CHEM 3331 (Richardson) Final Exam – Aug. 11, 2023

Your Name: Key

Student ID: _____

Recitation (fill in one circle):

O 211 (Charlie Lu)

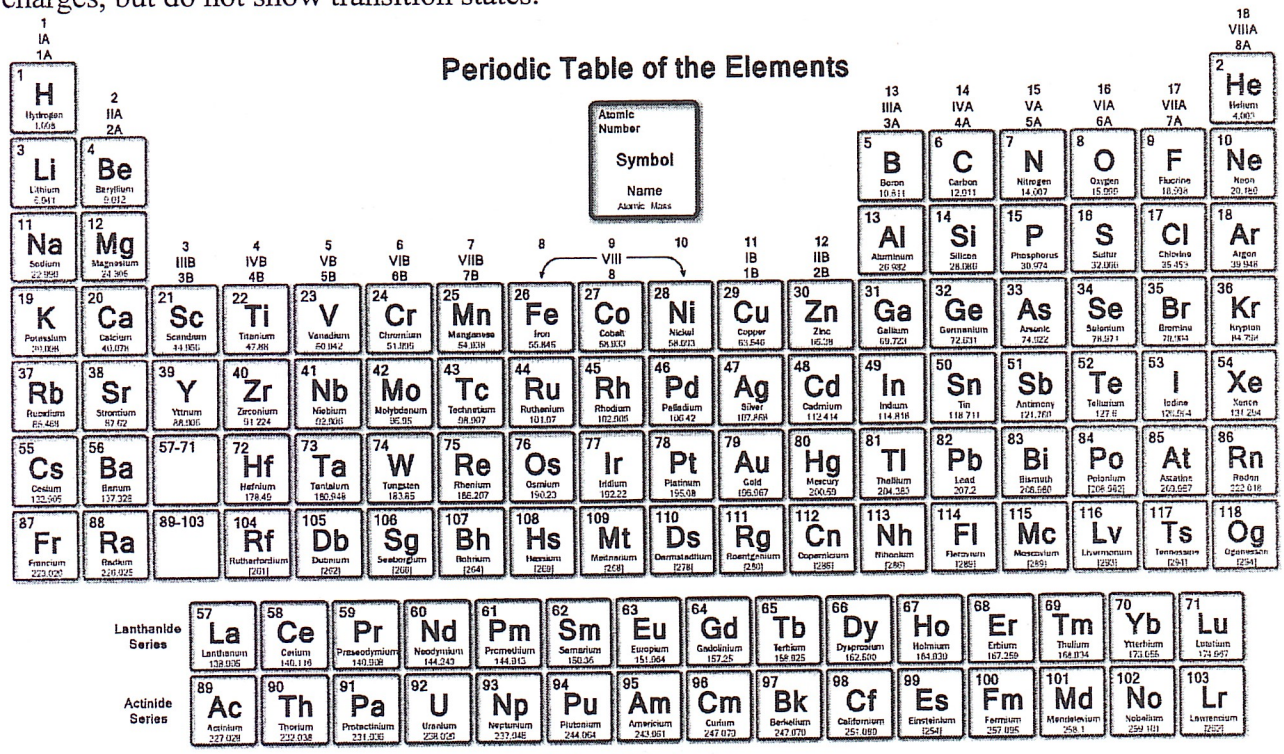
O 212 (Kajal)

O 213 (Mia Muse)

O 214 (Kyle Fisch)

Question	Score	Out of
1		40
2		20
3		40
4		30
5		~~40~~ 30
6		~~30~~ 40
7		10 e.c.
Total		200

This is a closed-book exam, except for one double-sided sheet 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.

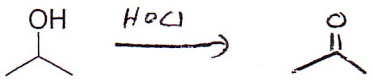


pKa Values

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

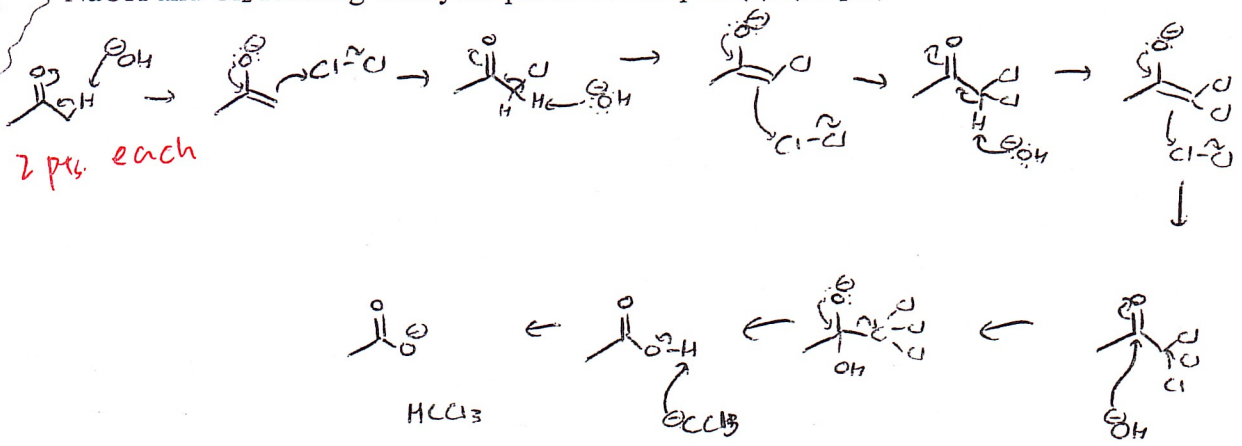
Avg 142
Curve 8
St. Dev. 55
Max 205

1) A common safety tip is "Never mix bleach and alcohol! It makes chloroform." (40 pts)
   a. Bleach (aqueous sodium hypochlorite, NaOCl) forms small amounts of hypochlorous acid (HOCl) at equilibrium. HOCl oxidizes alcohols to aldehydes or ketones, in a reaction you might remember from organic 1 lab. You don't have to show the mechanism here, but draw the overall reaction for isopropyl alcohol (shown below) being oxidized by HOCl. (5 pts)



   b. Bleach can also break down to form NaOH and Cl_2. You don't have to show the mechanism for the formation of these species, but instead, show the mechanism for NaOH and Cl_2 reacting with your product from part (a). (20 pts)

For every enolate, OK to show as or



2 pts. each

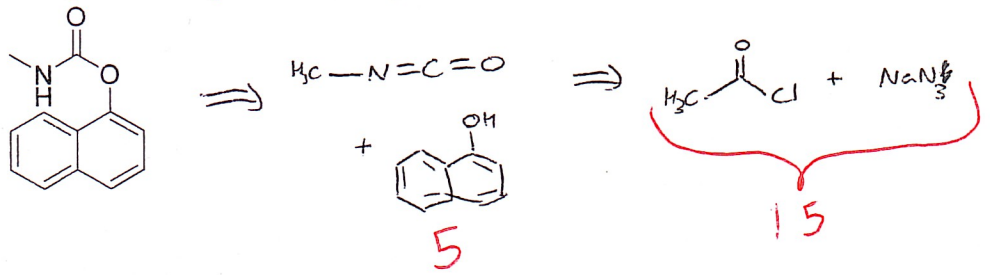
   c. Would these molecules also undergo both the reactions from steps (a) and (b)? Ethanol, methanol, t-butyl alcohol. If not, why not? (10 pts)

Ethanol: yes; b/c both steps a) & b) work (3 pts)
Methanol: no; step a) works but b) doesn't. (3 pts)
t-Butyl alcohol: no; step a) doesn't work. (4 pts)

   d. Based on your answers to part (c), what characteristics does an alcohol molecule need in order to produce chloroform when mixed with bleach? (5 pts)

The C w/ the OH needs at least 1 H (so it can be oxidized), & at least 1 $-CH_3$ (that leaves after becoming $-CCl_3$).

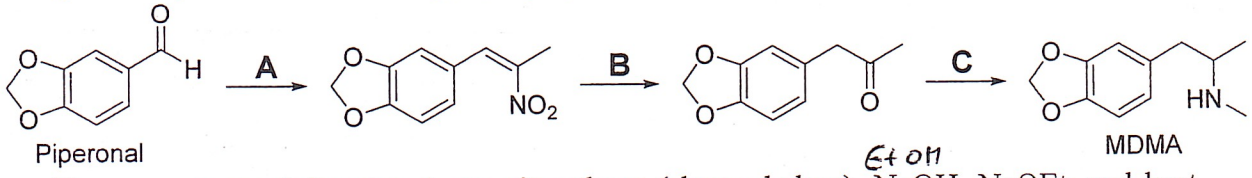
2) The insecticide carbaryl, shown below, can be prepared via a Curtius rearrangement. Show how you would perform this synthesis, using any starting materials. (20 pts ~~extra credit~~)



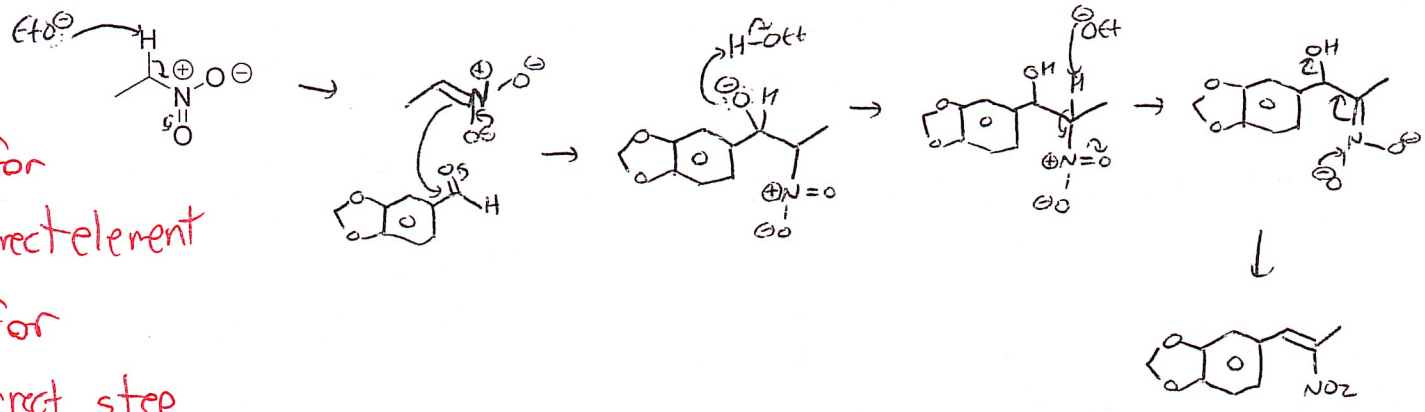
5 15

-2 if missing Na

3) The synthetic route shown below is one possible way to synthesize MDMA (3,4-methylene-dioxymethamphetamine or ecstasy). (40 pts)



a. The reagents used for step A are nitroethane (shown below), ~~NaOH~~, NaOEt, and heat. Show a mechanism for this reaction, bearing in mind that the alpha protons of a nitro group (pKa ~ 9) can be removed even more easily than the alpha protons of a ketone (pKa ~ 20), allowing it to perform aldol-like chemistry. (30 pts)



+2/1 for a correct element

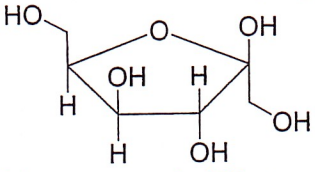
+5 for a correct step

b. What reagents are needed for step C? (10 pts)

H_2N-Me, $NaBH_3CN$ 5 5

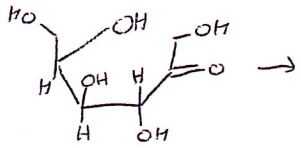
-5 if extra reagents incorrect

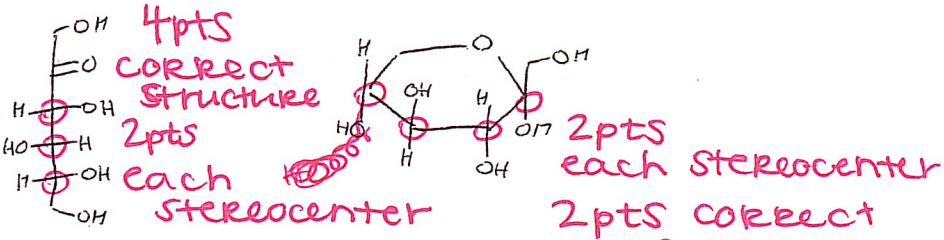
4) The furanose form of a carbohydrate is shown below. (30 pts)



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

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





4pts correct structure

2pts each stereocenter

2pts each stereocenter

2pts correct structure

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

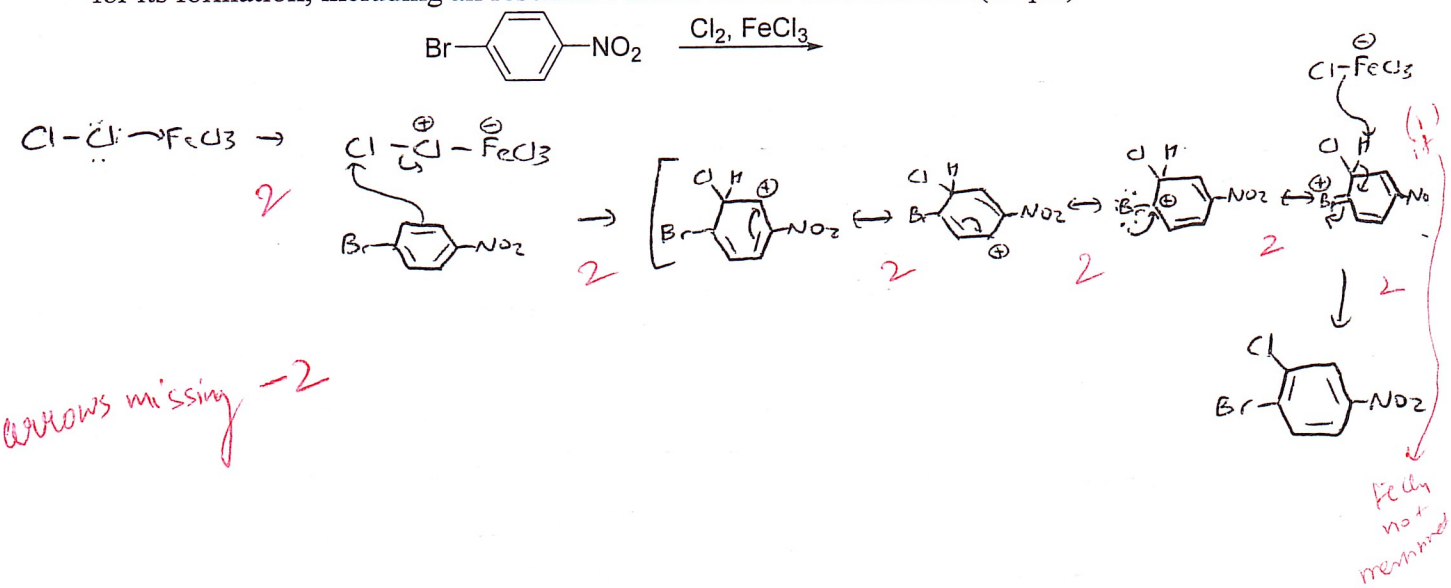
2 2 2

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

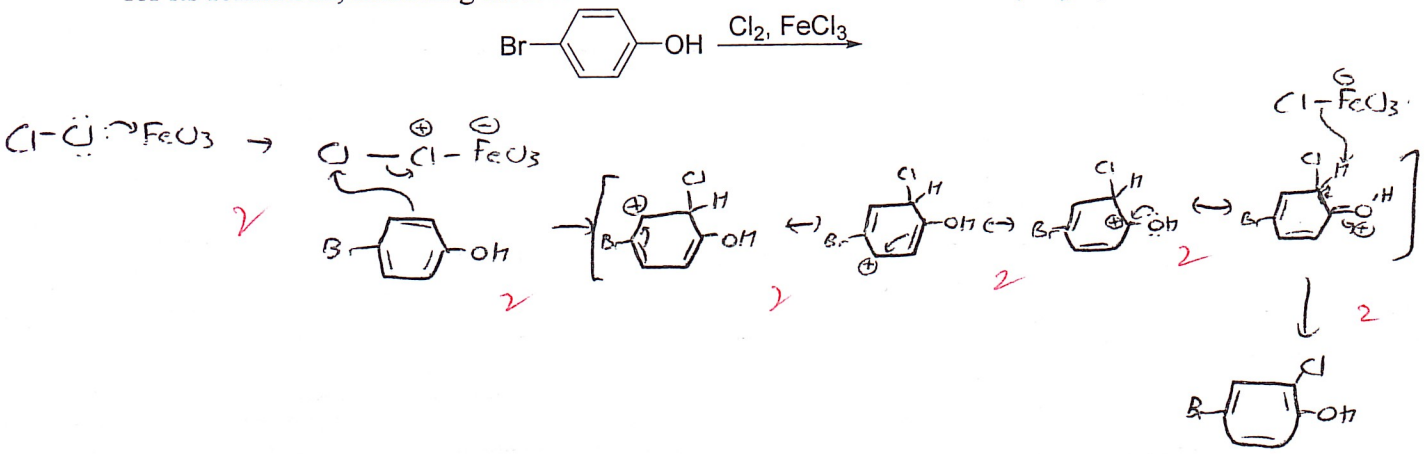
c. How many diastereomers does the acyclic form of this compound have? (2 pts) $2^3 - 2 = 6$

5) The directing effects of groups during electrophilic aromatic substitution reactions can be explained by resonance. (30 pts)

a. The reaction below produces a single isomer as the major product. Show the mechanism for its formation, including all resonance forms for the intermediate. (12 pts)



b. The reaction below produces a single isomer as the major product. Show the mechanism for its formation, including all resonance forms for the intermediate. (12 pts)



c. Which reaction would be faster, and why? (6 pts)

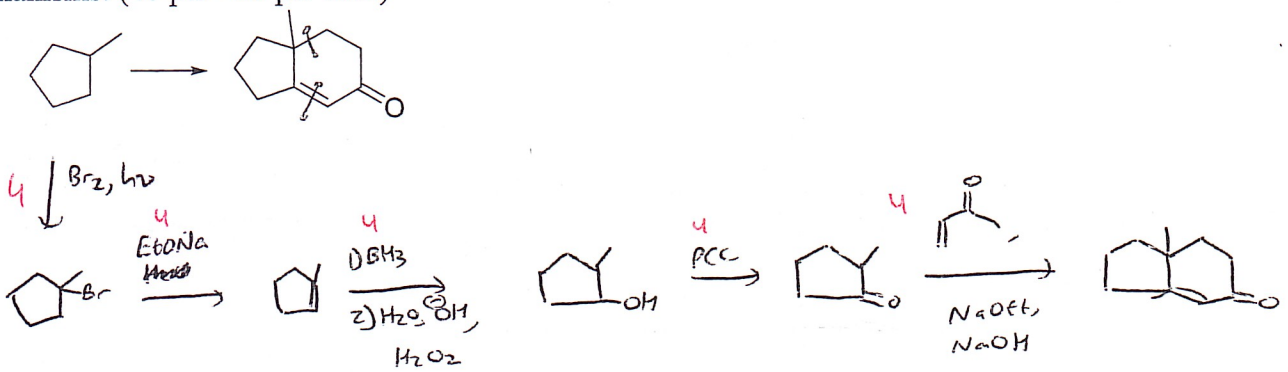
Bottom one, due to stronger activating group.

Correct (b) but not explanation (2)

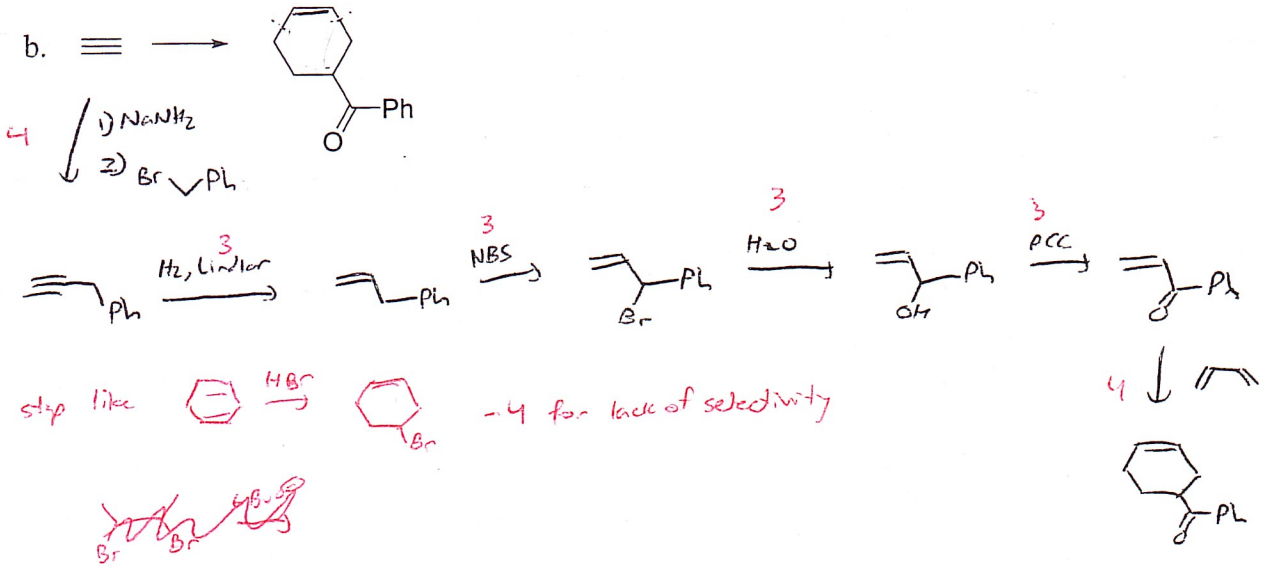
if partially right -on more resonance str. -3

6) Find a way to synthesize the desired product from the given starting material and any other reagents. If more than one step is necessary, show the product of each step. Do not show mechanisms. (40 pts - 20 pts each)

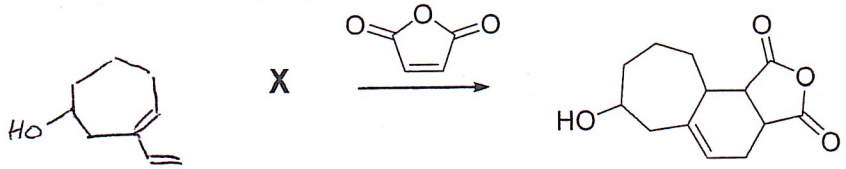
a.



b.



7) Use the structure of the Diels–Alder adduct to deduce the structure of the compound X in the reaction shown below. (10 pts extra credit)



6-mem: 5 pts if alkenes are otherwise good