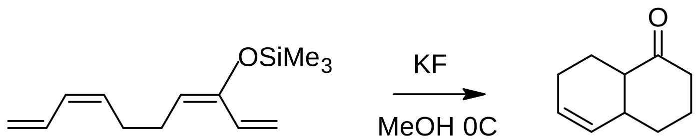
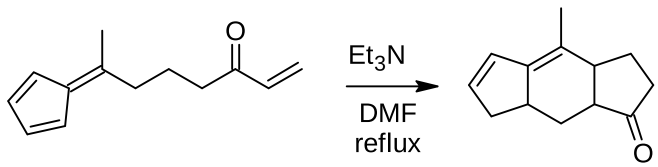
Chemistry 324, 2008
HW #2, Due M, Feb 11

1. Draw a plausible (detailed) mechanism for each reaction. Wherever a Diels-Alder reaction occurs, label the addition as *endo* or *exo*. Note: Each reaction leads to a single (racemic) compound, but the product stereochemistry has not been shown. Draw <u>all</u> of the hydrogens attached to bridgehead carbons to show the most likely product stereochemistry.

   a.

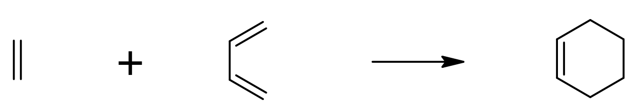


   b.



2. The following reaction enthalpies have been calculated using reasonably reliable molecular modeling tools.
   a. Explain why the top reaction is so exothermic by appealing to the types of bonds being formed and broken.
   b. Give a structure-based rationale for the other reaction enthalpies, i.e., why are they substantially more/less exothermic than the top reaction?
   c. Assuming that $-T\Delta S^o$ is approximately about 13 kcal/mol for a bimolecular addition reaction (in the gas phase), i.e., a reaction like A + B → C, estimate K_{eq} for each reaction at 298 K. Which of these reactions, if any, might be reversible?

ΔH^o
<u>(kcal/mol)</u>



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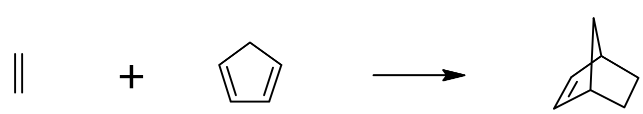

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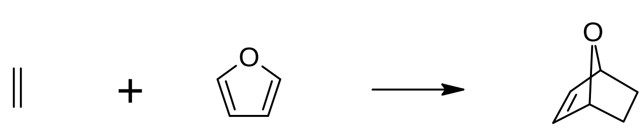

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3. This exercise examines how the initial concentration of starting materials affects the theoretical yield of a reaction.

   a. Reaction #1: $A \rightarrow B$

      Assume that $[B]_i = 0$ and $K_{eq} = 2$. Calculate the final (equilibrium) concentration of [B] assuming that $[A]_i = 1$ M. Repeat for $[A]_i = 0.1$ M. What would be the theoretical yield in case?

   b. Reaction #2: $A + B \rightarrow C$

      Assume that $[C]_i = 0$ and $K_{eq} = 2$. Calculate the final (equilibrium) concentration of [C] assuming that $[A]_i = [B]_i = 1$ M. Repeat for $[A]_i = [B]_i = 0.1$ M. What would be the theoretical yield in case?