NAME:_____ Section:_____ Student Number:_____

Spring 2019 **Chemistry 2600 Midterm 2** ____/ 65 marks

INSTRUCTIONS:

1) Please read over the test carefully before beginning. You should have 9 pages of questions in addition to this cover page and a periodic table.
2) You have also 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 any papers or other written materials in your model kit.
4) Electronic devices (including calculators) are **not** allowed for this test.
5) If your work is not legible, it will be given a mark of zero.
6) 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.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:00pm Mountain Time on Monday, March 18th, 2019. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/65 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____ Date: _____

Course: CHEM 2600 (Organic Chemistry II)
Semester: Spring 2019
The University of Lethbridge

Question Breakdown

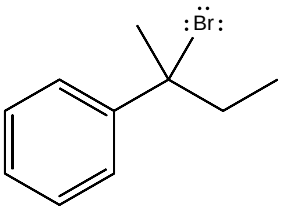
Q1	/ 6
Q2	/ 6
Q3	/ 5
Q4	/ 7
Q5	/ 8
Q6	/ 7
Q7	/ 7
Q8	/ 10
Q9	/ 9

Total	/ 65

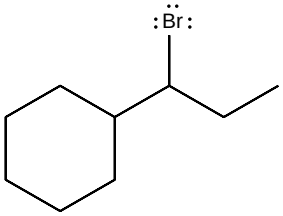
NAME:_____ Section:_____ Student Number:_____

1. *In this question, relative order is important – not absolute position. Incorrect lists that could be fixed by moving one molecule received 1 mark. Incorrect lists with either the first or last item correct received 0.5 mark. All other incorrect answers received 0 marks.* **[6 marks]**

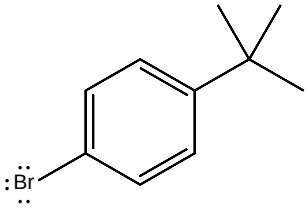
(a) Rank the following substrates in order from slowest E1 reaction rate to fastest. *[2 marks]*



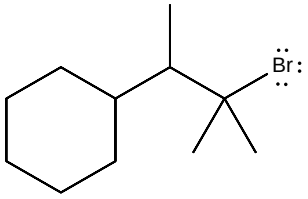
A



B



C

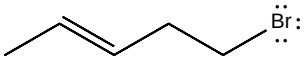


D

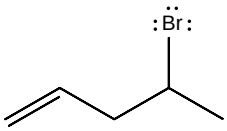
slowest _____C_____ _____B_____ _____D_____ _____A_____ fastest

Rate of E1 reaction is dependent on stability of the carbocation intermediate. The carbocation formed from A is 3° and benzylic. The carbocation formed from D is 3°. The carbocation formed from B is 2°. The carbocation formed from C would be a vinyl carbocation and those do not form.

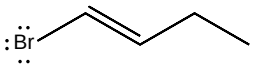
(b) Rank the following substrates in order from slowest S_N2 reaction rate to fastest. *[2 marks]*



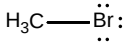
A



B



C

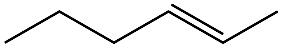


D

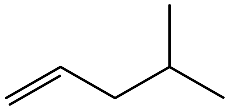
slowest _____C_____ _____B_____ _____A_____ _____D_____ fastest

Rate of S_N2 reaction is dependent on accessibility of the electrophilic site. D has the most accessible electrophilic site (three H attached). A is a primary alkyl halide, so it is next most accessible. B is a secondary alkyl halide so it can react slowly in S_N2 reactions. C is a vinylic halide, and S_N2 reactions do not proceed if the leaving group is not attached to an atom with tetrahedral electron group geometry.

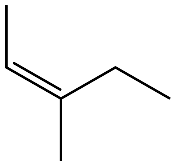
(c) Rank the following alkenes from least to most stable. *[2 marks]*



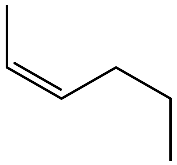
A



B



C



D

least stable _____B_____ _____D_____ _____A_____ _____C_____ most stable

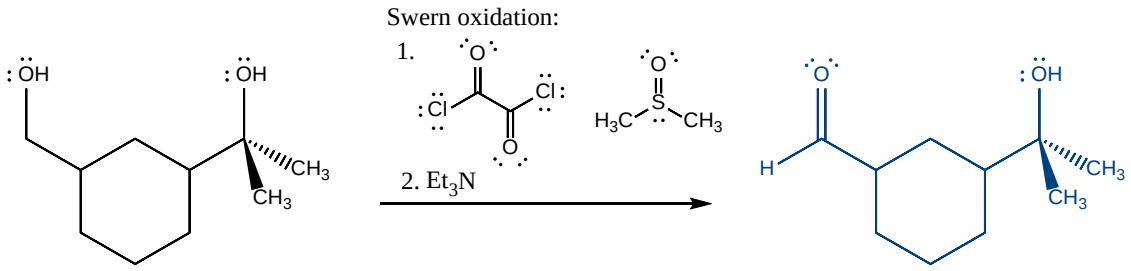
When comparing alkenes with the same molecular formula, isomers with more highly substituted double bonds are more stable. As such, C (trisubstituted double bond) is most stable and B (monosubstituted double bond) is least stable. D has a cis-double bond and A has a trans double bond, so we expect A to be more stable as it keeps the carbon chains farther apart.

NAME:_____ Section:_____ Student Number:_____

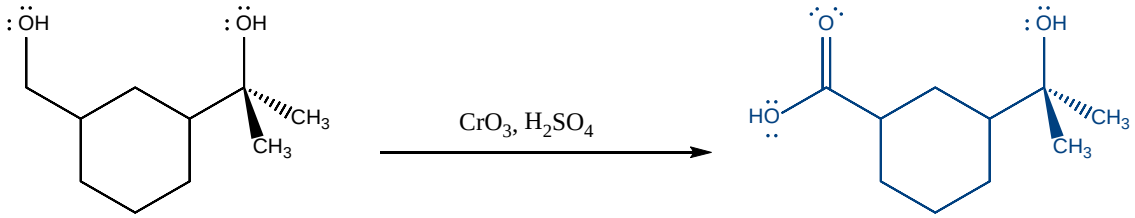
2. Draw the organic product for each of the following reactions: **[6 marks]**

These are all oxidation reactions. The 3° alcohol cannot be oxidized. (a) and (c) oxidize the 1° alcohol to an aldehyde. (b) oxidizes the 1° alcohol to a carboxylic acid.

(a)

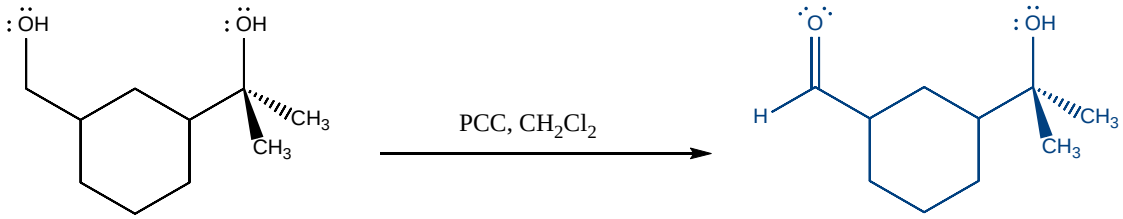


(b)



Students who also had an elimination reaction produce the most highly substituted alkene from the 3° alcohol received full credit (as long as they also oxidized the carboxylic acid). This is very likely to occur under these conditions.

(c)

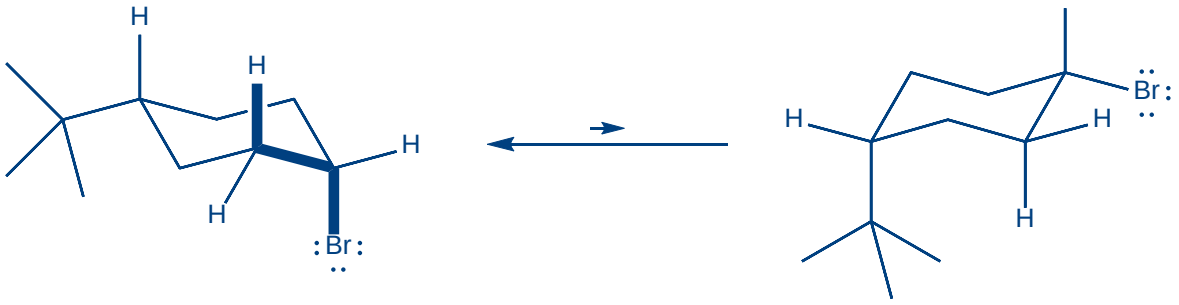


NAME:_____ Section:_____ Student Number:_____

3. The *cis* isomer of 1-bromo-4-*tert*-butylcyclohexane undergoes E2 elimination ~1000 times faster than the trans isomer. Explain why the *cis* isomer reacts faster. **[5 marks]**

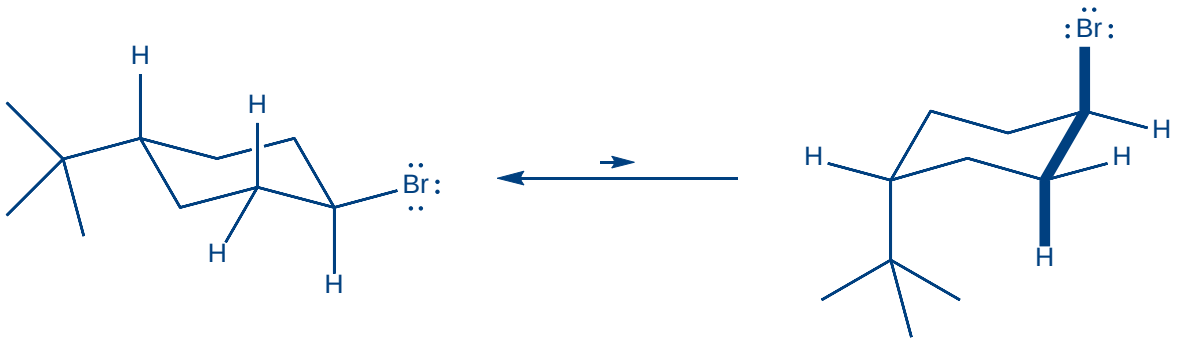
For full credit, your answer should include one or more diagrams.

tert-Butyl groups are very bulky, so the more stable conformer of any cyclohexane ring with a *tert*-butyl group attached will have the bulky group in an equatorial position:



major conformer of cis isomer
(Br is in axial position)

minor conformer of cis isomer
(Br is in equatorial position)



major conformer of trans isomer
(Br is in equatorial position)

minor conformer of trans isomer
(Br is in axial position)

An E2 reaction can only proceed when a β-hydrogen and leaving group are antiperiplanar to each other. This is only possible when the leaving group is in an axial position (see bolded bonds in diagram above).

Thus, the major conformer of *cis*-1-bromo-4-*tert*-butylcyclohexane can undergo E2 reaction; however, the major conformer of *trans*-1-bromo-4-*tert*-butylcyclohexane cannot; *trans*-1-bromo-4-*tert*-butylcyclohexane has to undergo a ring flip to the minor conformer before it can undergo E2 reaction.

While the tert-butyl group in the minor conformer of trans-1-bromo-4-tert-butylcyclohexane also introduces steric hindrance by making it difficult for the base to access the β-hydrogen, answers that did not address the fact that it is very unfavorable to have a bulky tert-butyl group in an axial position did not get full credit.

NAME:_____ Section:_____ Student Number:_____

4. A kinetic study of the reaction between an alkyl bromide (RBr) and a non-nucleophilic base ($base$) provided the following data: **[7 marks]**

$[RBr]$ $\left(\frac{mol}{L}\right)$	$[base]$ $\left(\frac{mol}{L}\right)$	Rate of reaction $\left(\frac{mol}{L \cdot s}\right)$
1	1	6
1	2	6
2	4	12
3	4	18

(a) Write the rate law for this reaction. Include a numerical value and units for k. *[4 marks]*
Clearly identify the order of each reactant.

Step 1: Write generic rate law

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

Step 2: Solve for n by comparing rows 1 and 2 (or observe that n must be zero by comparing those rows)

$\frac{6\frac{mol}{L \cdot s}}{6\frac{mol}{L \cdot s}} = \frac{k\left(1\frac{mol}{L}\right)^m\left(2\frac{mol}{L}\right)^n}{k\left(1\frac{mol}{L}\right)^m\left(1\frac{mol}{L}\right)^n}$ therefore $1 = \frac{\left(2\frac{mol}{L}\right)^n}{\left(1\frac{mol}{L}\right)^n}$ therefore $1 = 2^n$ therefore $n = 0$

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

$\frac{18\frac{mol}{L \cdot s}}{12\frac{mol}{L \cdot s}} = \frac{k\left(3\frac{mol}{L}\right)^m\left(4\frac{mol}{L}\right)^0}{k\left(2\frac{mol}{L}\right)^m\left(4\frac{mol}{L}\right)^0}$ therefore $1.5 = \frac{\left(3\frac{mol}{L}\right)^m}{\left(2\frac{mol}{L}\right)^m}$ therefore $1.5 = 1.5^m$ therefore $m = 1$

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

$6\ \frac{mol}{L \cdot s} = k\left(1\ \frac{mol}{L}\right)^1\left(2\ \frac{mol}{L}\right)^0$ therefore $6\ \frac{mol}{L \cdot s} = k\left(1\ \frac{mol}{L}\right)$ therefore $k = \frac{6\frac{mol}{L \cdot s}}{1\frac{mol}{L}}$

therefore $k = 6s^{-1}$

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

$rate = 6s^{-1}[RBr]$

It is fine to leave the $n = 0$ implicit in the final rate law as long as it was made explicitly clear that you knew that $n = 0$.

(b) Did this reaction proceed via an S_N1, S_N2, E1 or E2 mechanism? Explain your choice. It must be clear why all three alternative options were rejected. *[3 marks]*

E1

The reaction is first order therefore it cannot be E2 or S_N2 (both are second order).

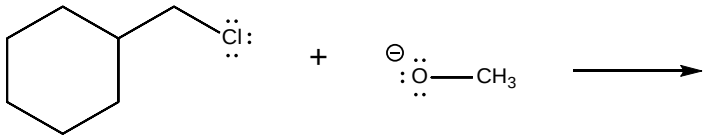
There is no nucleophile ("non-nucleophilic base") therefore it cannot be a substitution reaction (cannot be S_N1).

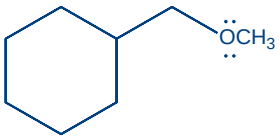
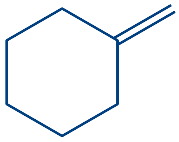
NAME:_____ Section:_____ Student Number:_____

5. 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: **[8 marks]**

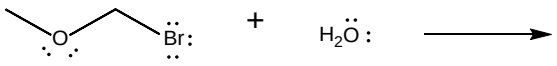
- For each 'yes', drawing the organic product(s) that will be observed.
- For each 'no', briefly explaining why you expect little-to-no reaction.

(a)



S_N1?	**S_N2?**	**E1?**	**E2?**
yes / (no)	(yes) / no	yes / (no)	(yes) / no
An S_N1 mechanism in this system would require a primary carbocation intermediate, and they are not stable		An E1 mechanism in this system would require a primary carbocation intermediate, and they are not stable.	

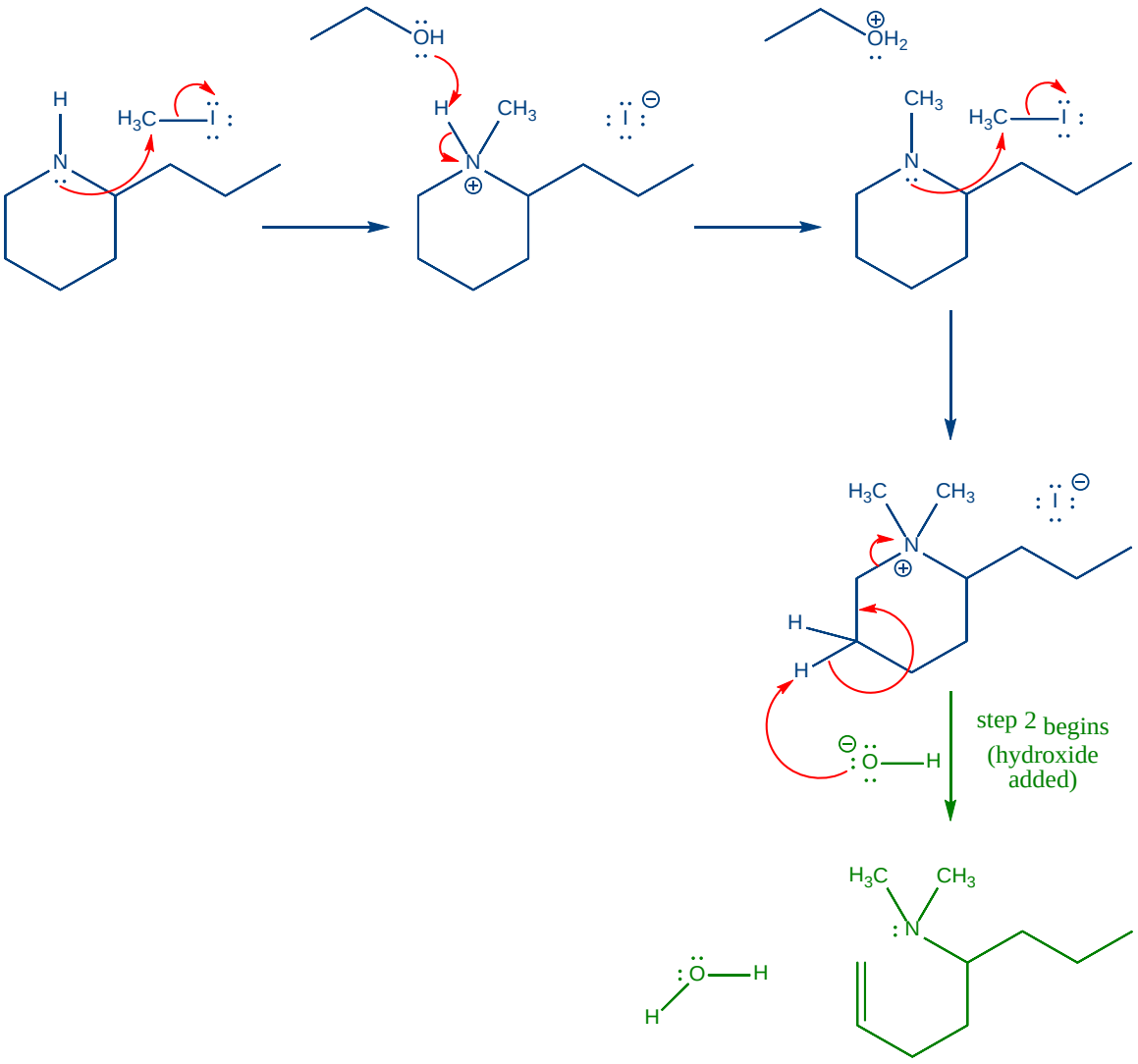
(b)



S_N1?	**S_N2?**	**E1?**	**E2?**
(yes) / no	yes / (no)	yes / (no)	yes / (no)
	Water is a weak nucleophile, and S_N2 reactions require good nucleophiles.	There is no β-H, so there cannot be an elimination reaction.	There is no β-H, so there cannot be an elimination reaction. Also, water is a weak base, and E2 reactions require strong bases.

NAME:_____ Section:_____ Student Number:_____

6. Propose a reasonable reaction mechanism for the following reaction: **[7 marks]**



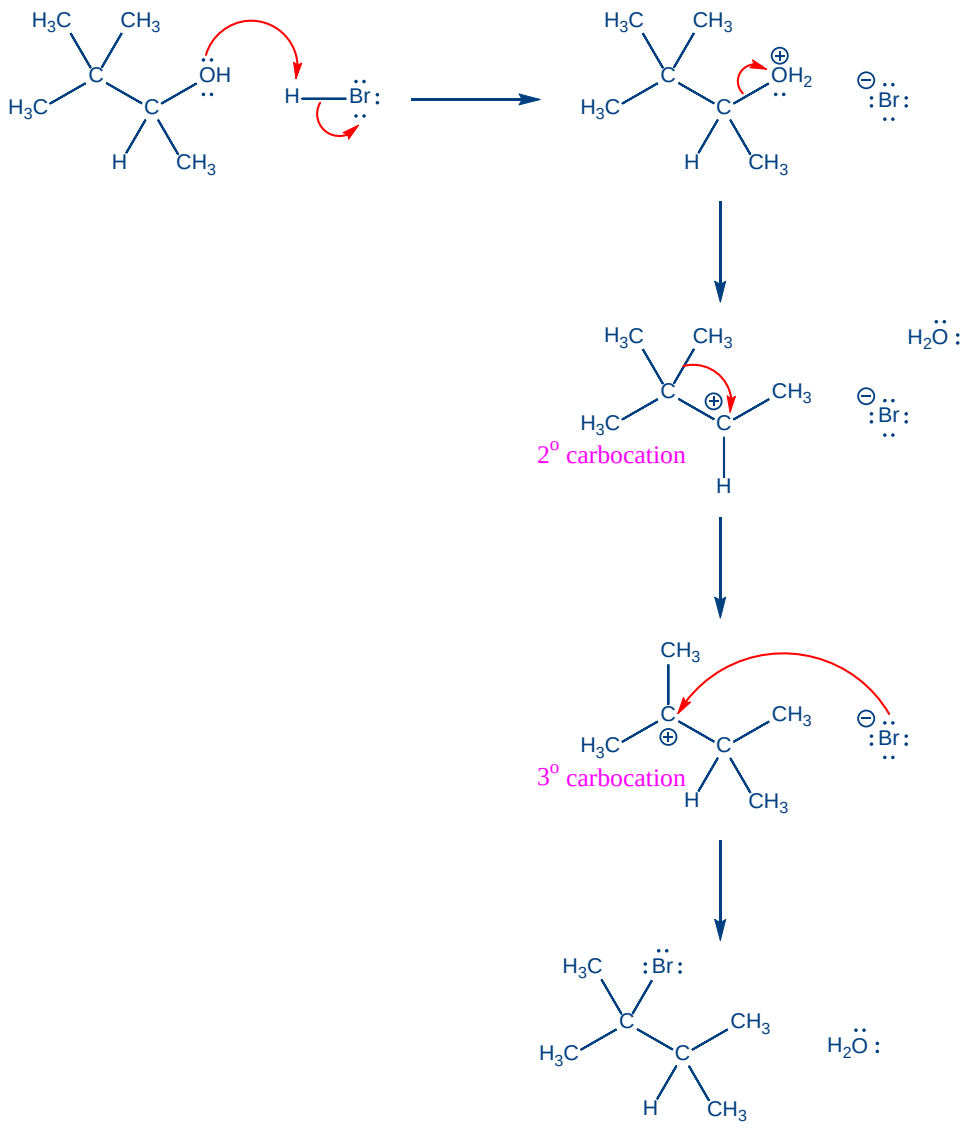
This is a series of S_N2 reactions followed by an E2 reaction. The S_N2 reactions set up a good leaving group for the E2 reaction.

It is important to note that the reaction is presented as two steps. That means that you must do something for step 1 before the hydroxide is added in step 2.

Many students started by deprotonating the amine. Amines have pK_a values of approximately 35. A typical neutral amine cannot be deprotonated by an alkoxide or hydroxide, and I don't know of any neutral amine that can be deprotonated by an alcohol. A protonated amine is much more acidic, so deprotonating the substitution product is reasonable.

NAME:_____ Section:_____ Student Number:_____

7. Propose a reasonable reaction mechanism for the following reaction: **[7 marks]**

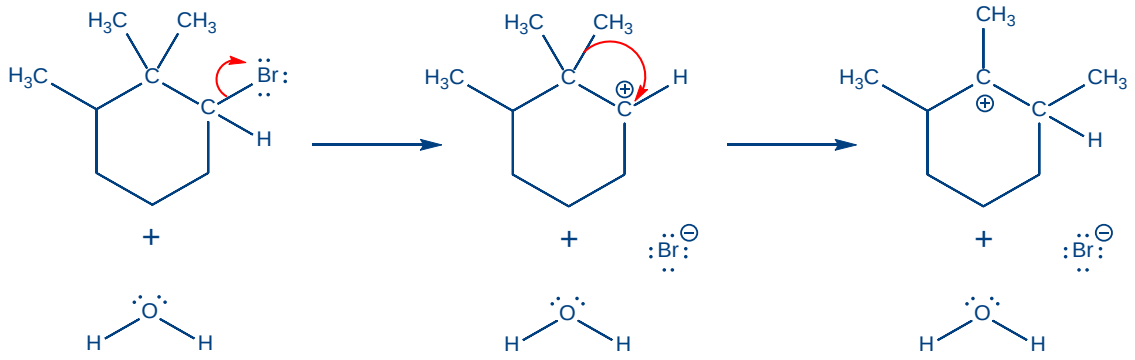


This mechanism was generally very well done. It is an S_N1 reaction in which a methyl shift converts the 2° carbocation into a more stable 3° carbocation before the nucleophile attacks.

NAME:_____ Section:_____ Student Number:_____

8. The following reaction gives 5 different products (not including stereoisomers): 2 different substitution products and 3 different elimination products. **[10 marks]**

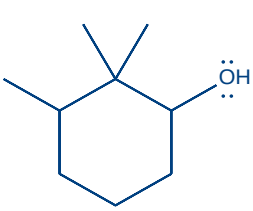
On the original version of the test, the methyl group on the left was accidentally left off. That meant that there were four possible elimination products instead of three. Students were given full marks for part (b) if they showed at least three of the four possible elimination products. The error did not affect the number of possible substitution products.



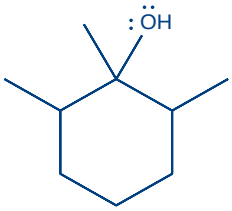
This alkyl bromide is secondary, so one could imagine that it could react through S_N1, S_N2, E1, or E2 mechanisms; however, S_N2 would not be favoured due to the two methyl groups on the carbon adjacent to the electrophilic site. Also, S_N2 reactions require good nucleophiles (water isn't one) and E2 reactions require good bases (water isn't one). So, we must be looking for products of S_N1 and E1 reactions.

A carbocation intermediate is further suggested by the fact that more products are observed than we could account for without the possibility of a carbocation rearrangement. A carbocation rearrangement should result in a more stable carbocation, so a hydride shift from the carbon drawn below the C^+ is not favoured (would give 2° carbocation from 2° carbocation). Instead, a methyl shift from the carbon drawn above and to the left of the C^+ is favoured (gives 3° carbocation from 2° carbocation).

(a) Draw the two substitution products. *[4 marks]*

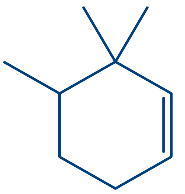


(no rearrangement)

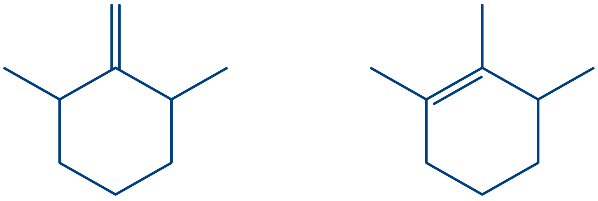


(methyl shift before nucleophile attacks)

(b) Draw the three elimination products. *[6 marks]*



(no rearrangement)



(methyl shift before base attacks)

NAME:_____ Section:_____ Student Number:_____

9. ^{1}H NMR analysis of Compound A (C_4H_9Cl) gives a spectrum with one singlet at 1.6 ppm.

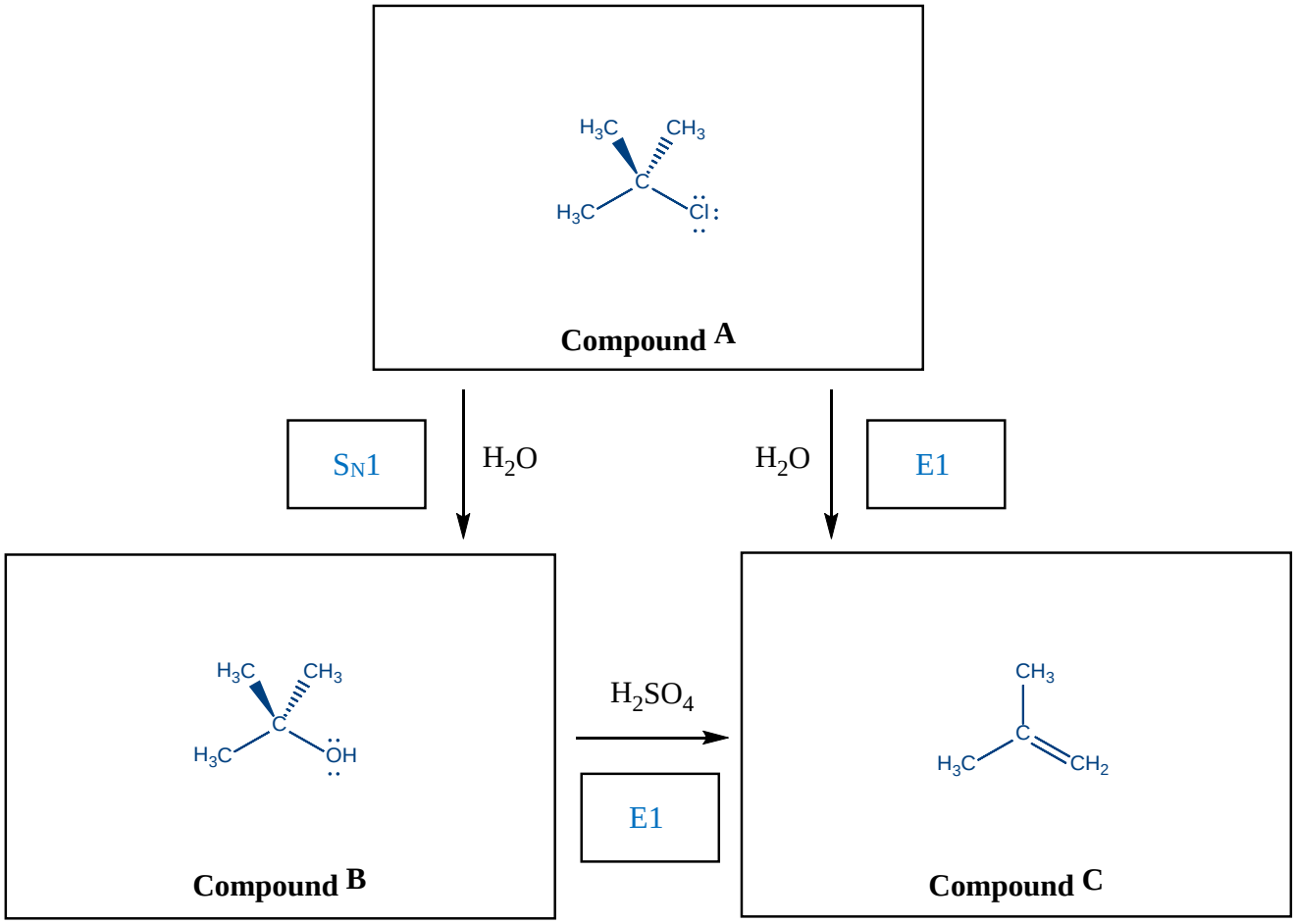
When Compound A is reacted with water, a mixture of two products is formed:

- ^{1}H NMR analysis of Compound B gives two signals: 1.3 ppm and 2.0 ppm
- ^{1}H NMR analysis of Compound C gives two signals: 1.7 ppm and 4.7 ppm.

If Compound B is treated with concentrated sulfuric acid, Compound C is produced.

Complete the diagram below by

- drawing the structures of Compounds A, B and C in the boxes provided, and
- identifying each reaction as proceeding via S_N1, S_N2, E1 or E2 mechanism in the boxes provided next to the arrows. **[9 marks]**



There is only one way to make all nine H shift equivalent for C_4H_9Cl, so compound A must be tBuCl.

Many students reversed compounds B and C. Reasons why the structures shown are correct:

- *Vinyl H (H directly attached to C of alkene) cannot appear as far upfield as 2.0 ppm (typical range is 4.5-6.5 ppm – though conjugation to a larger pi system can pull them farther downfield).*
- *Methyl groups attached to an alkene are more deshielded than those attached to the C of C–O.*
- *To make the tertiary alcohol from the alkene would require an addition reaction (with H_2O as well as the acid catalyst) – which was not one of the four reaction types listed in the question.*