

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

Your Name: Key

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.
<b>Total</b>		<b>200</b>

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 <b>H</b> 1.0079																	helium 2 <b>He</b> 4.0026						
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122																	boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305																	aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selecnium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80						
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29						
cesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	* 57-70	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	wolfram 74 <b>W</b> 183.84	reuterium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]					
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	* *	lanthanum 89 <b>La</b> [227]	cerium 90 <b>Ce</b> [228]	praseodymium 91 <b>Pr</b> [229]	neodymium 92 <b>Nd</b> [230]	promethium 93 <b>Pm</b> [231]	samarium 94 <b>Sm</b> [232]	europium 95 <b>Eu</b> [233]	gadolinium 96 <b>Gd</b> [234]	terbium 97 <b>Tb</b> [235]	dysprosium 98 <b>Dy</b> [236]	holmium 99 <b>Ho</b> [237]	erbium 100 <b>Er</b> [238]	thulium 101 <b>Tm</b> [239]	ytterbium 102 <b>Yb</b> [240]							
			actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> [232]	protactinium 91 <b>Pa</b> [231]	uranium 92 <b>U</b> [238]	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	esboium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]							

\* Lanthanide series

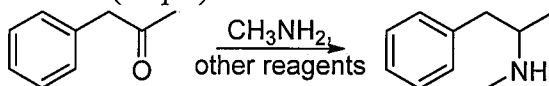
\*\* Actinide series

## pKa Values

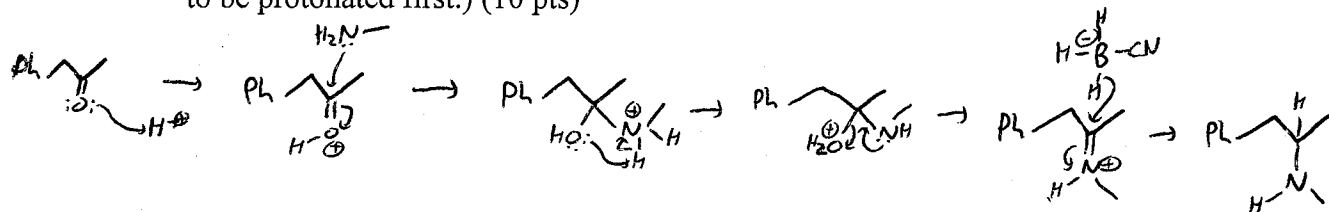
HI	-10	CH <sub>3</sub> COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN <sub>3</sub>	4.7	RSH	10-12	H <sub>2</sub>	35
HCl	-6	H <sub>2</sub> S	7.0	H <sub>2</sub> O	15.7	NH <sub>3</sub>	36
H <sub>3</sub> O <sup>+</sup>	-1.7	NH <sub>4</sub> <sup>+</sup>	9.3	ROH (R=alkyl)	16-18	H <sub>2</sub> C=CH <sub>2</sub>	45
HF	3.2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

Average: 151  
 St. Dev: 40.2  
 Max: 216  
 Min: 41

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

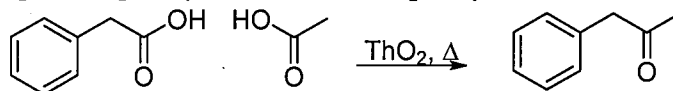


- a. What other reagents are typically needed for this reaction? Show the mechanism. (Hint: the mechanism for the last part is similar to reduction of a ketone, only the nitrogen needs to be protonated first.) (10 pts)

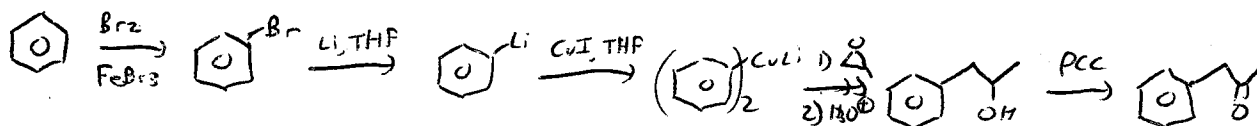
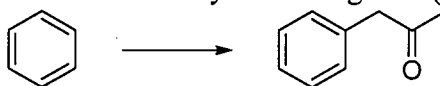


\* (2 pts per intermediate/set of arrows)

- 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.



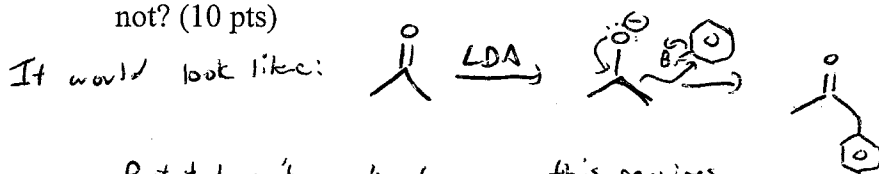
This is not a reaction that we've covered, so instead, show a way to synthesize phenylacetone starting with benzene and any other reagents. (10 pts)



\* 1 pt per intermediate prod

\* 1 pt per set of reagents

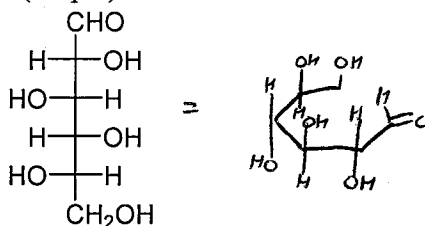
- c. Is it possible to synthesize phenylacetone from the  $\alpha$ -alkylation of a ketone? Why or why not? (10 pts)



But it doesn't work, because this requires

$\text{S}_{\text{N}}2$  on aryl bromide.

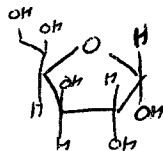
2) One enantiomer of idose is shown below. (25 pts)



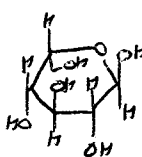
a. Is this the **L** or **D** enantiomer of idose? (3 pts)

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  $\beta$ -furanose form

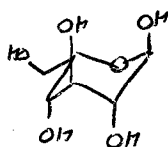


c. Haworth projection for  $\alpha$ -pyranose form



(OK not to show Hs explicitly for all of these)

d. One chair conformation for  $\alpha$ -pyranose form



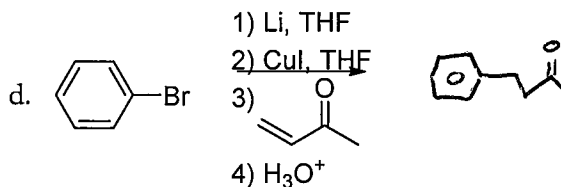
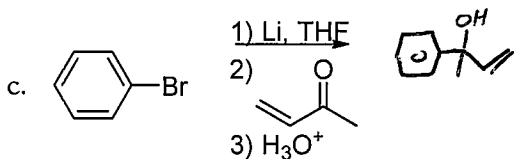
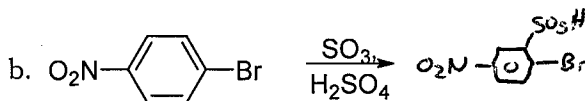
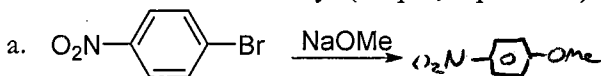
(No pts deduction for error carried forward from c)

e. The other chair conformation for  $\alpha$ -pyranose form

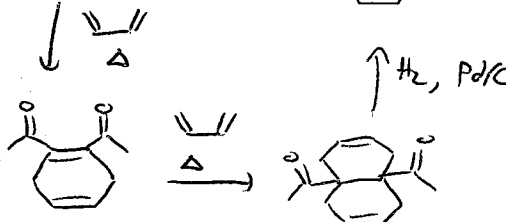
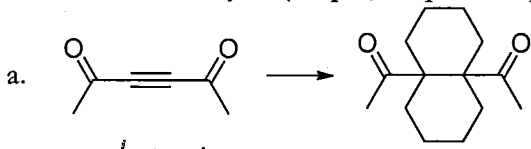


f. Circle all of the terms that describe this compound: **aldose**, ketose, pentose, **hexose** (2 pts)

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)

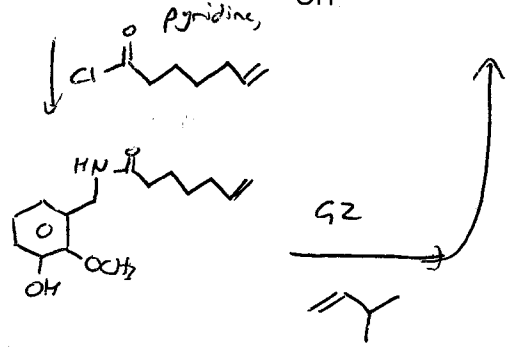
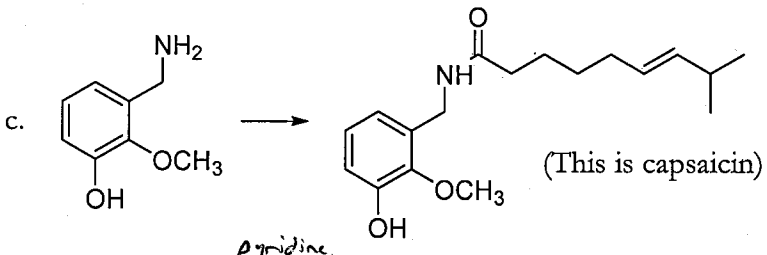
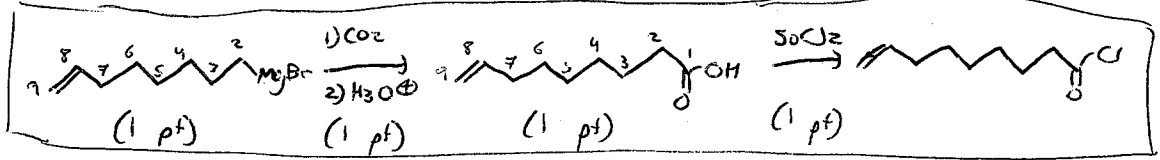
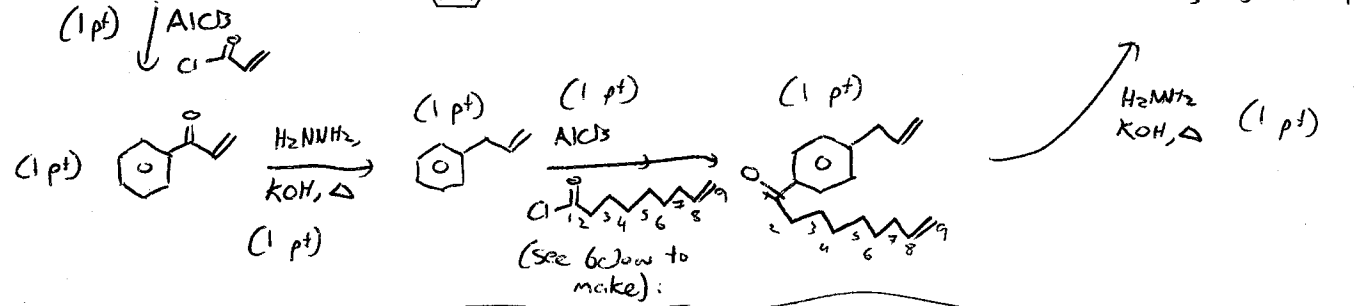
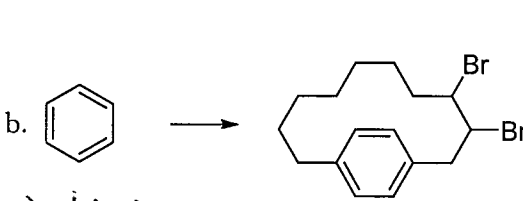


4) Find a way to synthesize the desired product from the given starting material plus any other reagents containing at most eight carbon atoms, or triphenylphosphine, or any transition metal-based catalyst. (45 pts; 15 pts each)



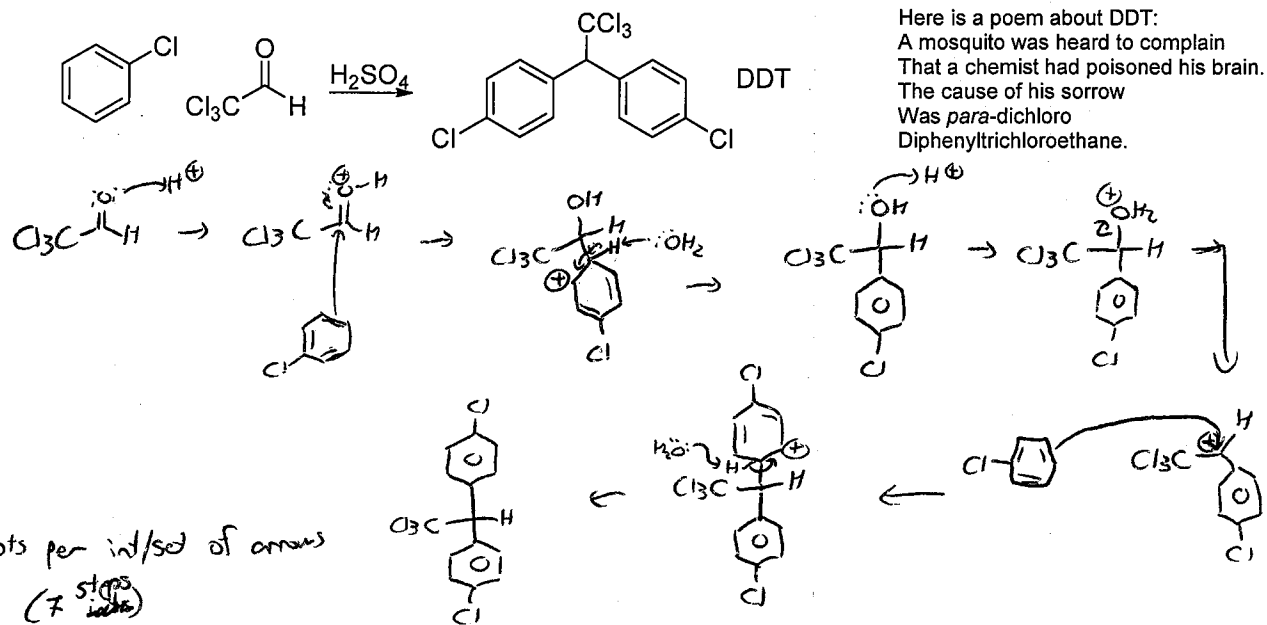
\* 3 pts per intermediate/set of reagents

\* 1 pt per int/set of reagents



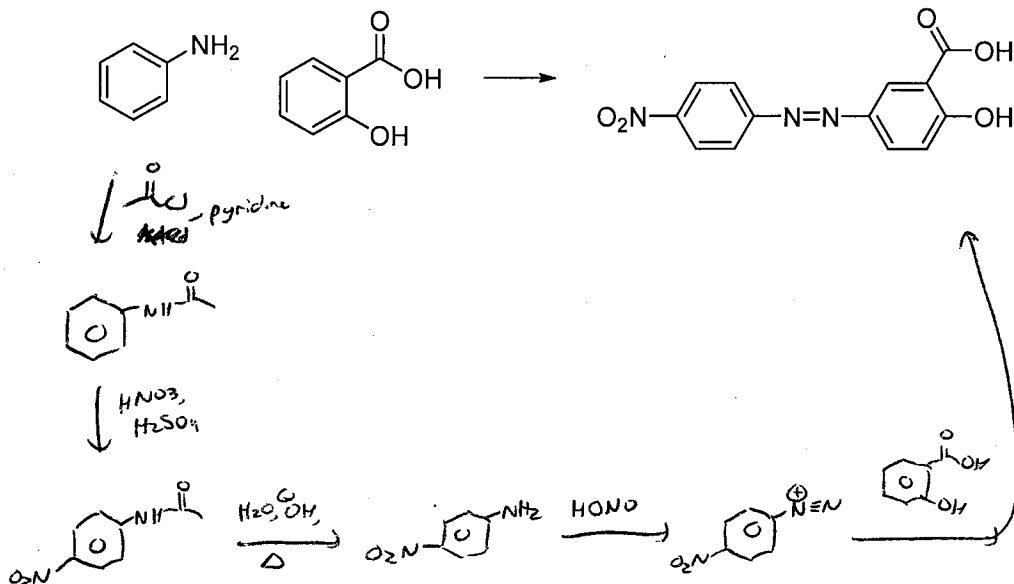
\* 5 pts per intermediate/set of reagents

- 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)



\* 4 pts per int/set of arrows  
 (7 steps)  
 \* 2 pts for product.

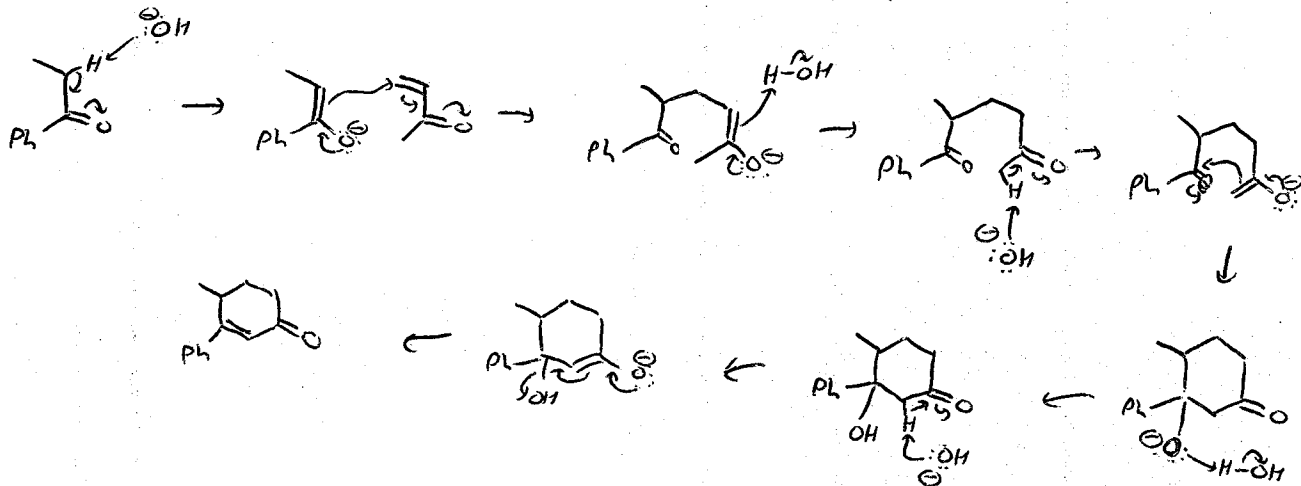
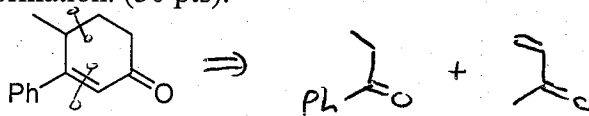
- 6) Show how to synthesize Alizarin Yellow R from aniline and salicylic acid. (Hint: you may need to modify the reactivity of the  $\text{NH}_2$  group before adding the  $\text{NO}_2$  group.) (20 pts)



\* 2 pts per  
intermediate/product  
 \* 2 pts per set  
of reagents

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

Note: showing  $\ominus$  form of enolate is OK



\* 6 pts for precursors

\* 4 pts for each set of arrows

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



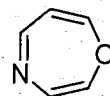
Antiaromatic



Aromatic



Nonaromatic



Nonaromatic



Aromatic