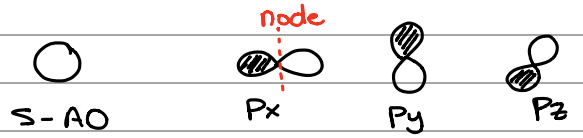
III - Intro to Molecular Orbital Theory

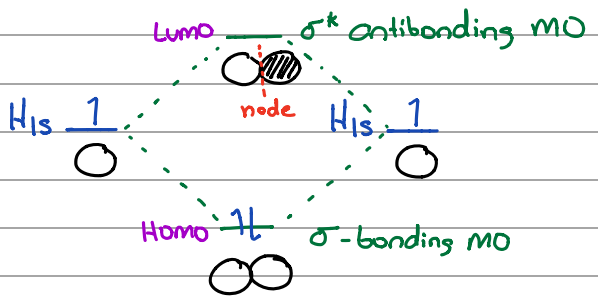
Atomic Orbitals = orbitals occupied by electrons in isolated atoms. Reading: Karty

Molecular Orbitals = orbitals occupied by the electrons in molecules. Fleming Ch 2



node = Site with zero probability of finding an e⁻

Ex: H_2

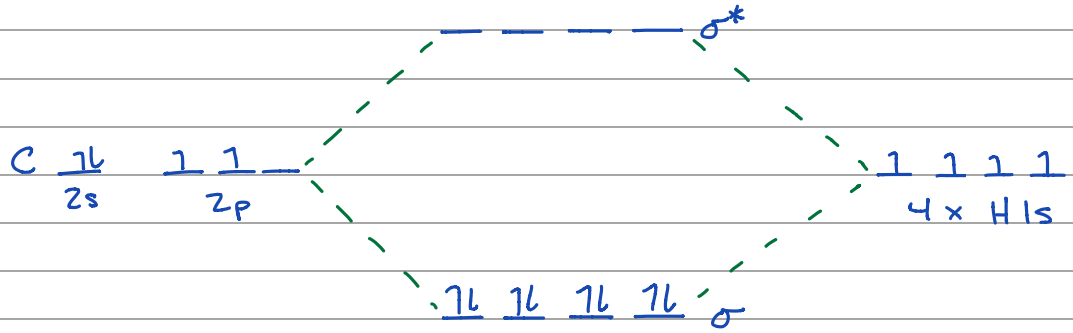


Lumo = Lowest Unoccupied MO

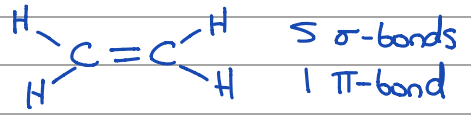
Homo = Highest Occupied MO

Total # AO's = Total # MO's

Ex: CH_4

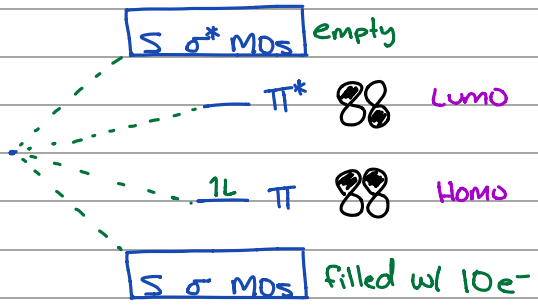


Ex: C_2H_4

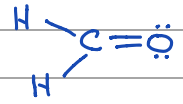


5 σ-bonds
1 π-bond

12 e⁻ total

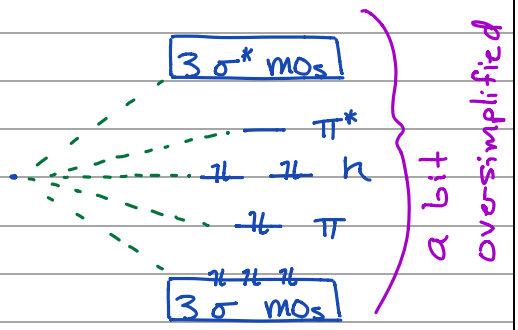


Non-bonding lone pair e⁻ reside in non-bonding orbitals (n)



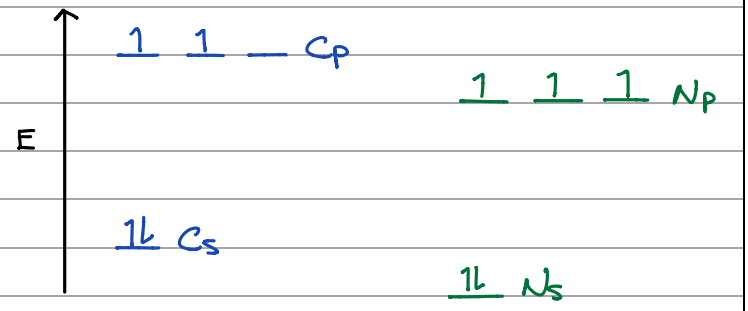
3 σ bonds
1 π bond
2 nb e⁻ pairs

12 e⁻ total

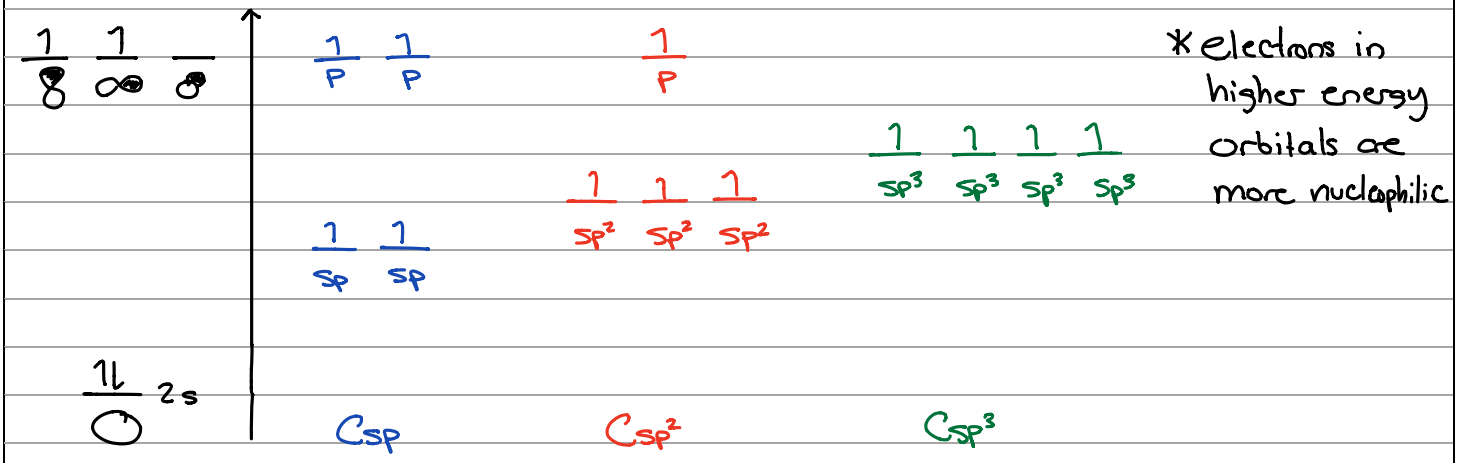


Relative Energy of Orbitals

Low E 1s < 2s < 2p High E
Electronegativity ↓ orbital energy



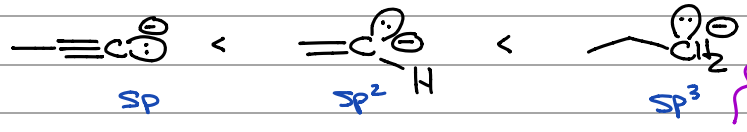
Higher e⁻neg sp < sp² < sp³ Lower e⁻neg
Lower E Higher E



*electrons in higher energy orbitals are more nucleophilic

Always assess the % p-character => more p-character in a bond / lone pair = More Nu

Relative Basicity

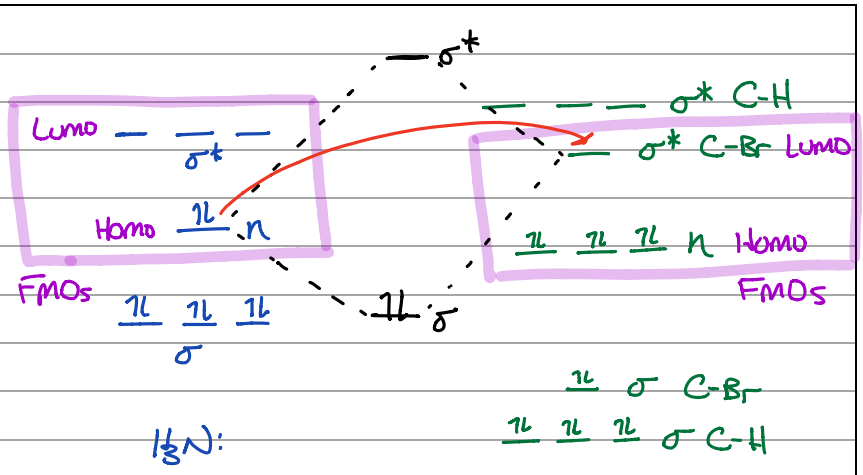


75% p-Character = most Nucleophilic

Frontier Molecular Orbitals (FMOs)

Consider $H_3N:$ + H_3C-Br

* Electron Pushing represents the interaction of filled orbitals w/ unfilled orbitals

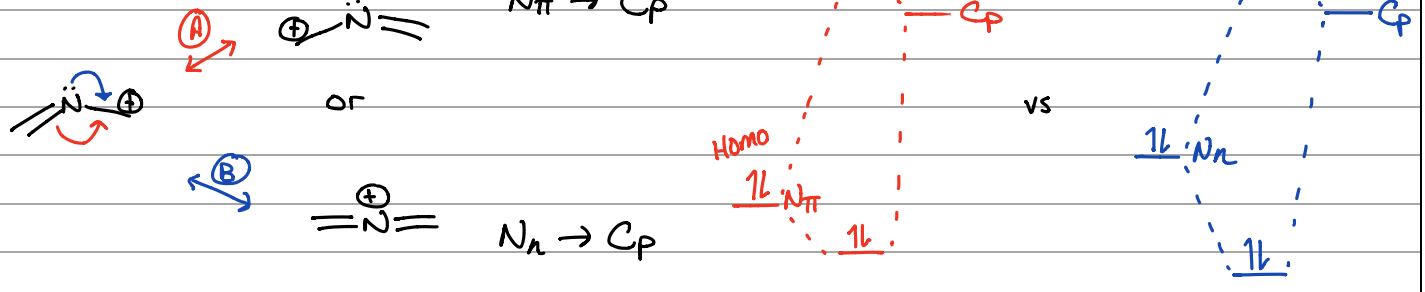


MO Interaction Diagram

The Six Frontier Molecular Orbitals:

- unfilled MOs: σ*, π*, p
- filled MOs: n, π, σ

n has mixed in s-character which lowers its E relative to a p-orbital

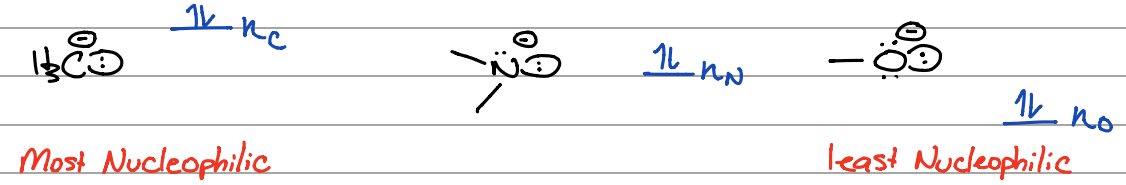


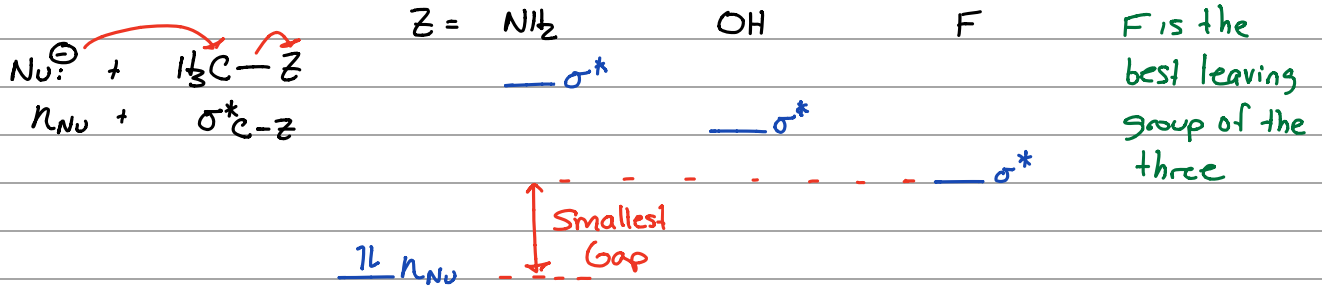
* A smaller HOMO-LUMO gap results in greater interaction energy.

FMO Trends

Electronegativity

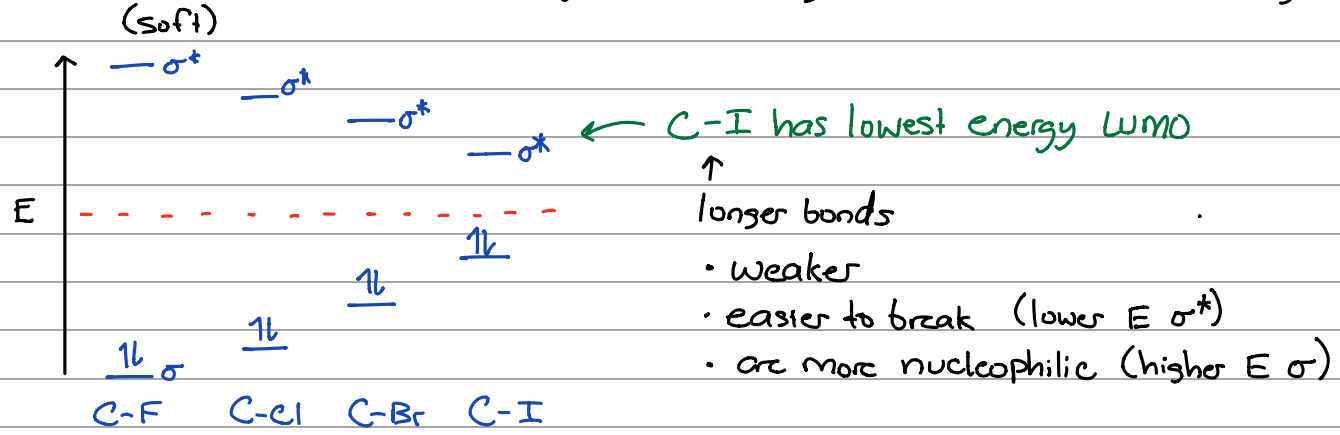
- More e⁻ neg atoms have lower energy MOs.





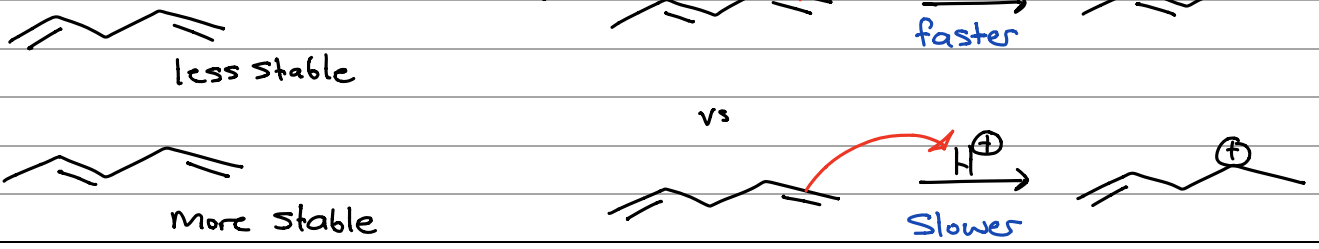
- Be careful with the halides

More polarizable bonds have higher E bonding MOs + lower E antibonding MOs.

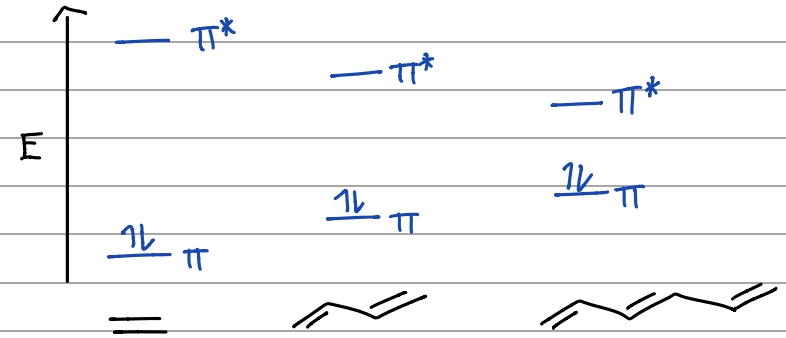


Conjugation (Hückel MO Theory)

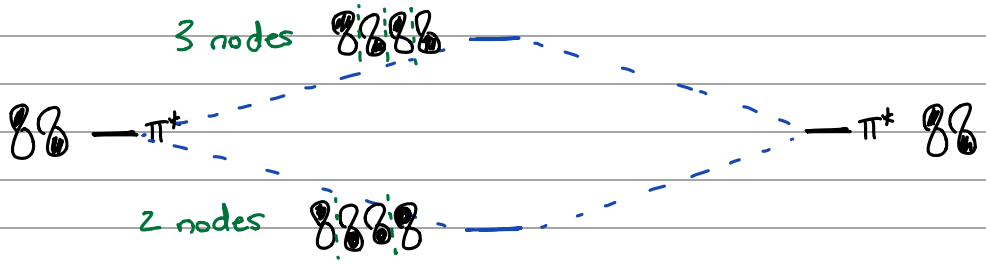
But...



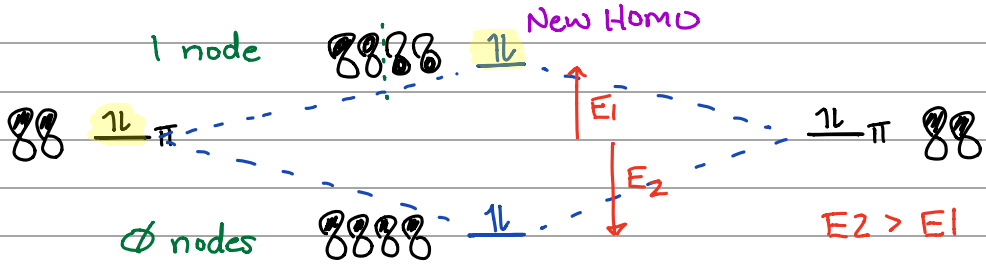
Conjugation ↑E of Homo
↓E of Lumo



Why



$H_2C=CH_2$ $H_2C=CH_2$



E2 > E1 = net Stabilization

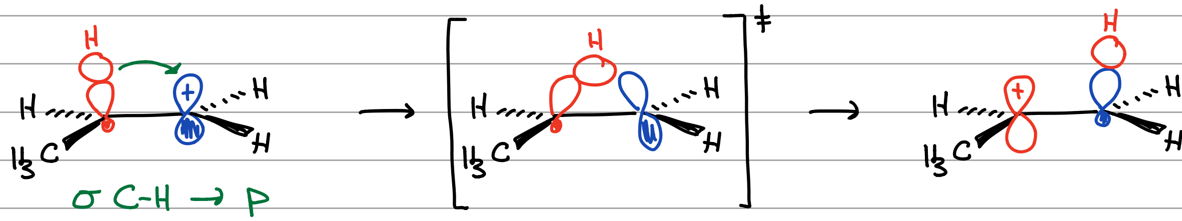
Salem - Klopman Equation

$$\Delta E = \underbrace{\sum (q_a + q_b)\beta_{ab} S_{ab}}_{\text{Sterics}} + \underbrace{\sum \frac{Q_k Q_l}{\varepsilon R_{kl}}}_{\text{Charges}} + \underbrace{\sum_r^{occ} \sum_s^{unoc} + \sum_s^{occ} \sum_r^{unoc} \frac{2(\sum_{ab} c_{ra} c_{sb} \beta_{ab})^2}{E_r \pm E_s}}_{\text{MO Interaction}}$$

Stereoelectronic Effects

↳ Stereochemical & regiochemical consequences due to the shape and orientation of the participating orbitals.
(e.g. backside attack in S_N2)

• Hyperconjugation

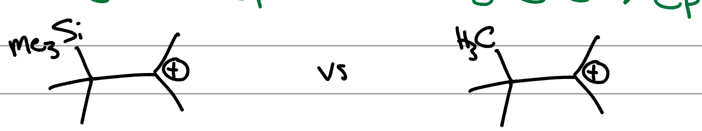


σ C-H → p

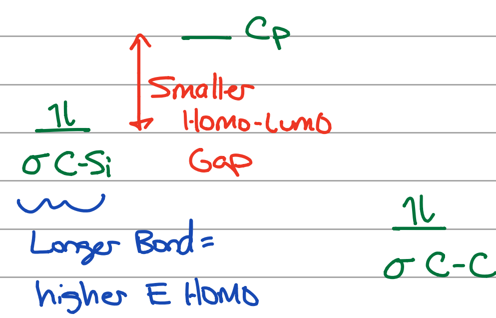
* 1,2- Hydride Shift

• β-Silicon Effect (JACS 1986, 107, 1496)

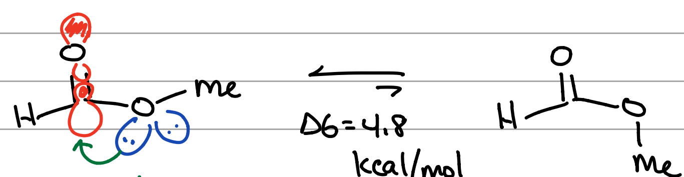
σ C-Si → Cp   σ C-C → Cp



38 kcal/mole more stable

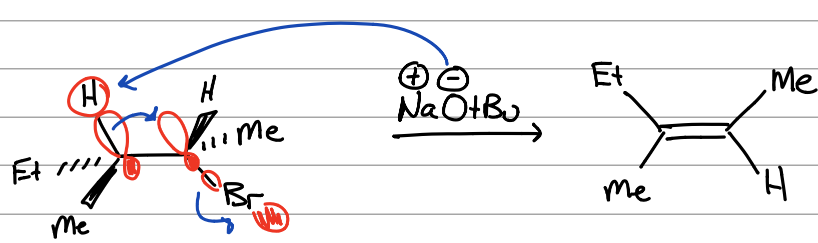


• Ester Conformation

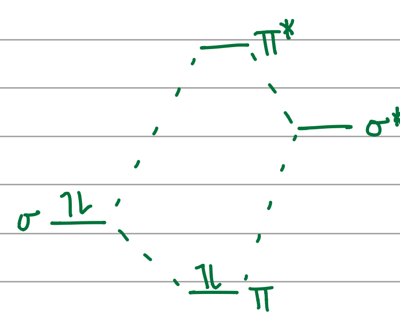


n → σ* C-O

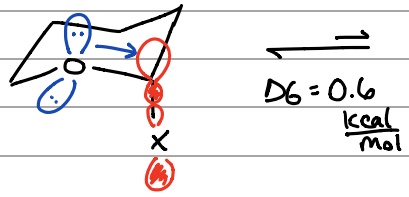
• E2 Antiperiplanar Elimination



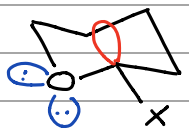
σ C-H ⟶ σ* C-Br



- The anomeric effect



$\Delta G = 0.6 \frac{kcal}{mol}$

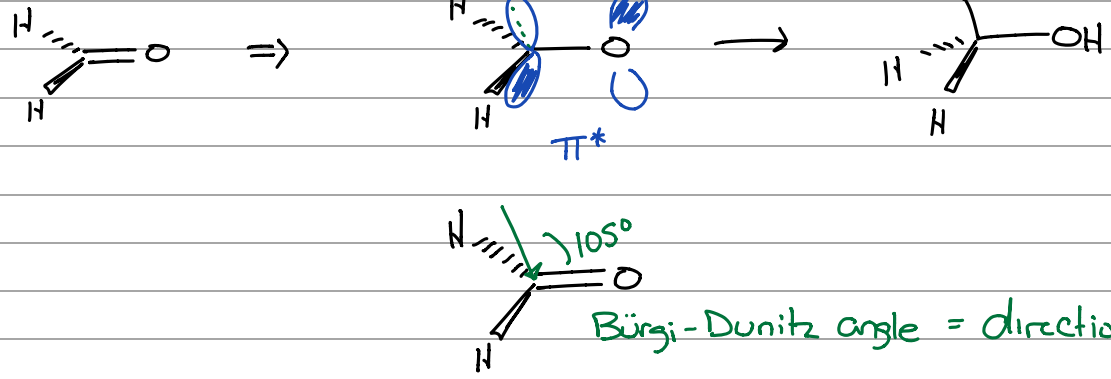


$n \rightarrow \sigma^*$ donation

incorrect orbital alignment for donation

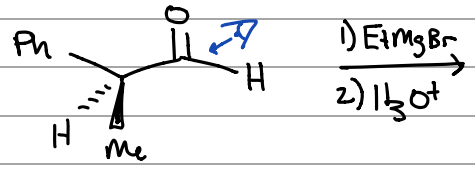
- Carbonyl Addition Rxns

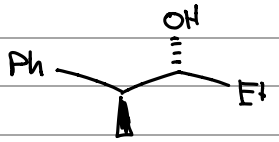
$n_{Nu} \rightarrow \pi^* C\text{-}O$



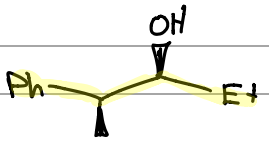
Bürgi-Dunitz angle = direction of attack

Consider:





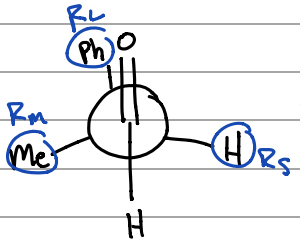
25%

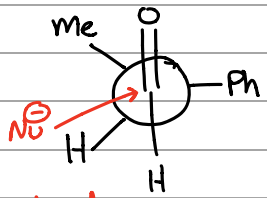


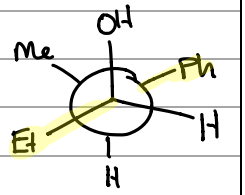
75% (50% de)

Felkin Ahn Model:

- Rotate so substituents are staggered
- Put R_L perpendicular to C=O
- Put R_M closest to C=O







unhindered approach @ B-D angle

$de = \frac{major - minor}{major + minor} \times 100$

• Baldwin's Rules (MPOC pg 568)

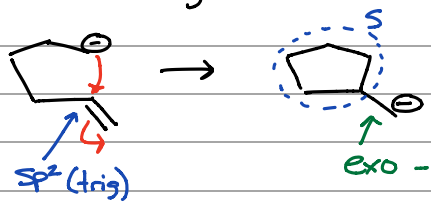
Provides a set of generalizations on the likelihood of ring closure

Applies to ⊕ ⊖ and • systems

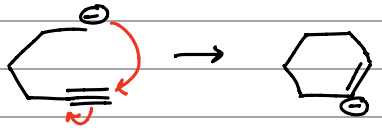
Nomenclature: Size of ring + mode + hybridization State

Size of ring	mode	hybridization State
3	endo	dig (sp)
4	exo	trig (sp^2)
5		tet (sp^3)
etc.		

Ex: 5-exo-trig



6-endo-dig



Baldwin's Rules for Ring Closure

	Exo			Endo		
Ring Size	*dig*	*trig*	*tet*	*dig*	*trig*	*tet**
3	U	F	F	F	U	U
4	U	F	F	F	U	U
5	F	F	F	F	U	U
6	F	F	F	F	F	U
7	F	F	F	F	F	U

F = Favored
U = Unfavored
*The endo-*tet* mode would proceed through a cyclic transition state to give an acyclic product. When the ring size is >9, the stereoelectronic requirement for the 180° Nu-C-LG bond angle can be met.

5-exo-trig (F) vs 5-endo-trig (U)