Fall 2021 **Chemistry 2600 Final Exam** ____/90 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam until after 4:30pm Mountain Time on Saturday, December 11th, 2021. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/90 on this exam.

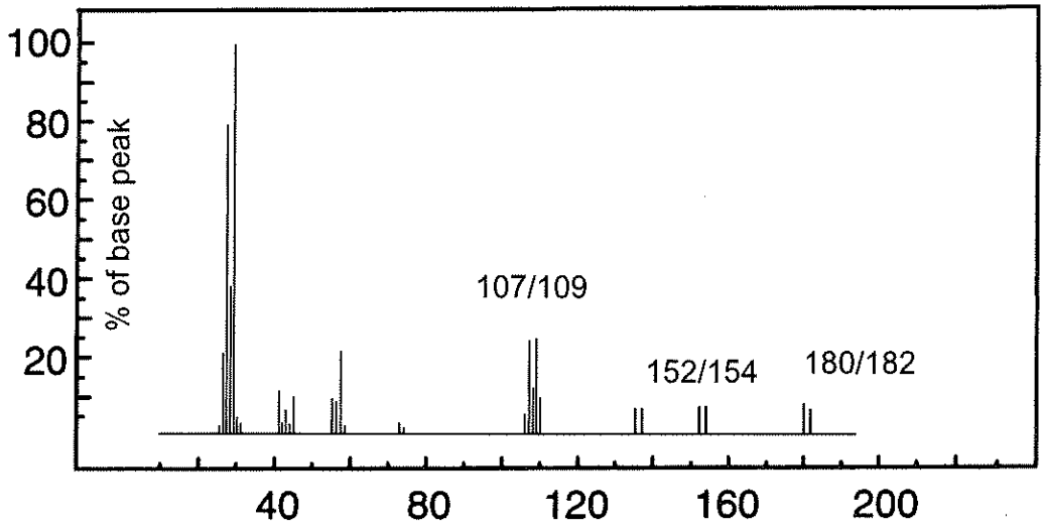
Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 12 pages of questions and a periodic table.
2) You have been given a 6-page Spectroscopy Data Package. **PLEASE DO NOT WRITE ON THE SPECTROSCOPY DATA PACKAGE**! If you need scrap paper, use the back of any page of the test. On questions with spectra, you may also do rough work directly on the spectra.
3) 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.
4) You may use a molecular model kit and ruler. You may not have written materials in your model kit.
5) You may use a calculator but only for calculation. No other electronic devices are allowed.
6) **DO NOT WRITE ON ANY QR CODE!!!** Work on pages without a QR code will not be graded.
7) If your work is not legible, it will be given a mark of zero. For full credit, explanations must be complete. In many cases, complete explanations include drawing relevant structures. If delocalization of electrons is invoked, the relevant resonance structures must be drawn.
8) Marks will be deducted for incorrect information added to an otherwise correct answer.
9) You have 9 hours to complete this test.

Question Breakdown

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9						Total
/ 3	/ 2	/ 22	/ 8	/ 7	/ 24	/ 18	/ 5	/ 1						/ 56

1. The following mass spectrum corresponds to a compound containing one halogen atom. **[3 marks]**



(a) Clearly label the molecular ion on the mass spectrum. *[1 mark]*

M^+ is m/z 180

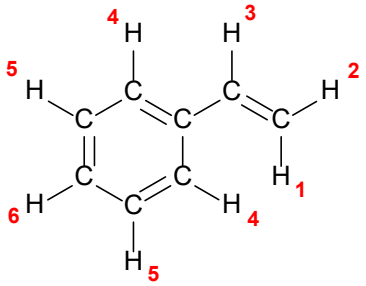
(b) Of which element is the halogen atom, and how can you tell? *[2 marks]*

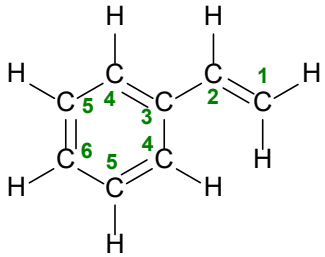
Bromine.

The molecular ion region has two peaks of approximately equal height (1 : 1 ratio) with a gap of m/z 2 between them – one for each isotope of bromine. (^{79}Br and ^{81}Br exist in approximately 1 : 1 ratio.)

This same pattern (two peaks in a 1 : 1 ratio with m/z 2 between them) can be seen at m/z 107 and 109 and at m/z 152 and 154.

2. For both parts of this question, assume that you are using an instrument capable of resolving all distinct peaks. In other words, do **not** attempt to account for peaks that might coincidentally overlap. **[2 marks]**





(a) How many peaks would you expect to see on the ^1H NMR of styrene (drawn above)?

6

(b) How many peaks would you expect to see on the ^{13}C NMR of styrene (drawn above)?

6

3. The following page contains spectra for Unknown X ($C_5H_9BrO_2$). **[22 marks]**

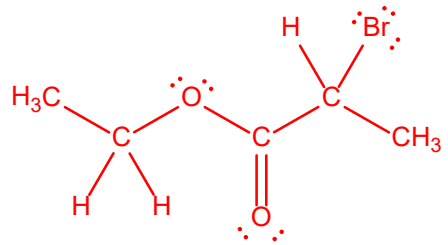
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your reasoning. **Calculation of integrals is required for full marks.**

(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, 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, clearly identifying which bond(s) correspond(s) to each peak.

Unknown X:



General breakdown of marks:
1 mark for correct answer
1 mark for calculating DU
2 marks for calculating integrals for ^{1}H NMR
1 mark for IR peak assignment
4 marks for ^{1}H NMR assignment (correct for correct answer; "reasonable" for incorrect answers)
4 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
9 marks for logic (this page plus legible rough work on spectra, etc.); verbal explanation is required for full credit

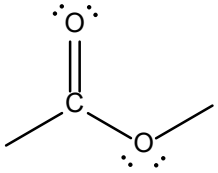
One Way to Arrive at the Answer

Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(5)+2-1-9}{2} = \frac{2}{2} = 1$
- The unknown therefore contains either a double bond or a ring.

Step 2: Look at IR for relevant peaks

- The large peak at 1740 cm^{-1} strongly suggests a $C = O$ bond that most likely corresponds to an ester.
  - There is a peak on the ^{13}C NMR at about 170 ppm. This chemical shift is consistent with the carbonyl of an ester or carboxylic acid.

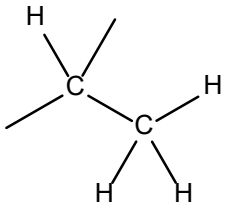


Step 3: Consider the peaks on ^{1}H NMR

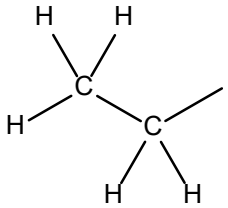
- There are four peaks on the ^{1}H NMR spectrum. The integral trail heights are approximately 3mm : 6mm : 9mm : 9mm, so the integral ratio is 1 : 2 : 3 : 3. This is consistent with the nine hydrogen atoms in the molecular formula.
- The four peaks are:
  - a quartet at ~4.4 ppm (1H) – CH next to CH_3
  - a quartet at ~4.2 ppm (2H) – CH_2 next to CH_3
  - a doublet at ~1.8 ppm (3H) – CH_3 next to CH

- a triplet at ~1.2 ppm (3H) – CH_3 next to CH_2

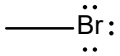
- The peaks for "CH next to CH_3" and "CH_3 next to CH" almost certainly correspond to adjacent groups, giving



- The peaks for "CH_2 next to CH_3" and "CH_3 next to CH_2" almost certainly correspond to adjacent groups, giving

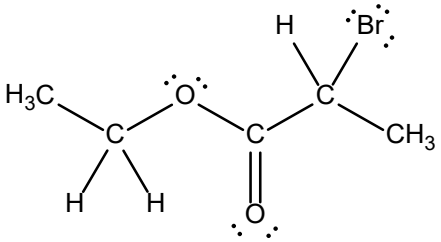


- The three pieces proposed so far use up all carbon, hydrogen and oxygen atoms in the molecular formula. The remaining piece must be a bromine atom

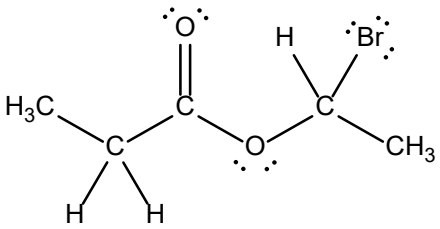


Step 4: Assemble the pieces and decide between the two options.

- There are two different ways in which these pieces can be assembled:

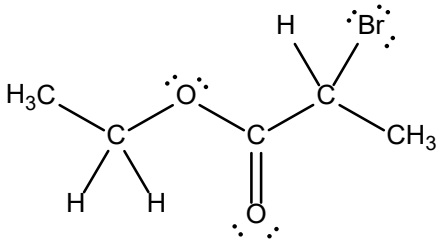


or



- The easiest way to distinguish between these two options is to look at the chemical shifts of the quartets:
  - The compound on the left would be expected to give a quartet (2H) at about 4 ppm for CH_2-O of an ester and another quartet (1H) at about 4.5-5 ppm for CH that is both attached to Br (deshields to ~4 ppm in isolation) and a carbonyl group (further deshields the CH group).
  - The compound on the right would be expected to give a quartet (2H) at about 2 ppm for CH_2 next to the carbonyl of an ester and another quartet (1H) at about 6-7ppm for CH that is both attached to O of an ester (deshields to ~5 ppm in isolation) and a Br (further deshields the CH group)
- Given that the two quartets both have chemical shifts between 4 and 4.5 ppm. It is clear that the structure on the right cannot be correct therefore the structure on the left must be correct.

Explanations which do not address both possibilities will not get full credit (unless previous logic includes a good reason why the incorrect one would not have been considered).

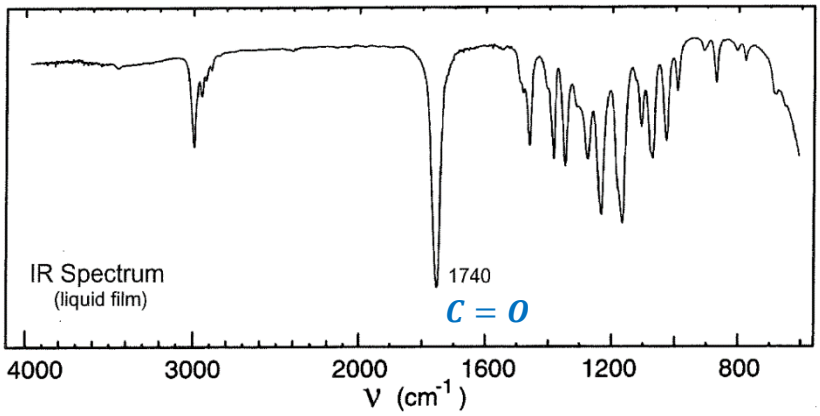


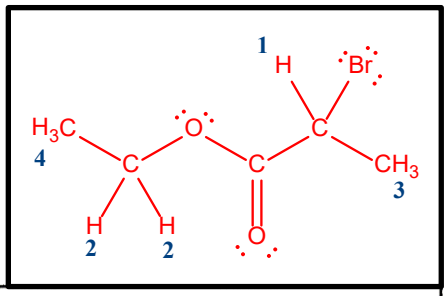
Step 5: Check your answer against the spectra and assign the peaks.

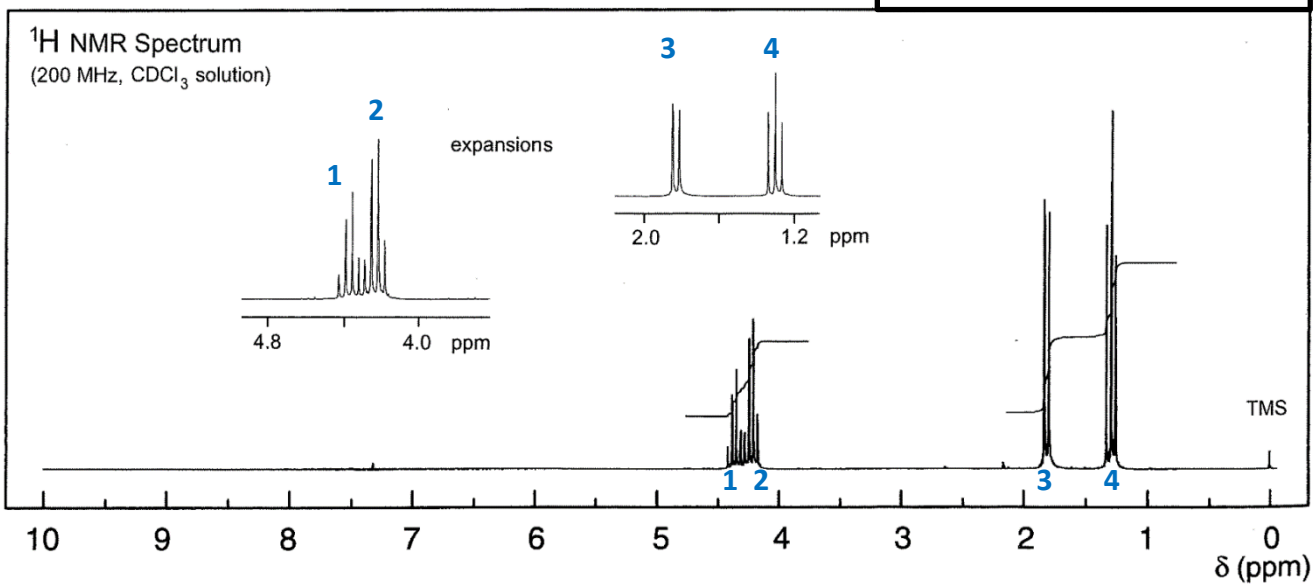
- IR
  - A $C = O$ stretch is visible at 1740 cm^{-1}. This is within the usual range for esters.
- ^{1}H NMR
  - The quartet at ~4.4 ppm on the ^{1}H NMR is consistent with a CH group attached to both Br and CO. It's a quartet because it's next to a CH_3 group. It integrates to 1H.
  - The quartet at ~4.2 ppm on the ^{1}H NMR is consistent with a CH_2 group attached to O of an ester. It's a quartet because it's next to a CH_3 group. It integrates to 2H.
  - The doublet at ~1.8 ppm on the ^{1}H NMR is consistent with a CH_3 group close to (but not directly attached to) deshielding groups. It's a doublet because it's next to a CH group. It integrates to 3H.
  - The triplet at ~1.2 ppm on the ^{1}H NMR is consistent with a CH_3 group close to (but not directly attached to) deshielding groups. It's a triplet because it's next to a CH_2 group. It integrates to 3H.
- ^{13}C NMR
  - The peak at ~170 ppm is consistent with $C = O$ of an ester.
  - The peak at ~60 ppm is consistent with $C - O$ (C on the other side of the ester).
  - The peak at ~40 ppm is consistent with CH attached to Br.
  - The peaks at ~12 ppm and ~22 ppm are consistent with the two CH_3 groups. It's likely that the peak at ~22 ppm is for the CH_3 group next to CHBr as that would be expected to be more deshielded than the one next to CH_2.

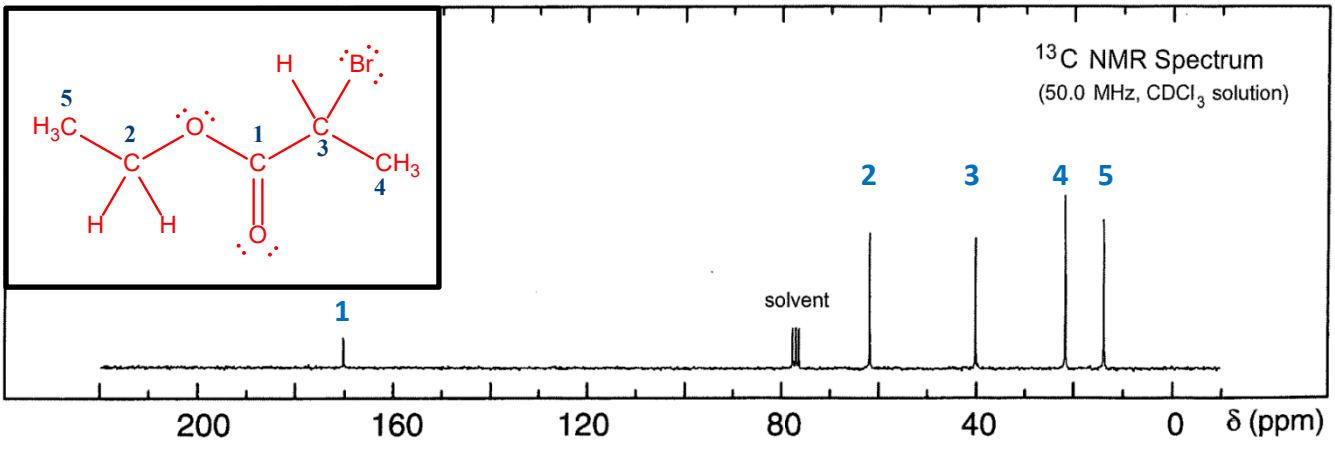
3. *…continued*

$C_5H_9BrO_2$







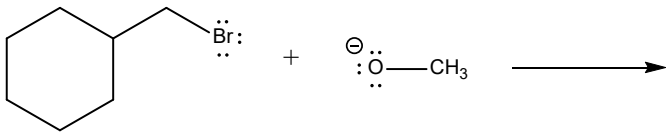


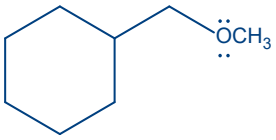
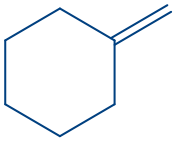
4. Indicate whether you would expect to see a significant amount of reaction according to each mechanism type by circling 'yes' or 'no'. In the bottom row of each table, justify your answer by: **[8 marks]**

- For each 'yes', drawing the organic product(s) that will be observed.
- For each 'no', briefly explaining why you expect little-to-no reaction.

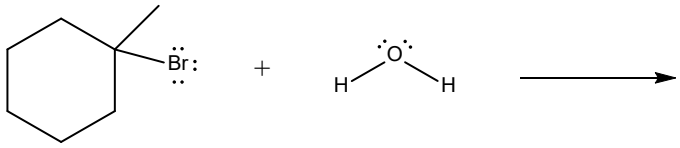
The marks are for the product(s) and/or explanations. The yes/no part is just to help you think.

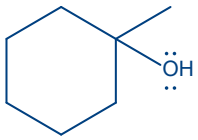
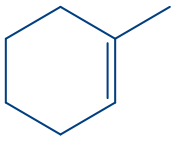
(a)



S_N1? yes / no	**S_N2?** yes / no	**E1?** yes / no	**E2?** yes / no
An S_N1 mechanism in this system would require a primary carbocation intermediate with no resonance stabilization.		An E1 mechanism in this system would require a primary carbocation intermediate with no resonance stabilization.	

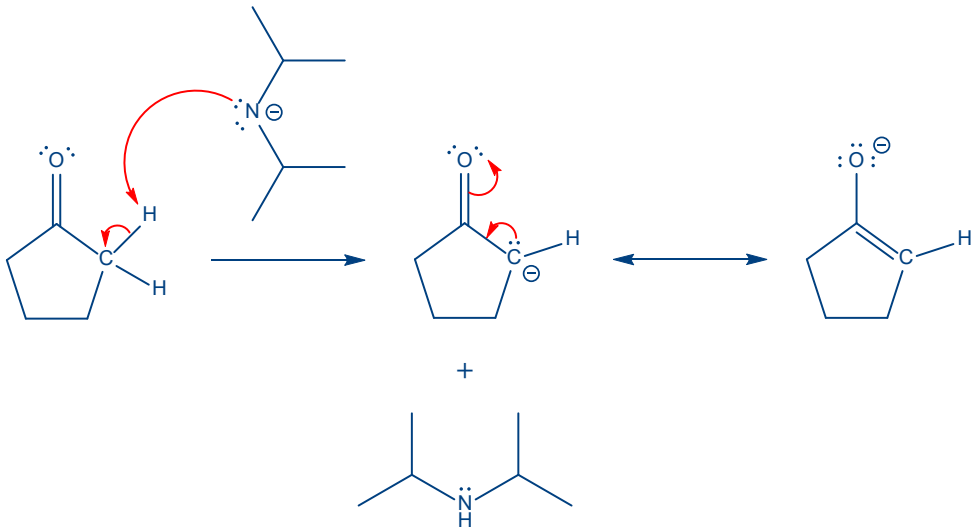
(b)



S_N1? yes / no	**S_N2?** yes / no	**E1?** yes / no	**E2?** yes / no
	The carbon atom attached to the leaving group is tertiary and therefore not sterically accessible. Also, water is not a strong enough nucleophile for an S_N2 reaction.		Water is not a strong enough nucleophile for an E2 reaction.

5. Use an argument based on resonance structures (which you must draw) to answer each of the following questions. **[7 marks]**

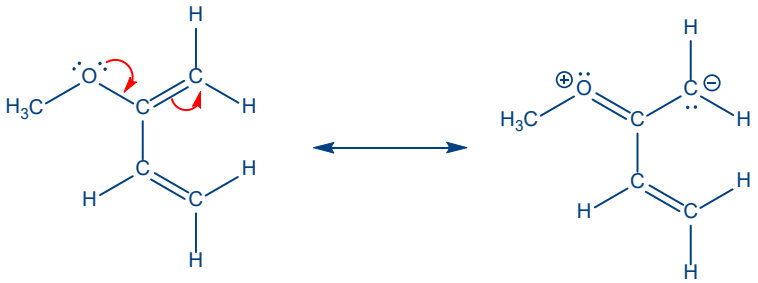
(a) When cyclopentanone is reacted with a strong base such as LDA, deprotonation always occurs at the carbon atom next to the carbonyl group. Why? *[4 marks]*



When deprotonation occurs at the carbon atom next to the carbonyl group, the negative charge of the resulting conjugate base is shared by two atoms (the deprotonated carbon atom and the oxygen atom). This delocalization of charge does not occur if you deprotonate elsewhere.

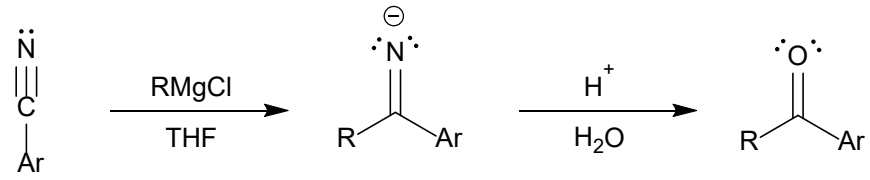
(b) 2-methoxy-1,3-butadiene is an electron-rich diene. At which end of the diene is it most electron-rich? Why? *[3 marks]*

The diene is most electron rich at the carbon atom next to the one with the methoxy group attached. This is due to delocalization of electron density from the electron-donating methoxy group:



6. A chemist wants to make a particular ketone so they can investigate its potential usefulness as a medicine. For the sake of simplicity, we'll use R and Ar to represent the groups on either side of the carbonyl.

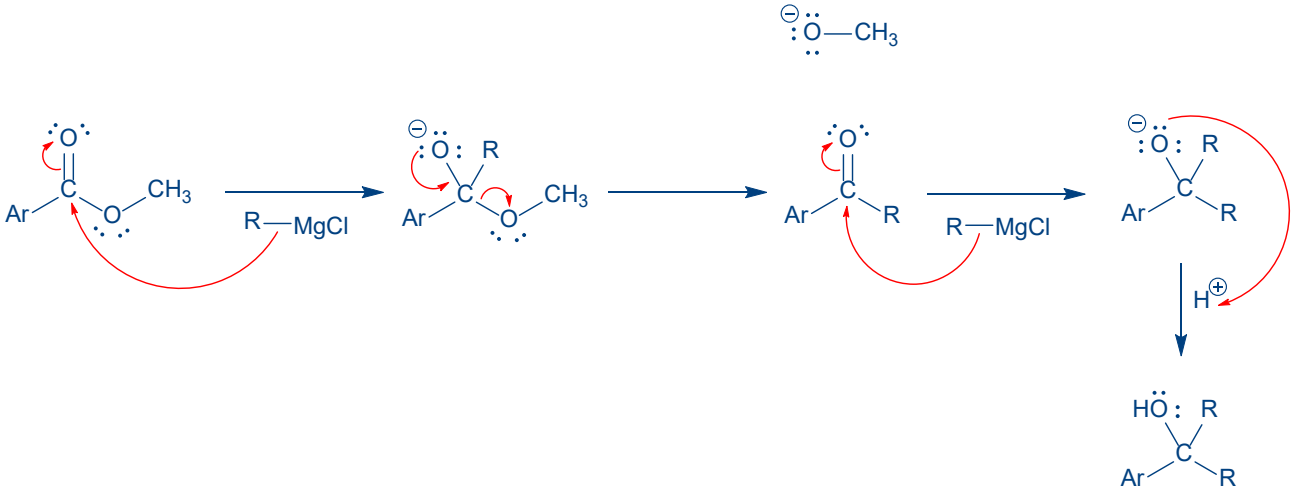
One approach would be to react a nitrile with one group attached (**A**) and a Grignard reagent with the other group (RMgCl) then add aqueous acid: **[24 marks]**



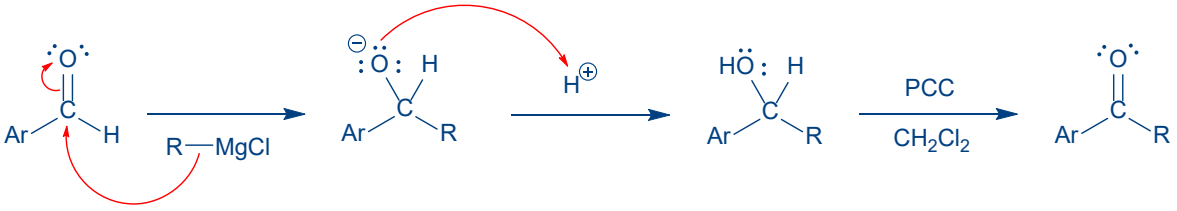
A **B** **C**

(a) At first glance, you might wonder why the chemist couldn't use an ester ($ArCO_2CH_3$) instead of nitrile **A**. Show what would happen if $ArCO_2CH_3$ was reacted with RMgCl. Your answer should include both the mechanism and product of the reaction. You may assume mild acidic work-up. *[8 marks]*

The reason that you can't make ketone **C** by reacting $ArCO_2CH_3$ with RMgCl is that, after the tetrahedral intermediate collapses to give the desired ketone, a second equivalent of RMgCl will attack the ketone. This cannot be prevented because ketones are better electrophiles than esters so RMgCl will preferentially react with the newly formed ketone over the remaining ester.

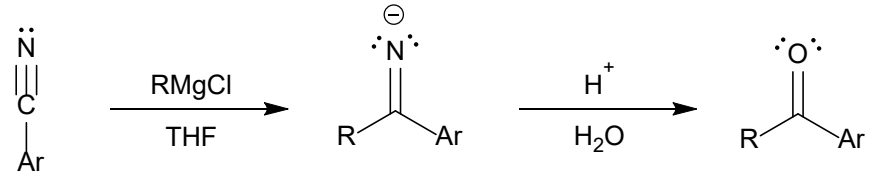


(b) It is possible to use an aldehyde (ArCHO) instead of nitrile **A**; however, an extra step would be needed to convert the product of that reaction into ketone **C**. Show the product of the reaction between ArCHO and RMgCl (before an after mild acidic work-up) **and** show one reagent (or set of reagents) that could be used to convert that product into ketone **C**. *[3 marks]*



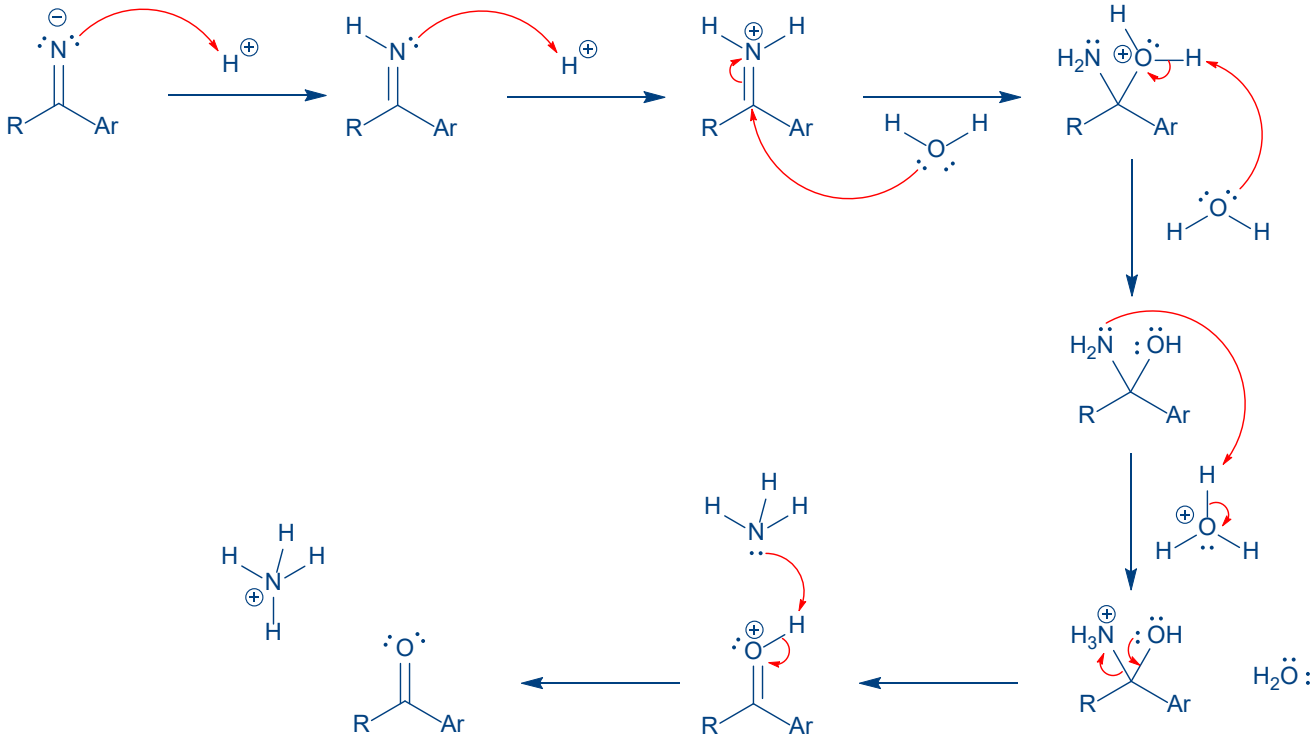
Alternatives to PCC/CH_2Cl_2 include PDC/CH_2Cl_2, Br_2/$NaHCO_3$, and the Swern oxidation (list reagents not just the name).

6. *…continued from previous page*



A **B** **C**

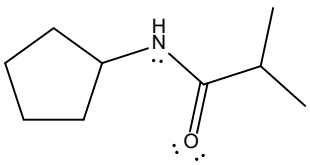
(c) Draw a valid mechanism for the acid-catalyzed conversion of intermediate **B** into ketone **C**. *[13 marks]*
You may use as much H^+ and H_2O as you like.

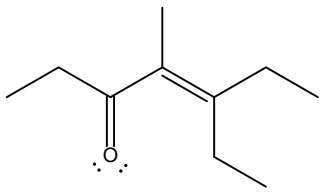


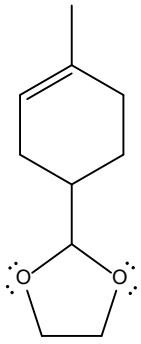
7. Choose any **three** of the molecules below and propose a synthesis for each one. **[18 marks]**

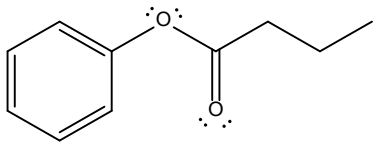
- If your synthesis involves more than one step, write an equation for each step. Show all required reactants. Number steps within a reaction if order of addition is important.
- All organic reactants must be stable compounds containing **no more than five carbon atoms**. They may be **hydrocarbons, 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).

Solutions presented are not the only possible way to make each compound. They are intended as representative examples. In most cases, you have learned how to do the same transformations using other reagents and, in many cases, entirely different approaches could be valid. When in doubt about the reasonableness of your proposal, show your it to an instructor.



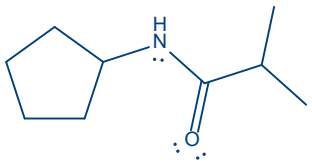




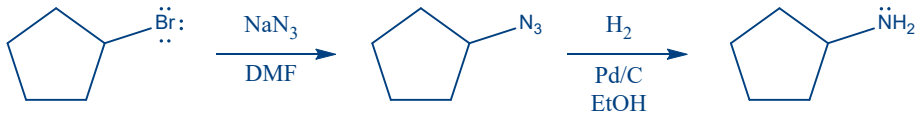


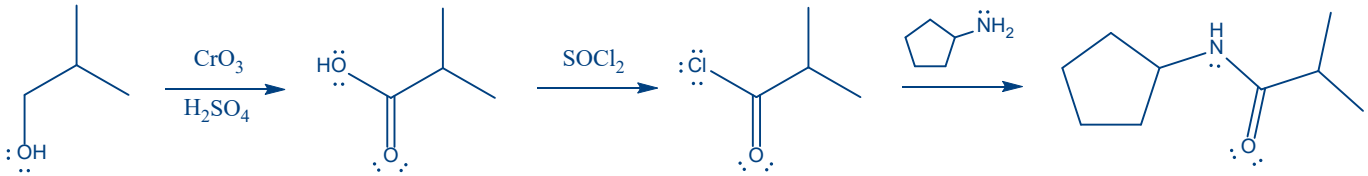
7. *continued…* *[6 marks]*

Synthetic Target #1:



Synthesis:



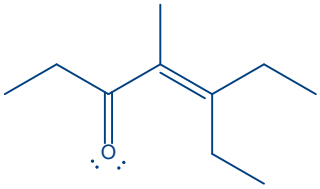


You could also use a phthalimide approach to make the secondary amine. Reductive amination with NH_3 would also work, but would take more steps (oxidize cyclopentanol to cyclopentanone then make the imine by reacting with NH_3 then reduce imine to amine). (NH_3 is allowed as a reactant because it's not organic. Cyanide and carbon dioxide are also considered "inorganic" despite containing carbon.)

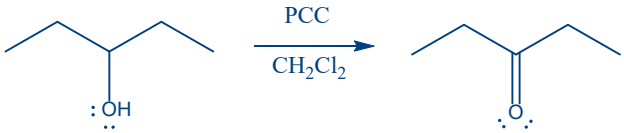
You could react the amine and carboxylic acid directly rather than going through the acid chloride intermediate; however, the acid chloride is more reactive and would likely give a better yield. If you chose to show the amine and carboxylic acid reacting directly, you would need to indicate that the mixture would require heating.

7. *continued…* *[6 marks]*

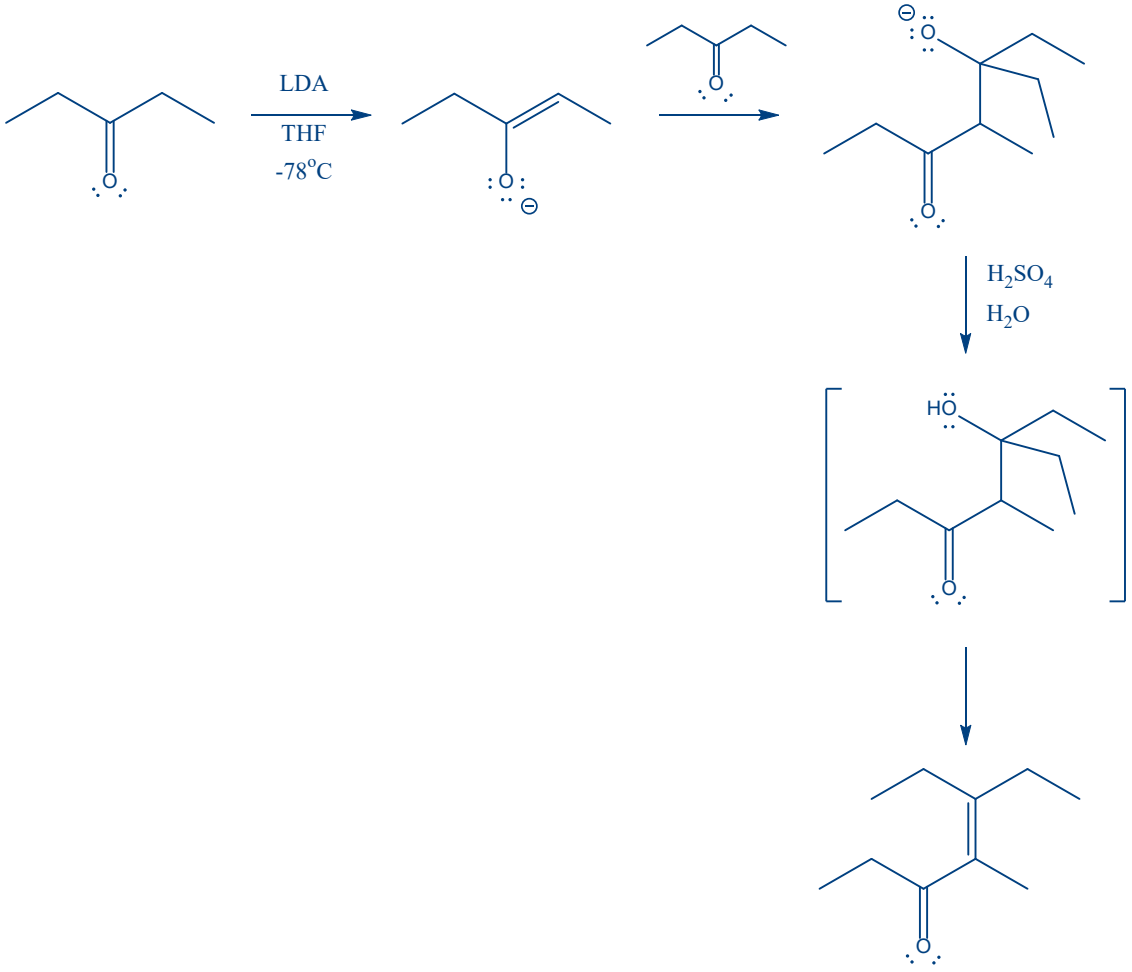
Synthetic Target #2:



Synthesis:

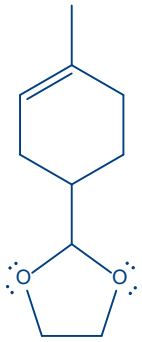


There are many valid alternative oxidizing agents that could be used instead of PCC.

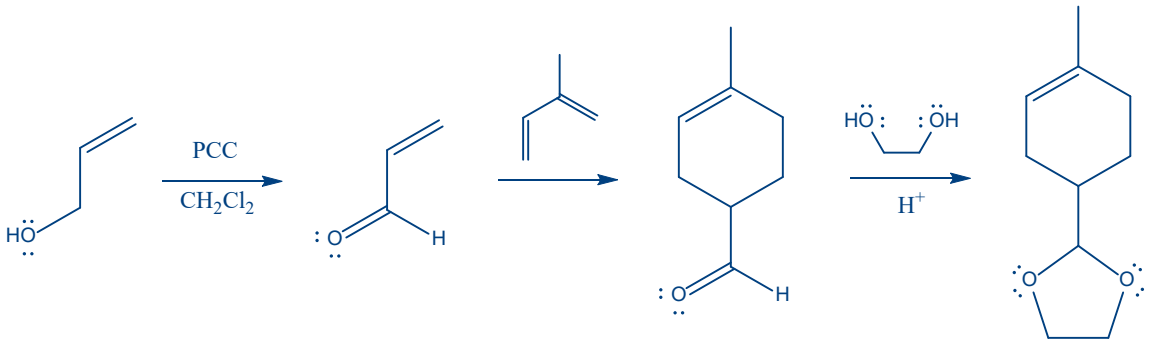


7. *continued…* *[6 marks]*

Synthetic Target #3:



Synthesis:

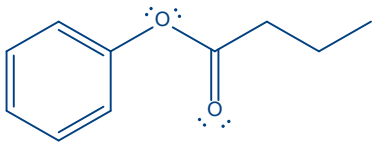


Recall that you're not allowed to use starting materials with more than five carbon atoms, so you cannot start with a pre-existing cyclohexene ring. The Diels-Alder reaction isn't the only way to make that – but it's the easiest! (Any other approach would take a LOT more steps, some of which you might not know all the reagents for.)

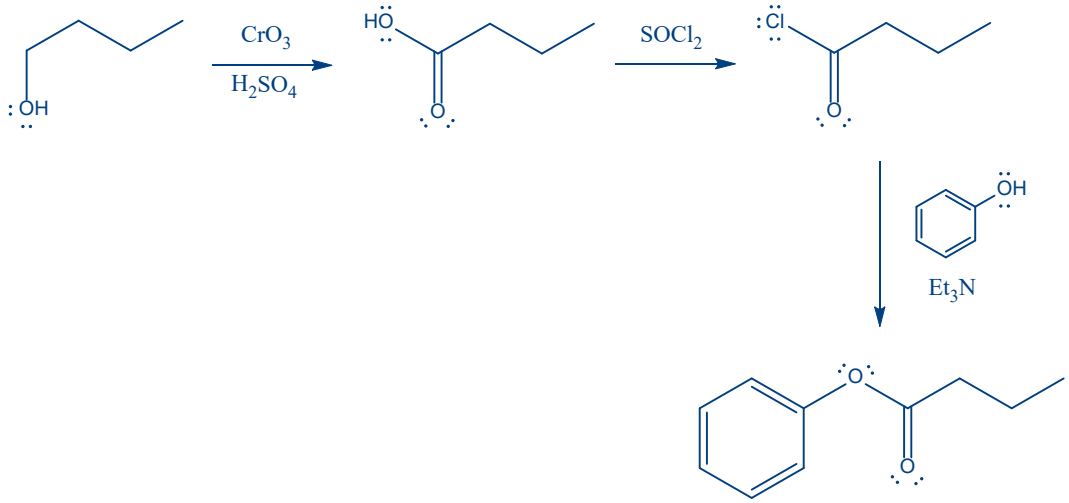
There are many valid alternative oxidizing agents that could be used instead of PCC.

7. *continued…* *[6 marks]*

Synthetic Target #4:



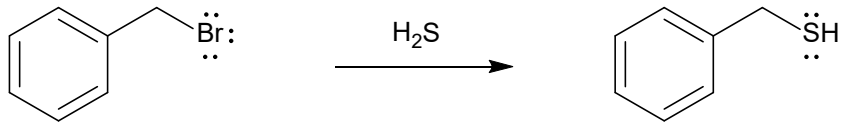
Synthesis:



Phenol is explicitly listed as an allowed starting material (exception to the "no more than 5 carbon atoms" rule). Please note that this means phenol itself – NOT phenols with other groups attached.

You could react the carboxylic acid directly with the phenol rather than going through the acid chloride intermediate; however, the acid chloride is more reactive and would likely give a better yield. If you chose to show the carboxylic acid and phenol reacting directly (in a Fischer esterification), you would need to indicate that the mixture would require heating with an acid catalyst.

8. Looking at the following reaction, it's not immediately obvious whether it would proceed primarily via S_N1 mechanism or S_N2 mechanism. Briefly explain how you could use kinetic data to decide. **[5 marks]**



Your answer should include:

- the rate law expected if the reaction proceeds exclusively via S_N1 mechanism,
- the rate law expected if the reaction proceeds exclusively via S_N2 mechanism,
- clear indication of what experimental parameter(s) would have to be varied, and
- clear indication of how the experimental data would tell you whether you were observing only S_N1 reaction, only S_N2 reaction or a mixture of both.

If the reaction proceeds exclusively via S_N1 mechanism, the rate law will be $rate = k[PhCH_2Br]$.
If the reaction proceeds exclusively via S_N2 mechanism, the rate law will be $rate = k[PhCH_2Br][H_2S]$.

As such, the way to distinguish between the two mechanisms is to keep the concentration of $PhCH_2Br$ constant while varying the concentration of H_2S. If the rate of reaction does not change, the reaction proceeds according to the S_N1 mechanism. If the rate of reaction changes in direct proportion to the concentration of H_2S, the reaction proceeds according to the S_N2 mechanism. If the rate of reaction increases as the concentration of H_2S increases – but not by as much as it would with the S_N2 mechanism, both reactions must be active.

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

…AND THAT'S ALL FOR CHEM 2600.

HAPPY HOLIDAYS!