CHEM 3331 (Richardson) Midterm Exam 2 – Mar. 12, 2019

Your Name: Key

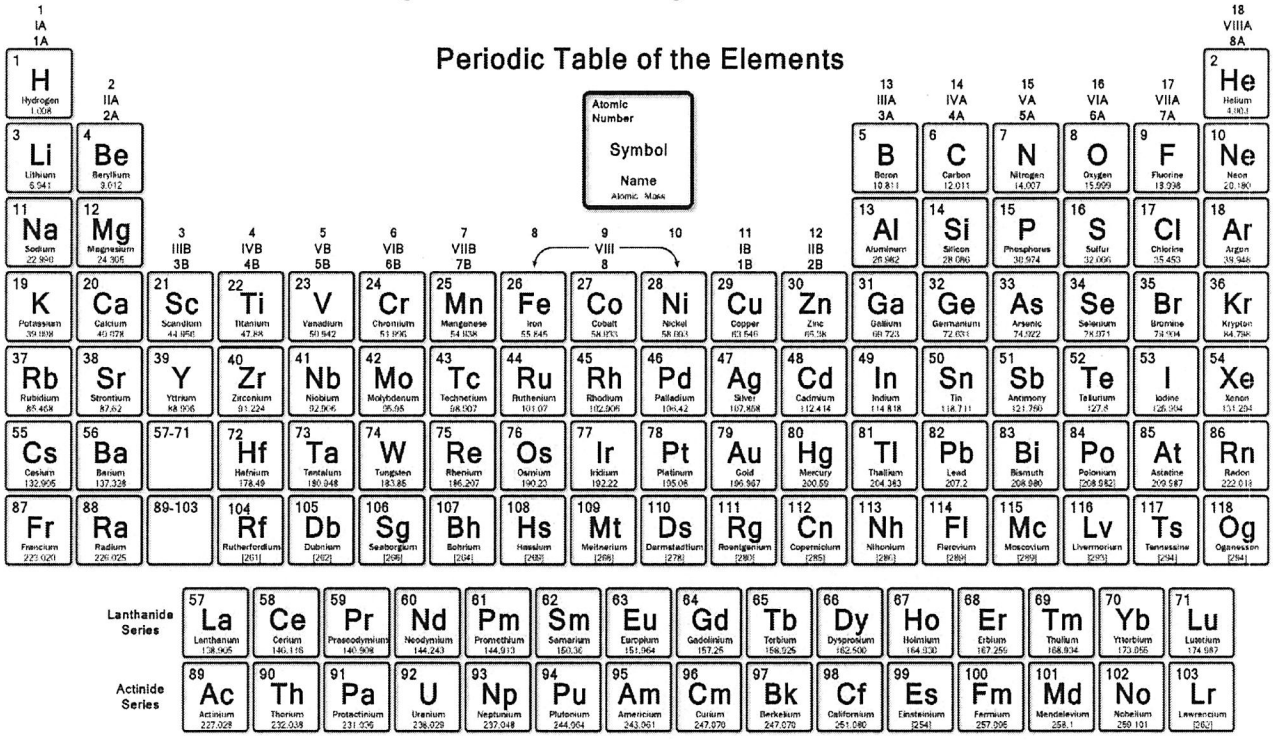
Student ID: _____

Recitation (check one)

O 130 (Wed 8:00 w/ Olivia)
O 134 (Wed 12:00 w/ Olivia)
O 136 (Wed 2:00 w/ Lacey)
O 138 (Wed 4:00 w/ Lacey)
O 141 (Thu 9:00 w/ Chance)
O 143 (Thu 11:00 w/ Chance)
O 145 (Thu 1:00 w/ Lacey)
O 147 (Thu 3:00 w/ Will)
O 149 (Thu 5:00 w/ Will)
O 235 (Wed 1:00 w/ Lauren)
O 237 (Wed 3:00 w/ Lauren)
O 239 (Wed 5:00 w/ Zepeng)
O 240 (Thu 8:00 w/ Zhenhao)
O 242 (Thu 10:00 w/ Lauren)
O 244 (Thu 12:00 w/ Lauren)
O 246 (Thu 2:00 w/ Brianna)
O 248 (Thu 4:00 w/ Brianna)

Question	Score	Out of
1		16
2		14
3		30
4		20
5		5
6		15
8		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 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.

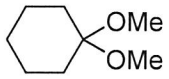


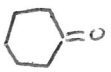
pKa Values

HI	-10	CH_3COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN_3	4.7	RSH	10-12	H_2	35
HCl	-6	H_2S	7.0	H_2O	15.7	NH_3	36
H_3O^+	-1.7	NH_4^+	9.3	ROH	16-18	$H_2C{=}CH_2$	45
HF	3.2	HCN	9.4	O=C-CH	9-25	CH_4	60

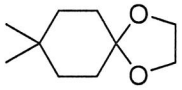
Average: 72.4
St. Dev: 20.3
Max: 101
Min: 6

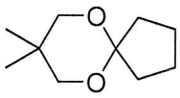
1) Show the product(s) formed if these compounds were exposed to H_3O^+ and heat. (16 pts)

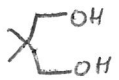
a. 

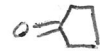


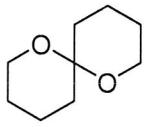
+ 2x HOMe

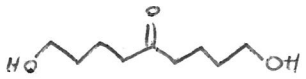
c. 

b. 



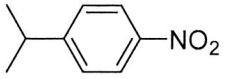
+ 

d. 

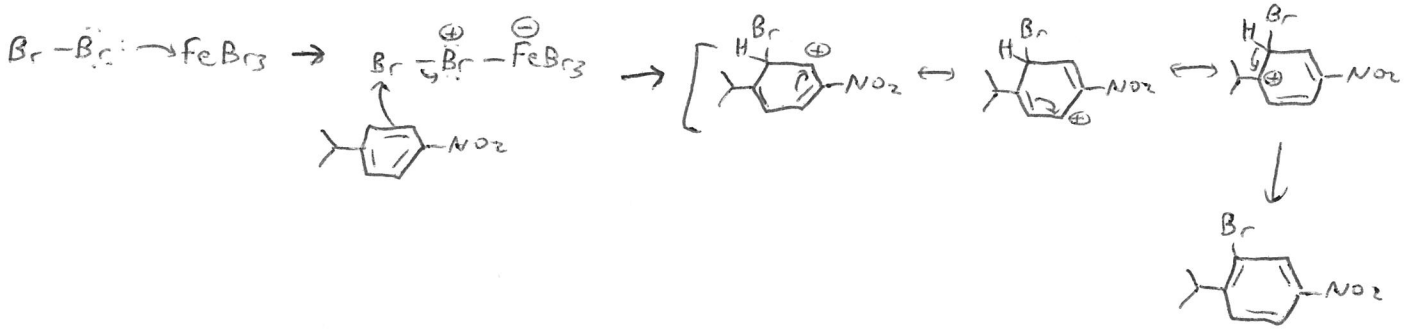


2) The directing effects of groups during electrophilic aromatic substitution reactions can be explained by resonance. (14 pts)

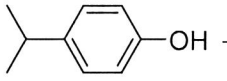
a. The reaction below produces a single isomer as the major product. Show the mechanism for its formation, including all resonance forms for the intermediate. (6 pts)



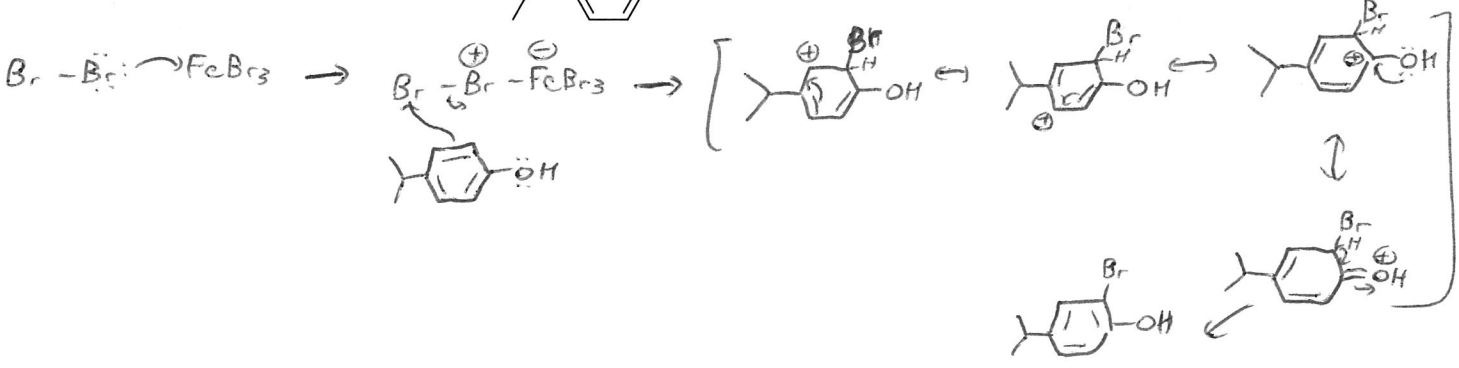
Br_2, $FeBr_3$



b. The reaction below produces a single isomer as the major product. Show the mechanism for its formation, including all resonance forms for the intermediate. (6 pts)

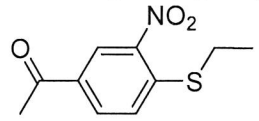


Br_2, $FeBr_3$

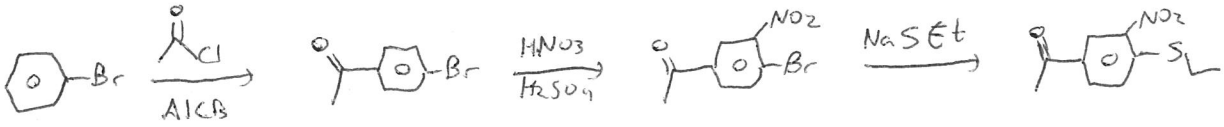


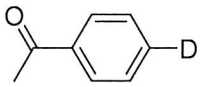
c. Which reaction would be faster? (2 pts) b) OH is a stronger activating group.

3) Find a way to synthesize the desired product from any reagents containing at most six carbon atoms, or triphenylphosphine, or any transition metal catalyst. (30 pts)

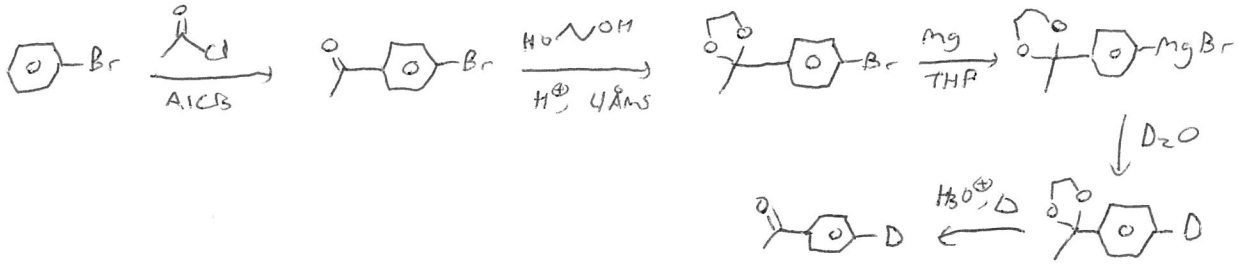
a. 

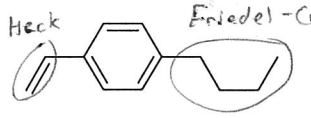
Do Friedel-Crafts before nitration



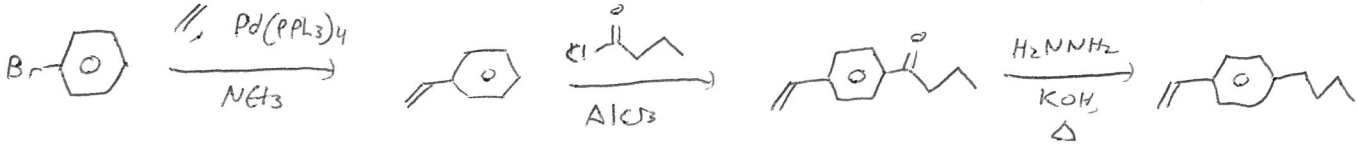
b. 

Protect carbonyl during Grignard formation/rxn



c. 

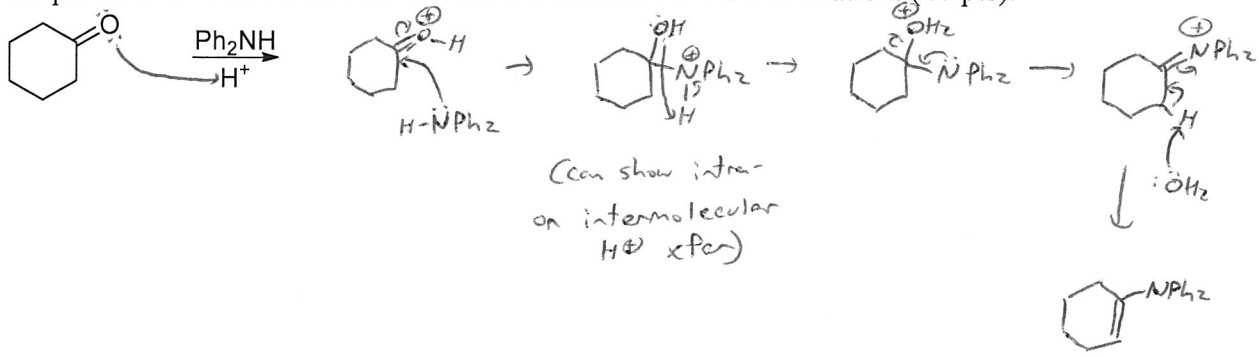
Friedel-Crafts acylation, then lose carbonyl (use base, not acid)



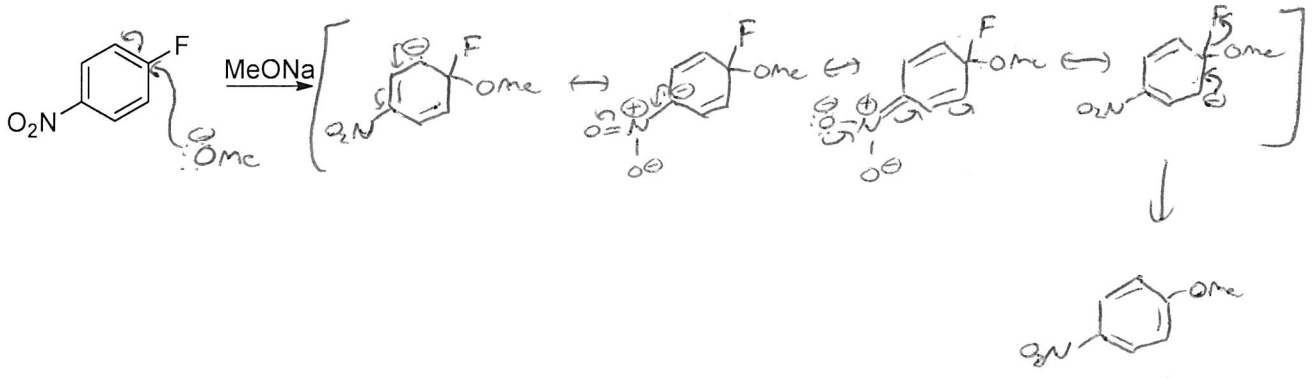
4) Show the products of these reactions and the mechanism for their formation. (20 pts).

Show res. forms of all ints.

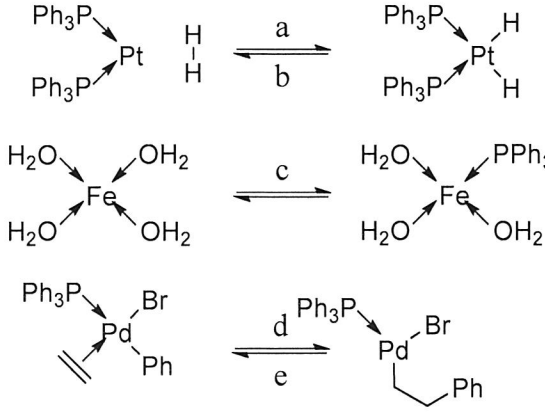
a.



b.



5) Label each of these basic transition metal-ligand reaction steps. (5 pts)



Describe each step:

a. oxidative insertion

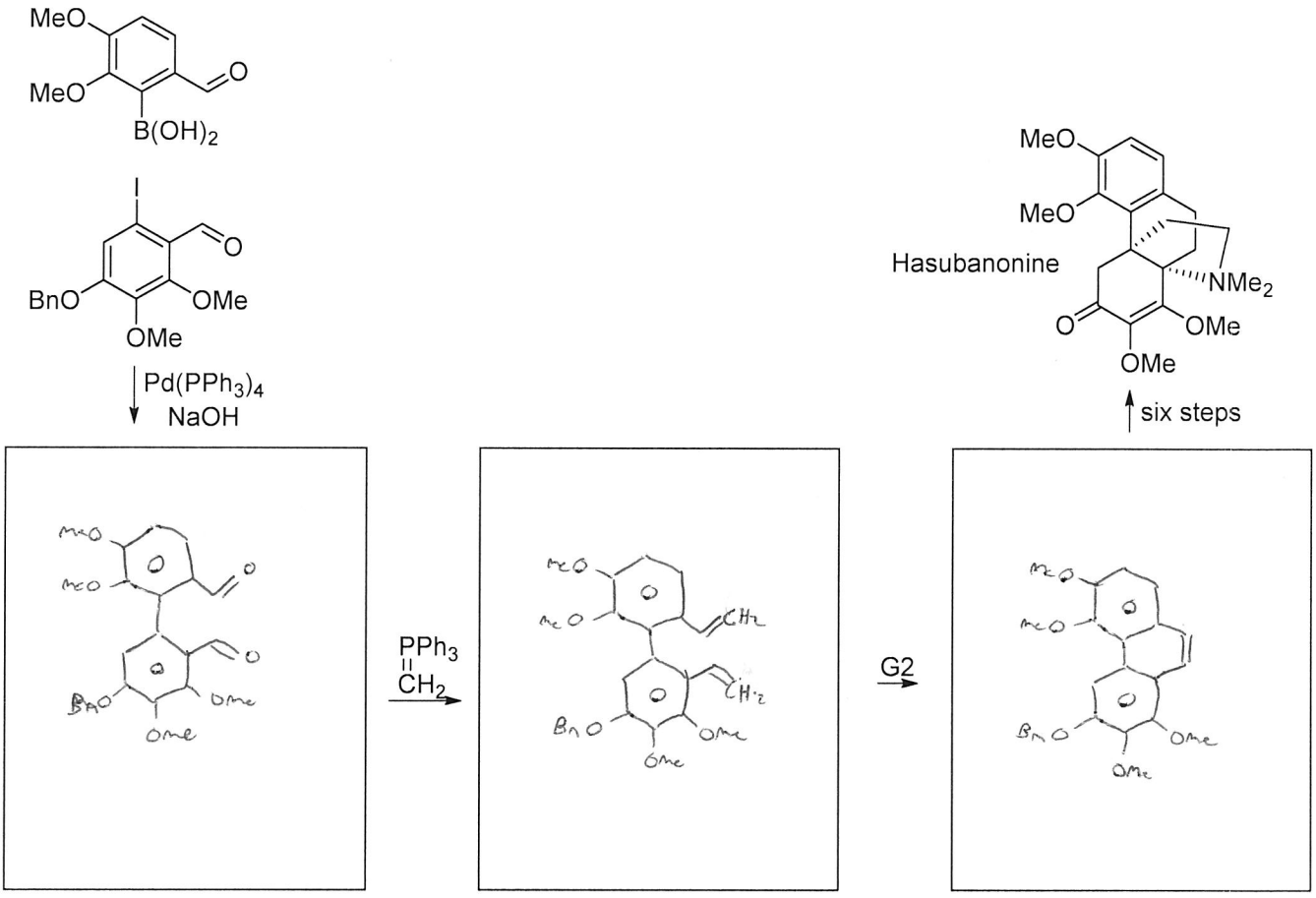
b. reductive elimination

c. ligand substitution

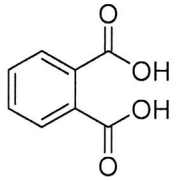
d. ligand insertion

e. β-elimination

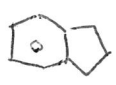
6) Hasubanonine was recently synthesized by the following route. Fill in the boxes. (15 pts)

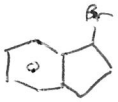


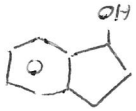
7) Extra credit! A hydrocarbon A, C_9H_{10}, is treated with N-bromosuccinimide to give a single monobromo compound B. When B is dissolved in aqueous acetone it reacts to give two nonisomeric compounds: C and D. Catalytic hydrogenation of D gives back A, and C can be separated into enantiomers. When optically active C is oxidized with CrO_3 and pyridine, an optically inactive ketone E is obtained. Vigorous oxidation of A with $KMnO_4$ affords phthalic acid (shown below). Propose structures for compounds A through E, and explain your reasoning. (10 pts e.c.)



Phthalic acid

A: 

B: 

C: 

D: 

E: