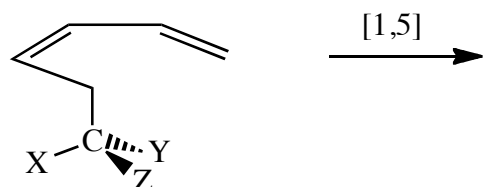


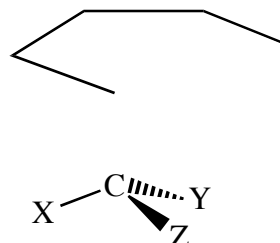
## Lecture outline

Aromatic transition state theory provides a simple explanation for these results —

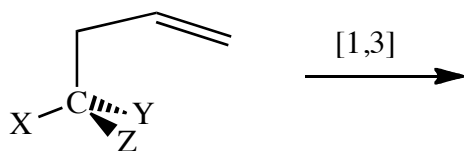
A [1,5] shift of C —



AO interaction diagram

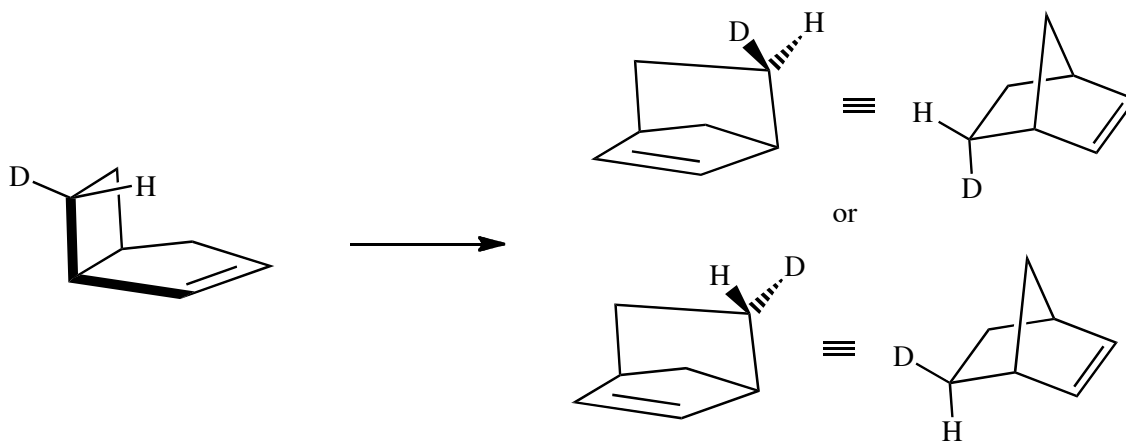


A [1,3] shift of C —



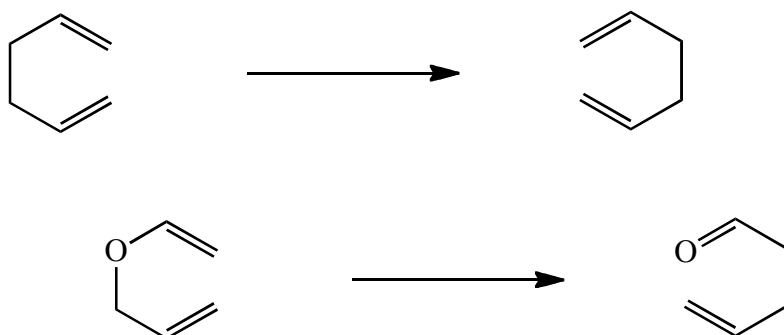
AO interaction diagram

and a classic experiment that confirmed the surprising prediction for the [1,3] C shift...



[3,3] sigmatropic shifts are also common —

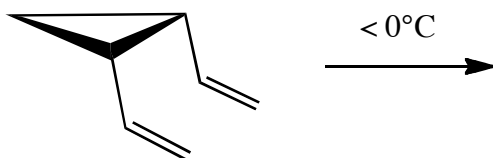
The Cope rearrangement and its oxygen-containing analog the Claisen rearrangement —



These rearrangements normally proceed via a chair-cyclohexane-like transition state.

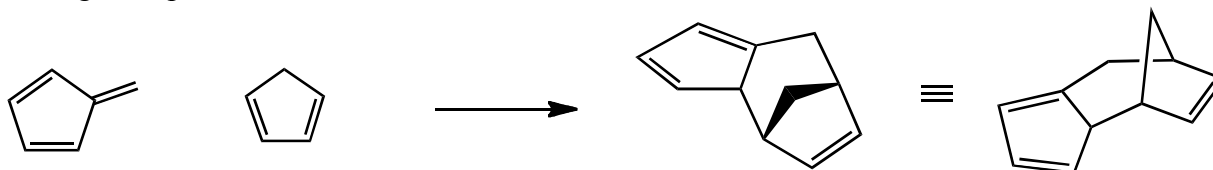


When the chair is geometrically inaccessible, the reaction can proceed via a boat-like conformation, such as in the rearrangement of *cis*-1,2-divinylcyclopropane, which goes at a remarkably low temperature.

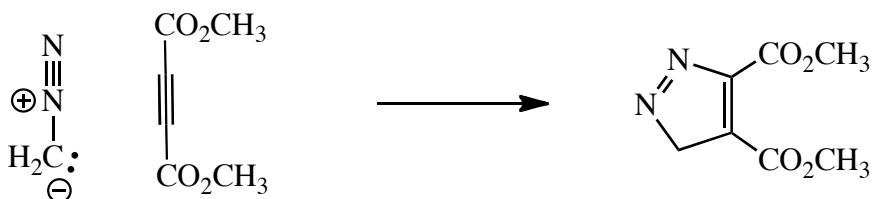


Note that many pericyclic reactions can be initiated by absorption of light rather than thermal energy. The "rules" for photochemical pericyclic reactions are generally the opposite of the rules for thermal reactions — reactions that are forbidden thermally are allowed photochemically and vice versa. We saw that the reason for this in cycloadditions was based on the  $\pi$ -MO interactions of an excited state reactant with a ground state reactant, but in general, a proper analysis of photochemical pericyclic processes is beyond the scope of this course.

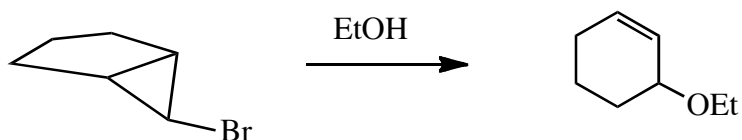
Here are some reactions that fall into the categories of cycloadditions, electrocyclic reactions, and sigmatropic shifts —



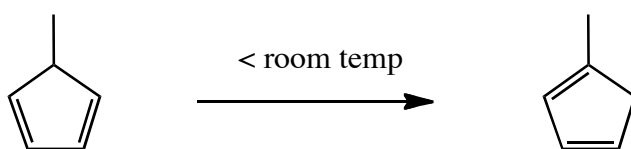
a "1,3-dipolar cycloaddition"



Hint: think  $\text{S}_{\text{N}}1$  solvolysis — but what happens to the carbocation?



What kind of sigmatropic shift is this?



Here's an enzyme-mediated Claisen rearrangement that plants use to synthesize phenylalanine and tyrosine...

