

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

Your Name: _____

Student ID: _____

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

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
caesium 55 Cs 132.91	barium 56 Ba 137.33	* 57-70	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	* * 89-102	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	duobium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbibium 112 Uub [277]	unquadium 114 Uuq [285]										

* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
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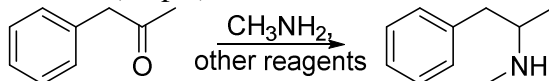
** Actinide series

actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]
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pKa Values

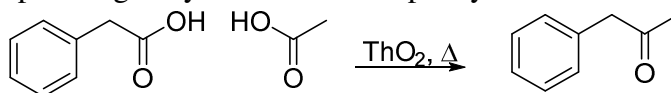
HI	-10	CH ₃ COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN ₃	4.7	RSH	10-12	H ₂	35
HCl	-6	H ₂ S	7.0	H ₂ O	15.7	NH ₃	36
H ₃ O ⁺	-1.7	NH ₄ ⁺	9.3	ROH (R=alkyl)	16-18	H ₂ C=CH ₂	45
HF	3.2	HCN	9.4	O=C-CH (α H)	9-25	CH ₄	60

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

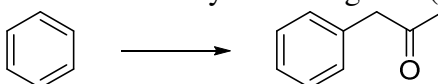


- a. What other reagents are typically needed for this reaction? Show the mechanism. (Hint: the mechanism for the last part is similar to reduction of a ketone, only the nitrogen needs to be protonated first.) (10 pts)

- 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.

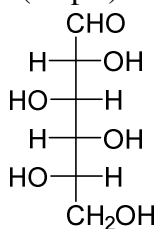


This is not a reaction that we've covered, so instead, show a way to synthesize phenylacetone starting with benzene and any other reagents. (10 pts)



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

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



a. Is this the **L** or **D** enantiomer 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

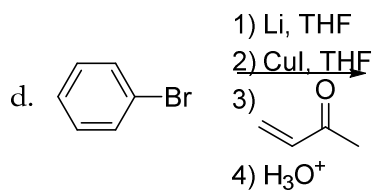
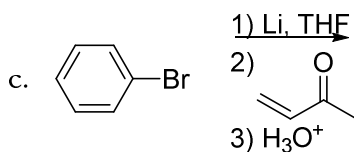
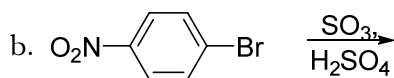
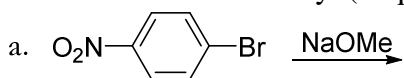
c. Haworth projection
for α -pyranose form

d. One chair conformation
for α -pyranose form

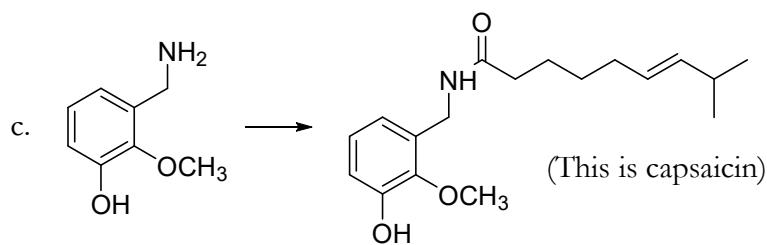
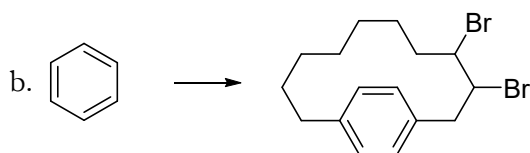
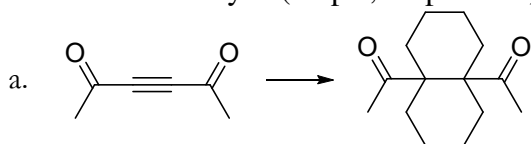
e. The other chair conformation
for α -pyranose form

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

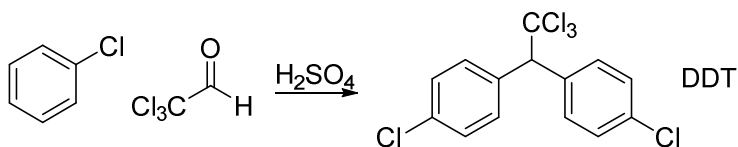
3) Predict the major product of the following reactions. If no reaction occurs, then write NR. Do not show stereochemistry. (20 pts; 5 pts each)



- 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)

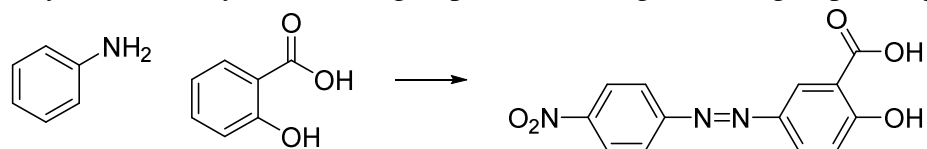


- 5) The insecticide DDT (*p*-dichlorodiphenyltrichloroethane) is prepared by following route. Suggest a mechanism for this reaction. (Hint: although Friedel-Crafts is the most common way to generate an alkyl electrophile, we've seen a couple of other ways to do it. How could you make one of these reagents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

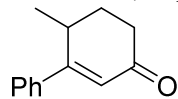


Here is a poem about DDT:
 A mosquito was heard to complain
 That a chemist had poisoned his brain.
 The cause of his sorrow
 Was *para*-dichloro
 Diphenyltrichloroethane.

- 6) Show how to synthesize Alizarin Yellow R from aniline and salicylic acid. (Hint: you may need to modify the reactivity of the NH₂ group before adding the NO₂ group.) (20 pts)



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



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

