

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

Your Name: _____

Student ID: _____

Recitation TA (fill in one circle):

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|---------------------------------------|--|
| <input type="radio"/> 134 (Phil Pham) | <input type="radio"/> 142 (Phil Pham) |
| <input type="radio"/> 135 (Phil Pham) | <input type="radio"/> 143 (Zhehao Yuan) |
| <input type="radio"/> 136 (Max Abreu) | <input type="radio"/> 144 (Tania Shahvali) |
| <input type="radio"/> 137 (Max Abreu) | <input type="radio"/> 147 (Tania Shahvali) |
| <input type="radio"/> 141 (Phil Pham) | |

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

Periodic Table of the Elements

The periodic table includes the following series at the bottom:

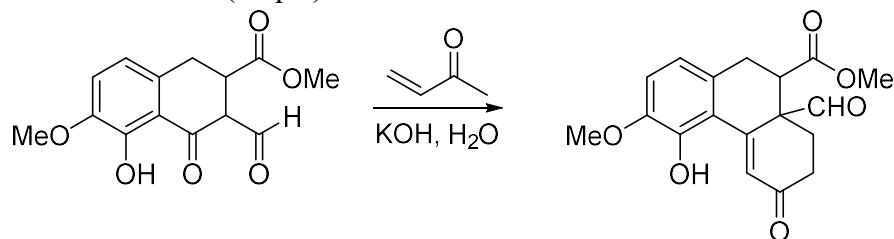
Lanthanide Series: 57 La, 58 Ce, 59 Pr, 60 Nd, 61 Pm, 62 Sm, 63 Eu, 64 Gd, 65 Tb, 66 Dy, 67 Ho, 68 Er, 69 Tm, 70 Yb, 71 Lu

Actinide Series: 89 Ac, 90 Th, 91 Pa, 92 U, 93 Np, 94 Pu, 95 Am, 96 Cm, 97 Bk, 98 Cf, 99 Es, 100 Fm, 101 Md, 102 No, 103 Lr

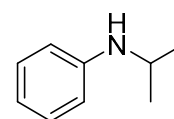
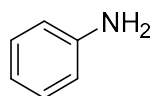
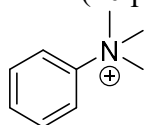
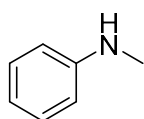
pKa Values

HI	-10	CH ₃ COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN ₃	4.7	RSH	10-12	H ₂	35
HCl	-6	H ₂ S	7.0	H ₂ O	15.7	NH ₃	36
H ₃ O ⁺	-1.7	NH ₄ ⁺	9.3	ROH	16-18	H ₂ C=CH ₂	45
HF	3.2	HCN	9.4	O=C-CH	9-25	CH ₄	60

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



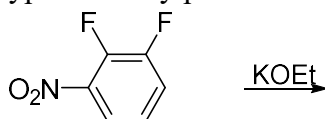
- 2) Several amines are shown below. (40 pts total)



- 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)

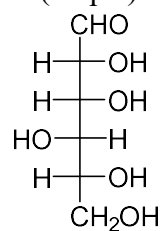
- c. Which of them could be synthesized by reductive amination (carbonyl + amine, NaBH_3CN , MeOH)? Show the starting materials for their formation. (10 pts)
- d. Which of them could be synthesized by acylation of amines followed by reduction (acyl chloride + amine, then LAH, then H_3O^+)? Show the starting 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)
- 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)

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



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)

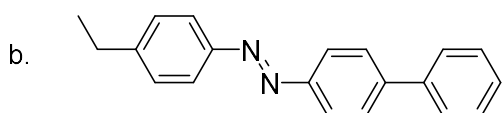
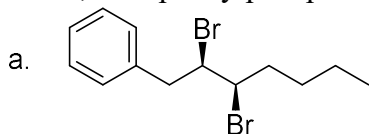
b. Haworth projection
for α -furanose form

c. Haworth projection
for β -pyranose form

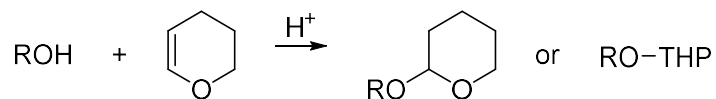
d. One chair conformation
for β -pyranose form

e. The other chair conformation
for β -pyranose form

- 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)



- 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.)