

① LECTURE 19: PERICYCLIC RXNS (CONT'D)

PS B: Due Thurs, 11/12

Midterm #2: Good Job!

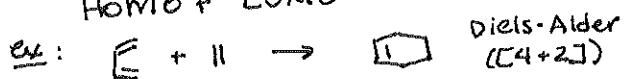
Mean: 65%

Answer Key, Exam & Statistics posted on-line.

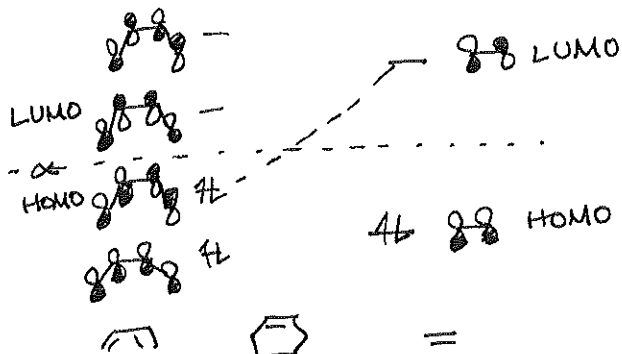
Final Exam: Tues, 12/16
3:30 - 6:30 pm
Gore 222

② Fukui: FMO theory

The idea: use FMO's
HOMO + LUMO



Hückel MO's:



③ Which HOMO & LUMO?

$$E \propto \frac{\text{overlap}}{\Delta G}$$

For C=CC=C + C=CC=C, it doesn't matter.
Either combo is equally good.

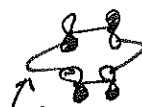
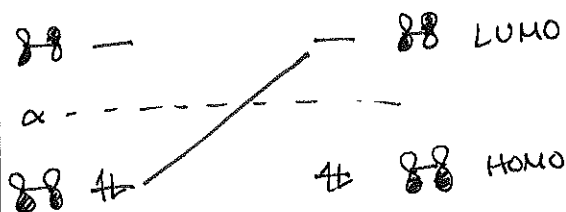
* Does symmetry lead to net bonding interaction?



HOMO + HOMO

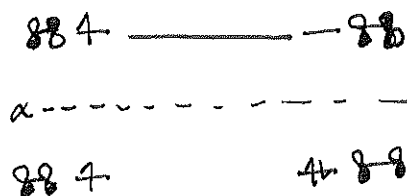
YES.

④ What about C=CC=C + C=CC=C >> C1C=CC=C1?

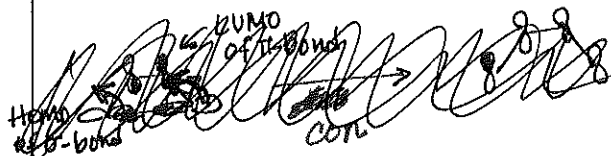
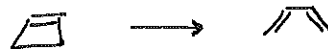


anti/non-bonding \Rightarrow "FORBIDDEN"

⑤ Good to predict cycloadditions, including photochemical rxns:



⑥ Less intuitive for electrocyclicizations
 \rightarrow Break into HOMO & LUMO



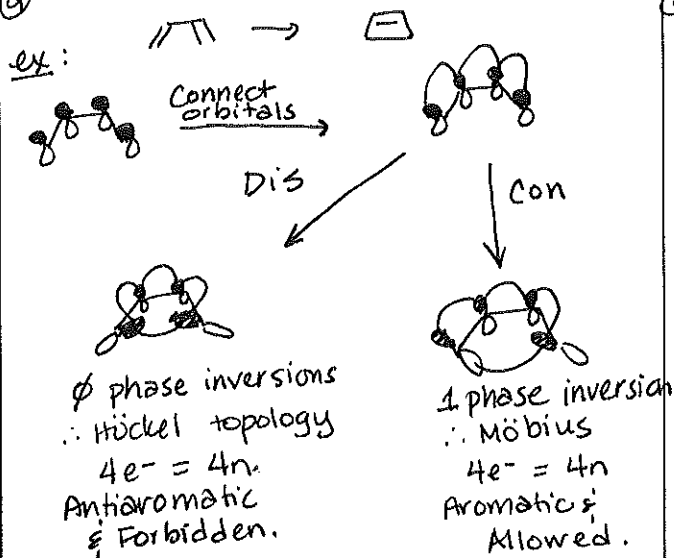
⑦ DEWAR-ZIMMERMAN: AROMATIC TS

Steps:

- 1) Choose basis set of 2p AO's (or 1s for H atoms).
- 2) Assign phases (any phases).
- 3) Connect orbitals that interact in SM.
- 4) Connect lobes that begin to interact in rxn.
- 5) Count # of phase inversions.
- 6) Identify topology:
 Odd # of phase inversions = Möbius
 Even # = Hückel
- 7) Assign TS as aromatic or antiaromatic.
 ↳ Photochemically allowed.
 ↳ Thermally allowed.

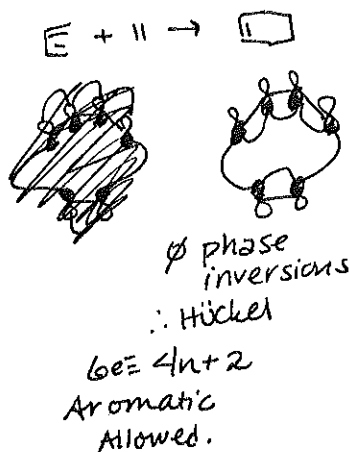
System	Aromatic	Antiaromatic
Hückel	$4n+2$	$4n$
Möbius	$4n$	$4n+2$

⑨



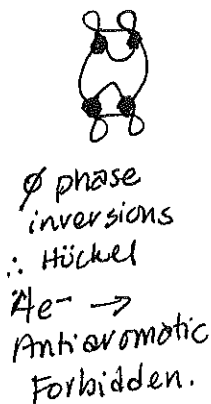
⑩

Cycloadditions:



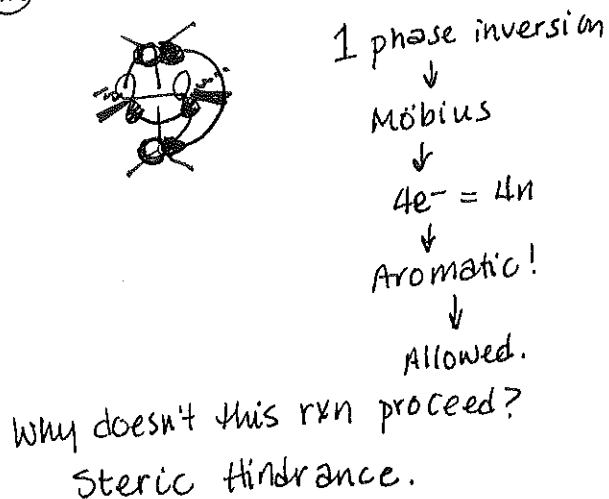
⑪

What about $\parallel + \parallel \rightarrow \square$



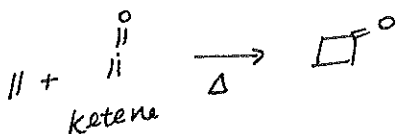
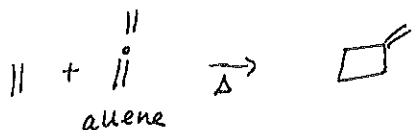
But if there was ≥ 2 phase inversion...

⑫



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If you remove steric hindrance:



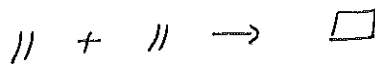
Challenge: Where is the symmetry element in a [2+2] to predict this rxn?
 Hint: C₂-symmetry.

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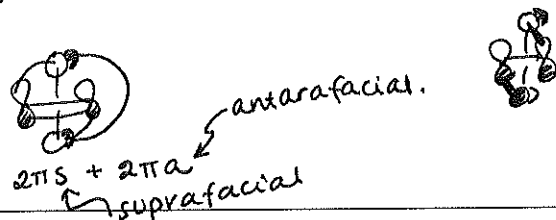
How do we describe this?

Suprafacial = same face of the π-system

Antarafacial = opposite faces of π-system.



FMO:



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Antarafacial ⇒ Phase Inversion
 Use Möbius rules for determining TS aromaticity.

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[1,3]-sigmatropic Rearr

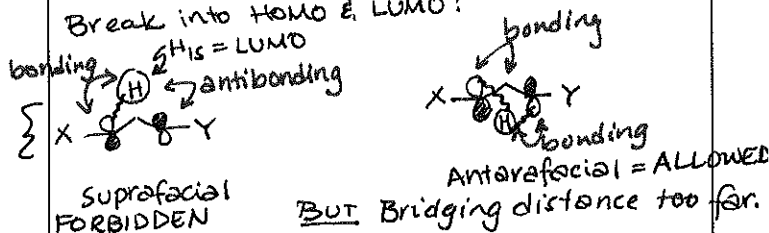
supra- or Antara-facial?

↕ Same face
 ↕ opposite faces

FMO Analysis:



Break into HOMO & LUMO:

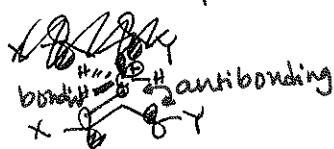


Allyl anion HOMO

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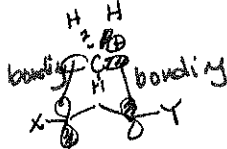


RETENTION @ CH₃



Suprafacial on allyl fragment & CH₃ FORBIDDEN

INVERSION @ CH₂



Supra on allyl Antara on CH₃ ALLOWED.

Note: Highly strained → Rare.

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What about Dewar-Zimmerman?



(suprafacial)

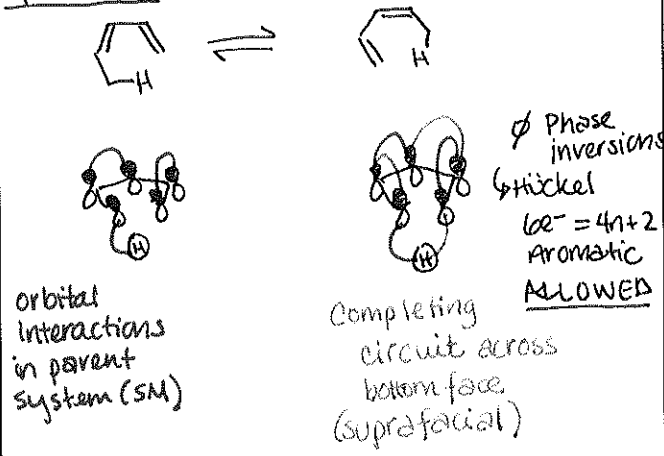
2 phase inversions
Hückel

4e⁻ → Antiaromatic FORBIDDEN.

What about [1,5] shifts?

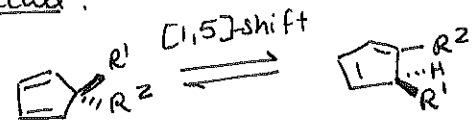
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1,5-shifts:



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Recall:



Why not [1,2]-shift?
 π -e-s are moving.

[1,2]-shift =

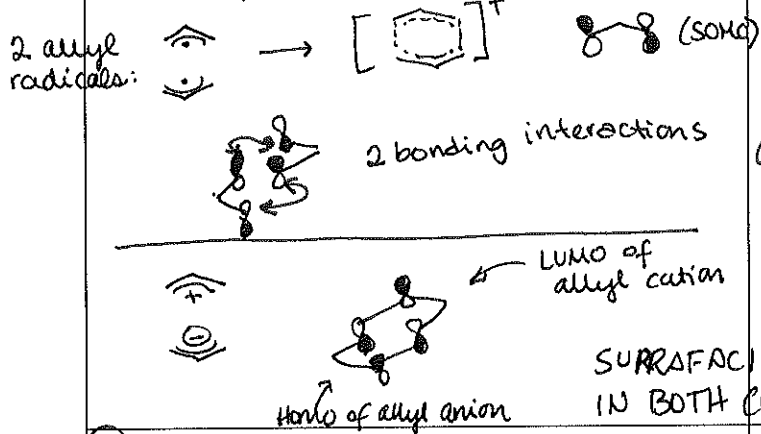


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[3,3]-Rearrangements

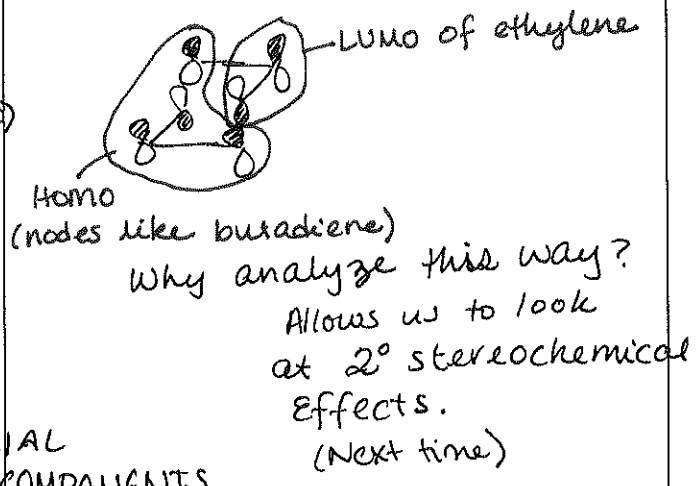


FMO Analysis:



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Alternate FMO analysis:



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Summary

- 3 Theories to explain reactivity & stereochemistry of pericyclic rxns.
- Thermal vs. Photochemical
- Conrotatory vs. Disrotatory
- Suprafacial vs. Antarafacial
- Retention vs. Inversion

*you may "memorize" what's allowed or forbidden.

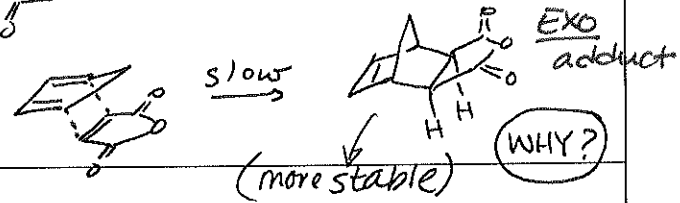
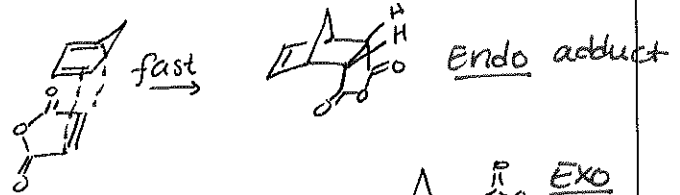
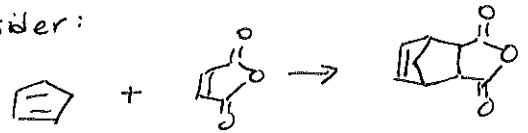
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① LECTURE 20 :

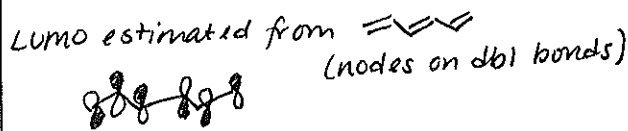
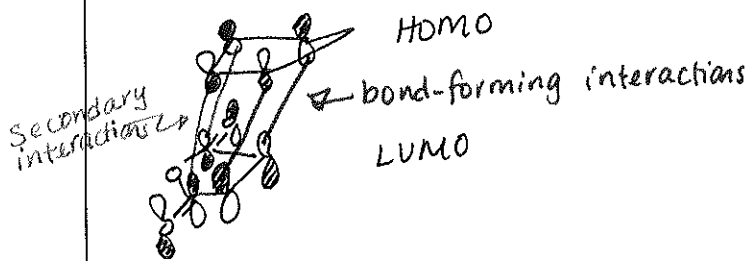
② SECONDARY STEREOCHEMICAL EFFECTS

- explained by FMO Theory.

Consider:

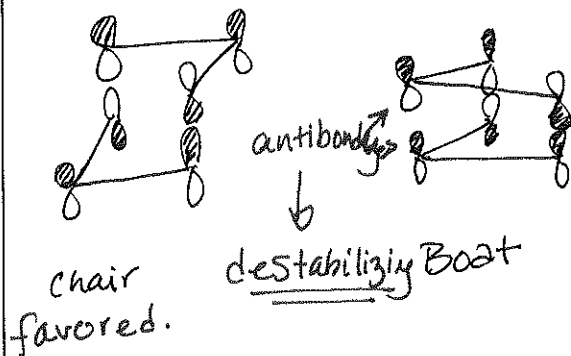


③ Orbital interactions not in bond-forming...



④ These 2° interactions lower energy of TS on endo pathway.

⑤ What about the Cope Rearr.?
Chair vs. Boat



⑥ What about: (exo) vs. (endo)

