Final Exam
March 19, 2013
Organic Chemistry 335

Portland State UNIVERSITY

I will not accept answers on scratch paper

This exam is 110 minutes long (8-9:50). I will post a key on D2L when I have all the exams back. There will be no make-up exams. A missed final will result in an incomplete for the course. Please be considerate of your fellow classmates when leaving. Don't stand by the doors and discuss the exam.

All cell phones and personal audio devices must be turned off and put away. The use of calculators, notes, the textbook, or **your neighbors test** is not permitted during the exam. You may use molecular models, but they cannot be shared during the exam.

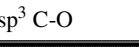
Please put your in-class number and your name on the second page **and back of the exam**.

You may tear off this page for easier use of the tables.
If your test becomes unstapled, please let me know

IR Data

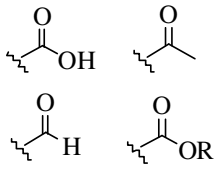
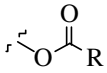
Bond	IR Range cm^{-1}	General Shape (intensity strong = s, middle = m, weak = w)
O-H alcohol	3600-3200	**broad** (s/m)
O-H Carboxylic Acid	3600-2500	**broad** (s/m/w)
N-H Amine/Amide	3500-3350	**"fangs"** (s/m/w)
sp C-H	3320-3310	**sharp** (s/m/w)
sp^2 C-H	3100-3000	**sharp** (s/m/w)
sp^3 C-H	3000-2900	**sharp** (s/m)
-C≡N nitrile	2240-2280	**sharp** (w/m/s)
-C≡C sp-sp alkyne	2100-2200	**sharp** (m)
-C=O (carbonyl)	1750-1650	**sharp** (s)
-C=C sp^2-sp^2	1680-1600	**sharp** (m/w)
-sp^2 C-O	1250-1200	**sharp** (m/w)
-sp^3 C-O	1200-1025	**sharp** (m/w)

^{13}C NMR Chemical Shift Ranges

Type of Carbon	Chemical Shift (δ) range in ppm
R<u>C</u>H_3	0 to 35
R_2<u>C</u>H_2	15 to 40
R_3<u>C</u>H	25 to 50
R_4<u>C</u>	30 to 40
R<u>C</u>=<u>C</u>R	65 to 90
R_2<u>C</u>=<u>C</u>R_2	100 to 150
	110 to 175
R<u>C</u>HBr	20 to 40
R<u>C</u>HBr	20 to 40
R<u>C</u>HCl	25 to 50
R<u>C</u>H_2NH_2	35 to 50
R<u>C</u>H_2OH R<u>C</u>H_2OR	50 to 65
R<u>C</u>≡N	110 to 125
	160 to 185
	190 to 220

Predicting the chemical shift of proton/s on a sp^3 carbon in a ^1H NMR spectrum

methyl (XCH_3): starting point is 0.9 ppm.
methene (X_2CH_2): starting point is 1.3 ppm.
methine (X_3CH): starting point is 1.5 ppm

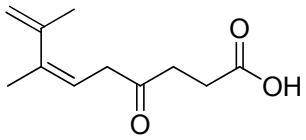
Group (X)	Increment (ppm)
⟆-CH_3 (or any alkyl group)	0.0
⟆-$CH{=}CH_2$ (or an alkene group)	0.9
⟆—C≡CH ⟆—C≡CR (an alkyne group)	0.9
⟆-SH, ⟆-SR	1.2
	1.2
⟆—C≡N	1.2
⟆-NH_2, ⟆-NHR ⟆-NR_2	1.2
⟆—I	1.3
⟆—Ph 	1.4
⟆—Br	1.8
⟆—Cl	2.1
⟆—OH ⟆—OR	2.4
	2.8
⟆—O— 	3.0
⟆—F	3.2

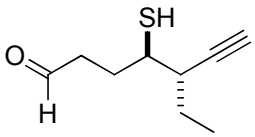
^1H NMR Chemical Shift Ranges for H attached to non sp^3 Carbons

Type of Proton	Chemical Shift (δ) range in ppm
	10 to 12
	9 to 10
	6.5 to 8.5
	4.5 to 5.5
RC≡C-**H**	2 to 3
R_2CO-**H**	1 to 5.5
R_2CHN-**H**	1 to 4

Organic Chemistry 335 In-class # _____
Final Exam
March 19, 2013 Name _____
(Last, First)

1. Name the following compounds (12 points)

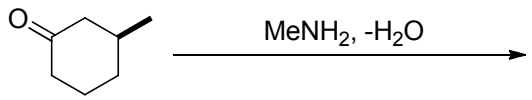


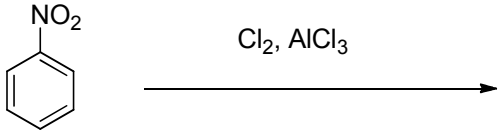


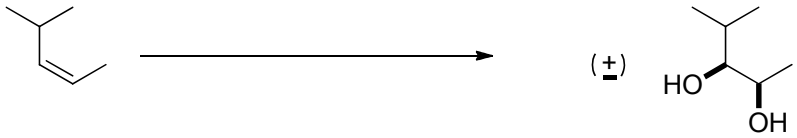
2. Draw the following compounds. (12 points)

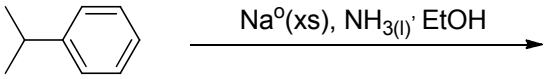
(*S*)-3-ethoxyhexane (2*S*,3*S*)-2,3-dimethyloxetane 3-acetyl-5-bromobenzoic acid

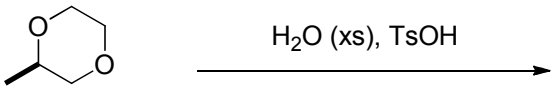
3. What was the starting material, reagents, or product/s for the following chemical transformations? If there is no reaction write "no reaction"
Do not forget about stereochemistry (84 points)

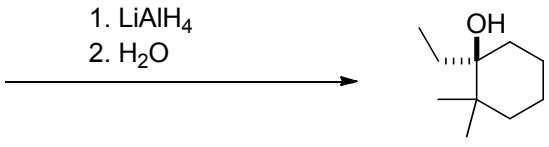




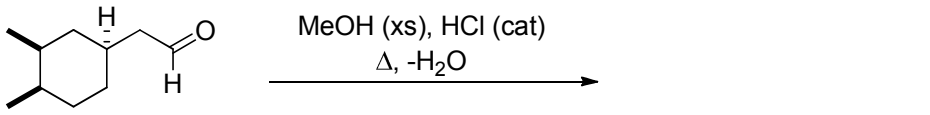


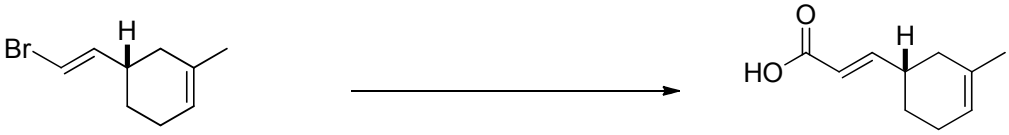


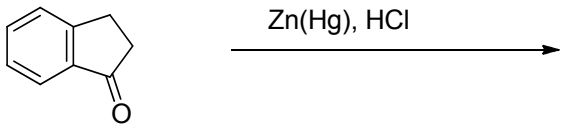


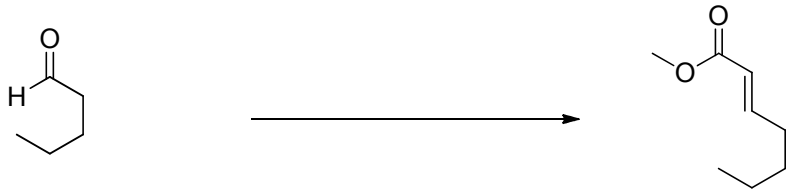


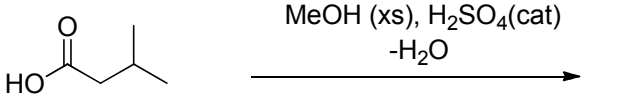
3. Continued

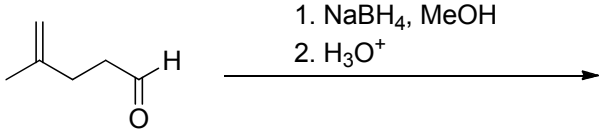

H
O
H
MeOH (xs), HCl (cat)
Δ, -H2O


Br
H
O
HO
H

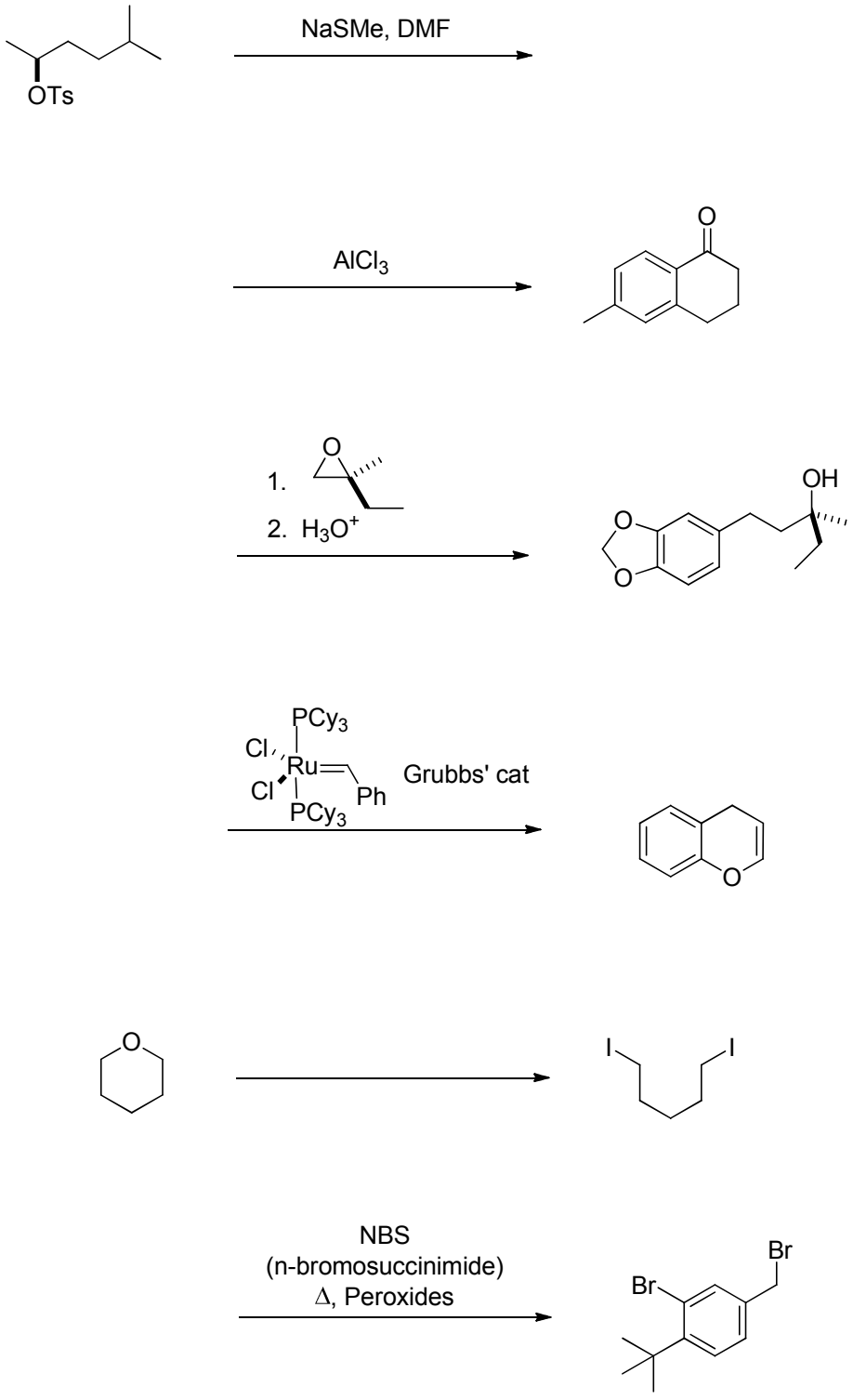

O
Zn(Hg), HCl


O
H
O
O

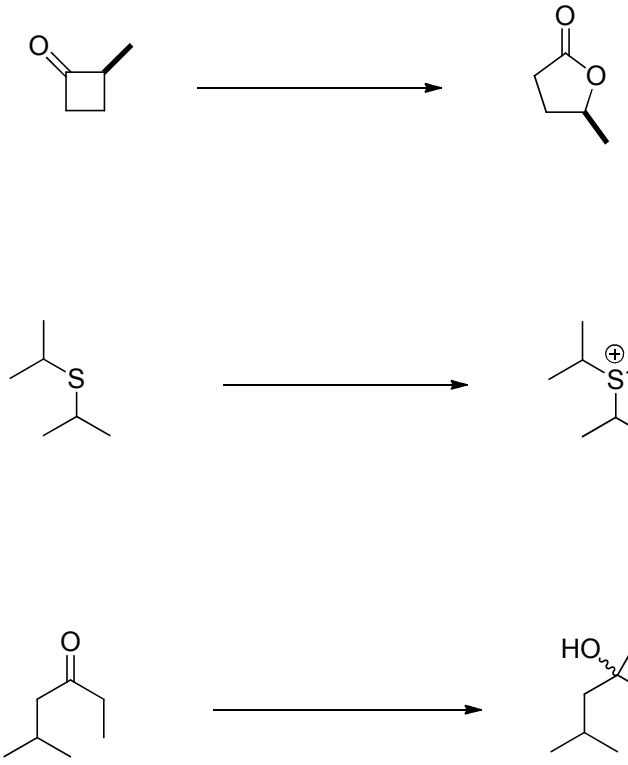

O
HO
MeOH (xs), H2SO4(cat)
-H2O


H
O
1. NaBH4, MeOH
2. H3O+

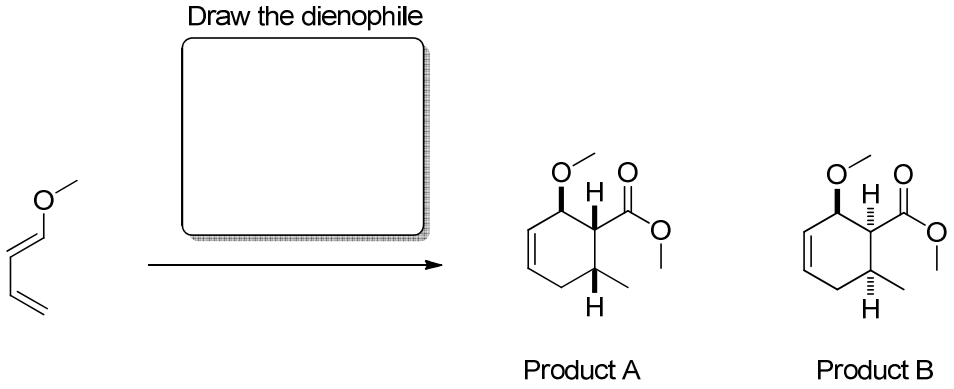
Problem 3 continued.



Problem 3 continued.

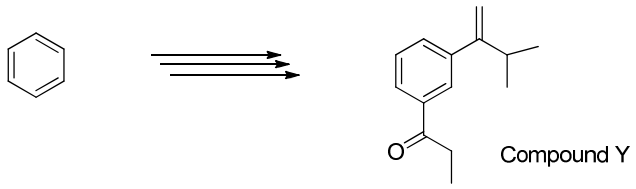


4. a. Draw the dienophile for the following reaction. 3 points
   b. **Circle** the product that is formed from an ***Exo*** **transition state**. 3 Points

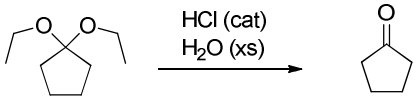


5. Design a synthesis of compound Y. (16 points)

* The synthesis must start with benzene.
* You can use any reaction you have learned this year.
*** All carbons (except benzene)that end up in the product must start from carbon dioxide and/or alcohols that has three carbons or less.**
* **You need to show the how you make the reagents and intermediate products**.
* The major product must be carried on to the next step.
* You do not need to show the mechanisms.



6. Draw the complete mechanism acid catalyzed removal of the diethyl ketal. (16 points)

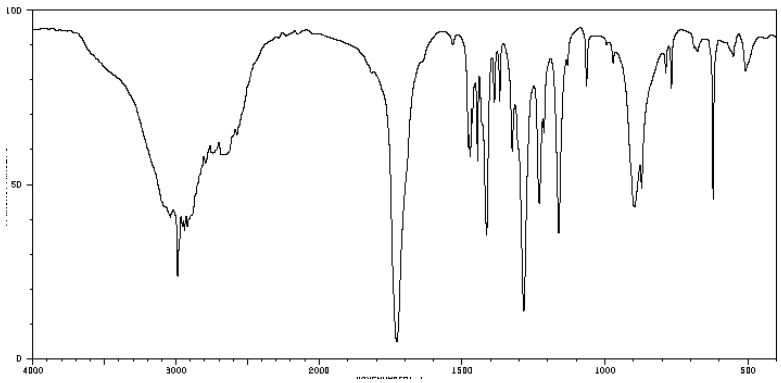


7. What is the following structure? $C_7H_{12}O_4$ (17 points: these 17 point are broken up in the problem)

What are the degrees of unsaturation or IHD? (3 point)

degrees of unsaturation or IHD

IR: 3041, 2994, 1729, 1285 cm^{-1}



^{13}C NMR data (ppm)
185
178
44
35
34
25

List four types of bonds the IR show this molecule has. (4 points)

1. 2. 3. 4.

Please tell me what you think each peak in the ^{1}H NMR represents (CH_X, OH, NH_x …) and how you get its splitting pattern (5 points)

^{1}H NMR

11.9 (s, 1H)

11.7 (s, 1H)

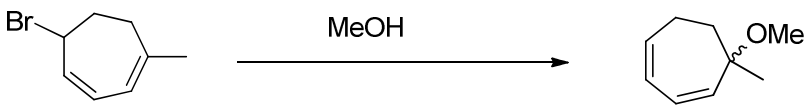
2.4 (t, 2H)

1.9 (t, 2H)

1.1 (s, 6H)

Draw the structure that best fits all the data. (5 Points)

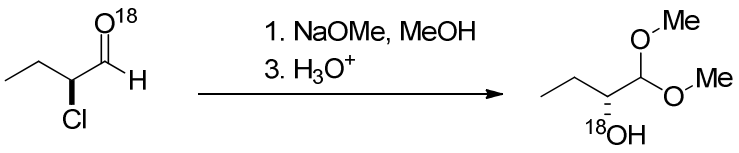
8. Draw a complete mechanism for the following S_N1 reaction . (6 points)



9. Provide a **short** explanation (pictures are worth a 1000 words) why there is a drastic difference in the acidity of the methylenes of cyclopentadiene and cycloheptatriene. (6 points)

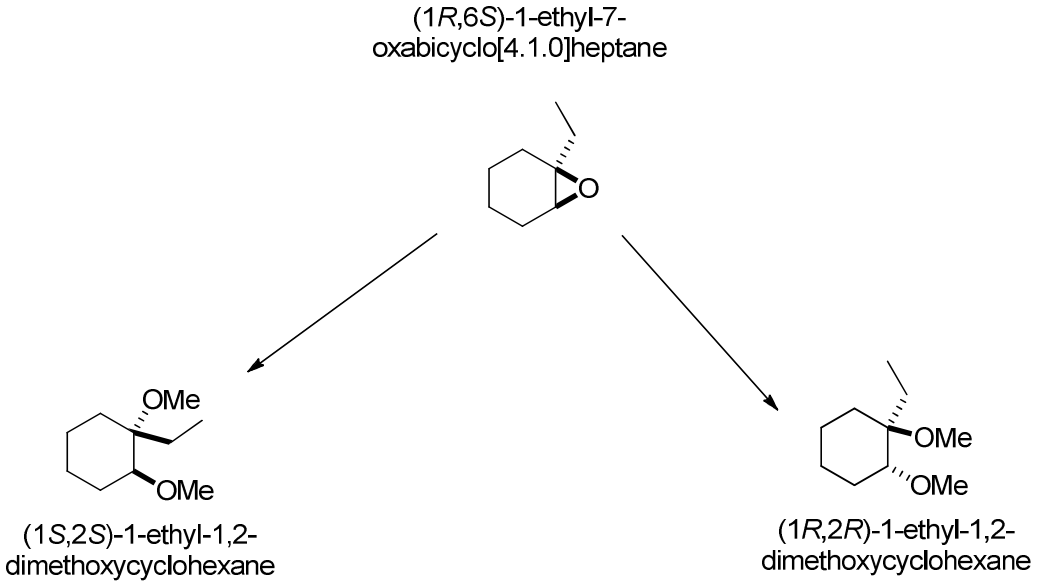
cyclopentadiene $pK_a = 16$ vs cycloheptatriene $pK_a = 36$

10. Draw a mechanism for the following reaction. (5 points)



**********Insurance question: 10 points**********

IQ1. Starting from pure (1R,6S)-1-ethyl-7-oxabicyclo[4.1.0]heptane X design a synthesis of pure (1S,2S)-1-ethyl-1,2-dimethoxycyclohexane and pure (1R,2R)-1-ethyl-1,2-dimethoxycyclohexane . (4 points)



IQ2. Draw the complete mechanism for the following reaction. (6 points)