

**B.Sc. Semester-VI
Group A / DSE-4
Organic Synthesis**



II. Pericyclic Reactions


10. Symmetry Control in Pericyclic Reactions



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Ranchi**

Pericyclic Reactions

•Polar react. (nucleophiles and electrophiles) Nu : 

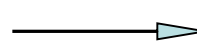
•Radical react. 

•Pericyclic react. (concerted, cyclic TS#)

•**Electrocyclic react.**

•Cycloadditions (i.e. Diels Alder)

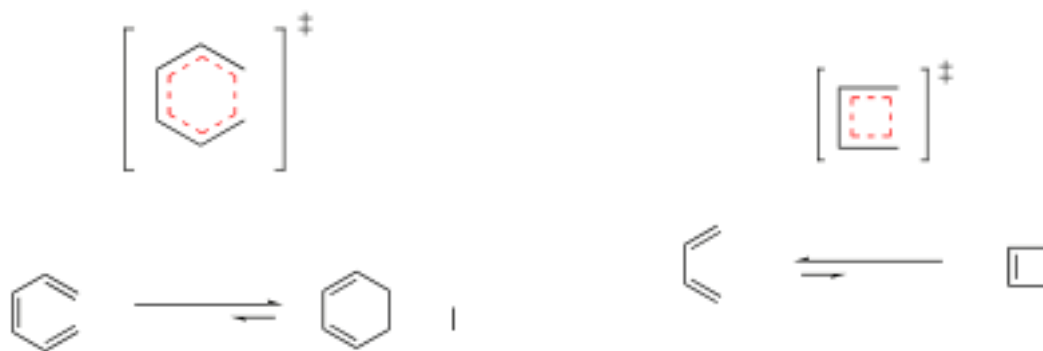
•Sigmatropic rearrangement



•Rearrangement of polyene

•Termal (react. in ground state)
or photochemical

(react of excited state)

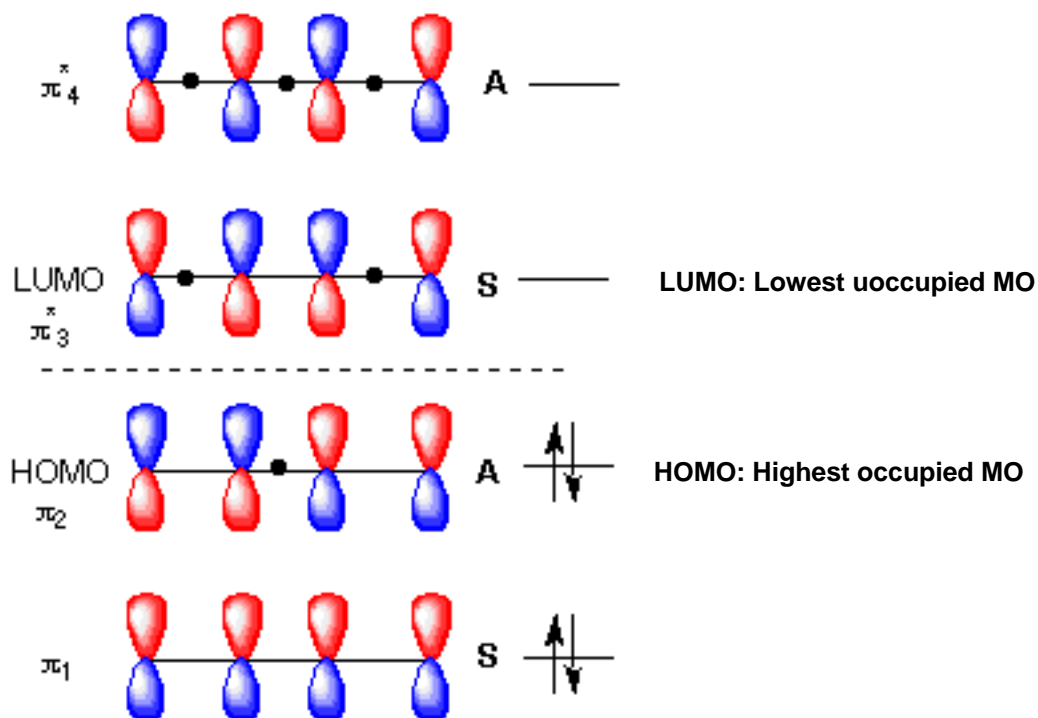


Symmetry Allowed Reaction

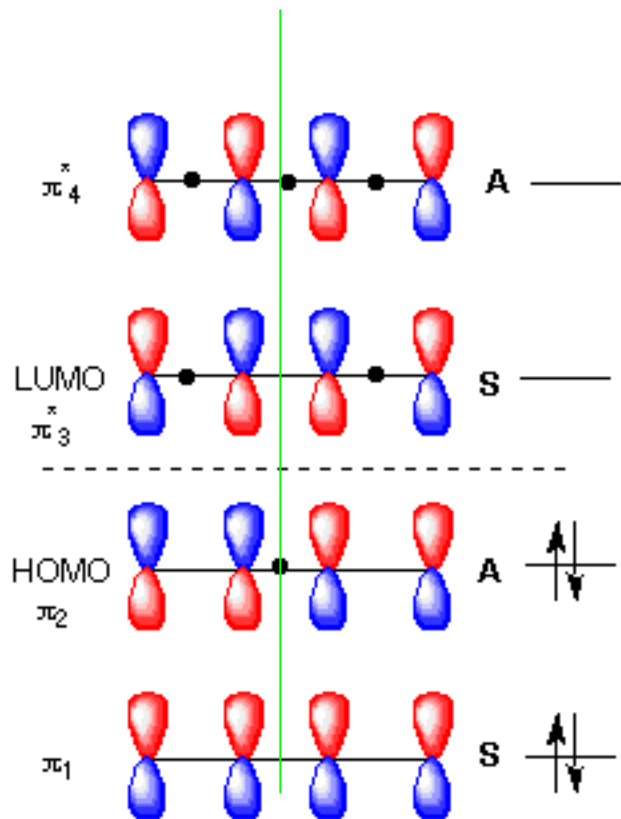
Woodward Hoffmann rules

Symmetry in reactants are preserved during pericyclic react.

Results can generally be predicted just by looking at Front Orbitals (FMO; HOMO and LUMO) - Fukui

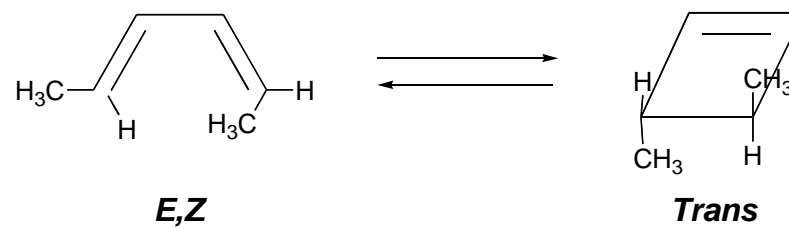
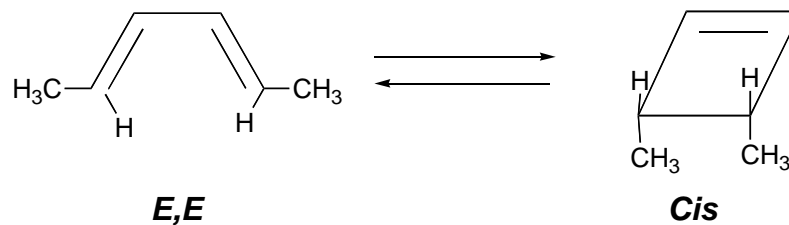


Molecular orbitals 1,3-butadiene

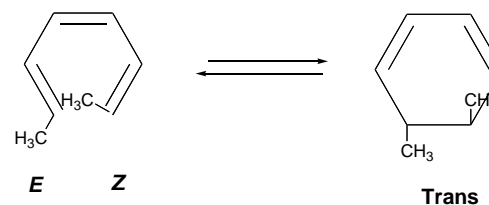
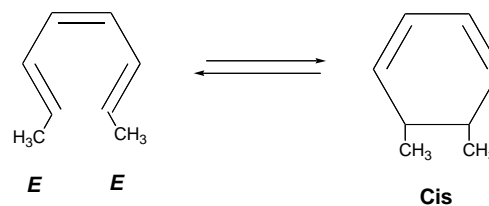
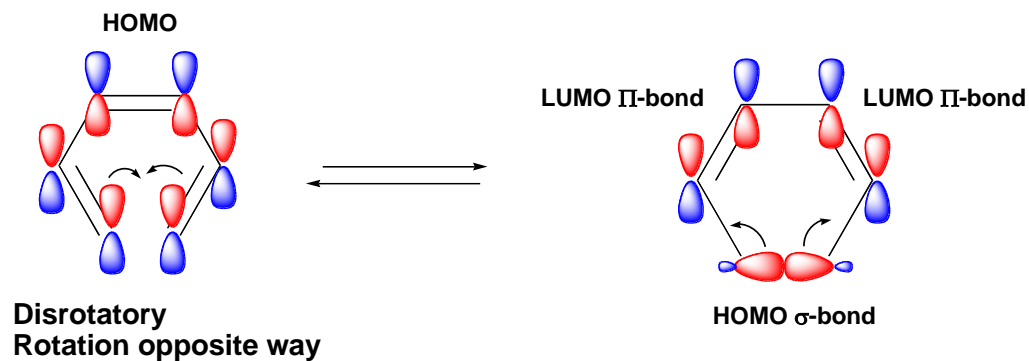
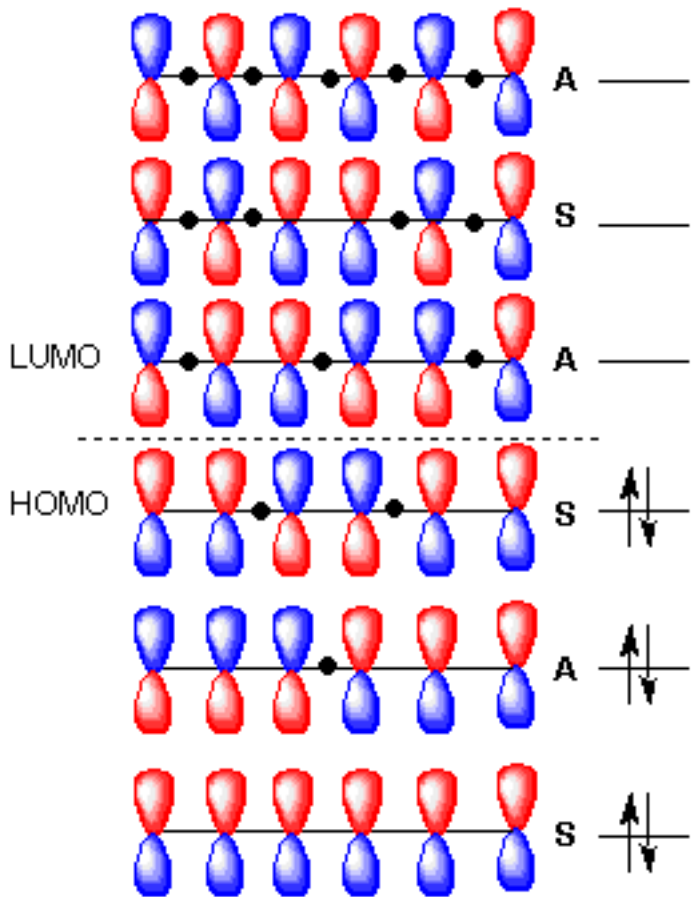
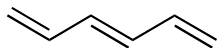


S: Symmetric
A: Antisym.

Stereospecific react.



Molecular orbitals hexatriene



Symmetry allowed react

No. of electrons

Reactions in the ground state

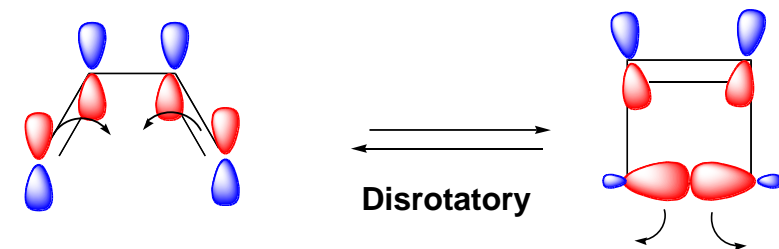
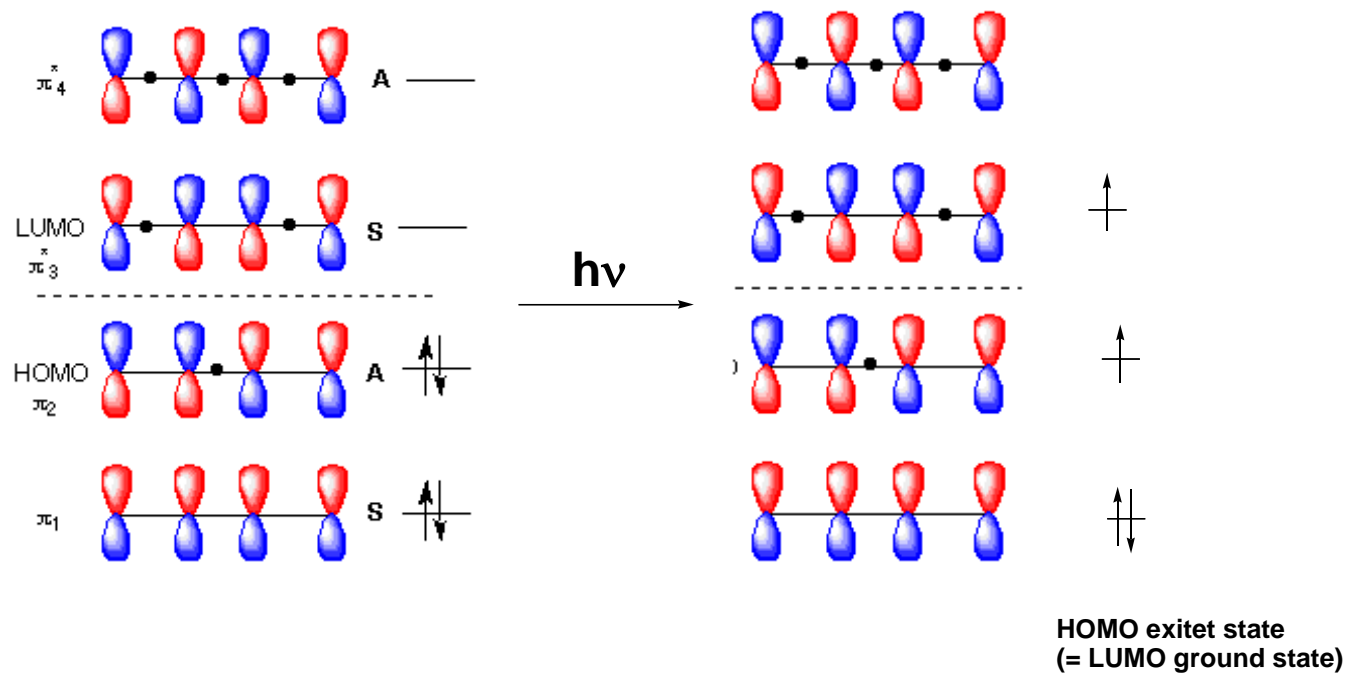
4n

Conrotatory

4n + 2

Disrotatory

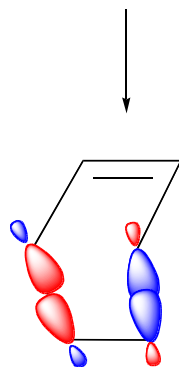
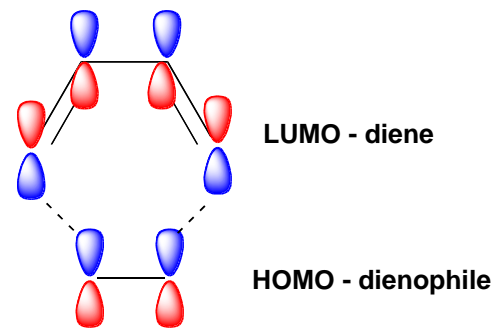
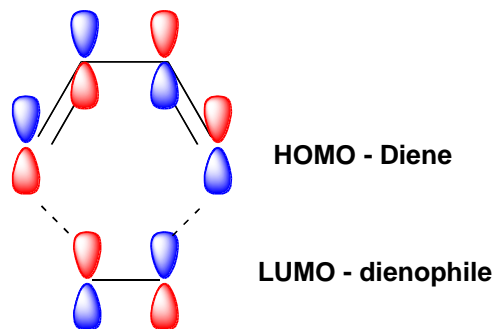
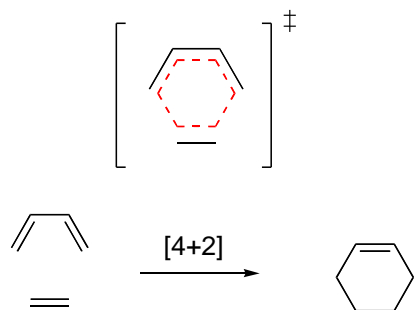
Photochemical electrocyclic reaction



No. of electrons	Reactions in the ground state (thermal)	Reactions in excited state (Photochem.)
4n	Conrotatory	Disrotatory
4n + 2	Disrotatory	Conrotatory

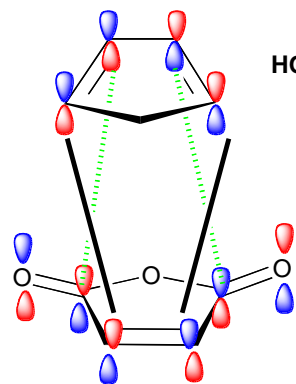
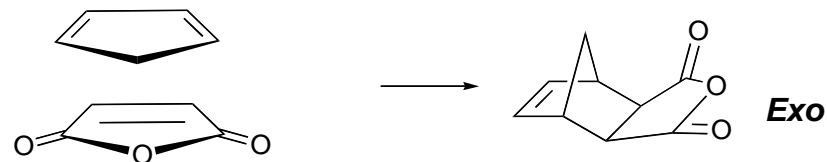
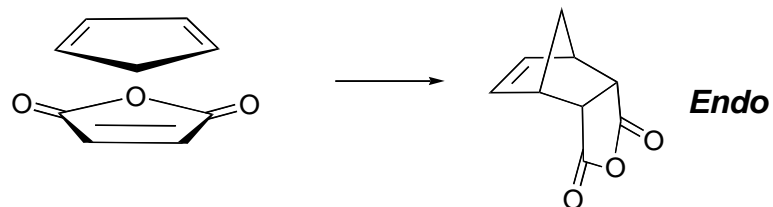
Cycloadditions (i.e. Diels Alder Reaction)

Suprafacial cycloadd.

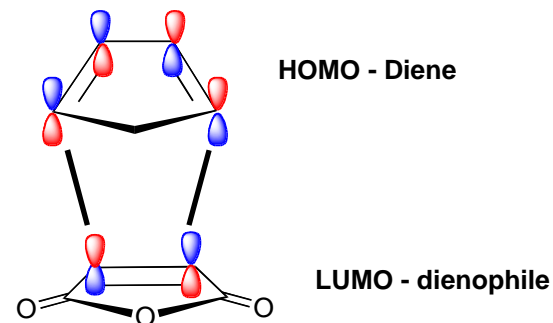


Stereospecific react.

endo - exo selectivity

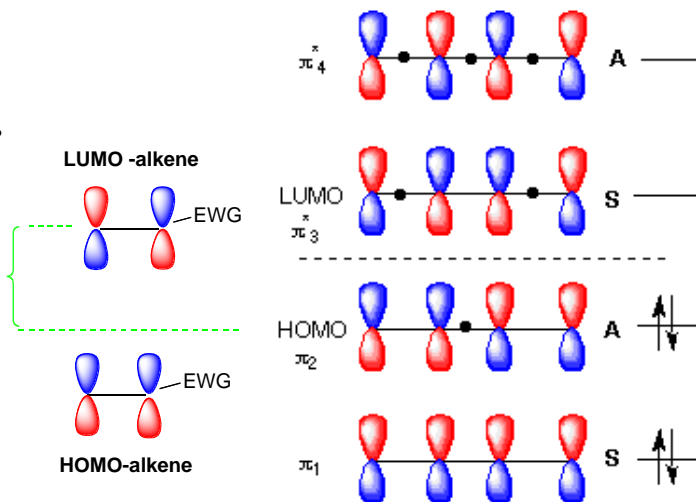


— Primary interact., bond formation
 - - - - Secondary interact., extra TS[#] stabil.

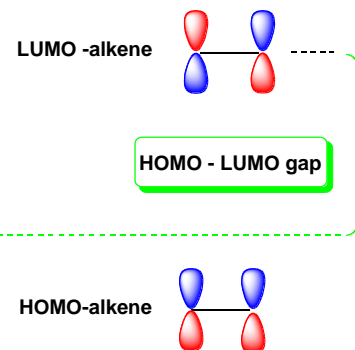


Normal electron demand DA - Electron poor dienophile (Michael accept.)

Michael accept.
 Lower LUMO

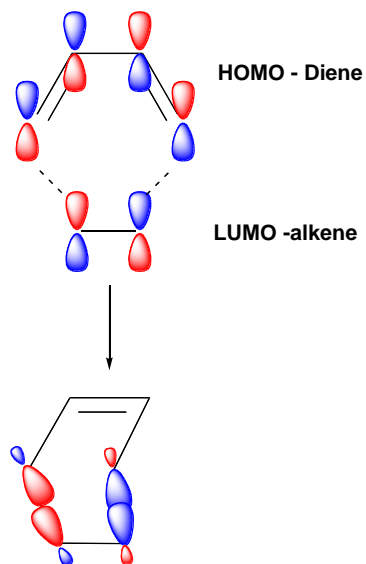


Ethene etc, very low react.

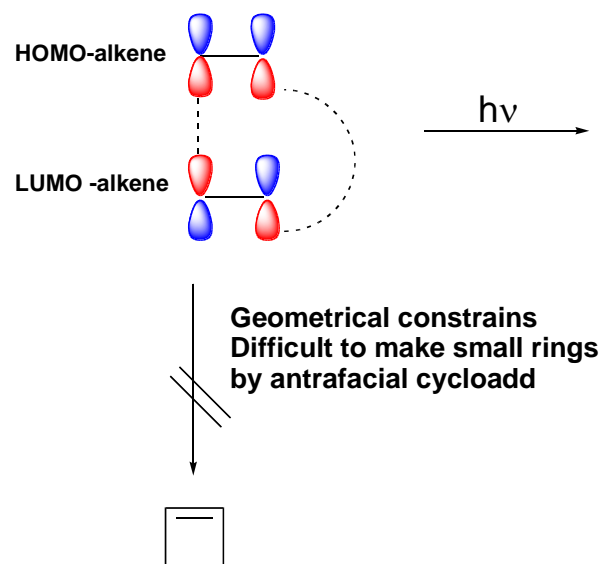


[2+2] Cycloadditions

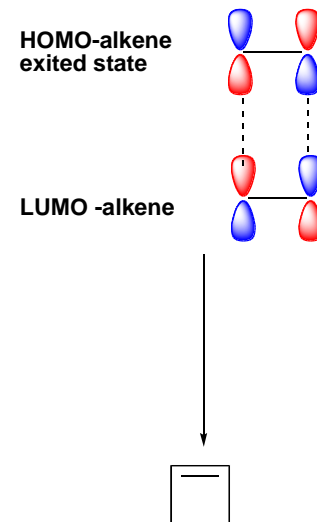
Suprafacial cycloadd.



Antarafacial cycloadd. (thermal cond.)



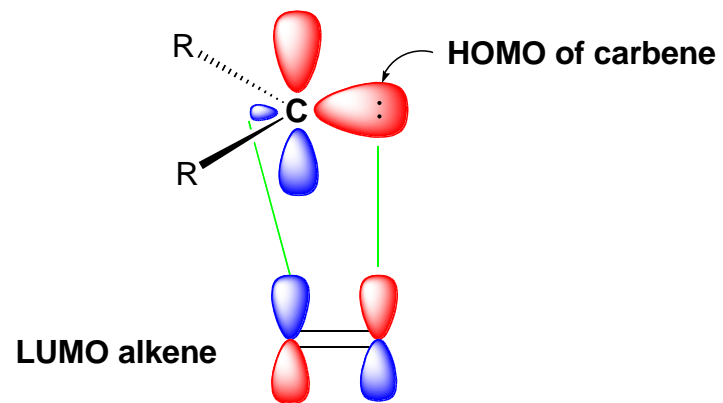
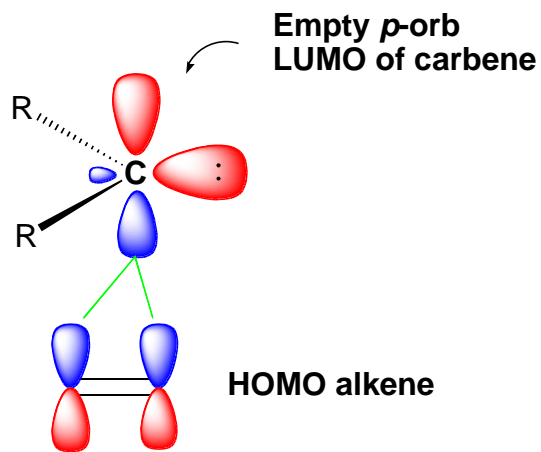
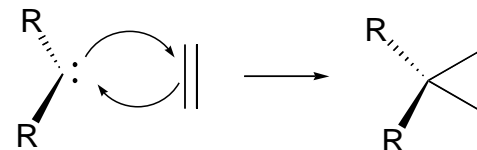
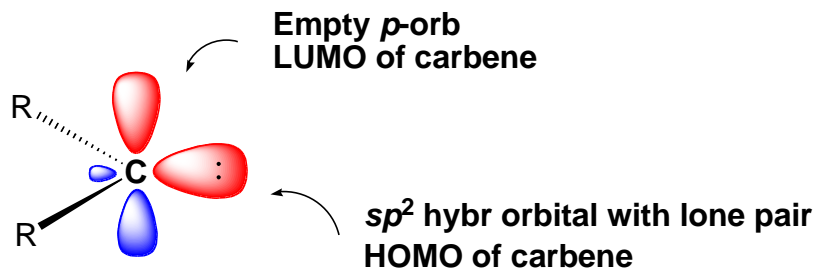
Suprafacial cycloadd. (photochem. cond.)



No. of electrons	Reactions in the ground state (thermal)	Reactions in exited state (Photochem.)
$4n$	Antarafacial	Suprafacial
$4n + 2$	Suprafacial	Antarafacial

Carbene Cycloadditions

Singlet Carbene

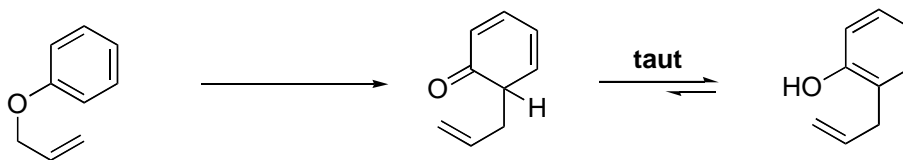
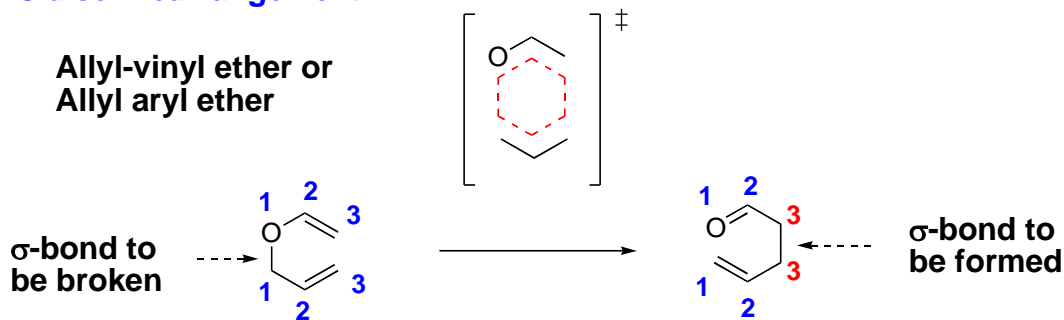


Sigmatropic Rearrangements

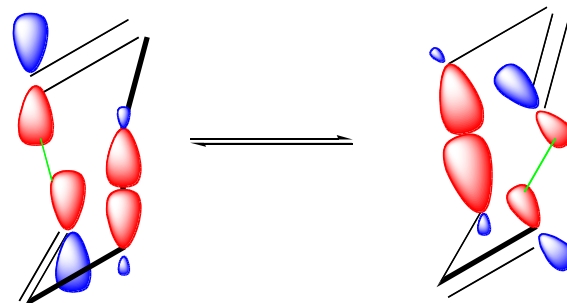
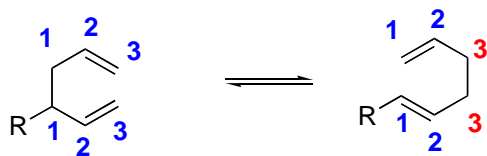
[3,3] Rearrangements; Claisen rearrang. etc.

Claisen rearrangement:

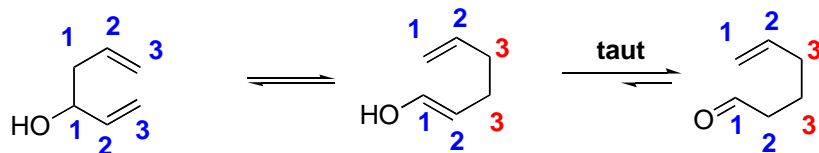
Allyl-vinyl ether or
Allyl aryl ether



Cope rearrangement:

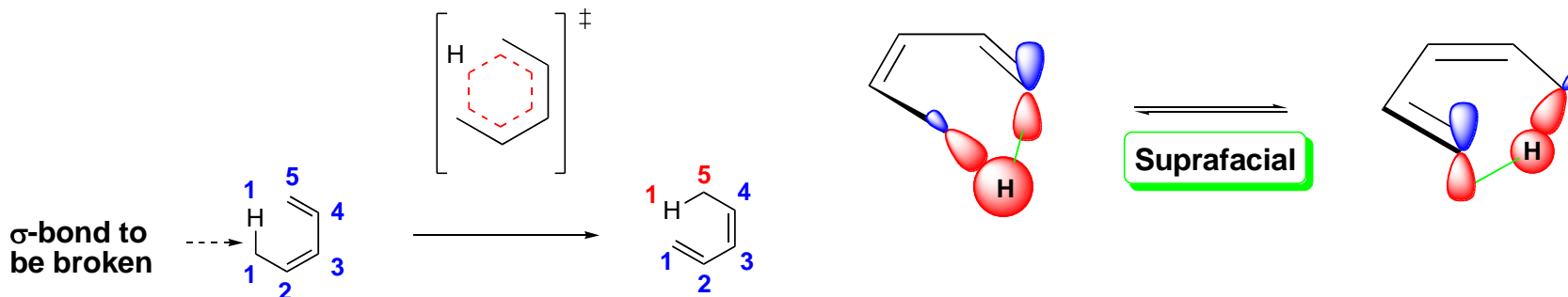


Oxy-Cope rearrangement:



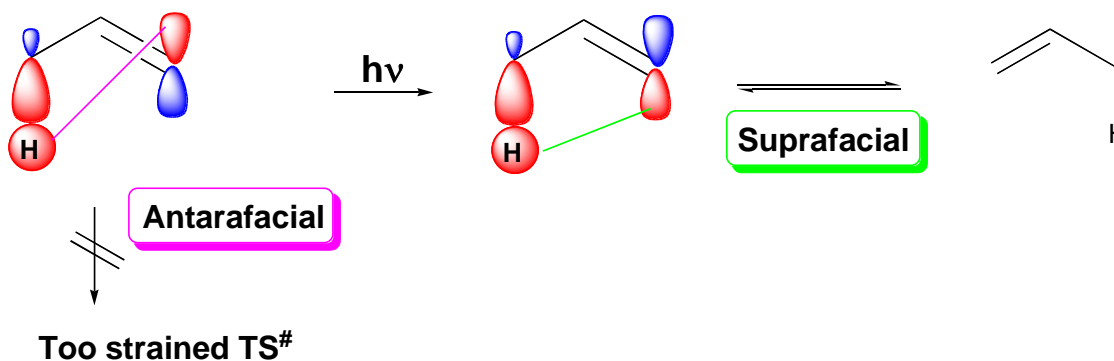
Suprafacial

[1,5] Rearrangement (H-shift)

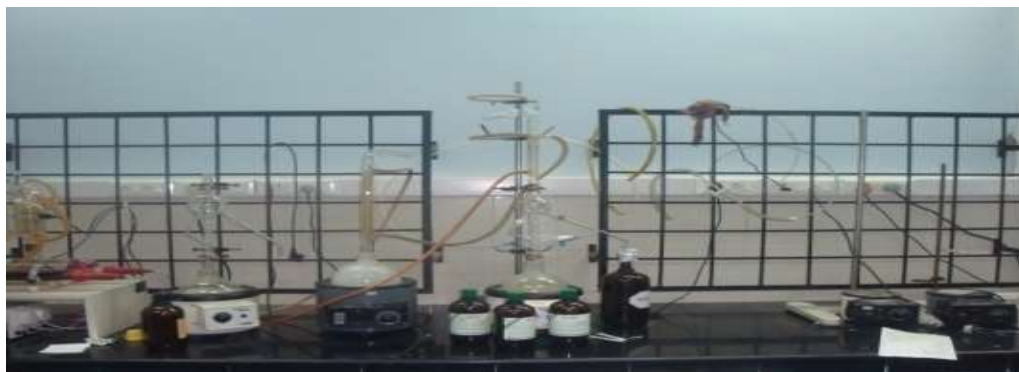


No. of electrons	Reactions in the ground state (thermal)	Reactions in excited state (Photochem.)
$4n$	Antarafacial	Suprafacial
$4n + 2$	Suprafacial	Antarafacial

[1,3] Rearrangement (H-shift)



Thank You



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