Organic Chemistry 2
First Examination
February 17, 2006
Prof. Malachowski

Name:___Dick Cheney_____

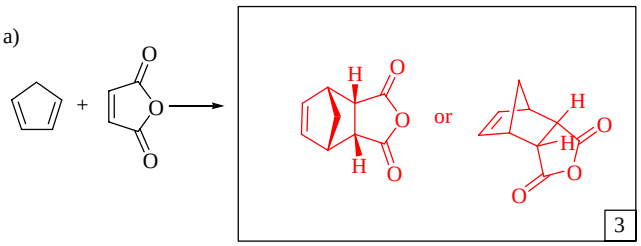
The examination has seven questions on four pages. The point values for each question are found with the question. Partial credit where appropriate will be given.

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.

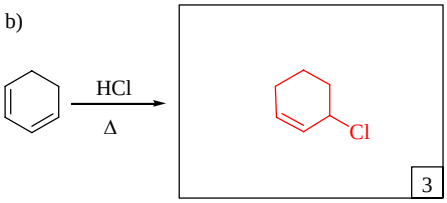
In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include lone pairs of electrons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

1. Complete the following reactions by providing the necessary information: starting material, reagent or major product, unless otherwise instructed. Be sure to include stereochemical information where applicable. (points listed in corner of box)

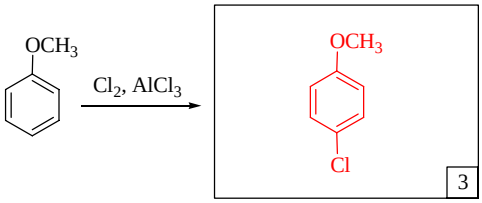
a)



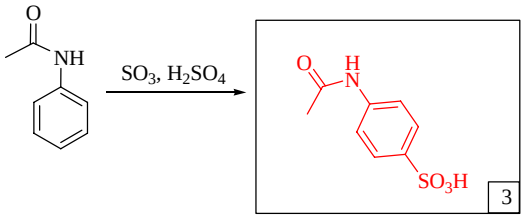
b)



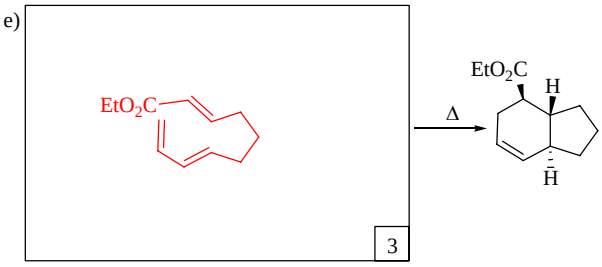
c)



d)



e)



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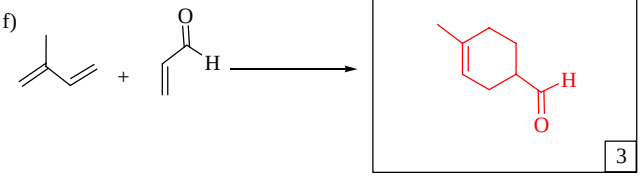
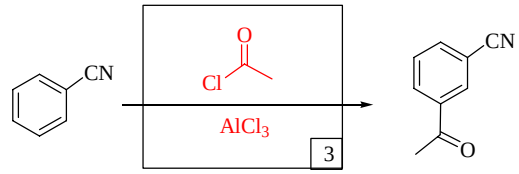
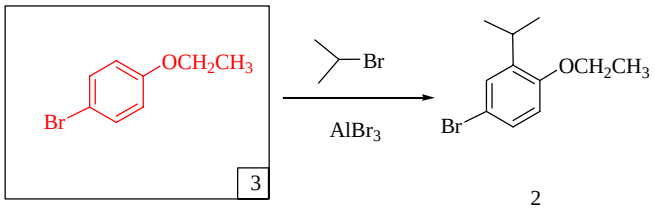


g)

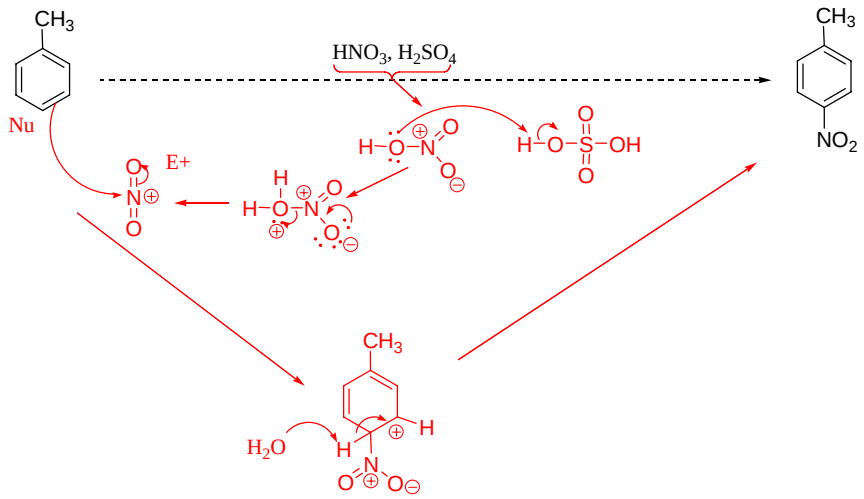


h)



24 total pts.

2. a) Draw the mechanism of the following reaction. You do not need to draw resonance structures. (10 pts.)



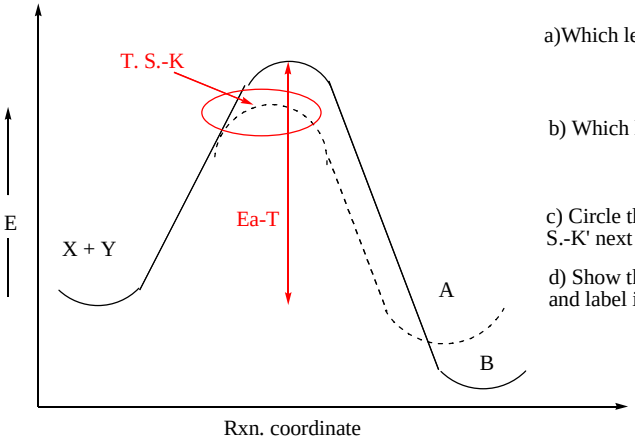
b) What type of reaction mechanism is shown in part a? (2 pts.) electrophilic aromatic substitution

c) What is the name of the reactive intermediate formed by the combination of nitric acid and sulfuric acid? (2 pts.)

nitronium ion

d) Label the nucleophile in part a with 'Nu' and the electrophile with 'E+'. (2 pts.)

3. The following energy diagram represents a reaction between X and Y that can follow two different paths to afford either A or B. The processes are all reversible under the reaction conditions. Answer the following questions about the energy diagram.



a)Which letter represents the kinetic product? (3 pts.)

A

b) Which letter represents the thermodynamic product? (3 pts.)

B

c) Circle the transition state for the kinetic product and write 'T. S.-K' next to it. (3 pts.)

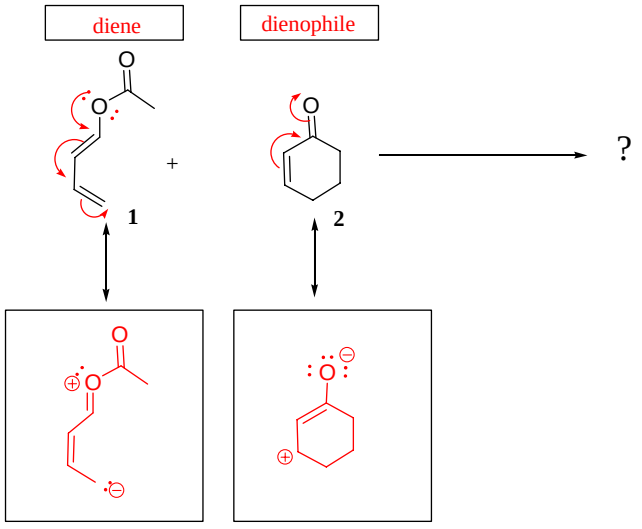
d) Show the energy of activation for the thermodynamic product and label it with 'Ea-T'. (3 pts.)

28 total pts.

4. The reaction between compound **1** and **2** shown below is a Diels-Alder reaction. Answer the related questions.

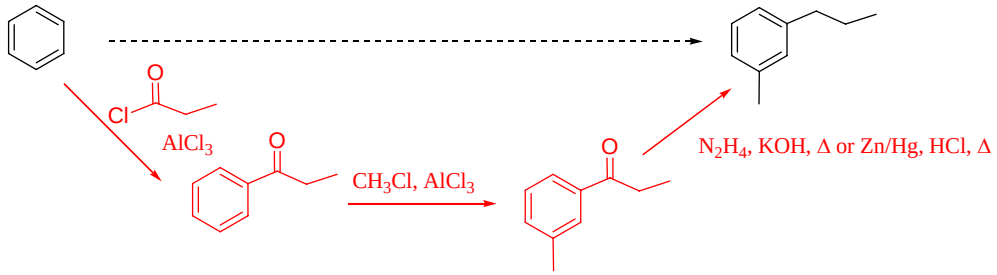
a) Label the diene and dienophile in the reaction. (3 pts.)

b) Draw a resonance structure of the diene and one of the dienophile that helps to explain the regioselectivity seen in the product. Remember to include lone pairs and formal charges where necessary. Show curved electron flow arrows that rationalize the resonance structure that you have drawn. (12 pts.)



resonance structures

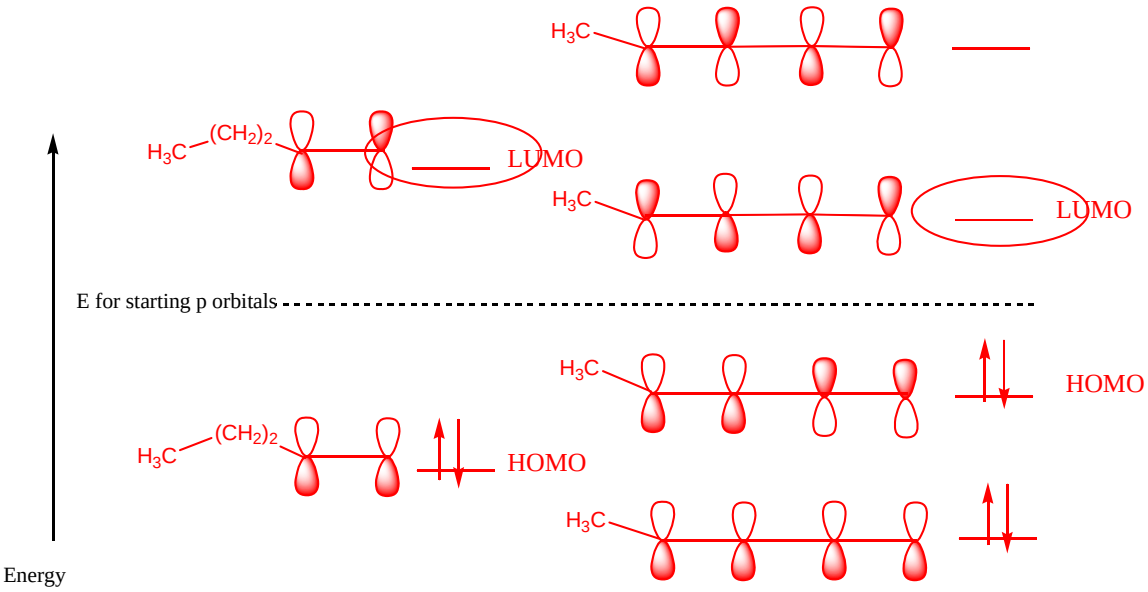
5. Provide a synthesis of the molecule on the right from the starting material on the left. You may use any reagents. (10 pts.)



25 total pts.

6. Birch reductions are great organic reactions that involve the addition of one electron from Na, K or Li into alkene systems. However, the alkene system must be conjugated. Answer the following questions to try to understand why the alkene system be conjugated.

a) Generate the π molecular orbitals for 1-pentene and 1,3-pentadiene. (6 pts.)



1-pentene 1,3-pentadiene

b) Put electrons into the orbitals to show the ground state electronic structure of each molecule. (3 pts.)

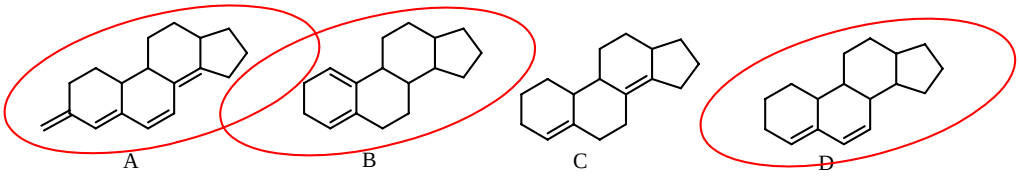
c) Identify the HOMO and LUMO of each. (4 pts.)

d) Circle the orbital into which an electron from Na, K or Li would add. (2 pts.)

e) Based on differences in the molecular orbitals of 1-pentene and 1,3-pentadiene, suggest a reason why 1-pentene does not react, but 1,3-pentadiene does add one electron. (3 pts.)

1,3-Pentadiene has a lower energy LUMO, so it is easier for the electron of Na, K or Li to add to this orbital.

7. You have just been hired to monitor drug use of Olympic atheletes. Dodge ball, now an Olympic sport, has a new star from Pennsylvania who has been tearing up the field and it looks very suspicious. He was a chemistry professor at a small college outside Philadelphia, but he is showing himself to be quite the dodge ball dominator, while clearly past his physical prime. We suspect that he has been using performance enhancing drugs, but we need to figure out a way to detect these new steroid like structures. Circle the structures below that should show UV/vis absorption and rank them from lowest λ_{max} to highest λ_{max}. (5 pts.)



Trend: D < B < A

lowest λ_{max} highest λ_{max}

23 total pts.