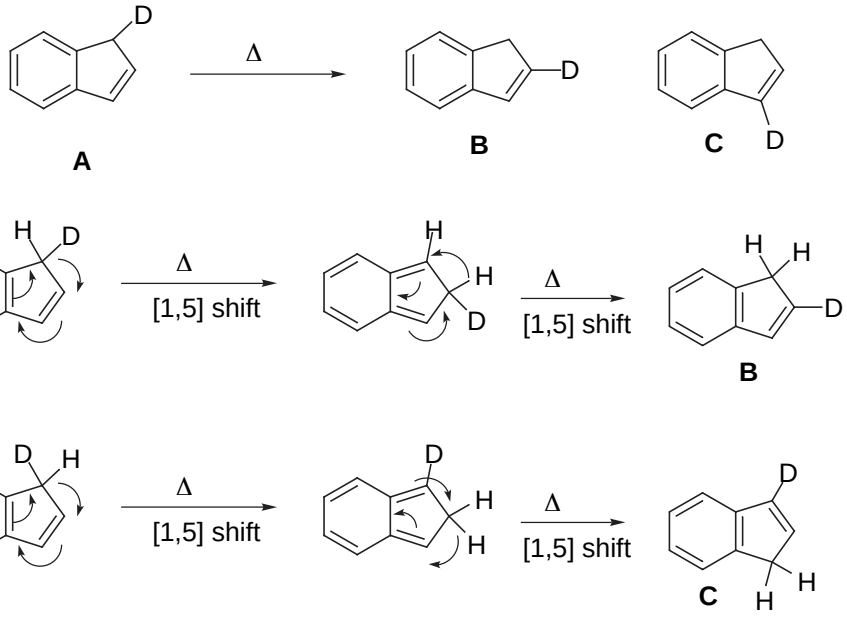
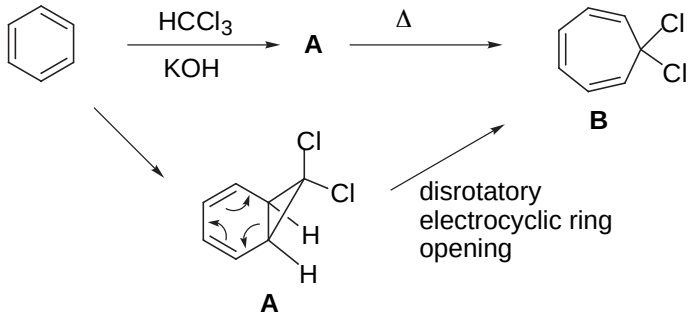
Answers to Problem Set # 5 , Chem 332, Spring 2003, Prof. Fox

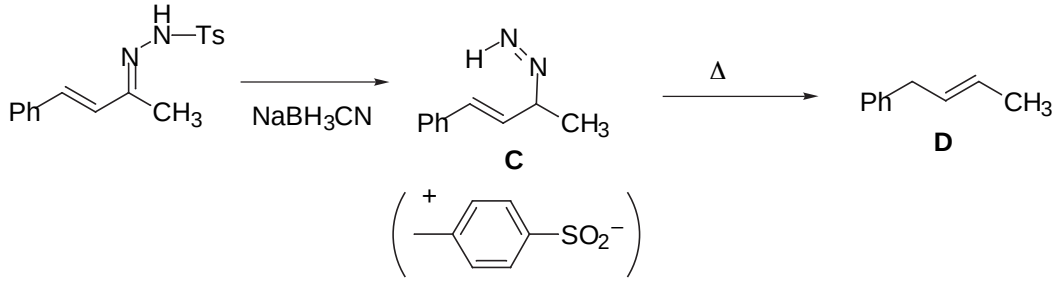
1. Provide a mechanism

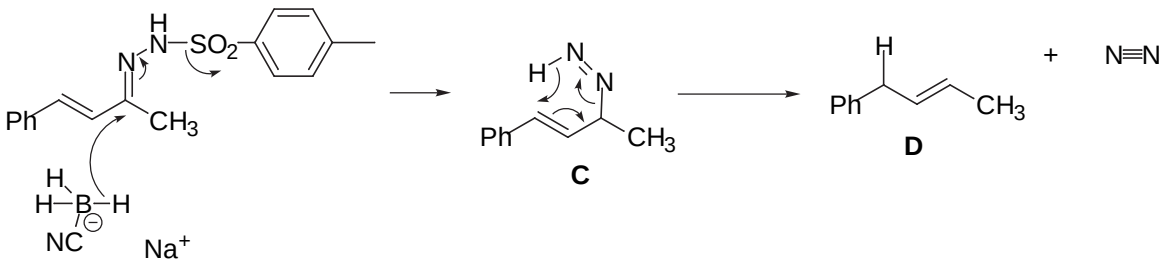


2. Provide a structure for **A** and a mechanism for the conversion to **B**

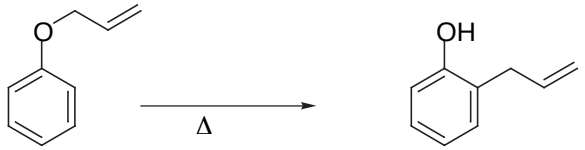


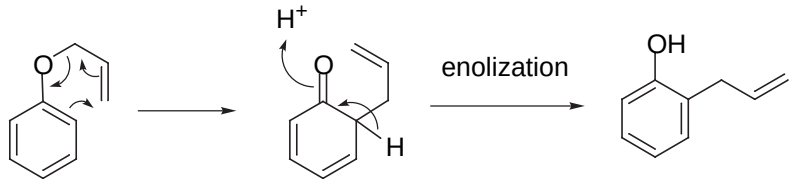
3. Provide mechanisms for the formation of **C** and **D**.



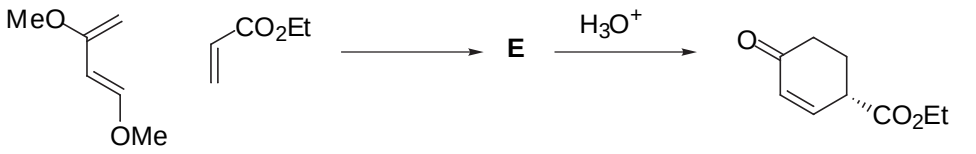


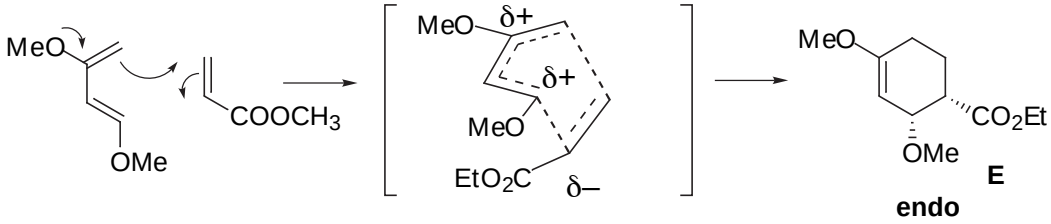
4. Provide a mechanism



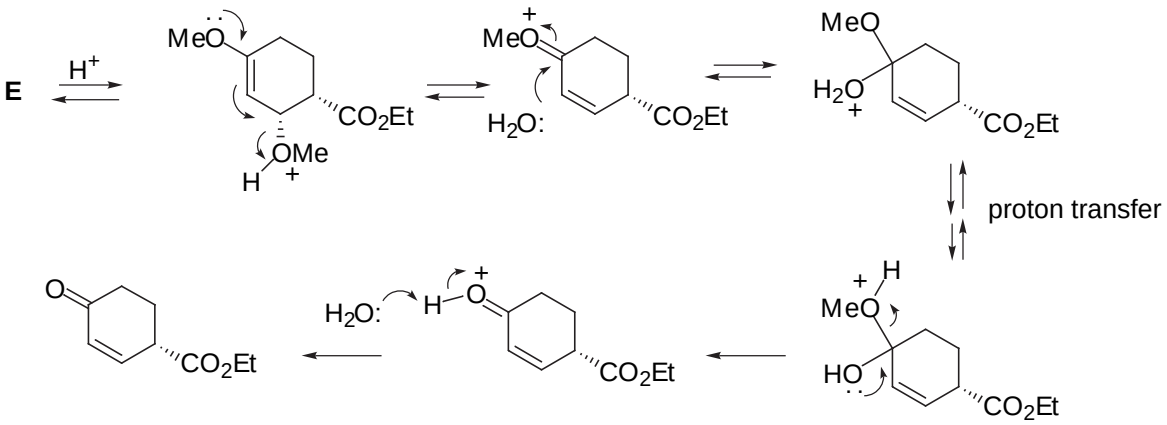


5. Provide a structure for **E** (stereochemistry is important) and a mechanism for the formation of **F**.



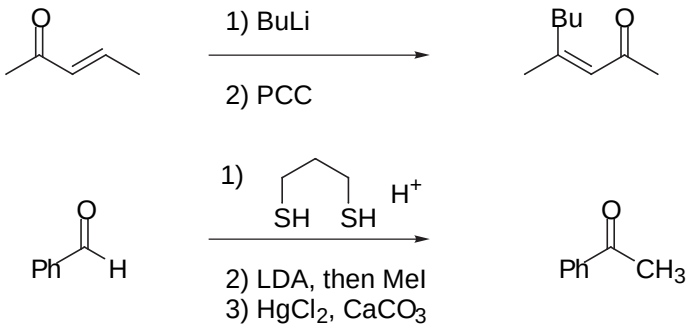


endo transition state for Diels Alder
"ortho/para directing
groups" stabilize the transition
state

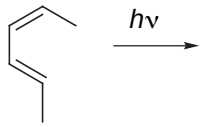


Exam practice questions

1. Provideproducts for the following tranformations

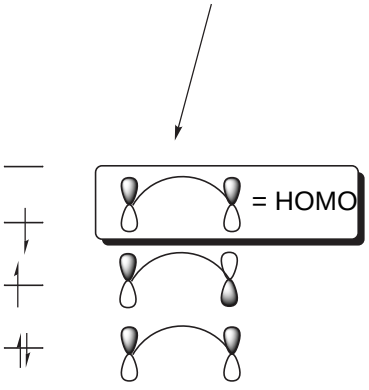


2. Provide products for the following transformations, and use MO diagrams to explain the stereochemistry



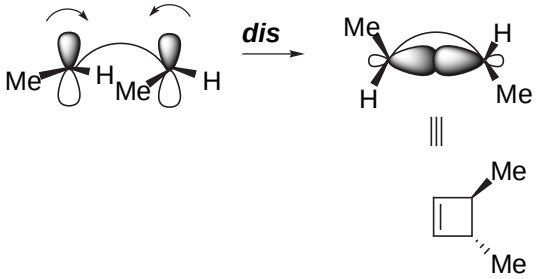
step 1. Draw the MO energy levels and fill in the electrons

step 2. Determine the symmetry of the Highest Occupied Molecular Orbital (HOMO)



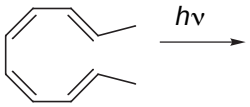
step 3. Decide if the reaction must be conrotatory or disrotatory

step 4. follow the stereochemistry



methyls are trans

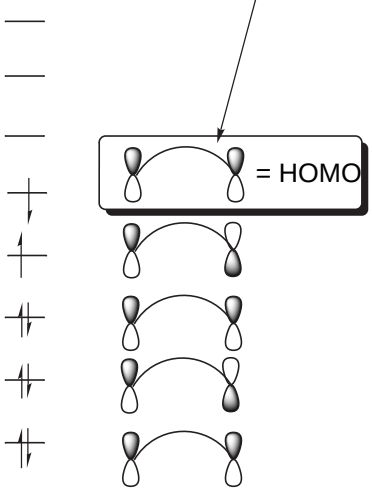
2. Provide products for the following transformations, and use MO diagrams to explain the stereochemistry



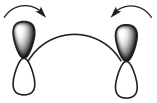
step 1. Draw the MO energy levels and fill in the electrons

8 pi electrons; 8 MO's

step 2. Determine the symmetry of the Highest Occupied Molecular Orbital (HOMO)

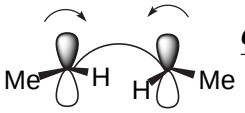


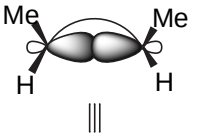
step 3. Decide if the reaction must be conrotatory or disrotatory



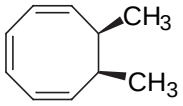
dis

step 4. follow the stereochemistry

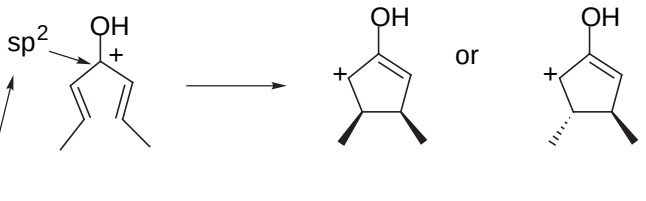




methyls are cis



3. Circle the (initially formed) product for the rearrangment below, and provide an explaination using your knowledge of MO theory

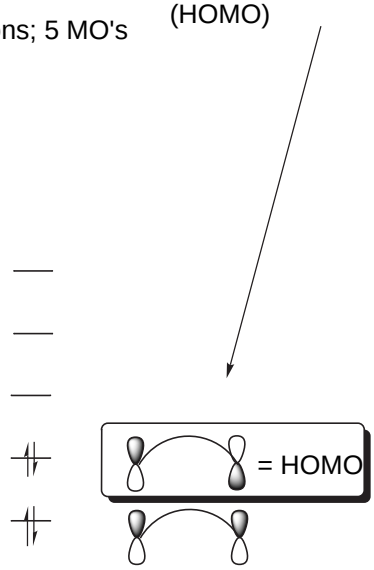


This is a thermal rearrangment of 5 contiguous sp^2 centers, and therefore the same rules would apply as for concerted electrocyclic ring closure. We have 4 pi electrons in a 5 carbon pi system, and so the MO picture is as shown below

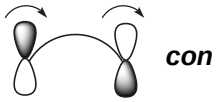
step 1. Draw the MO energy levels and fill in the electrons

4 pi electrons; 5 MO's

step 2. Determine the symmetry of the Highest Occupied Molecular Orbital (HOMO)

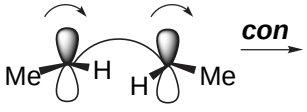


step 3. Decide if the reaction must be conrotatory or disrotatory

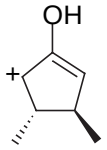


con

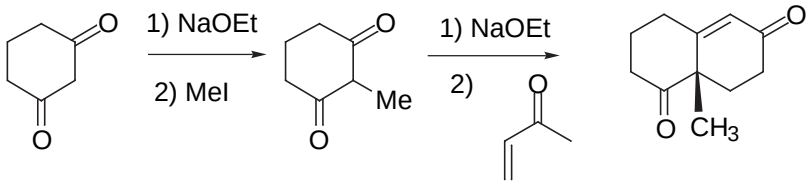
step 4. follow the stereochemistry



methyls are trans



4. Provide a multistep synthesis starting from 6 carbons or less



5. Provide a structure and mechanism for **A** and a mechanism for **B**