Fall 2021 **Chemistry 2600 Midterm #2** ____/56 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:30pm Mountain Time on Thursday, November 18th, 2021. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/56 on this exam.

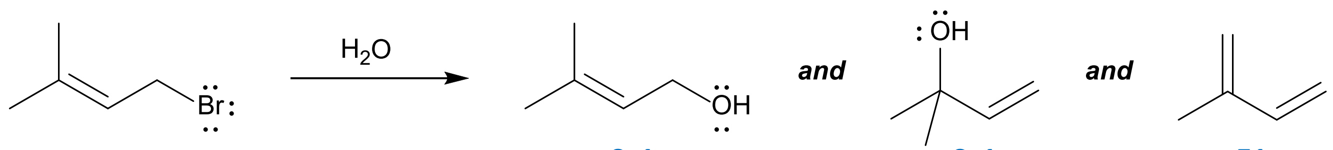
Signature: _____ Date: _____

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/extra space, use the back of any test page.
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**
/ 20	/ 6	/ 6	/ 14	/ 10									/ 56

1. A student adds water to 1-bromo-3-methyl-2-butene and observes three products: **[20 marks]**

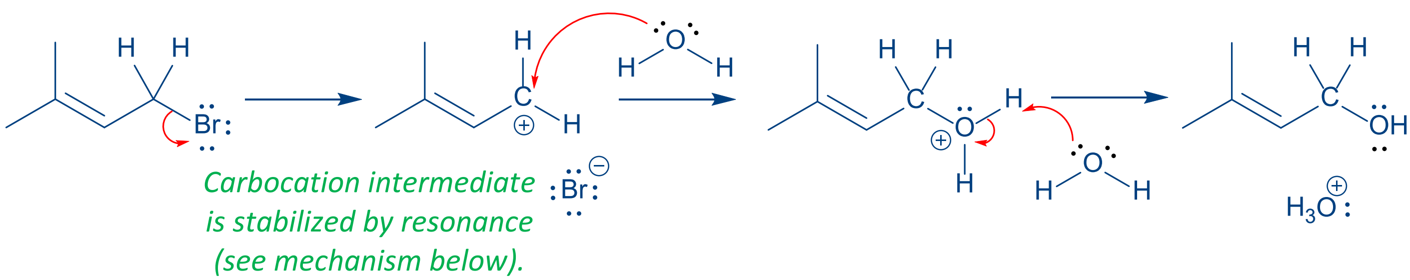


S_N1 S_N1 **E1**

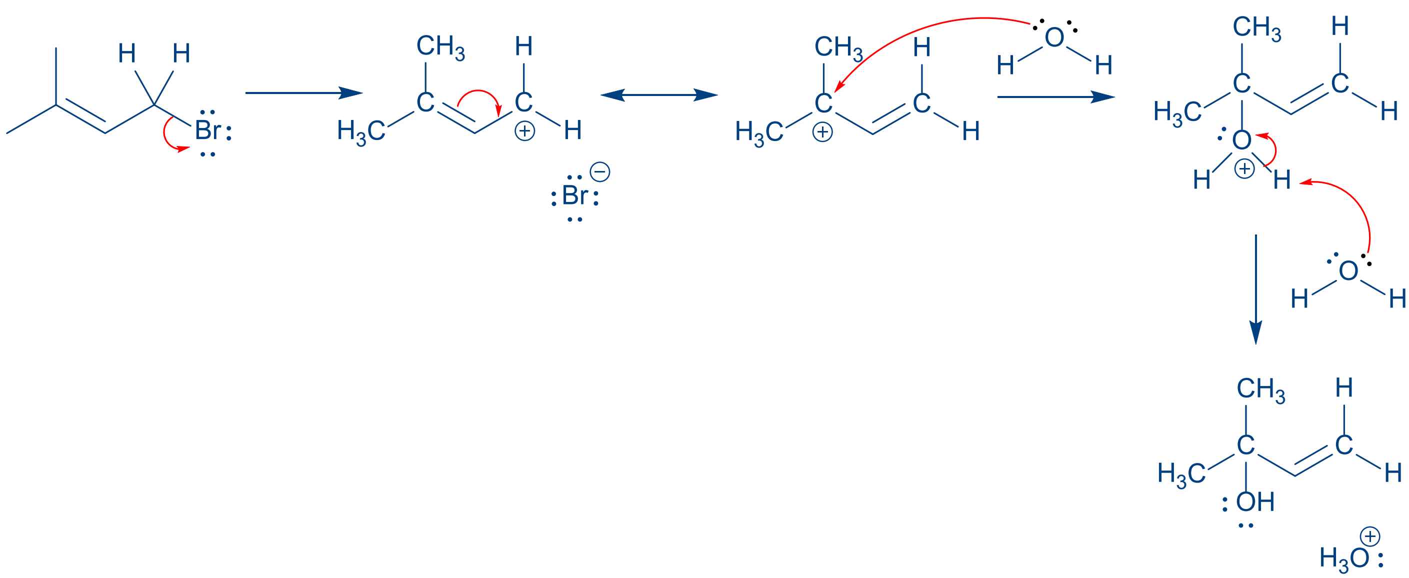
(a) For each product: *[14 marks]*

- Classify the reaction giving that product as S_N1, S_N2, E1 or E2 *(see above)*, and
- Use curved arrows to show the mechanism for its formation.

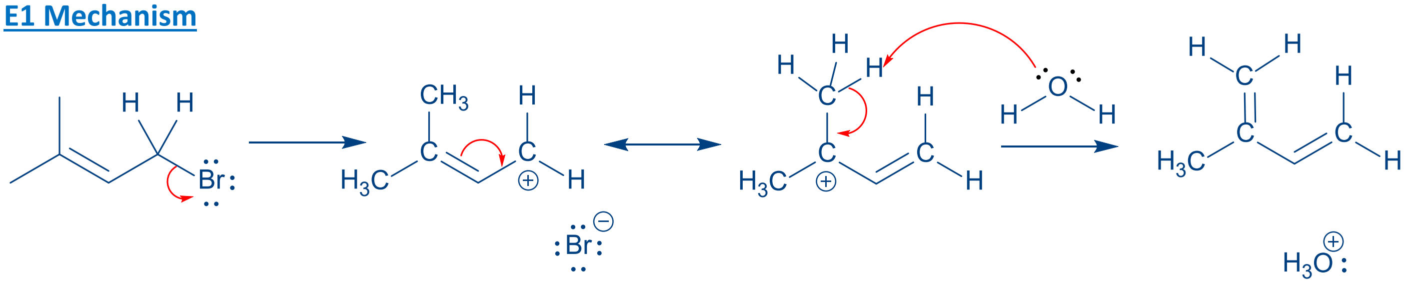
S_N1 Mechanism (with nucleophilic attack at one partially positive carbon atom)



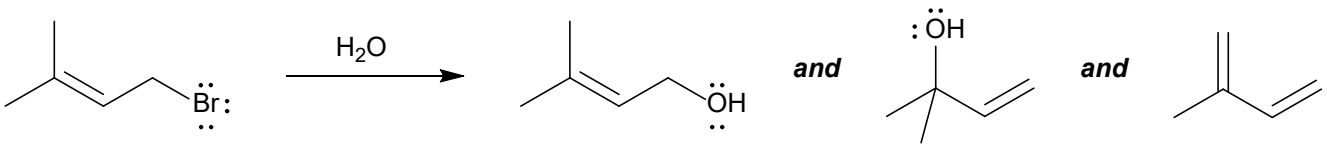
S_N1 Mechanism (with nucleophilic attack at the other partially positive carbon atom)



E1 Mechanism



1. *…continued from previous page*



A **B** **C**

The answers below give more detail than was required for full marks, but these are the main points that allow differentiation between the products.

It was necessary to talk about the peaks on the spectra (number of peaks, chemical shift, integration and/or multiplicity) – not just identify different features of the molecules.

(b) Briefly explain how you could use ^{1}H NMR to distinguish between the three products. *[3 marks]*

It is not necessary to provide complete descriptions of the spectra. Identify key differences between them.

A will give 5 peaks.

- Two peaks will each integrate to 3H (the two methyl groups).
- One will be a broad singlet integrating to 1H (the OH).
- One will be a doublet integrating to 2H at around 3.5 ppm (for CH_2O).
- One will appear near 5-6 ppm and will integrate to 1H (for the vinyl H)

B will give 5 peaks.

- One will integrate to 6H (the two equivalent methyl groups).
- One will be a broad singlet integrating to 1H (the OH).
- Three will appear near 5-6 ppm. Each will integrate to 1H and be a doublet of doublets.

C will give 6 peaks.

- One will integrate to 3H (the methyl group).
- The other five will appear near 5-6 ppm. Each will integrate to 1H, but they will likely overlap.

(c) Briefly explain how you could use ^{13}C NMR to distinguish between the three products. *[3 marks]*

It is not necessary to provide complete descriptions of the spectra. Identify key differences between them.

A will give 5 peaks.

- Two of the peaks will appear in the alkene region (110-150 ppm).
- One peak will appear in the region for primary C-O (40-70 ppm)

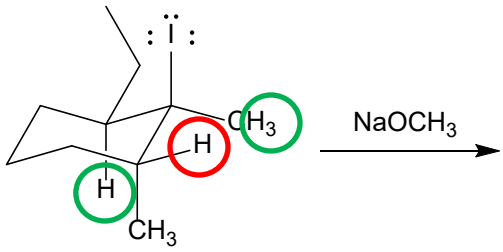
B will give 4 peaks.

- Two of the peaks will appear in the alkene region (110-150 ppm).
- One peak will appear in the region for tertiary C-O (70-90 ppm)

C will give 5 peaks.

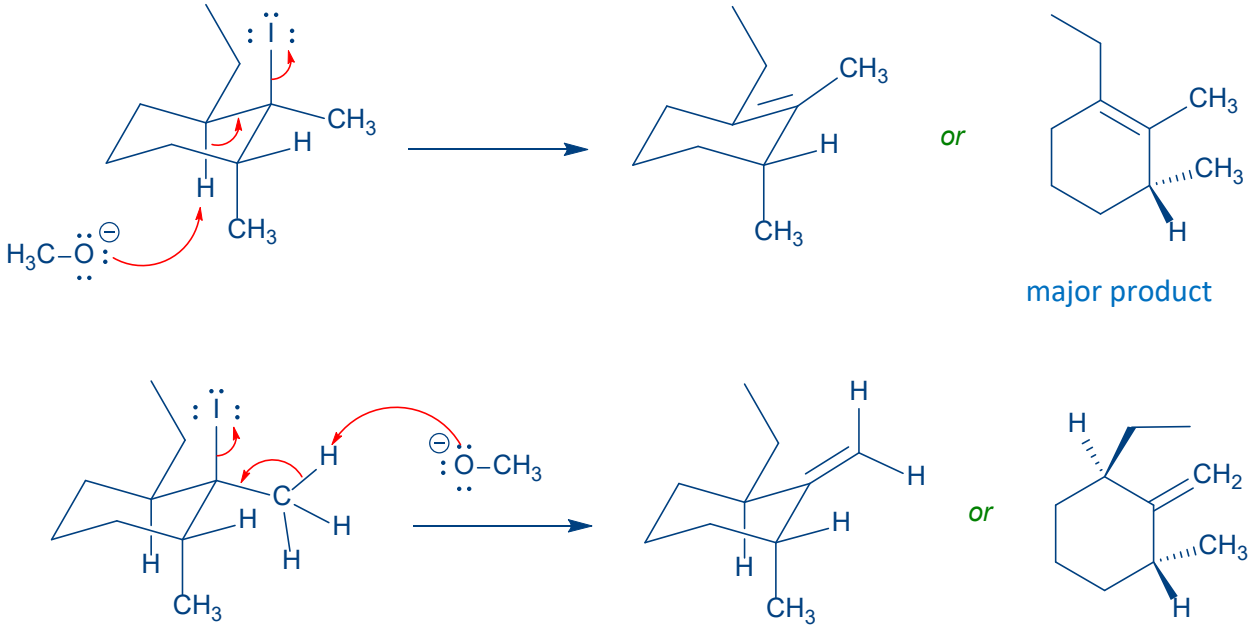
- Four of the peaks will appear in the alkene region (110-150 ppm).

2. Consider the following reaction mixture: **[6 marks]**



Two organic products are possible if the reaction proceeds according to an E2 mechanism. Draw both. Clearly label the major product, and briefly explain why it is favoured (especially at high temperatures).

There are three unique types of beta hydrogen circled on the molecule above; however, only two of them can adopt any position that would be antiperiplanar to the iodine atom. These two are circled in green. Deprotonation at each of these two sites gives a different elimination product:



major product

The alkene produced in the top reaction is tetrasubstituted whereas the alkene produced in the bottom reaction is only disubstituted. Since isomers containing more highly substituted alkenes tend to be lower energy, we expect the product of the top reaction to be the thermodynamic product.

Another contributing factor is that the C=C double bond in the first product is endocyclic (inside the ring) whereas the C=C double bond in the second products is exocyclic (sticking out of the ring). Isomers containing endocyclic double bonds are usually lower energy than those with exocyclic double bonds.

3. Use the data provided in the table below to determine whether the reaction between the alkyl chloride (RCl) 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.

$[RCl]$ $\left(\frac{mol}{L}\right)$	$[base]$ $\left(\frac{mol}{L}\right)$	Rate of reaction $\left(\frac{mol}{L \cdot s}\right)$
0.030	0.030	0.072
0.030	0.060	0.144
0.045	0.045	0.162
0.045	0.060	0.216

Step 1: Write generic rate law

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

Step 2: Solve for n by comparing rows 1 and 2

$$\frac{0.144\,\frac{mol}{L \cdot s}}{0.072\,\frac{mol}{L \cdot s}} = \frac{k\left(0.030\,\frac{mol}{L}\right)^m\left(0.060\,\frac{mol}{L}\right)^n}{k\left(0.030\,\frac{mol}{L}\right)^m\left(0.030\,\frac{mol}{L}\right)^n} \text{ therefore } 2 = \frac{\left(2\,\frac{mol}{L}\right)^n}{\left(1\,\frac{mol}{L}\right)^n} \text{ therefore } 2 = 2^n \text{ therefore } n = 1$$

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

$$\frac{0.216\,\frac{mol}{L \cdot s}}{0.144\,\frac{mol}{L \cdot s}} = \frac{k\left(0.045\,\frac{mol}{L}\right)^m\left(0.060\,\frac{mol}{L}\right)^1}{k\left(0.030\,\frac{mol}{L}\right)^m\left(0.060\,\frac{mol}{L}\right)^1} \text{ therefore } 1.5 = \frac{\left(0.045\,\frac{mol}{L}\right)^m}{\left(0.030\,\frac{mol}{L}\right)^m} \text{ therefore } 1.5 = 1.5^m \text{ therefore } m = 1$$

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

$$0.072\ \frac{mol}{L \cdot s} = k\left(0.030\ \frac{mol}{L}\right)^1\left(0.030\ \frac{mol}{L}\right)^1 \text{ therefore } 0.072\ \frac{mol}{L \cdot s} = k\left(0.030\ \frac{mol}{L}\right)\left(0.030\ \frac{mol}{L}\right)$$

$$\text{therefore } k = \frac{0.072\,\frac{mol}{L \cdot s}}{\left(0.030\,\frac{mol}{L}\right)\left(0.030\,\frac{mol}{L}\right)} \text{ therefore } k = 80\,\frac{L}{mol \cdot s}$$

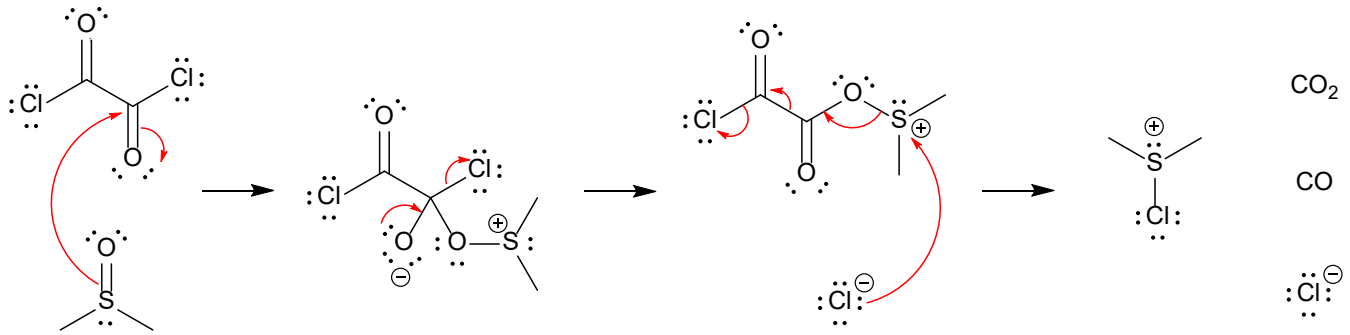
Step 5: Answer question (i.e. write rate law)

$$rate = 80\,\frac{L}{mol \cdot s}[RCl][base]$$

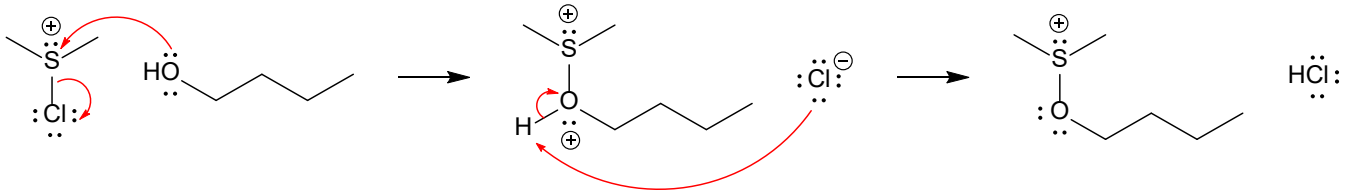
This reaction is first order in alkyl chloride and first order in base. That makes it second order overall. Since E1 reactions are first order while E2 reactions are second order, this is an E2 reaction.

4. The Swern oxidation is an effective (if smelly) method of oxidizing alcohols. **[14 marks]**

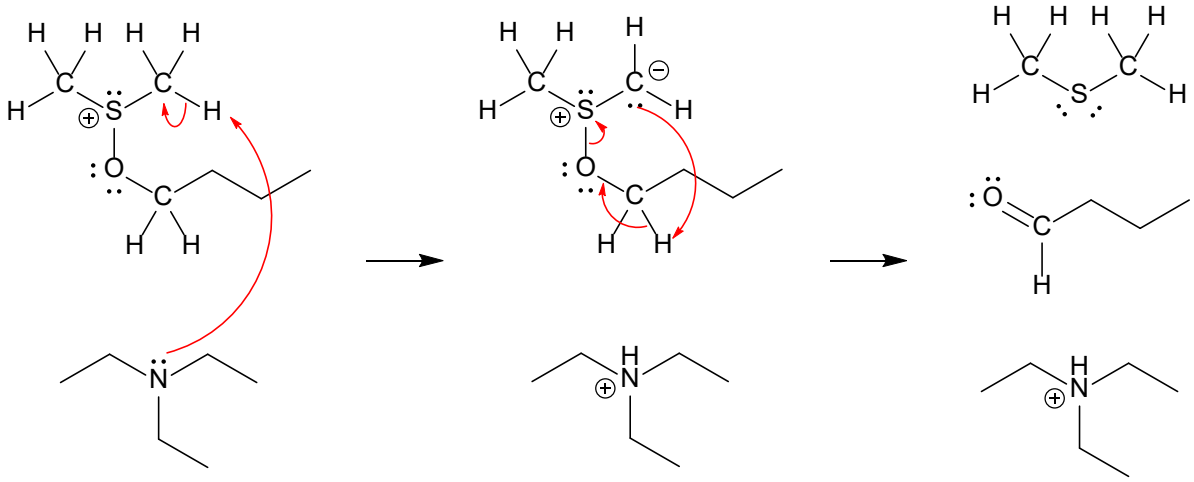
In the first step of a Swern oxidation, dimethyl sulfoxide and oxalyl chloride are combined at low temperature:



In the second step, an alcohol is added to the mixture:



In the third step, triethylamine is added:



continues on next page…

4. *…continued from previous page*

(a) Add curved arrows to the diagrams on the previous page to show the movement of electrons in each step of this reaction. *[7 marks]*

see previous page

(b) Given that it proceeds at low temperature, the first step of the Swern oxidation must be highly favourable. What makes this step so favourable? Your answer should include the name of the key property. *[2 marks]*

This reaction is strongly favoured by entropy because it produces two gases.

(c) In the second step of the Swern oxidation, a chloride ion is used as a base. This is highly unusual. Why is it possible to use chloride as a base in this case? *[1 mark]*

The hydrogen attached to O^+ is unusually acidic due to the adjacent positive charges on O and S.

(d) The second step of the Swern oxidation (in which the alcohol reacts with the sulfur-containing cation) contains a substitution reaction. Is it best classified as S_N1 or S_N2? Why? *[2 marks]*

S_N2.

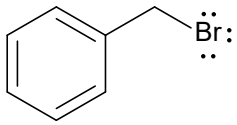
This step is bimolecular. The leaving group leaves in the same step as the nucleophile attacks.

(e) The final step of the Swern oxidation contains an elimination reaction. Is it best classified as E1 or E2? Why? *[2 marks]*

E2. *It's an intramolecular E2 reaction, but it's still E2.*

The leaving group leaves in the same step as the carbanion deprotonates C to form the new pi bond.

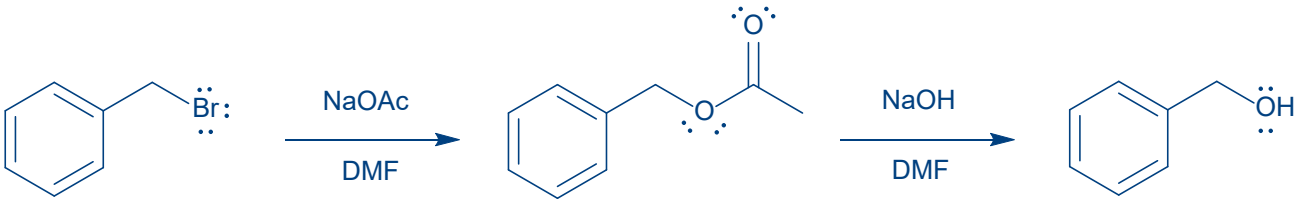
5. Use benzyl bromide *(shown below)* as your starting material for each synthesis. **[10 marks]**

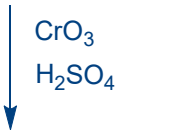


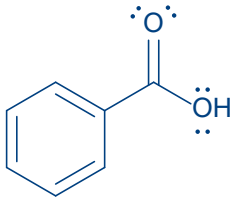
There are multiple valid methods to prepare each of the molecules shown below. This answer key shows one representative answer for each.

(a) **CHOOSE <u>ONE</u> OF THE PRODUCTS BELOW.** Show how it could be prepared from benzyl bromide using any reactions discussed in CHEM 2500 or CHEM 2600. *[4 marks]*

<u>One Route to Benzoic Acid</u>

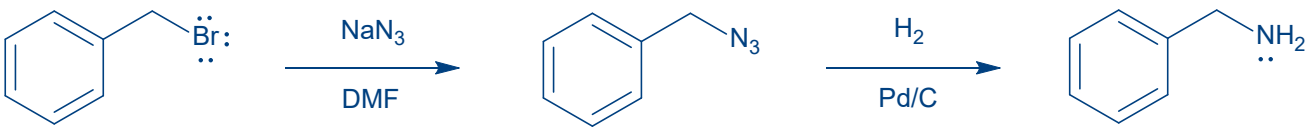






In this case, it is not necessary to use the NaOAc/NaOH two-step approach to convert the bromide into the alcohol because there are no beta hydrogens so elimination cannot compete with substitution. As such, you could do a direct substitution using either NaOH (via S_N2) or H2O (via S_N1).

<u>One Route to Benzylamine</u>



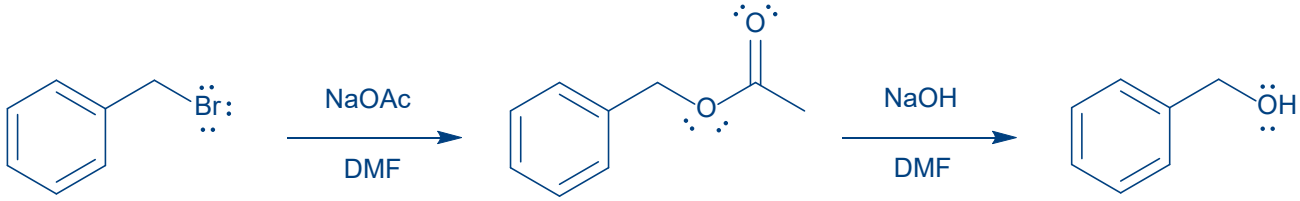
continues on next page…

5. *…continued from previous page*

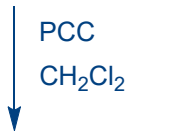
(b) **CHOOSE <u>ONE</u> OF THE PRODUCTS BELOW.** Show how it could be prepared from benzyl bromide using any reactions discussed in CHEM 2500 or CHEM 2600. *[6 marks]*

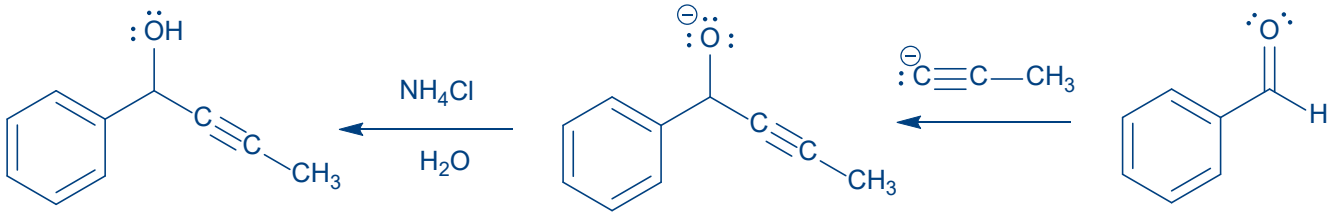
Please note that Grignard reagents are not able to act as nucleophiles in S_N1 or S_N2 reactions; they can only react with electrophiles containing pi bonds.

One Route to the Alcohol Product

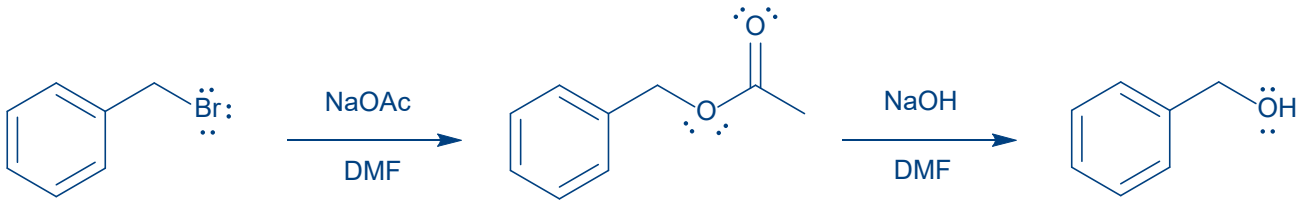


See comment on previous page for alternative routes from benzyl bromide to benzyl alcohol.
Also, we learned about several different oxidizing agents that convert primary alcohols into aldehydes (Swern, Br_2/$NaHCO_3$, PCC, PDC, etc.)

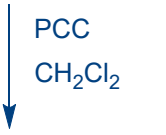


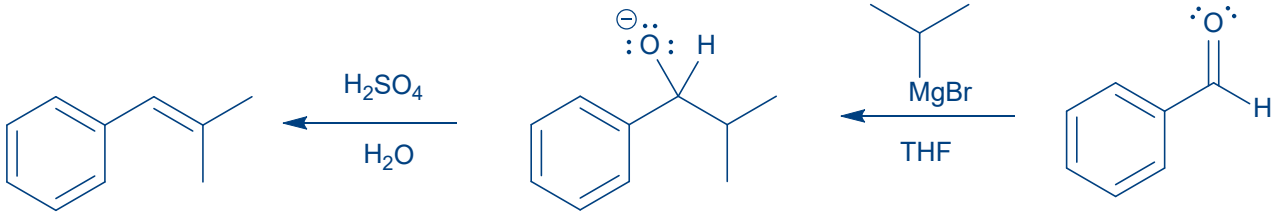


One Route to the Alkene Product



See comment on previous page for alternative routes from benzyl bromide to benzyl alcohol. See above for a variety of alternative oxidizing agents.





The acid first protonates O^- to give the alcohol. Then, if a strong non-nucleophilic acid is used, the O can be protonated again and an E1 reaction gives the alkene.