Winter 2025 **Chemistry 2600 Final Exam** ____/95 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam with (or in the presence of) any CHEM 2600 student who has yet to write it. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/95 on this exam.

Signature: _____ Date: _____

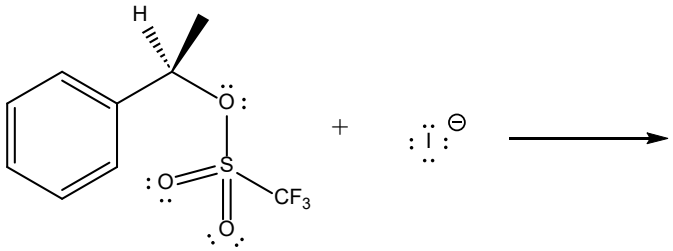
1) Please read the test carefully before starting. It has thirteen pages of questions and a periodic table.
2) You have been given a 6-page Spectroscopy Data Package. **PLEASE DO NOT WRITE ON THE SPECTROSCOPY DATA PACKAGE**! If you need scrap paper, use the back of any page of the test. On questions 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 3 hours to complete this test.

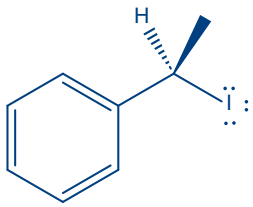
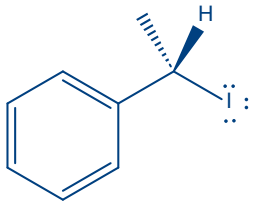
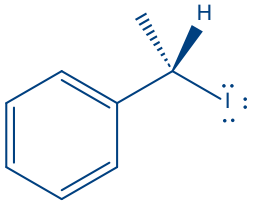
Question Breakdown

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10					Total
/ 5	/ 6	/ 4	/ 9	/ 9	/ 10	/ 18	/ 28	/ 5	/ 1					/ 95

1. Indicate whether or not 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: **[5 marks]**
   - For each 'yes', drawing the organic product(s) that will be observed. If multiple regioisomers and/or stereoisomers can be produced via that mechanism, draw each of them.
   - 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.



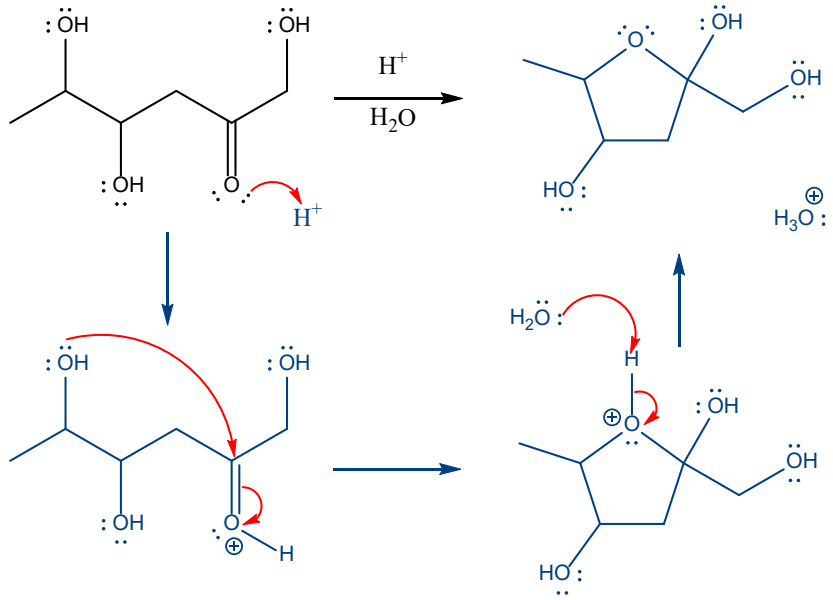
S_N1? yes / no	**S_N2?** yes / no	**E1?** yes / no	**E2?** yes / no
 and 		$E1$ reactions require a base, and there is no base available.	$E2$ reactions require a strong base, and there is no base available.

Because S_N2 reactions are concerted (leaving group leaves in same step as nucleophile attacks), they will only give the product in which the configuration of the electrophilic carbon has been inverted.

Because S_N1 reactions proceed via a planar carbocation intermediate, this reaction would give a racemic product (50/50 mixture of both enantiomers).

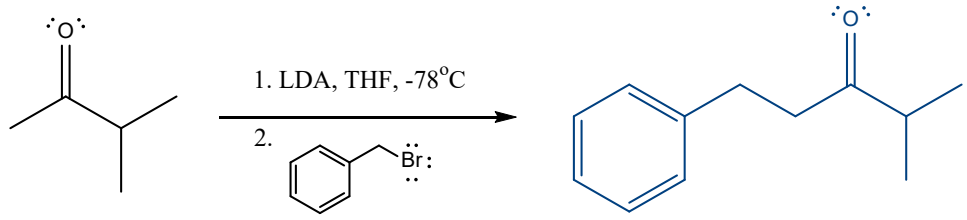
I^- and $CF_3SO_3^-$ are both conjugate bases of extremely strong acids ($pK_a \approx -10$ for HI and $pK_a \approx -15$ for CF_3SO_3H) and, as such, are too weak to act as bases under normal reaction conditions.

2. Draw the hemiacetal that is expected to form when the sugar below is in aqueous acid **and** draw a reasonable mechanism for its formation. **[6 marks]**



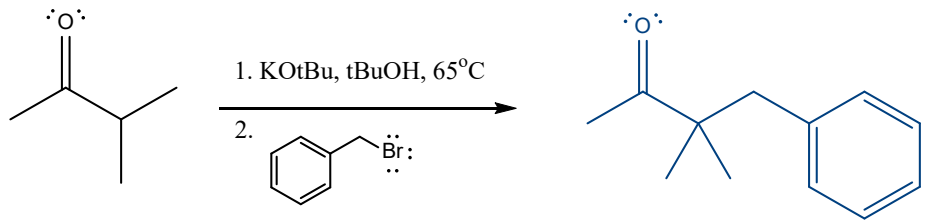
3. Draw the major organic product for each of the following reactions. **[4 marks]**

(a)



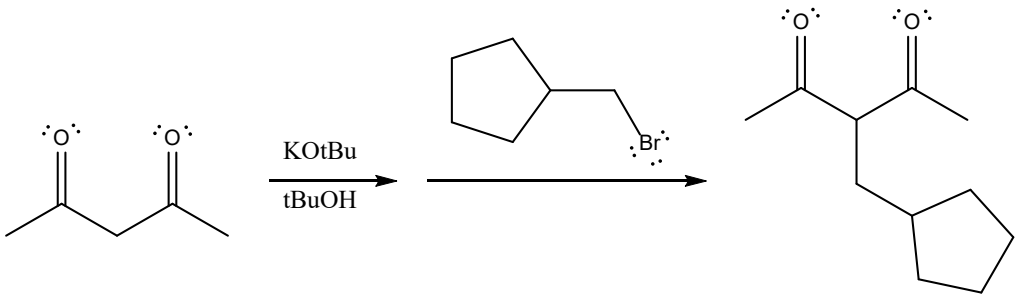
At low temperatures, bulky bases like LDA attack the most accessible hydrogen atoms, giving the kinetic enolate.

(b)



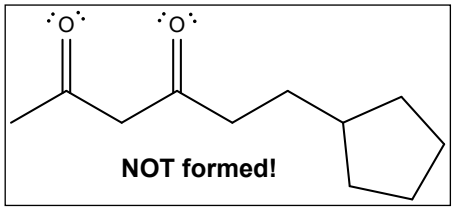
At high temperatures, deprotonation is reversible and, as such, the thermodynamic enolate will dominate.

4. Consider the following reaction. **[9 marks]**

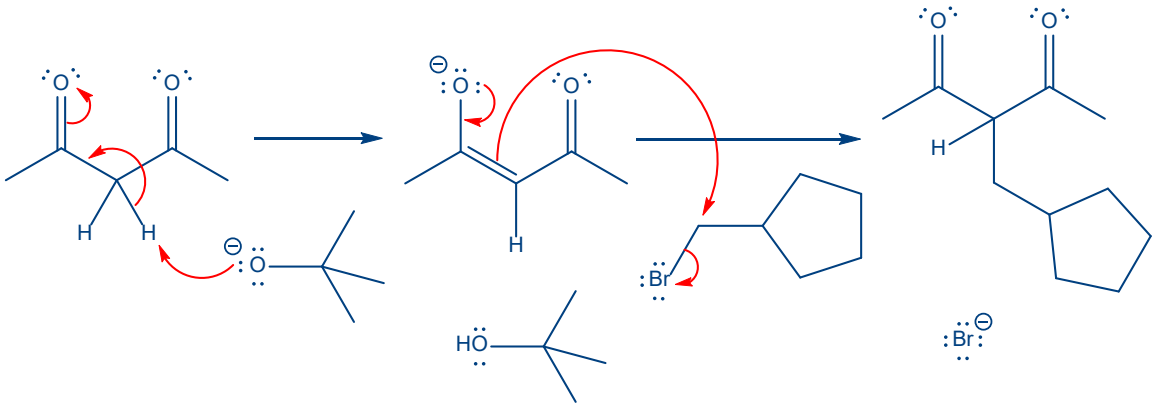


(a) Draw a reasonable mechanism for this reaction. *[3 marks]*

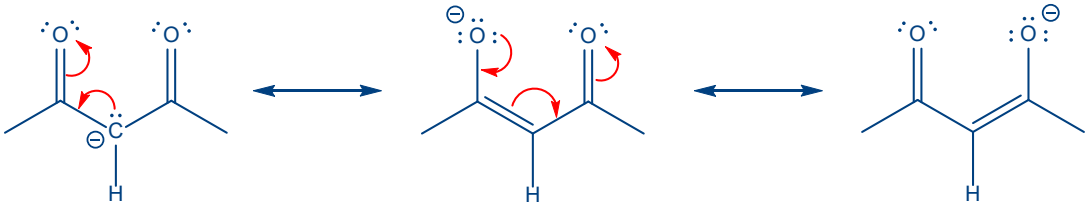
(b) Explain why the compound at the right is **not** also formed. *[6 marks]*



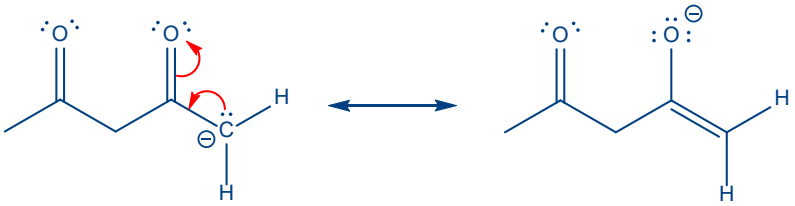
(a)



(b) The enolate formed by deprotonation of the central CH_2 group has negative charge shared by three atoms:



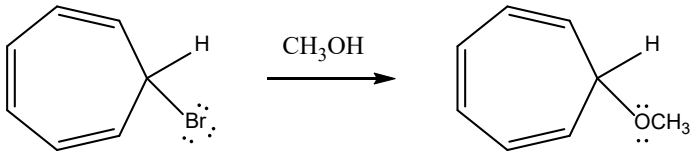
The enolate formed by deprotonation of either CH_3 group has negative charge shared by only two atoms:



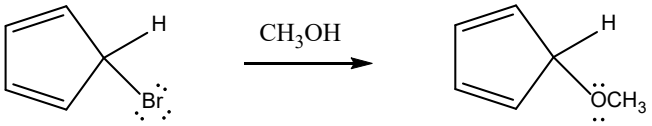
Because of this greater delocalization of charge, the first enolate is favoured over the second enolate.

5. Reaction A proceeds much more rapidly than Reaction B. **[9 marks]**

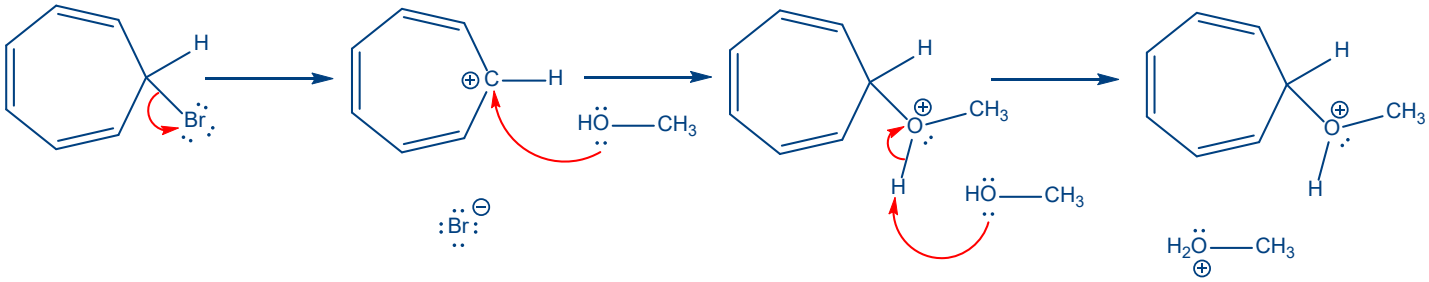
Reaction A



Reaction B



(a) Draw a reasonable mechanism for Reaction A. *[5 marks]*



(b) Explain why Reaction A is faster than Reaction B. *[4 marks]*

For full marks your answer must address the key component(s) of both reactions.

The speed of a reaction is determined by its rate determining step.

The rate determining step for these S_N1 reactions is the step in which bromide leaves and the carbocation is formed.

Since the leaving group is the same for both reactions, we must look for differences between the carbocations.

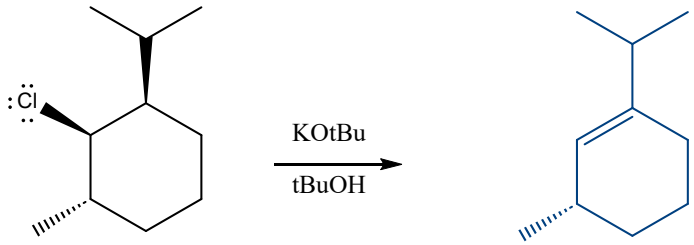
The carbocation intermediate in Reaction A is aromatic and therefore one of the most highly favourable carbocations to form.

The carbocation intermediate in Reaction B is antiaromatic and therefore highly unfavourable.

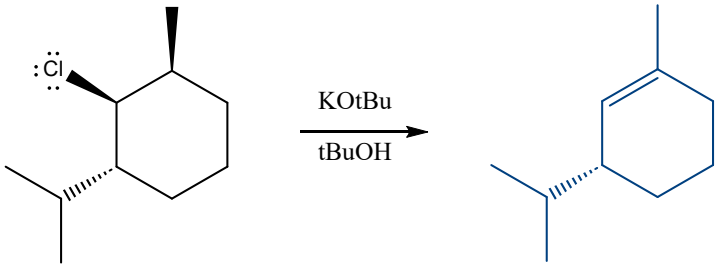
As such, Reaction A should proceed much faster than Reaction B (which might not even occur at all).

6. Consider the following reactions, each of which proceeds via an $E2$ mechanism. **[10 marks]**

Reaction A



Reaction B



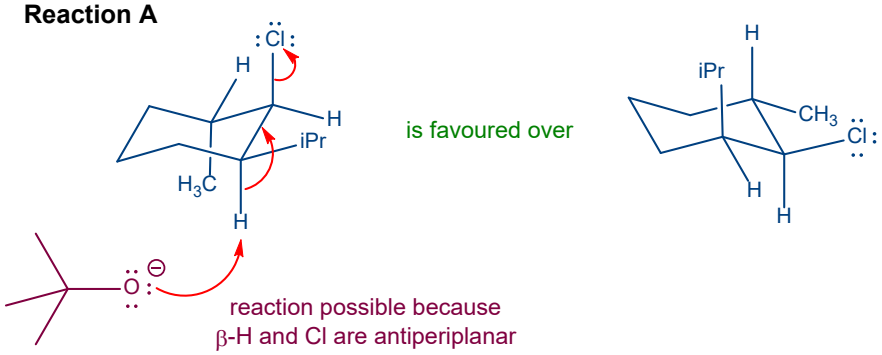
(a) Complete each reaction equation by drawing the major organic product. *[4 marks]*

(b) Which of these two reactions would you expect to proceed faster? Why? *[6 marks]*

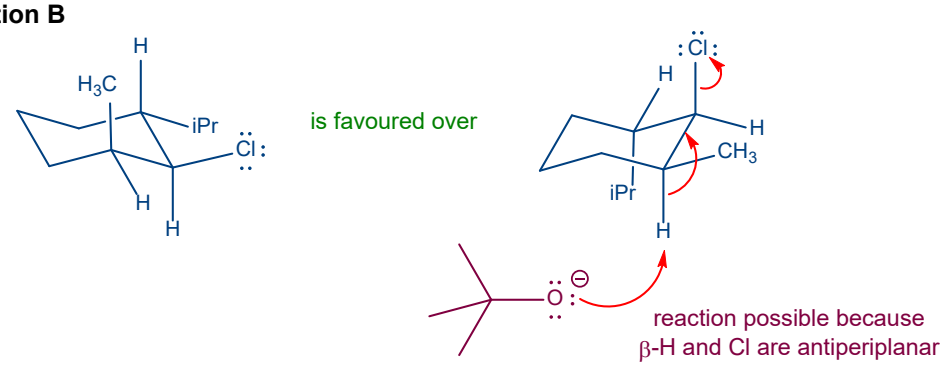
Reaction A will proceed faster.

$E2$ reactions require an antiperiplanar relationship between the $\beta - H$ and the leaving group. When both components are attached to a cyclohexane ring, they must therefore both be axial. The major conformer of a cyclohexane ring is the one in which the largest substituent occupies an equatorial site. As such, Reaction A involves reaction of the major conformer while Reaction B requires reaction of the minor conformer:

Reaction A

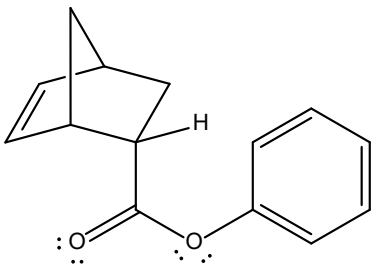


Reaction B

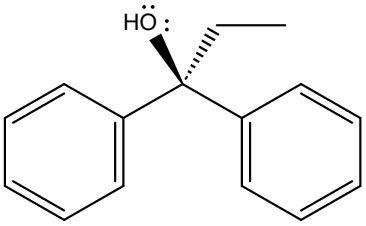


7. Choose any **three** of the molecules below and propose a synthesis for each one. **[18 marks]**

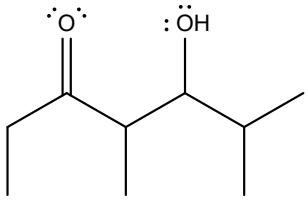
- If your synthesis involves more than one step, write an equation for each step. Show all required reactants. Number steps within a reaction if order of addition is important.
- All organic reactants must be stable compounds containing **no more than five carbon atoms**. They may be **hydrocarbons,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



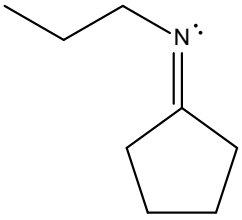
Looks like a Diels-Alder adduct…



Looks like addition of two Ph^- to an ester…
(due to C w/ O and two identical Ph attached)



Looks like an aldol product…
(due to three C in a row w/ an O at each end)



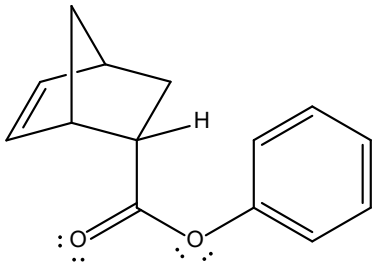
This is an imine. Make from ketone and amine.

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.

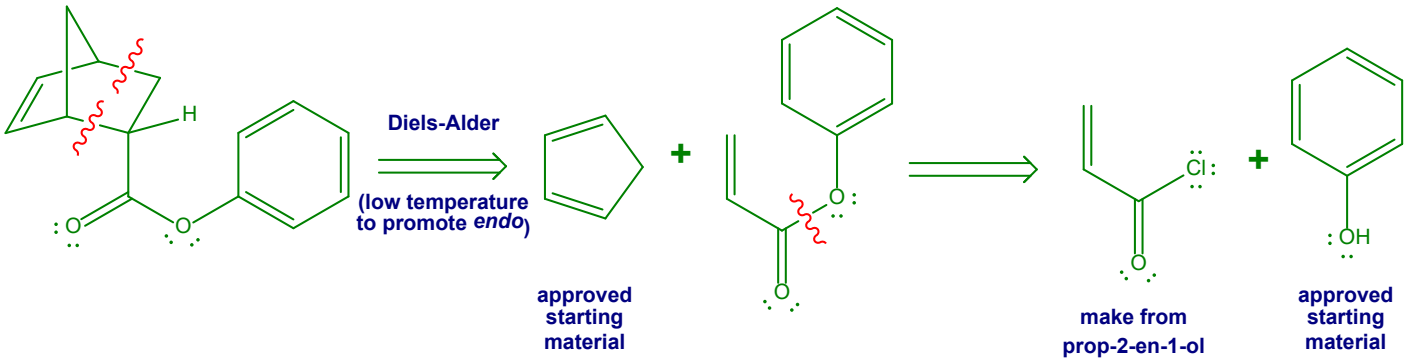
7. *continued…* *[6 marks]*

Synthetic Target #1:

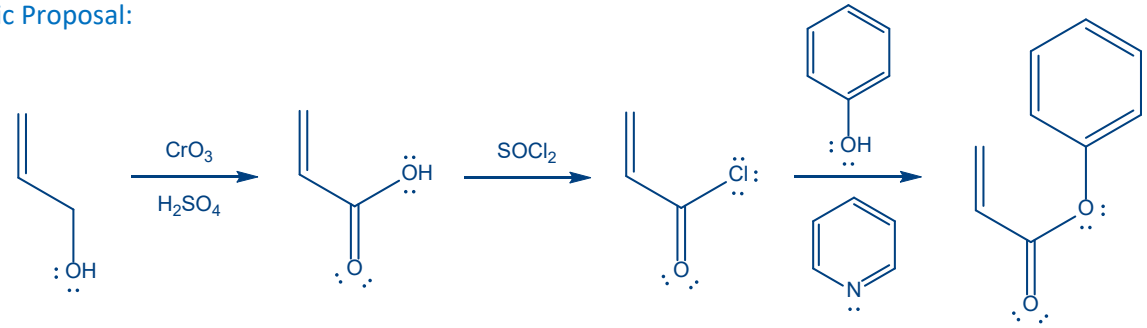


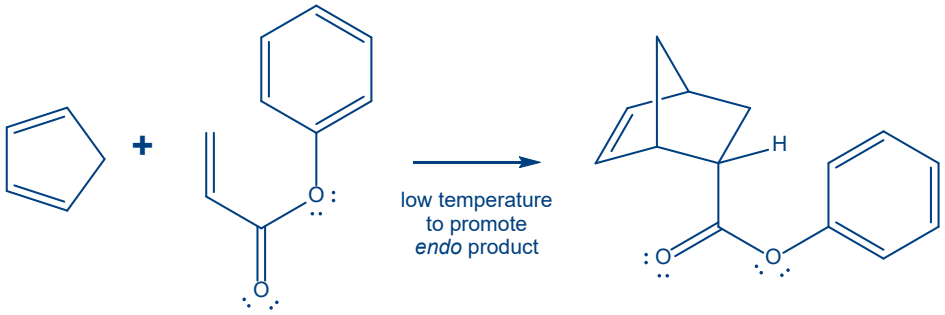
Synthesis:

Retrosynthetic analysis (aka "The Plan"):



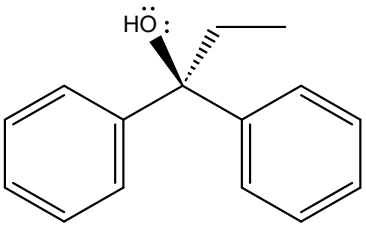
Synthetic Proposal:





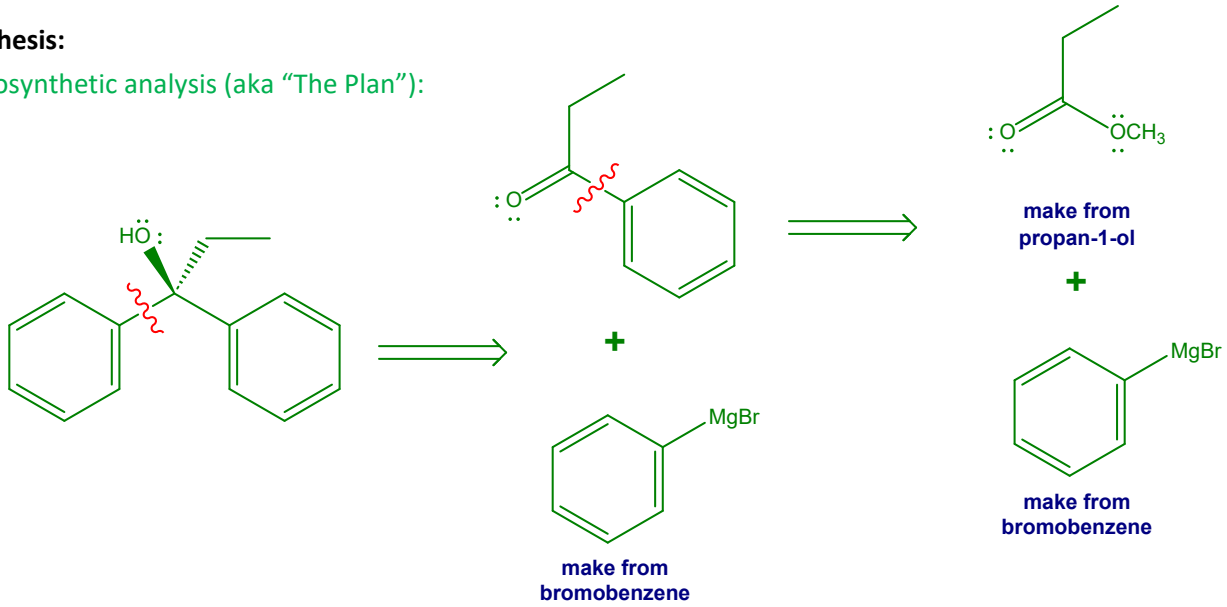
7. *continued…* *[6 marks]*

Synthetic Target #2:

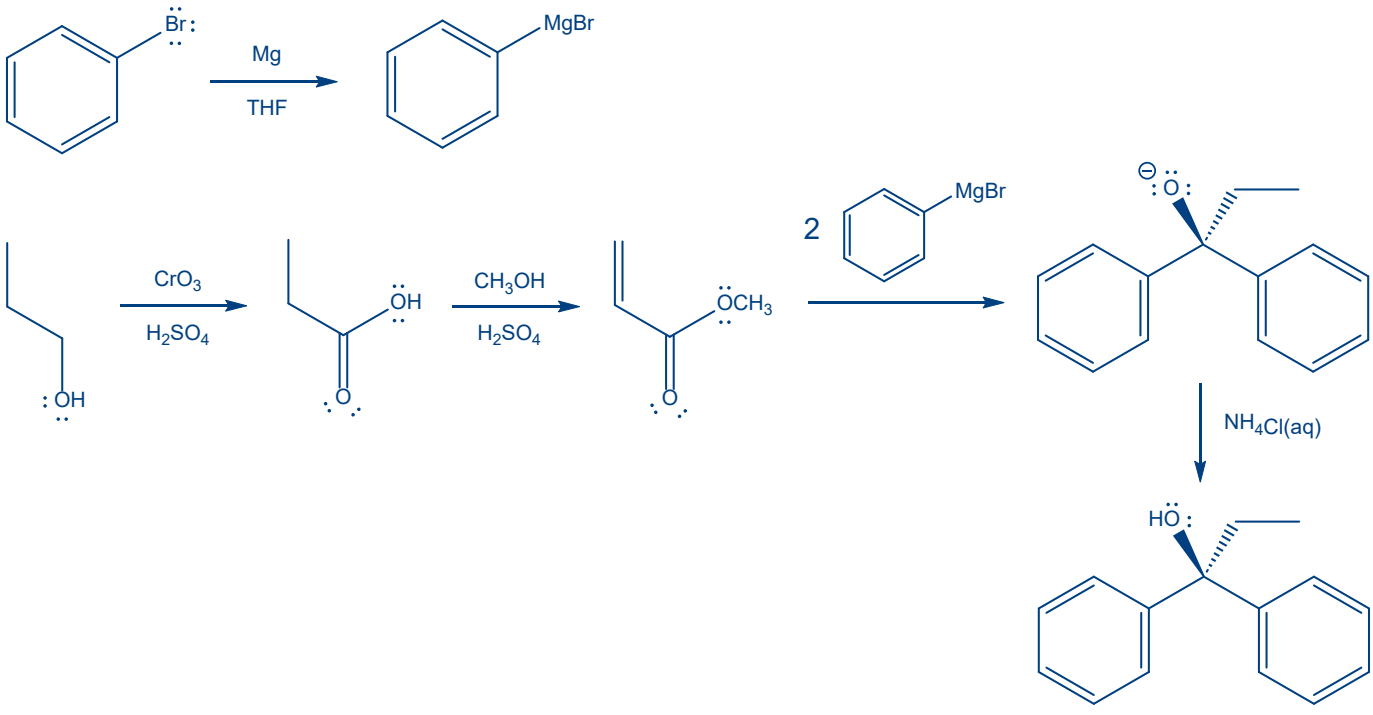


Synthesis:

Retrosynthetic analysis (aka "The Plan"):

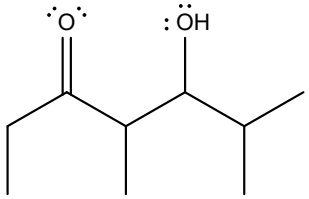


Synthetic Proposal:



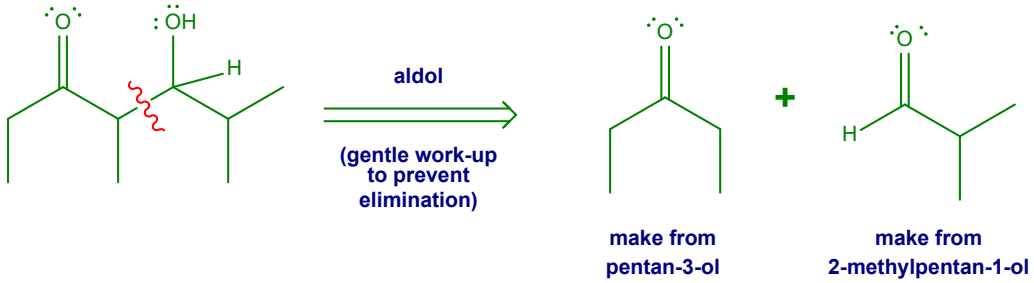
7. *continued…* *[6 marks]*

Synthetic Target #3:

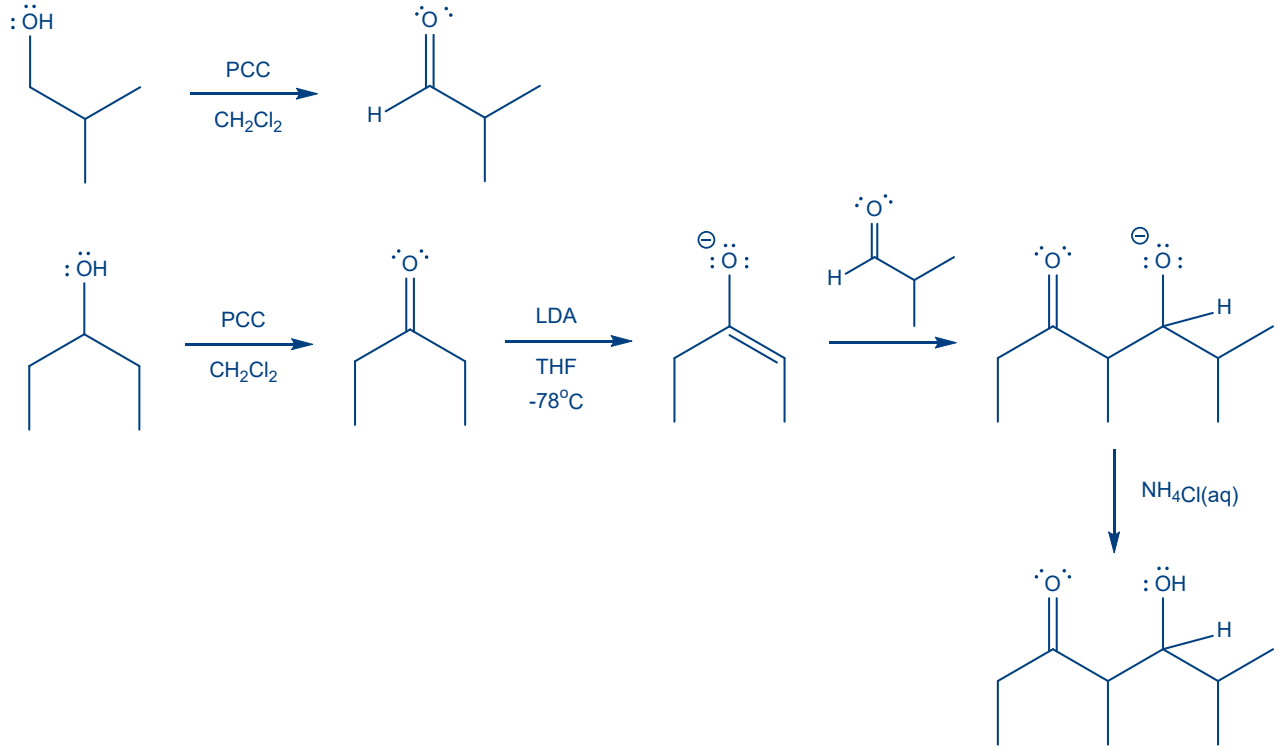


Synthesis:

Retrosynthetic analysis (aka "The Plan"):

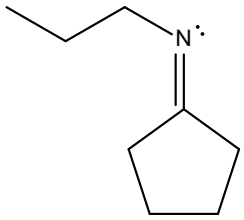


Synthetic Proposal:



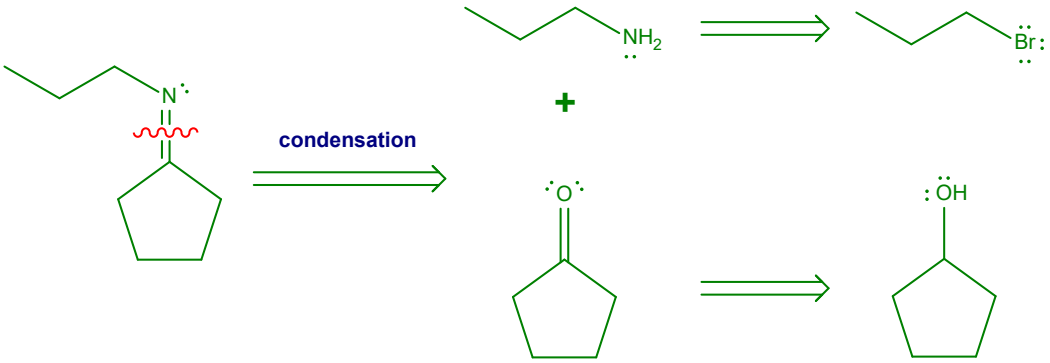
7. *continued…* *[6 marks]*

Synthetic Target #4:

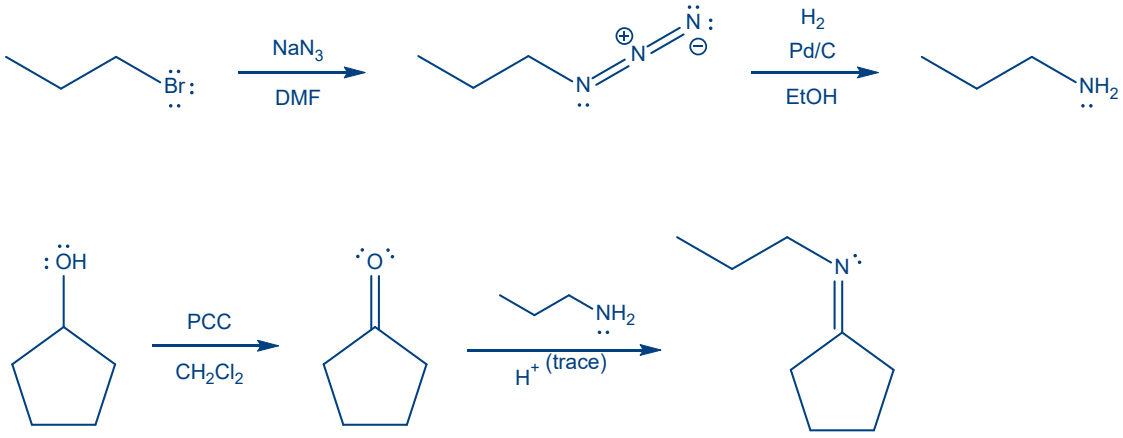


Synthesis:

Retrosynthetic analysis (aka "The Plan"):



Synthetic Proposal:



8. The following pages contain spectra for Unknown X ($C_9H_8O_4$). **[28 marks]**

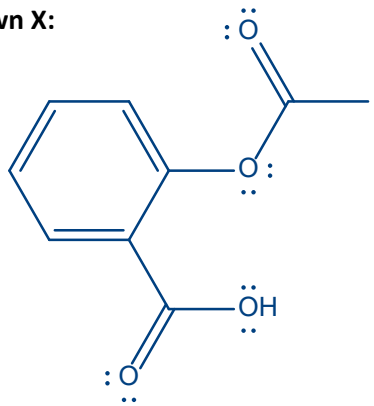
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your reasoning. Integrals have been provided under each peak or set of peaks on the ^{1}H NMR spectrum, so you do not need to calculate them this time.

(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:



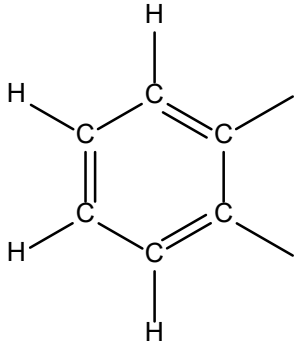
General breakdown of marks:
1 mark for correct answer
1 mark for calculating DU
3 marks for IR peak assignment
3 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
6 marks for ^{1}H NMR assignment (correct for correct answer; "reasonable" for incorrect answers)
14 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)

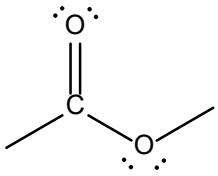
- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(9)+2-8}{2} = \frac{12}{2} = 6$
- Anytime we have four or more degrees of unsaturation, we look for evidence of a benzene ring:
  - There are six peaks on the ^{13}C NMR between 120 and 150 ppm.
  - There are four peaks on the ^{1}H NMR between 7 and 8.5 ppm.
  - There are peaks on the IR at ~1450 cm^{-1} and 1606 cm^{-1} that could be aromatic C=C stretches.
- 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:

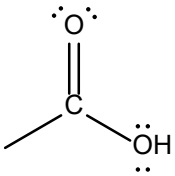


Step 2: Look at IR for relevant peaks

- The large peak at 1754 cm^{-1} strongly suggests a $C = O$ bond that most likely corresponds to an ester.
  - There are two peaks on the ^{13}C NMR at 170 ppm. This chemical shift is consistent with the carbonyl of an ester or carboxylic acid. One of these peaks could be for the ester.
- The large peak at 1693 cm^{-1} strongly suggests another $C = O$, and the broad peak from 3300-2500 cm^{-1} strongly suggests a carboxylic acid $O - H$.
  - The other peak at 170 ppm on the ^{13}C NMR could correspond to a carboxylic acid
  - The peak at 11.5 ppm on ^{1}H NMR is also consistent with a carboxylic acid group (CO_2H peak)
- The ester and carboxylic acid would account for the remaining 2 degrees of unsaturation (4 for the benzene ring, 1 for ester $C = O$, 1 for carboxylic acid $C = O$)

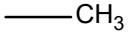


and



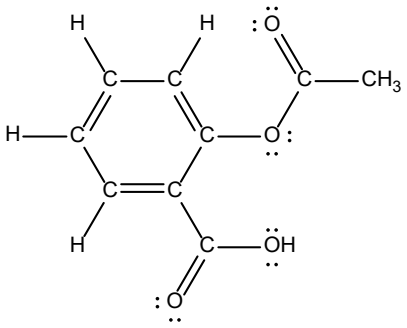
Step 3: Consider the remaining peaks on ^{1}H NMR and ^{13}C NMR

- Thus far, we have used $C_8H_5O_4$ of the $C_9H_8O_4$ in the molecular formula. That leaves CH_3 unaccounted for. That's most likely a methyl group.
  - There is a peak at ~20ppm on ^{13}C NMR, consistent with CH_3 that is not attached to oxygen
  - There is a singlet at ~2.3ppm on ^{1}H NMR, consistent with CH_3 attached to either $C = O$ or a benzene ring (but not attached to an oxygen atom as that would deshield the peak to 3.5+ ppm). This singlet integrates to 3H, also consistent with CH_3.

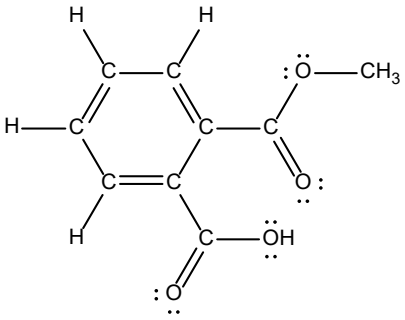


Step 4: Assemble the pieces and decide between the options.

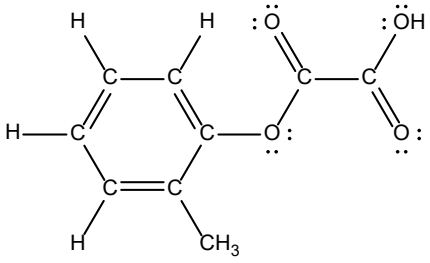
- There are two terminal groups (CH_3 and CO_2H) and two central groups (ester and benzene). We must remember that the ester can have two different orientations. That gives a preliminary set of options:



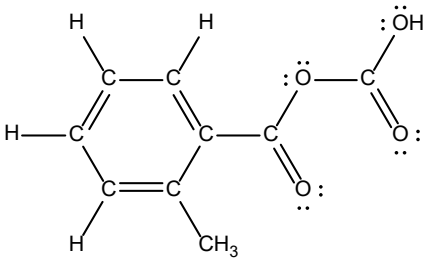
Option A



Option B

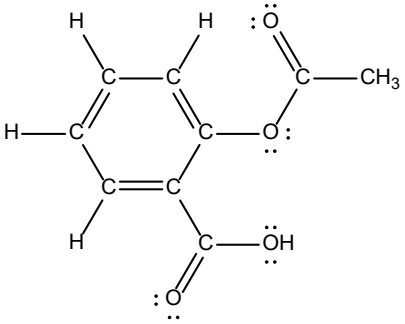


Option C



Option D

- We can eliminate Option B because the chemical shift of the CH_3 group on ^{1}H NMR is too far upfield (~2.3 ppm) for OCH_3 of an ester (~4ppm)
- We can eliminate Option C because it has two electron-donating groups attached to the benzene ring so there's no way for any of the aromatic peaks to be as far downfield at 8.1 ppm on the ^{1}H NMR
- We can eliminate Option D because the ^{13}C NMR has one aromatic peak substantially downfield of the rest, indicative of one carbon atom in the benzene ring being attached to an oxygen atom.
- That leaves Option A as the only viable option for Unknown X:

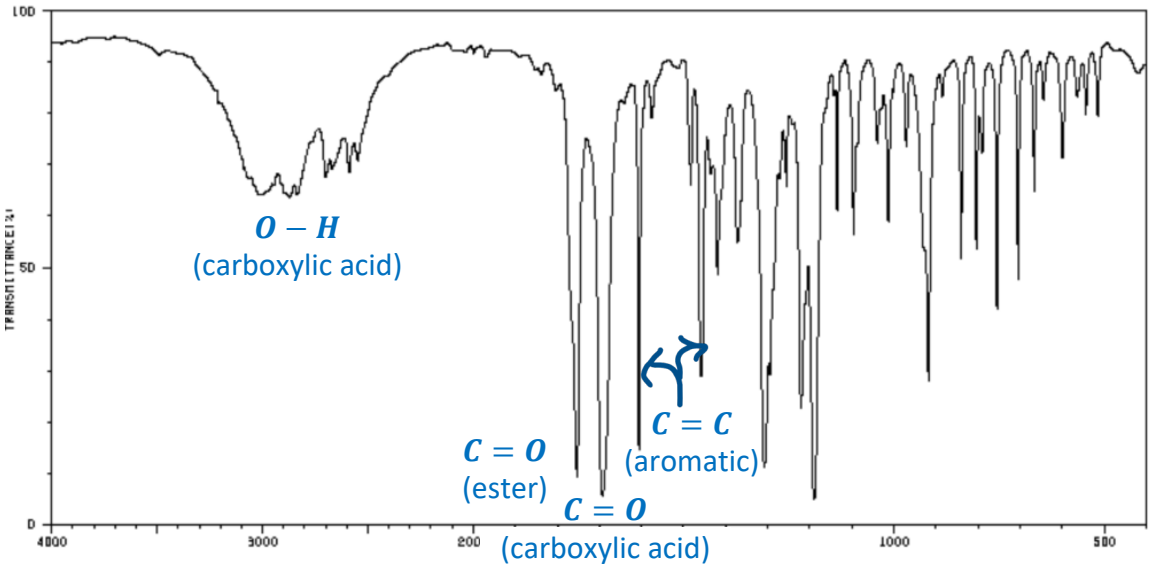


Step 5: Check your answer against the spectra and assign the peaks.

- IR
  - A very broad stretch is visible from 3300 to 2500 cm^{-1}. This is consistent with a carboxylic acid $O-H$.
  - $C-H$ stretches are 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).
  - A $C=O$ stretch is visible at 1754 cm^{-1}. This is close to the usual range for esters.
  - A $C=O$ stretch is visible at 1693 cm^{-1}. This is within the usual range for conjugated carboxylic acids.
  - $C=C$ stretches are visible at 1606 cm^{-1} and ~1450 cm^{-1}, consistent with an aromatic ring.
- ^{1}H NMR
  - The singlet at ~11.5 ppm integrating to 1H is consistent with the CO_2H.
  - The doublet of doublets at ~8.1ppm integrating to 1H is consistent with an aromatic hydrogen atom *ortho* to an electron-withdrawing group such as a carboxylic acid.
  - The peak at ~7.1 ppm must be a doublet (of doublets) because the line spacing between the three rightmost lines in the aromatic region is not even so there cannot be a triplet there. It makes sense that the aromatic hydrogen atom *ortho* to the electron-donating ester group (connected through the oxygen atom) would be the furthest upfield of the aromatic peaks.
  - That leaves a triplet of doublets at ~7.65 ppm and a triplet of doublets at ~7.35 ppm. The H that is *para* to the electron-withdrawing carboxylic acid group will be further downfield (~7.65ppm) while the H that is *para* to the electron-donating ester group will be further upfield (~7.65ppm).
  - Calculation of chemical shifts for the aromatic protons using the Spectroscopy Data Package gives the following results:
    - 8.15 ppm for H *ortho* to carboxylic acid
    - 7.57 ppm for H *para* to carboxylic acid
    - 7.32 ppm for H *para* to ester
    - 7.20 ppm for H *ortho* to ester
  - The singlet at ~2.3 ppm is consistent with the CH_3 group attached to $C=O$.
- ^{13}C NMR
  - The two peaks at 170 ppm are consistent with $C=O$ of an ester and $C=O$ of a carboxylic acid.
  - The peak at ~150 ppm is consistent with $C-O$ where C is in a benzene ring.
  - The five peaks between 120 ppm and 140 ppm are consistent with the other five carbon atoms in the benzene ring (which is not symmetrically substituted).
  - The peak at ~20 ppm is consistent with the CH_3 group.

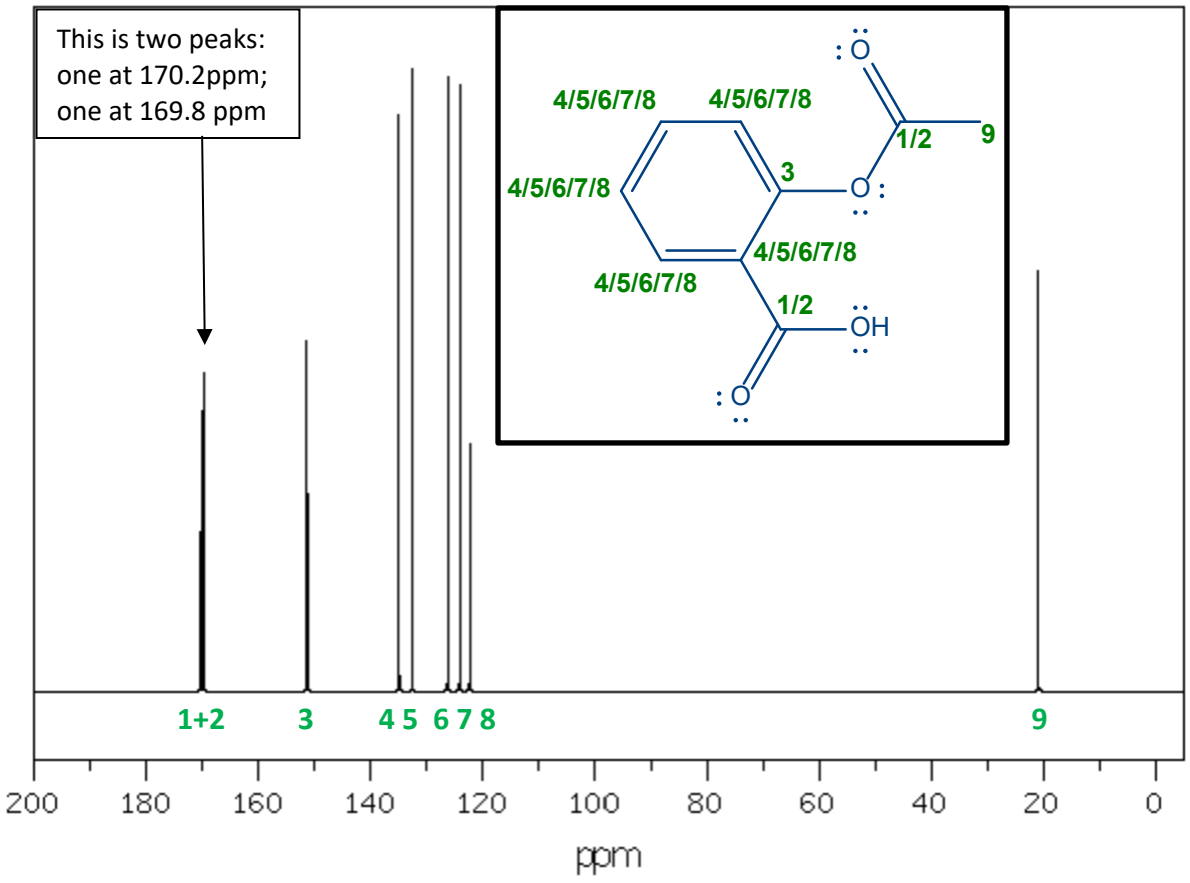
8. *…continued*

$C_9H_8O_4$



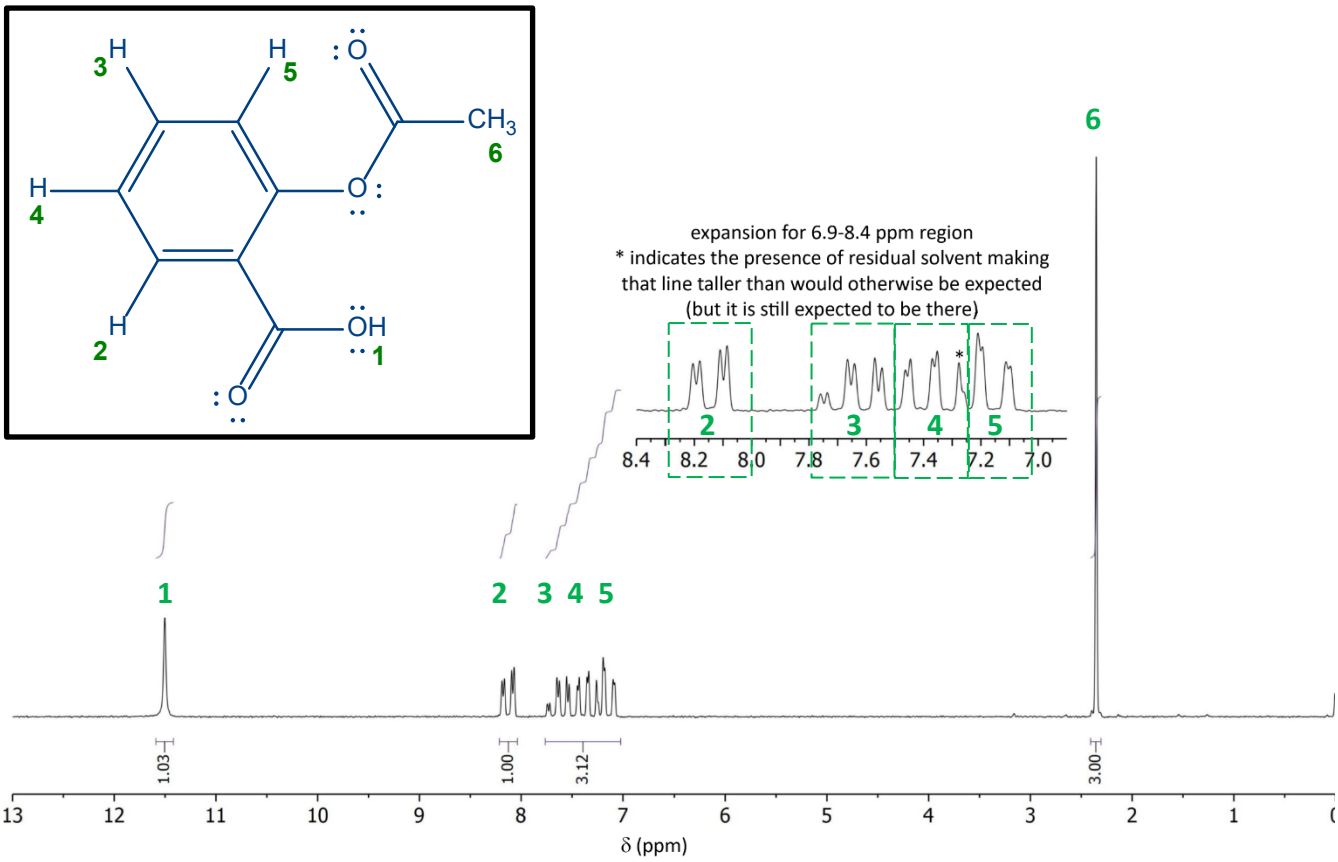
Some Longer Peaks

3006 cm^{-1}	62%
2983 cm^{-1}	62%
2891 cm^{-1}	62%
2824 cm^{-1}	62%
2701 cm^{-1}	66%
2548 cm^{-1}	66%
1754 cm^{-1}	8%
1693 cm^{-1}	6%
1606 cm^{-1}	16%



8. *…continued*

$C_9H_8O_4$



An answer worth full marks will assign every peak on the ^1H NMR spectrum to a specific hydrogen atom or set of equivalent hydrogen atoms.

9. Of the four spectroscopic techniques discussed in CHEM 2600 (IR, ^{1}H NMR, ^{13}C NMR and MS), which would be the most effective if you needed to distinguish between a bottle of chlorobenzene and a bottle of bromobenzene whose labels had both fallen off? Briefly explain which peak(s) would be most distinctive for each compound and where on each spectrum you would expect to see them. Be specific. **[5 marks]**

Mass spectrometry

- Chlorobenzene:
  - $3:1$ ratio between the M^+ and $[M+2]^+$ peaks
  - M^+ will be found at $^m/_z$ 112; $[M+2]^+$ will be found at $^m/_z$ 114
- Bromobenzene
  - $1:1$ ratio between the M^+ and $[M+2]^+$ peaks
  - M^+ will be found at $^m/_z$ 156; $[M+2]^+$ will be found at $^m/_z$ 158

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

…AND THAT'S ALL FOR CHEM 2600.

HAVE A GREAT SUMMER!