CHEM95002: Orbitals in Organic Chemistry - Pericyclics

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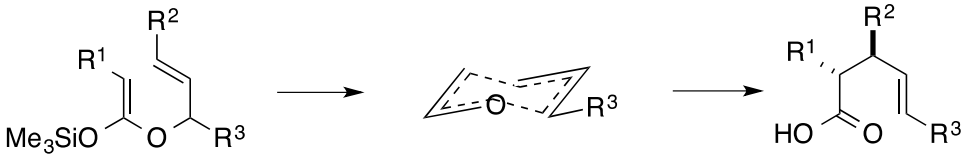
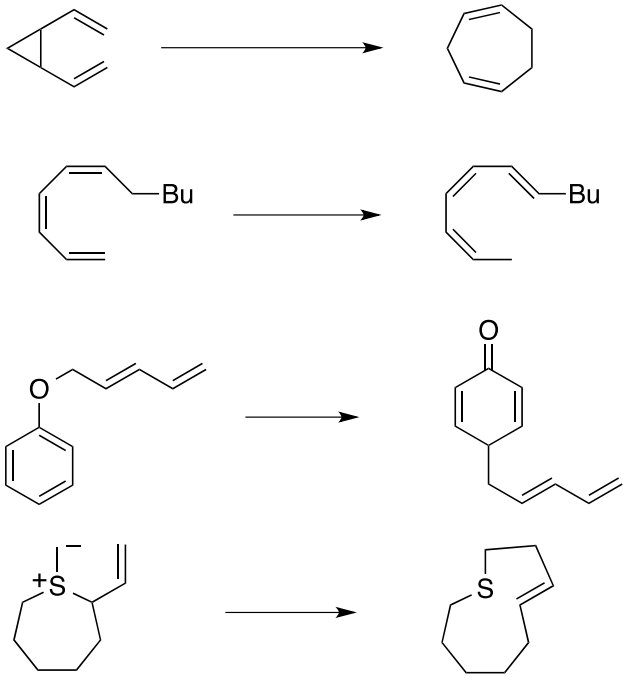
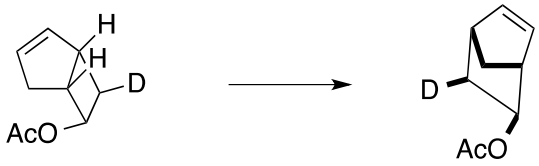
1. Complete the chair transition state to rationalize the outcome of the Ireland-Claisen rearrangement shown below.



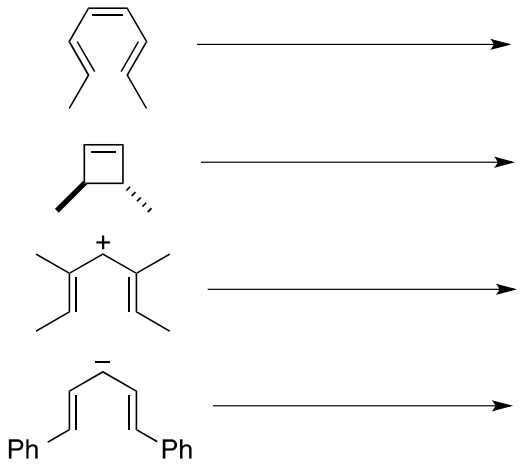
2. Draw curly arrow mechanisms for the following thermal reactions and classify them as [x,y]-sigmatropic rearrangements:



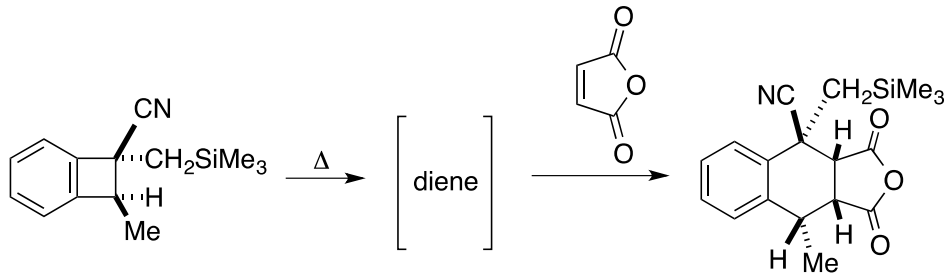
3. Consider the [1,3]-sigmatropic rearrangement shown below. Carry out a Woodward-Hoffmann analysis on the starting material that demonstrates that the observed inversion of stereochemistry at the migrating carbon is thermally allowed.



4. Draw curly arrow mechanisms for the following thermal reactions, deduce the number of electrons involved, whether the reaction is conrotatory or disrotatory, and hence predict the stereochemistry of the product.



5. Heating the benzocyclobutane shown below in the presence of maleic anhydride generates the tricyclic product indicated *via* a transient diene.



(a) How many electrons are involved in the initial electrocyclic reaction?

(b) Is the reaction conrotatory or disrotatory?

(c) What is the stereochemistry of the transient diene?

(d) Draw an approach trajectory between the diene and maleic anhydride to explain all the stereochemistry in the product.