Course Chem 345 Instructor Gellman
Day Monday Date 5 May 2014
Notes Taken By Kaz Skubi Total # of Pages 5

Submit notes to the Undergraduate Chemistry Office for posting.
PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

Office hours this week:

After class today and Friday

5-6 PM Today

Review: 5:30-6:30

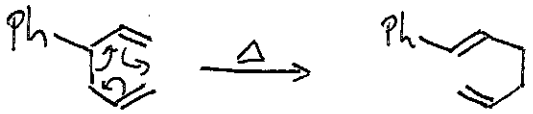
Friday (B371)

Recall: Pericyclic Rxns....

1) Electrocyclic reactions
2) Cycloaddition reactions
3) Today: Sigmatropic rearrangements

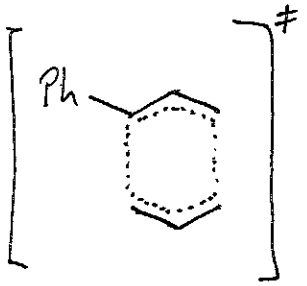
→ σ and π bonds exchange places. Unimolecular Processes (one molecule).

Ex: Cope Rearrangement

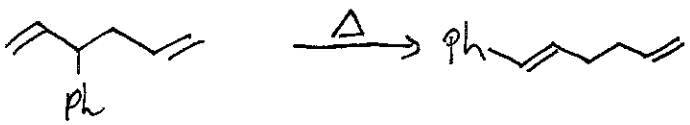


1,5-diene a different 1,5-diene

TS:



Perception can be challenging!



Literally same reaction, just drawn in a different orientation.

Look for 1,5-dienes

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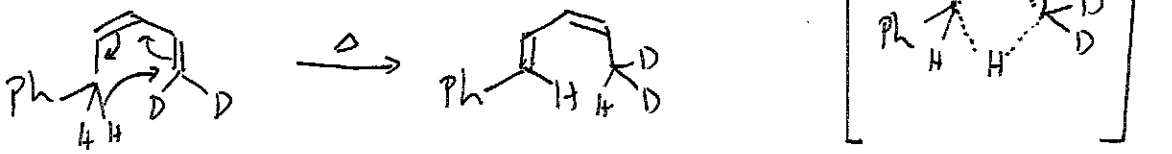
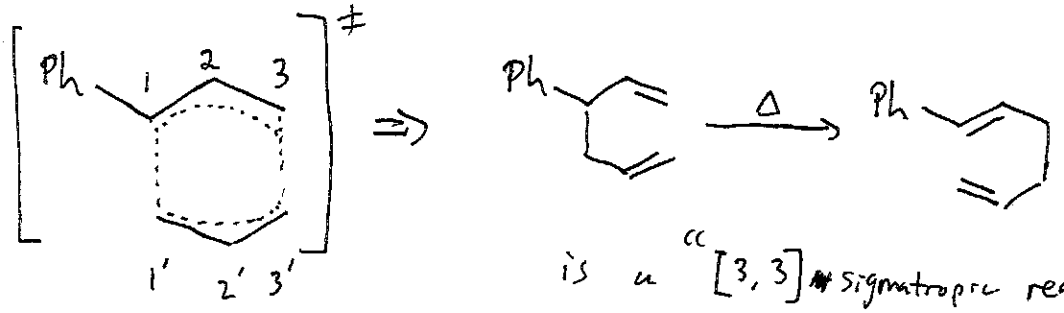
Another example:



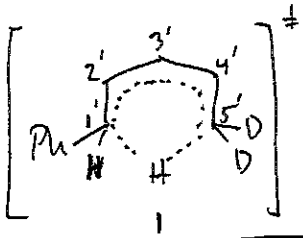
Systematic classification: based on fragments over which σ bonding is maintained at the transition state

e.g. for the Cope Rearrangement



is a "[3, 3] sigmatropic rearrangement"

Other example:



so this is a "[1, 5] sigmatropic rearrangement"

MO Analysis of [1,5] sigmatropic rearrangement.

Envision the "fragments" as radicals. The text uses a different system, but both will arrive at the same conclusion.

→ Focus on singly-occupied MOs (SOMOs)

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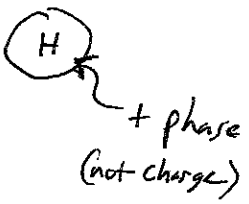
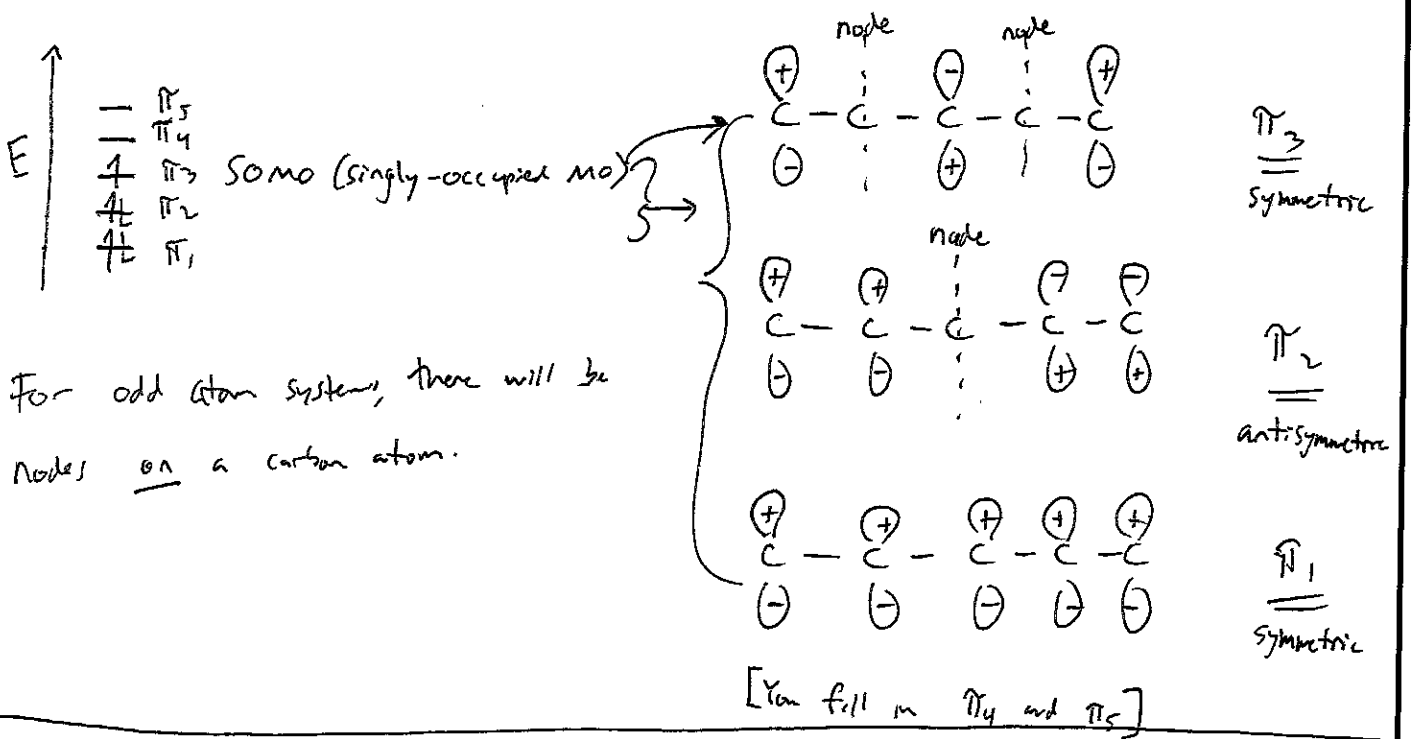
$H^\bullet$ ← e^- in 1s orbital → spherically symmetric
→ same sign (phase) everywhere



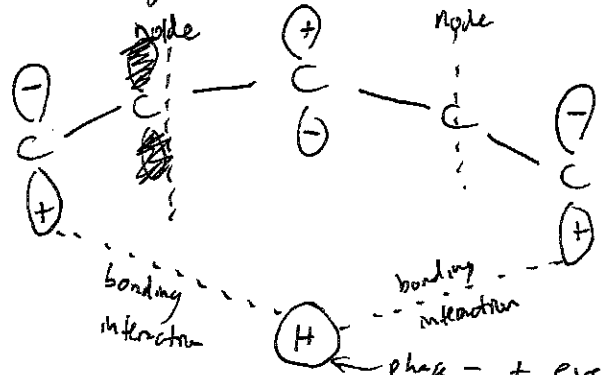
For the 5-C "fragment" (5 electrons)



For odd atom systems, there will be nodes <u>on</u> a carbon atom.

[You fill in π_4 and π_5]

π_3 (SOMO) is symmetric. At transition state:



∴ Thermal [1,5] rearrangement is <u>allowed</u>

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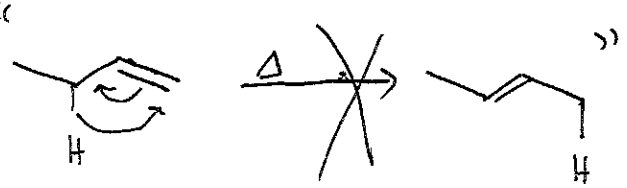
Consider thermal [1,3] sigmatropic rearrangement (not observed)



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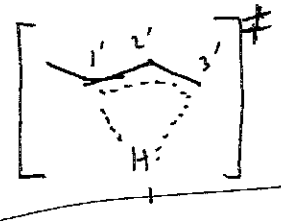
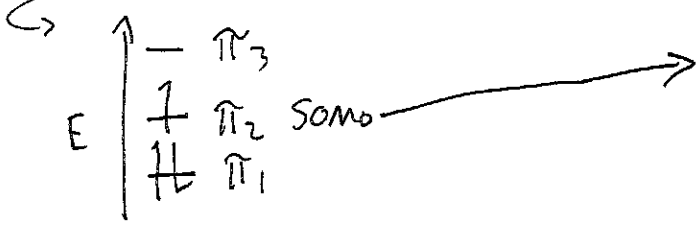
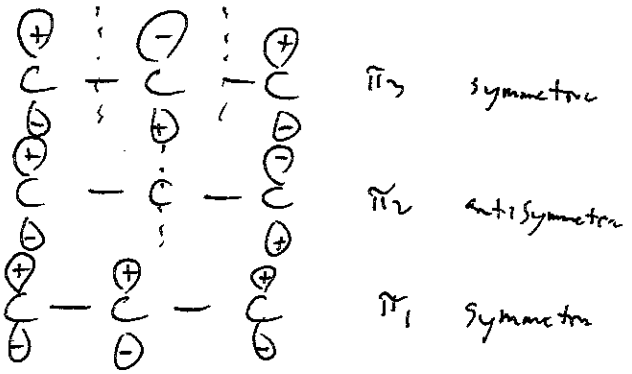


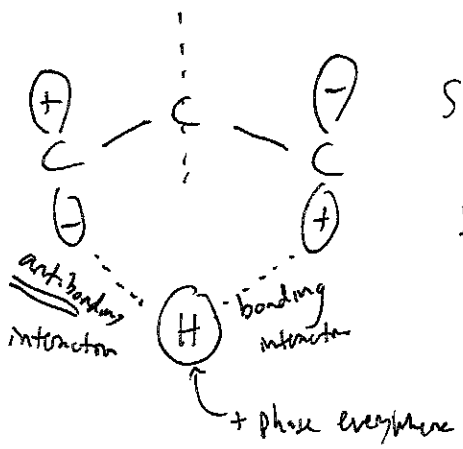
Arrow pushing looks fine, but can our MO analysis explain why this does not occur?

Must consider allyl radical π MO





Thus:



Signs don't align on one interaction, antibonding.

So this is thermally forbidden

In theory, could undergo the rearrangement in an antarafacial manner, but this is not physically possible for such a small, 3-carbon fragment.

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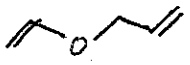
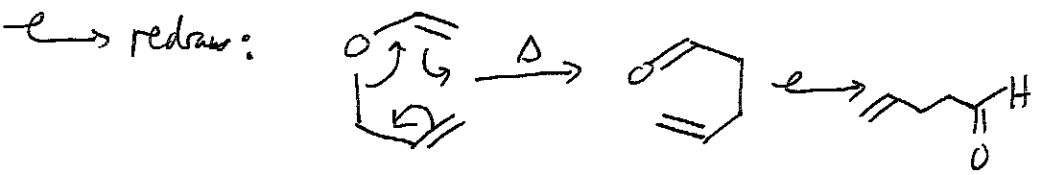
Variant on [3,3] - "Claisen Rearrangement"

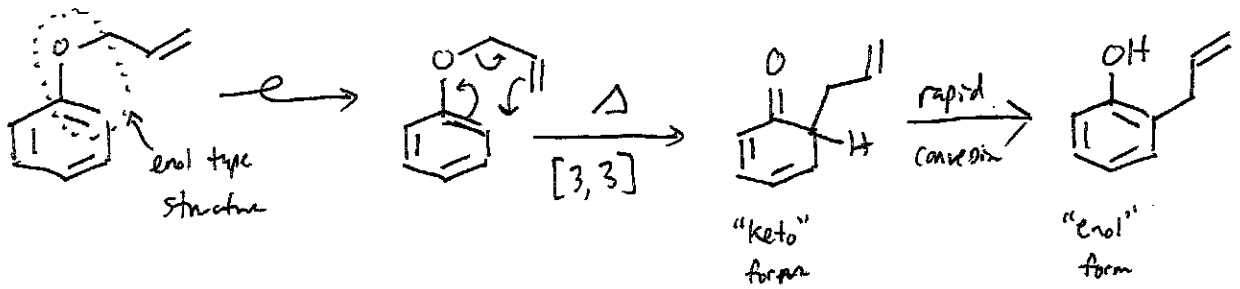


vinyl allyl ether
(still 1,5-diene)



Aromatic version:

Allyl ethers of phenols:

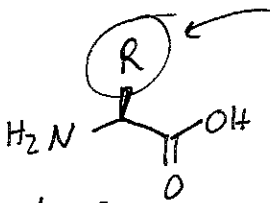


End of ch. 27

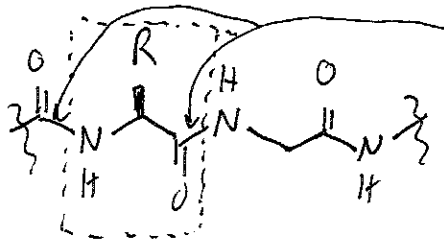
Proteins & Peptides ⇒ Amides (Ch. 26, no assigned problems)

Peptide Synthesis (chemical)

Building blocks = α-amino acids



20 different R groups in proteins.



amide bonds (peptide bonds)

"α-AA residue"