Exam #1

Chemistry 334

Principles of Organic Chemistry II

Tuesday March 14, 2006

Name:_____.

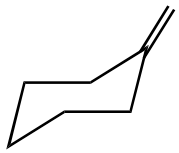
The exam is worth a total of 100 points; there are five questions. Please show all work to receive full credit for an answer.

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

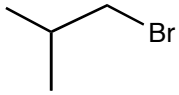
Molecular models are allowed for this exam. Calculators are not needed.

Good Luck!

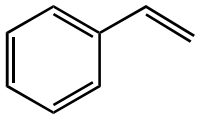
1. Predict the products of the following reactions. ***Remember to indicate stereochemistry where relevant.*** (20 pts)

a. 

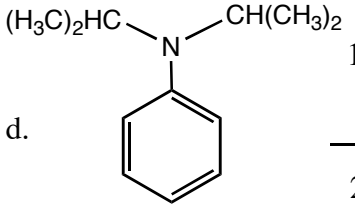
1. O_3, DMS
2. NH_2NH_2
3. KOH,heat

b 

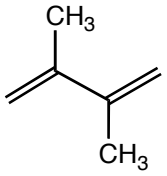
1. PPh_3
2. n-BuLi
3. CH_3CHO

c 

1. OsO_4, NMO
2. $NaIO_4$
3. CH_3OH, H^+ ($-H_2O$)

d. 

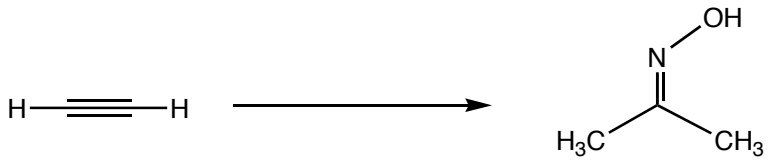
2. Zn(Hg), HCl (aq)
3. Li, NH_3, *t*-BuOH

e. 

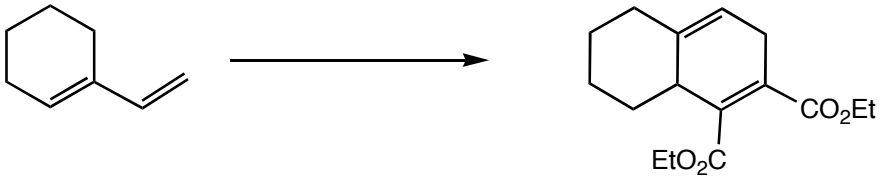
1. HBr, 40°C
2. NaSPh

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

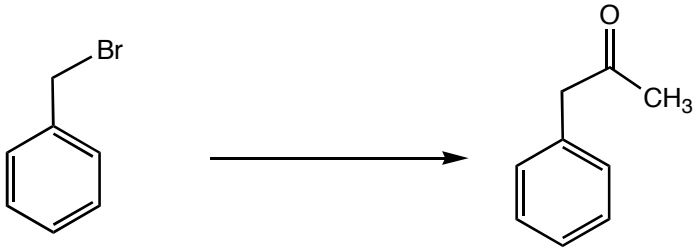
a.



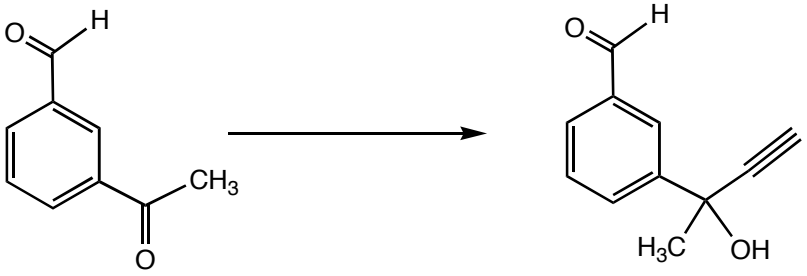
b.



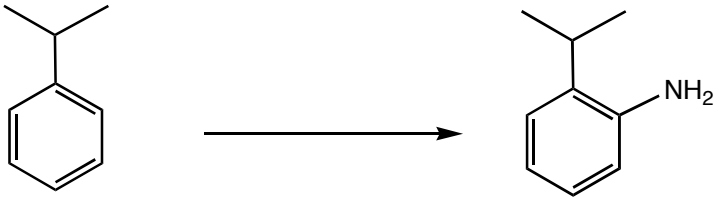
c.



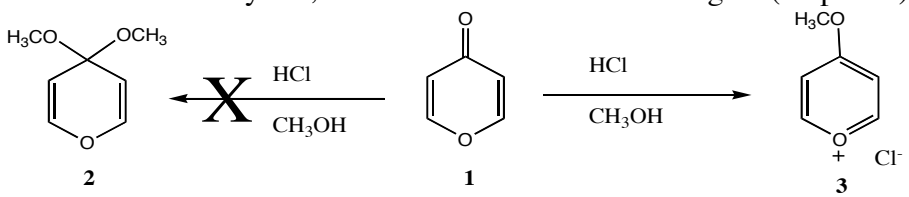
d



e.



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)



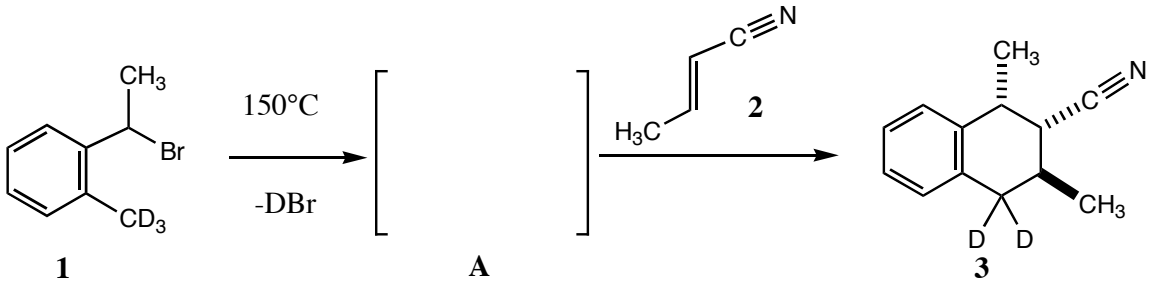
2 **1** **3**

a. Draw resonance structures for the intermediate formed upon protonation of **1**; 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.**

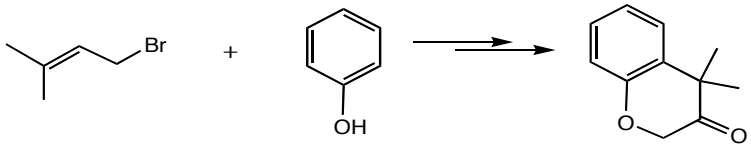
c. Why is acetal **2** not formed? What sequence of steps is necessary to convert **1** into **3**?

4. Heating deuterated benzylic bromide **1** to 150°C results in loss of DBr and formation of a highly reactive intermediate diene **A**, which is capable of rapidly combining with alkene **2** to give compound **3** with the relative stereochemistry shown. Draw the structure of **A** and rationalize how **3** is formed with the regiochemistry and stereochemistry indicated. (25 points). (Recall that deuterium (D) is simply a heavier isotope of hydrogen)



1 **A** **3**

5. Showing all steps <u>and</u> intermediate compounds formed, devise a synthesis of ketone **C** from prenyl bromide **A** and phenol **B**. Potentially useful reagents include: BF_3•OEt_2, NaOH, PCC, and MCPBA. (20 points)

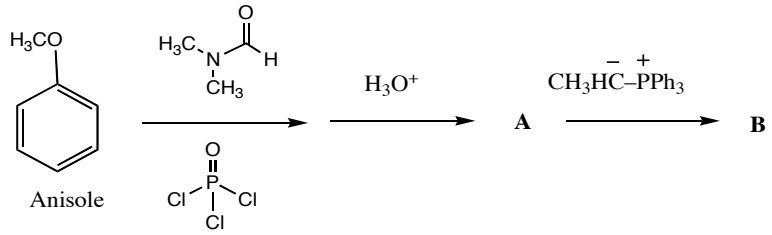


A **B** **C**

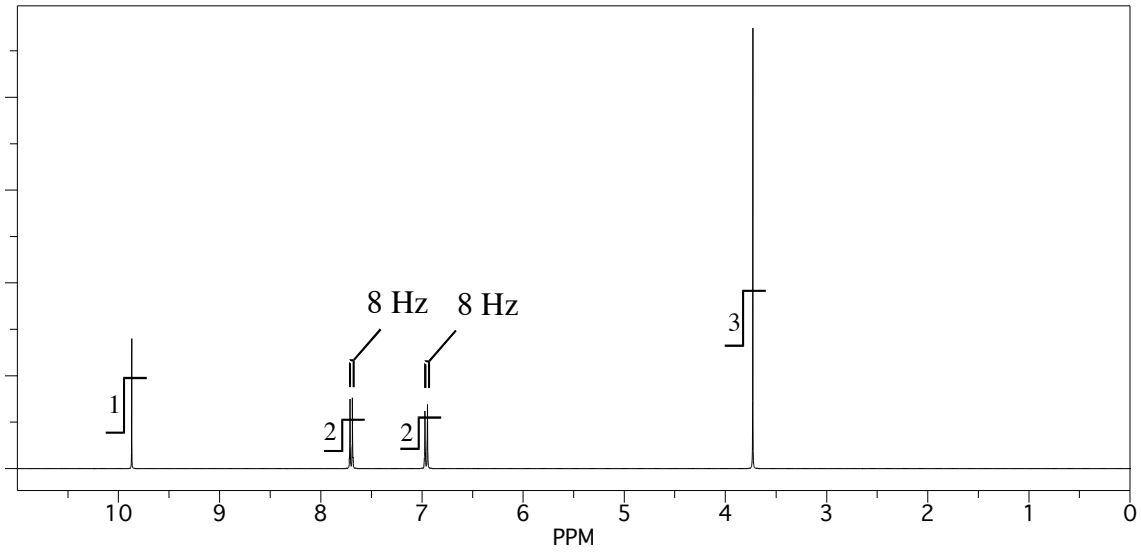
phenol

Bonus (10 pts)

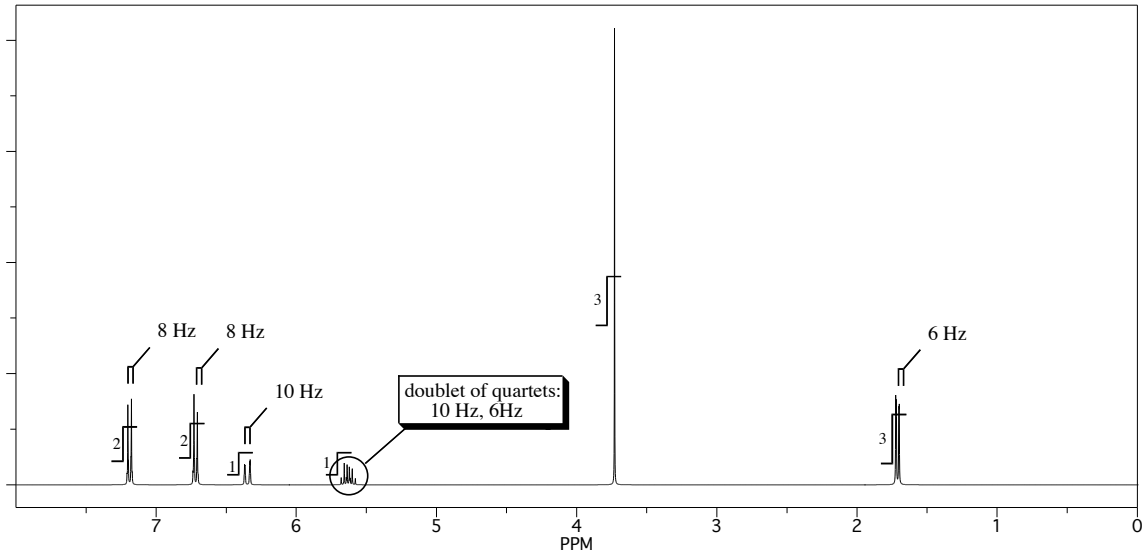
Treatment of the electron-rich aromatic compound anisole with the reagent combination DMF/$POCl_3$ leads to production of compound **A**, which when treated with $CH_3CH{=}PPh_3$ forms compound **B**. Draw structures for **A** and **B** based on the following ^{1}H NMR spectra:



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



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



Structure A:

Structure B:

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

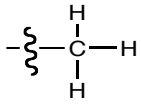
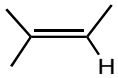
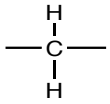
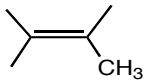
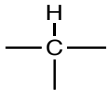
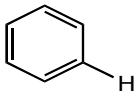
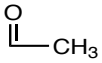
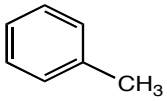
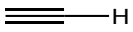
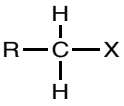
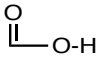
Congratulations!
Score:

1. _____/20
2. _____/20
3. _____/15
4. _____/25
5. _____/20

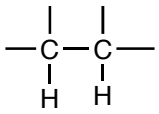
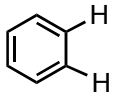
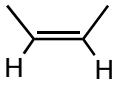
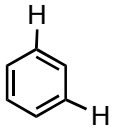
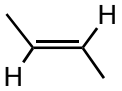
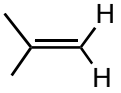
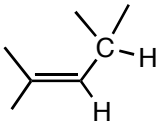
Bonus: _____/15

Total: _____/100

Chemical Shifts in ^{1}H NMR:

	δ		δ
	0.9		5-6
	1.3		1.7
	1.4		7.2
	2.1		2.3
	2.5		9-10
	3-4		10-12

Typical Coupling constants observed in ^{1}H NMR:

free rotation:	J_{Hz}		J_{Hz}
	7 Hz		8 Hz
	10 Hz		2 Hz
	15 Hz		
	2 Hz		
	6 Hz		

Chemical Shifts in ^{13}C NMR: