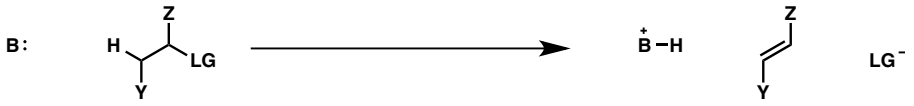
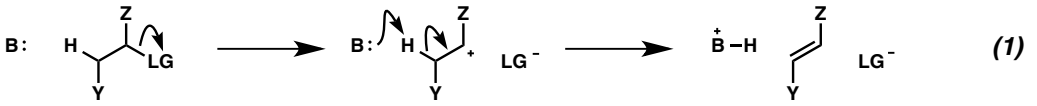
Attempt all questions. All parts are related and information one part may be helpful in another. Read all the questions before you begin working. Present your answers **clearly** and **legibly** in the order that they appear below. Label each section in your answer book according to the problem numbering. ***(100 total points)***

Consider the following equation for an elimination reaction to form a C–C double bond:



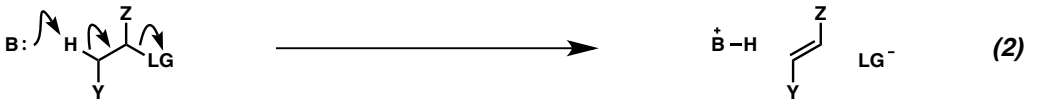
1. One mechanistic possibility for this transformation is shown in equation 1. For the following questions (a–g), assume that this mechanism is the sole operating mechanism.



(1)

   a. Predict which step in equation 1 is likely the rate determining step. Justify your reasoning. ***(3 points)***
   b. Predict the overall kinetic order of the reaction. ***(2 points)***
   c. Draw a reaction coordinate diagram consistent with your prediction in part a. Clearly label the intermediates indicated on your diagram. ***(5 points)***
   d. Predict how you would expect the reaction rate to be affected by modifying the Y group from electron releasing, to electron neutral, to electron withdrawing. Will the effect be small, moderate, or large? ***(5 points)***
   e. Predict how you would expect the reaction rate to be affected by modifying the Z group from electron releasing, to electron neutral, to electron withdrawing. Will the effect be small, moderate, or large? ***(5 points)***
   f. Predict how you would expect the reaction rate to be affected by modifying the leaving group (LG) from OMe, to Cl, to SMe_2. Will the effect be small, moderate, or large? ***(6 points)***
   g. Predict the approximate magnitude of a separate flask k_H/k_D kinetic isotope effect experiment (replacing the indicated H with D). ***(2 points)***

2. A second mechanistic possibility for this transformation is shown in equation 2. For the following questions (a–f), assume that this mechanism is the sole operating mechanism.

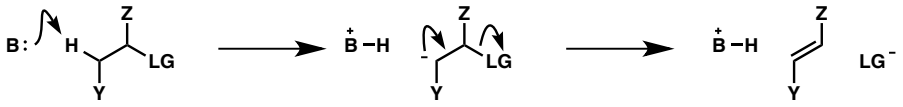


(2)

   a. Predict the overall kinetic order of the reaction. ***(2 points)***
   b. Predict how you would expect the reaction rate to be affected by modifying the Y group from electron releasing, to electron neutral, to electron withdrawing. Will the effect be small, moderate, or large? ***(5 points)***
   c. Predict how you would expect the reaction rate to be affected by modifying the Z group from electron releasing, to electron neutral, to electron withdrawing. Will the effect be small, moderate, or large? ***(5 points)***
   d. Predict the magnitude of a separate flask k_H/k_D kinetic isotope effect experiment (replacing the indicated H with D). ***(2 points)***
   e. Draw a Newman projection that predicts the transition state of the elimination reaction. ***(2 points)***
   f. Predict the magnitude of the entropy of activation for this mechanism. Will it be large or small relative to the mechanisms in parts 1 & 2? ***(2 points)***

(over)

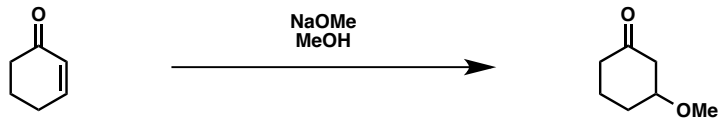
3. A third mechanistic possibility for this transformation is shown in equation 3. For the following questions (a–e), assume that this mechanism is the sole operating mechanism.



(3)

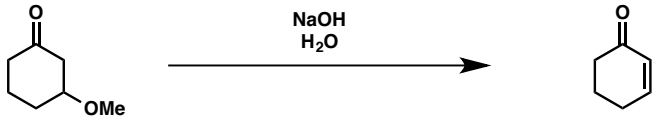
   a. In this case there are two plausible possibilities for the rate-determining step. Draw two reaction coordinate diagrams that are consistent with these two possibilities. Clearly label the intermediates indicated on your diagrams. ***(10 points)***
   b. Considering your reaction coordinate diagrams from part a, predict the overall kinetic order of the reaction for each of the two possibilities. ***(4 points)***
   c. Suppose you perform the elimination reaction in a deuterated solvent, but stop the experiment before it is complete and isolate the remaining starting material. For each possibility, predict whether the remaining starting material contains a signifcant amount of deuterium. ***(4 points)***
   d. For each possibility, predict how you would expect the reaction rate to be affected by modifying the Y group from electron releasing, to electron neutral, to electron withdrawing. Will the effect be small, moderate, or large? ***(12 points)***
   e. For each possibility, predict how you would expect the reaction rate to be affected by modifying the Z group from electron releasing, to electron neutral, to electron withdrawing. Will the effect be small, moderate, or large? ***(12 points)***

4. Provide a mechanism for the following transformation. ***(5 points)***



(4)

5. Based on your insights from the preceding parts, provide a mechanism for the following transformation. ***(5 points)***



(5)

6. What chemical principle can be cited for the relationship between the mechanisms in parts 4 & 5? ***(2 points)***