Name: _____ Student Number: _____

Chemistry 2600 Final Exam (Version A)
December 14th, 2019

INSTRUCTIONS

1) Read the exam carefully before beginning. There are 9 questions on pages 2 to 14 followed by a periodic table and a blank page for rough work. You are also provided with a Spectroscopy Data Package (as posted on the class website). **Please ensure that you have a complete exam. If not, let an invigilator know immediately**. All pages must be submitted.
2) You are allowed to bring one index card (maximum size 3"x5") into the exam with you as a "cheat sheet". This card must be submitted with your exam.
3) You are allowed to bring a ruler and a molecular model kit.
4) You may use a calculator. It may not have wireless capability. You may not have any other electronic devices (phone, iPod, etc.) with you when you write the exam.
5) If your work is not legible, it will be given a mark of zero.
6) Marks will be deducted for incorrect information added to an otherwise correct answer.
7) When drawing molecules, clearly show any relevant stereochemistry. If a mixture of diastereomers is produced, draw both/all of them.
8) **DO NOT OPEN THE EXAM UNTIL YOU ARE TOLD TO BEGIN.**
   Beginning prematurely will result in removal of your exam paper and a mark of 0.
9) You have **3 hours** to complete this exam. Nobody may leave the exam room during the first hour or the last 15 minutes of the exam.

Q	Mark
1	/ 10
2	/ 8
3	/ 15
4	/ 12
5	/ 6

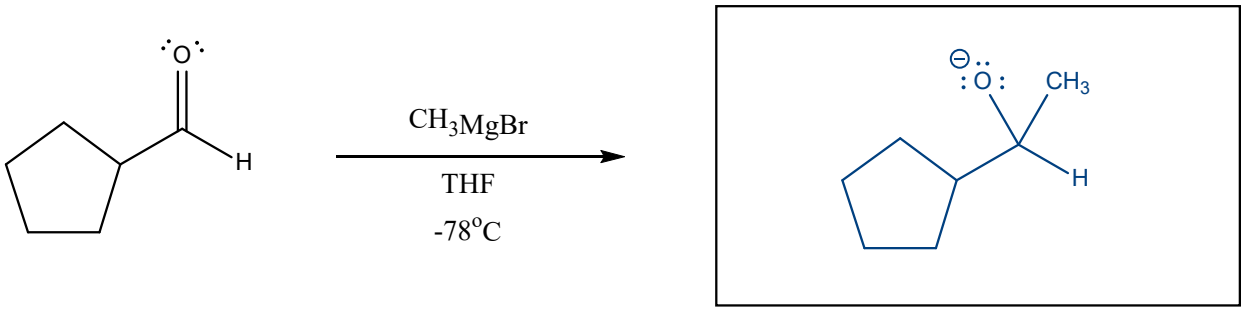
Q	Mark
6	/ 26
7	/ 18
8	/ 4
9	/ 1
10	

Total	/ 100

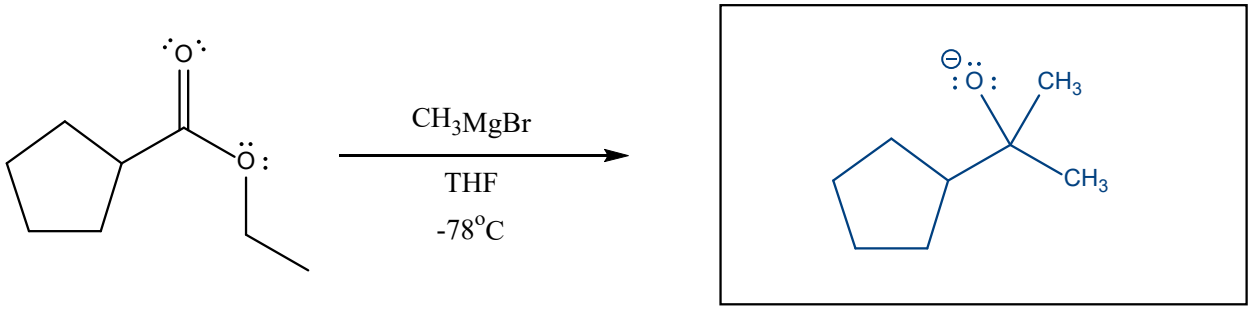
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1. For each of the following reactions, draw the major organic product. **[10 marks]**
Reagents listed above or below the arrow are present in sufficient quantity to allow for full reaction. Do **not** assume an aqueous work-up if none is shown.

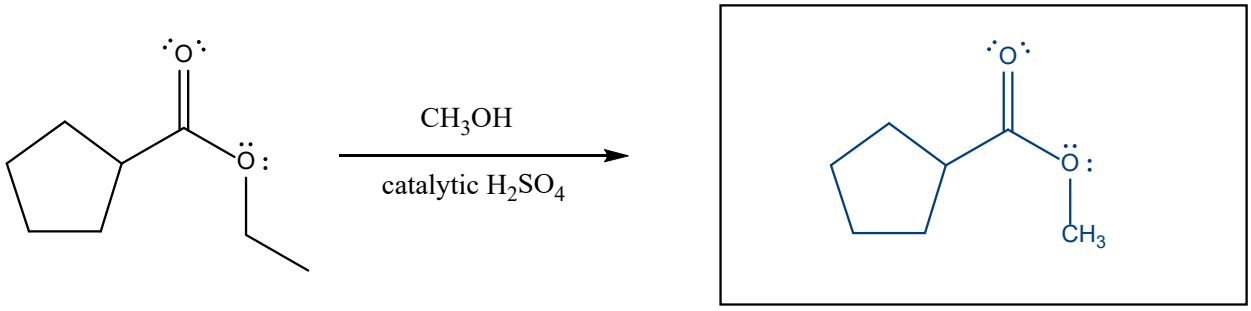
(a)



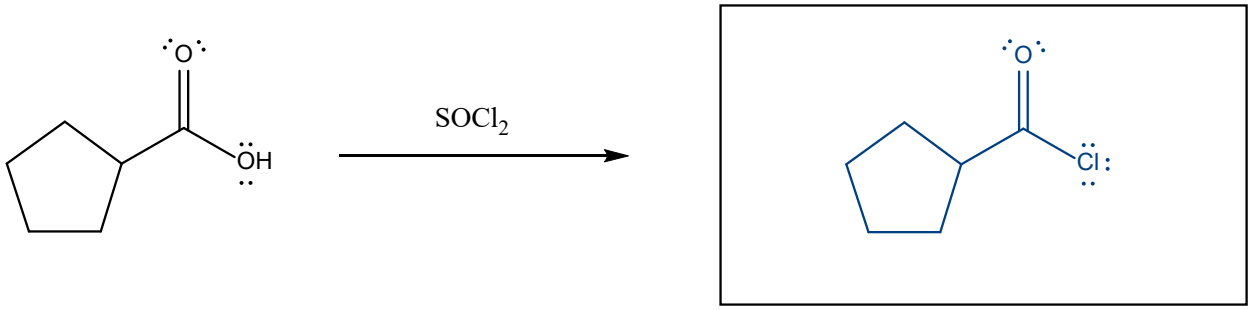
(b)



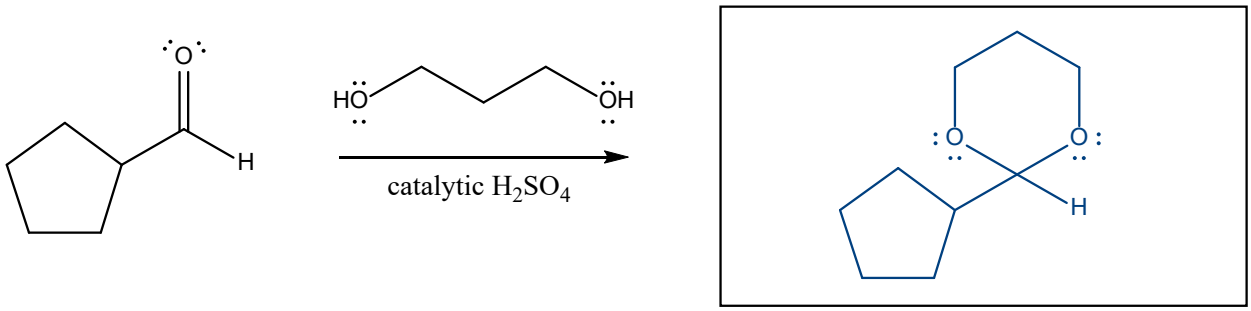
(c)



(d)

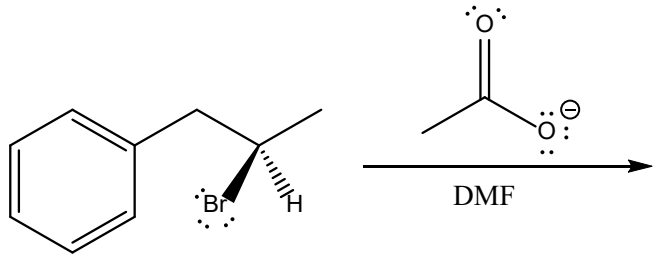


(e)



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2. *(R)*-(2-bromopropyl)benzene is reacted with sodium acetate (CH_3CO_2Na): **[8 marks]**

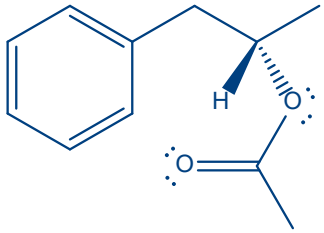


(a) Draw the organic product(s) that you would expect to observe if this reaction proceeded according to an S_N1 mechanism. Clearly show any relevant stereochemistry. *[2 marks]*



An S_N1 reaction proceeds via a trigonal planar carbocation intermediate. The nucleophile can therefore attack the electrophilic carbocation from either side, so both enantiomers of substitution product can form.

(b) Draw the organic product(s) that you would expect to observe if this reaction proceeded according to an S_N2 mechanism. Clearly show any relevant stereochemistry. *[2 marks]*



An S_N2 reaction proceeds via backside attack, so only the enantiomer corresponding to inversion at the electrophilic carbon atom can form.

(c) Briefly, describe an experiment that would use kinetics to determine which mechanism is followed for this reaction. What parameters would you vary, and what results would support each mechanism? *[4 marks]*

S_N1 reactions are first order (with the rate of reaction depending only on the concentration of electrophile). S_N2 reactions are second order (with the rate of reaction depending on both the concentration of nucleophile and of electrophile).

As such, if you performed several reactions with each having the same concentration of *(R)*-(2-bromopropyl)benzene but a different concentration of sodium acetate (CH_3CO_2Na) and measured the rate of each reaction, you could determine which mechanism is followed:

- If all the reactions had the same rate, the mechanism would be S_N1.
- If doubling the concentration of sodium acetate doubled the rate of reaction, the mechanism would be S_N2.
- If doubling the concentration of sodium acetate increased the rate of reaction but by less than a factor of two, both mechanisms would be active.

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3. If 2-hexanol is reacted with sulfuric acid, three elimination products are possible. **[15 marks]**

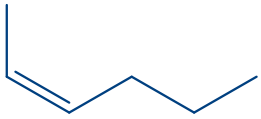
(a) Draw all three potential elimination products. *[3 marks]*



1-hexene



trans-2-hexene



cis-2-hexene

(b) Which of your answers to part (a) would you expect to be the thermodynamic product? Justify your choice. *[3 marks]*

The thermodynamic product will be *trans*-2-hexene.

Both isomers of 2-hexene have a more highly substituted double bond than 1-hexene (favouring both over 1-hexene from a thermodynamic standpoint).

The alkyl groups attached to each end of the double bond are more spread out in *trans*-2-hexene than they are in *cis*-2-hexene. As such, there is less steric hindrance (or steric strain) in *trans*-2-hexene.

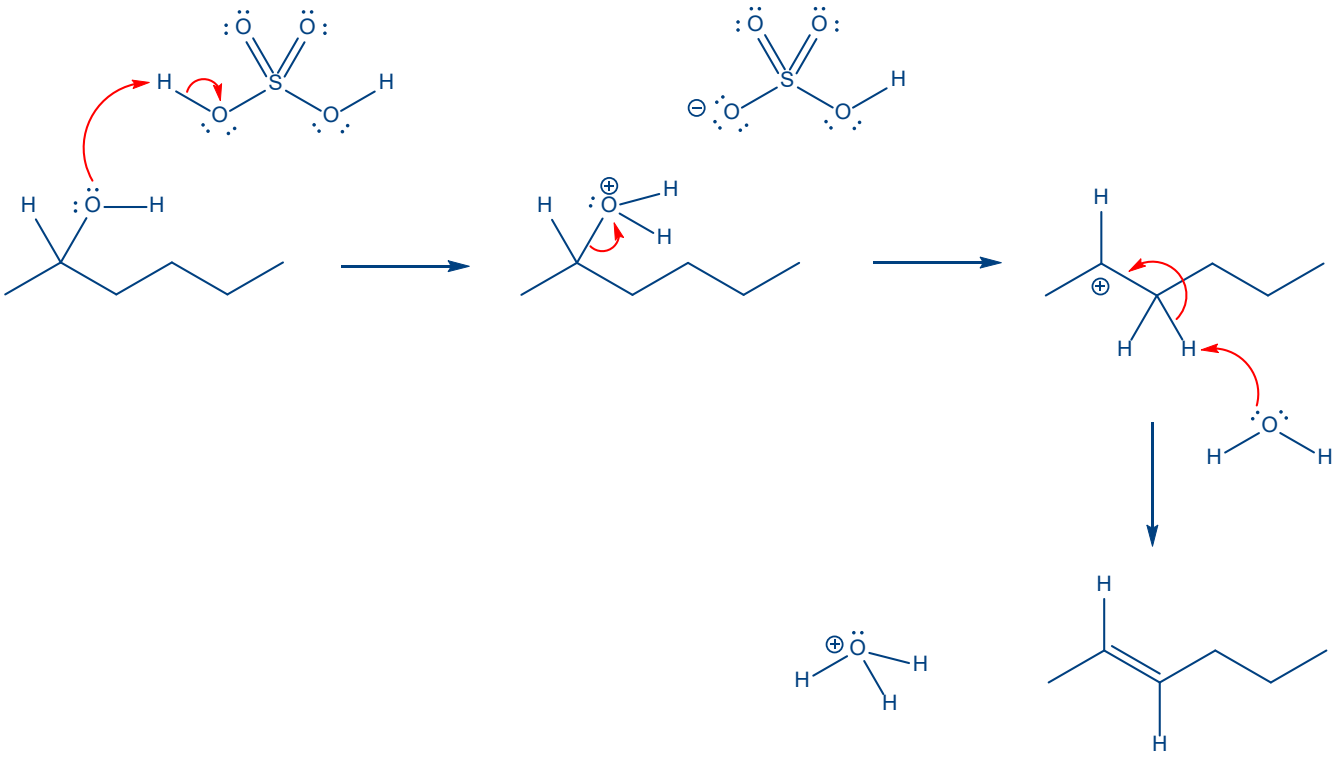
(c) How would you favour production of the thermodynamic product over the other two potential elimination products? Give two suggestions. *[2 marks]*

Performing the reaction at high temperature will favour the thermodynamic product.

Allowing the reaction to run for a long enough time that equilibrium can be reached will favour the thermodynamic product.

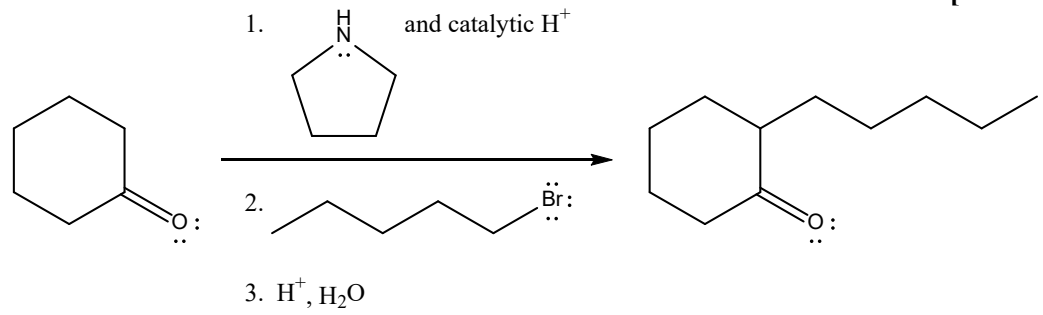
(d) Draw a mechanism for the reaction of 2-hexanol with sulfuric acid to produce the thermodynamic equilibrium product **and** classify your mechanism as E1 or E2. *[7 marks]*

This is an E1 reaction. *Water is not a strong enough base for an E2 reaction. Hydrogen sulfate is an even weaker base than water.*

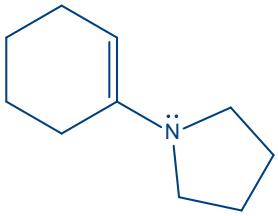


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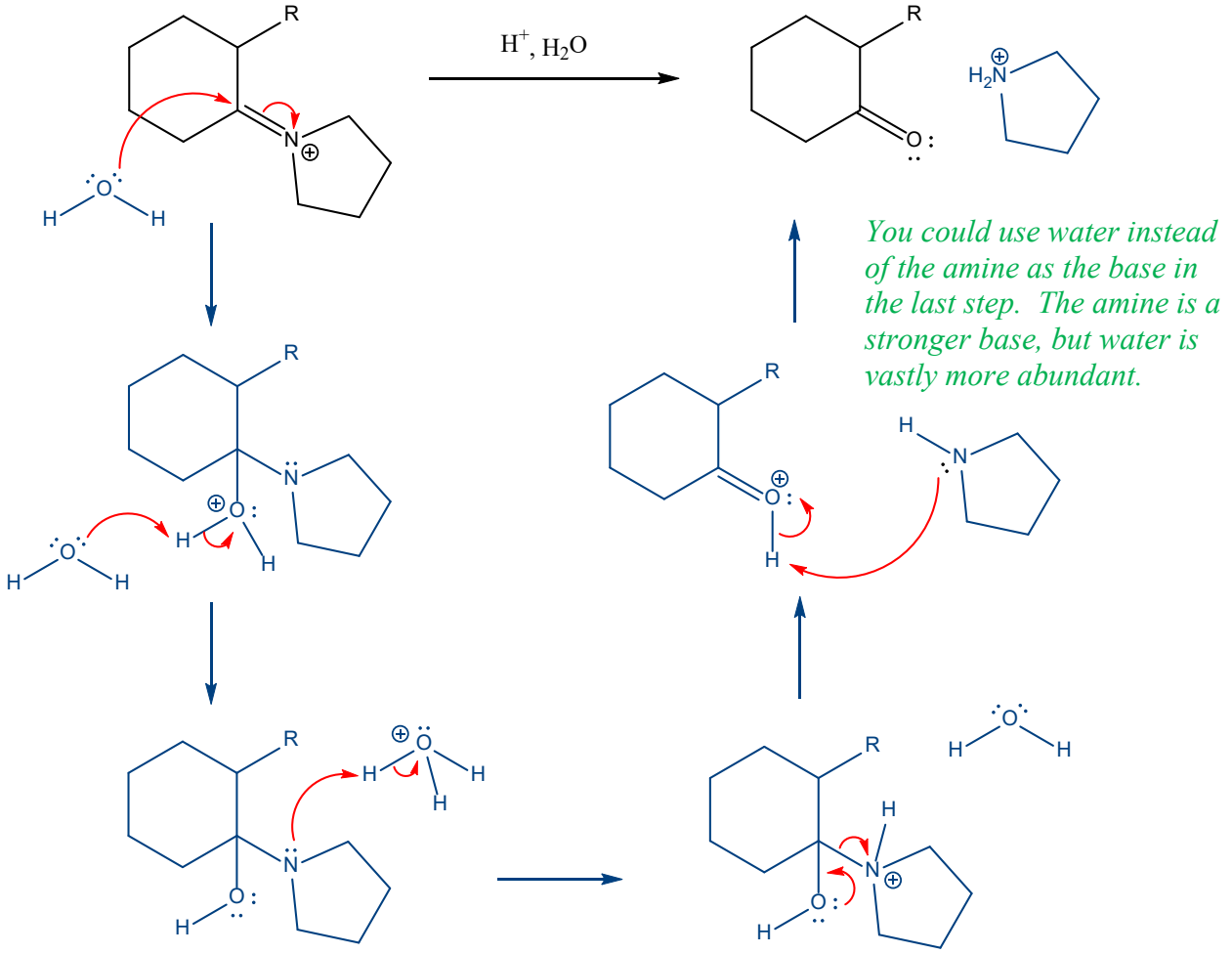
4. A student decides to use an enamine strategy to prepare 2-pentylcyclohexanone from cyclohexanone: **[12 marks]**



(a) Draw the structure of the enamine made in step 1 of the three-step process outlined above. *[2 marks]*

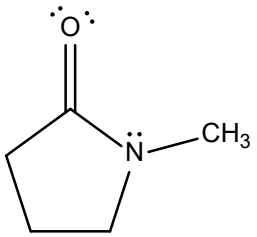


(b) The product of step 2 is an iminium ion *(see below)*. Propose a reasonable mechanism for the hydrolysis of the iminium ion to the desired ketone. *[10 marks]*

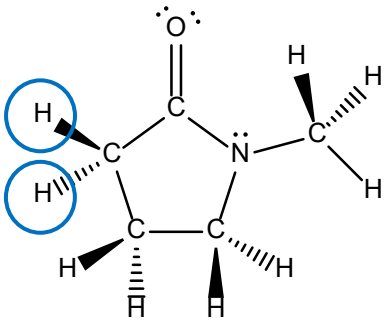


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5. Consider the following molecule. The nitrogen atom is trigonal planar. **[6 marks]**

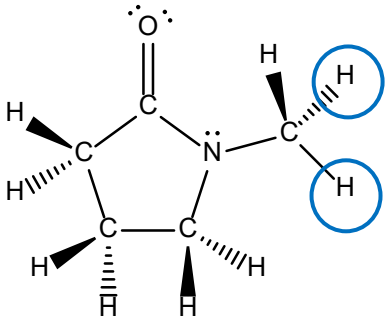


(a) On the picture below, circle two hydrogen atoms which are enantiotopic: *[2 marks]*



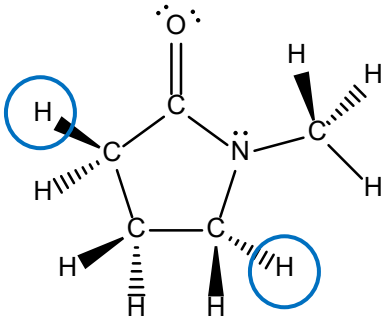
Any two hydrogen atoms attached to the same carbon atom (except the methyl carbon)

(b) On the picture below, circle two hydrogen atoms which are homotopic: *[2 marks]*



Any two of the three hydrogen atoms of the methyl group

(c) On the picture below, circle two hydrogen atoms which are constitutionally different: *[2 marks]*



Any two hydrogen atoms attached to different carbon atoms

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6. The following **two** pages contain spectra for Unknown X. **[26 marks]**

(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

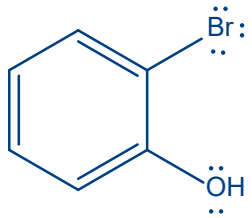
(b) Use this page to explain your logic (including how you determined the molecular formula).

(c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, drawing Unknown X in the box provided on the spectrum, and labeling each carbon or hydrogen atom with the appropriate peak number. *For atoms that cannot be assigned with certainty, list the signals to which they might reasonably correspond.*

(d) Label any important peaks on the IR.

(e) Identify the fragment corresponding to the peak at m/z 93 on the Mass Spectrum.

Unknown X:

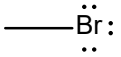


General breakdown of marks (to the best of my recollection):
1 mark for correct answer
1 mark for correct molecular formula
4 marks for showing how to determine correct molecular formula
1 mark for calculating DU
2 marks for calculating integrals for ^{1}H NMR
1 mark for identifying fragment corresponding to the peak at m/z 93 on the Mass Spectrum
1 mark for IR peak assignment (the O-H peak)
2 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
5 marks for ^{1}H NMR assignment (correct for correct answer; "reasonable" for incorrect answers)
8 marks for logic (this page plus legible rough work on spectra, etc.); verbal explanation is required for full credit

One Way to Arrive at the Answer

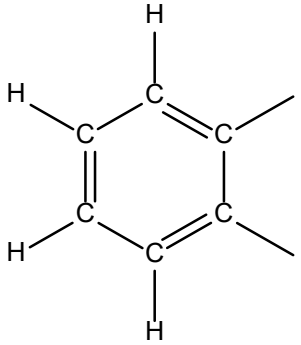
Step 1: Calculate Molecular Formula

- M^+: $[M+2]^+ = 1:1$ so there is one bromine atom
- M^+ is $^m/_z$ 172 so molar mass (when bromine is ^{79}Br) is $172\,\frac{g}{mol}$
  - That means the rest of the molecule is $172\,\frac{g}{mol} - 79\,\frac{g}{mol} = 93\,\frac{g}{mol}$
- There are 6 peaks on the ^{13}C NMR so there are at least 6 carbon atoms
  - That means we have C_6Br and the rest is $93\,\frac{g}{mol} - 72\,\frac{g}{mol} = 21\,\frac{g}{mol}$
- There is a broad peak on the IR at 3490 cm^{-1} and a broad singlet that exchanges with D_2O on the ^{1}H NMR. These peaks suggest either OH or NH (with the IR peak looking more like an OH). If the molecule contained a single nitrogen atom, the molecular ion would be odd. $^m/_z$ 172 is even, so it must contain an oxygen atom instead. Also, the ^{1}H NMR also has four peaks in the aromatic region, and the integral ratio appears to be 1: 1: 1: 1: 1 so the number of hydrogen atoms should be a multiple of five.
  - One oxygen atom $\left(16\,\frac{g}{mol}\right)$ and five hydrogen atoms add up to $21\,\frac{g}{mol}$
- Therefore, the molecular formula must be C_6H_5BrO



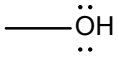
Step 2: Calculate Unsaturation Index (Degrees of Unsaturation)

- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(6)+2-1-5}{2} = \frac{8}{2} = 4$
- Anytime we have four or more degrees of unsaturation, we look for evidence of a benzene ring:
  - There are six peaks on the ^{13}C NMR between 110 and 160 ppm.
  - There are four peaks on the ^{1}H NMR between 6.5 and 7.5 ppm.
- There is probably a disubstituted benzene ring. Since there are four different aromatic H peaks, the two substituents must be different. There are three possible substitution patterns: *ortho*, *meta* and *para*.
  - A *para* disubstituted benzene ring has symmetry, giving two doublets on ^{1}H NMR. We have four peaks in the aromatic region, so the benzene ring is not *para* substituted.
  - A *meta* disubstituted benzene ring gives one singlet, two doublets and one triplet on ^{1}H NMR. There are no singlets in the aromatic region (or extremely narrow doublets/triplets due to a proton that only experiences 4-bond coupling), so the benzene ring is not *meta* substituted.
  - An *ortho* disubstituted benzene ring gives two doublets and two triplets on ^{1}H NMR. This matches what we see on the spectrum provided – the fine splitting of each of those peaks will be due to 4-bond coupling.
- So, Unknown X contains an *ortho*-disubstituted benzene ring:



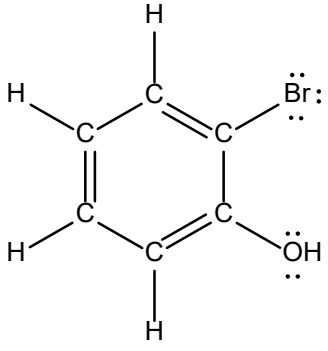
Step 2: Look at IR for relevant peaks

- The large peak at 3490 cm^{-1} strongly suggests a $O-H$ bond.
  - There is also a broad singlet that exchanges with D_2O at 5.5 ppm on the ^{1}H NMR. This chemical shift is consistent with an alcohol and is too far upfield for a carboxylic acid.



Step 3: Assemble the pieces (now that we've used up all the atoms in the molecular formula)

- There is only one way to assemble these three pieces. Attach Br and OH to the *ortho*-disubstituted benzene ring:



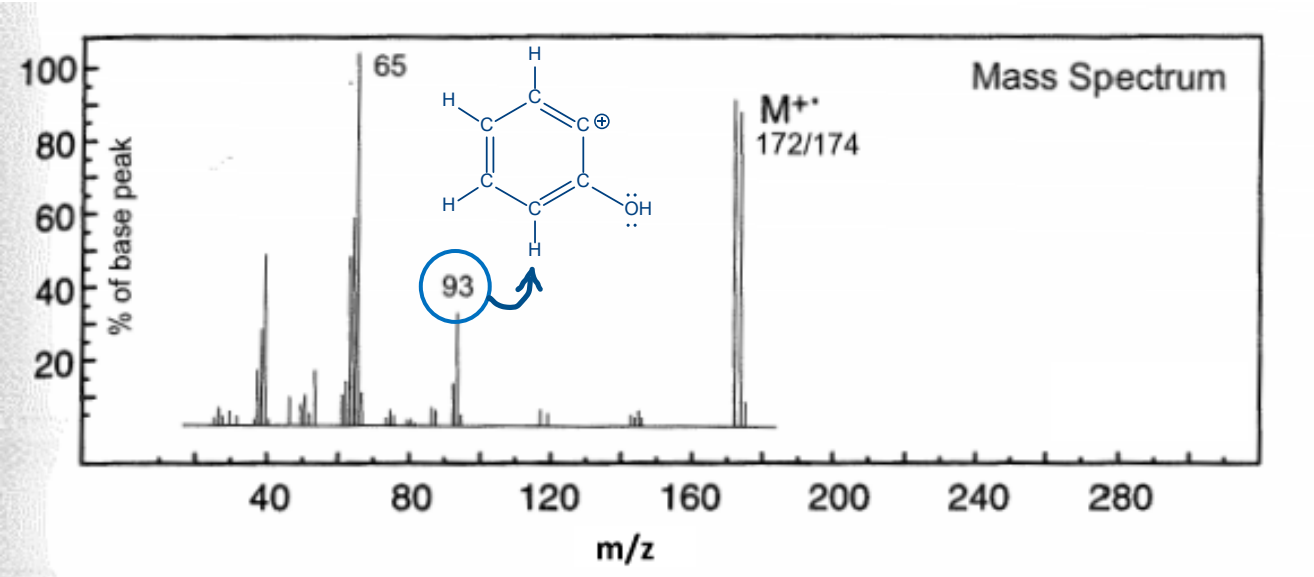
Step 4: Check your answer against the spectra and assign the peaks.

- MS
  - M^+: $[M+2]^+ = 1:1$ consistent with having one bromine atom
  - M^+ is $^m/_z$ 172 consistent with our molecular formula
  - The peak at $^m/_z$ 93 is consistent with fragmentation of the bromine atom
    - $172 - 79 = 93$ so $^m/_z$ 93 is $[C_6H_4OH]^+$
- IR
  - A broad stretch is visible at 3490 cm^{-1}. This is consistent with the phenol $O-H$.
  - $C-H$ stretches are barely visible just above 3000 cm^{-1} (for the trigonal planar carbon atoms) and just below 3000 cm^{-1} (for the tetrahedral carbon atom of the methyl group).
  - $C=C$ stretches are visible at ~1600 cm^{-1} and ~1450 cm^{-1}, consistent with an aromatic ring.
- ^{1}H NMR
  - The broad singlet at ~5.5 ppm integrating to 1H that exchanges with D_2O is consistent with the phenol OH.
  - The four peaks between 6.5 ppm and 7.5 ppm each integrating to 1H are the four aromatic hydrogen atoms.
    - The two doublets of doublets (~7.0 ppm and ~7.4 ppm) must correspond to the hydrogen atoms that are *ortho* to a substituent
      - Oxygen is a better electron donor through resonance so the OH group is expected to shield the hydrogen atom *ortho* to it more effectively than the Br group does. Therefore, the peak at ~7.0 ppm is *ortho* to OH while the peak at ~7.4 ppm is *ortho* to Br.
    - The two triplets of doublets (~6.75 ppm and ~7.15 ppm) must correspond to the hydrogen atoms that are not *ortho* to a substituent
      - Oxygen is a better electron donor through resonance so the OH group is expected to shield the hydrogen atom *para* to it more effectively than the Br group does. Therefore, the peak at ~6.75 ppm is *para* to OH (and *meta* to Br) while the peak at ~7.15 ppm is *para* to Br (and *meta* to OH).
  - Alternatively, calculation of predicted chemical shifts for the aromatic protons using the Spectroscopy Data Package gives the following results:
    - 7.33 ppm for H *ortho* to Br (*meta* to OH) – must be a doublet of doublets
    - 7.11 ppm for H *para* to Br (*meta* to OH) – must be a triplet of doublets
    - 6.74 ppm for H *para* to OH (*meta* to Br) – must be a triplet of doublets
    - 6.64 ppm for H *ortho* to OH (*meta* to Br) – must be a doublet of doublets
  - *Please note that while the calculated values suggest that the hydrogen atom ortho to OH is expected to be further upfield than we observe, experimental evidence (the peak shapes) always trumps theoretical predictions (the predicted chemical shifts). The observed chemical shift is still within 0.5 ppm of the observed value, and the other three are all very good matches.*
- ^{13}C NMR
  - The peak at ~150 ppm is consistent with $C-O$ where C is in a benzene ring.
  - The five peaks between 110 ppm and 140 ppm are consistent with the other five carbon atoms in the benzene ring (which is not symmetrically substituted).

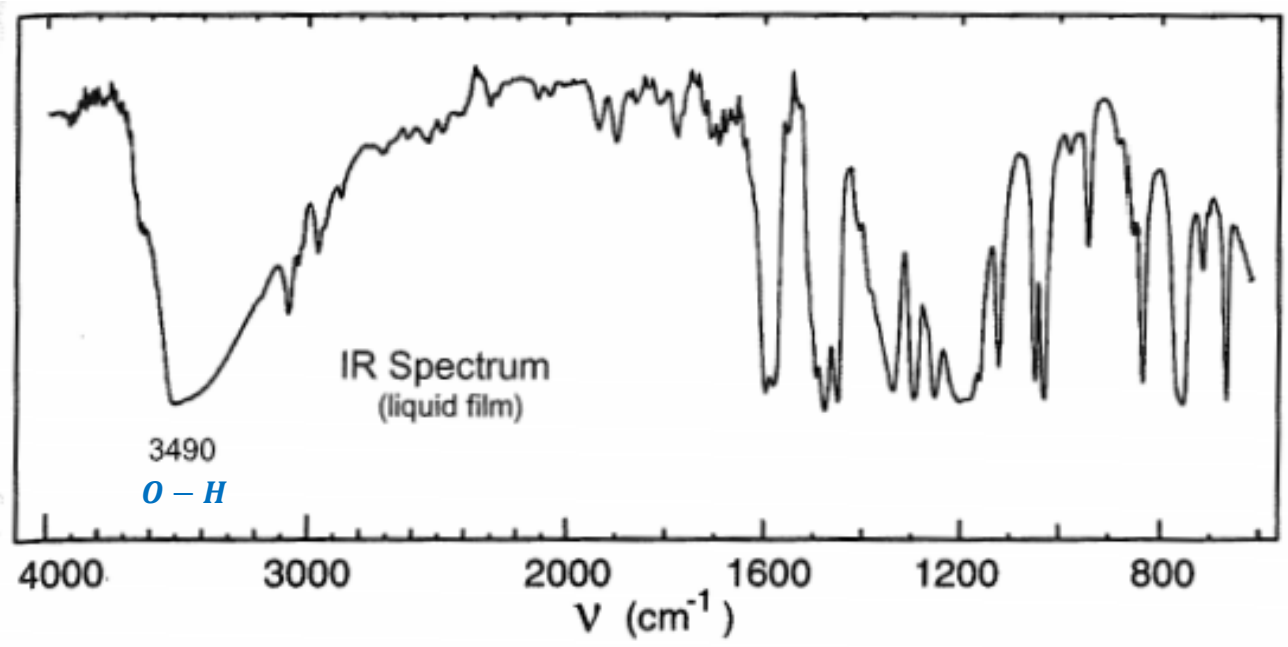
Name: _____ Student Number: _____

6. *…continued…*

Mass Spectrum



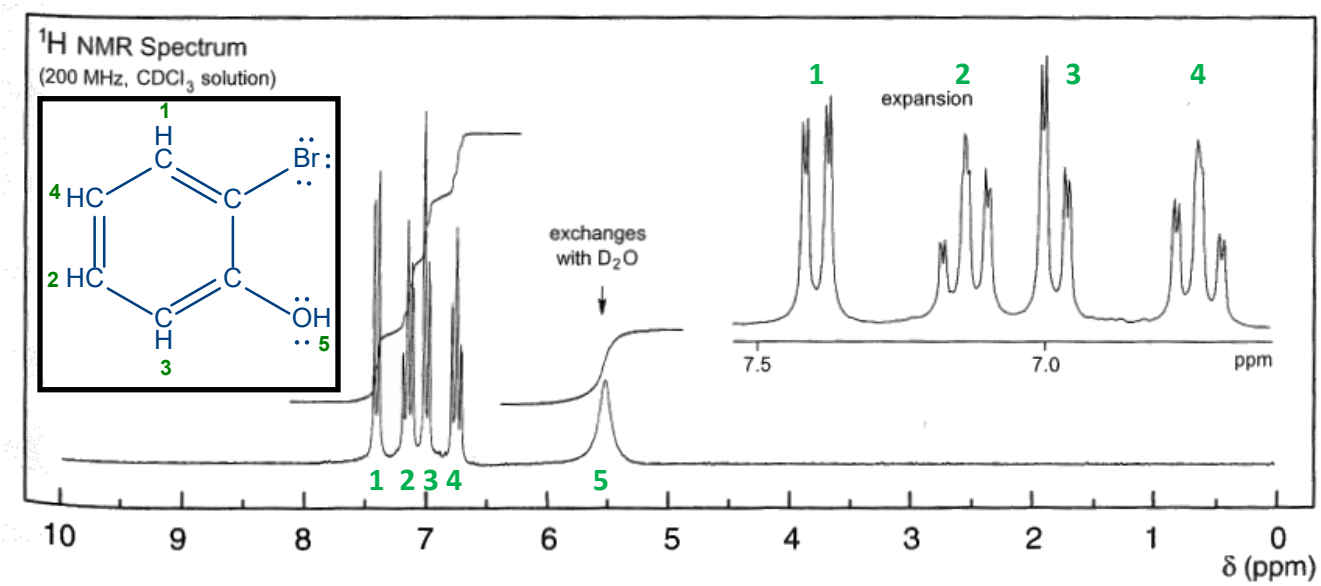
IR



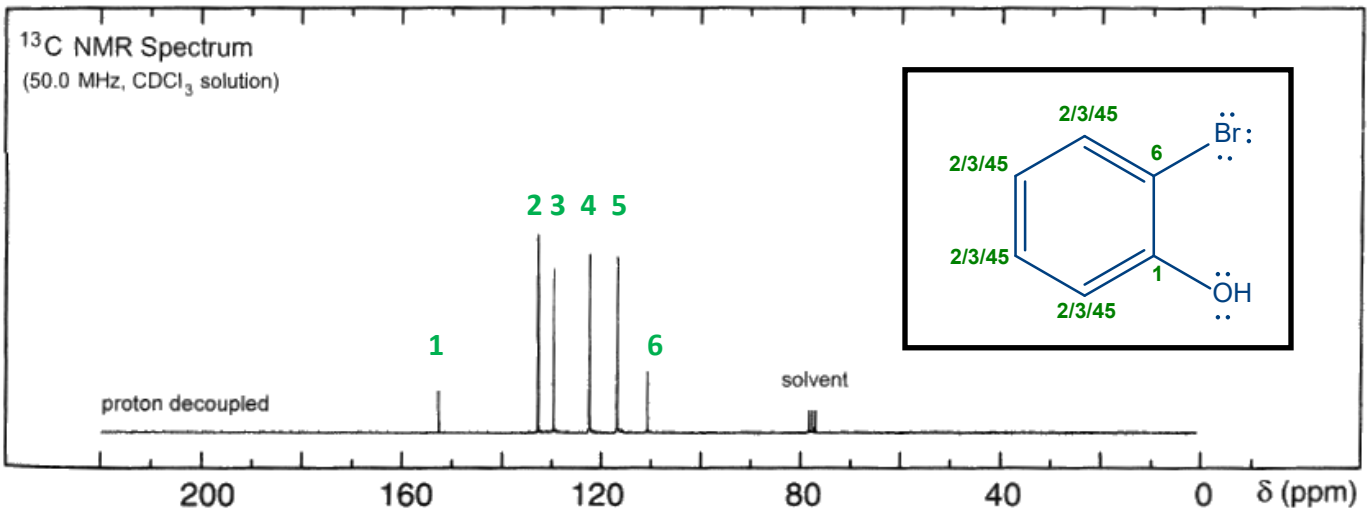
Name: _____ Student Number: _____

6. *…continued…*

^{1}H NMR



^{13}C NMR

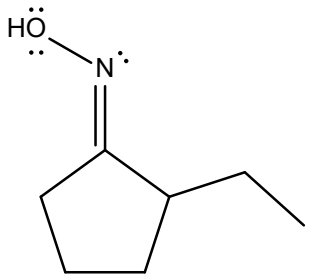


The two short peaks are for the quaternary carbon atoms. Oxygen is significantly more electronegative than bromine, so it is the one that deshields the attached carbon atom downfield to 150 ppm. (Resonance effects only affect carbon atoms ortho or para to an EWG or EDG. So, in this case, OH shields carbon 6 via resonance but deshields carbon 1 inductively.) It's likely that 4 and 5 are the CH ortho and para to OH (stronger shielding via resonance) while 2 and 3 are the CH ortho and para to Br, but I was not expecting that degree of detail for the ^{13}C NMR peak assignments because there are no peak shapes to help.) I was expecting students to be able to identify the carbon giving peak 1 though.

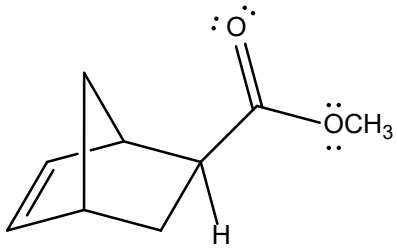
Name: _____ Student Number: _____

7. Choose any **three** of the molecules below and propose a synthesis for each one. **[18 marks]**

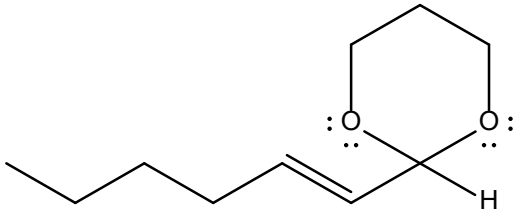
- If your synthesis involves more than one step, write an equation for each step. Show all required reactants. Number steps within a reaction if order of addition is important.
- All organic reactants must be stable compounds containing **no more than five carbon atoms**. They may be **hydrocarbons, alkyl halides or alcohols** and may contain C=C or C≡C bonds. The only exception to this rule is that you are **also allowed** to use **benzene, bromobenzene or phenol**.
- If you wish to use an organic reactant (including Grignard reagent) that does not meet these requirements, you must show how to make it from starting materials that do.
- You may use any inorganic reagents, acids, bases, catalysts, etc.
- Acids, bases, catalysts, etc. do not need to meet the "organic reactant" requirements if the organic part will not be present in the final product.
- Clearly indicate stereochemistry of reaction products where appropriate. Assume that all stereochemistry shown is relative and that you are to make racemic product.
- You are **not** required to show mechanisms for this question.
- There are three pages after this page. Use one of those pages for each synthesis and clearly identify the synthetic target at the top of the page. This page is scrap paper.
- If you give more than three syntheses, I will only mark the first three (ignoring any that are crossed out).



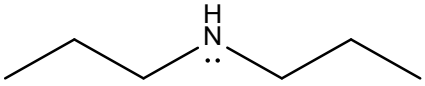
Make the hydroxylamine from a ketone. Before doing that, use enolate chemistry to attach the ethyl group alpha to C=O.



Looks like a Diels-Alder adduct…



Looks like an acetal made from an aldol product…



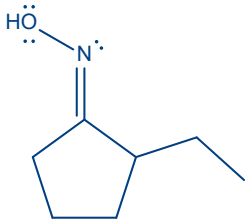
This is a secondary amine. Reaction of a primary amine with an alkyl halide would give a tertiary amine, so do reductive amination instead (i.e. start with aldehyde and primary amine).

The answers in this answer key are representative. There will be other ways each molecule can be made. You were not asked to provide a retrosynthetic analysis; however, I have included one here to more clearly show the logic behind the synthetic proposal.

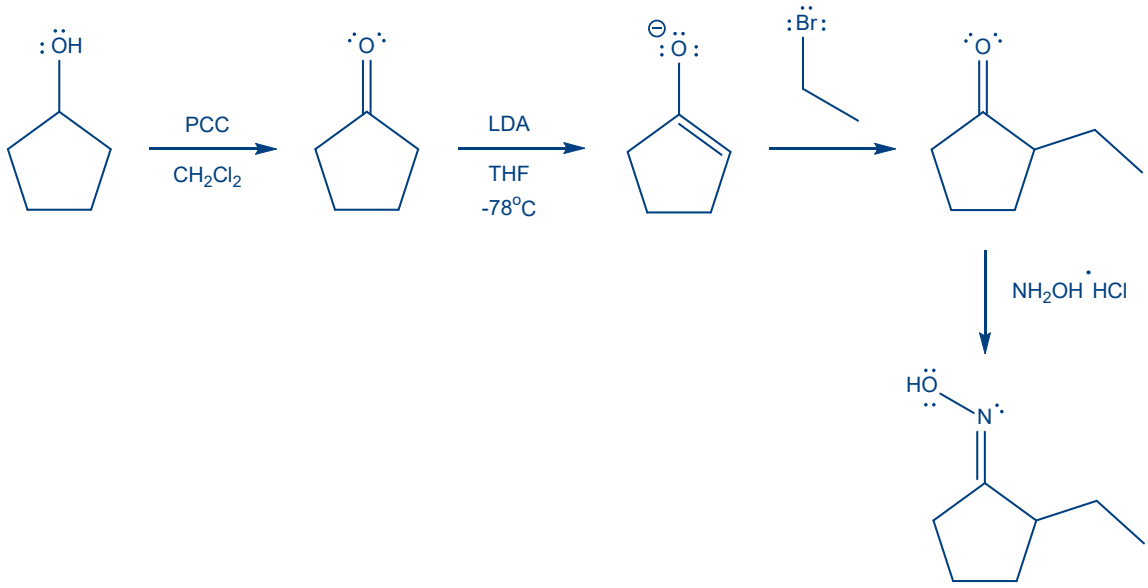
Name: _____ Student Number: _____

7. *continued…* *[6 marks]*

Synthetic Target #1:



Synthesis:



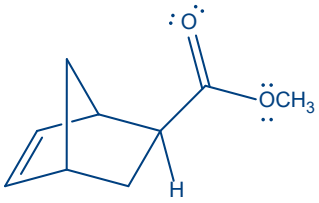
There are many different options for oxidizing agents that will convert a secondary alcohol to a ketone.

Instead of alkylating via enolate chemistry, you could also alkylate via enamine chemistry.

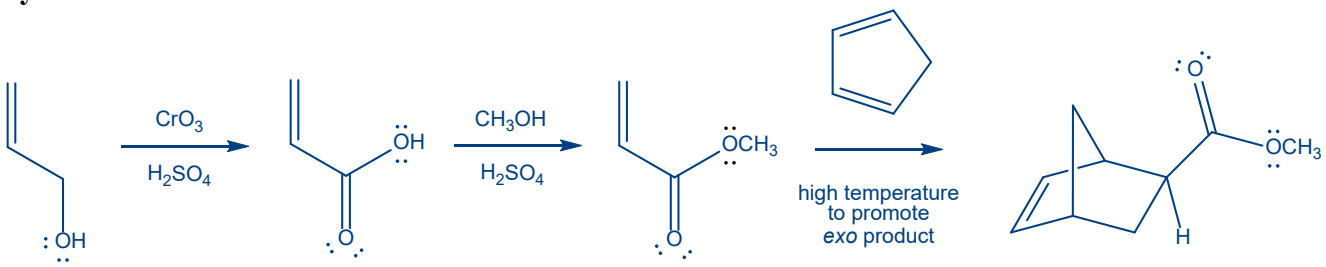
Name: _____ Student Number: _____

7. *continued…* *[6 marks]*

Synthetic Target #2:



Synthesis:

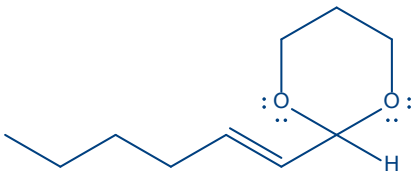


Instead of the Fischer esterification shown above, you could use $SOCl_2$ to convert the carboxylic acid into an acid chloride and then react the acid chloride with methanol to give the methyl ester.

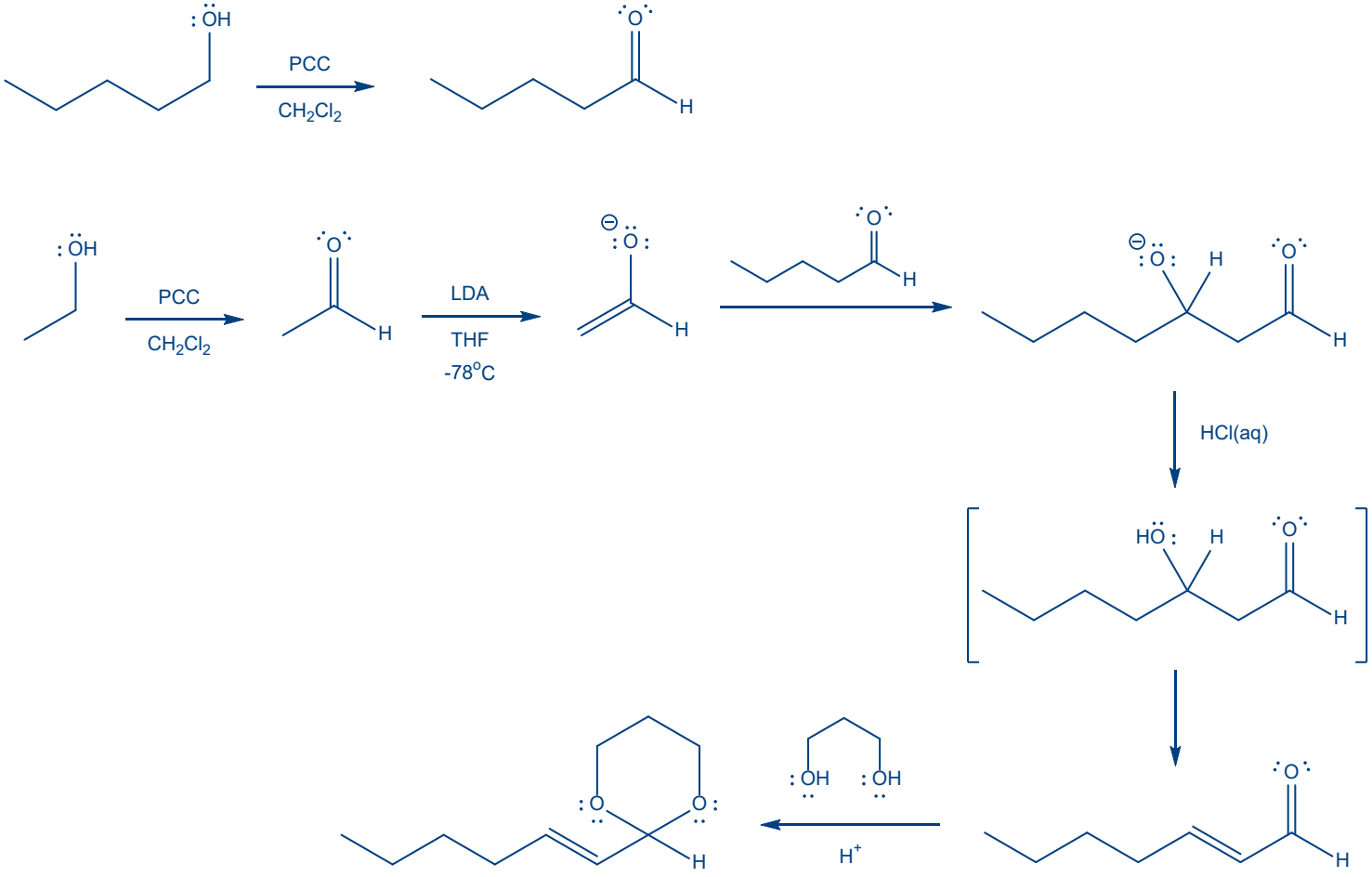
Name: _____ Student Number: _____

7. *continued…* *[6 marks]*

Synthetic Target #3:



Synthesis:

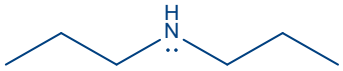


There are many different options for oxidizing agents that will convert a primary alcohol to an aldehyde (but be careful to avoid those that go all the way to the carboxylic acid).

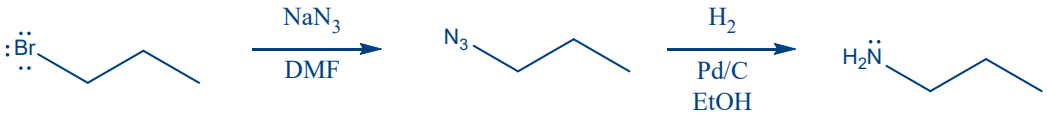
Name: _____ Student Number: _____

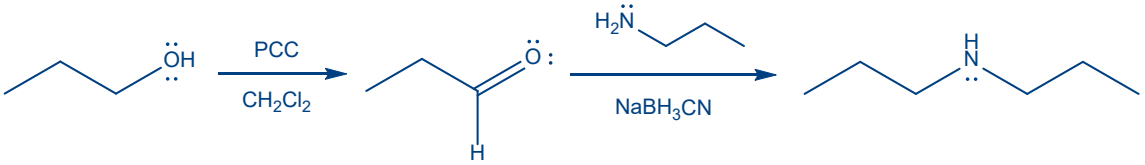
7. *continued…* *[6 marks]*

Synthetic Target #4:



Synthesis:



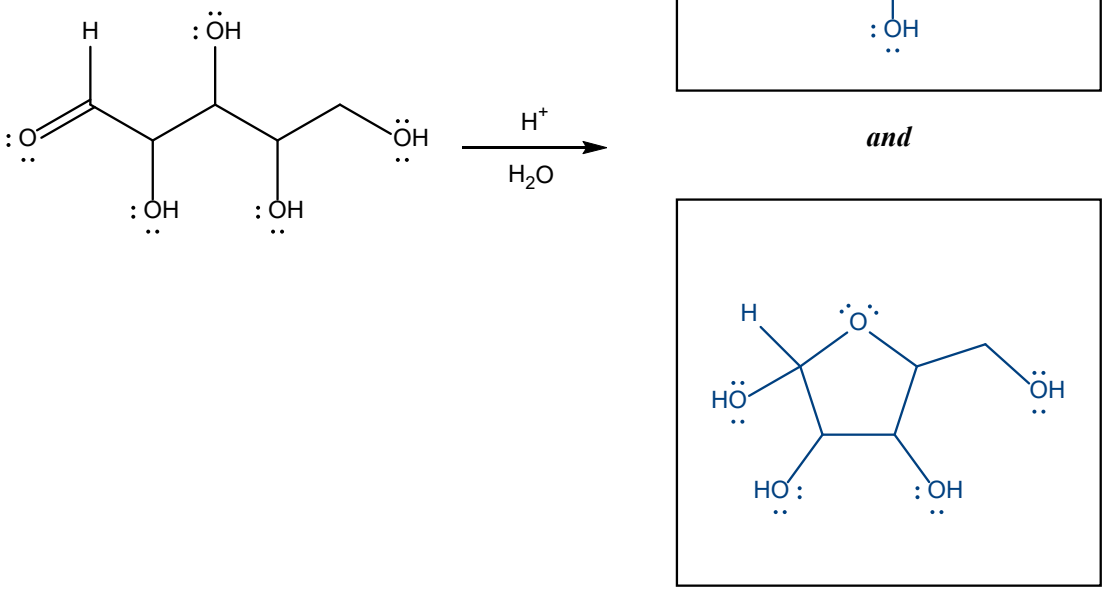


There are many different options for oxidizing agents that will convert a primary alcohol to an aldehyde (but be careful to avoid those that go all the way to the carboxylic acid).

It would also be possible to prepare propan-1-amine using the same reductive amination method shown in the second line (but using NH_3 as the nitrogen nucleophile).

Name: _____ Student Number: _____

8. The sugar below can form two different hemiacetals. Draw them in the boxes provided. *You do not need to show the mechanisms for these reactions; however, you may find it helpful to work through them in order to determine what products are formed.* **[4 marks]**



9. What was the most interesting and/or useful thing you learned in CHEM 2600? **[1 mark]**

…AND THAT'S ALL FOR CHEM 2600.
HAPPY HOLIDAYS!

DATA SHEET/SCRAP PAPER

CHEM 1000 Standard Periodic Table

1												13	14	15	16	17	18
1.0079 **H** 1	**2**																4.0026 **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(265) **Rf** 104	(268) **Db** 105	(271) **Sg** 106	(270) **Bh** 107	(277) **Hs** 108	(276) **Mt** 109	(281) **Ds** 110	(280) **Rg** 111	(285) **Cn** 112	(284) **Nh** 113	(289) **Fl** 114	(288) **Mc** 115	(293) **Lv** 116	(294) **Ts** 117	(294) **Og** 118

138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(262) **Lr** 103

Developed by Prof. R. T. Boeré (updated 2016)