

**Advanced Organic Chemistry (CHE 311/511)**  
**Final Examination**  
**Dec. 11-17, 2004**  
**Prof. W. P. Malachowski**

Name: \_\_\_\_\_

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics. The exam has a total of nine pages and seven questions.

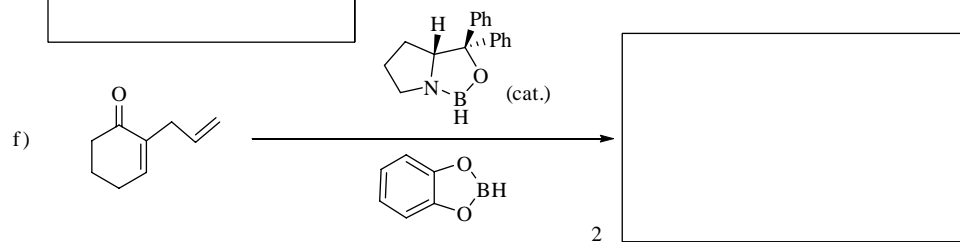
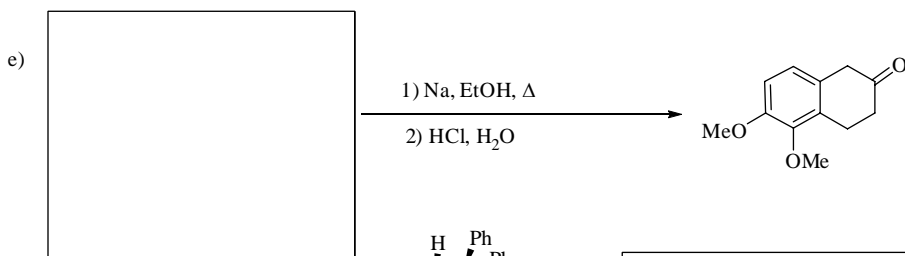
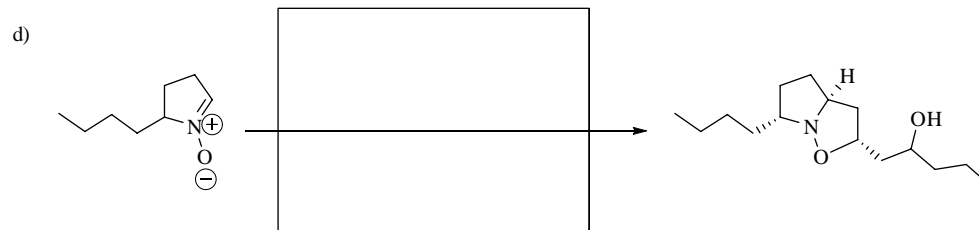
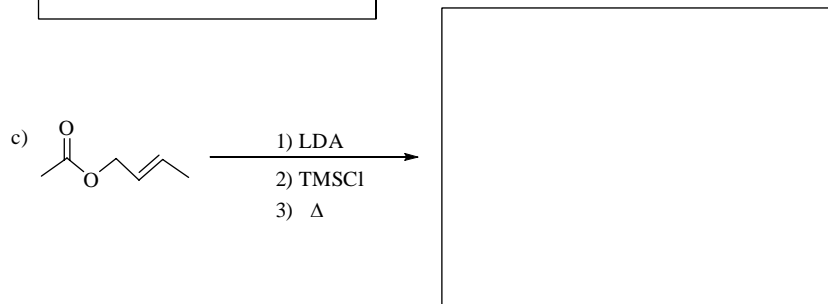
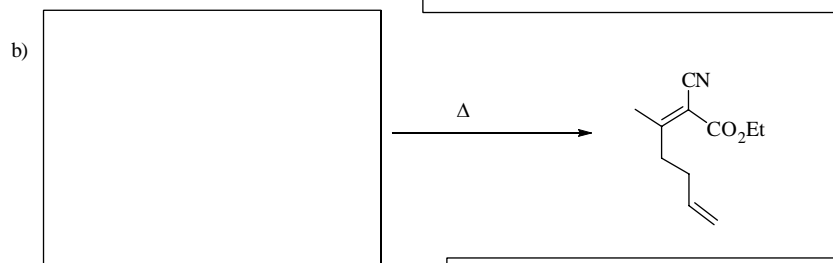
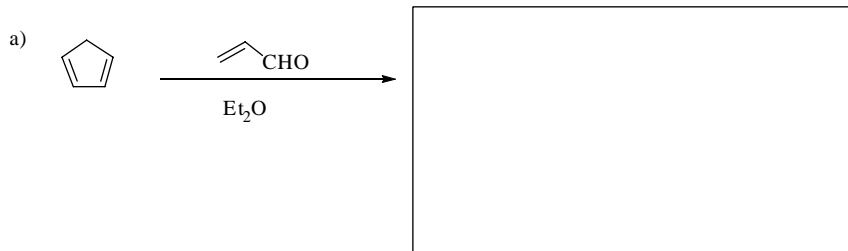
In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include formal charges when appropriate.

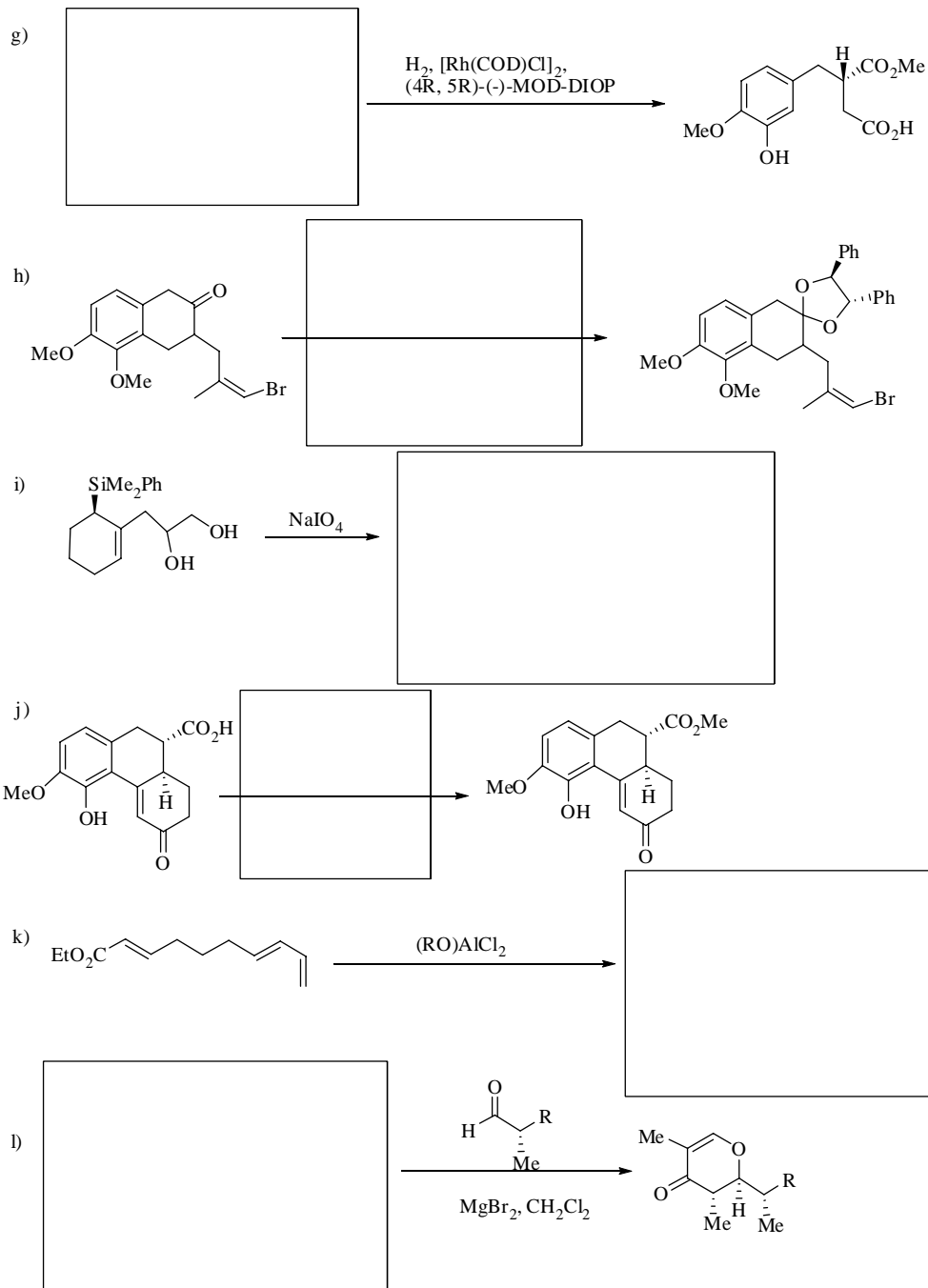
You may use models to assist in determining answers. You may use scrap paper to work out problems before entering your final answer on the exam sheets. In addition, feel free to use the back side of the exam sheets for scrap. If necessary, you may enter exam answers on the back side of the exam sheets, however you must clearly indicate which problems are located on the back of the exam pages.

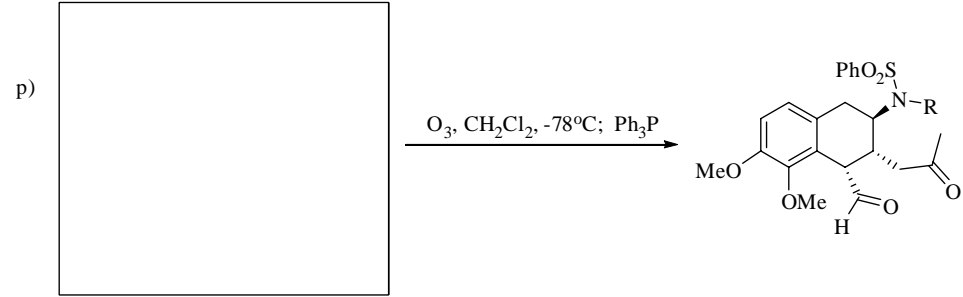
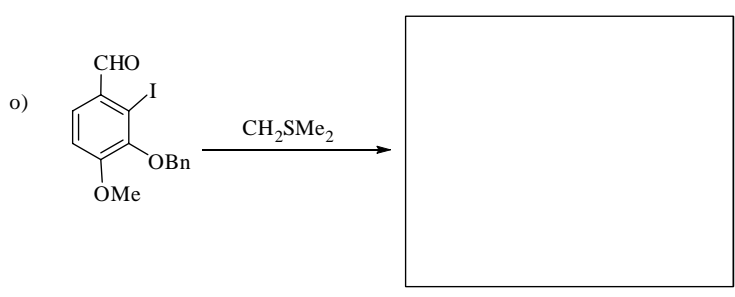
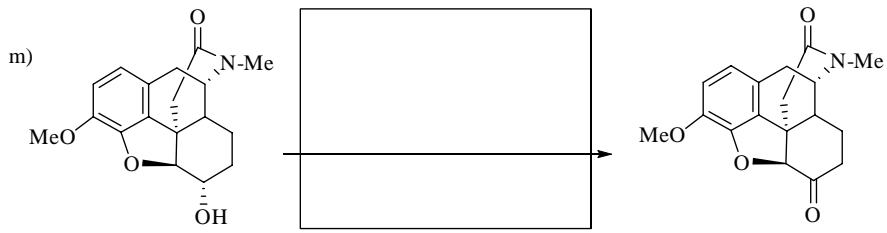
Note that question 4 on pages 6-7 and question 7 on page 9 have different requirements of graduate students and undergraduate students. Although the point total for the questions is the same, *graduate students must answer four of six parts in question 4 and two of three parts in question 7. Undergraduate students only need to answer three of six parts of question 4 and one of three parts in question 7.*

Bonus points: Bonus points will be awarded for extra correct answers in question 1, 4 and 7.

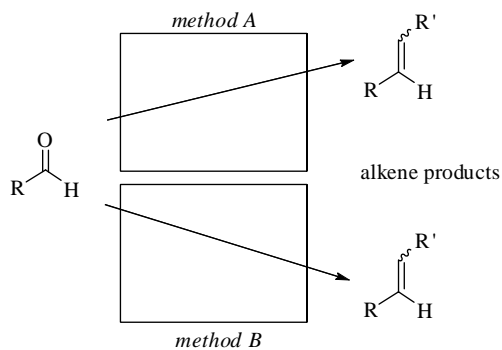
1. Provide the necessary information (product, reagent or starting material) to complete the following reactions and answer the associated questions. Answer 10 of the 16 questions. (5 pts. each) One bonus point for each additional correct answer.





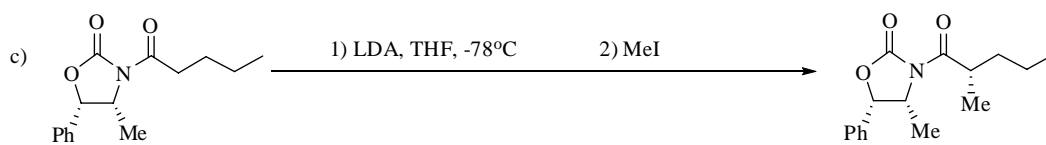
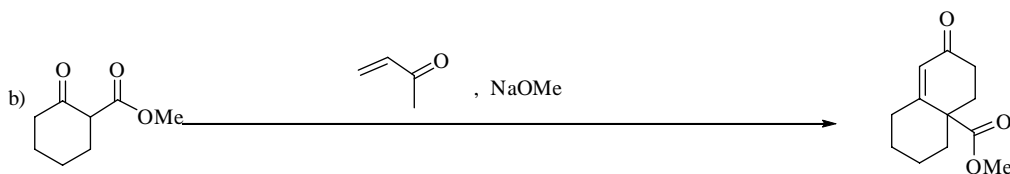
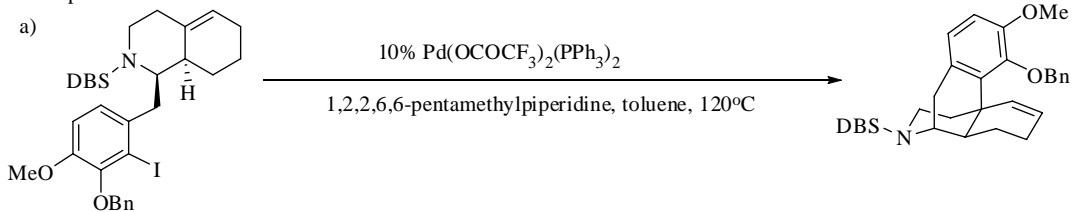


2. Over the semester, we have seen three different ways to make alkenes from aldehydes. Show two of these methods by putting a reagent in the boxes below and briefly describing the reaction. (11 pts.)

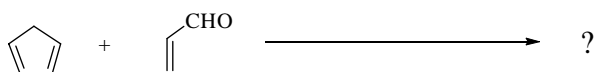


3. Our morphine synthesis presentations included two ways to make carbenes or carbenoids, which subsequently reacted to form important C-C bonds in the morphine skeleton. Describe one way in which carbenes/carbenoids can be made. A chemical reaction with reagents is also an acceptable way to illustrate a method of carbene/carbenoid formation. (11 pts.)

4. **Graduate students:** Draw the mechanism for four of the following six reactions, including at least two from a-c. (9 pts. each) **Undergraduate students:** Draw the mechanism for three of the following six reactions, including at least one from a-c. (12 pts. each) Structural abbreviations are permissible if the essence of the reaction mechanism is not compromised. Three bonus points will be awarded for each additional correct mechanism.



e) The mechanism for problem 1 a), including an accurate depiction of the transition state.

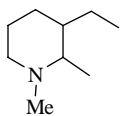


f) The mechanism for problem 1 b), including an accurate depiction of the transition state.



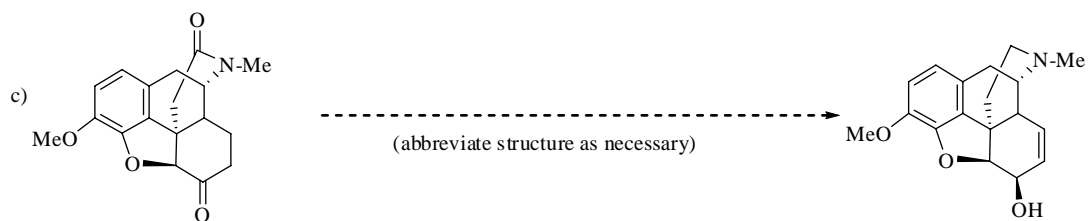
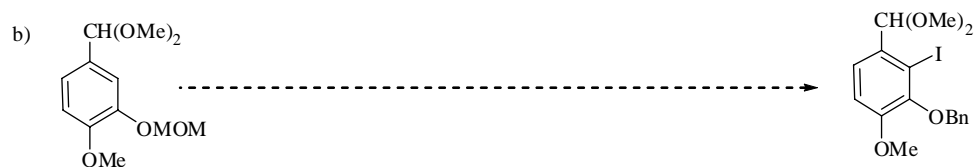
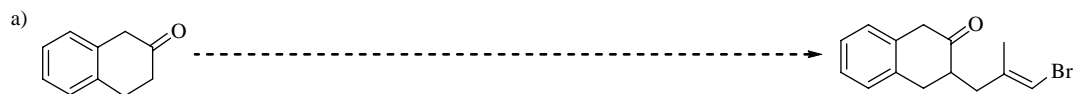
g) The mechanism for problem 1 c) part 3 (heating step), including an accurate depiction of the transition state.

5. The morphine syntheses that we reviewed included three different approaches to creating the piperidine D ring of morphine. Other synthetic methods were discussed during the semester which could be adapted to create piperidine rings. Describe two methods to make the piperidine ring shown below. You should include important intermediates and briefly describe reaction conditions or key transformations. (12 pts.)



6. Describe two ways to increase the rate and/or efficiency of a Diels-Alder reaction. (12 pts.)

7. Provide reactions to transform the starting material on the left to the product on the right. You may use any reagents or reactants to accomplish this task. **Undergraduate students:** Answer one of the three synthesis questions below. (18 pts.) **Graduate students:** Answer two of the three synthesis questions. (9 pts. each) Note: when the synthesis indicates a stereochemically pure product is formed, then full credit will result from strategies that properly address this challenge. Five bonus points will be awarded for each additional synthesis that is correct.




---

18 total pts.