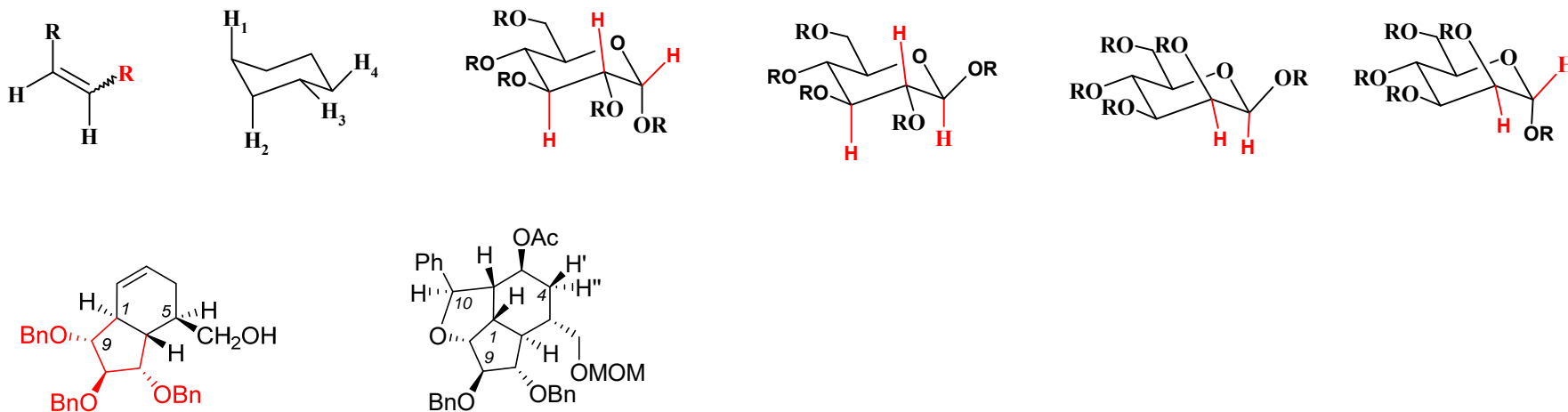
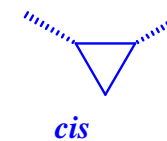
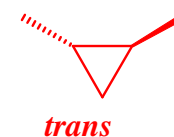
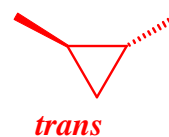


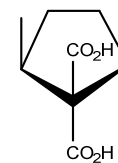
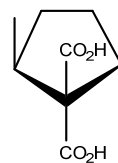
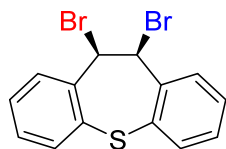
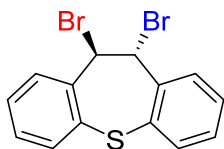
Assignment of the configuration by spectral analysis: COUPLING CONSTANTS ^1H NMR



chemical methods

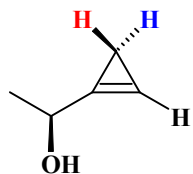
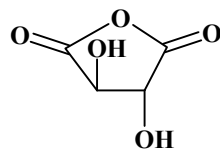
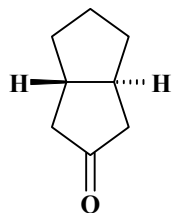
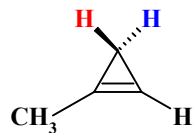
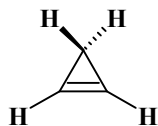
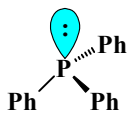
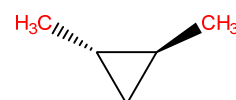
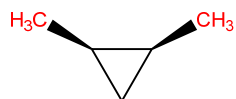
How to distinguish these isomers ???



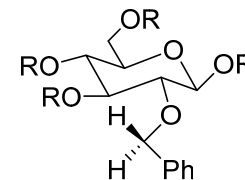
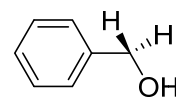
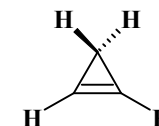
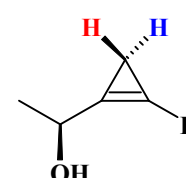
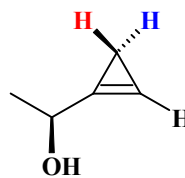
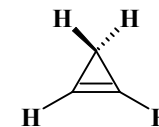
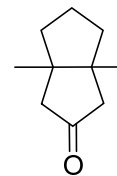
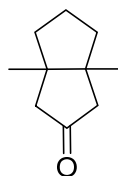


Topic relations

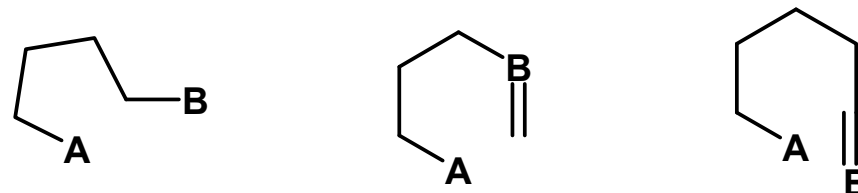
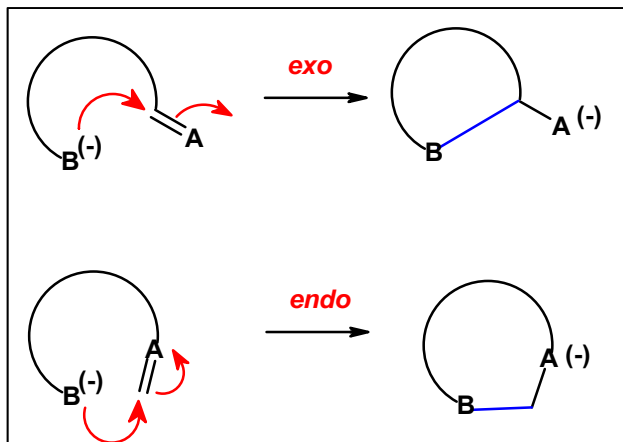
1. Homotopic
2. Enantiotopic
3. Diastereotopic



Substitution test



Baldwin Rules



3-7-exo-Tet are allowed. 5-6-Endo-Tet NO

3-7-exo-Trig and 6-7-Endo-Trig are allowed. 3-5-Endo-Trig NO

5-7-exo-Dig and 3-7-Endo-Dig are allowed. 3-4-Exo-Dig NO

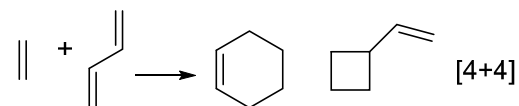
	EXO			ENDO		
	Tet	Trig	Dig	Tet	Trig	Dig
3	YES	YES	NO		NO	YES
4	YES	YES	NO		NO	YES
5	YES	YES	YES	NO	NO	YES
6	YES	YES	YES	NO	YES	YES
7	YES	YES	YES		YES	YES

J. E. Baldwin, *J. Chem. Soc., Chem. Commun.* **1976**, 734; J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman, R. C. Thomas, *J. Chem. Soc., Chem. Commun.* **1976**, 736; J. E. Baldwin, R. C. Thomas, L. Kruse, L. Silberman, *J. Org. Chem.*, **1977**, 42, 3846; K. Gilmore, R.K. Mohamed, I.V. Alabugin, *WIREs Comput Mol Sci* **2016**, 6:487 (doi: 10.1002/wcms.1261)

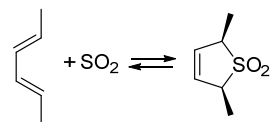
Pericyclic reactions

1. Cycloaddition: [2+2], [4+2], [4+4], [8+2], [6+4], etc.

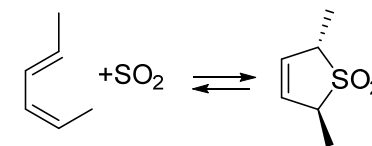
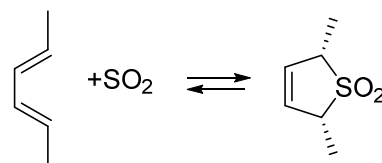
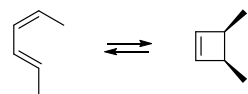
also 1,3-dipolar cycloaddition (formally [4+2])



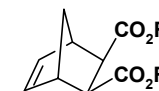
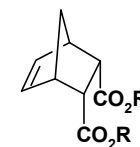
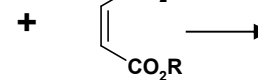
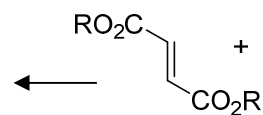
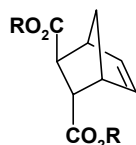
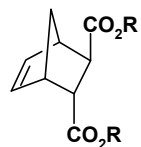
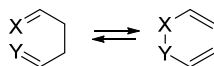
2. Cheletropic reactions



3. Electrocyclic reactions



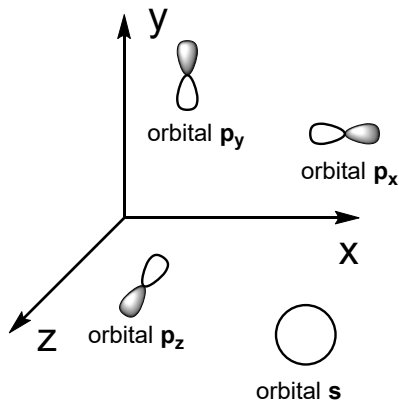
4. Sigmatropic rearrangement



Selectivity of many reactions can be predicted by **FRONTIER ORBITAL THEORY**

Nobel 1981: Roald Hoffmann, Kenichi Fukui

Types of orbitals

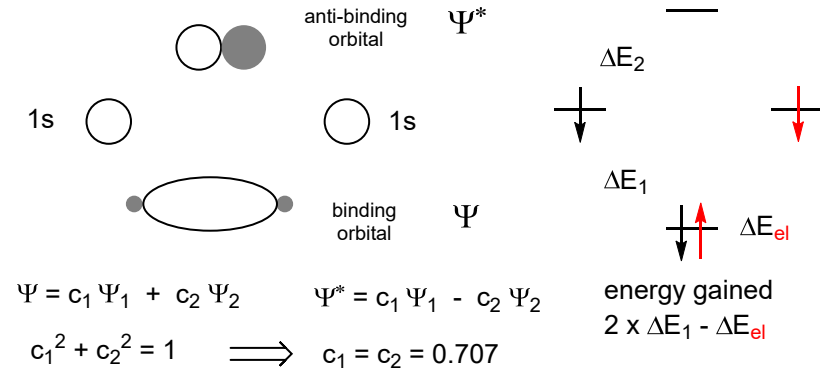


orbital
Probability of finding electron
 $\sim |\phi|^2$

This probability is the SAME
in both 'spheres'
Only the sign ϕ is opposite

LCAO MO

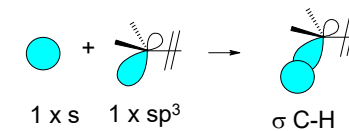
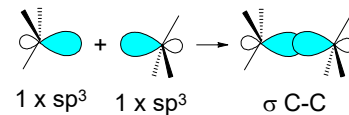
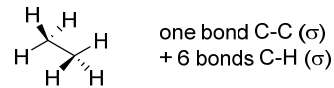
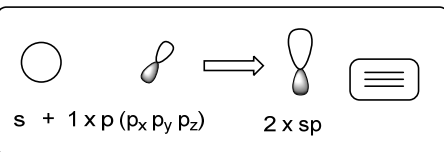
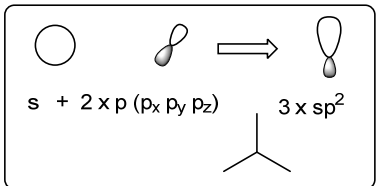
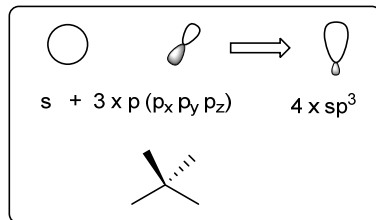
Molecule of hydrogen H-H



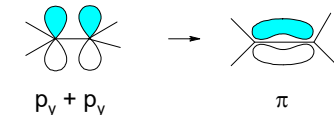
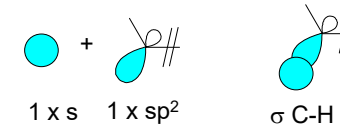
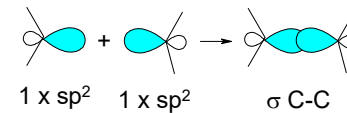
LCAO MO = Linear Combination of Atomic Orbitals Molecular Orbitals

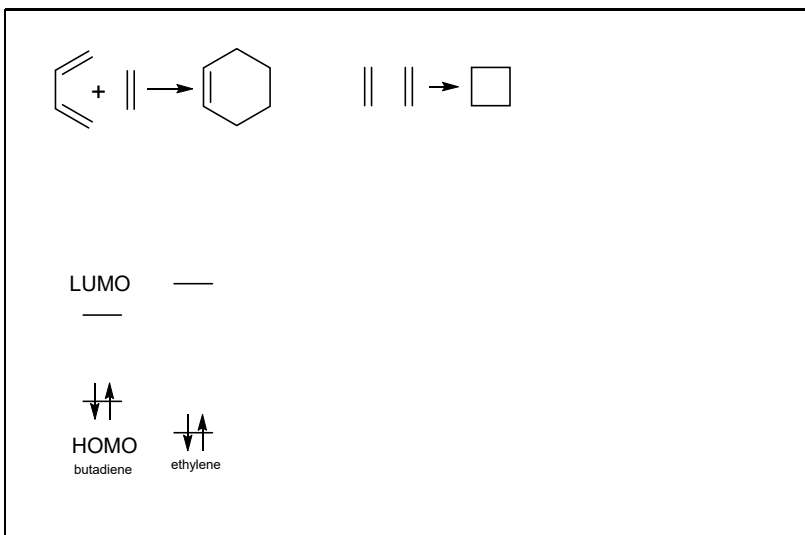
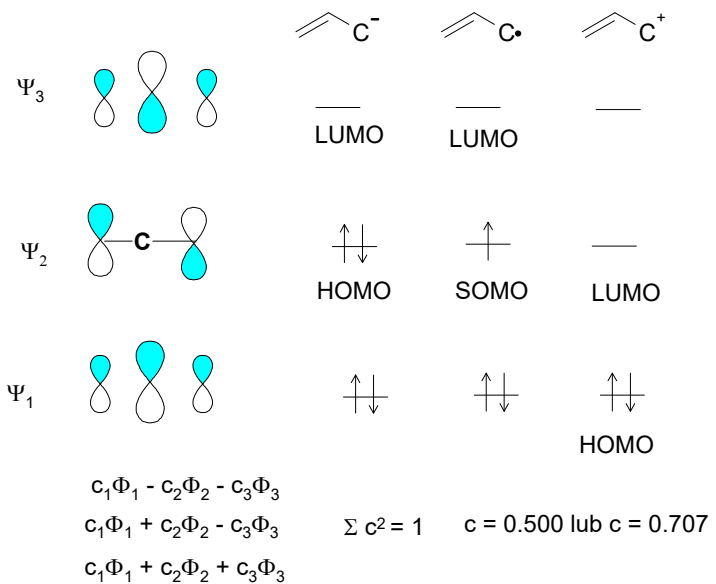
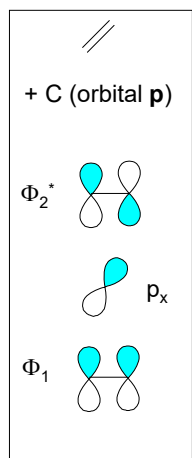
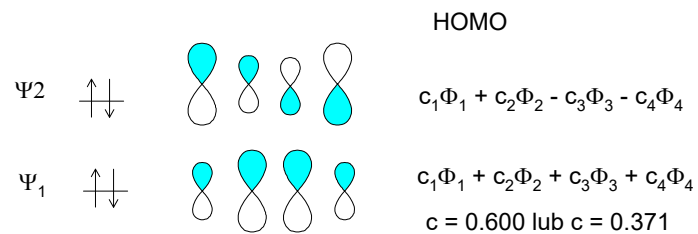
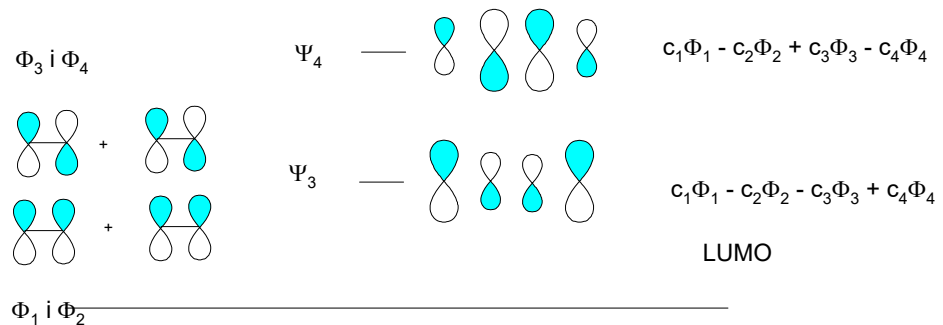
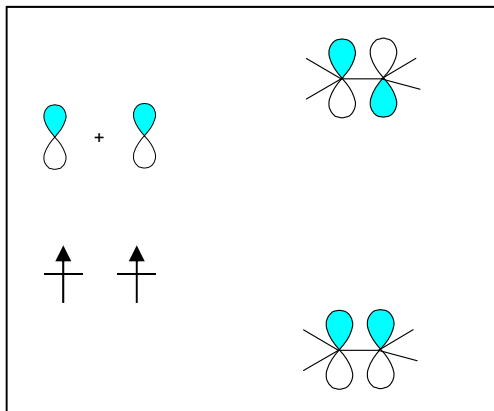
Electron configuration at carbon atom: C: $(1s)^2 (2s)^2 (2p)^2$; Hund's rule: $2s^1 2p_x^1 2p_y^1 2p_z^1$

HYBRIDIZATION: (sp^3 , sp^2 , sp)

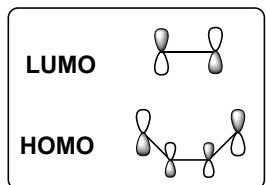
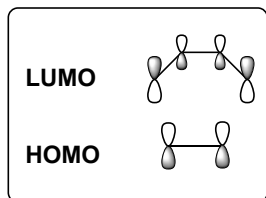


ethylene
one bond C-C (σ)
+ 4 bonds C-H (σ)
1 bond π



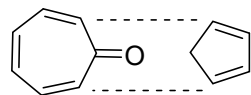
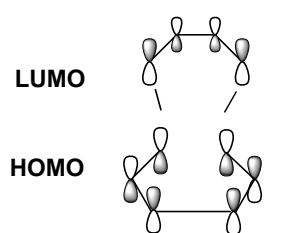


[4+2]



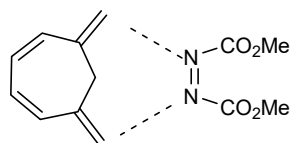
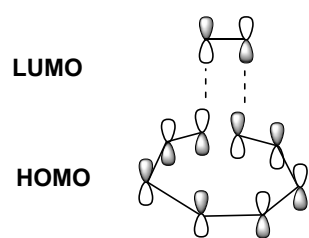
$$2n+1 = 3$$

[6+4]

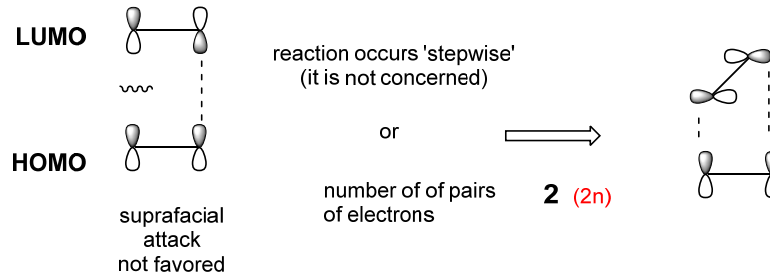


$$5 = 2n+1$$

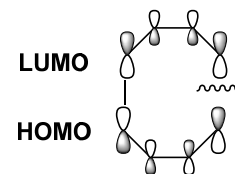
[8+2]



$$5 = 2n+1$$

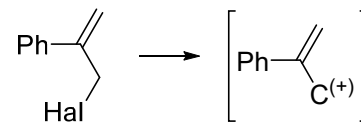
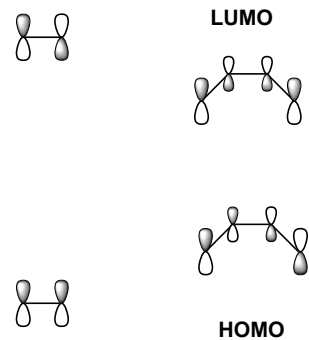
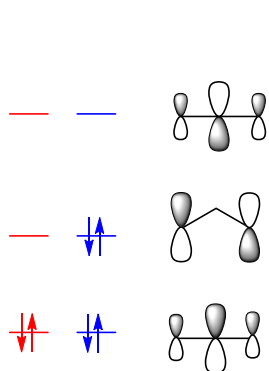
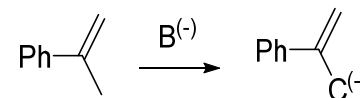
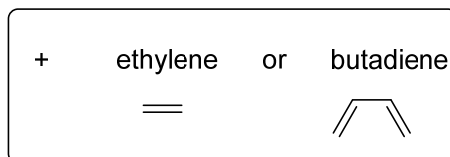


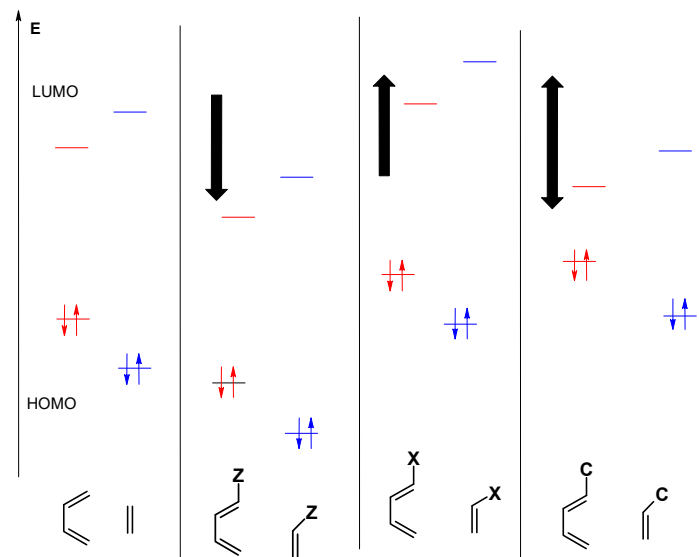
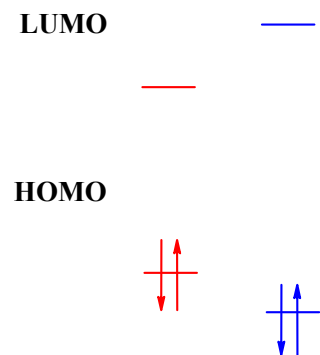
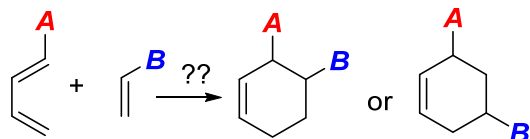
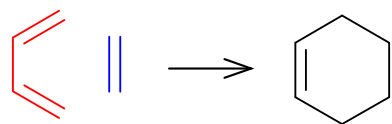
[4+4]



number of of pairs of electrons **4 (2n)**

Allyl ions





Typical coefficients

