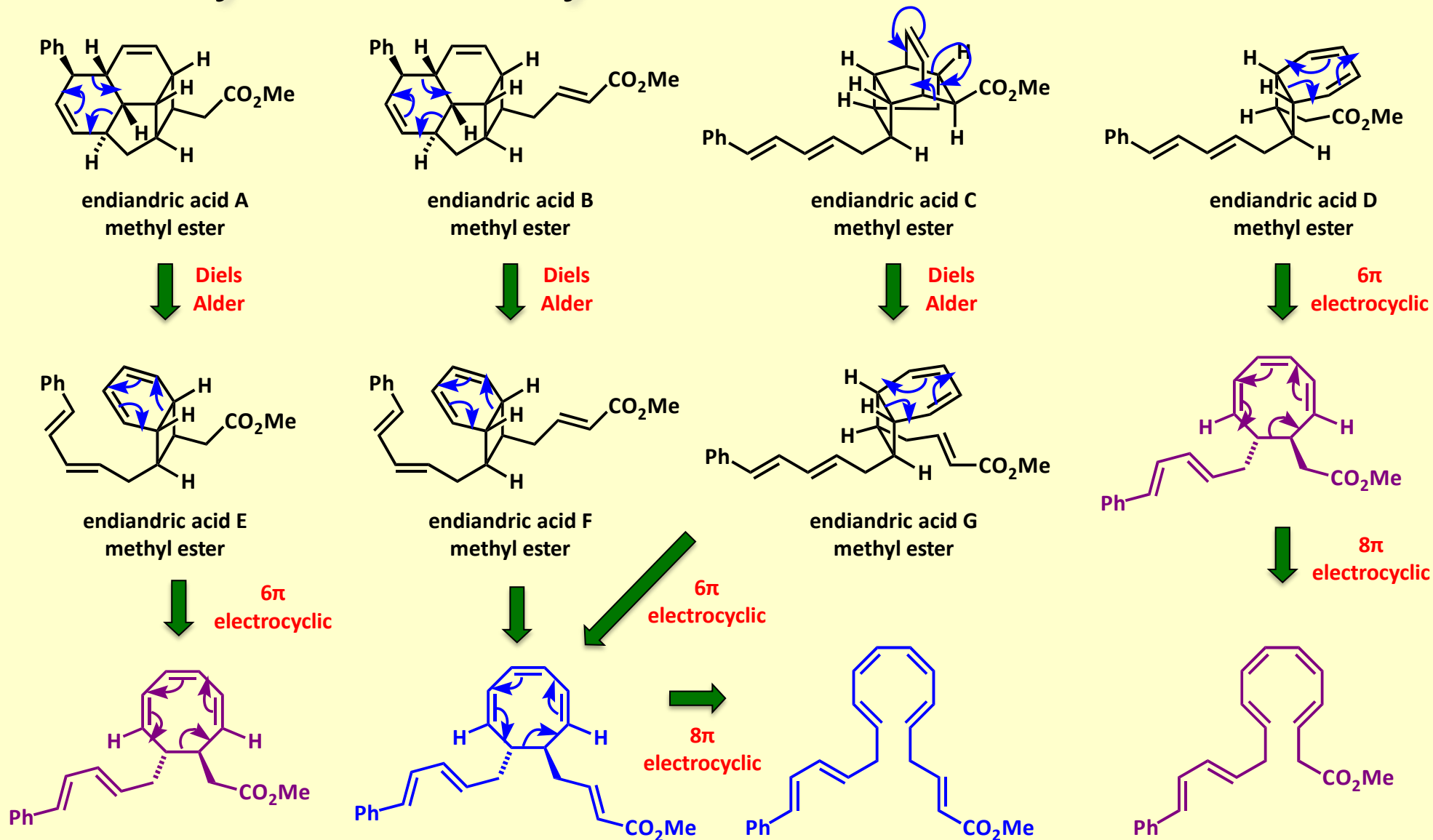
- **Photochemical electrocyclic butadiene ring-closure [$4n = 4$ ($n = 1$)]**

- cf. Lectures 2 and 4 – symmetry allowed for disrotatory processes:



FMO approach

Pericyclics in biosynthesis: *the endiandric acids*



Pericyclics in synthesis: *the endiandric acids*

