Fall 2023 **Chemistry 2600 Midterm #2** ____/56 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 0/56 on this exam.

Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 8 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 may use a molecular model kit and ruler. You may not have written materials in your model kit.
4) You may use a calculator but only for calculation. No other electronic devices are allowed.
5) **DO NOT WRITE ON ANY QR CODE!!!** Work on pages without a QR code will not be graded.
6) 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.
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 2 hours to complete this test.

Question Breakdown

Q1	**Q2**	**Q3**	**Q4**	**Q5**										**Total**
/ 6	/ 8	/ 12	/ 22	/ 8										/ 56

1. Use the data provided in the table below to determine whether the reaction between the alkyl iodide (RI) and base proceeds via E1 or E2 mechanism. **[6 marks]**

   For full marks, your answer must include the rate law for this reaction including a numerical value and units for k. It must also include a brief verbal explanation of your choice between E1 and E2.

$[RI]\ \left(\frac{mol}{L}\right)$	$[base]\ \left(\frac{mol}{L}\right)$	Rate of reaction $\left(\frac{mol}{L \cdot s}\right)$
0.025	0.040	3.6×10^{-5}
0.025	0.060	5.4×10^{-5}
0.075	0.040	1.08×10^{-4}
0.075	0.060	1.62×10^{-4}

Step 1: Write generic rate law

$$rate = k[RI]^m[base]^n$$

Step 2: Solve for n by comparing rows 1 & 2 (or rows 3 & 4)

$$\frac{5.4\times10^{-5}\ \frac{mol}{L\cdot s}}{3.6\times10^{-5}\ \frac{mol}{L\cdot s}} = \frac{k\left(0.025\ \frac{mol}{L}\right)^m\left(0.060\ \frac{mol}{L}\right)^n}{k\left(0.025\ \frac{mol}{L}\right)^m\left(0.040\ \frac{mol}{L}\right)^n}$$

$$1.5 = \frac{\left(0.060\ \frac{mol}{L}\right)^n}{\left(0.040\ \frac{mol}{L}\right)^n} \quad \text{therefore} \quad 1.5 = 1.5^n \quad \text{therefore} \quad n = 1$$

Step 3: Solve for m by comparing rows 1 & 3 (or any other pair that isn't rows 1 & 2 or rows 3 & 4)

$$\frac{1.08\times10^{-4}\ \frac{mol}{L\cdot s}}{3.6\times10^{-5}\ \frac{mol}{L\cdot s}} = \frac{k\left(0.075\ \frac{mol}{L}\right)^m\left(0.040\ \frac{mol}{L}\right)^1}{k\left(0.025\ \frac{mol}{L}\right)^m\left(0.040\ \frac{mol}{L}\right)^1}$$

$$3 = \frac{\left(0.075\ \frac{mol}{L}\right)^m}{\left(0.025\ \frac{mol}{L}\right)^m} \quad \text{therefore} \quad 3 = 3^m \quad \text{therefore} \quad m = 1$$

Step 4: Solve for rate constant (k) using any row (row 1 shown below)

$$3.6 \times 10^{-5}\ \frac{mol}{L\cdot s} = k\left(0.025\ \frac{mol}{L}\right)^1\left(0.040\ \frac{mol}{L}\right)^1$$

$$k = \frac{3.6\times10^{-5}\ \frac{mol}{L\cdot s}}{\left(0.025\ \frac{mol}{L}\right)\left(0.040\ \frac{mol}{L}\right)}$$

$$k = 0.036\ \frac{L}{mol\cdot s}$$

Step 5: Answer question (i.e. write rate law)

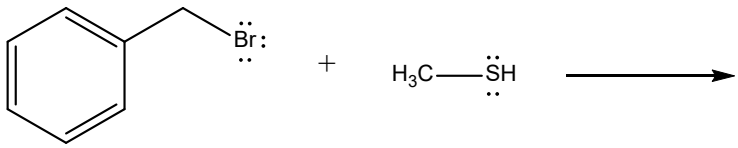
$$rate = 0.036\ \frac{L}{mol\cdot s}[RI][base]$$

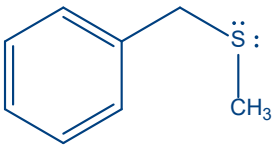
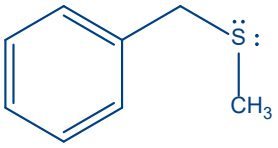
Since this reaction is second order (first order in substrate *and* first order in base), it must proceed via an $E2$ mechanism.

2. 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:
   - For each 'yes', drawing the organic product(s) that will be observed.
   - For each 'no', briefly explaining why you expect little-to-no reaction. **[8 marks]**

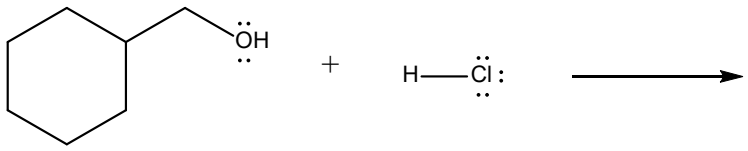
   The marks are for the product(s) and/or explanations. The yes/no part is just to help you think.

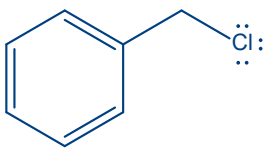
(a)



S_N1? yes / no	**S_N2?** yes / no	**E1?** yes / no	**E2?** yes / no
		There is no β-hydrogen so there cannot be an elimination reaction.	There is no β-hydrogen so there cannot be an elimination reaction. Also, there is no strong base, and $E2$ reactions require a strong base.

(b)

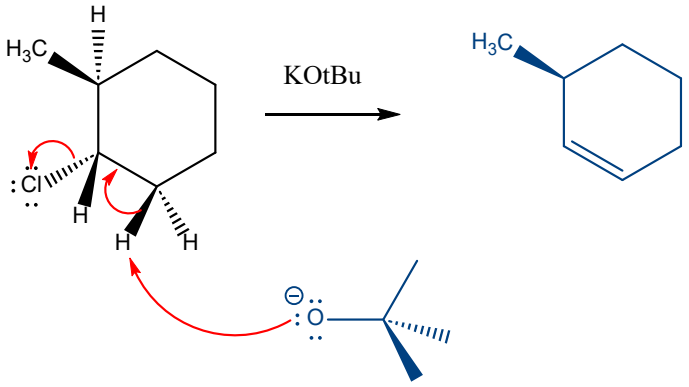


S_N1? yes / no	**S_N2?** yes / no	**E1?** yes / no	**E2?** yes / no
An S_N1 mechanism in this system would require a primary carbocation intermediate with no resonance stabilization.		An $E1$ mechanism in this system would require a primary carbocation intermediate with no resonance stabilization.	$E2$ reactions require a strong base, and there is no strong base in this system. (Cl^- is not a base and water is a very weak base.)

Note that, while HO^- is not a good enough leaving group for any of these four reaction mechanisms, the alcohol can deprotonate HCl. After that, water becomes available as a leaving gtoup.

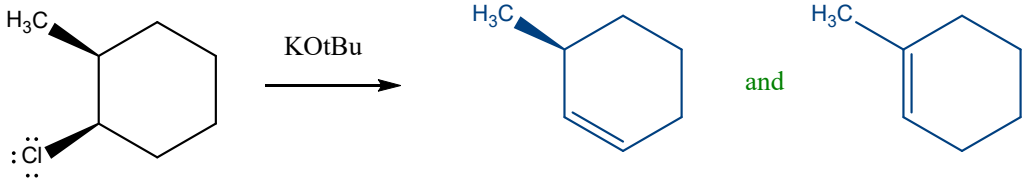
3. You are working on a project to optimize conditions for elimination reactions. **[12 marks]**

(a) Your first reaction works well, giving you a single organic product. Use curved arrows to show the mechanism for this reaction, and draw the resulting product. *[4 marks]*



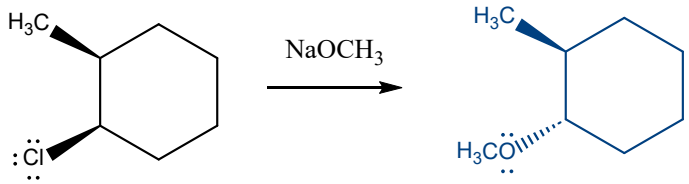
Note that the only β-hydrogen atoms that can be antiperiplanar to the leaving group are those trans- to it. In this substrate, that means that only the β-hydrogen atom attacked in the mechanism above can participate in the elimination reaction. This is easiest to see by redrawing the substrate in a chair conformation with Cl occupying an axial site.

(b) Buoyed by your success, you attempt the reaction shown below. It gives you a mixture of two organic products. Draw them both. *[4 marks]*



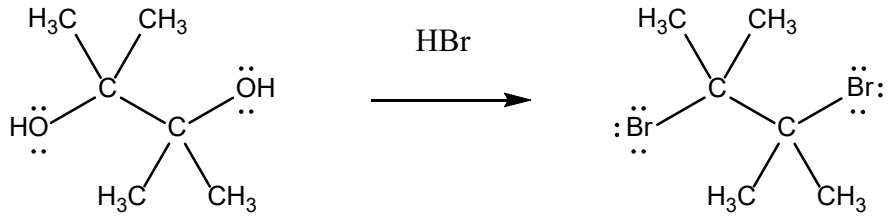
For this substrate, there are two β-hydrogen atoms that can be antiperiplanar to Cl so there are two possible products. Again, this is easiest to see by redrawing the substrate in chair conformation.

(c) You run out of potassium *tert*-butoxide but find a bottle of sodium methoxide in the lab. When you repeat the reaction in part (b) using sodium methoxide instead of potassium tert-butoxide, now you're up to **<u>three</u>** different organic products! Two of them are the same as your answer to part (b). Draw the third one and briefly explain why it started to form. *[4 marks]*



$NaOCH_3$ is a much less bulky base than $KOtBu$. As such, it can also act as a nucleophile and we also see formation of the S_N2 product shown above. Note that the configuration of the electrophilic carbon atom is always inverted in an S_N2 reaction.

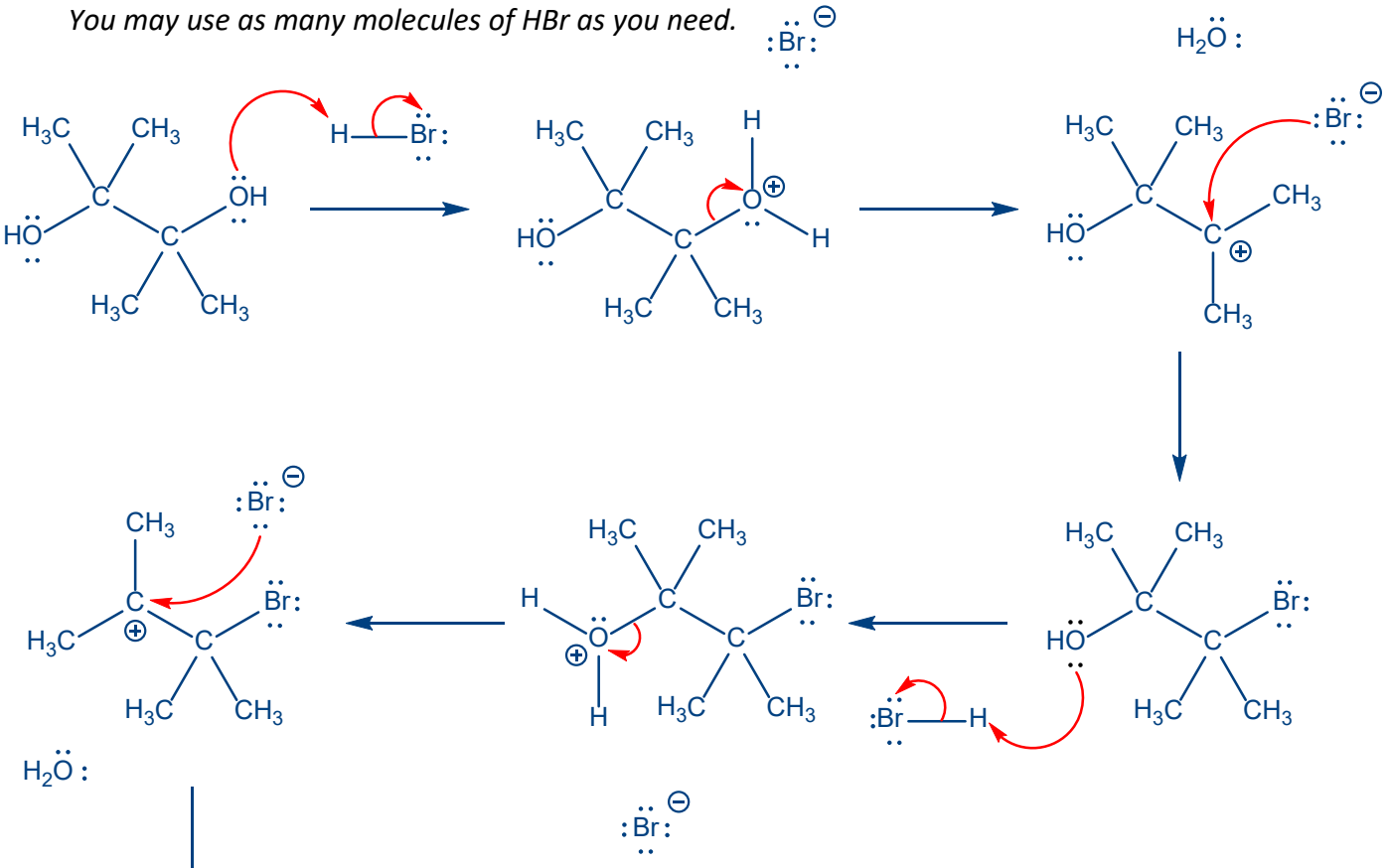
4. You wish to prepare 2,3-dibromo-2,3-dimethylbutane (**B**), so you try reacting 2,3-dimethylbutane-2,3-diol (**A**) with hydrobromic acid: **[22 marks]**



A **B**

(a) Use curved arrows to propose a valid mechanism for the reaction shown above. *[10 marks]*

You may use as many molecules of HBr as you need.

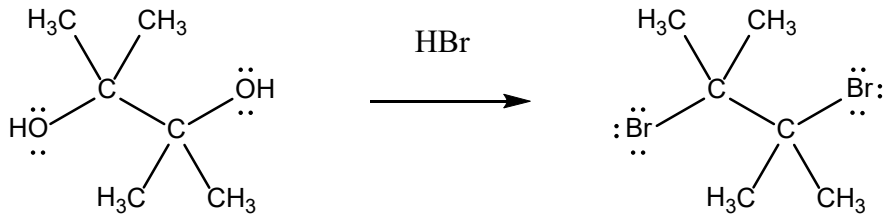


This reaction is performed in acid, so basic reactants are not available (no HO^-, etc.).

When drawing a reaction mechanism, you must draw each step separately. This not only communicates that you know which curved arrows "go together" in the same step, it also ensures that you draw all reaction intermediates. Intermediates are an essential component of any reaction mechanism.

When water leaves, a tertiary carbocation is formed. As such, S_N1 reaction is viable. S_N2 reaction is not viable because the electrophilic carbon atom is tertiary and therefore not accessible. In addition to not recognizing the inaccessible electrophilic site, students who drew S_N2 mechanisms failed to draw the carbocation intermediate.

4. *…continued*



A **B**

(b) You decide to monitor this reaction by ^{1}H NMR. *[3 marks]*

For chemical shifts, ranges are fine – as are approximate values.

i. What do you expect to see on the ^{1}H NMR for reactant **A**? Your answer should address multiplicity, integration and approximate chemical shift (where appropriate) for each peak.

^{1}H NMR spectrum for **A** is expected to have two peaks with an integral ratio of 1 : 6 (or 2 : 12)

- A broad singlet integrating to 1H
- A singlet at ~1.4 ppm integrating to 6H (1-2 ppm was accepted as valid estimated range)

ii. What do you expect to see on the ^{1}H NMR for product **B**? Your answer should address multiplicity, integration and approximate chemical shift (where appropriate) for each peak.

^{1}H NMR spectrum for **B** is expected to have one peak

- A singlet at ~1.8 ppm integrating to 6H (1-2 ppm was accepted as valid estimated range)

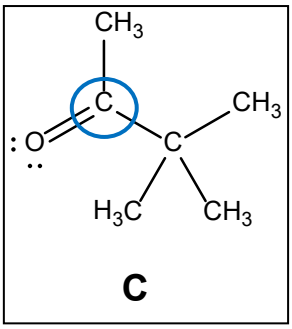
(c) Much to your dismay, the ^{1}H NMR spectrum you obtain does not match the one you predicted for product **B**. Astounded, you analyze the sample by ^{13}C NMR and are shocked to see four peaks, one of which is at 214 ppm!!! IR analysis shows a strong peak at 1708 cm^{-1}. With the help of your lab partner, you deduce that the only possible structure compatible with the spectra you obtained is that of 3,3-dimethylbutan-2-one (**C**), shown at the right. *[2 marks]*

i. Which carbon atom is responsible for the peak at 214 ppm?

see circle on diagram

ii. Which bond is responsible for the peak at 1708 cm^{-1}?

$C = O$



C

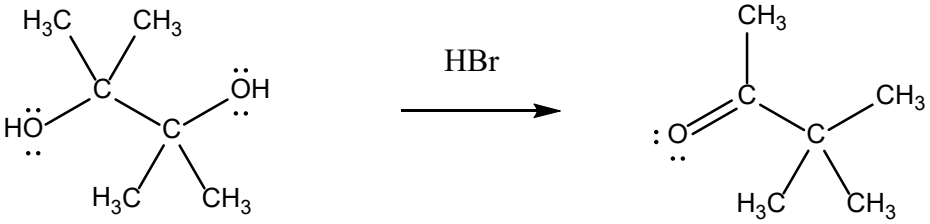
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4. *…continued*

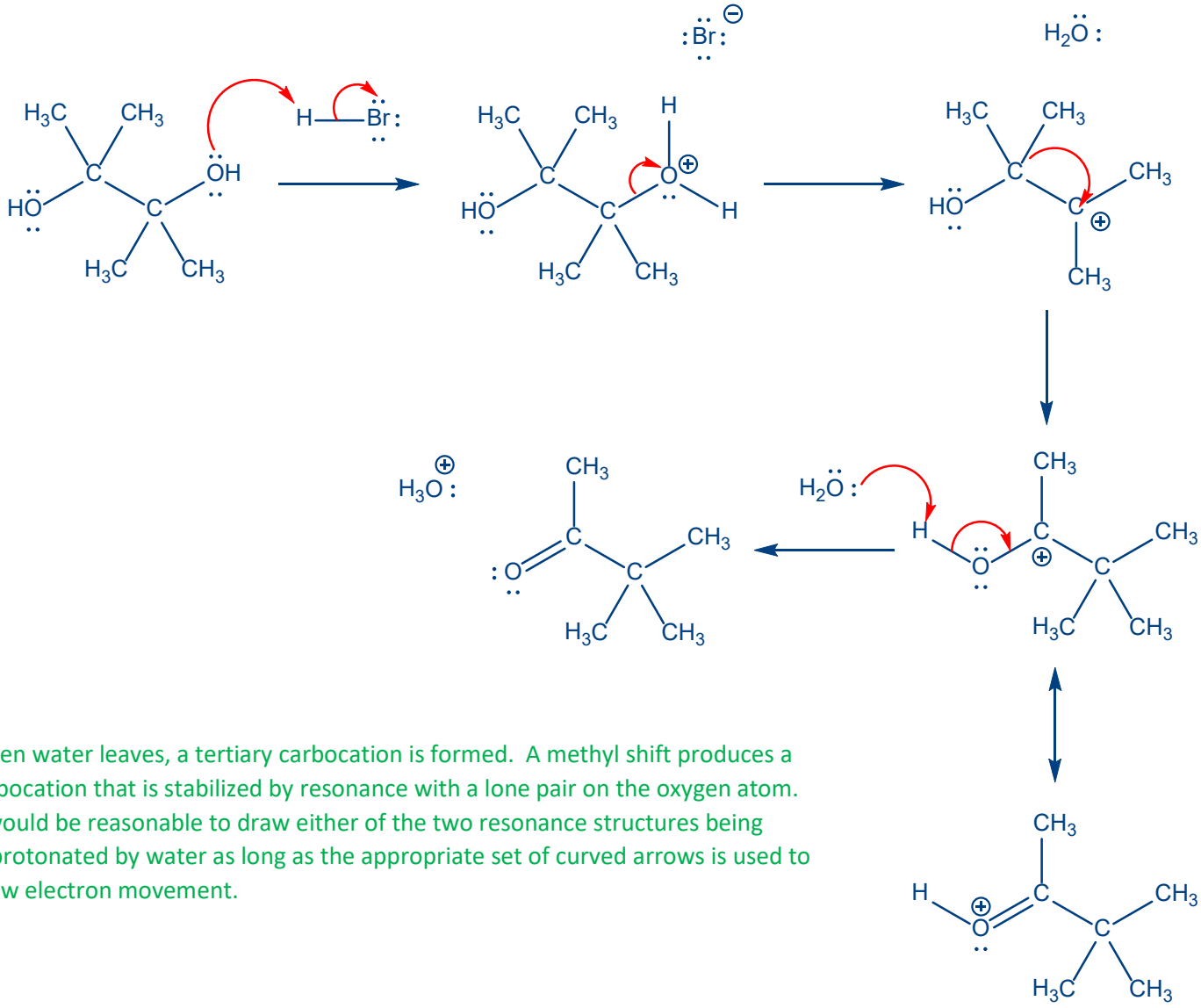
(d) What happened?!?!?!

Use curved arrows to propose a valid mechanism for the reaction shown below. *[7 marks]*

You may use as many molecules of HBr as you need.



A **C**



When water leaves, a tertiary carbocation is formed. A methyl shift produces a carbocation that is stabilized by resonance with a lone pair on the oxygen atom. It would be reasonable to draw either of the two resonance structures being deprotonated by water as long as the appropriate set of curved arrows is used to show electron movement.

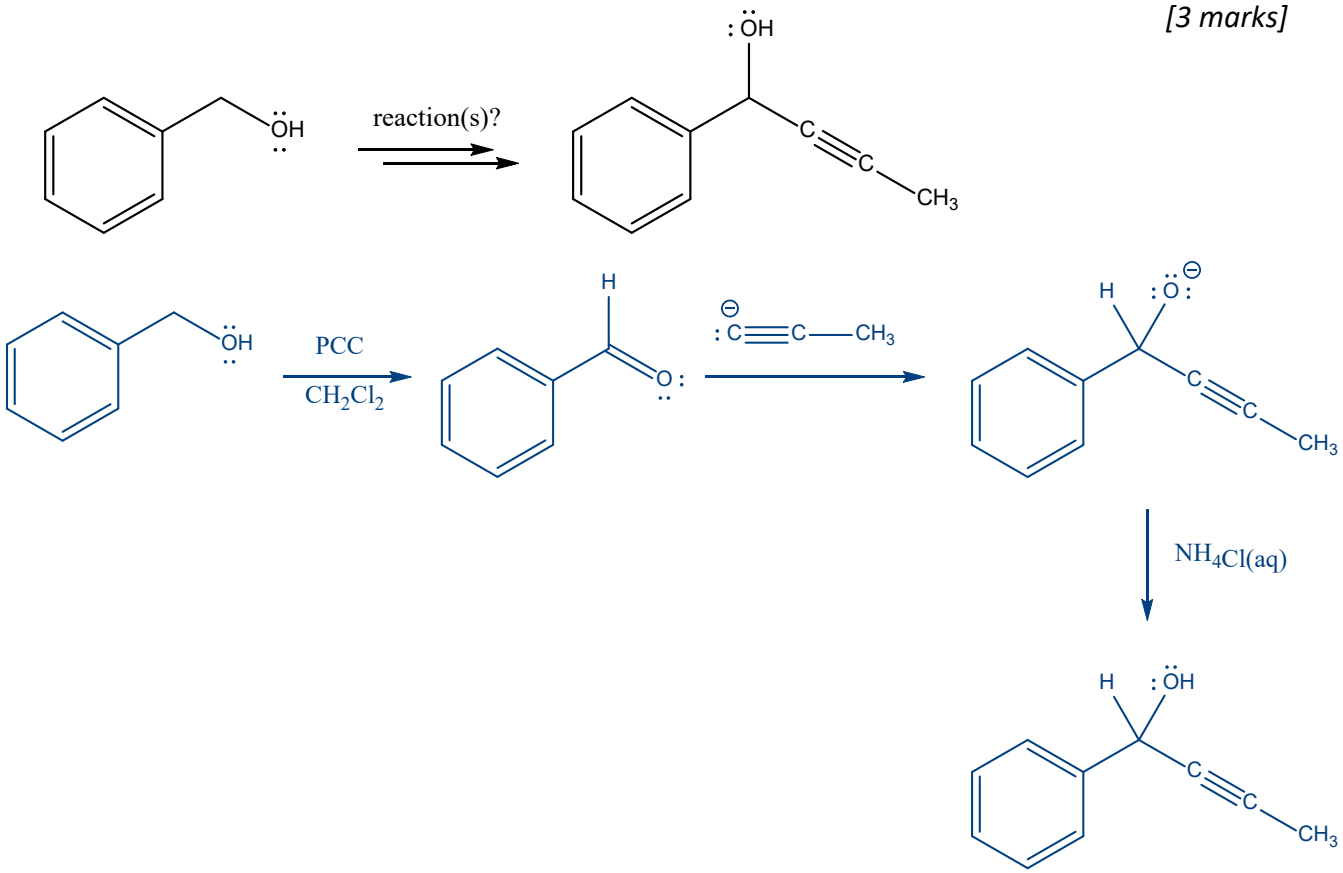
5. Propose a route to make each product from the given starting material. **[8 marks]**

In cases where more than one reaction is required, please draw each reaction with its own arrow and draw the product of each reaction. We are NOT asking for mechanisms. But we are asking that if you react A and B to make C and then, in a later step, react C with D to make E, that there be two separate arrows (one for each reaction) and that the structure of C be shown:



If you wish to use a reaction which requires that you add multiple reagents in a given sequence, showing that using numbered steps over a single arrow is fine. That's still one arrow per reaction. If you're not sure, err on the side of showing more.

(a) *[3 marks]*



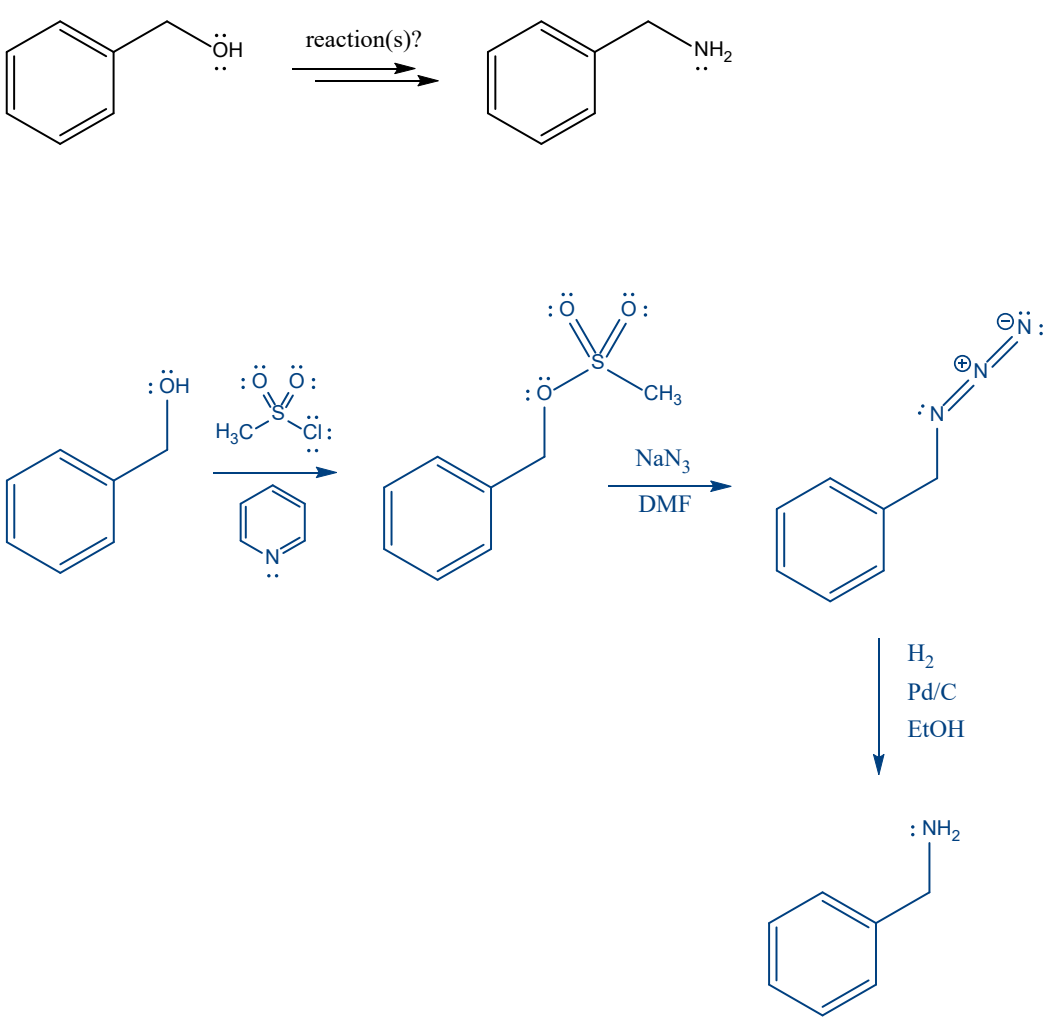
The most straightforward approach to this question is to oxidize the primary alcohol to an aldehyde then react the resulting aldehyde with the acetylide shown (the acetylide is the nucleophile; the aldehyde is the electrophile).

We saw many different reaction conditions that can oxidize primary alcohols to aldehydes; any of those would be acceptable. (PCC in CH_2Cl_2, PDC in CH_2Cl_2, $Br_2/NaHCO_3(aq)$, Swern oxidation, etc.)

continued on next page…

5. *…continued*

(b) *[5 marks]*



The answer above is representative; there are many other valid answers.

Important points to keep in mind for this question:

- *Hydroxide is a bad leaving group. You cannot just add a nucleophile and do either S_N1 or S_N2.*
- *While adding acid would convert the OH group into a good leaving group, you cannot add any basic species to $PhCH_2OH_2^+$ and expect a substitution reaction to proceed. The basic species would deprotonate $PhCH_2OH_2^+$ instead of acting as a nucleophile.*
- *Because of the two points above, it is necessary to convert the alcohol into a better electrophile such as a sulfonate ester or halide. (e.g. To make benzyl bromide, react benzyl alcohol with HBr.)*
- *Ammonia (NH_3) is not a good choice of nucleophile because, while it would react with a sulfonate ester or alkyl halide, the product of that reaction would be a better nucleophile than the ammonia was, so you would get reaction of multiple electrophiles with each nitrogen atom. Azide (N_3^-) or the phthalimide discussed in class are much better choices of nucleophile.*