CHEM 3311 (Richardson) Final Exam – May 7, 2015

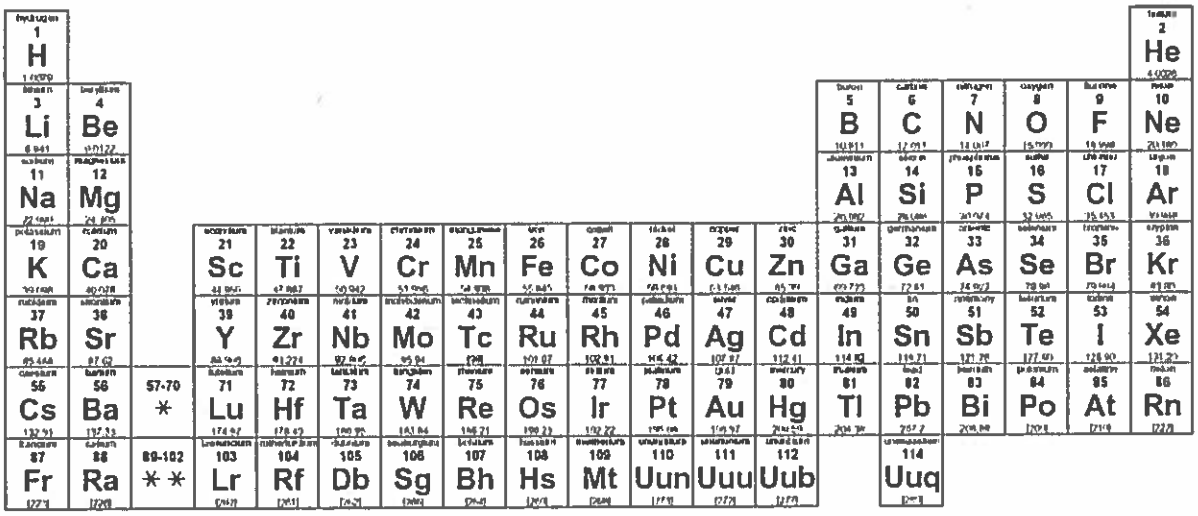
Your Name Key

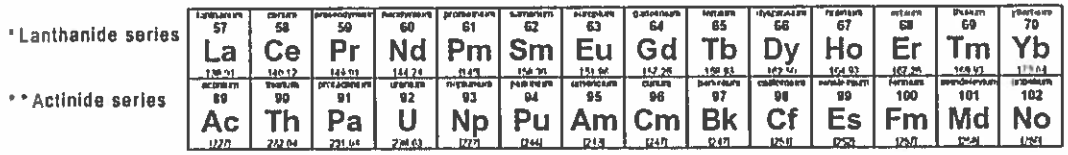
Student ID _____

Recitation Time 12:00 Monday, 1:00 Monday, 11:00 Tuesday, 1:00 Tuesday, 12:00 Wednesday

Question	Score	Out of
1		20
2		20
3		30
4		30
5		30
6		20
7		20
8		10
9		20
10		10 e.c.
Total		200

This is a closed-book exam. The use of notes, calculators, or cell phones will not be allowed during the exam. You may use models sets brought in a clear ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states.





Average: 134.10
St. Dev: 36.7
Max: 198
Min: 36

pKa Values

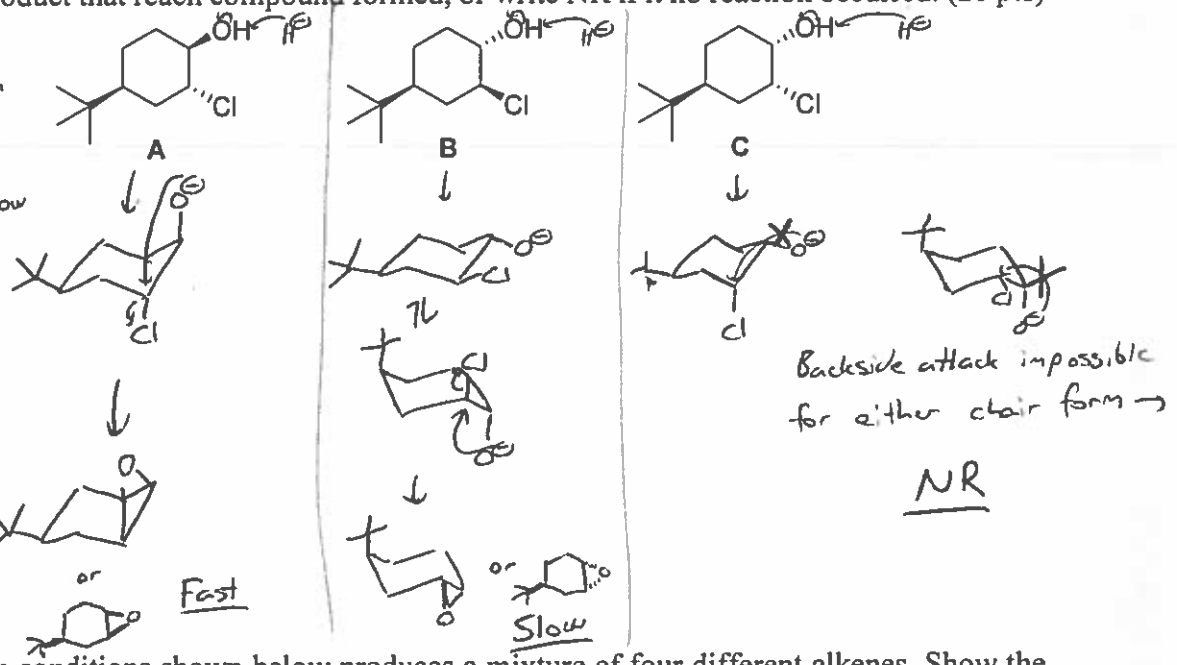
HI	-10	CH_3COOH	4.7	Phenol (PhOH)	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	Alcohol (ROH)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

 Name_____

1) The three compounds below were reacted with NaH in an attempt to form a neutral product. One reacted very quickly, one reacted very slowly, and one did not react at all. Which is which? Show the product that reach compound formed, or write NR if it no reaction occurred. (20 pts)

5 pts for each correct product

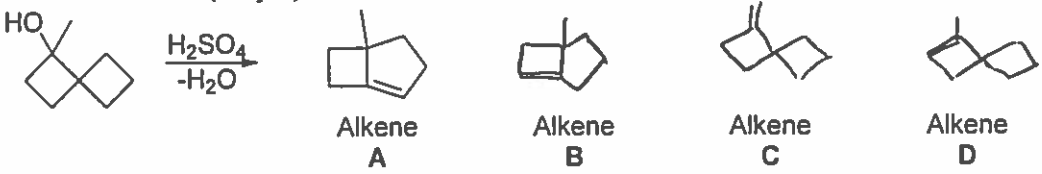
5 pts for fast/slow



Backside attack impossible for either chair form →

NR

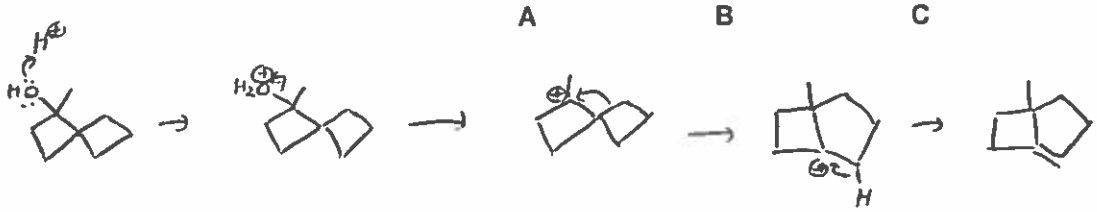
2) The reaction conditions shown below produces a mixture of four different alkenes. Show the structures of these alkenes (one has already been provided), and show the mechanism for the formation of alkene A. (20 pts)



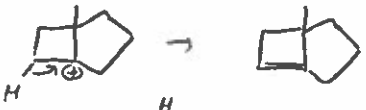
4 pts per product

8 for mech for A's formation

Mech for A:



Mech for B: Same as for A, but last step is



Mech for C: Same as for A in first 2 steps, then

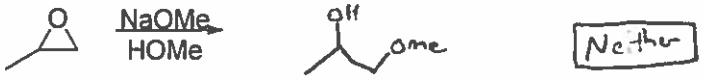
Mech for D:

 Name_____

3) **Predict the product** of the following reactions, and **choose the appropriate descriptor** (reduction, oxidation, or neither) for what happens to the organic molecule during each reaction. If no reaction occurs then write NR. (30 pts - 3 pts each)

(2 pts for structure, 1 pt for descriptor)

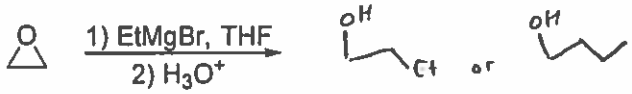
(-1 pt for incorrect regiochem)

a. 

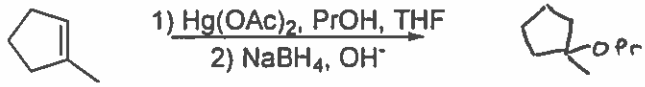
Neither

b. 

Neither

c. 

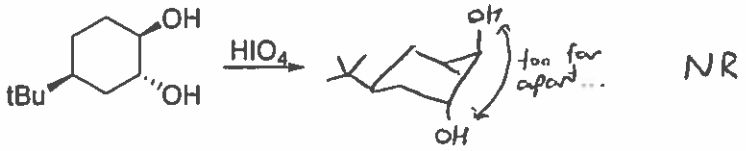
Reduction

d. 

Neither

e. 

Oxidation

f. 

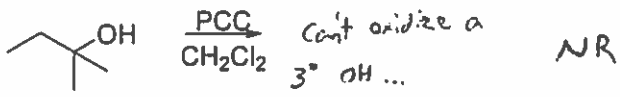
NR

g. 

Neither

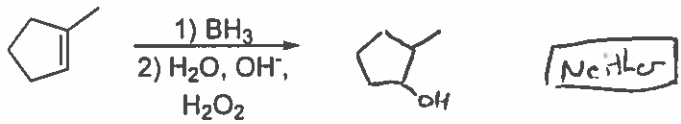
h. 

Reduction

i. 

Can't oxidize a 3° OH ...

NR

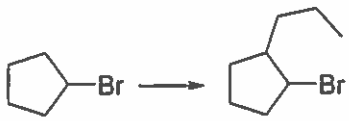
j. 

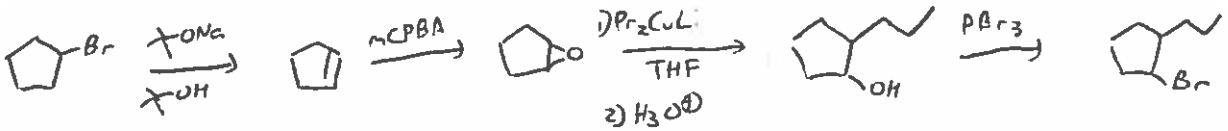
Neither

 Name_____

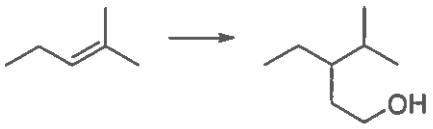
4) Synthesize the desired product from the given starting material. If more than one step is necessary, show the product of each step. Do not show mechanisms. (30 pts - 10 pts each)

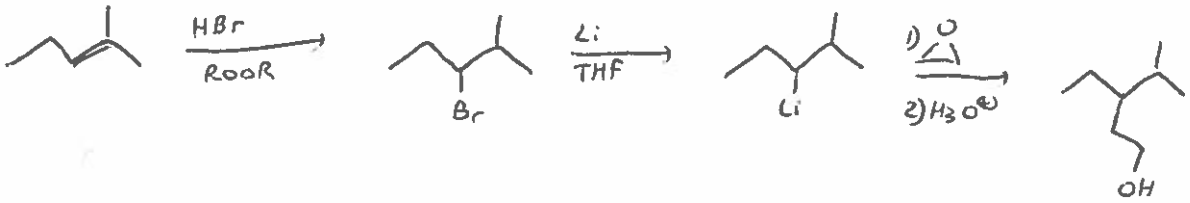
a.



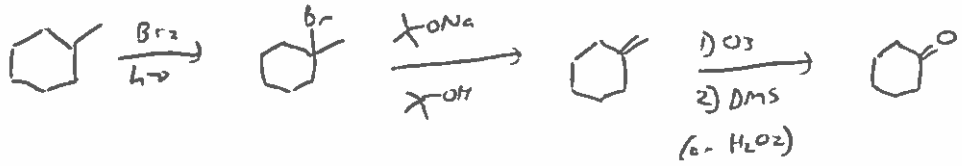


b.



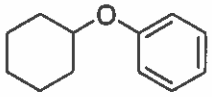


c.

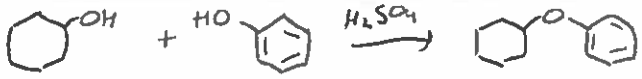


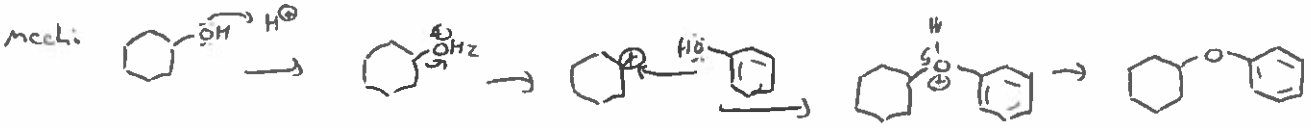
 Name_____

5) **Show what reagents** you would use to synthesize this ether by each of the following methods, and **show the mechanism** by which the ether forms in each reaction. (30 pts - 10 pts each)

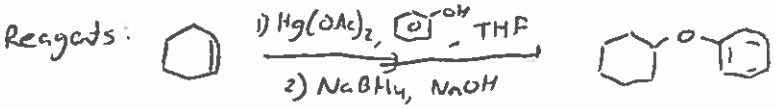


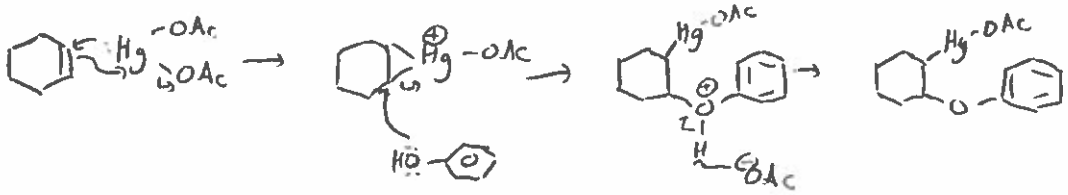
a. Acid-catalyzed ether formation from alcohols

Reagents: 

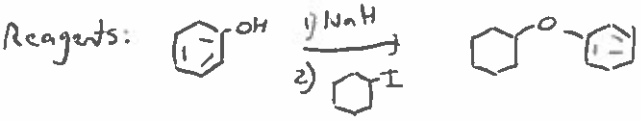
mech: 

b. Alkoxymercuration-reduction (do not show mechanism for reduction step)

Reagents: 

mech: 

c. Williamson ether synthesis

Reagents: 

Phenoxide ($PhO^{\ominus}$) is a weak base & good Nucleophile → S_N2 favored

 Name_____

6) Rank each group of molecules by increasing heat of formation and explain the reason for the ordering in under twenty words per group. (20 pts)

a. Methylcyclopentane, cyclohexane, 1,1-dimethylcyclobutane

(2 pts for ranking, 3 pts for explanation)


middle


lowest


highest

Six-membered ring is most stable and instability (heat of formation) increases as ring size drops below 6.

b. *cis*-2-butene, *trans*-2-butene, 1-butene


middle


lowest


highest

More substitution on alkene = more stable; after that trans is more stable than cis.

c. Hexane, propane, butane


lowest

highest


middle

If structures are similar, more stuff = larger magnitude of ΔH_f (more negative for hexane).

d. *cis*-2-hexene, 2,3-dimethylbutene, 2-methyl-2-pentene

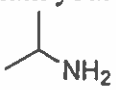

highest

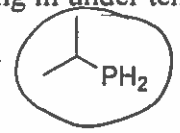

lowest


middle

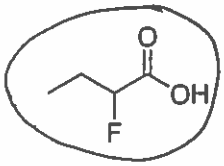
More substitution on alkene: more stable.

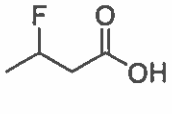
7) For each pair of compounds shown below, select the more acidic of the two compounds and explain your reasoning in under ten words. (20 pts) (2 pts per circle, 3 pts per explanation)



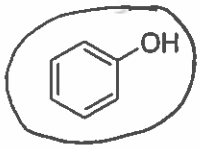
vs.


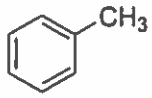
Reason: Element effect: in same column of periodic table, acidity increases downwards.



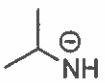
vs.


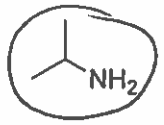
Reason: F is closer to ⊖ charge → stronger inductive effect.



vs.


Reason: Element effect: in same row of periodic table, acidity increases to right.



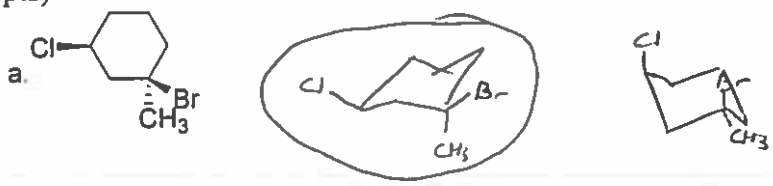
vs.


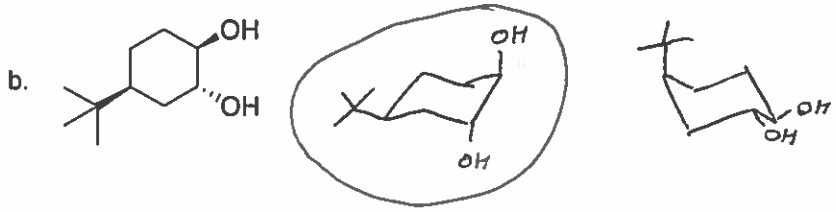
Reason: Charge effect: neutral atom is more acidic than ⊖.

 Name_____

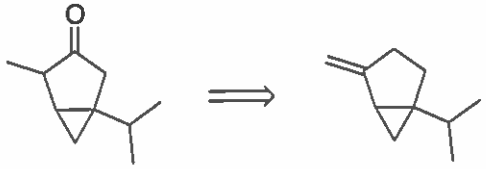
8) Draw the following molecules in **both** chair conformations, and circle the most stable. (10 pts)

(2 pts per structure, 1 pt per circle)

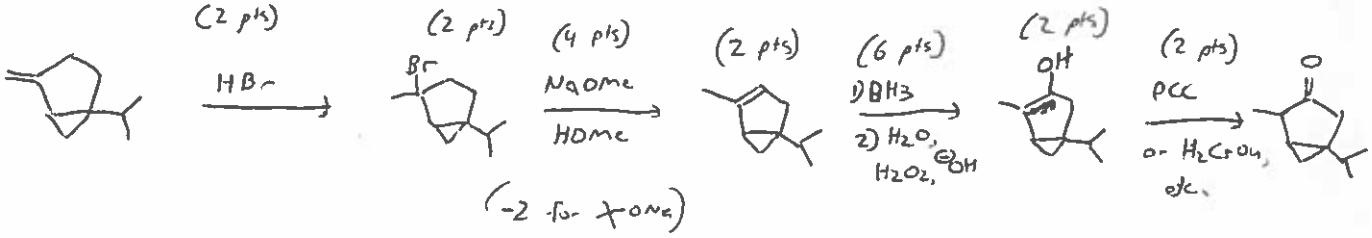
a. 

b. 

9) α-Thujone is a monoterpene that was once believed to be responsible for the psychedelic effects of absinthe. Although it is typically isolated directly from wormwood, it can also be synthesized from similar precursors, including sabinene. Show the steps necessary to do this, ignoring stereochemistry. (20 pts)

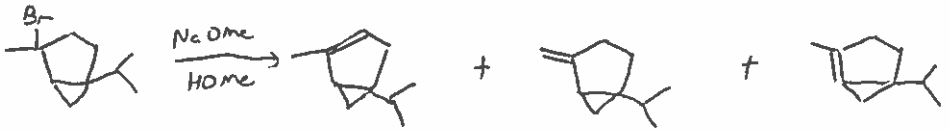


α-Thujone Sabinene



10) Extra credit! In the previous problem, there was one step where three different elimination products could potentially form, but two of those products were disfavored. What are these products, and why is each of them disfavored? (10 pts extra credit)

(2 pts per structure, 3 pts per explanation)



Disfavored due to Zaitsev's rule

Disfavored b/c it puts sp^2 C in 3-membered ring - bond angles are very strained