

Exam #1

Chemistry 334

Principles of Organic Chemistry II

Tuesday March 14, 2006

Name: KEY.

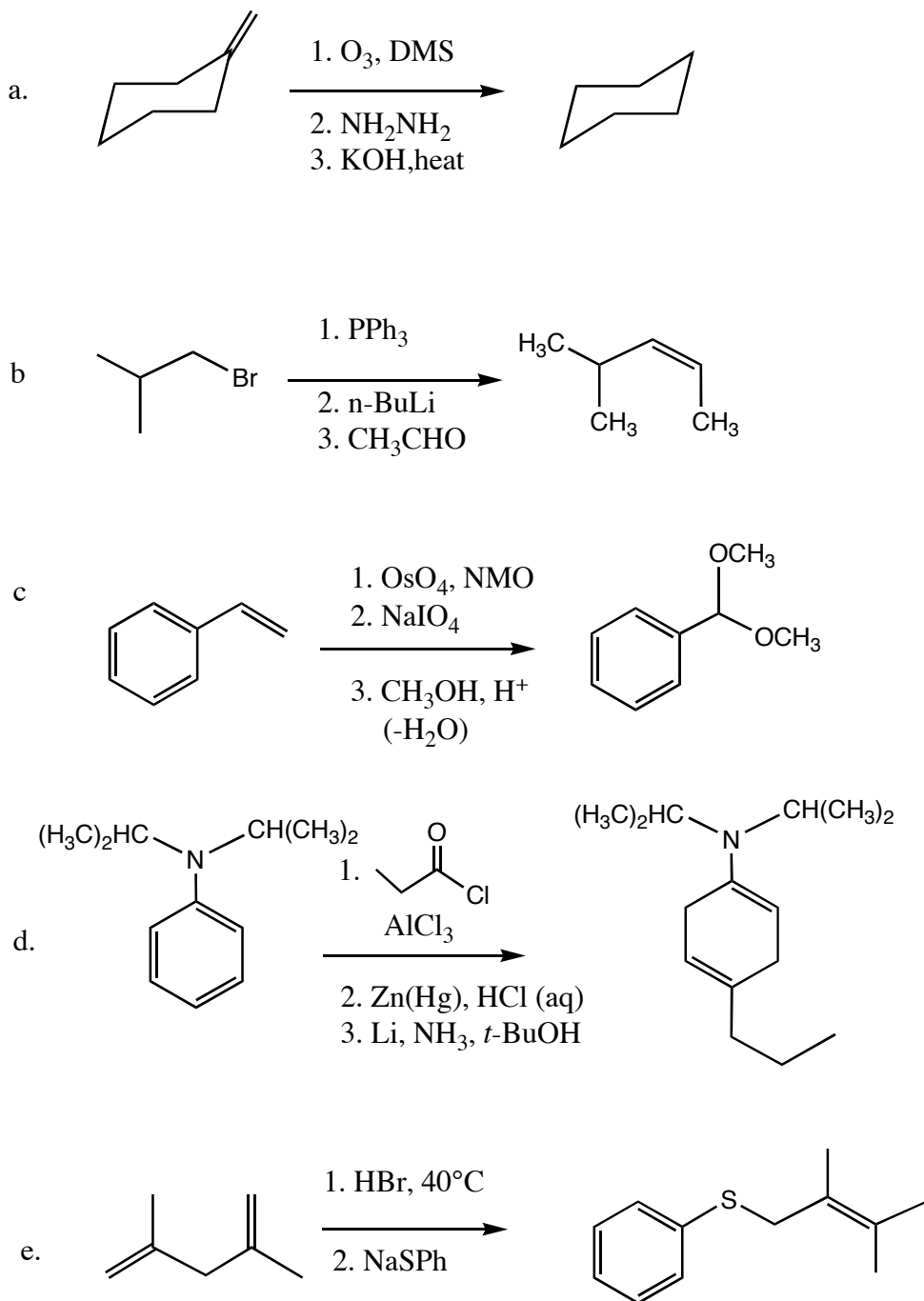
The exam is worth a total of 100 points; there are five questions. Please show all work to receive full credit for an answer.

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

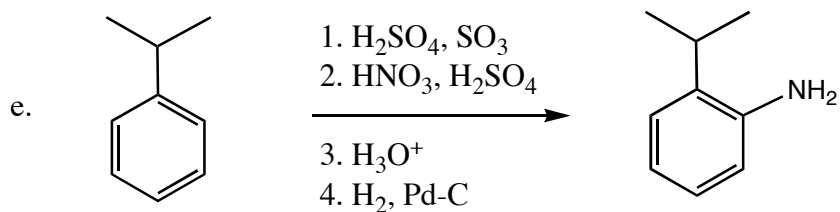
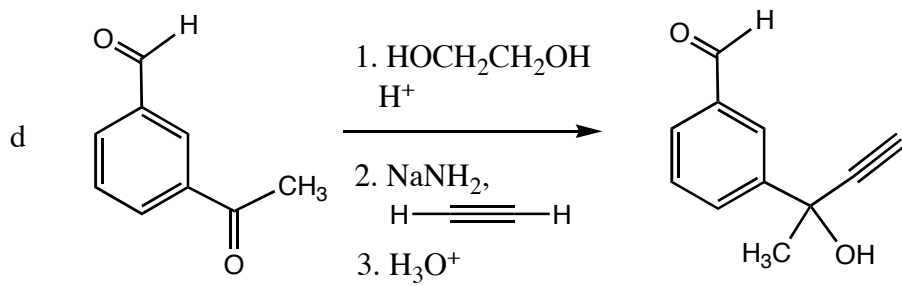
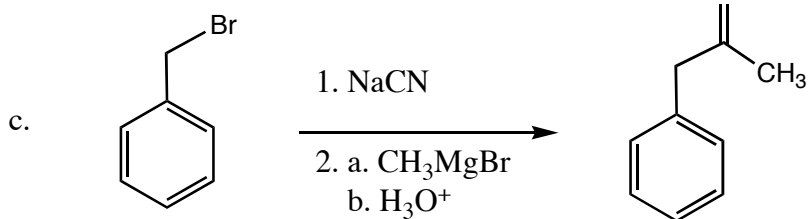
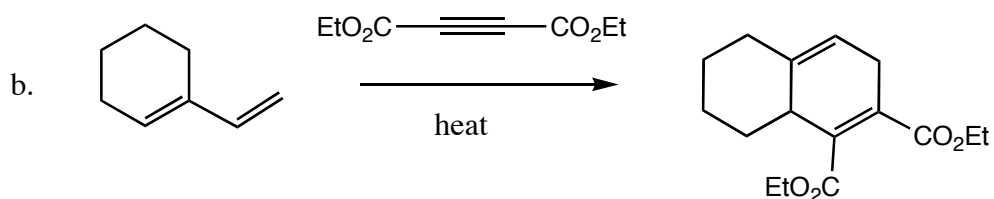
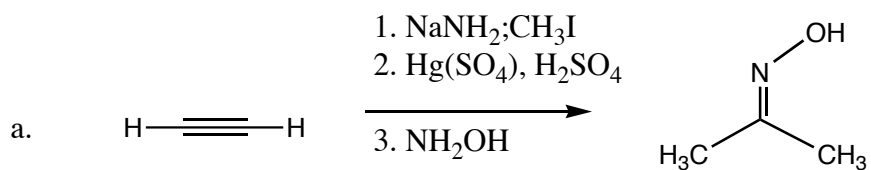
Molecular models are allowed for this exam. Calculators are not needed.

Good Luck!

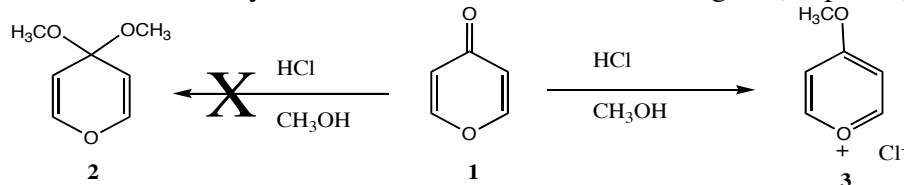
1. Predict the products of the following reactions. **Remember to indicate stereochemistry where relevant.** (20 pts)



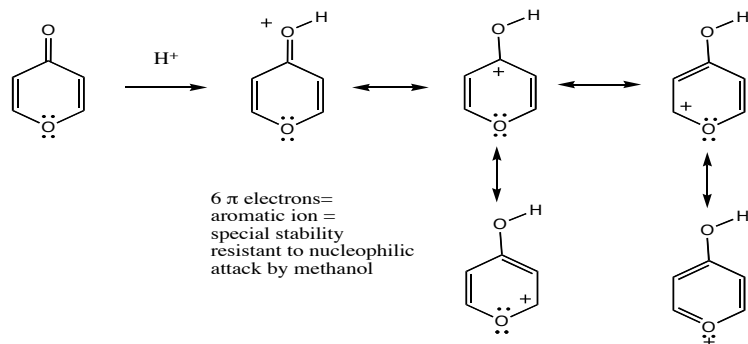
2. Indicate reagents to accomplish the following transformations.(20 pts)



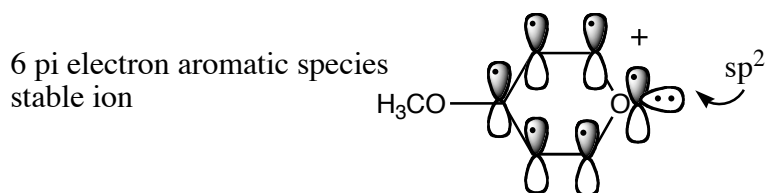
3. Treatment of pyrone **1** with HCl in methanol as solvent leads not to acetal **2** but to pyrilium salt **3** in 30% yield; 70% of **1** is recovered unchanged. (15 points)



- a. Draw resonance structures for the intermediate formed upon protonation of **1** and explain why this compound is relatively unreactive under these conditions.

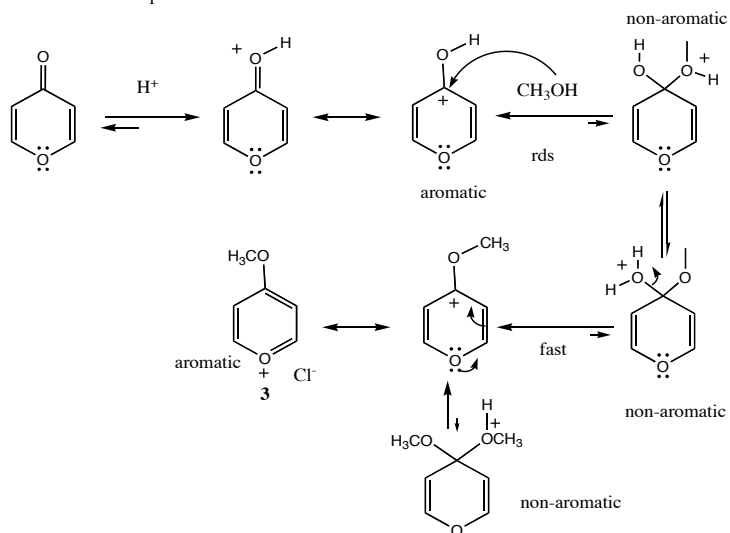


- b. Drawing a 3-dimensional orbital picture of the molecule, explain the special stability of ion **3**.

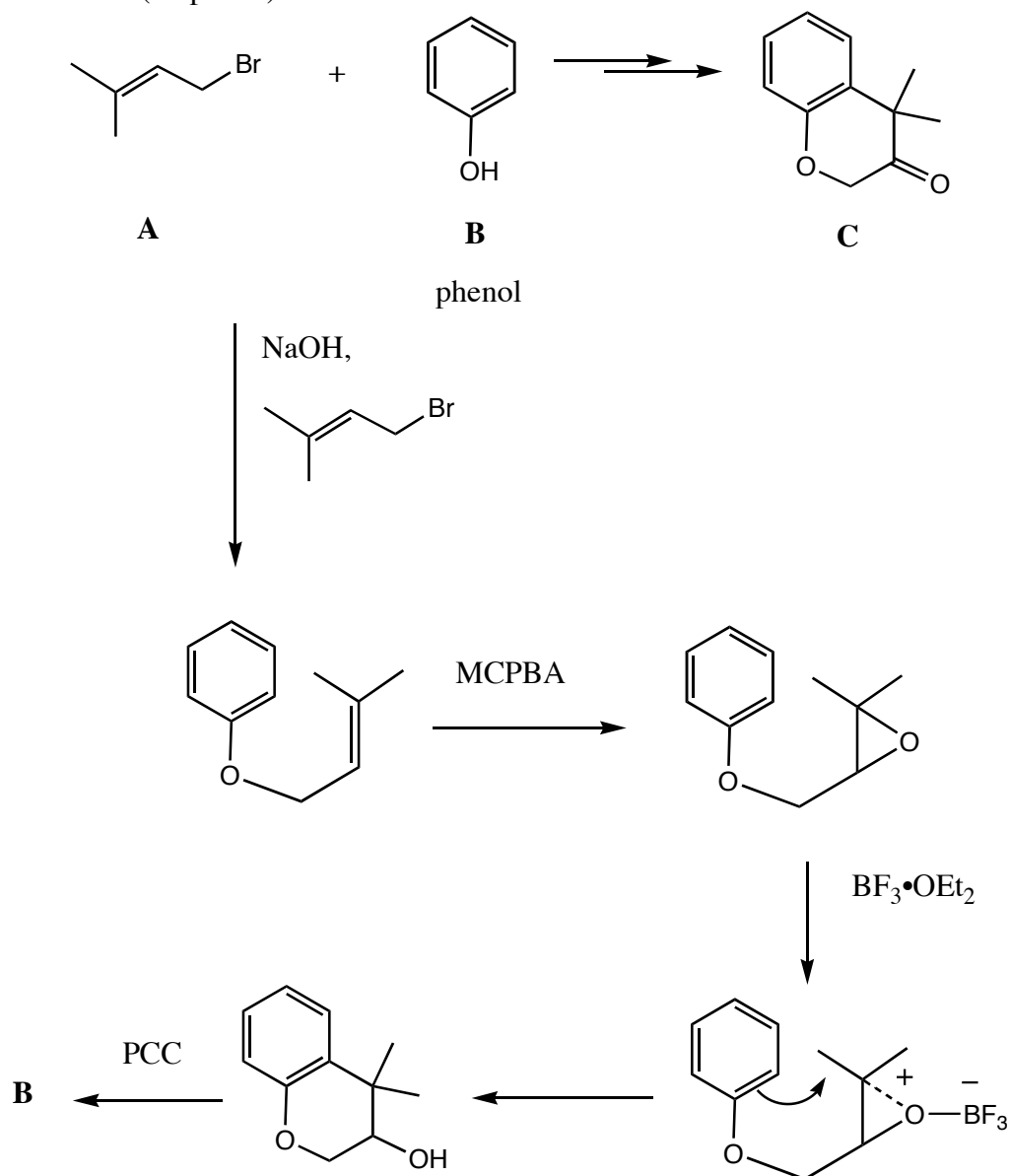


- c. Why is acetal **2** not formed? What sequence of steps is necessary to convert **1** into **3**?

Acetal **2** is non-aromatic, resembling the sigma complex or arylum ion formed during electrophilic aromatic substitution, and is formed at the cost of the stability of an aromatic ion (protonated **1**); on the other hand, ion **3** has the same stability as protonated **1**, because it is aromatic also. Formation of **3** occurs by way of slow, rate-determining nucleophilic attack on the aromatic ion of protonated **1**, followed by proton transfer and rapid loss of water to form **3**.

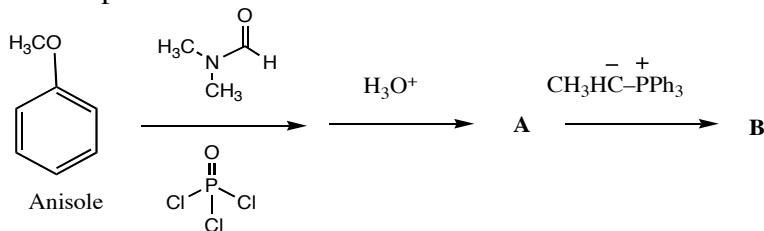


5. Using the following reagents, prepare ketone **C** from prenyl bromide **A** and phenol **B**. Potentially useful reagents include: $\text{BF}_3 \cdot \text{OEt}_2$, NaOH , PCC , and MCPBA . (20 points)

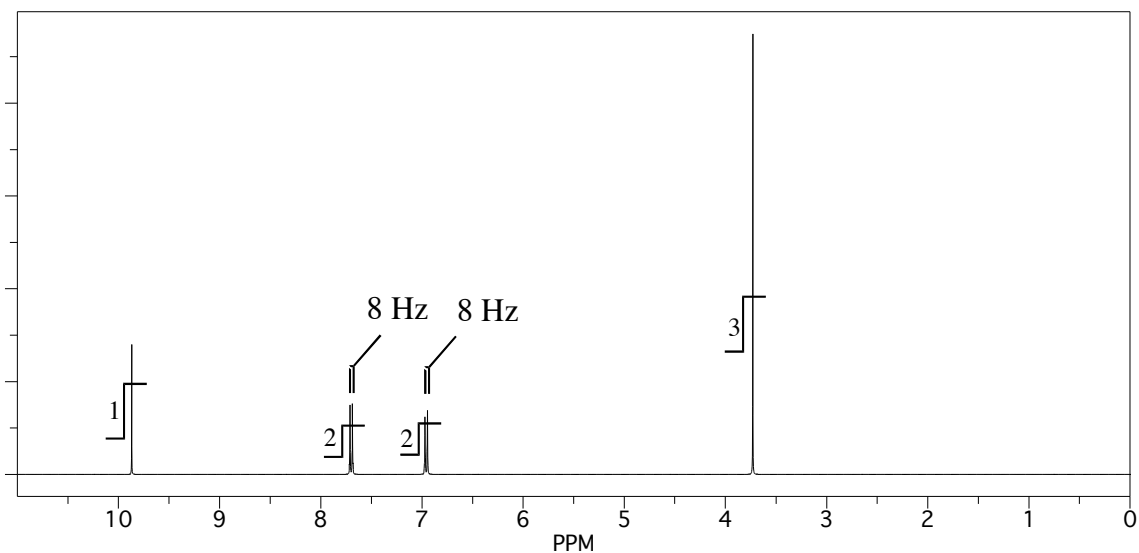


Bonus (10 pts)

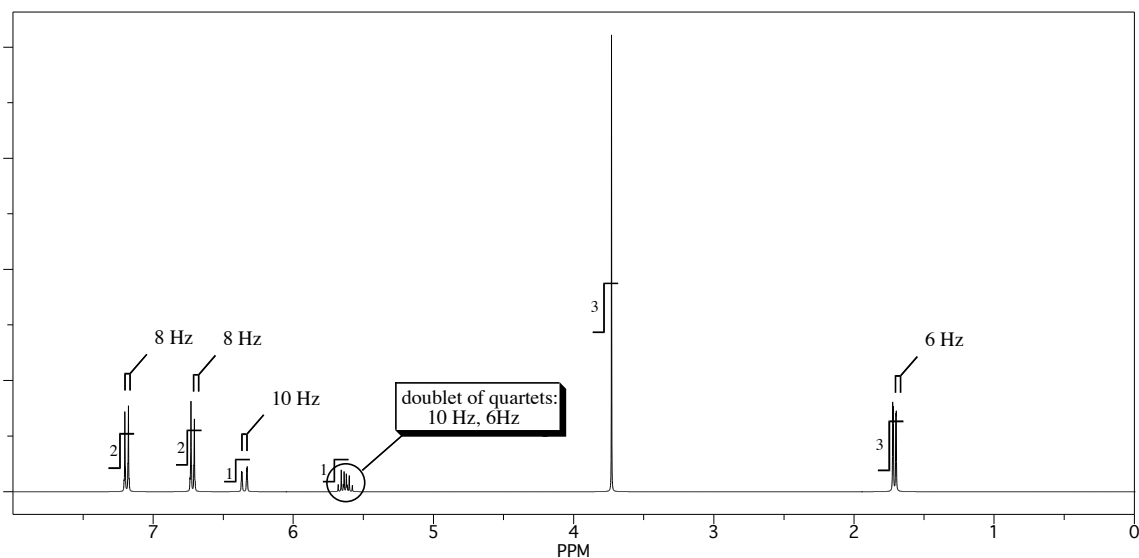
Treatment of the electron-rich aromatic anisole with the reagent combination DMF/ POCl_3 leads to production of compound **A**, which when treated with $\text{CH}_3\text{CH}=\text{PPh}_3$ forms compound **B**. Draw structures for **A** and **B** based on the following ^1H NMR spectra:



^1H NMR spectrum of **A**:



^1H NMR Spectrum of **B**:



Structure A:

Structure B:

(5 points): Suggest a mechanism for the transformation of anisole into **A**

Congratulations!

Score:

1. _____ /20

2. _____ /20

3. _____ /15

4. _____ /20

5. _____ /10

Bonus: _____ /15

Total: _____ /100

