CHEM 3331 (Richardson) Final Exam – Dec. 14, 2024

Your Name: Key

Student ID: _____

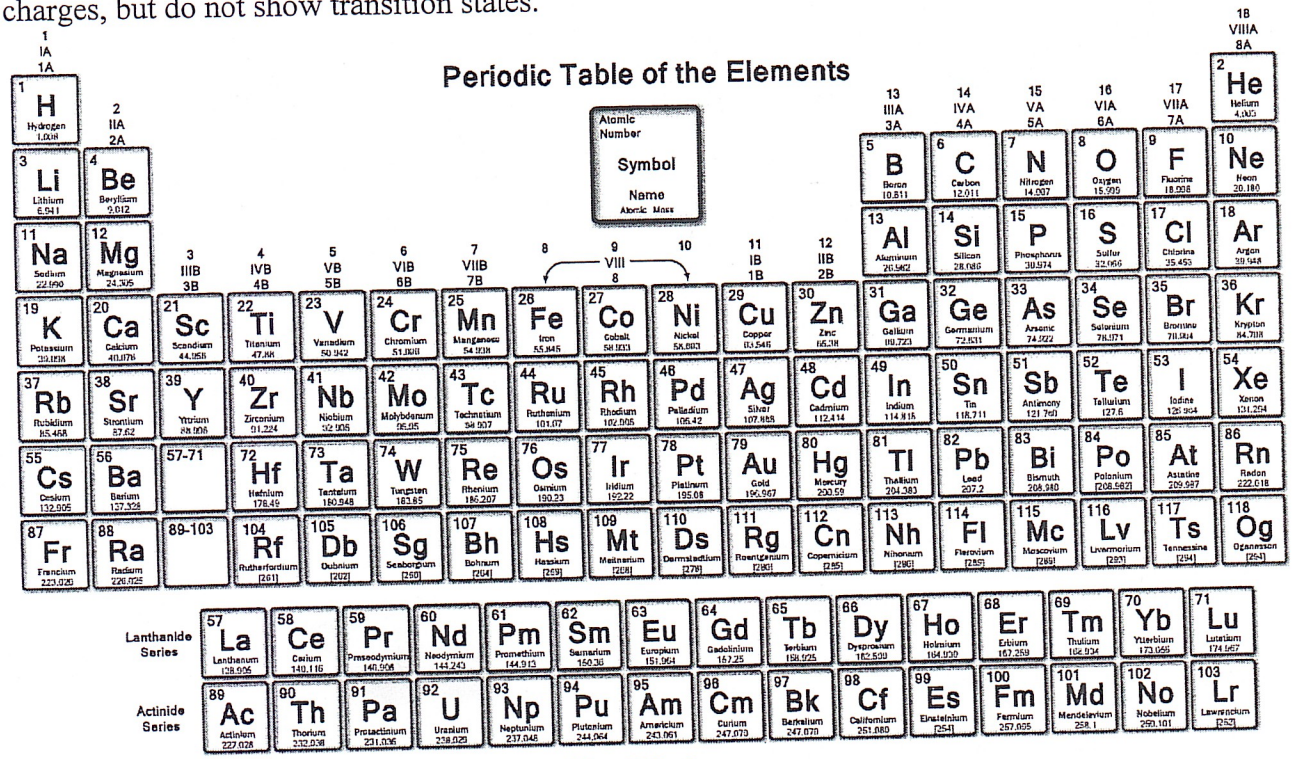
Recitation TA (fill in one circle):

- O 134 (Phil Pham)
- O 135 (Phil Pham)
- O 136 (Max Abreu)
- O 137 (Max Abreu)
- O 141 (Phil Pham)
- O 142 (Phil Pham)
- O 143 (Zhehao Yuan)
- O 144 (Tania Shahvali)
- O 147 (Tania Shahvali)

Question	Score	Out of
1		30
2		40
3		~~30~~ 40
4		50
5		50
6		20 e.c.
Total		200

Wloops, mislabeled this Q. This means that test is really out of 230 pts, not 220, but it's still scored as being out of 200.

This is a closed-book exam, except for two double-sided sheets of 8.5 x 11" paper. The use of 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.

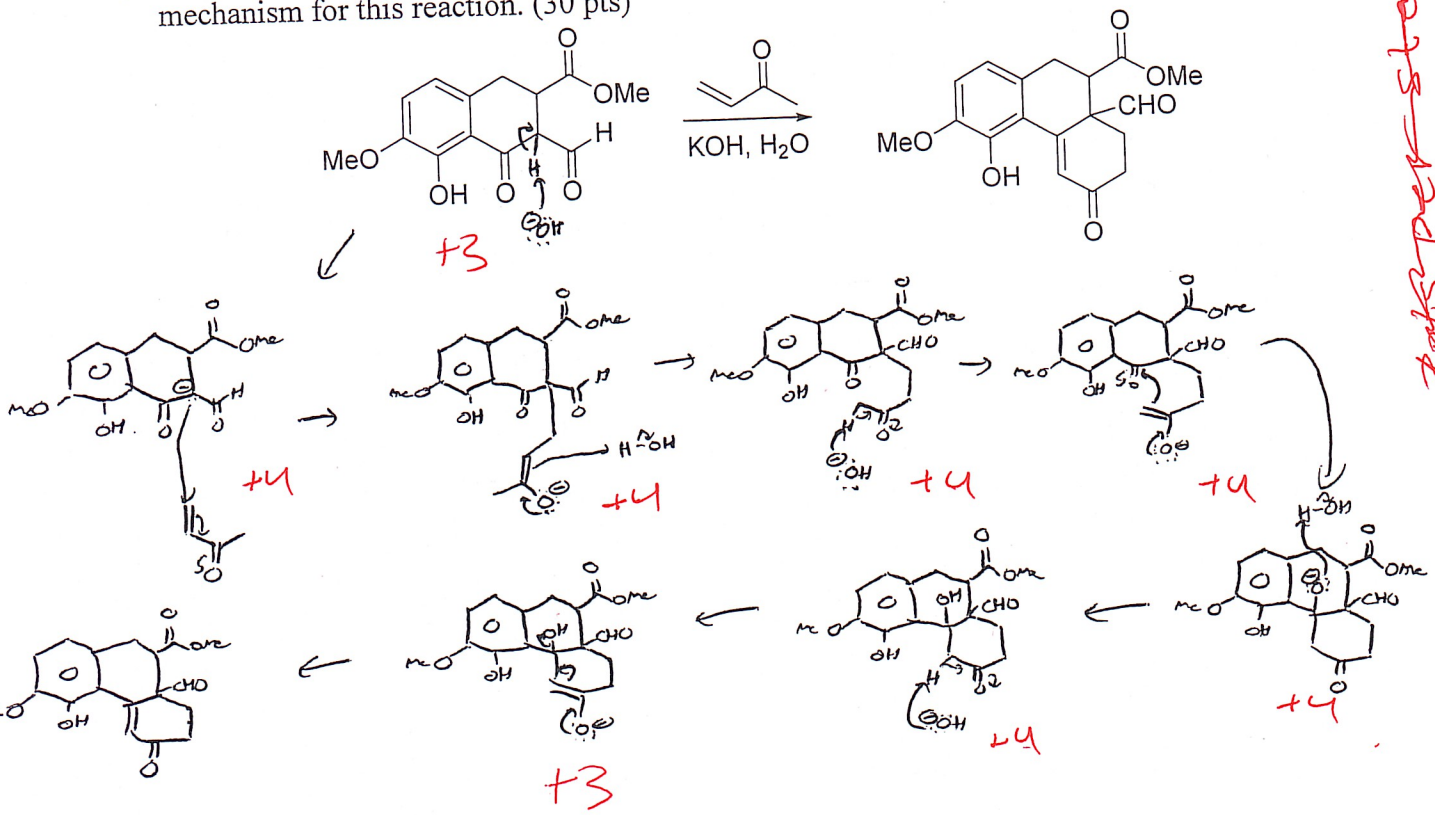


pKa Values

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

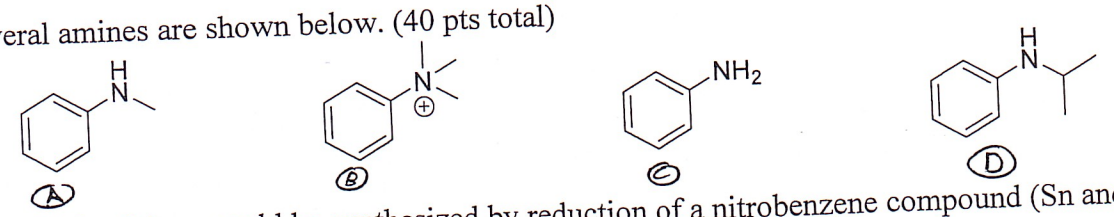
Avg: 153.8
Curve: 0
St. Dev: 50.4
Max: 225

1) A recently-published synthesis of codeine includes a Robinson annulation. Draw out the mechanism for this reaction. (30 pts)

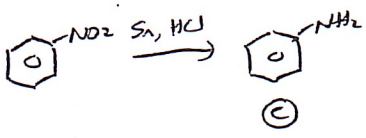


-1 pts for HOEt/⊖OEt

2) Several amines are shown below. (40 pts total)

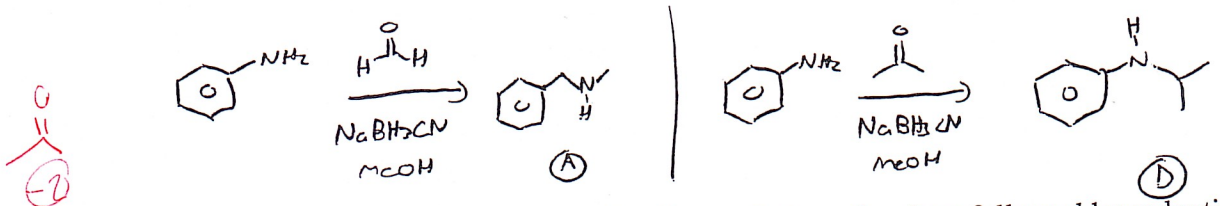


a. Which of them could be synthesized by reduction of a nitrobenzene compound (Sn and HCl)? Show the starting materials for their formation. (10 pts)



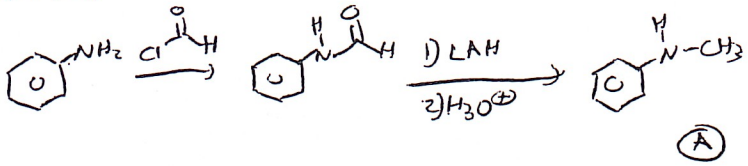
b. Which of them could be synthesized by direction alkylation with alkyl halides (amine + alkyl halide)? Show the starting materials for their formation. (10 pts)

c. Which of them could be synthesized by reductive amination (carbonyl + amine, $NaBH_3CN$, MeOH)? Show the starting materials for their formation. (10 pts)

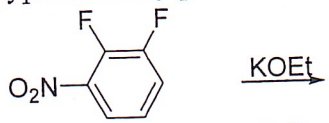


-2

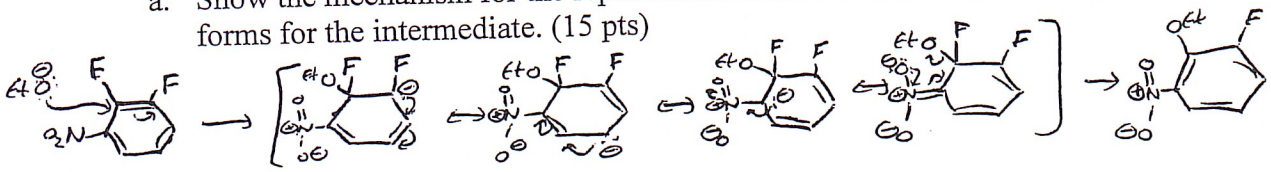
d. Which of them could be synthesized by acylation of amines followed by reduction (acyl chloride + amine, then LAH, then H_3O^+)? Show the starting materials for their formation. (10 pts)



3) The reaction shown below could hypothetically produce multiple products. (40 pts)



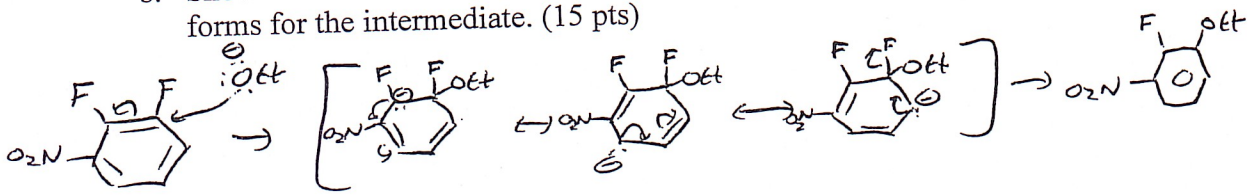
a. Show the mechanism for the replacement of the left fluorine, including all resonance forms for the intermediate. (15 pts)



⊕, not ⊖ -5
Backwards arrows -5
extra/missing 1 res form -3
messed up NO2 resonance -3
~~Reactivity first only~~

"Et" as "tE" -1
OEt violation -5

b. Show the mechanism for the replacement of the right fluorine, including all resonance forms for the intermediate. (15 pts)

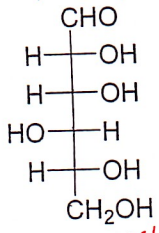


c. In twenty words or less, explain which of these outcomes is favored and why. (10 pts)

The left fluorine, because it allows you to put ⊖ onto O with extra resonance form.

5 pts for left vs. right
5 pts for reasoning

4) One enantiomer of gulose is shown below. (50 pts)

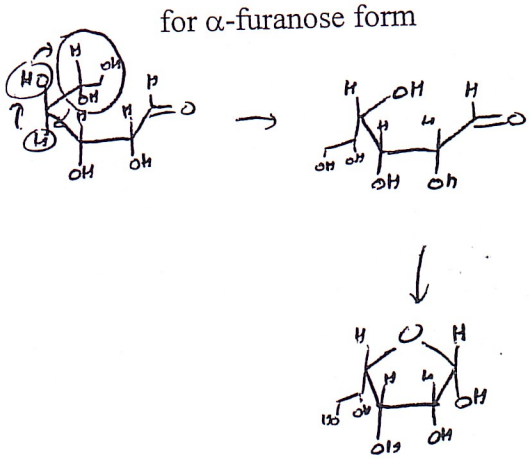


+4 +3 +3

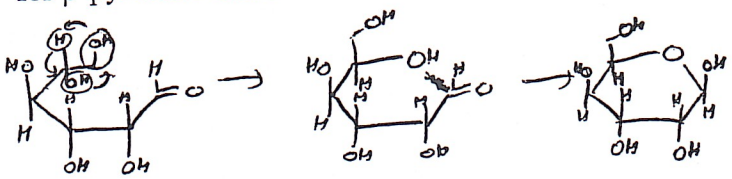
a. Circle the terms to describe this compound: **L**, **D**, aldose, ketose, pentose, hexose (10 pts)

Draw the following structures for this compound (you don't need to show stereochemistry on parts that are outside the ring). (10 pts each)

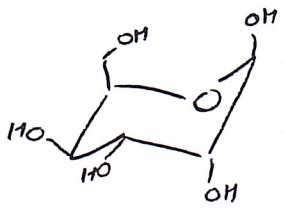
b. Haworth projection
for α-furanose form



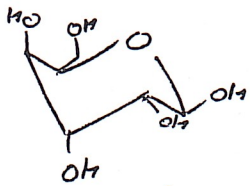
c. Haworth projection
for β-pyranose form



d. One chair conformation
for β-pyranose form



e. The other chair conformation
for β-pyranose form



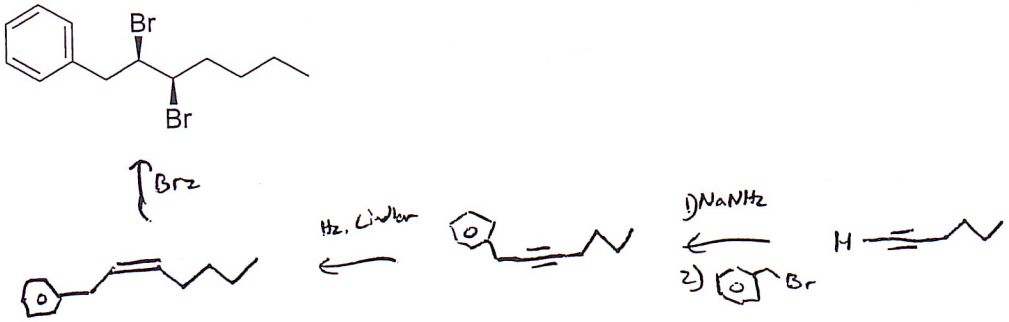
+3 for correct ring size

+5 for α / β

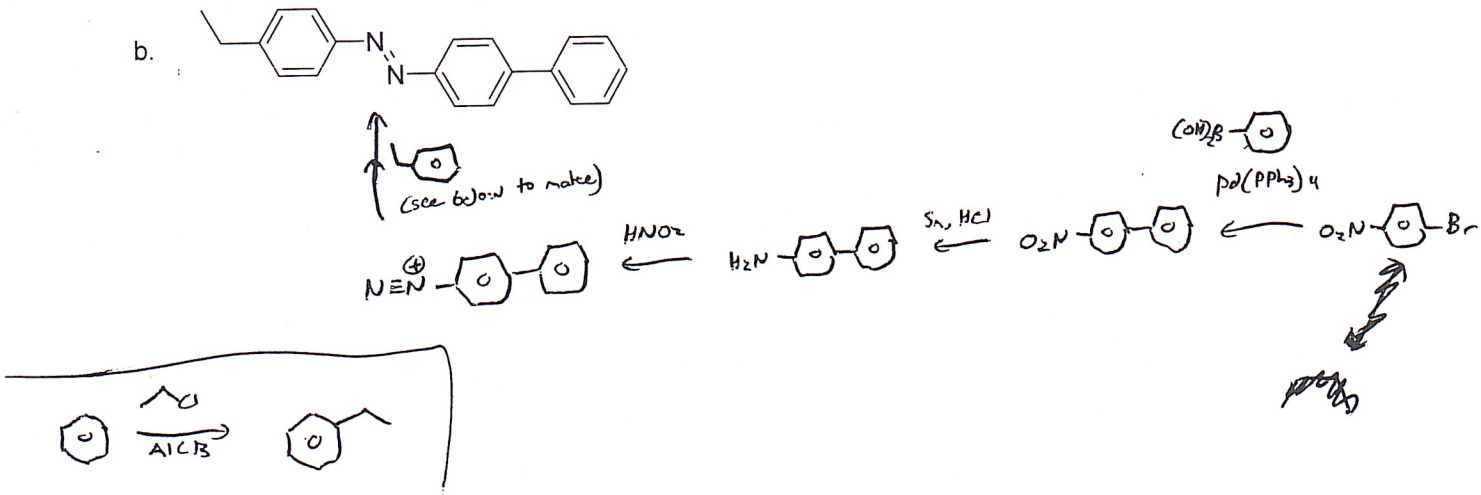
+2 for general correctness

5) Find a way to synthesize the desired product from any reagents containing at most six carbon atoms, or triphenylphosphine, or any transition metal catalyst. (50 pts – 25 pts each)

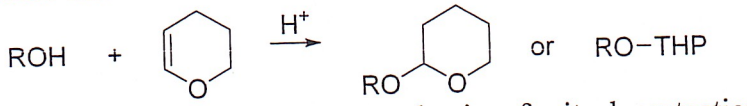
a.



b.

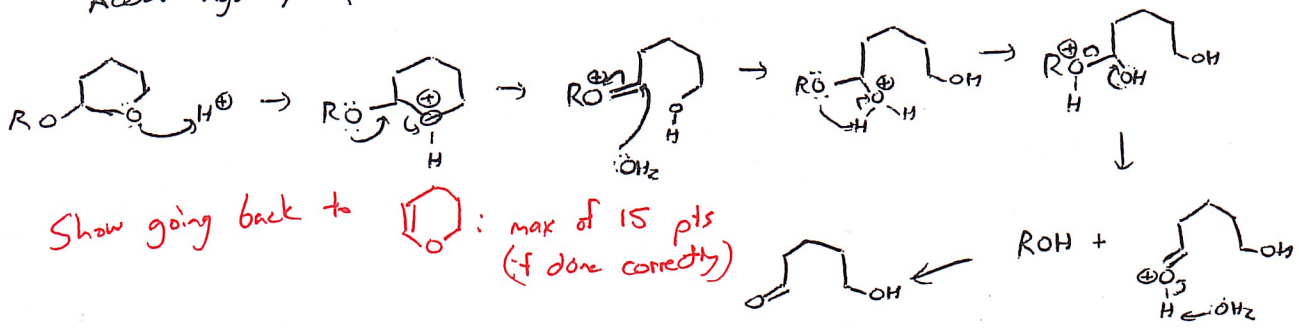


6) Extra credit! We've looked at using acetal protecting groups for carbonyls, but it's also possible to use acetals as protecting groups for alcohols. The THP (tetrahydropyranyl) protecting group can be installed as shown below.



This group deprotects in aqueous acid. Show a mechanism for its deprotection. (20 pts e.c.)

Acetal hydrolysis!



Show going back to : max of 15 pts (if done correctly)