

Unit 2

Molecular Orbitals and Pericyclic Reactions

2.10 Molecular Orbital Theory - 1

9/27: • See Georgia's notes on Canvas (also included below).

Lecture 10: MO Theory (1/2)

NO 1
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!

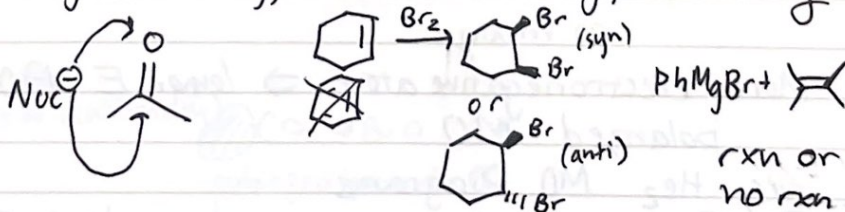
What's Next?

- 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

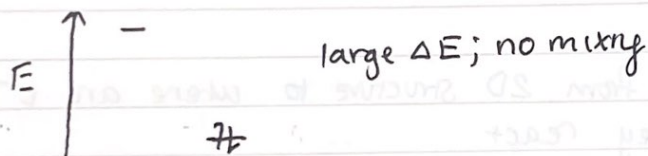
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Lecture 10: (cont)

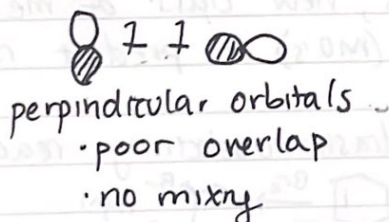
- orbitals are wavefunctions that describe the ability to find an electron in space
- ↳ they interact constructively & destructively

Rules:

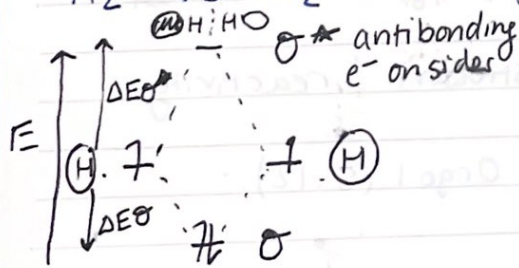
- ① # atomic orbitals (AOs) in = # MO's out
- ② interacting orbitals must have similar energy
 - if large ΔE ; no mixing
 - if same E ; best mixing



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



- ④ More electronegative atom \Rightarrow lower E AO = more polarized MO

H₂ vs He₂ MO Diagramsbonding; e^- in middleNOTE: $|\Delta E_{\text{antibonding}}| > |\Delta E_{\text{bonding}}|$

antibonding is more destabilizing than the bonding is stabilizing

H₂ MO more stable than 2 \times H \cdot AO

↳ why H₂ bond forms



- 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

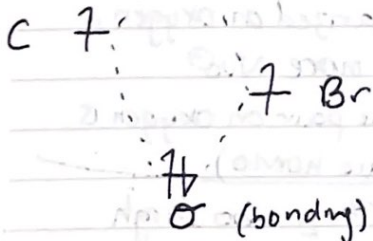
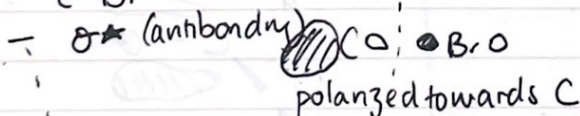
SN₂ MO Picture



Why backside attack?
• identify HOMO & LUMO

HOMO highest occupied MO = 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



σ C-Br σ
polarized towards Br

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Lecture 10: (cont)



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

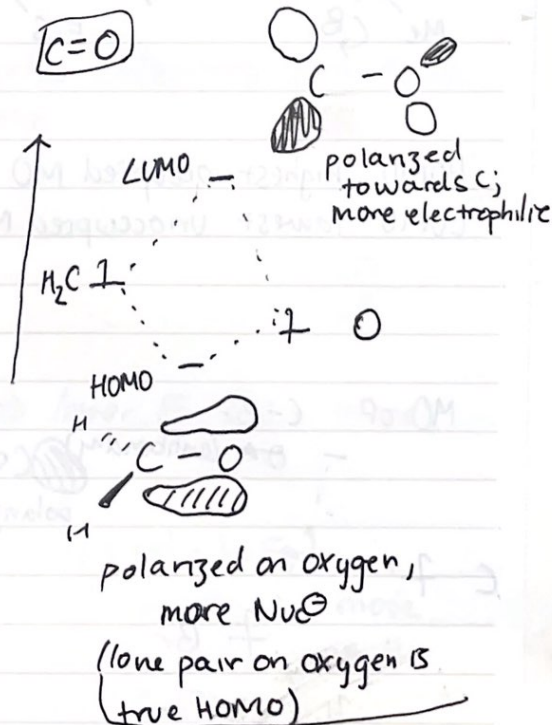
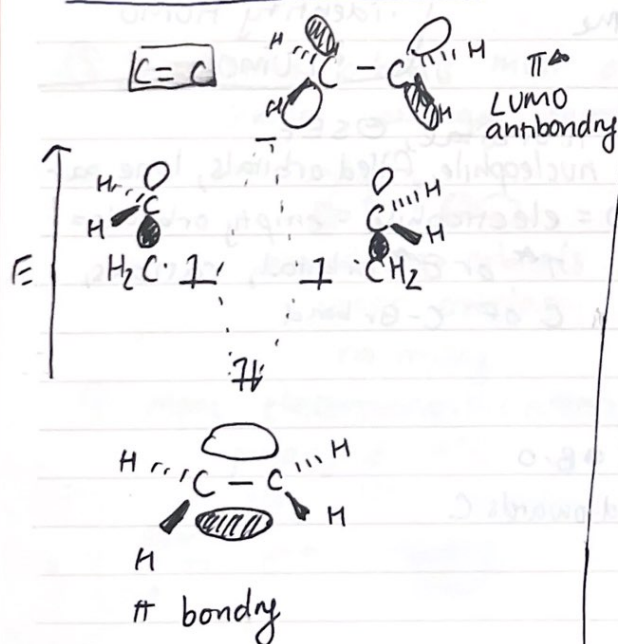
meanwhile



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 polonized
ex: C=C=O

C=O electrophilic on carbon