CHEM 3331 (Richardson) Final Exam – Dec. 14, 2022

Your Name: _____

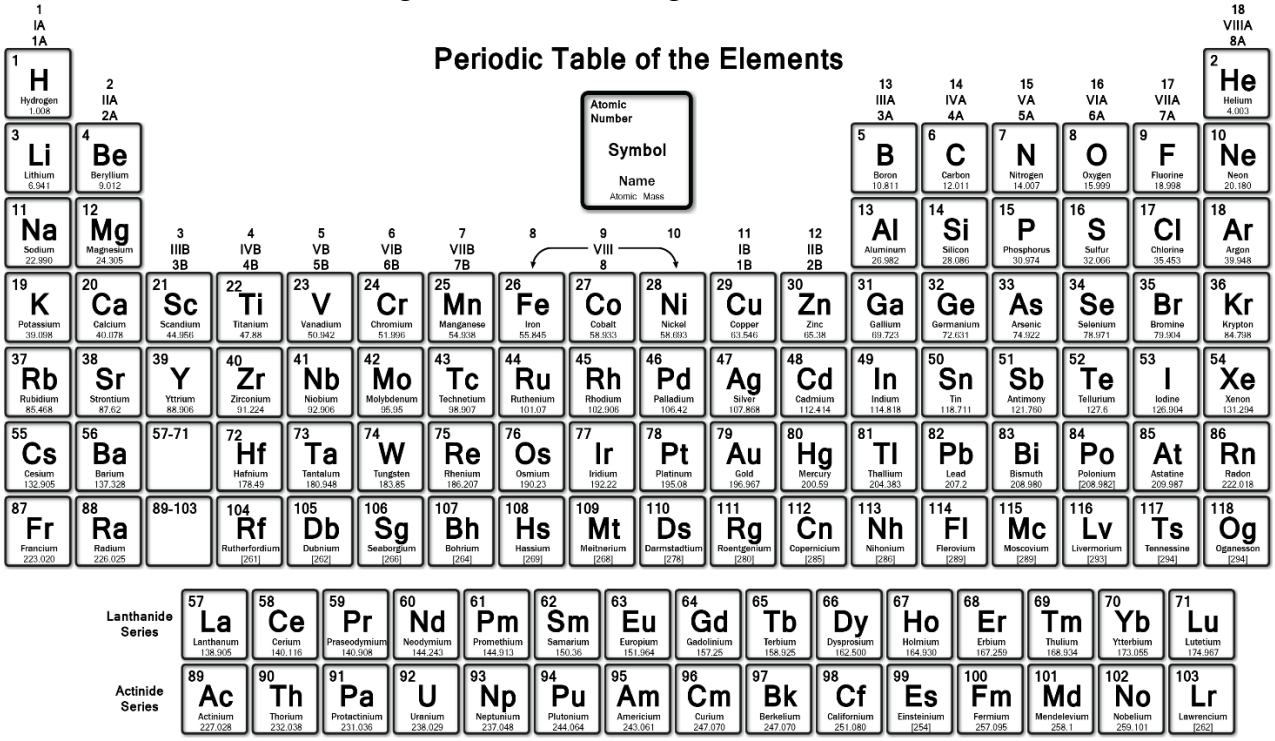
Student ID: _____

Recitation (fill in one circle):

O 134 (Wed 12:20 w/ Will)
O 135 (Wed 1:25 w/ Will)
O 136 (Wed 2:30 w/ Will)
O 137 (Wed 3:35 w/ Will)
O 142 (Thu 10:10 w/ Ethan)
O 143 (Thu 11:15 w/ Ethan)
O 144 (Thu 12:20 w/ Ethan)
O 147 (Thu 3:35 w/ Hongxuan)

Question	Score	Out of
1		30
2		20
3		20
4		30
5		40
6		30
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 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.

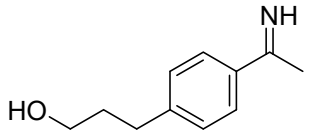


pKa Values

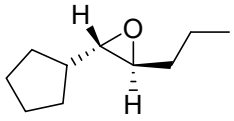
HI	-10	CH_3COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN_3	4.7	RSH	10-12	H_2	35
HCl	-6	H_2S	7.0	H_2O	15.7	NH_3	36
H_3O^+	-1.7	NH_4^+	9.3	ROH	16-18	$H_2C{=}CH_2$	45
HF	3.2	HCN	9.4	O=C-CH	9-25	CH_4	60

1) Find a way to synthesize the desired products from any reagents containing at most six carbon atoms, or triphenylphosphine. (30 pts; 15 pts each)

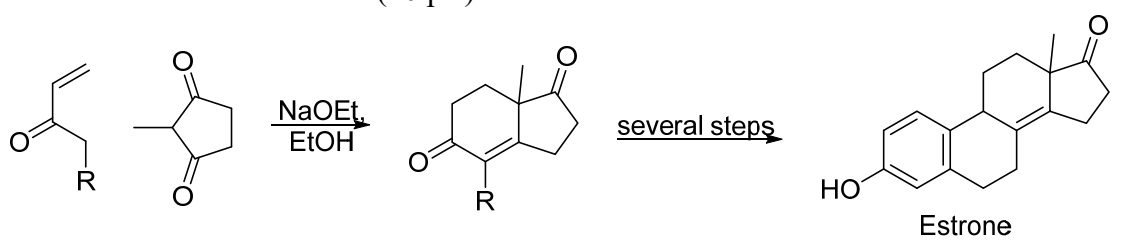
a.



b.



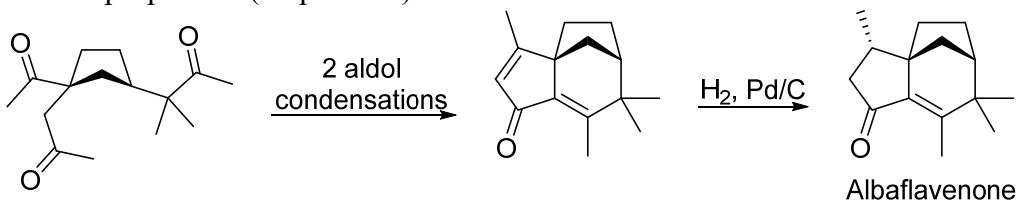
2) Estrone, shown below, is a precursor to the active components in many contraceptive drugs. One of its precursors is formed by Robinson annulation, as shown below. Draw out the mechanism for this reaction. (20 pts)



Estrone

3) **D**-Ribose is an aldopentose that can link into long chains which form the backbone of DNA (deoxy**ribo**nucleic acid). In an attempt to figure out the structure of **D**-ribose, you oxidize it with dilute nitric acid (converting both end groups to carboxylic acids) and find it to be optically inactive. You also perform a Kiliani-Fischer synthesis (extending the upper end of the chain by one carbon and creating a new stereocenter) on D-xylose and get two different hexoses. After oxidizing these with nitric acid, you find that one is optically active and one is optically inactive. Draw the structure of **D**-ribose. (20 pts)

4) The reactions shown below are the last two steps of the synthesis of albaflavenone, a terpene with antibiotic properties. (30 pts total)



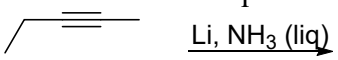
Albaflavenone

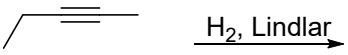
a. In the middle structure, draw the disconnect lines across the bonds that were formed during the aldol condensations. (4 pts)

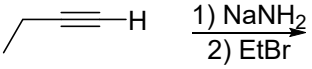
b. Draw a reasonable mechanism for the two aldol condensations. You can show either one of them happening first. (20 pts)

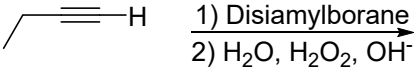
c. During the hydrogenation step shown, only one of the two alkenes is reduced. Given the different levels of substitution of these alkenes, why do you think the left alkene is reduced preferentially? (6 pts)

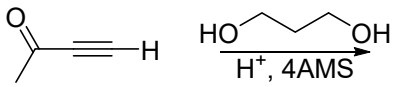
5) Predict the major product of the following reactions. If no reaction occurs, then write NR. Do not show stereochemistry. If an aldol-type reaction occurs, assume it only occurs once and does not involve subsequent additions. (40 pts; 4 pts each)

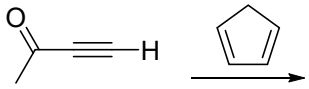
a. 

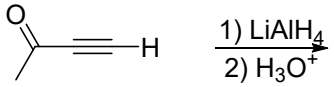
b. 

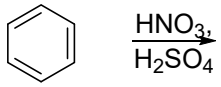
c. 

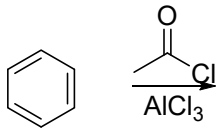
d. 

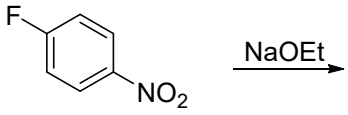
e. 

f. 

g. 

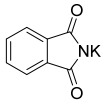
h. 

i. 

j. 

6) Several amines are shown below. (30 pts total)

a. Which of them could be synthesized by Gabriel amine synthesis (potassium phthalimide (shown below) + alkyl halide, then NaOH)? Show the starting materials for their formation. (5 pts)



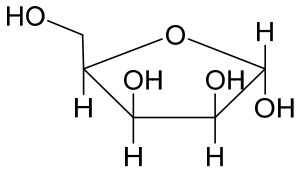
potassium phthalimide

b. Which of them could be synthesized by reductive amination (carbonyl + amine, $NaBH_3CN$, MeOH)? Show the starting materials for their formation. (15 pts)

c. 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. (5 pts)

d. Which of them could be synthesized by direction alkylation with alkyl halides (amine + alkyl halide)? Show the starting materials for their formation. (5 pts)

7) The furanose form of a carbohydrate is shown below. (30 pts)



Draw the following structures for this compound. (10 pts each)

a. Fischer projection for acyclic form b. Haworth projection for α-pyranose form

a. Which terms describe this compound? **L**, **D**, aldose, ketose, pentose, hexose. (6 pts)

b. How many enantiomers does the acyclic form of this compound have? (2 pts)

c. How many diastereomers does the acyclic form of this compound have? (2 pts)

8) Extra credit! The compound shown below, 1,5-dimethyl-1-vinyl-4-hexenyl butyrate, is the principal component of lavender oil. Devise a synthesis for this compound from any other compounds with 4 carbon atoms or fewer (or triphenylphosphine). (20 pts extra credit)