CHEM 3331 (Richardson) Second Midterm Exam – Mar. 13, 2018

Your Name: Key

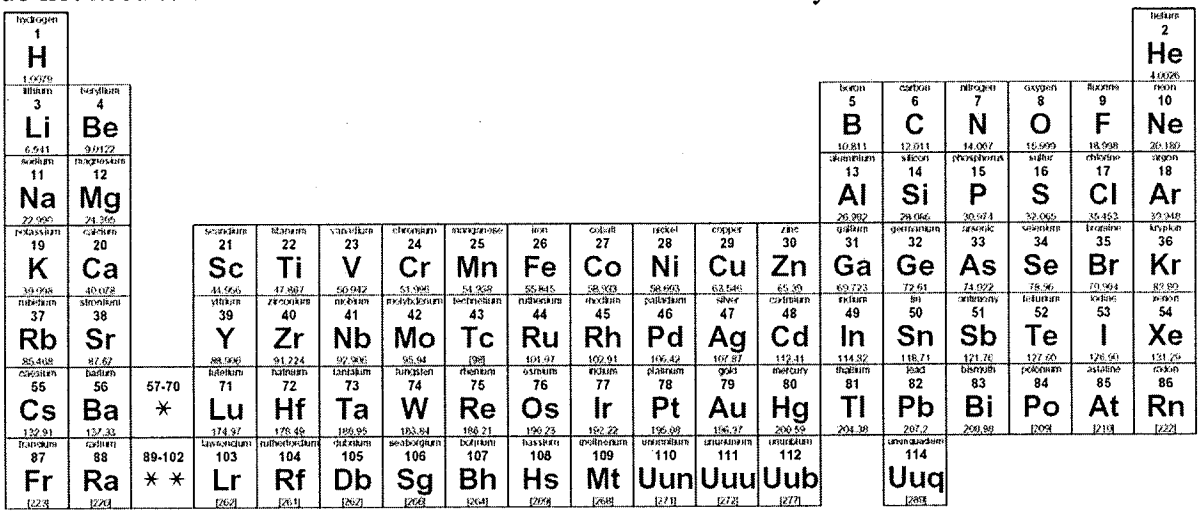
Student ID: _____

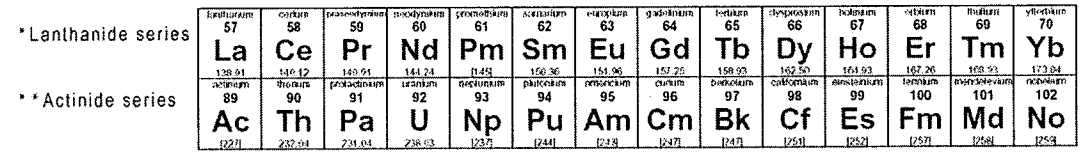
Recitation (check one)

O 12:00 Wed (Patrick Li)
O 4:00 Wed (Michael Ortiz)
O 11:00 Thu (Josh Kamps)
O 3:00 Thu (Rachel Weintraub)
O 8:00 Wed (Rachel Weintraub)
O 2:00 Wed (Patrick Li)
O 9:00 Thu (Josh Kamps)
O 1:00 Thu (Aaron Hinds)
O 5:00 Thu (Rachel Weintraub)

Question	Score	Out of
1		30
2		15
3		5
4		30
5		15
6		5
7		10 e.c.
Total		100

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. For synthesis, show the product of each synthetic step, but do not show mechanisms. You do not need to show the exact structure of transition metal catalysts.



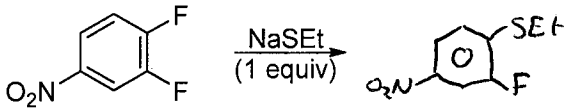


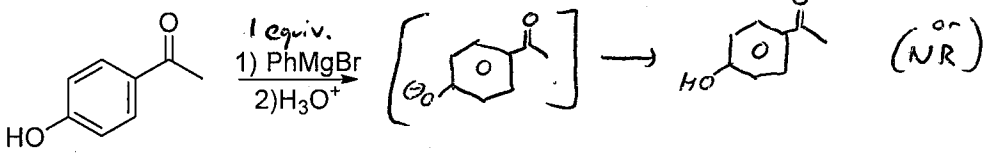
pKa Values

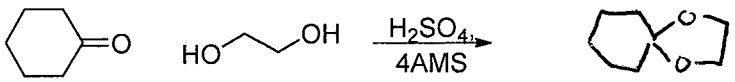
HI	-10	CH_3COOH	4.7	ArOH	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	ROH (R=alkyl)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

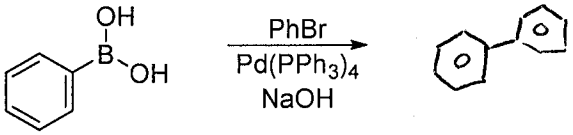
Average: 80
St Dev: 19
max: 108
min: 15

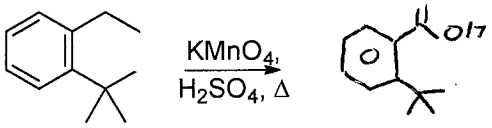
1) Predict the major product of the following reactions. If no reaction occurs, then write NR. Do not show stereochemistry. (30 pts; 3 pts each)

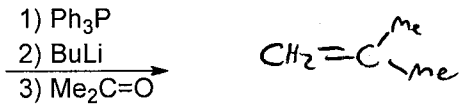
a. 

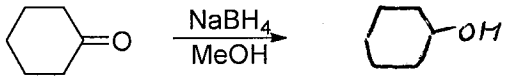
b. 

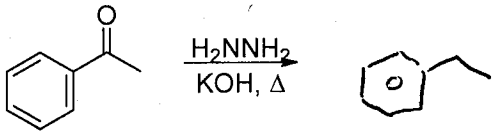
c. 

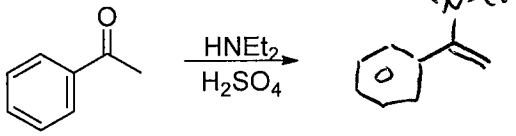
d. 

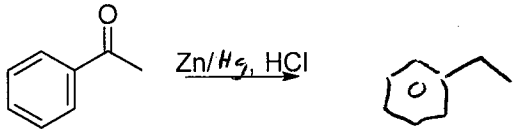
e. 

f. CH_3I 

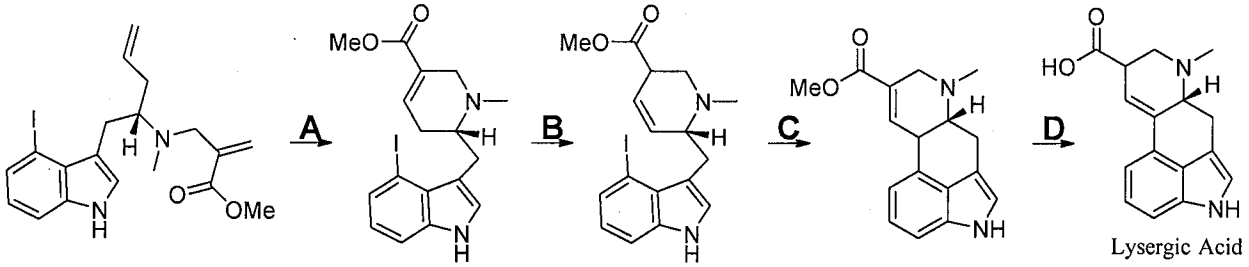
g. 

h. 

i. 

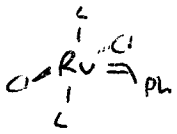
j. 

2) Lysergic acid is a precursor for a wide range of psychoactive compounds including LSD (lysergic acid diethylamide). A new synthesis of lysergic acid was recently published; a few steps of this synthesis are shown below. (15 pts)



a. What reaction is happening in step A? What reagents are used for this step? (5 pts)

Grubbs metathesis → G2, or Grubbs, or

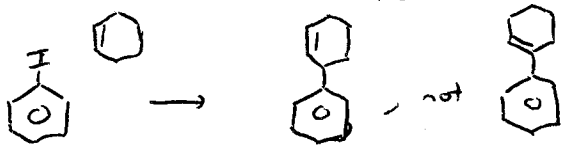


b. What reaction is happening in step C? What reagents are used for this step? (5 pts)

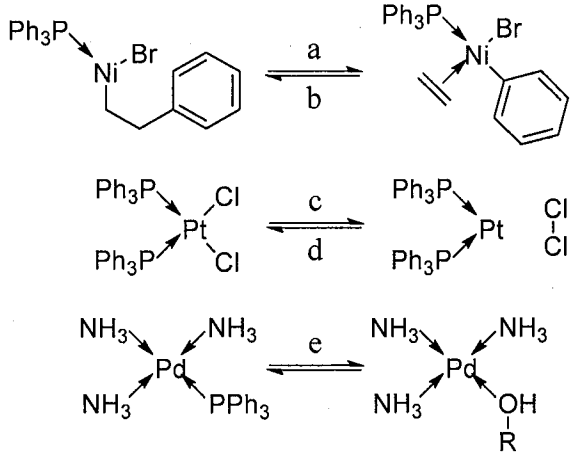
Heck rxn → $Pd(PAr_3)_4$ + Et_3N

c. What changes occur to the molecule during step D? Given the regiochemical outcome of step C, why is step D necessary? (5 pts)

Heck rxn on cycloalkenes produces alkene in wrong location, compared to where it needs to be in D. (Also in D, ester at top left has become an acid).



3) Label each of the steps in terms of basic transition metal-ligand reaction steps. (5 pts)



Describe each step:

a. β-elimination

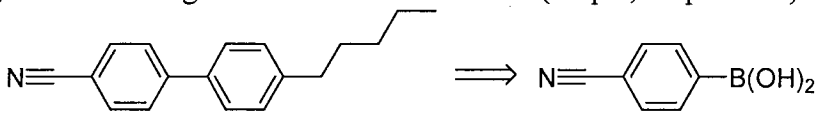
b. ligand insertion

c. reductive elimination

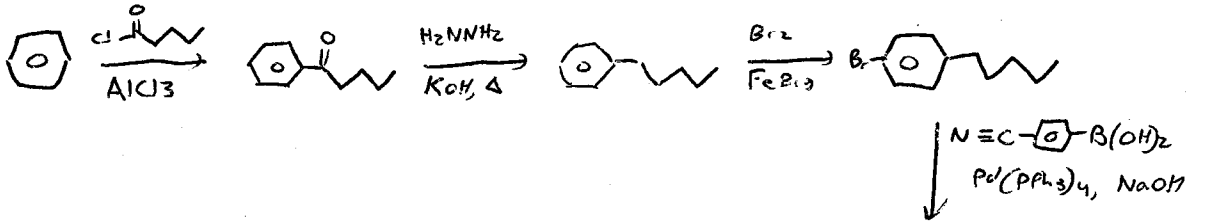
d. oxidative addition

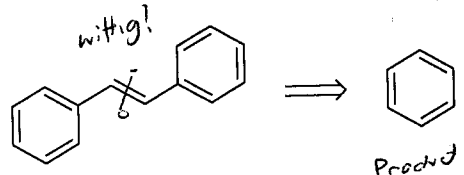
e. ligand substitution

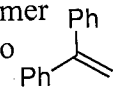
4) Find a way to synthesize the desired product from the given starting material plus any other reagents containing at most six carbon atoms. (30 pts; 10 pts each)

a. 

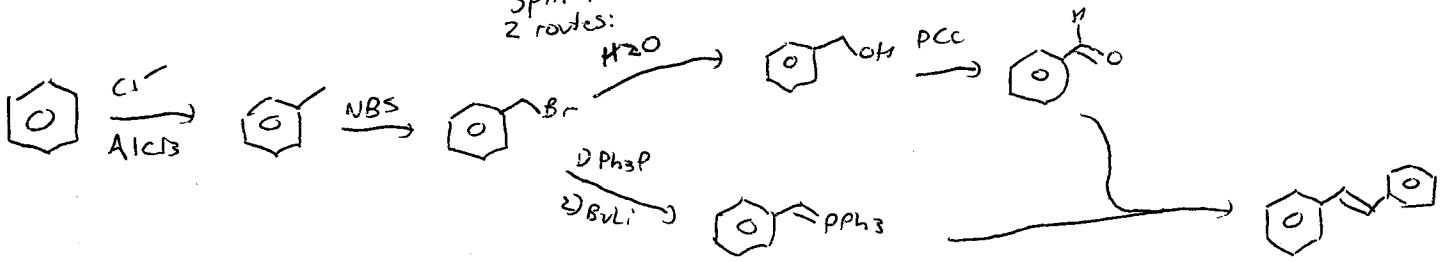
Make right side:

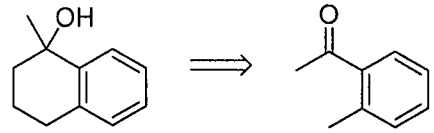


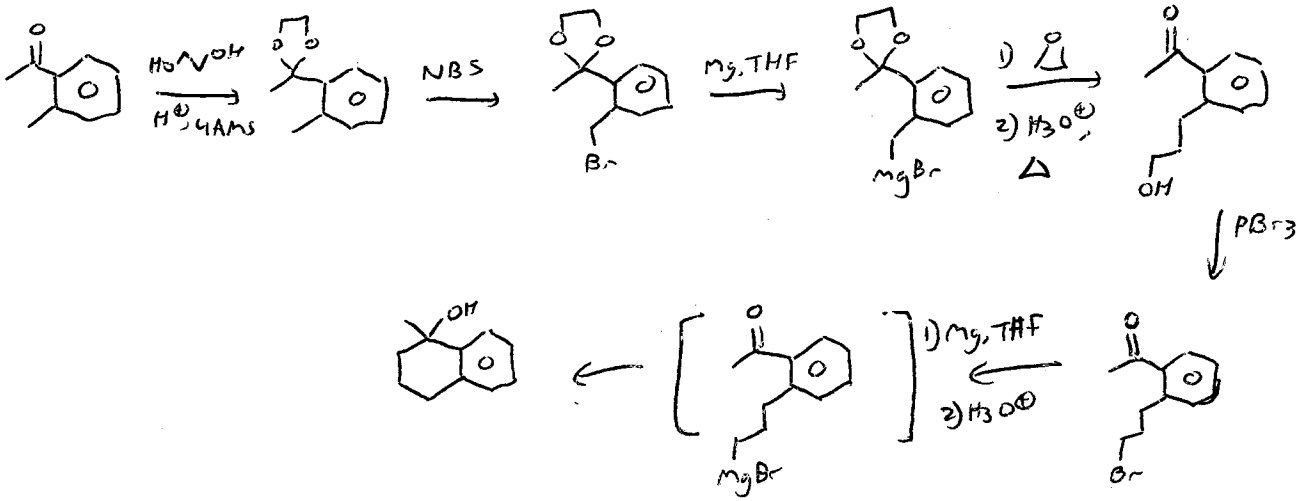
b. 

This should be the **only** regioisomer formed - no 

Product is split into 2 routes:

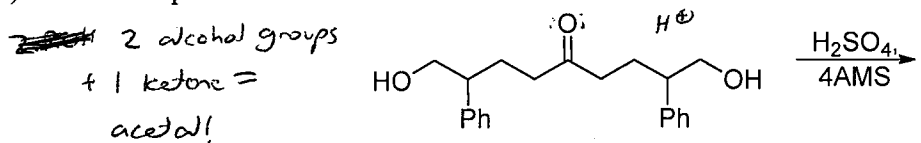


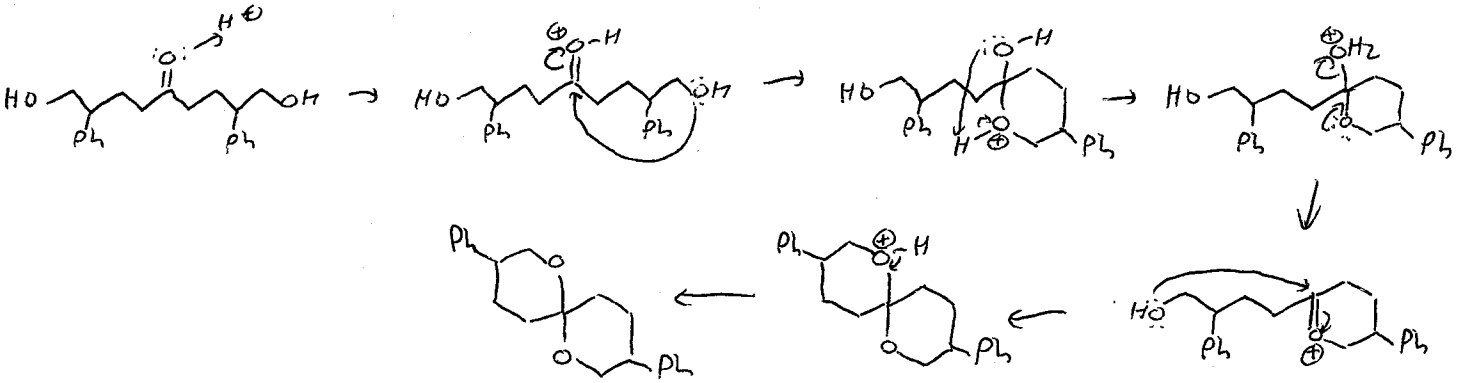
c. 



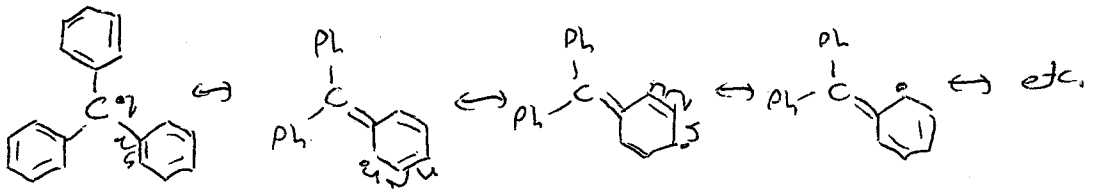
5) Show the product of this reaction and the mechanism for its formation. (15 pts)

~~2~~ 2 alcohol groups + 1 ketone = acetal!





6) Moses Gomberg was the first chemist to synthesize the trityl radical, $Ph_3C\cdot$, which is extraordinarily stable for a radical. Explain its stability in 20 words or less. (5 pts)



This radical is triply benzylic, so there are (3 locations per ring) + (1 location on central C) = 10 possible locations for radical & it's very heavily resonance-stabilized.

7) Extra credit! Rank these compounds by how much they favor forming the gem-diol (1 = largest amount of gem-diol at equilibrium). (10 pts e.c.)