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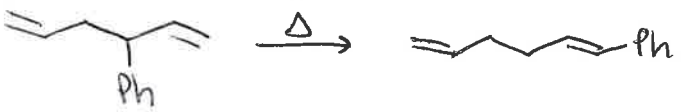
Monday — 5/4/15
Notes by Cassie Jans — Total pages: 3

- Recall: Electrocyclic Reactions...

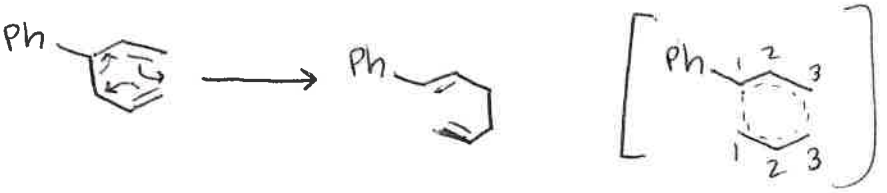
3) Sigmatropic Rearrangements

* Two variations:

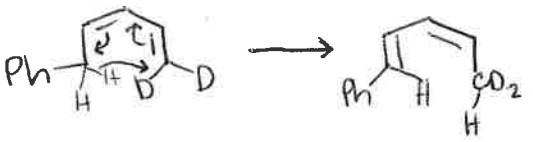
(i) [3,3]-rearrangement



(Alternative view):

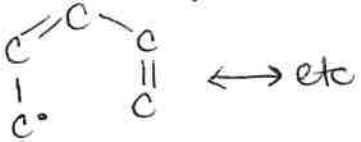


(ii) [1,5]-rearrangement



* MO symmetry analysis of [1,5]-sigmatropic rearrangement. Consider the "fragments" as radicals (text considers fragments as ⊕/⊖).

Thus,



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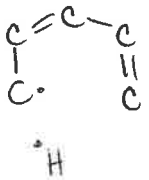
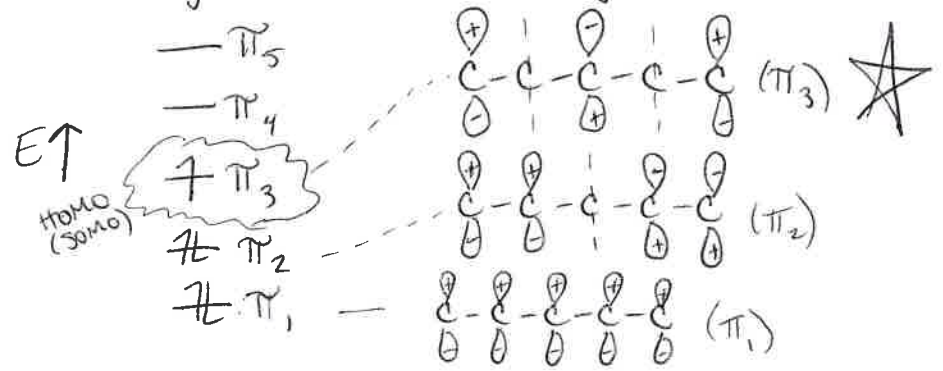
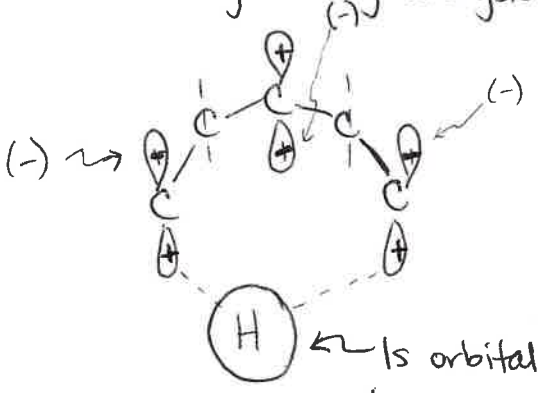


Pentadienyl radical - MO analysis (π):

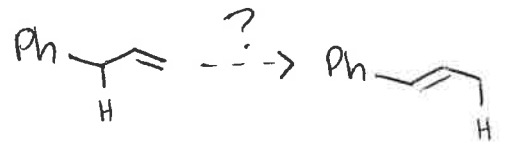


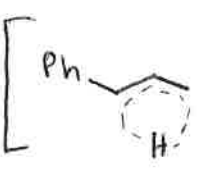
- MO symmetry analysis of [1,5] rearr. T.S.:



∴ [1,5] rearr. allowed according to π MO symmetry

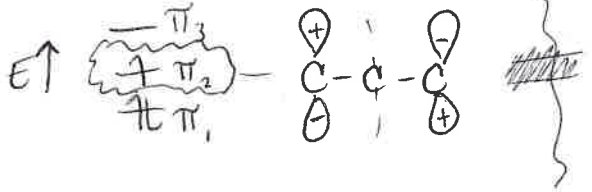
* consider a hypothetical thermal [1,3] rearrangement

E.g., 

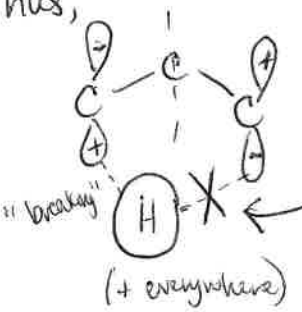
via 

NOT OBSERVED

- Allylic radical π MOs



Thus,



∴ Forbidden

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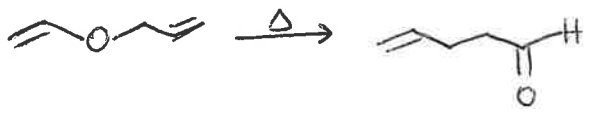
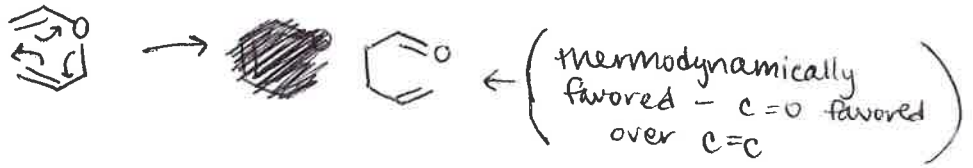
(see text on π MO symmetry in context of [3,3] rearr.)

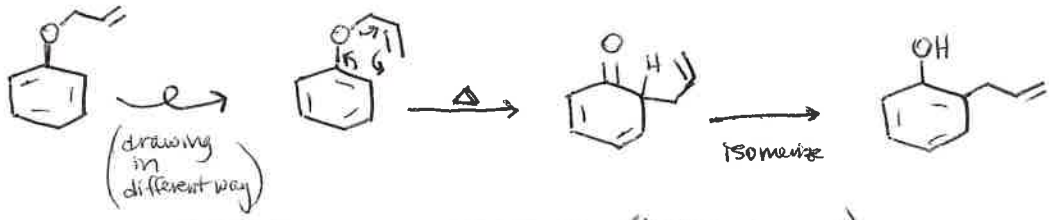
* [3,3] rearr. variations:



"Claisen rearrangement"



↳ Aromatic variation:



(keto → enol)
= restores aromaticity that was lost when did Claisen rearrangement

overall:

• Peptide Synthesis and Solid-phase Methods:

→ Chp. 26 (§ 26.6)

* Proteins – constituents are α-amino acids

α-amino acid:

Among proteins, 20 variations on "R" ("side chain")

- proteins are large molecules formed by linking α-amino acids to one another via amide bonds...