

Exam #1

Chemistry 334

Organic Chemistry II

Tuesday October 6, 2009

Name: _____ KEY _____.

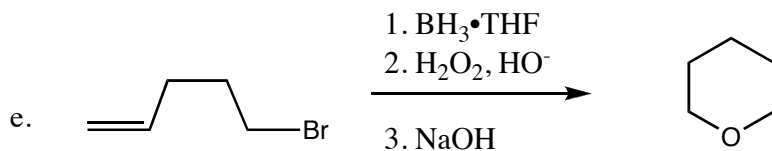
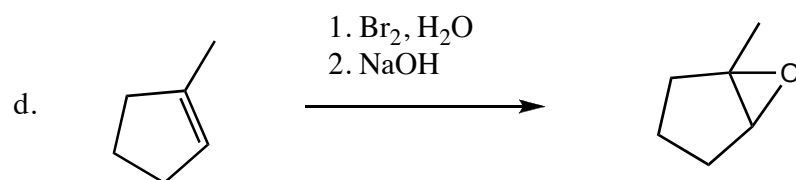
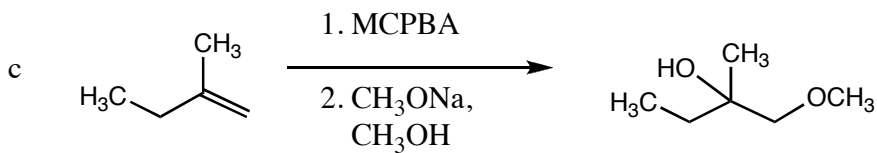
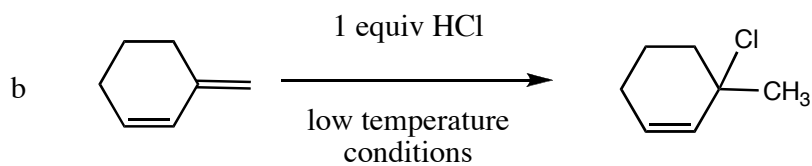
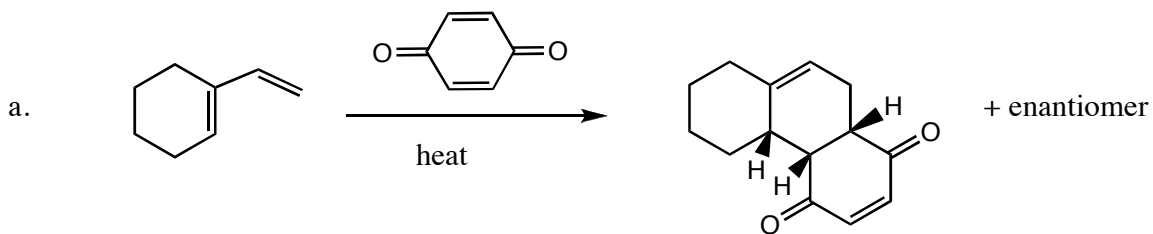
The exam is worth a total of 100 points; there are six questions. Please show all work to receive full credit for an answer.

By putting your name on this exam, you agree to abide by California State University, Northridge policies of academic honesty and integrity

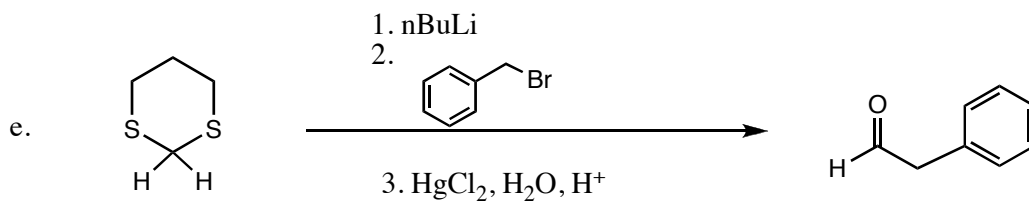
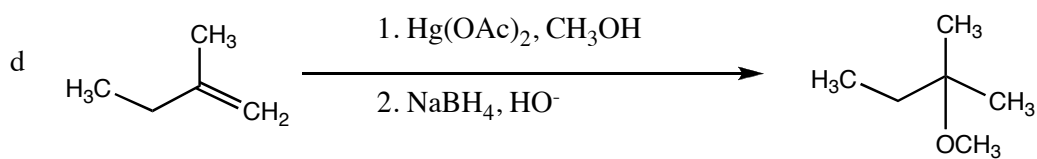
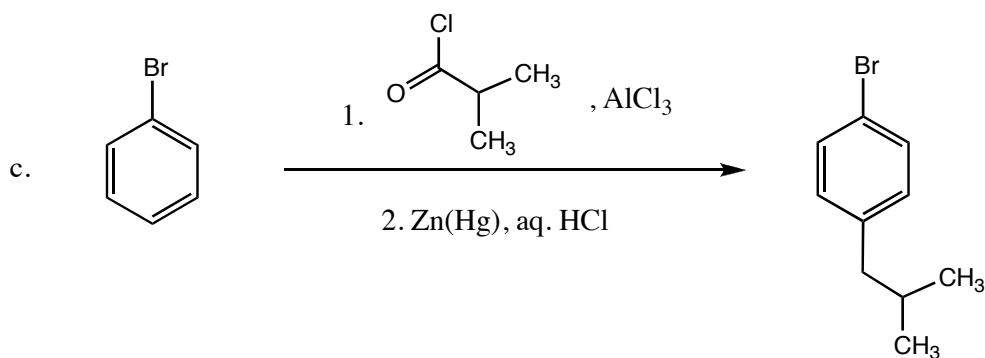
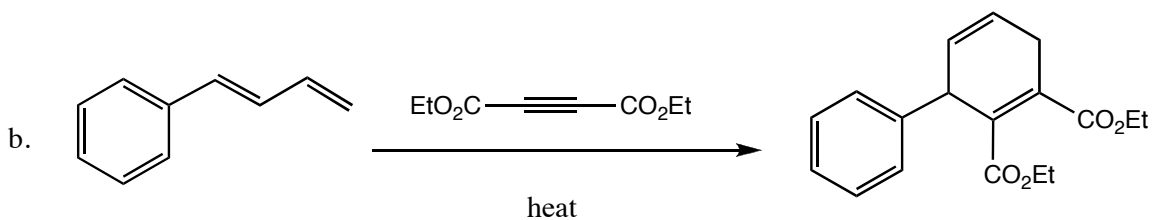
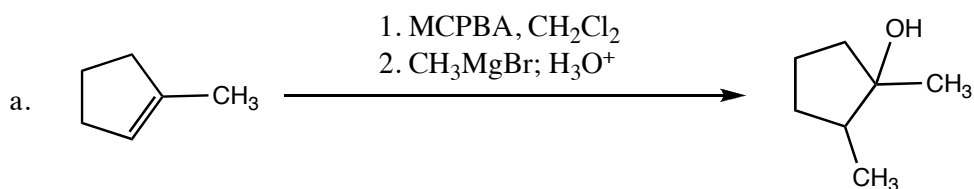
Molecular models are allowed for this exam. Calculators are not needed.

Good Luck!

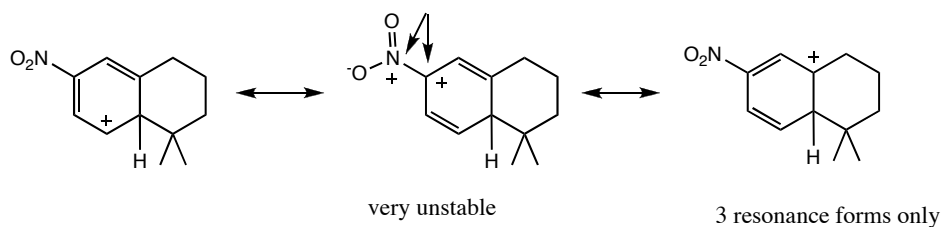
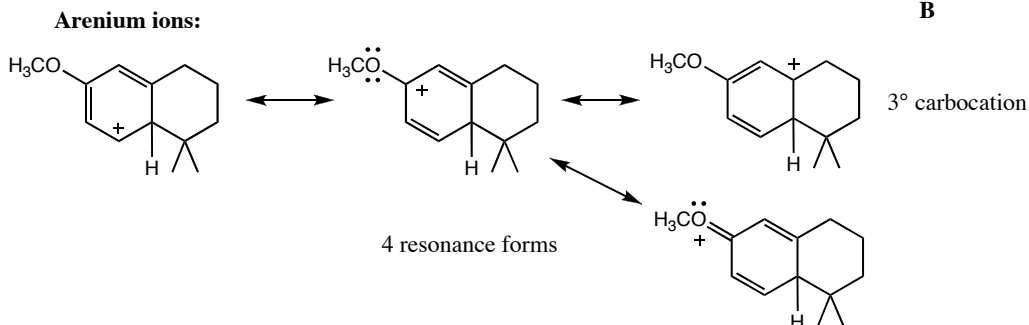
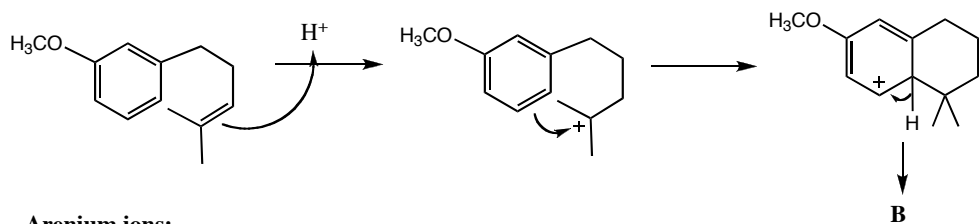
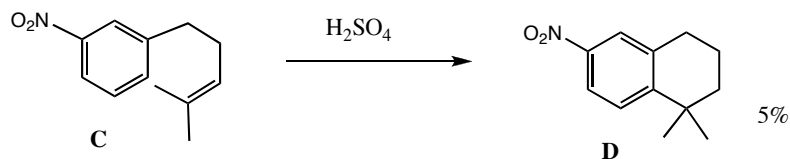
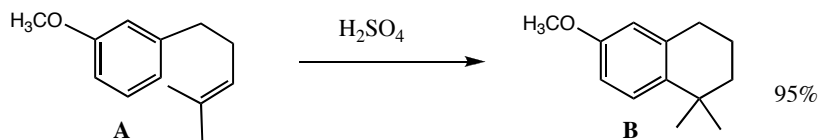
1. Predict the products of the following reactions. **Remember to indicate stereochemistry where relevant.** (20 pts)



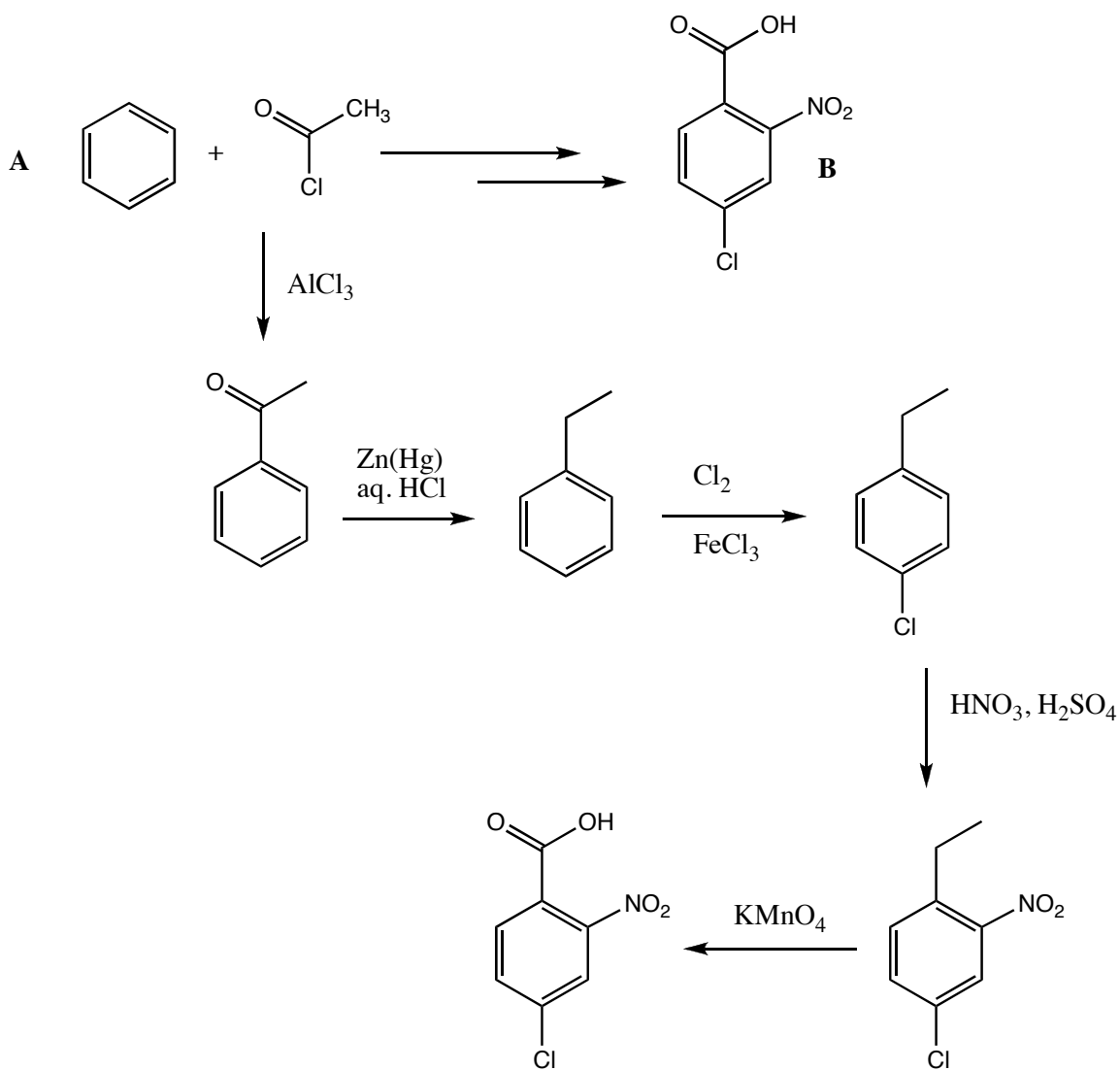
2. Indicate reagents to accomplish the following transformations. **More than one step may be required!!** (20 pts)



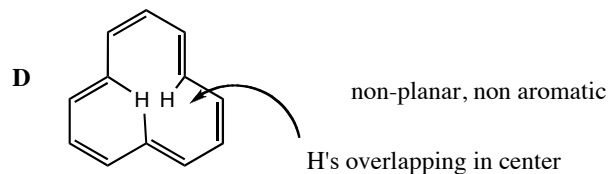
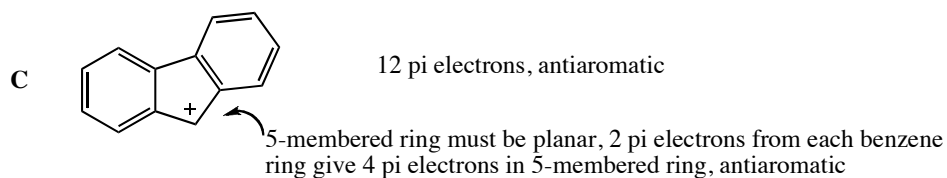
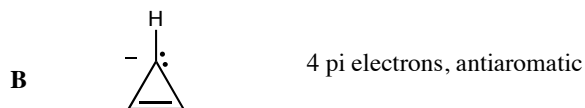
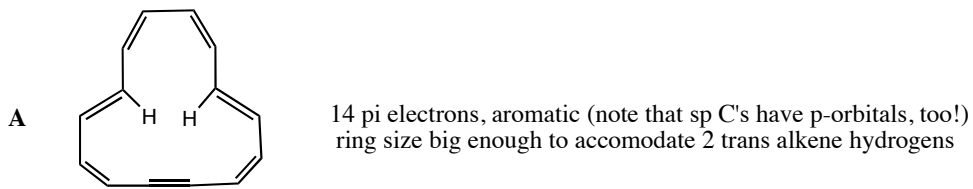
3. Treatment of compound **A** with catalytic amounts of sulfuric acid produces compound **B** in 95% yield *via intramolecular Friedel-Crafts alkylation*. However, subjecting compound **C** to the same reaction conditions produces only 5% of **D**. Draw the mechanism of the reaction **A**→**B** using the curved arrow notation (remember to include all lone pairs on heteroatoms) and explain, using resonance forms for the intermediate arenium ions, why compound **A** is more reactive toward Friedel-Crafts alkylation than compound **B**. (15 points)



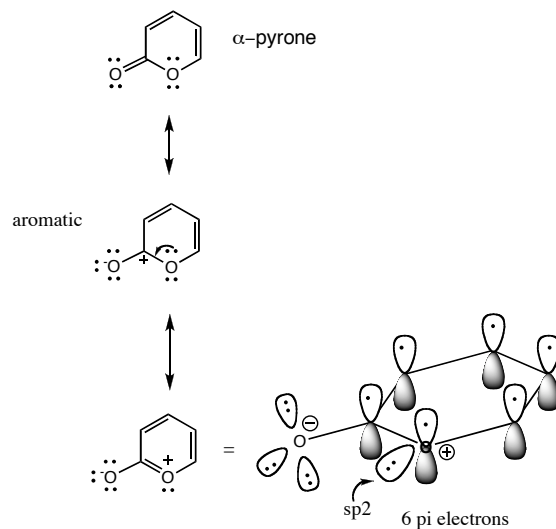
4. Design a synthesis of compound **B** starting from benzene and acetyl chloride. Useful reagents include Cl_2 , AlCl_3 , Zn(Hg) , HNO_3 , KMnO_4 , FeCl_3 , H_2SO_4 . (15 pts)



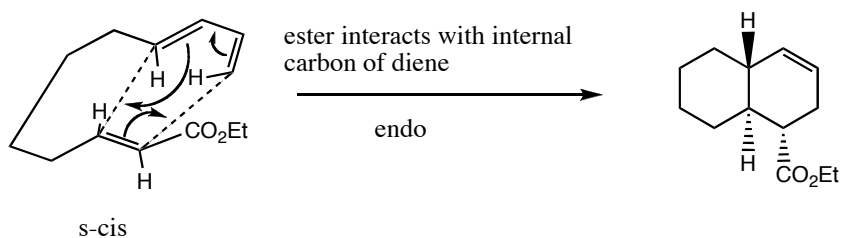
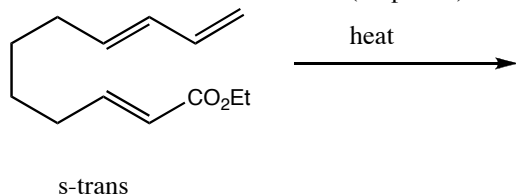
5. Identify whether each of the following compounds is **aromatic, antiaromatic, or non-aromatic**, **and explain why**. (15 points)



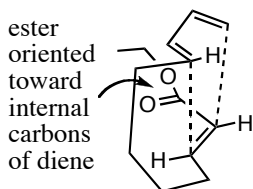
E Considering any alternate resonance forms of the carbonyl group, draw out the orbital structure of α -pyrone, showing explicitly the overlapping p orbitals of the pi system and any orbitals bearing lone pairs. *Is this compound aromatic, antiaromatic, or non-aromatic?*



6. Draw the product of the following *intramolecular* Diels-Alder reaction (where the diene and dienophile are in the **same** molecule), being careful to denote stereochemistry at asymmetric carbon atoms. Provide a definition of the term “endo transition state”, and indicate if this reaction proceeds *via* an *endo* transition state. (15 points)



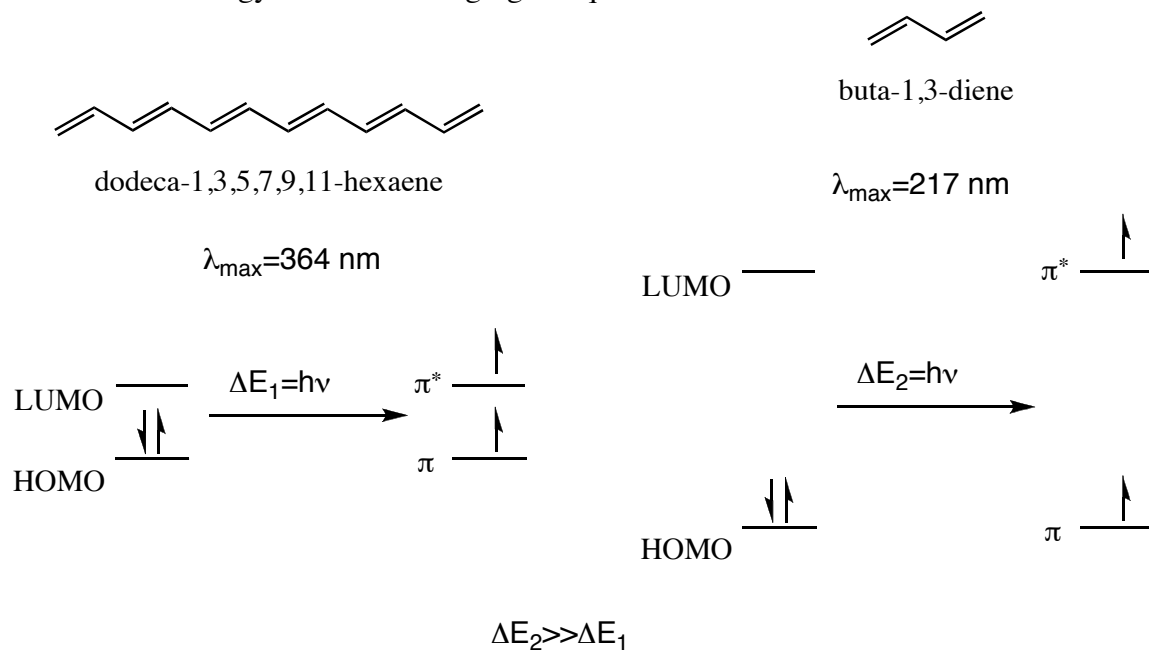
the *endo* transition state involves the orbital overlap of the electron withdrawing substituent on the dienophile with the internal carbons of the diene. This "secondary orbital overlap" lowers the energy of the *endo* transition state relative to the *exo* transition state due to the additional charge delocalization possible. The reaction shown above is geometrically constrained to proceed via the *endo* transition state because the dienophile is *trans*, which means the ester is positioned toward the back carbons of the diene.



Bonus (10 pts)

Explain in detail why the wavelength of maximum absorption (λ_{\max}) of 1,3,5,7, 9, 11 dodecahexaene (364 nm) is significantly greater than the λ_{\max} of 1,3-butadiene (217 nm). Use orbital energy levels/diagrams to illustrate.

The more double bonds in conjugation, the lower the HOMO-LUMO gap, and thus the lower the energy of the incoming light required to excite electrons from π to π^*



Congratulations!

Score:

1. _____ /20
2. _____ /20
3. _____ /15
4. _____ /15
5. _____ /15
6. _____ /15
- Bonus: _____ /10
- Total: _____ /100