

CHEMISTRY 2500: Organic Chemistry I

MIDTERM-2

Thursday, November 7, 2019

Instructions:

- This exam paper consists of 10 questions.
- The exam is worth a total of 50 marks. Most of these marks are for explanation/showing your work rather than for reaching the correct answer. Explain all of your answers fully using diagrams where appropriate (a picture really is worth a thousand words!).
- Marks will be deducted for poorly drawn structures.
- No calculators allowed. No other electronic devices can be present with you during the exam unless authorized by the instructor.
- You may use a molecular model kit.
- There is a 2-hour time limit.
- If your work is not legible, it will be given a mark of zero.
- **Read the questions carefully.** Good luck.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until they have all been marked and returned. I understand that, if I were to break this agreement, I would be choosing to commit academic misconduct, a serious offense that will be punished. The minimum punishment would be a mark of 0 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____

Date: _____

Course: CHEM 2500 (Organic Chemistry I)

Semester: Fall 2019

The University of Lethbridge

Question Breakdown

Q1	/6	Q7	/4
Q2	/4	Q8	/4
Q3	/6	Q9	/5
Q4	/5	Q10	/5
Q5	/5		
Q6	/6		

Total	/50
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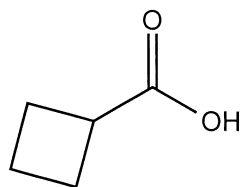


I SEE YOU, HOBBS!
MAN, WHAT A LOUSY
SHOT! TIGERS CAN'T
THROW WORTH A...



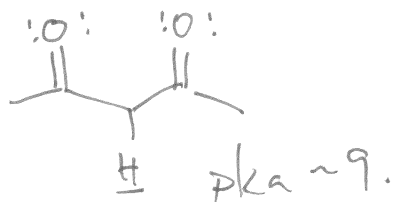
1. Consider the following compound with molecular formula $C_5H_8O_2$:

[6 marks]

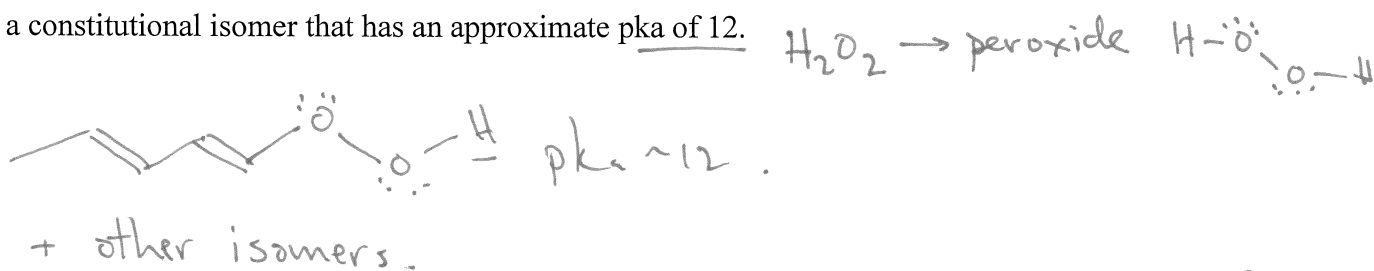


$C_5H_8O_2$

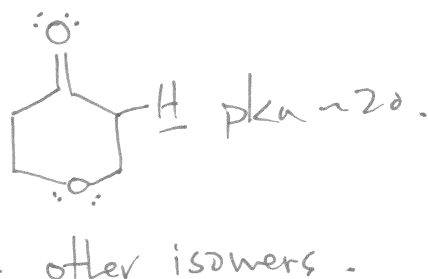
(a) Draw a constitutional isomer that has an approximate pK_a of 9.



(b) Draw a constitutional isomer that has an approximate pK_a of 12.



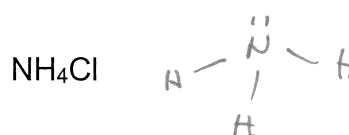
(c) Draw a constitutional isomer that has an approximate pK_a of 20.



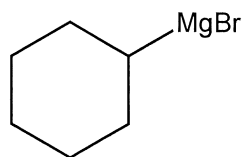
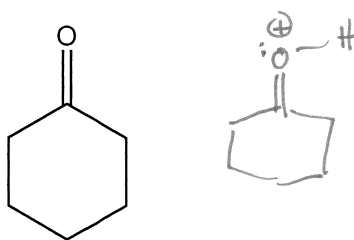
2.

(a) Draw the conjugate base beside each of the following acids.

[4 marks]



(b) Draw the conjugate acid beside each of the following bases.



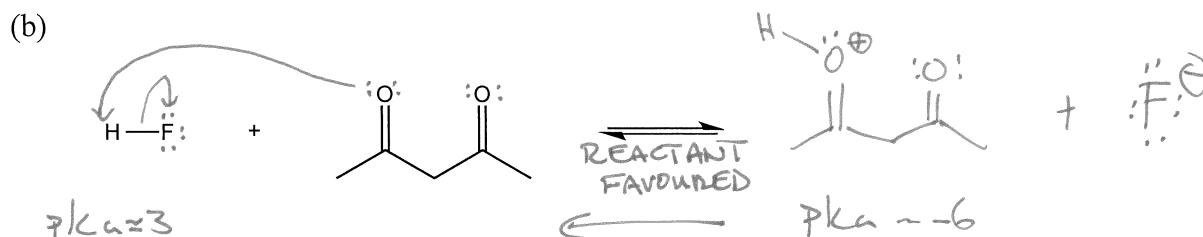
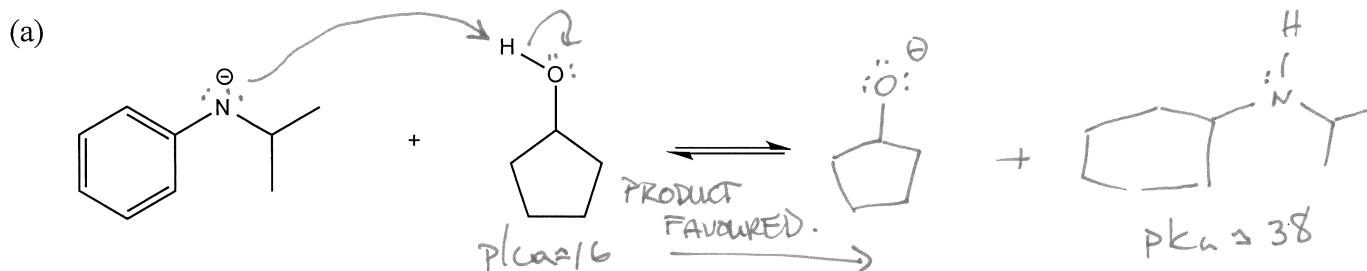
3. For each of the following reactions:

(i) Add all lone pairs and identify the acid and base.

(ii) Draw the mechanistic arrows showing the proton transfer reaction.

(iii) Draw the products of that proton transfer reaction and then predict the position of the equilibrium (reactant or product favoured).

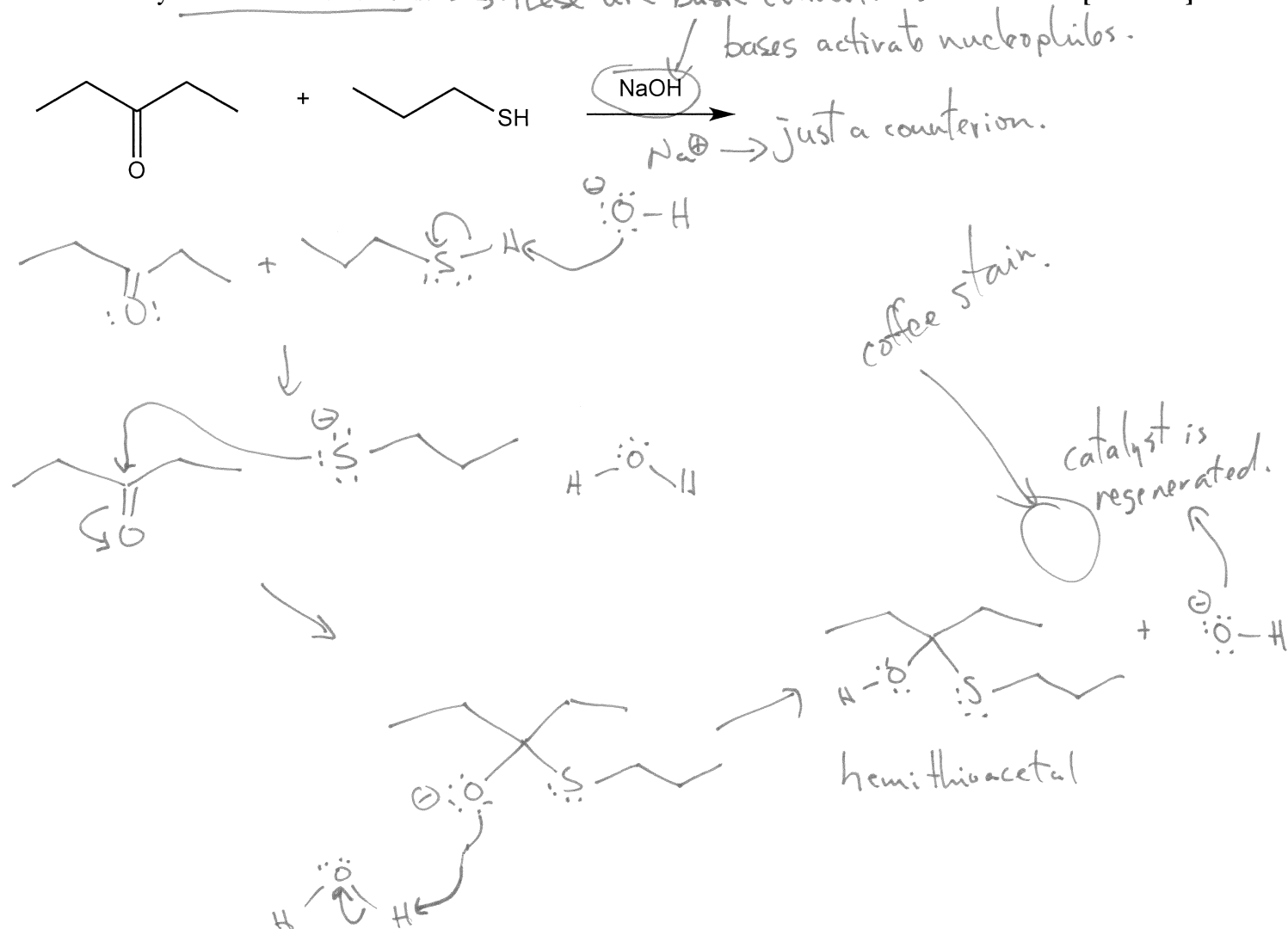
[6 marks]



4. Thiols are good nucleophiles and, like alcohols, can react with carbonyl groups to form hemithioacetals.

Provide a mechanism using curved arrows to predict the product of the following reaction. Be sure to consider your reaction conditions. $\rightarrow$ these are basic conditions.

[5 marks]

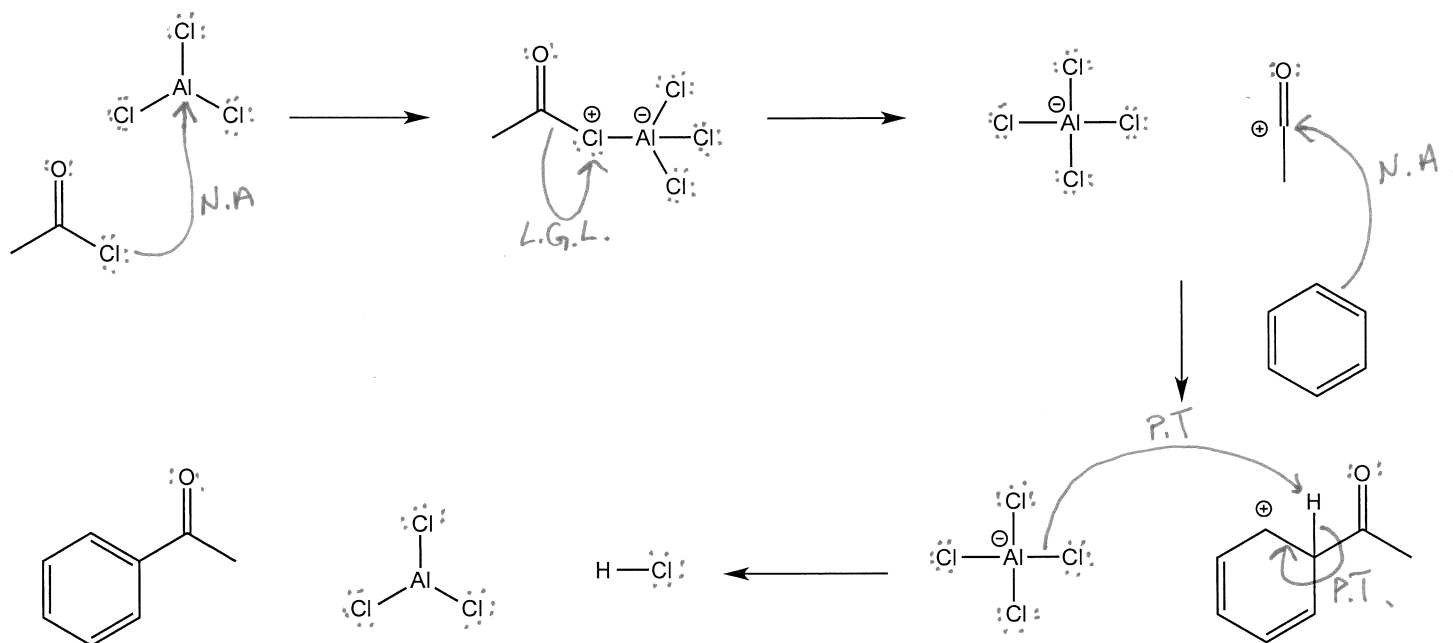


5. Consider the following Friedel-Crafts acylation reaction:

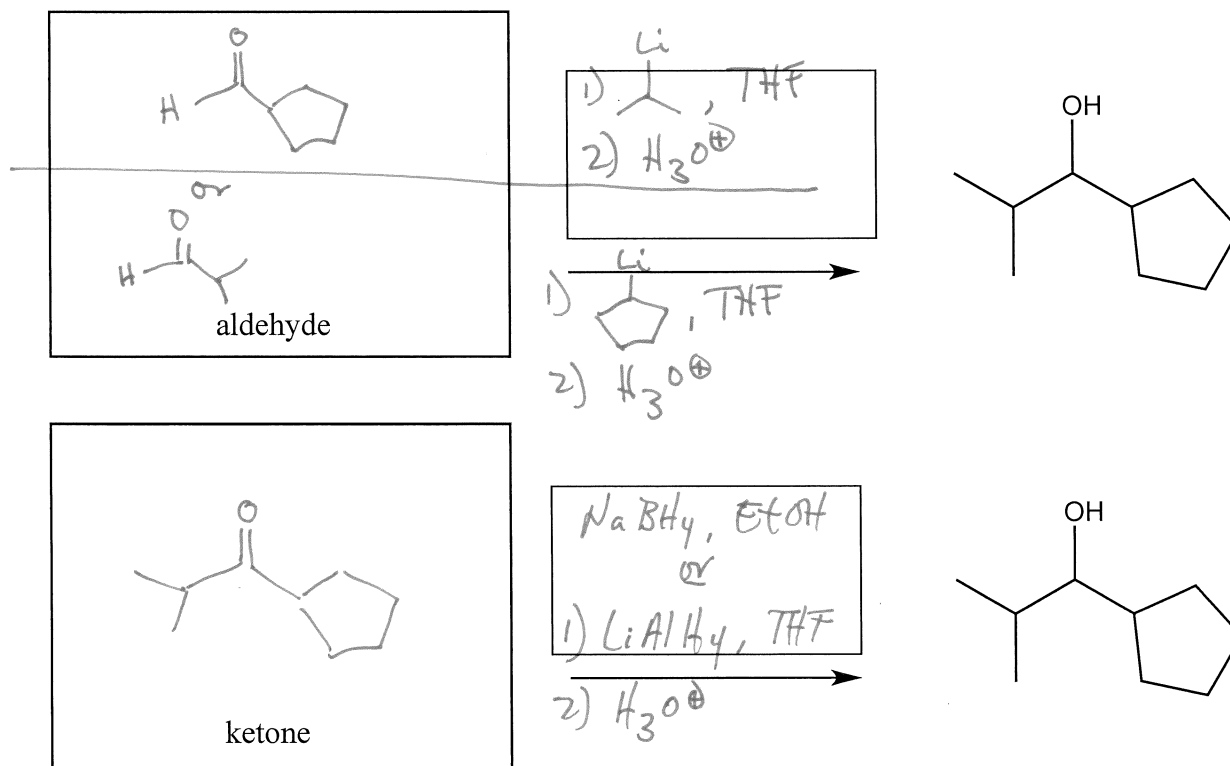
(i) Add all lone pairs.

(ii) Add mechanistic arrows to show the flow of electrons.

(iii) Label each arrow as either Proton Transfer (P.T), Nucleophilic Attack (N.A.), or Leaving Group Loss (L.G.L.) [5 mark]

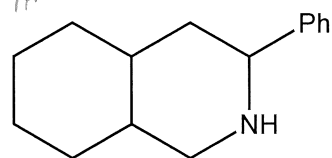
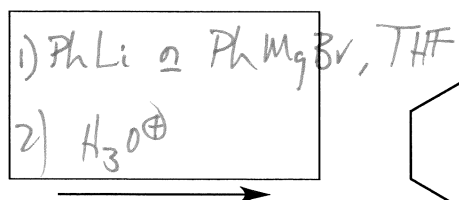
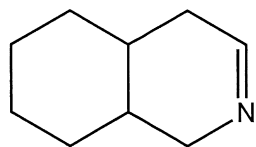
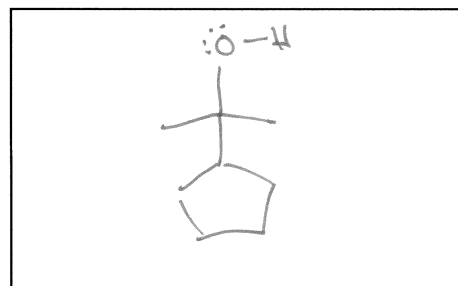
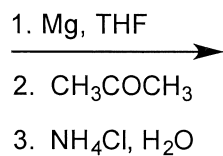
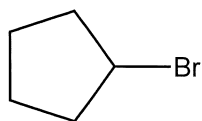
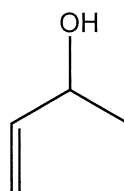
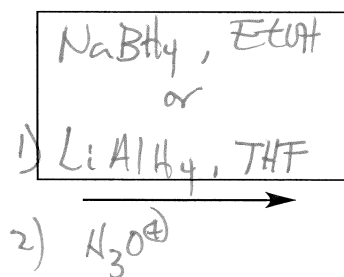
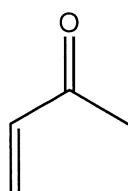
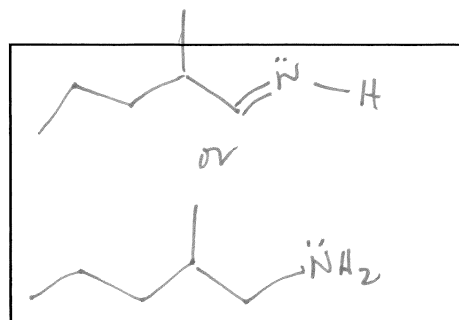
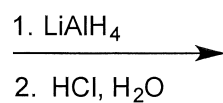
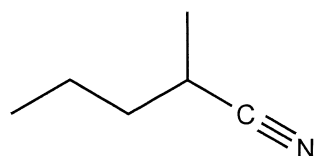


6. Suggest reagents that could be used to synthesize the following molecule in two different reactions; one from an aldehyde and one from a ketone. [6 marks]



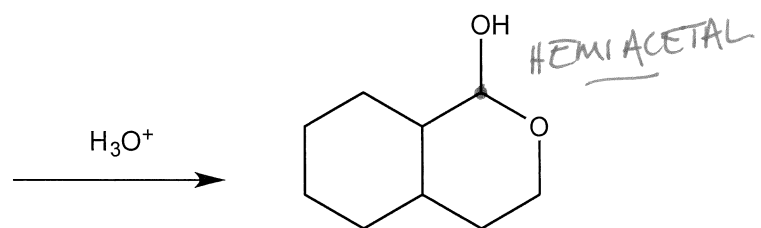
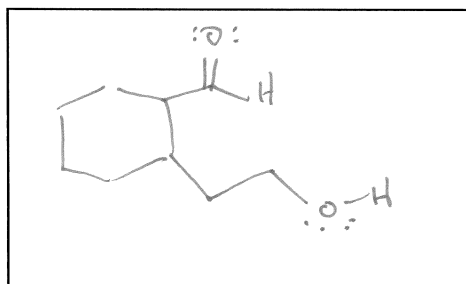
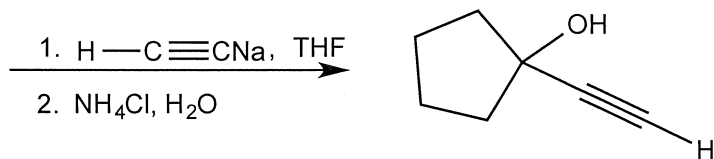
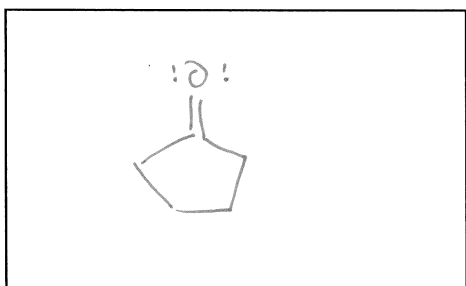
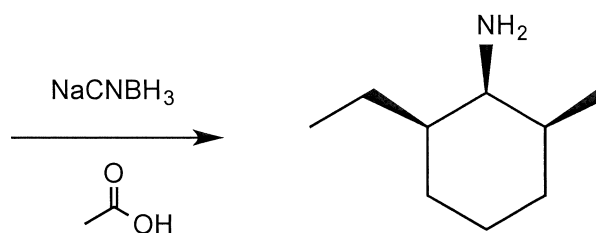
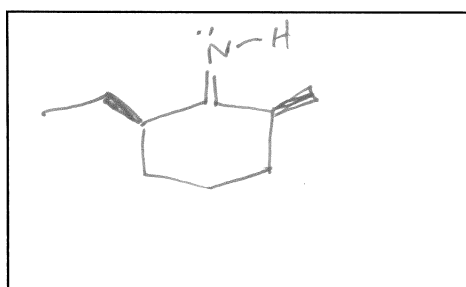
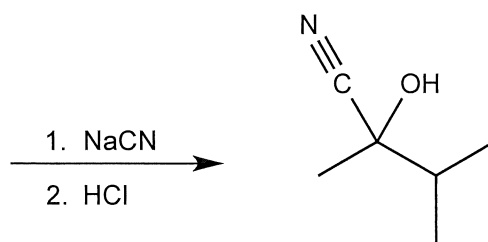
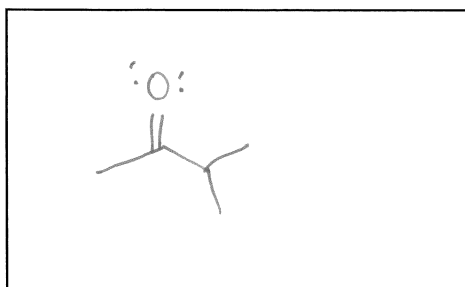
7. For each of the following reactions, provide the missing reagents or products.

[4 marks]

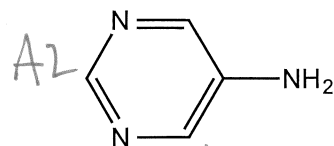
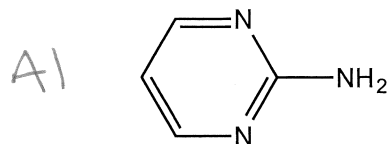


8. For each of the following reactions, fill in the missing organic starting reagents.

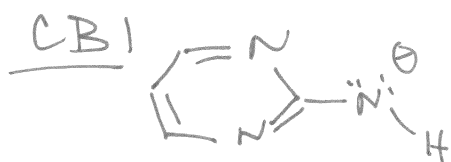
[4 marks]



9. Predict which of the following compounds is more acidic and explain your choice. [5 marks]

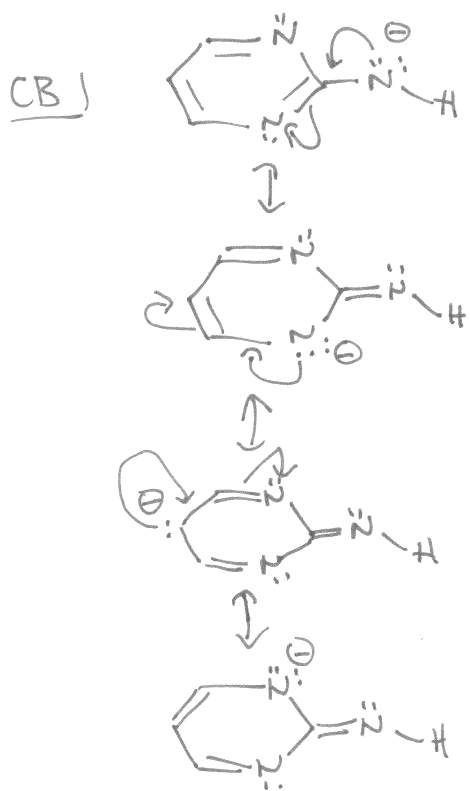


Both acids are neutral therefore we need to look at their conjugate bases.



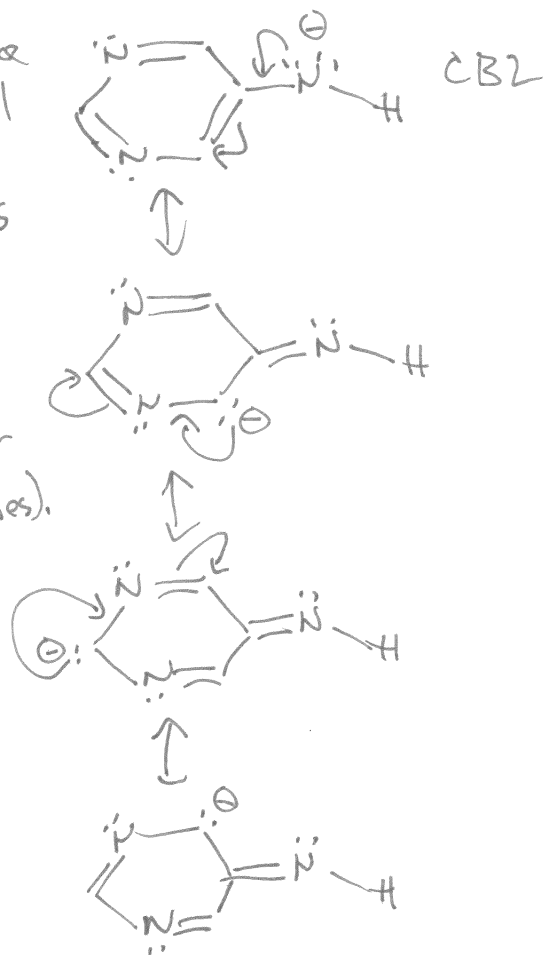
Initially, both conjugate bases have a negative charge on nitrogen. Therefore, electronegativity and atom size is not a factor. Hybridization is also the same so that is not a factor. The two nitrogen atoms in the ring are in different positions in both CBs but any inductive effects would be minimal at best (N is not that electronegative).

Both CBs have resonance:

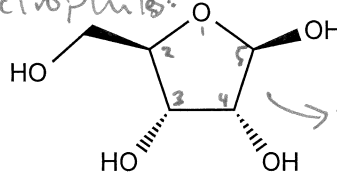
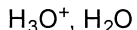
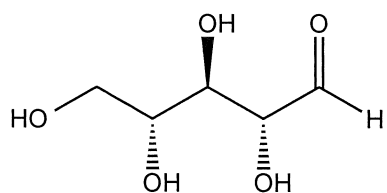


Both CBs have 4 resonance structures, however, in CB1 the negative charge is delocalized over 3 N atoms and 1 C atom. In CB2, the charge is spread over 3 C atoms & 1 N atom.

The negative charge is better on N than C (electronegativities). Therefore, CB1 is more stable and a weaker base making A1 a stronger acid than A2.



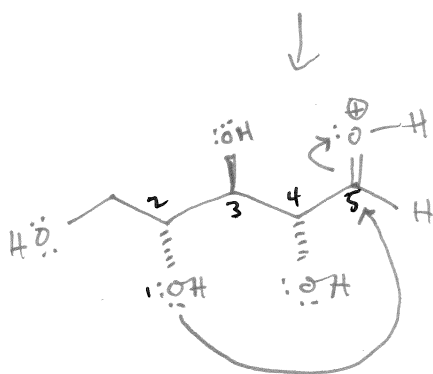
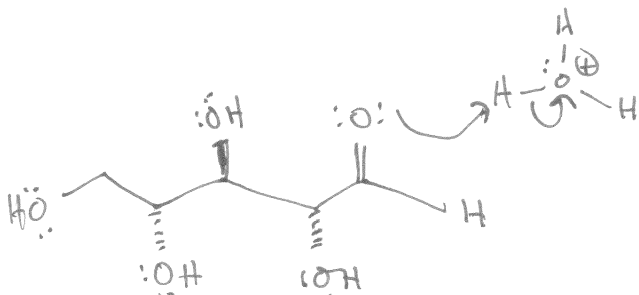
10. Under acidic conditions, D-ribose is converted to the hemiacetal, D-ribofuranose. Use curved arrows to draw a plausible mechanism for the following reaction. Be sure to consider your reaction conditions. [5 marks]



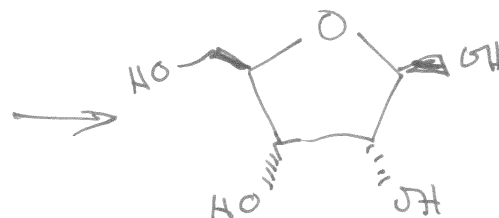
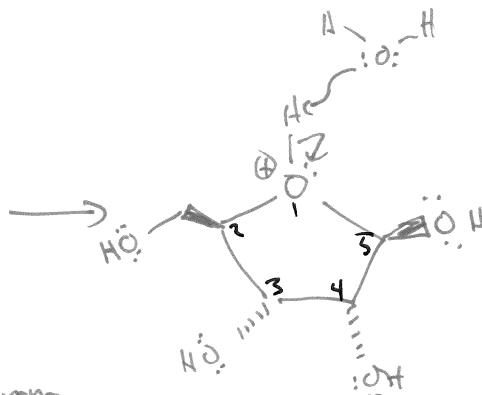
*these are acidic conditions.
acids activate electrophiles.*

[5 marks]

*→ this is a hemiacetal.
→ alcohol attacks an aldehyde → ketone.*



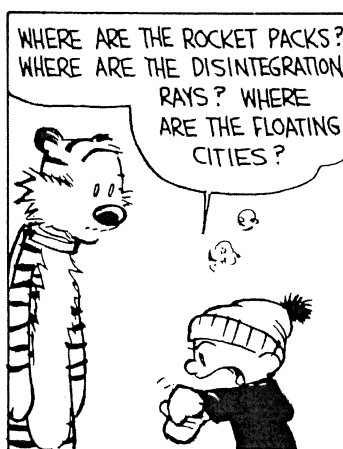
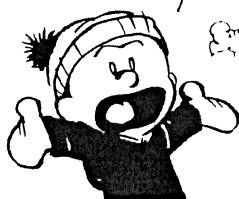
*many alcohols to choose from
but only 1 gives a 5-membered
ring.*



regenerated.

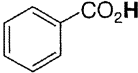
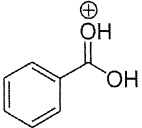
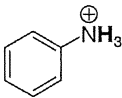
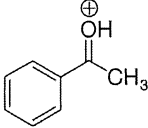
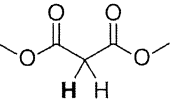
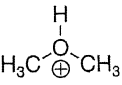
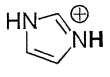
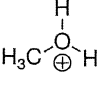
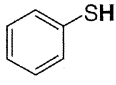
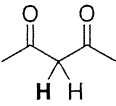
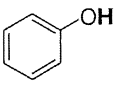
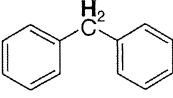
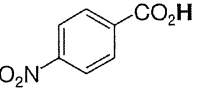
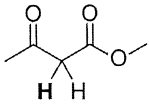
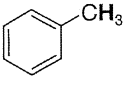


WHERE ARE THE FLYING CARS?
WHERE ARE THE MOON COLONIES?
WHERE ARE THE PERSONAL
ROBOTS AND THE ZERO GRAVITY
BOOTS, HUH? YOU CALL THIS A
NEW DECADE?! YOU CALL THIS
THE FUTURE?? HA!



APPENDIX C

pK_a Values¹ of Selected Organic Compounds

Compound	pK _a	Compound	pK _a	Compound	pK _a
HBr	-9		4.2	CH ₂ (C≡N) ₂	11
	-8		4.6	H ₂ O ₂	11.6
	-6	CH ₃ CO ₂ H	4.8	CCl ₃ CH ₂ OH	12.2
HCl	-7		5.2		13
	-3.8	H ₂ CO ₃	6.4	CHCl ₂ CH ₂ OH	12.9
H ₂ SO ₄	-3		6.9	CH ₃ CHO	13.6
	-2.2	H ₂ S	7.0	CH ₂ ClCH ₂ OH	14.3
CH ₃ SO ₃ H	-2.6		7.8		15
H ₃ O ⁺	-1.7	CH ₃ C(O)OOH	8.2	CH ₃ OH	15.5
HNO ₃	-1.3		9	H ₂ O	15.7
CF ₃ CO ₂ H	-0.2	NH ₄ ⁺	9.2	CH ₃ CONH ₂	15.1
CCl ₃ CO ₂ H	0.6	H-C≡N	9.4	(CH ₃) ₃ COH	17
CHCl ₂ CO ₂ H	1.3	-CO ₂ CH ₂ NH ₃ ⁺	9.7	CH ₃ COCH ₃	20
CH ₂ (NO ₂)CO ₂ H	1.6	(CH ₃) ₃ NH ⁺	9.8	HC≡CH	24
H ₃ PO ₄	2.1		10.0	N≡C-CH ₃	25
CH ₂ ClCO ₂ H	2.9	CH ₃ CH ₂ SH	10.5		34
HF	3.2	CH ₃ NO ₂	10.3	H ₂	36
	3.4		11	NH ₃	38
CH ₃ OCH ₂ CO ₂ H	3.6				41
HCO ₂ H	3.8				43
				CH ₂ =CH-CH ₃	43
				CH ₂ =CH ₂	44
				CH ₃ CH ₃	48

¹ pK_a values obtained in aqueous solutions at 25 °C. pK_a values less than 0 and greater than 15.7 are corrected values from measurements in other solvents.

hydrogen 1 H	helium 2 He
lithium 3 Li	beryllium 4 Be
sodium 11 Na	magnesium 12 Mg
potassium 19 K	calcium 20 Ca
rubidium 37 Rb	strontium 38 Sr
cesium 55 Cs	barium 56 Ba
francium 87 Fr	radium 88 Ra
Key: element name atomic number symbol atomic weight (mean relative mass)	
1.0078	
beryllium 4 Be	
magnesium 12 Mg	
calcium 20 Ca	
strontium 38 Sr	
barium 56 Ba	
radium 88 Ra	
1.0079	
lithium 3 Li	
beryllium 4 Be	
boron 5 B	
carbon 6 C	
nitrogen 7 N	
oxygen 8 O	
fluorine 9 F	
neon 10 Ne	
sodium 11 Na	
magnesium 12 Mg	
aluminum 13 Al	
silicon 14 Si	
phosphorus 15 P	
sulfur 16 S	
chlorine 17 Cl	
argon 18 Ar	
potassium 19 K	
calcium 20 Ca	
scandium 21 Sc	
titanium 22 Ti	
vanadium 23 V	
chromium 24 Cr	
manganese 25 Mn	
iron 26 Fe	
cobalt 27 Co	
nickel 28 Ni	
copper 29 Cu	
zinc 30 Zn	
gallium 31 Ga	
germanium 32 Ge	
arsenic 33 As	
selenium 34 Se	
bromine 35 Br	
krypton 36 Kr	
rubidium 37 Rb	
strontium 38 Sr	
yttrium 39 Y	
zirconium 40 Zr	
niobium 41 Nb	
molybdenum 42 Mo	
technetium 43 Tc	
ruthenium 44 Ru	
rhodium 45 Rh	
palladium 46 Pd	
silver 47 Ag	
cadmium 48 Cd	
indium 49 In	
tin 50 Sn	
antimony 51 Sb	
tellurium 52 Te	
iodine 53 I	
xenon 54 Xe	
barium 56 Ba	
lanthanum 57-70 *	
cerium 58 Ce	
praseodymium 59 Pr	
neodymium 60 Nd	
promethium 61 Pm	
samarium 62 Sm	
europium 63 Eu	
gadolinium 64 Gd	
terbium 65 Tb	
dysprosium 66 Dy	
holmium 67 Ho	
erbium 68 Er	
thulium 69 Tm	
ytterbium 70 Yb	
lutetium 71 Lu	
hafnium 72 Hf	
tantalum 73 Ta	
tungsten 74 W	
rhenium 75 Re	
osmium 76 Os	
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mercury 80 Hg	
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lead 82 Pb	
bismuth 83 Bi	
polonium 84 Po	
astatine 85 At	
radon 86 Rn	
francium 87 Fr	
radium 88 Ra	
actinium 89-102 **	
thorium 90 Th	
protactinium 91 Pa	
uranium 92 U	
neptunium 93 Np	
plutonium 94 Pu	
americium 95 Am	
curium 96 Cm	
berkelium 97 Bk	
californium 98 Cf	
einsteinium 99 Es	
fermium 100 Fm	
mendelevium 101 Md	
nobelium 102 Nb	
lawrencium 103 Lr	
rutherfordium 104 Rf	
dubnium 105 Db	
seaborgium 106 Sg	
bohrium 107 Bh	
hassium 108 Hs	
meitnerium 109 Mt	
darmstadtium 110 Ds	
roentgenium 111 Rh	
unbinilium 112 Uub	
ununilium 113 Uuh	
unununium 114 Uuq	
unbium 115 Uub	
ununseptium 116 Uus	
ununoctium 117 Uuo	
unseptium 118 Uus	
unnilium 119 Uun	
ununium 120 Uuu	
unbinilium 121 Uub	
untrium 122 Uut	
unquadrium 123 Uuq	
unquadium 124 Uuq	
unpentium 125 Uup	
unhexium 126 Uuh	
unheptium 127 Uuh	
unoctium 128 Uuo	
unnonium 129 Uun	
unnilium 130 Uun	
unbihexium 131 Uub	
unbihexium 132 Uub	
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unbihexium 162 Uub	
unbihexium 163 Uub	
unbihexium 164 	

*lanthanoids

actinoids

lanthanum	57	cerium	58	praseodymium	59	neodymium	60	promethium	61	samarium	62	europium	63	gadolinium	64	terbium	65	dysprosium	66	holmium	67	erbium	68	thulium	69	ytterbium	70
La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb	
138.91		140.12		140.91		144.24		[145]		150.36		151.96		157.25		158.93		162.50		164.93		167.26		168.93		173.04	
actinium	89	thorium	90	protactinium	91	uranium	92	neptunium	93	plutonium	94	americium	95	curium	96	berkelium	97	californium	98	einsteinium	99	fermium	100	mendeleevium	101	nobelium	102
Ac		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No	
227.03		232.04		231.04		238.03		237.04		244.06		243.06		247.07		247.07		251.08		252.08		257.10		258.10		259.10	