CHEM 3331 (Richardson) Final Exam – May 8, 2018

Your Name: Key

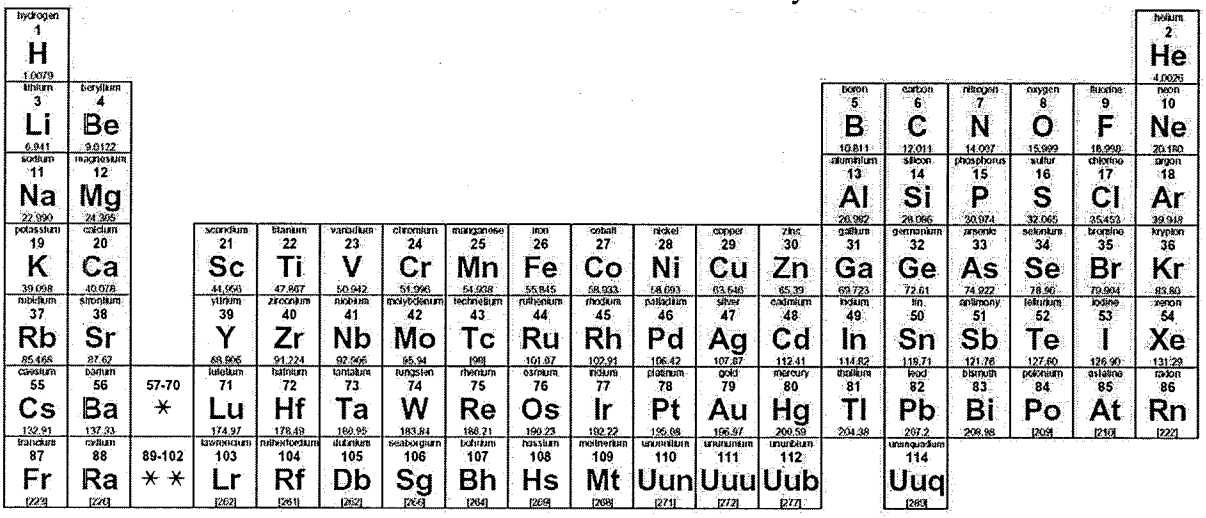
Student ID: _____

Recitation (check one)

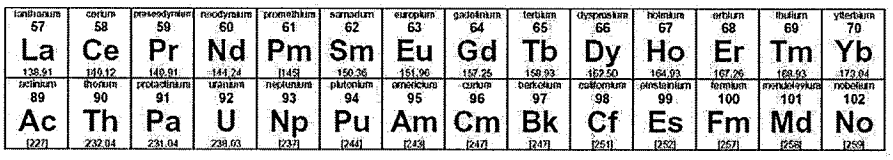
O 12:00 Wed (Patrick Li)
O 4:00 Wed (Michael Ortiz)
O 11:00 Thu (Josh Kamps)
O 3:00 Thu (Rachel Weintraub)
O 8:00 Wed (Rachel Weintraub)
O 2:00 Wed (Patrick Li)
O 9:00 Thu (Josh Kamps)
O 1:00 Thu (Aaron Hinds)
O 5:00 Thu (Rachel Weintraub)

Question	Score	Out of
1		30
2		25
3		20
4		45
5		30
6		20
7		30
8		20 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. 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.



*Lanthanide series



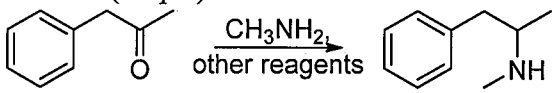
**Actinide series

pKa Values

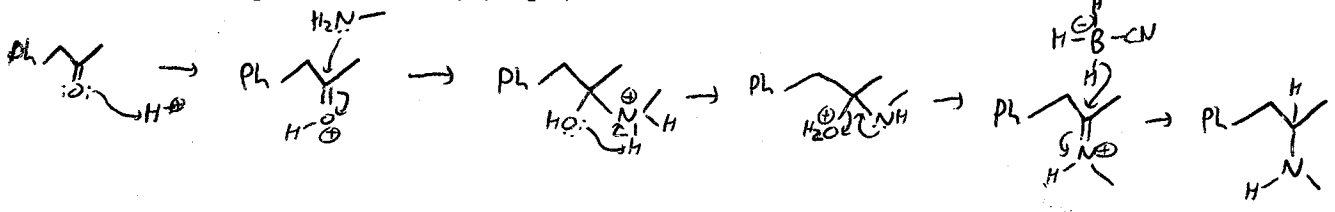
HI	-10	CH_3COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN_3	4.7	RSH	10-12	H_2	35
HCl	-6	H_2S	7.0	H_2O	15.7	NH_3	36
H_3O^+	-1.7	NH_4^+	9.3	ROH (R=alkyl)	16-18	$H_2C{=}CH_2$	45
HF	3.2	HCN	9.4	O=C-CH (α H)	9-25	CH_4	60

Average: 151
St. Dev: 40.2
Max: 216
Min: 41

1) In the television series "Breaking Bad", Walt and Jesse synthesize methamphetamine from phenylacetone and methylamine. (30 pts)

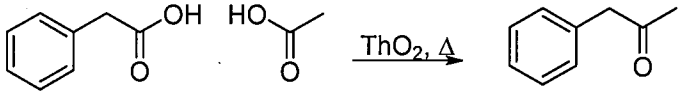


a. What other reagents are typically needed for this reaction? Show the mechanism. (Hint: the mechanism for the last part is similar to reduction of a ketone, only the nitrogen needs to be protonated first.) (10 pts)

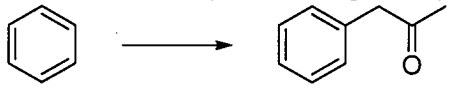


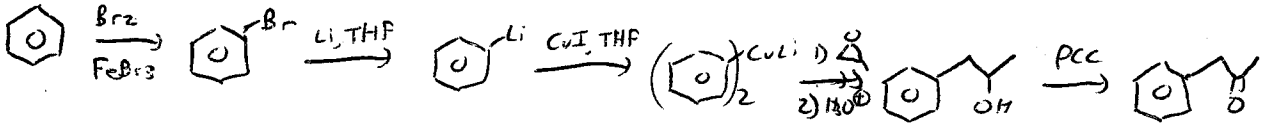
*(2 pts per intermediate/set of arrows)

b. Since phenylacetone is on the controlled substances list precisely because it is used for this purpose, they end up having to synthesize it from phenylacetic acid and acetic acid.



This is not a reaction that we've covered, so instead, show a way to synthesize phenylacetone starting with benzene and any other reagents. (10 pts)

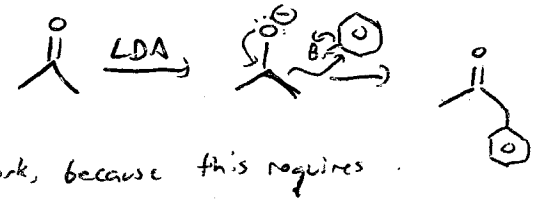




*1 pt per intermediate prod
*1 pt per set of reagents

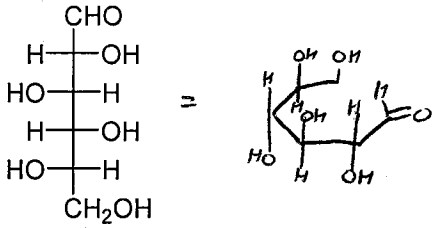
c. Is it possible to synthesize phenylacetone from the α-alkylation of a ketone? Why or why not? (10 pts)

It would look like:



But it doesn't work, because this requires SN2 on aryl bromide.

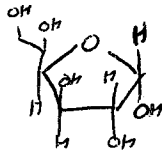
2) One enantiomer of idose is shown below. (25 pts)



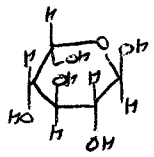
a. Is this the (L) or **D** enanatiomer of idose? (3 pts)

Draw the following structures for this compound (you don't need to show stereochemistry on parts that are outside the ring). (5 pts each)

b. Haworth projection
for β-furanose form

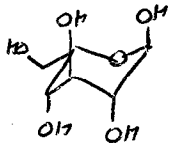


c. Haworth projection
for α-pyranose form



(OK not to show Hs explicitly for all of these)

d. One chair conformation
for α-pyranose form

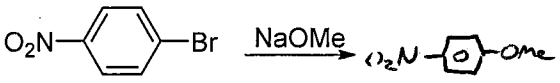


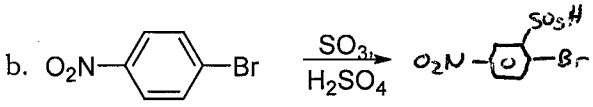
(No pts deduction for error carried forward from c)

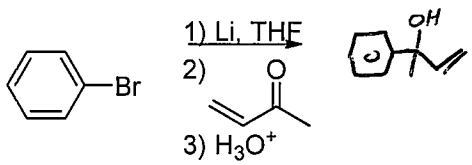
e. The other chair conformation
for α-pyranose form

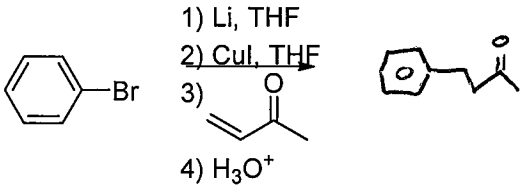
f. Circle all of the terms that describe this compound: (aldose) ketose, pentose, (hexose) (2 pts)

3) Predict the major product of the following reactions. If no reaction occurs, then write NR. Do not show stereochemistry. (20 pts; 5 pts each)

a. 

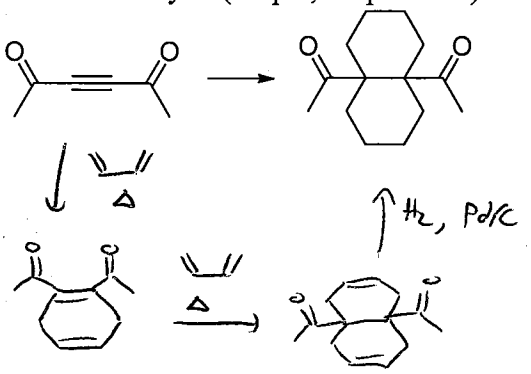
b. 

c. 

d. 

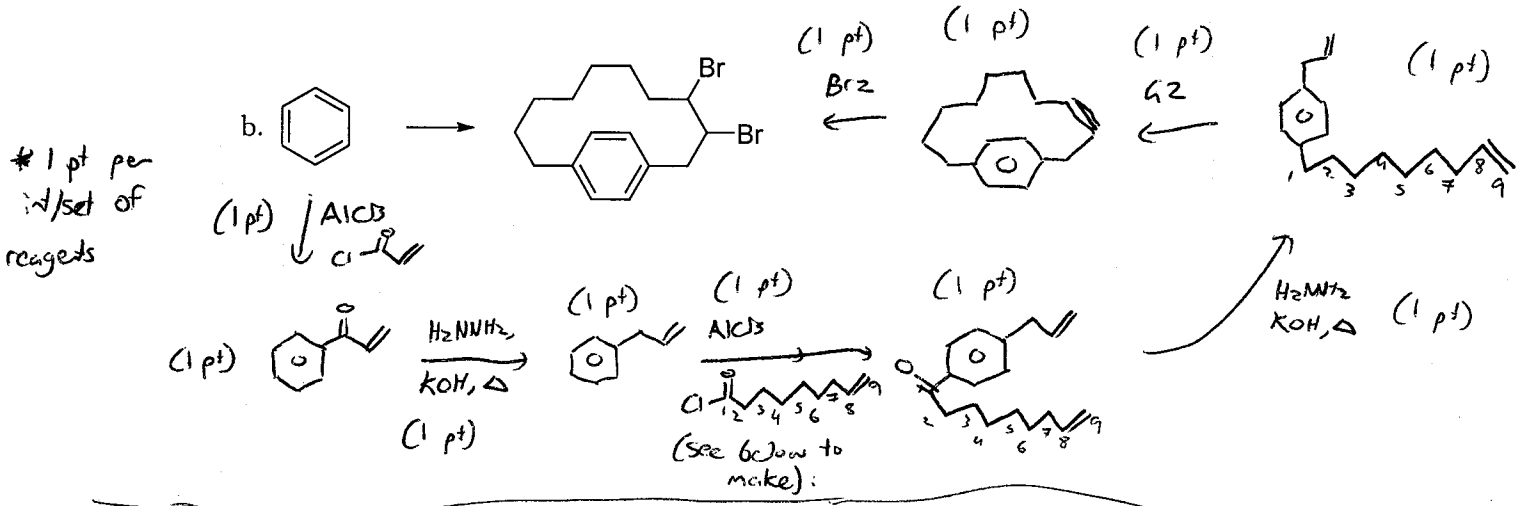
4) Find a way to synthesize the desired product from the given starting material plus any other reagents containing at most eight carbon atoms, or triphenylphosphine, or any transition metal-based catalyst. (45 pts; 15 pts each)

a.

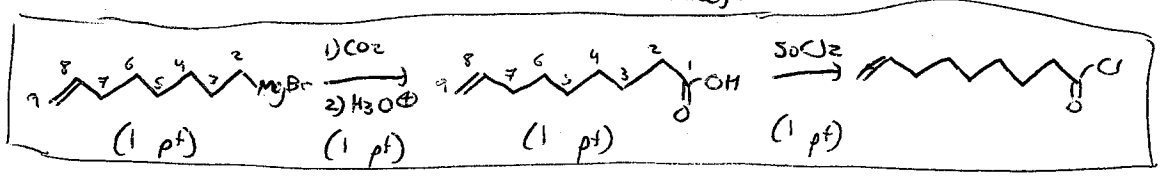


* 3 pts per intermediate/set of reagents

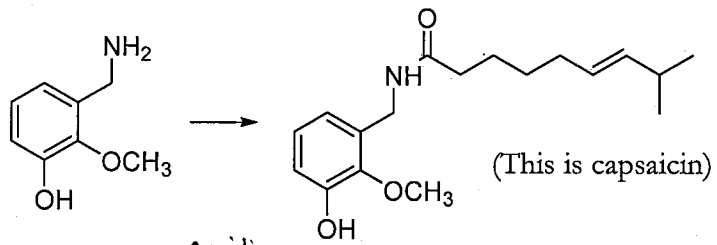
b.



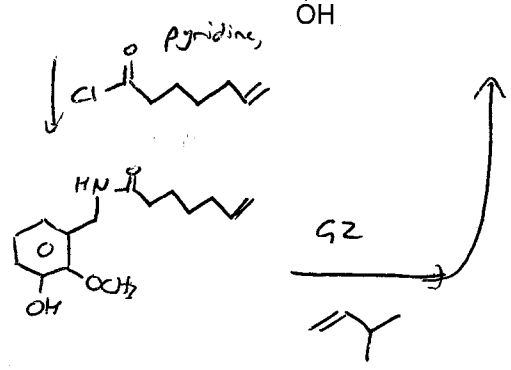
* 1 pt per int/set of reagents



c.

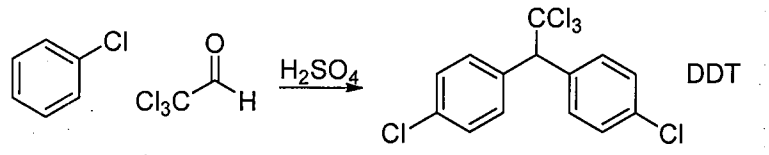


(This is capsaicin)

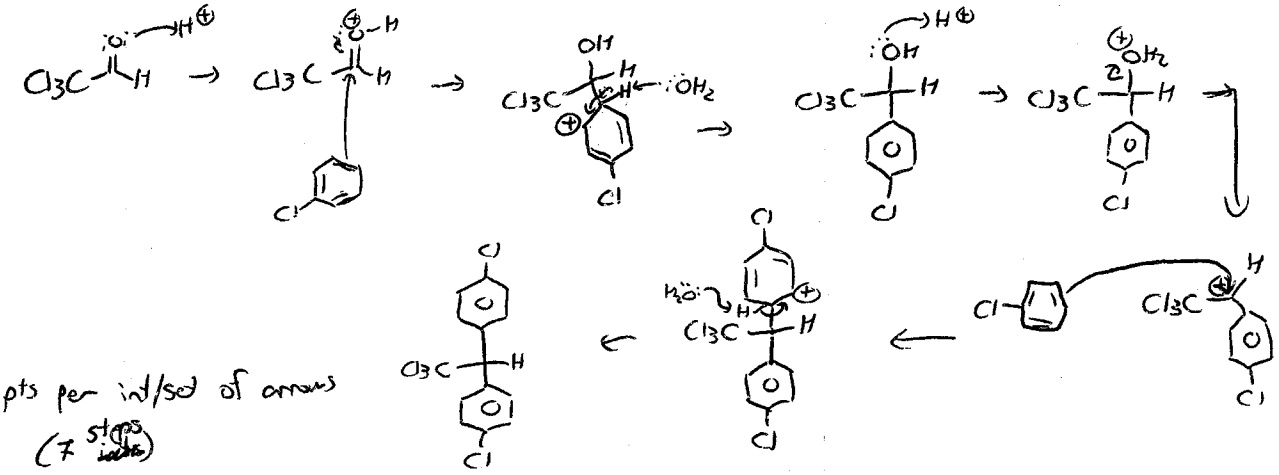


* 5 pts per intermediate/ set of reagents

5) The insecticide DDT (*p*-dichlorodiphenyltrichloroethane) is prepared by following route. Suggest a mechanism for this reaction. (Hint: although Friedel-Crafts is the most common way to generate an alkyl electrophile, we've seen a couple of other ways to do it. How could you make one of these reagents more electrophilic, under these circumstances?) (30 pts)



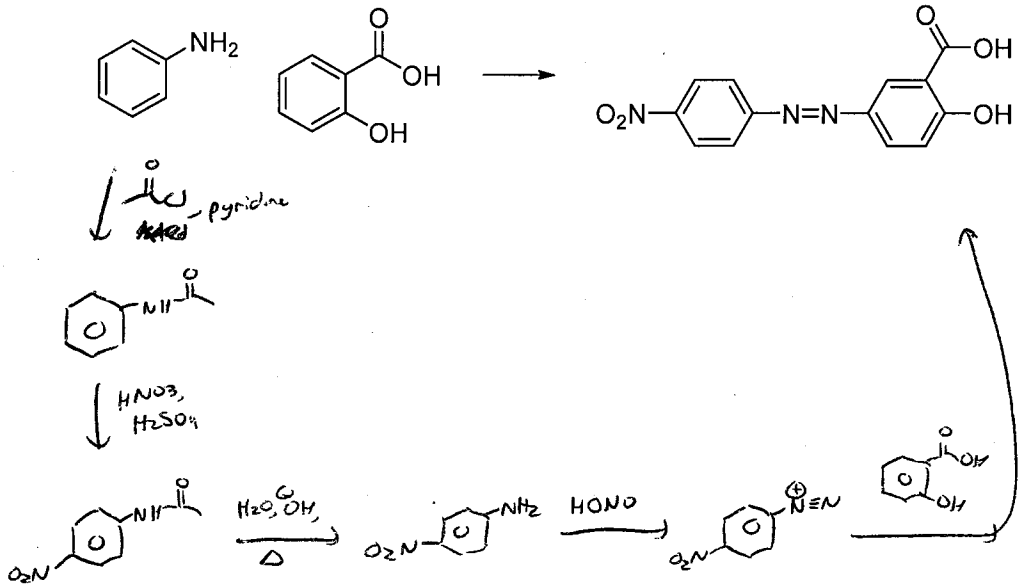
Here is a poem about DDT:
A mosquito was heard to complain
That a chemist had poisoned his brain.
The cause of his sorrow
Was *para*-dichloro
Diphenyltrichloroethane.



*4 pts per int/set of arrows (7 steps)

* 2 pts for product.

6) Show how to synthesize Alizarin Yellow R from aniline and salicylic acid. (Hint: you may need to modify the reactivity of the NH_2 group before adding the NO_2 group.) (20 pts)

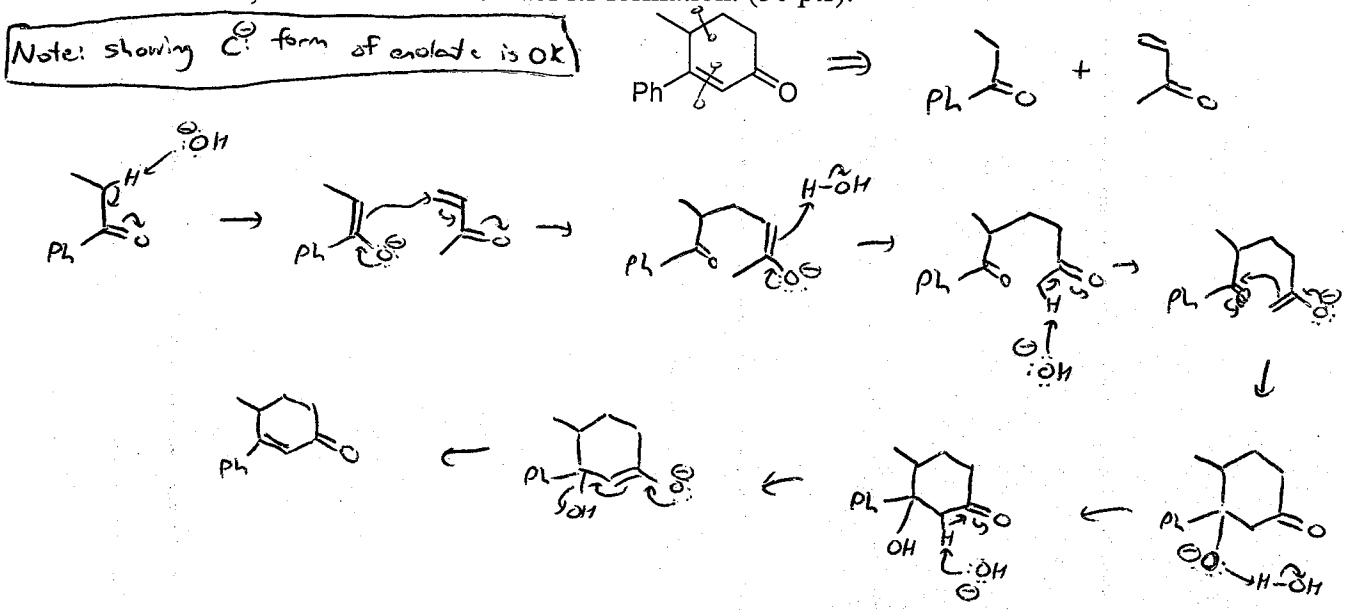


*2 pts per intermediate/product

*2 pts per set of reagents

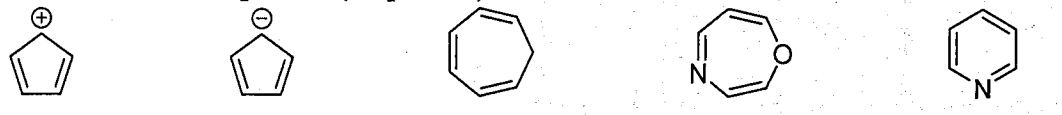
7) Show the precursors you would use to synthesize the following compound via the Robinson annulation, and the mechanism for its formation. (30 pts).

Note: showing $C^{\ominus}$ form of enolate is OK



* 6 pts for precursors
* 4 pts for each set of arrows

8) Extra credit! Describe each of the structures below as aromatic, nonaromatic, or antiaromatic. Assume each structure is planar. (20 pts e.c.)



Antiaromatic Aromatic Nonaromatic Nonaromatic Aromatic