Lecture 10: MO Theory (1/2)

DATE 27 Sept 2024

Exam Reflections

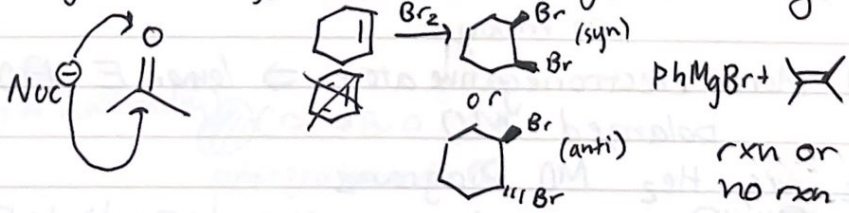
- You all did great
- "How did I do?"
  - 90-100 excellent
  - 80-90 good
  - <80 adequate, reach out
- exams hand back in recitations
- these guidelines are exam specific
  - ↳ first exam typically best
- You learned structure determination!

What's Next?

- how do you go from 2D structure to where are e⁻ where do they react

Unit 2 Molecular Orbitals & Pericyclic Reactions

- deeper look at e⁻ movement
- new types of reactions, new class of mechanism
- use molecular orbitals (MO's) to predict reaction outcomes
  - ↳ regioselectivity, diastereoselectivity, reactivity



- MO's provide insight into structure & reactivity

Background/Review & Study

- review gen chem (5.11/5.12) & Orgo I (5.12)
- Clayden: ch. 4, 5, 6

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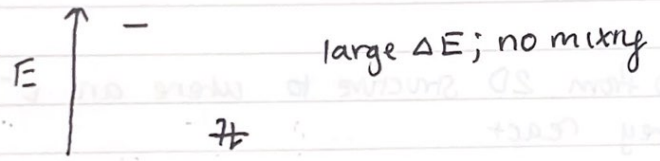
- orbitals are wavefunctions that describe the ability to find an electron in space
  ↳ they interact constructively & destructively

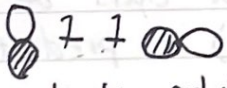
Rules:

① # atomic orbitals (AOs) in = # MO's out

② interacting orbitals must have similar energy
- if large ΔE ; no mixing
- if same E ; best mixing



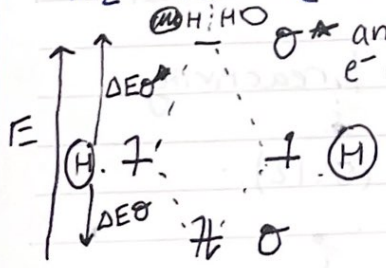
③ interacting orbitals must overlap efficiently and have similar ~~energy~~ symmetry



perpindicular orbitals
- poor overlap
- no mixing

④ More electronegative atom ⇒ lower E AO = more polarized MO

H_2 vs He_2 MO Diagrams



HOH

bonding; e⁻ in middle

Note: $|\Delta E_{\sigma^*}| > |\Delta E_{\sigma}|$
antibonding is more destabilizing than the bonding is stabilizing

H_2 MO more stable than 2 × H· AO
↳ why H_2 bond forms

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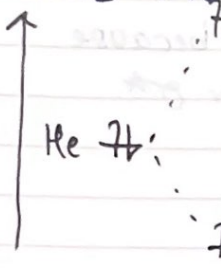
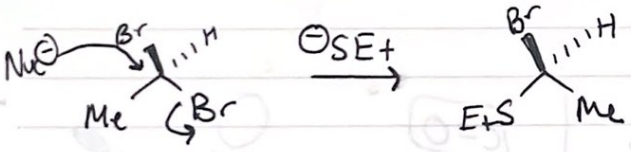
He_2 MO Diagram



- antibonding MO filled!
- this is less stable than two individual H atoms
- forming He-He requires filling σ* (which is more destabilizing) than

- this is the MO explanation for the full octet rule

S_N2 MO Picture

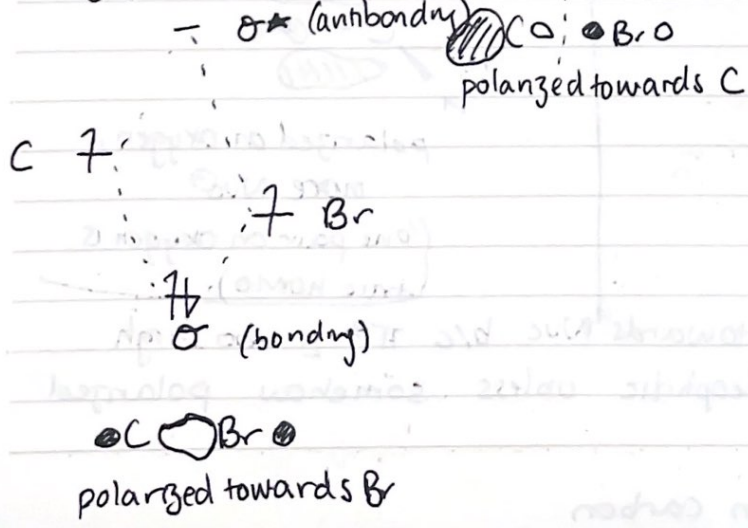


Why backside attack?
- identify HOMO & LUMO

HOMO highest occupied MO = π orbital, ⊖SEt nucleophile, filled orbitals, lone pair

LUMO lowest unoccupied MO = electrophile = empty orbitals = π* or σ* orbital, cations, C of C-Br bond

MO of C-Br



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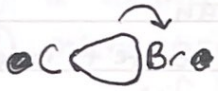
HOMO

backside attack because there is a larger σ^* lobe there

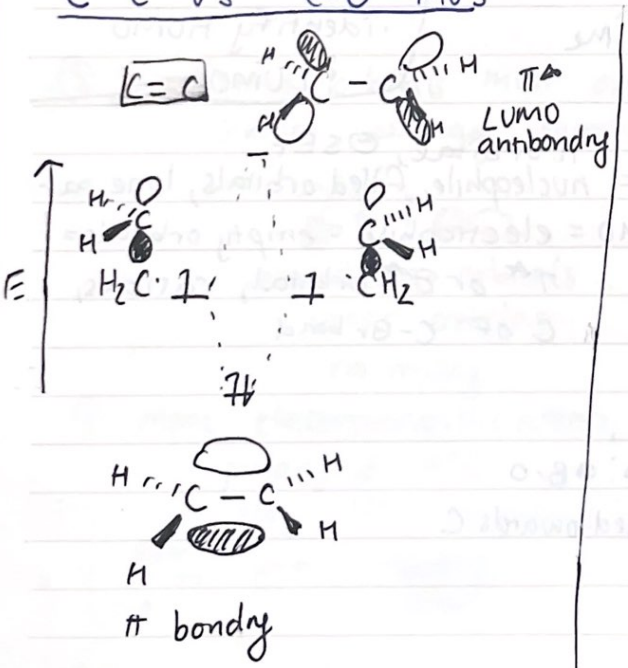
meanwhile

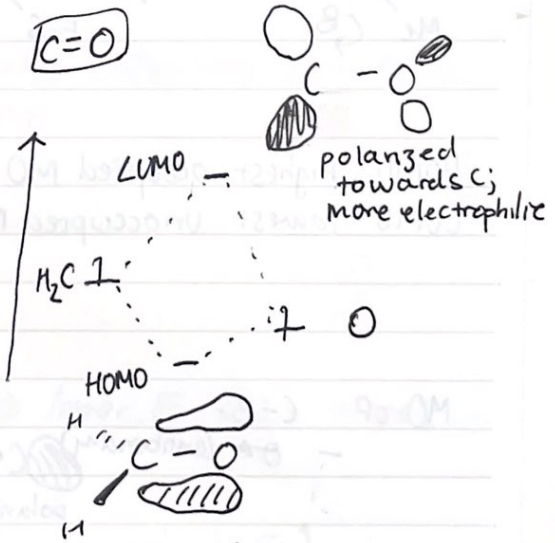


σ bond breaks because σ^* populated

our mechanistic arrows show this

C=C vs C=O MOs

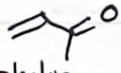




Consequences:

C=C less reactive towards Nuc b/c π^* E too high

C=C generally nucleophilic unless somehow polarized

ex: 

C=O electrophilic on carbon