Fall 2023 **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 13 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.

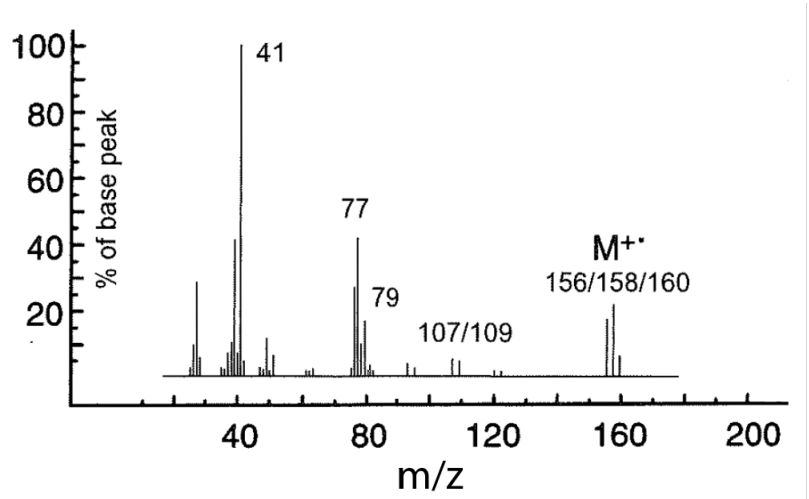
Question Breakdown

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8							Total
/ 15	/ 12	/ 15	/ 17	/ 11	/ 18	/ 6	/ 1							/ 95

1. **[15 marks]**

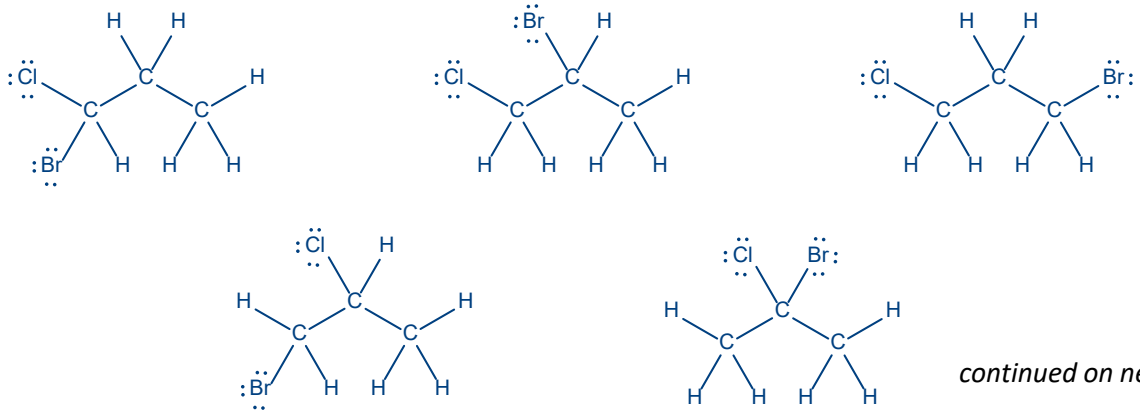
(a) The mass spectrum for Unknown **X** is shown below. The peak height ratio for the lines at m/z 156, m/z 158 and m/z 160 is 3: 4: 1. Unknown **X** contains only carbon, hydrogen and halogen atoms.

Determine the molecular formula for Unknown **X**. Show your work. *[4 marks]*



- $M^+ : [M+2]^+ : [M+4]^+ = 3:4:1$ so Unknown X contains one chlorine atom $\left(3:1\ {}^{35}Cl:{}^{37}Cl\right)$ and one bromine atom $\left(1:1\ {}^{79}Br:{}^{81}Br\right)$
- $35 + 79 = 114$, so total mass of remaining atoms is $156 - 114 = 42$ g/mol. Since all atoms are either carbon, hydrogen or halogen, this must be from carbon and hydrogen atoms. *(The mass of iodine is too high and, while you could theoretically have one or two fluorine atoms, the math doesn't work. If there were two fluorine atoms, that'd be 38 g/mol and there wouldn't be enough mass left for any carbon atoms. If there was one fluorine atom, that'd be 19 g/mol so you'd have 23 g/mol left and $CH_{11}FClBr$ is not a viable molecular formula.)*
- Three is the highest number of carbon atoms that can fit into 42 g/mol $(3x12 = 36)$. Fewer carbon atoms than that would require an unreasonably high number of hydrogen atoms.
- That leaves 6 g/mol which must be six hydrogen atoms.
- Therefore, the molecular formula is C_3H_6ClBr.

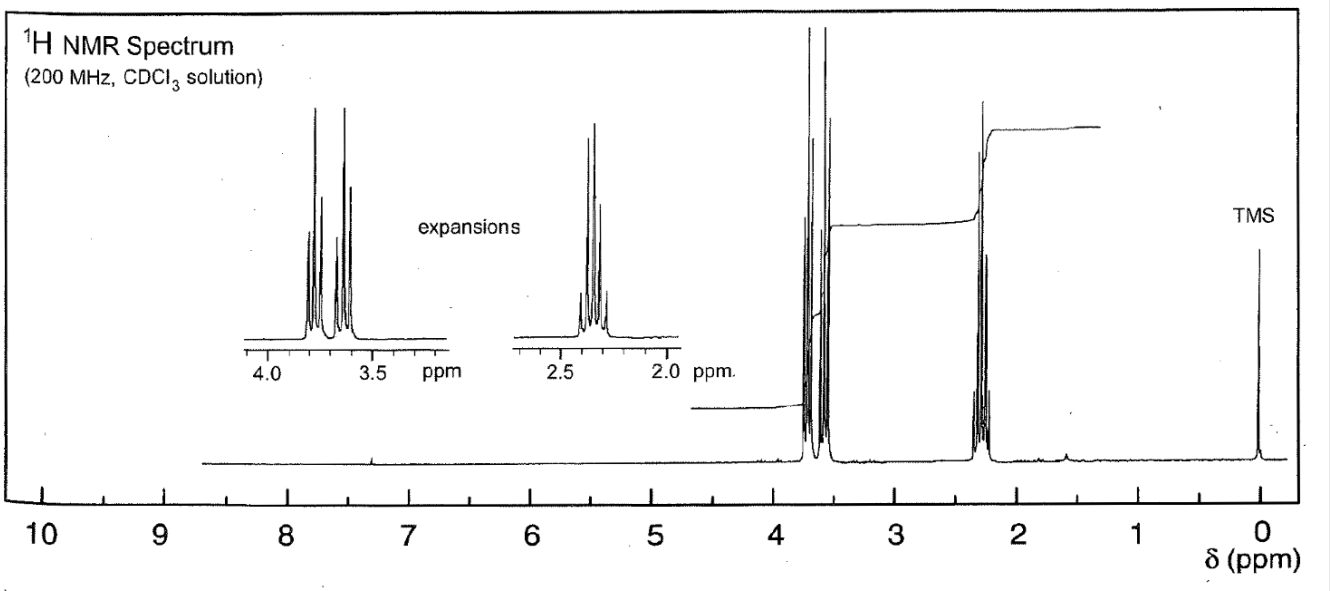
(b) There are five possible structural isomers for Unknown **X**'s molecular formula. Draw them all. *[5 marks]*



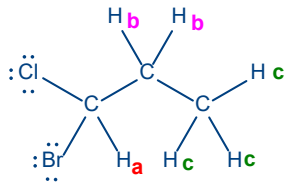
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1. *continued…*

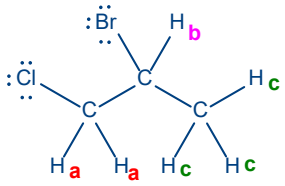
(c) The ^{1}H NMR spectrum for Unknown **X** is shown below. Use this spectrum to determine which of the five structural isomers drawn in part (b) must correspond to Unknown **X**. Clearly explain your reasoning. *[6 marks]*



The spectrum above shows two triplets and one pentet with a 1:1:1 integral ratio.
The peaks expected for each structural isomer are listed below its diagram:

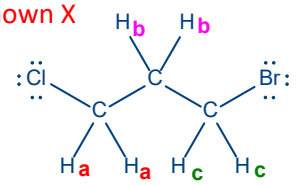


a gives triplet integrating to 1H
b gives pentet integrating to 2H
c gives triplet integrating to 3H
splitting patterns match
integral ratio doesn't match

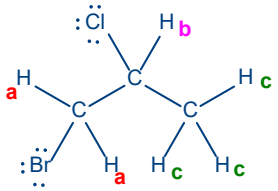


a gives doublet integrating to 2H
b gives sextet integrating to 1H
c gives doublet integrating to 3H
splitting patterns don't match
integral ratio doesn't match

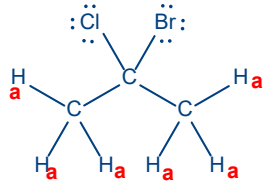
Unknown X



a gives triplet integrating to 2H
b gives pentet integrating to 2H
c gives triplet integrating to 2H
splitting patterns match
integral ratio matches



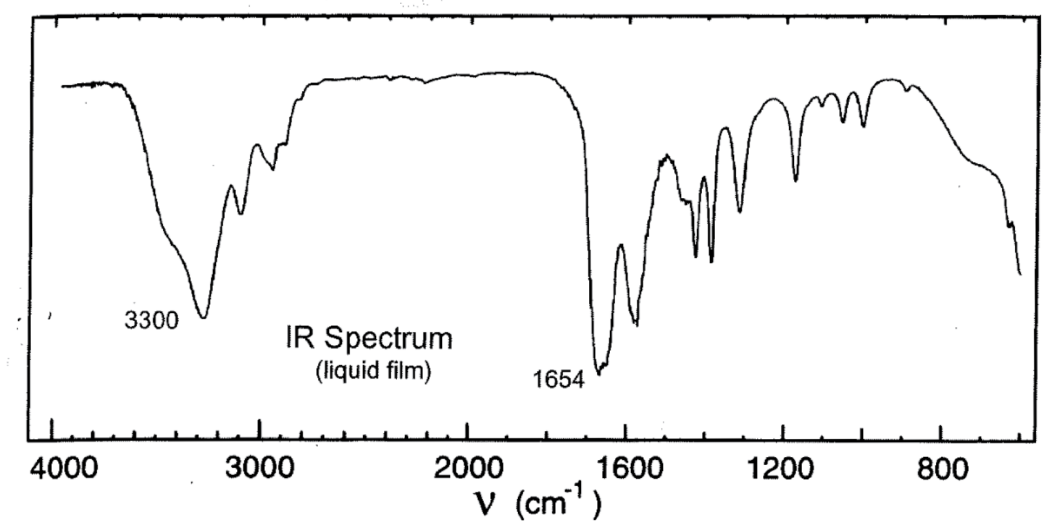
a gives doublet integrating to 2H
b gives sextet integrating to 1H
c gives doublet integrating to 3H
splitting patterns don't match
integral ratio doesn't match

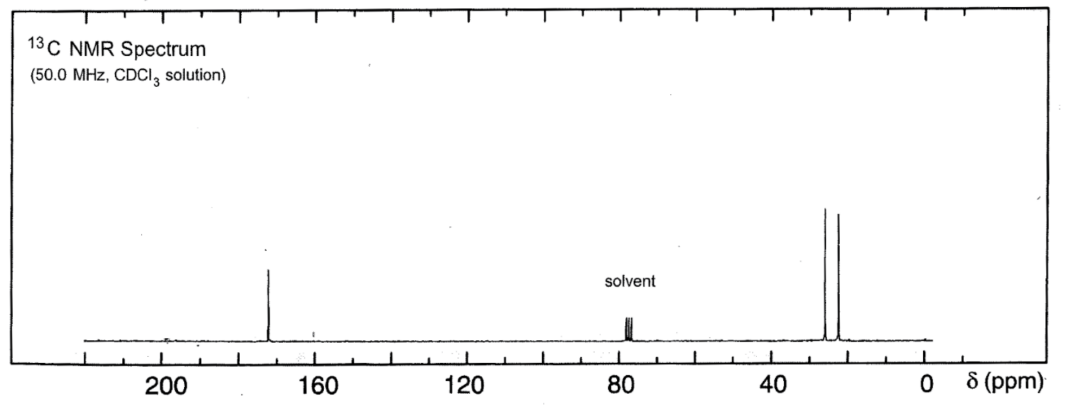


a gives singlet (the only peak)
number of peaks doesn't match
splitting patterns don't match
integral ratio doesn't match

2. The molecular formula of Unknown **Y** is C_3H_7NO. **[12 marks]**

(a) The infrared spectrum and ^{13}C NMR spectrum for Unknown **Y** are shown below. What can you conclude about Unknown **Y** based on these two spectra? Clearly explain your reasoning for each conclusion with direct reference to specific peaks on the relevant spectrum or spectra. *[6 marks]*





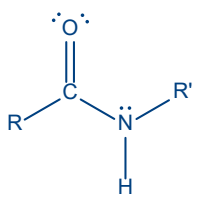
^{13}C NMR:

- three peaks, so all three carbon atoms must be in unique environments
- peak at ~170 ppm probably corresponds to a $C = O$ group
- peaks at ~20 ppm and ~25 ppm correspond to tetrahedral carbon atoms (CH_3 *or* CH_2)

IR:

- peak at 1654 cm^{-1} is most likely a $C = O$ stretch; it cannot be conjugated as there are no alkene peaks on ^{13}C NMR and only one degree of unsaturation, so this is most likely an amide
- broad peak at 3300 cm^{-1} will be either $N - H$ or $O - H$. Given that there appears to be a carbonyl group and there's only one oxygen in the molecular formula, $N - H$ is most likely.

This molecule is most likely a secondary amide:



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2. *…continued*

(b) A ^{1}H NMR spectrum for Unknown **Y** shows three peaks with integral ratios of $1:3:3$. *[4 marks]*

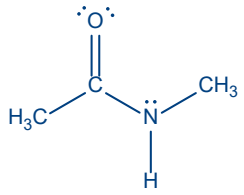
- A broad singlet at 7.4 ppm (1H) which exchanges with D_2O upon warming
- A sharp singlet at 2.8 ppm (3H)
- A sharp singlet at 2.0 ppm (3H)

What can you conclude about Unknown **Y** based on this information? Clearly explain your reasoning for each conclusion with direct reference to the relevant feature(s) of the peaks being discussed.

^{1}H NMR:

- three peaks with integral ratio of $1:3:3$ so two CH_3 groups and one other hydrogen
- broad singlet at 7.4 ppm (1H) exchanges with D_2O so it's either OH or NH (exchangeable hydrogens don't couple so we cannot tell whether it has any neighbouring hydrogens)
- sharp singlet at 2.8 ppm (3H) is a CH_3 group attached to something somewhat deshielding – possibly a nitrogen atom (this is not far enough downfield to be OCH_3); since it is a sharp singlet, it does not have any neighbouring hydrogens with which it can couple (remembering that exchangeable hydrogens don't couple)
- sharp singlet at 2.0 ppm (3H) is a CH_3 group attached to something somewhat deshielding – possibly a carbonyl group (based on the strong evidence for one on the IR and ^{13}C NMR); since it is a sharp singlet, it does not have any neighbouring hydrogens with which it can couple (remembering that exchangeable hydrogens don't couple)

(c) Identify Unknown Y. *[2 marks]*

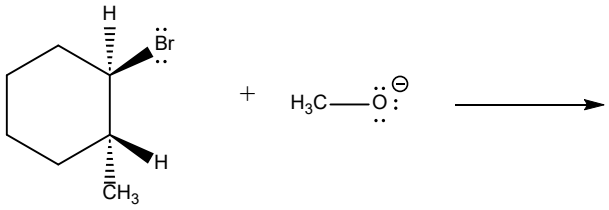


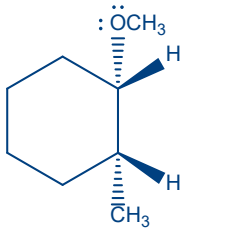
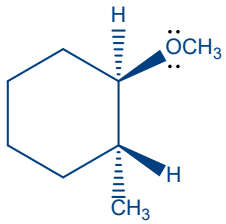
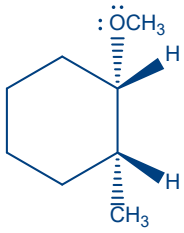
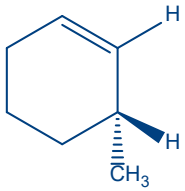
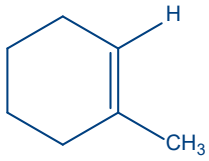
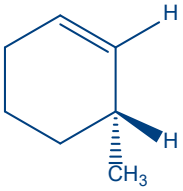
3. Indicate whether or not you would expect to see a significant amount of reaction according to each mechanism type by circling 'yes' or 'no'. In the bottom row of each table, justify your answer by: **[15 marks]**

- 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.

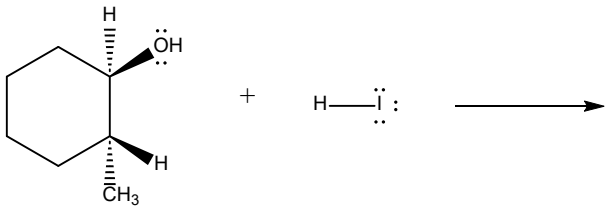
The marks are for the product(s) and/or explanations. The yes/no part is just to help you think.

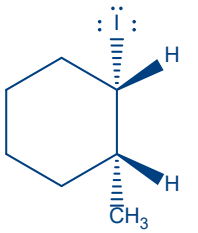
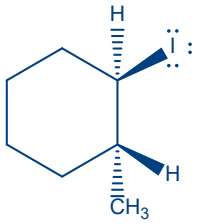
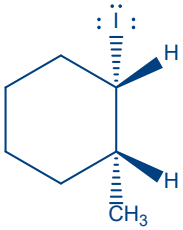
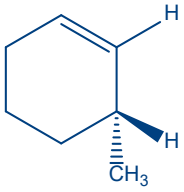
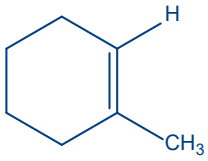
(a)



S_N1? yes / no	**S_N2?** yes / no	**E1?** yes / no	**E2?** yes / no
 and  *It would be reasonable to circle "no" based on the argument that S_N1 reactions require protic solvents (which would be deprotonated by the strong base) to stabilize the carbocation intermediate and/or that S_N2 reaction would be much faster than S_N1 reaction. If you circled "yes", you must show both diastereomers due to the trigonal planar carbocation intermediate.*	 *Stereochemical configuration of electrophilic atom is inverted in an S_N2 reaction. Configuration of the other chirality center is preserved since it's not involved in the reaction.*	 and  *It would be reasonable to circle "no" based on the argument that E1 reactions require protic solvents (which would be deprotonated by the strong base) to stabilize the carbocation intermediate and/or that E2 reaction would be much faster than E1 reaction. If you circled "yes", you must show both isomers due to the trigonal planar carbocation intermediate.*	 *In an E2 reaction, the base removes a β-hydrogen that is antiperiplanar to the leaving group. As such, the double bond can only form in one position.*

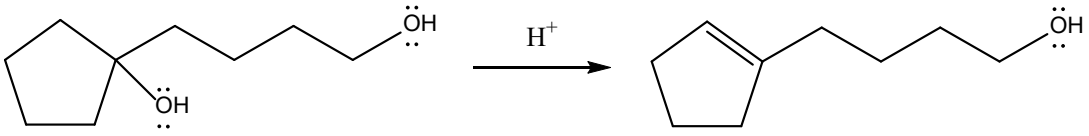
(b)



S_N1? yes / no	**S_N2?** yes / no	**E1?** yes / no	**E2?** yes / no
 and  *Two diastereomers are formed due to the trigonal planar carbocation intermediate.*	 *Stereochemical configuration of electrophilic atom is inverted in an S_N2 reaction. Configuration of the other chirality center is preserved since it's not involved in the reaction.*	 and  *E1 reactions have trigonal planar carbocation intermediates. As such, the β-hydrogen does not need to be antiperiplanar to the leaving group as it does in E2 reactions. There are thus two potential elimination products.*	$E2$ reactions require a strong base, and the only base available is water (after it leaves) which is a weak base.

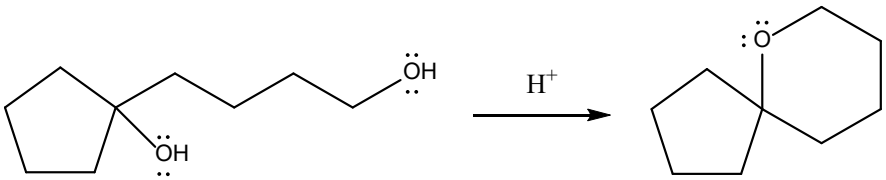
First, HI protonates the alcohol, creating a leaving group (water).

4. When I was a graduate student, I needed to prepare Compound **B** from Compound **A**: **[17 marks]**



A **B**

This was challenging because many acid catalysts would convert Compound **A** into Compound **C** instead:



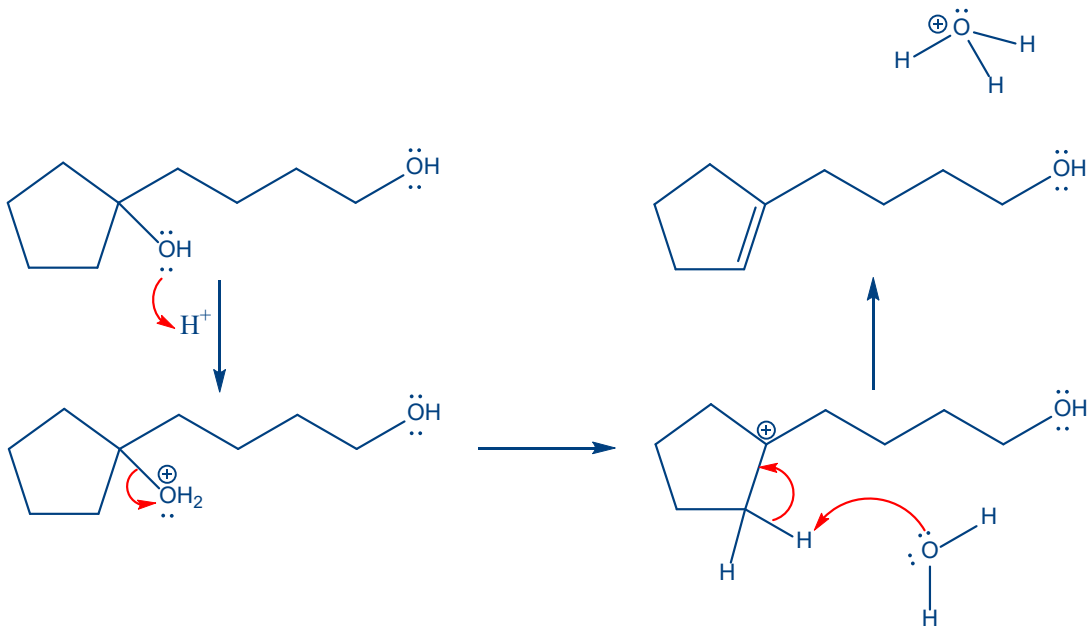
A **C**

Fortunately, I was eventually able to find an acid/solvent combination that favoured the production of Compound **B** over Compound **C**.

(a) Draw a reasonable mechanism for the formation of Compound **B** from Compound **A**. Clearly label your mechanism as either E1 or E2. *[6 marks]*

This is an E1 reaction.

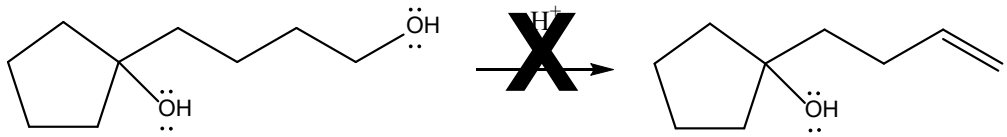
There is no base available until after water leaves and no strong base at all, so it cannot be E2.



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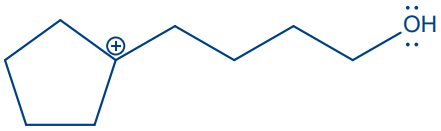
4. *…continued*

(b) Why did I not need to worry about production of Compound **D** as a side reaction? *[2 marks]*

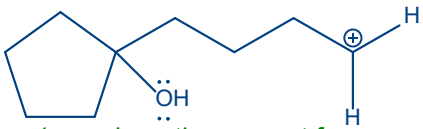


A **D**

While it is possible to protonate either oxygen atom, protonation of the tertiary alcohol allows water to act as a leaving group (giving a tertiary carbocation) whereas protonation of the primary alcohol cannot lead to carbocation formation since it would give a primary carbocation:

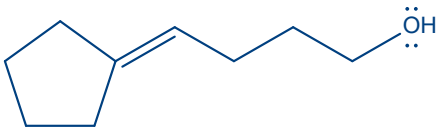


3° carbocation can form

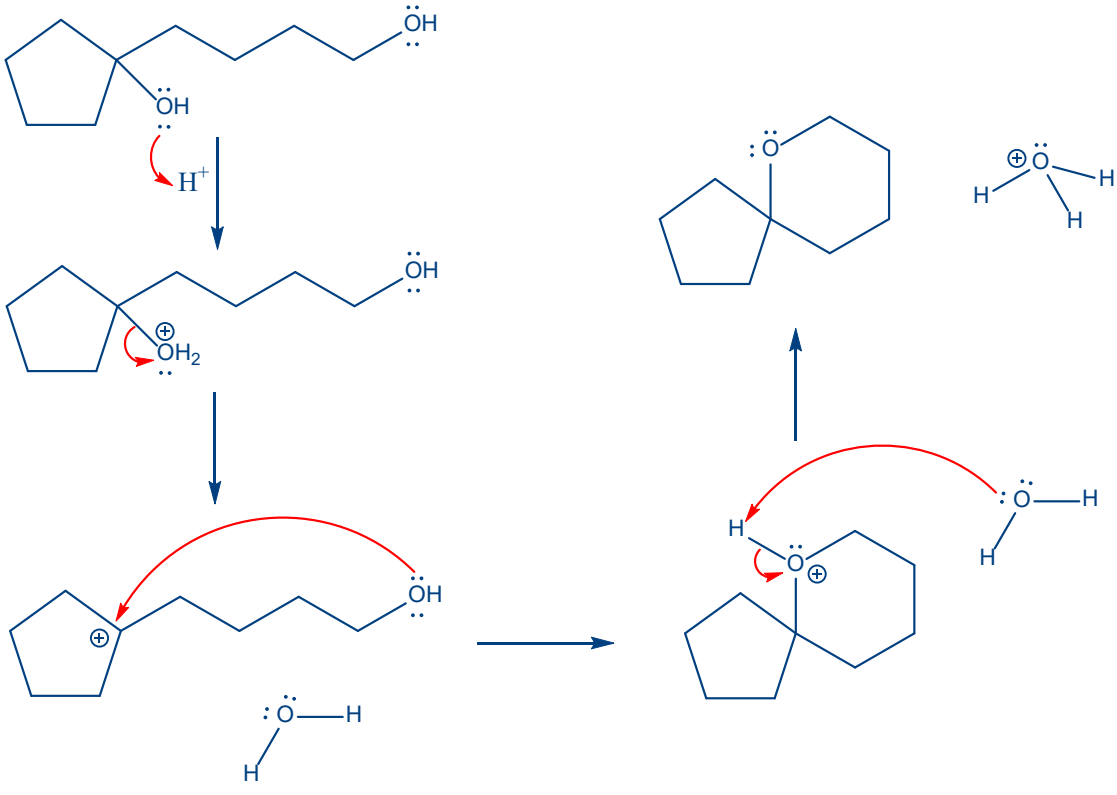


1° carbocation cannot form

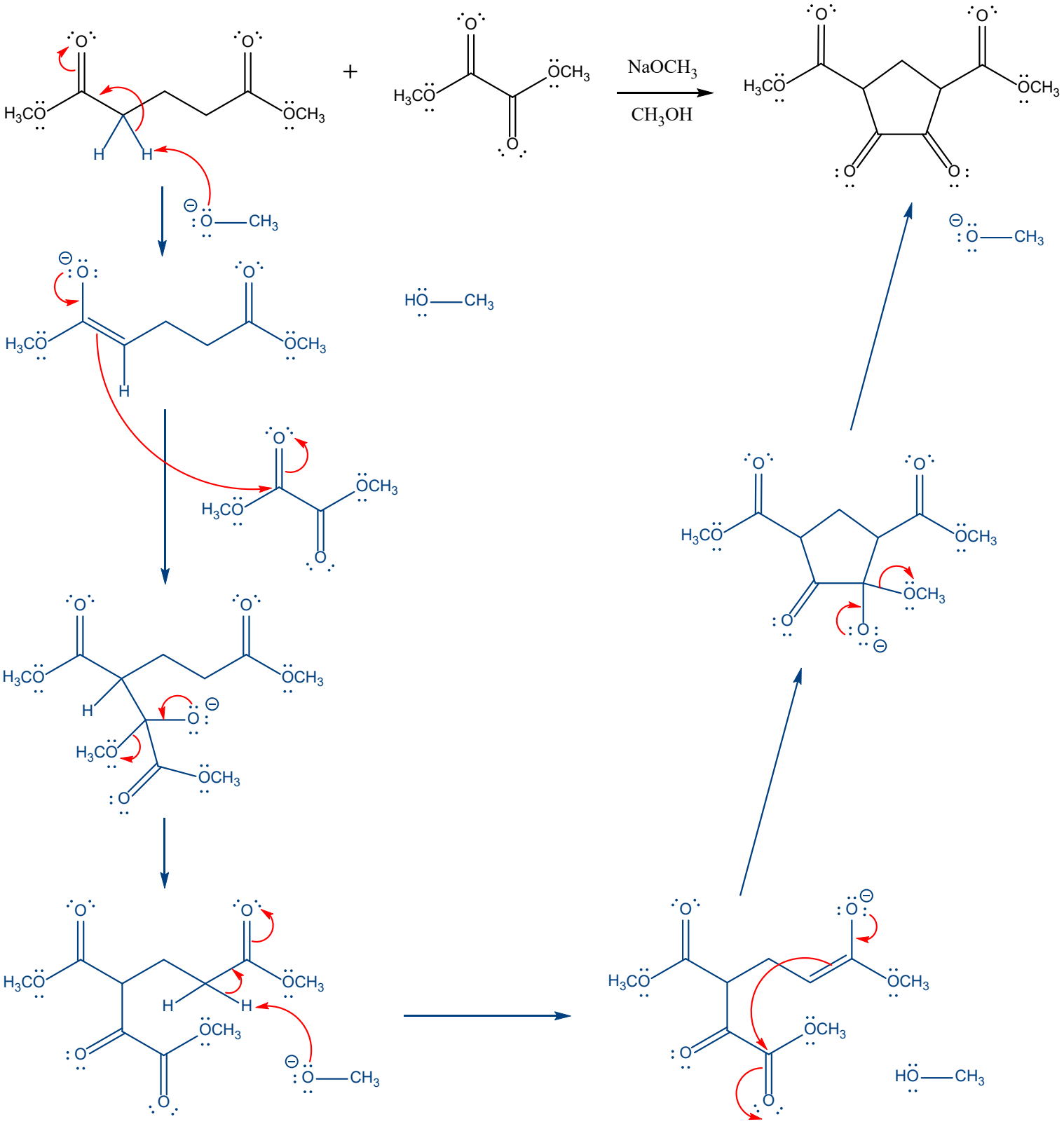
(c) I did see one other elimination product when I reacted Compound **A** with acid. I was able to minimize its formation but never entirely eliminate it. What would you expect to be the other elimination product formed when Compound **A** is reacted with an acid catalyst? *[2 marks]*



(d) Draw a reasonable mechanism for the formation of Compound **C** from Compound **A**. *[7 marks]*

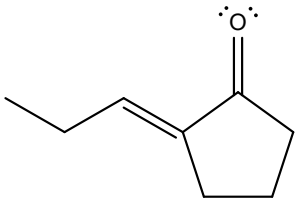


5. Propose a reasonable mechanism for the following reaction. **[11 marks]**

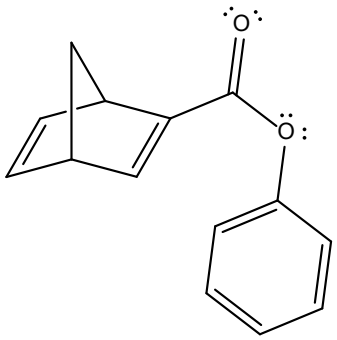


6. Choose any **three** of the molecules below and propose a synthesis for each one. **[18 marks]**

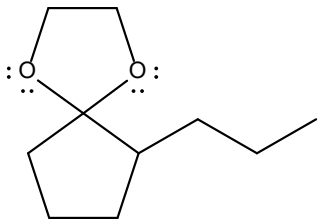
- If your synthesis involves more than one step, write an equation for each step. Show all required reactants. Number steps within a reaction if order of addition is important.
- All organic reactants must be stable compounds containing **no more than five carbon atoms**. They may be **hydrocarbons,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



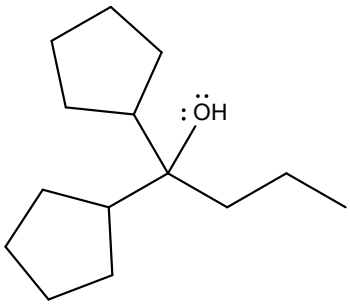
Looks like an aldol condensation product…



Looks like a Diels-Alder adduct…



Looks like alkylation of an enolate then turn the ketone into an acetal



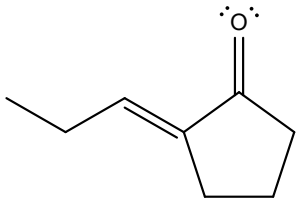
Looks like addition of two $C_5H_9^-$ to an ester… (due to C w/ O and two identical rings attached)

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.

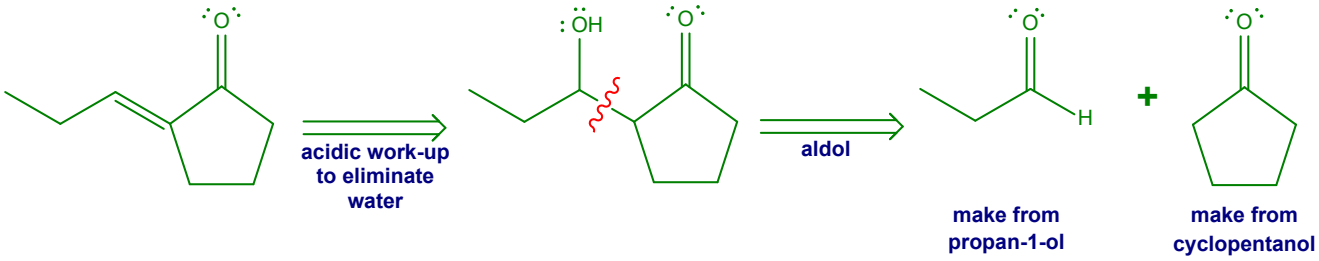
6. *continued…* *[6 marks]*

Synthetic Target #1:

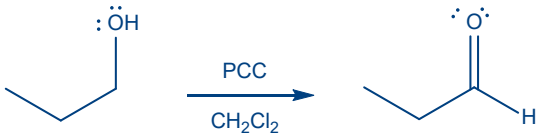


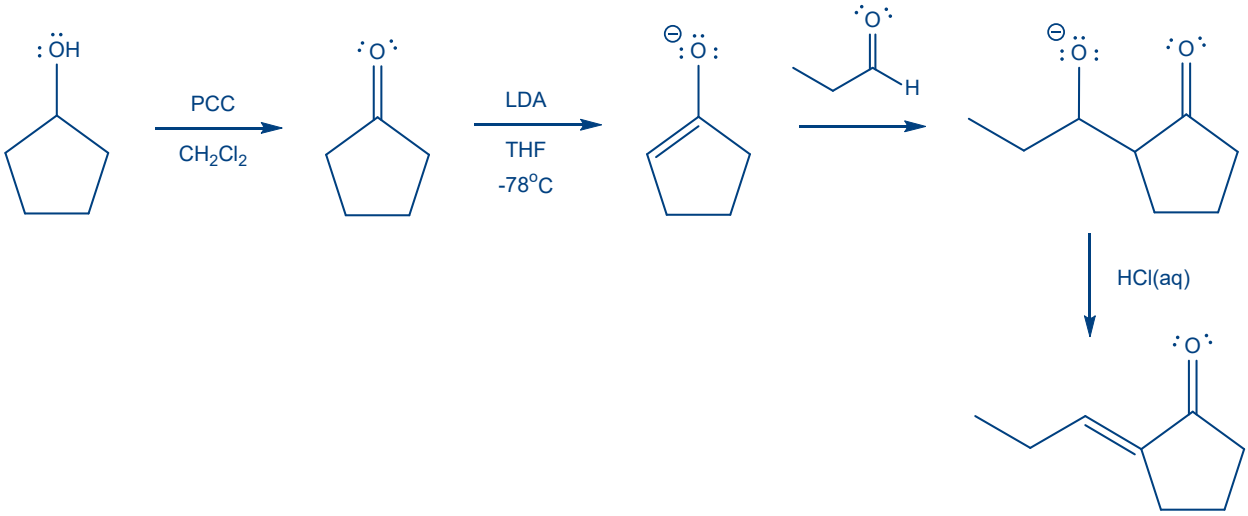
Synthesis:

Retrosynthetic analysis (aka "The Plan"):



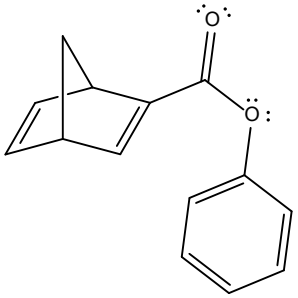
Synthetic Proposal:





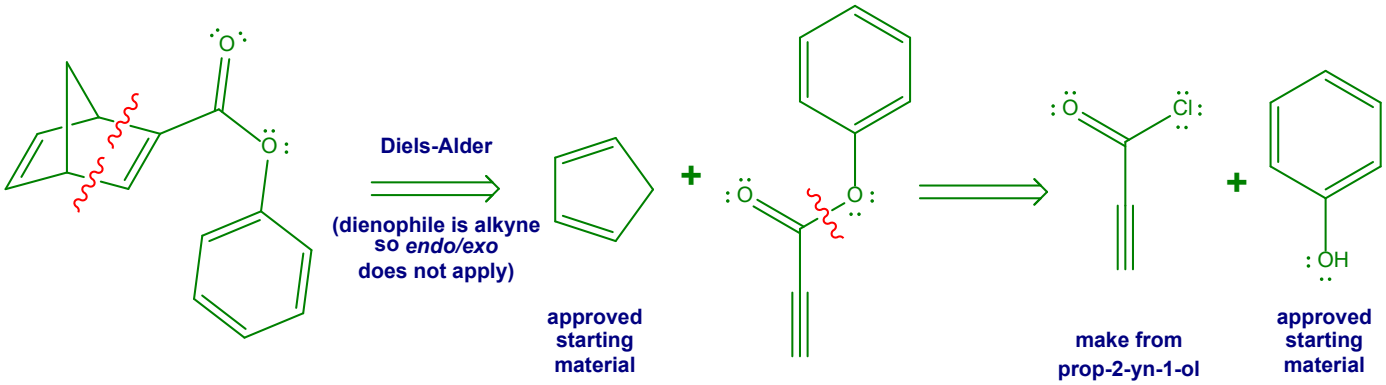
6. *continued…* *[6 marks]*

Synthetic Target #2:

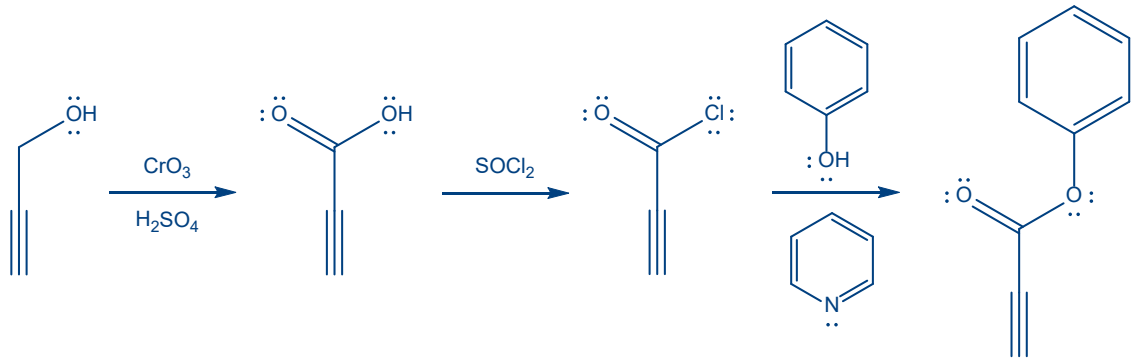


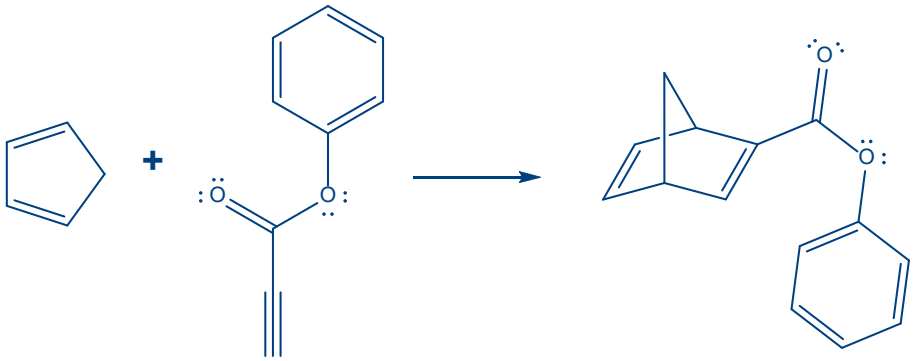
Synthesis:

Retrosynthetic analysis (aka "The Plan"):



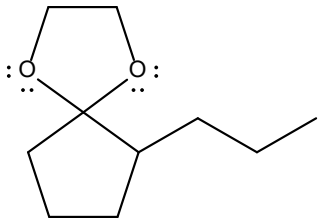
Synthetic Proposal:





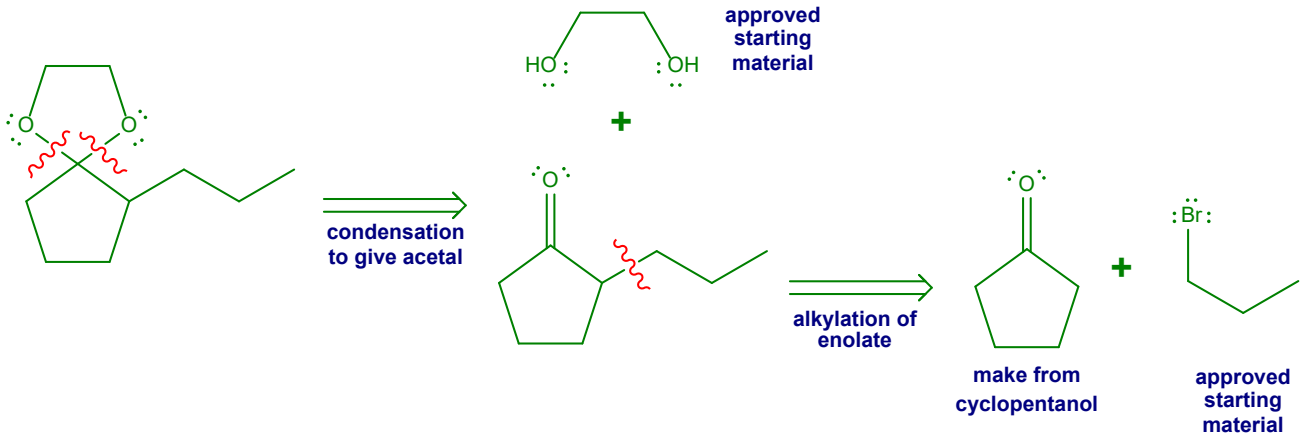
6. *continued…* *[6 marks]*

Synthetic Target #3:

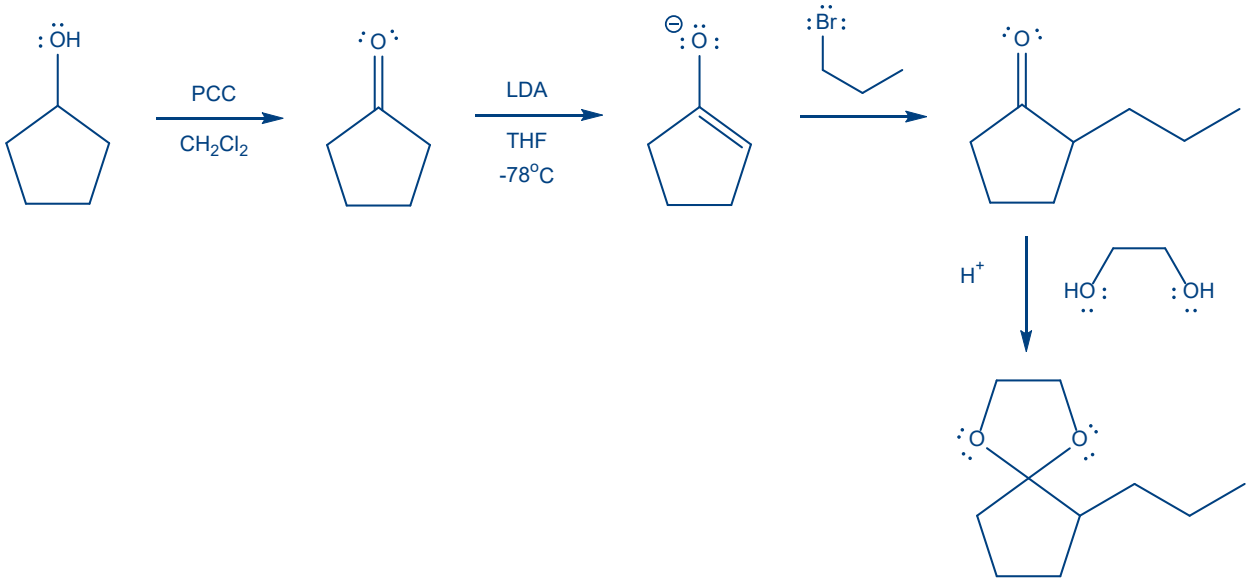


Synthesis:

Retrosynthetic analysis (aka "The Plan"):

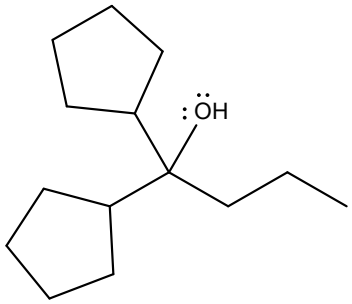


Synthetic Proposal:



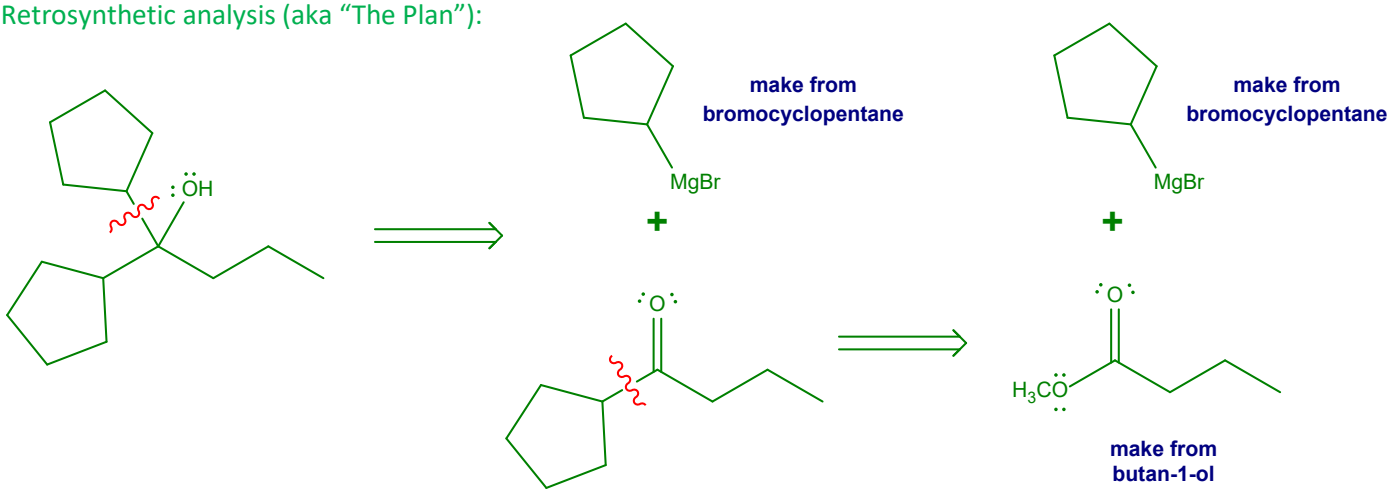
6. *continued…* *[6 marks]*

Synthetic Target #4:

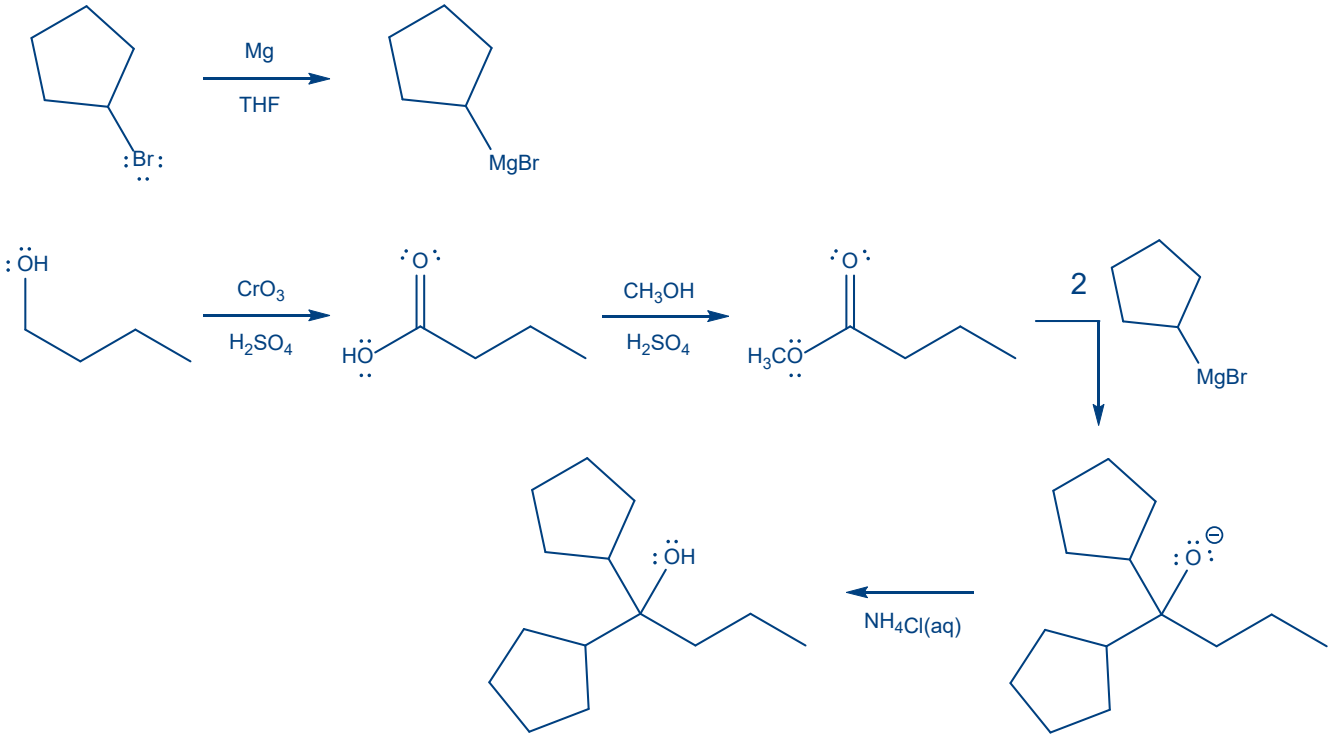


Synthesis:

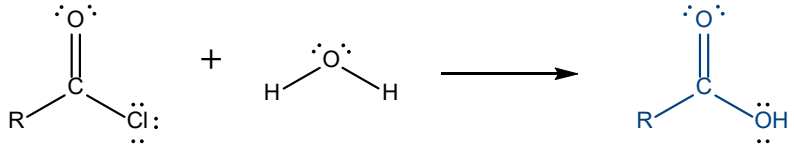
Retrosynthetic analysis (aka "The Plan"):



Synthetic Proposal:



7. A solvolysis is a reaction in which the solvent is one of the reactants. For example, if an acid chloride is added to a beaker of water, solvolysis of the acid chloride will occur: **[6 marks]**



(a) Draw the organic product of this reaction in the space provided above. *[2 marks]*

(b) This is a second order reaction. Write the rate law for this reaction. You do not need to provide a numerical value for k. *[2 marks]*

$rate = k[RCOCl][H_2O]$

(c) Using kinetic data to prove that this is a second order reaction would be challenging. Briefly explain why having one of the reactants be the solvent makes it difficult to collect experimental data that clearly demonstrates reaction order. *[2 marks]*

Kinetic experiments vary the concentration of each reagent independently (i.e. change the concentration of one reagent while keeping the concentration of the other one constant) and measure how the rate of reaction changes (or doesn't change) in response to changing reagent concentration.

When a reagent is the solvent, its concentration is so high that it cannot be varied meaningfully (without making it no longer the solvent).

8. 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!