

# CHEM 3331 (Richardson) Final Exam – May 8, 2019

Your Name: Key

Student ID:

- |                             |                             |
|-----------------------------|-----------------------------|
| O 149 (Thu 5:00 w/ Will)    | O 149 (Thu 5:00 w/ Will)    |
| O 235 (Wed 1:00 w/ Lauren)  | O 235 (Wed 1:00 w/ Lauren)  |
| O 237 (Wed 3:00 w/ Lauren)  | O 237 (Wed 3:00 w/ Lauren)  |
| O 239 (Wed 5:00 w/ Zepeng)  | O 239 (Wed 5:00 w/ Zepeng)  |
| O 240 (Thu 8:00 w/ Zhenhao) | O 240 (Thu 8:00 w/ Zhenhao) |
| O 242 (Thu 10:00 w/ Lauren) | O 242 (Thu 10:00 w/ Lauren) |
| O 244 (Thu 12:00 w/ Lauren) | O 244 (Thu 12:00 w/ Lauren) |
| O 246 (Thu 2:00 w/ Brianna) | O 246 (Thu 2:00 w/ Brianna) |
| O 248 (Thu 4:00 w/ Brianna) | O 248 (Thu 4:00 w/ Brianna) |

Question	Score	Out of
1		20
2		30
3		45
4		45
5		40
6		20
7		10 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.

Periodic Table of the Elements																	
1 IA 1A H Hydrogen 1.008	2 IIA 2A Be Beryllium 9.012	3 III A 3A Li Lithium 6.941	4 IVB 4B Mg Magnesium 24.306	5 VB 5B Na Sodium 22.989	6 VIB 6B Mg Magnesium 24.306	7 VII B 7B Cl Chlorine 35.453	8 VIII 8 Ar Argon 39.948	9 VII A 7A F Fluorine 18.998	10 VIA 6A Ne Neon 20.180	11 IIIB 3B K Potassium 39.096	12 IIB 4B Ca Calcium 40.078	13 IIIA 3A Sc Scandium 44.956	14 IVA 4A Ti Titanium 47.867	15 VA 5A V Vanadium 50.942	16 VIA 6A Cr Chromium 51.961	17 VIIA 7A Mn Manganese 54.938	18 VIIIA 8A He Helium 4.003
19 K Potassium 39.096	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.961	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.931	28 Ni Nickel 58.931	29 Cu Copper 63.546	30 Zn Zinc 65.401	31 Ga Gallium 69.721	32 Ge Germanium 72.631	33 As Arsenic 74.921	34 Se Selenium 78.921	35 Br Bromine 79.914	36 Kr Krypton 83.814
37 Rb Rubidium 85.465	38 Sr Strontium 87.62	39 Y Yttrium 88.916	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.96	43 Tc Technetium 98.007	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.901	46 Pd Palladium 106.42	47 Ag Silver 107.869	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.790	52 Te Tellurium 127.8	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.06	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium 208.982	85 At Astatine 209.987	86 Rn Rutherfordium 222.013
87 Fr Francium 223.028	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 264	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Ds Darmstadtium 270	111 Rg Roentgenium 272	112 Cn Copernicium 273	113 Nh Nihonium 279	114 Fl Flerovium 289	115 Mc Moscovium 289	116 Lv Livermorium 293	117 Ts Tennessine 294	118 Og Oganesson 294

## pKa Values

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

Aug: 146

Curve: 4

St. Dev: 37.3

Max: 204

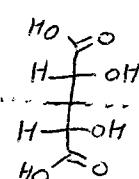
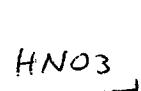
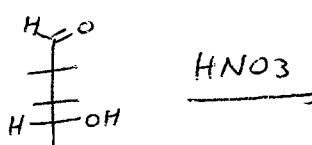
Min: 16

- 1) D-Xylose is an aldopentose that was first isolated from wood. It can be hydrogenated to form xylitol, a sweetener used in "sugar-free" gum and candy. In an attempt to figure out the structure of D-xylose, 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 Kilian-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, both of which are optically active.

Draw the structure of D-Xylose. (20 pts)

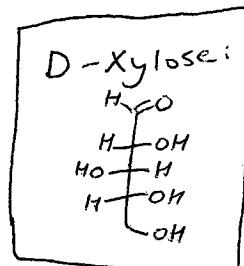
Anounced during exam: this should say "followed by oxidation w/ dilute  $HNO_3$ "

General structure  
for D-aldopentose:



1st & 3rd

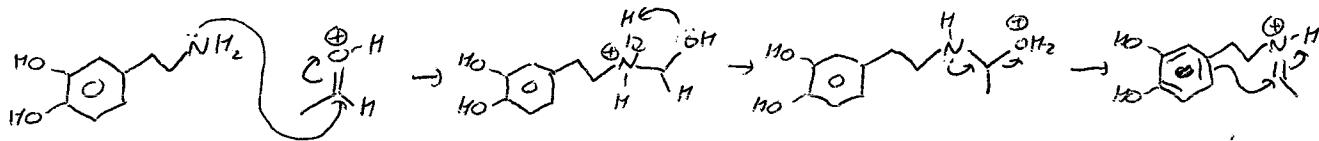
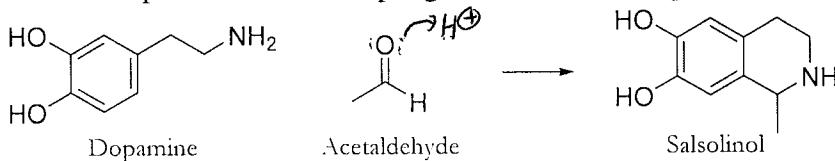
stereocenters must be  
symmetric b/c it's optically  
inactive.



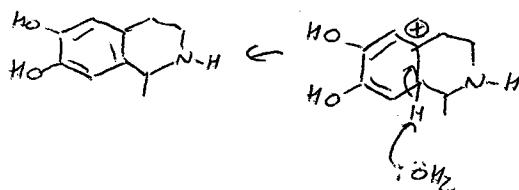
Full pts if correct, otherwise 5 pts  
for each stereocenter +

5 pts for  
aldopentose  
backbone.

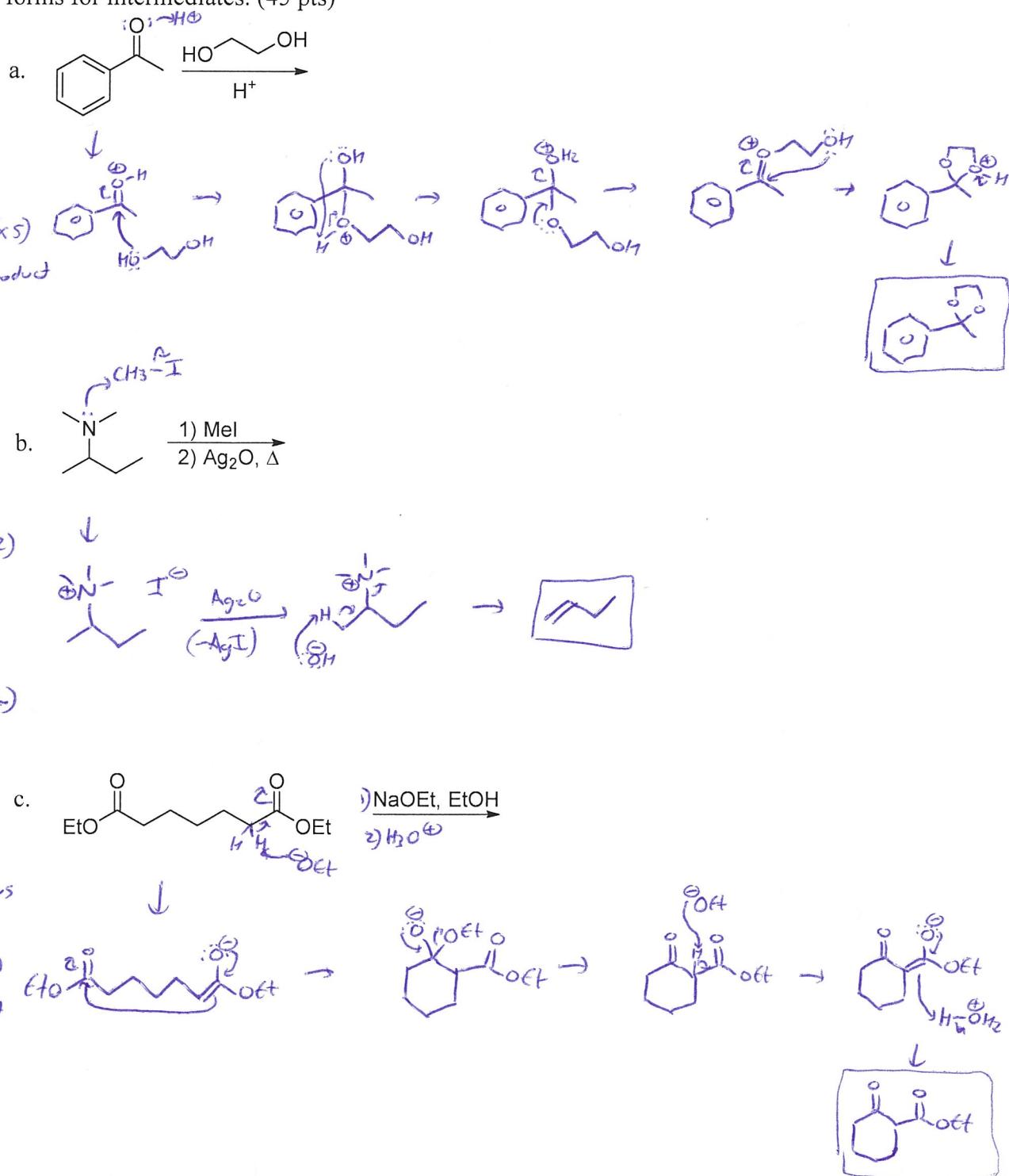
- 2) Salsolinol, shown below, is formed in the brain when acetaldehyde reacts with dopamine. Draw a reasonable mechanism for this reaction. Assume acids and bases are present as needed. (This is an example of the Pictet-Spengler reaction.) (30 pts)



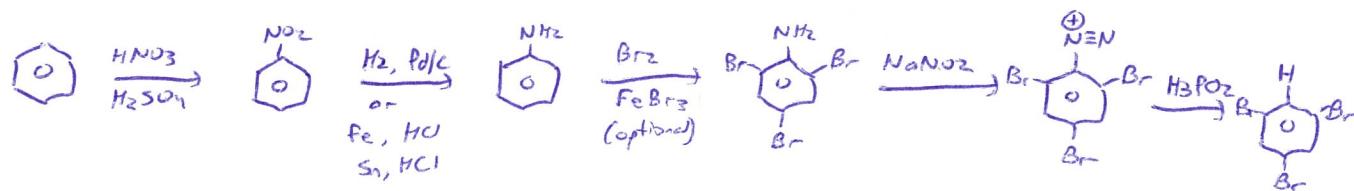
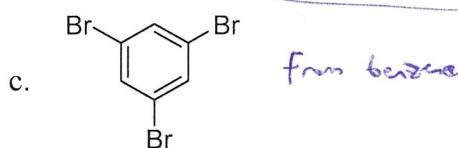
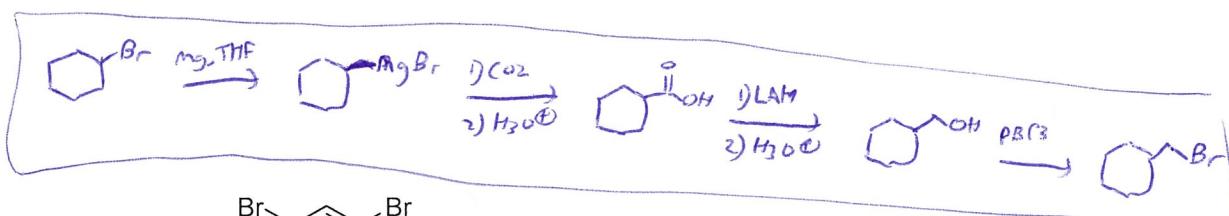
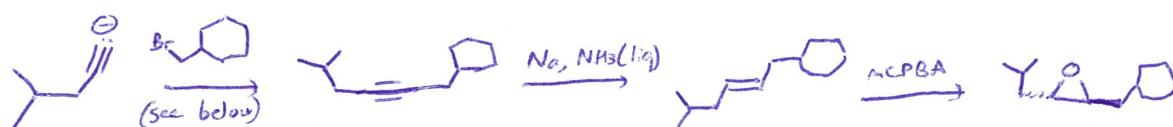
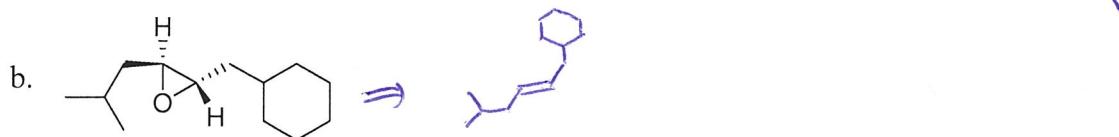
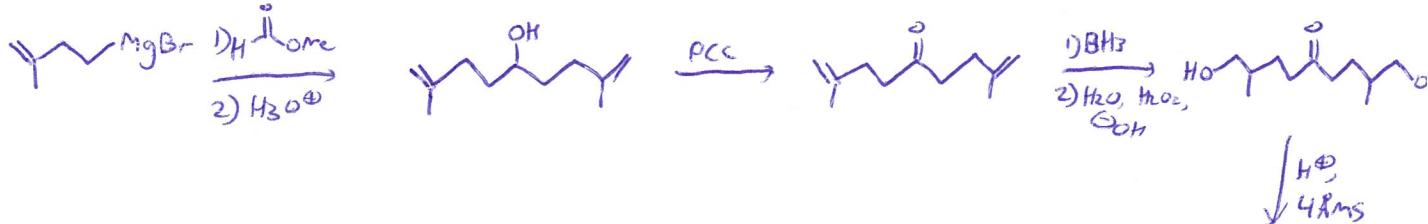
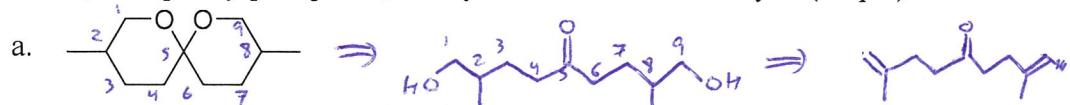
6 pts per intermediate set of arrows



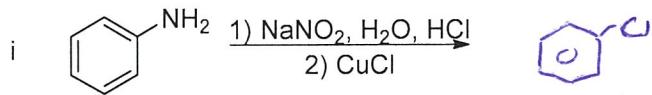
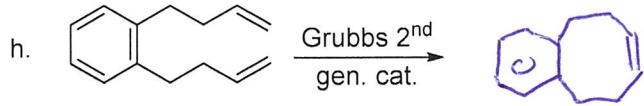
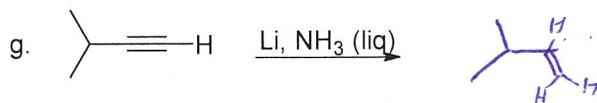
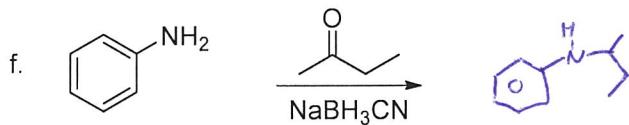
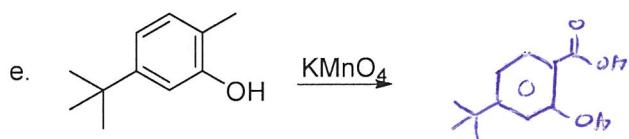
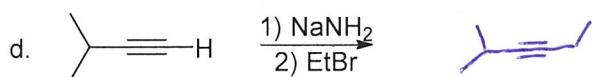
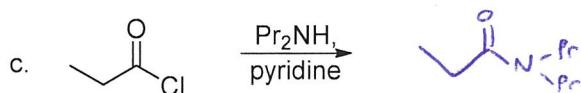
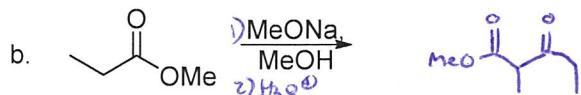
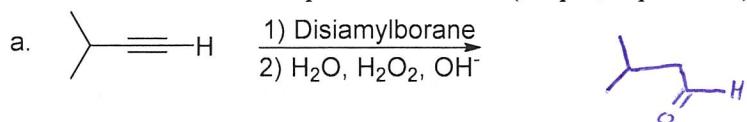
3) Show the mechanism and product for these reactions. You do not need to show resonance forms for intermediates. (45 pts)



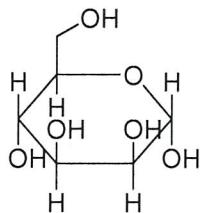
- 4) Find a way to synthesize the desired product from any reagents containing at most six carbon atoms, or triphenylphosphine, or any transition metal catalyst. (45 pts)



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)



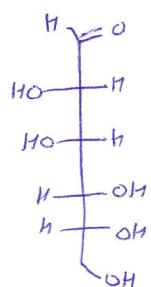
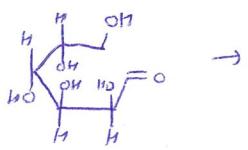
- 6) The pyranose form of a carbohydrate is shown below. (20 pts)



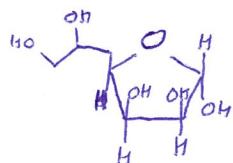
Draw the following structures for this compound. (5 pts each)

a. Fischer projection for acyclic form

Break ring first:



b. Haworth projection for  $\alpha$ -furanose form  
(you don't need to show stereochemistry on parts that are outside the ring)



(1 pt per stereocenter,  
1 pt for overall form)

+2 for correct answer

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

d. How many enantiomers does the acyclic form of this compound have? (2 pts) 1

e. How many diastereomers does the acyclic form of this compound have? (2 pts) 14

- 7) Extra credit! Most alkyl bromides are water-insoluble liquids. But when 7-bromo-1,3,5-cycloheptatriene was first isolated, its high melting point of 203 °C and its water solubility led its discoverers to comment that it behaves more like a salt. Explain the salt-like behavior of this compound in under thirty words. (10 points e.c.)

