Winter 2025 **Chemistry 2600 Midterm #2** ____/55 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 0/55 on this exam.

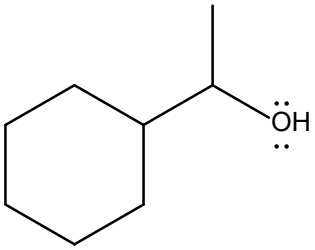
Signature: _____ Date: _____

1) Please read the test carefully before starting. It has eight 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**	**Q6**									**Total**
/ 14	/ 9	/ 8	/ 6	/ 10	/ 8									/ 55

1. When the alcohol below is reacted with hydrobromic acid $(HBr_{(aq)})$, **<u>two</u>** different organic substitution products are possible. The two products are constitutional isomers. **[14 marks]**

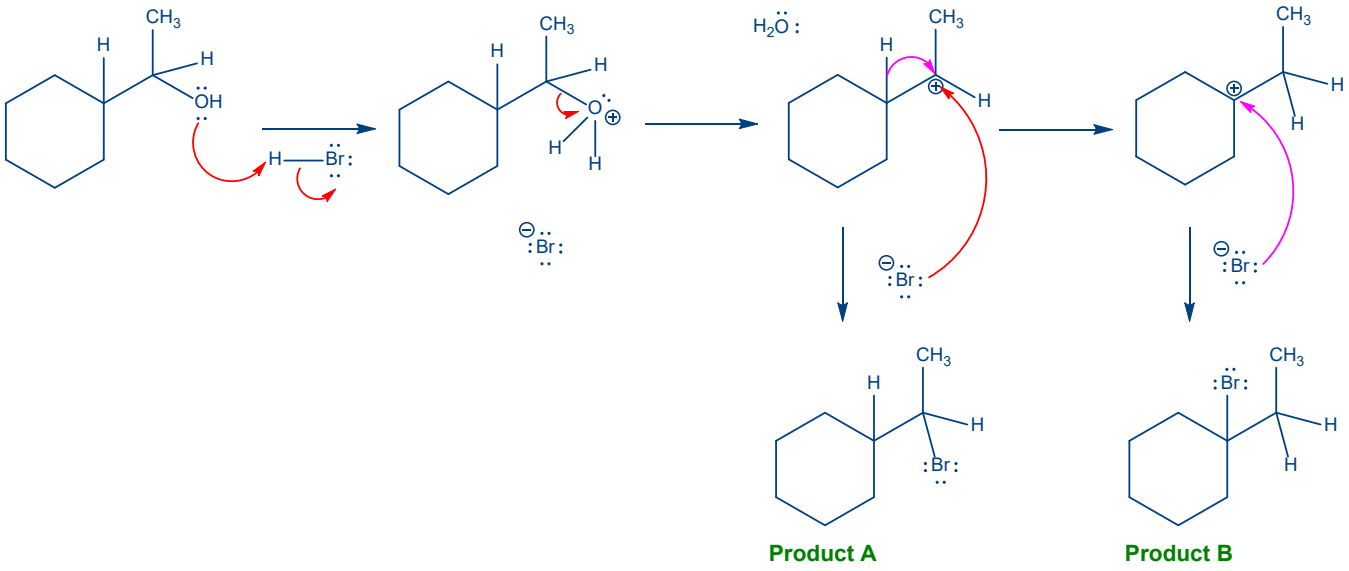


(a) What does the fact that this reaction can produce either of two constitutional isomers tell you about whether it is expected to proceed via S_N1 and/or S_N2? Explain briefly. *[2 marks]*

At least some of the reaction must proceed according to an S_N1 mechanism because the only way to get a different substitution product is for the system to undergo a carbocation rearrangement and those are only possible in S_N1 reactions.

Without information about reactant and product stereochemistry, it is not possible to know whether the system reacts entirely via S_N1 or whether it undergoes a mixture of S_N1 and S_N2.

(b) Use curved arrows to propose valid mechanisms for formation of each of the two products. *[10 marks]*

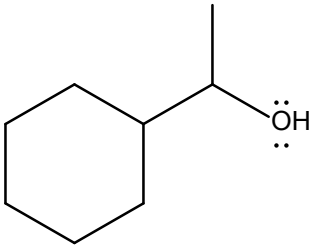


(c) Briefly explain how you could use $^1H\ NMR$ to distinguish between the two products. *[2 marks]*

Product A is expected to have a pentet integrating to 1H at approximately 4ppm for the hydrogen attached to the same carbon as the bromine.

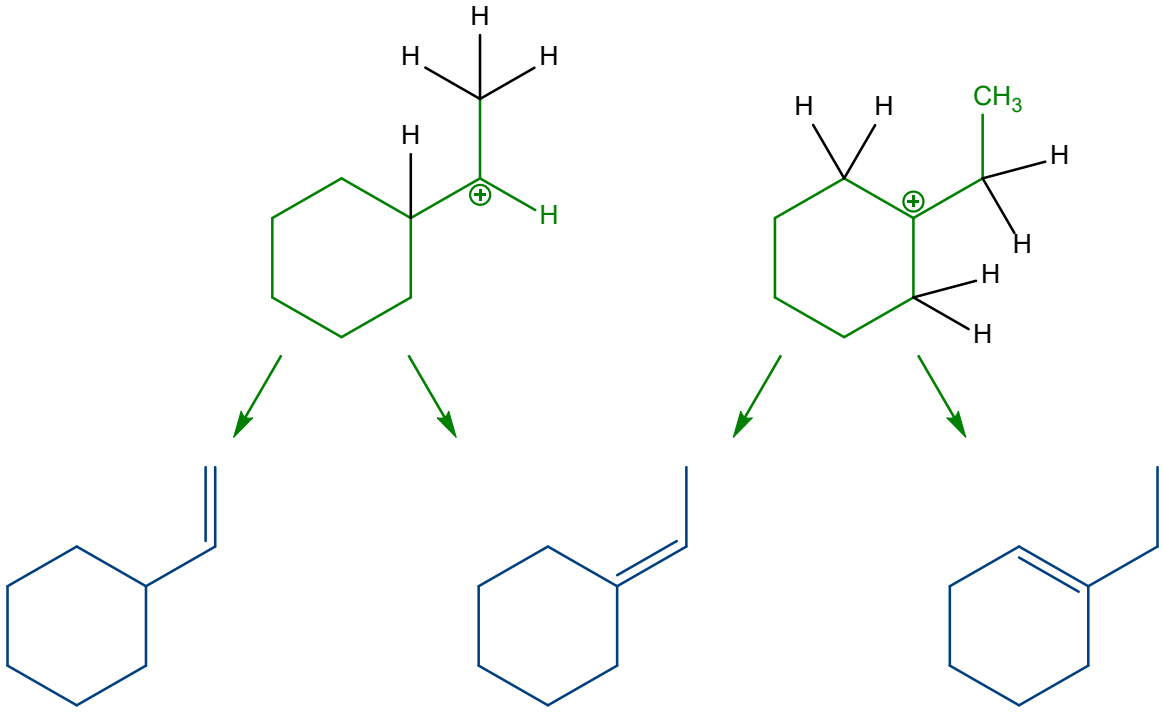
Product B is not expected to have any peak with a chemical shift greater than 3 ppm, but it should show the classic "triplet integrating to 3H and quartet integrating to 2H" pattern for the ethyl group. (The peak integrating to 3H for Product A will be a doublet rather than a triplet.)

2. When the alcohol below is reacted with sulfuric acid $(H_2SO_{4(aq)})$, **three** different organic elimination products are possible. Draw all three elimination products, classify each as a major product or a minor product, and briefly justify your classifications. **[9 marks]**



*You are **not** required to show mechanisms for this question; however, there will be no penalty for including them.*

Students did not need to draw the carbocations in green below. They are included here so that you can see where the β-hydrogen atoms (drawn in black) were:



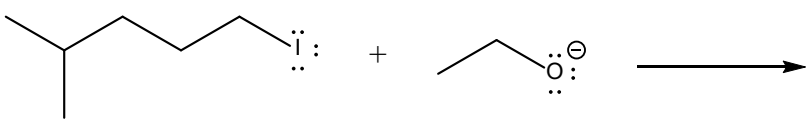
Minor Product | Major Product B | Major Product A

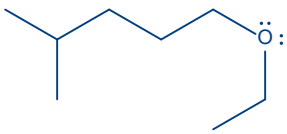
The double bond in Minor Product is disubstituted. This is less favourable than the trisubstituted double bonds found in Major Product A and Major Product B. Major Product A is slightly favoured over Major Product B because it is preferable to have an endocyclic (within the ring) double bond over an exocyclic double bond (pointing out of the ring).

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:
   - 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]**

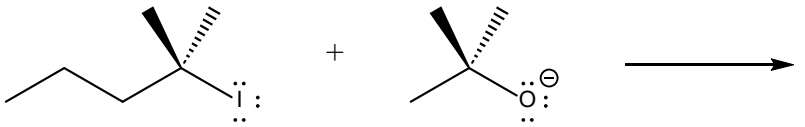
   The marks are for the product(s) and/or explanations. The yes/no part is just to help you think.

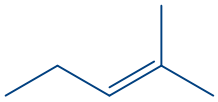
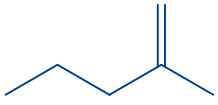
(a)



S_N1? yes / (no)	**S_N2?** (yes) / no	**E1?** yes / (no)	**E2?** (yes) / no
An S_N1 mechanism in this system would require a primary carbocation intermediate with no resonance stabilization.		An S_N1 mechanism in this system would require a primary carbocation intermediate with no resonance stabilization.	

(b)



S_N1? yes / (no)	**S_N2?** yes / (no)	**E1?** yes / (no)	**E2?** (yes) / no
$tBuO^-$ is too bulky to act as a nucleophile to any significant degree	The carbon atom attached to the leaving group is tertiary and therefore this carbon is not an accessible electrophilic site. Also, $tBuO^-$ is too bulky to act as a good nucleophile.	Theoretically, an E1 mechanism is not forbidden; however, the E2 mechanism will be MUCH faster so E1 will not occur in practice. If it were to occur, you would only get the thermodynamic product shown as an option for E2.	 and 

4. 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 $\left(\frac{mol}{L \cdot s}\right)$
0.15	0.20	3.6×10^{-4}
0.15	0.40	3.6×10^{-4}
0.30	0.60	7.2×10^{-4}
0.60	0.80	1.44×10^{-3}

Step 1: Write generic rate law

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

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

$$\frac{3.6\times10^{-4}\ \frac{mol}{L\cdot s}}{3.6\times10^{-4}\ \frac{mol}{L\cdot s}} = \frac{k\left(0.15\ \frac{mol}{L}\right)^m\left(0.40\ \frac{mol}{L}\right)^n}{k\left(0.15\ \frac{mol}{L}\right)^m\left(0.20\ \frac{mol}{L}\right)^n}$$

$$1 = \frac{\left(0.40\ \frac{mol}{L}\right)^n}{\left(0.20\ \frac{mol}{L}\right)^n} \quad \text{therefore} \quad 1 = 2^n \quad \text{therefore} \quad n = 0$$

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

$$\frac{7.2\times10^{-4}\ \frac{mol}{L\cdot s}}{3.6\times10^{-4}\ \frac{mol}{L\cdot s}} = \frac{k\left(0.30\ \frac{mol}{L}\right)^m\left(0.60\ \frac{mol}{L}\right)^0}{k\left(0.15\ \frac{mol}{L}\right)^m\left(0.20\ \frac{mol}{L}\right)^0}$$

$$2 = \frac{\left(0.30\ \frac{mol}{L}\right)^m}{\left(0.15\ \frac{mol}{L}\right)^m} \quad \text{therefore} \quad 2 = 2^m \quad \text{therefore} \quad m = 1$$

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

$$3.6 \times 10^{-4}\ \frac{mol}{L\cdot s} = k\left(0.15\ \frac{mol}{L}\right)^1\left(0.20\ \frac{mol}{L}\right)^0$$

$$k = \frac{3.6\times10^{-4}\ \frac{mol}{L\cdot s}}{\left(0.15\ \frac{mol}{L}\right)}$$

$$k = 0.0024\ s^{-1}$$

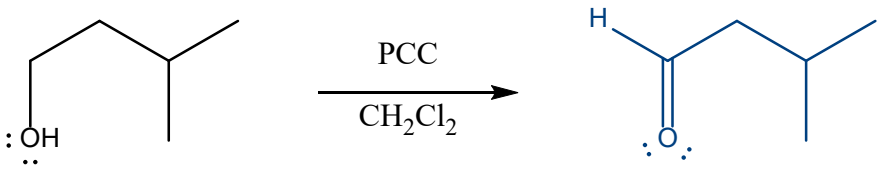
Step 5: Answer question (i.e. write rate law)

$$rate = 0.0024\ s^{-1}[RCl]$$

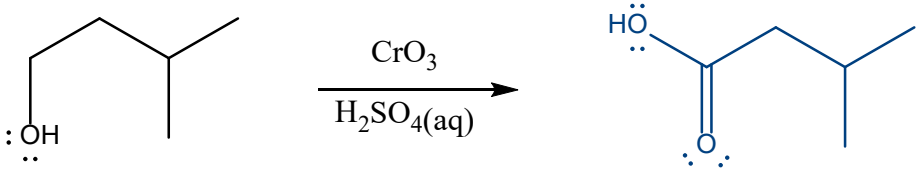
Since this reaction is first order, it must proceed via an $E1$ mechanism.

5. Draw the major organic product for each of the following reactions. **[10 marks]**

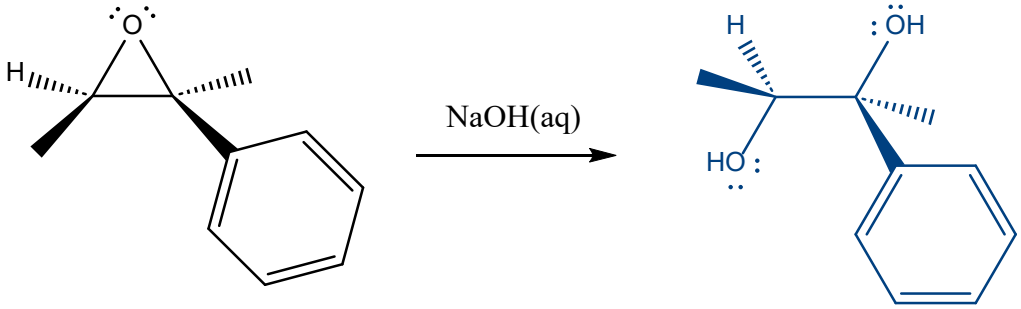
(a)



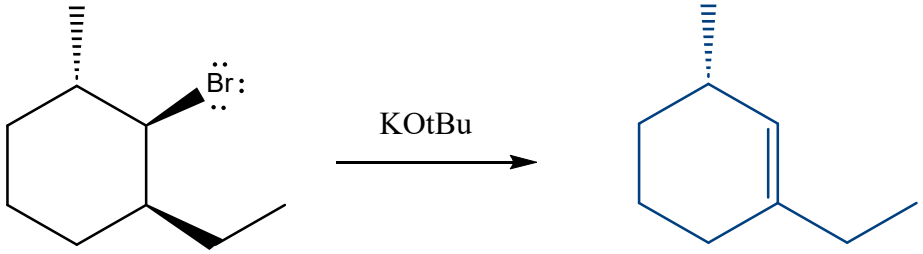
(b)



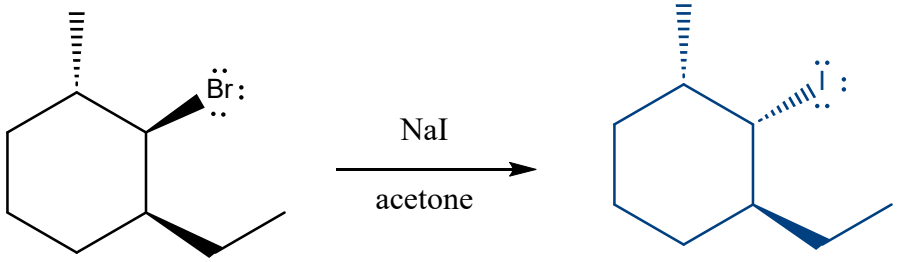
(c)



(d)



(e)



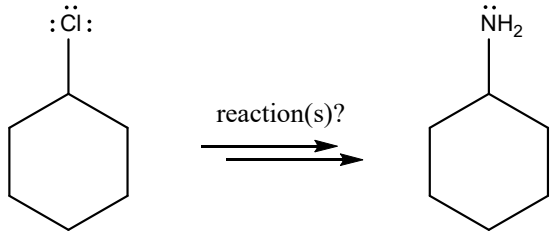
6. Propose a route to make each product from the given starting material. **[8 marks]**

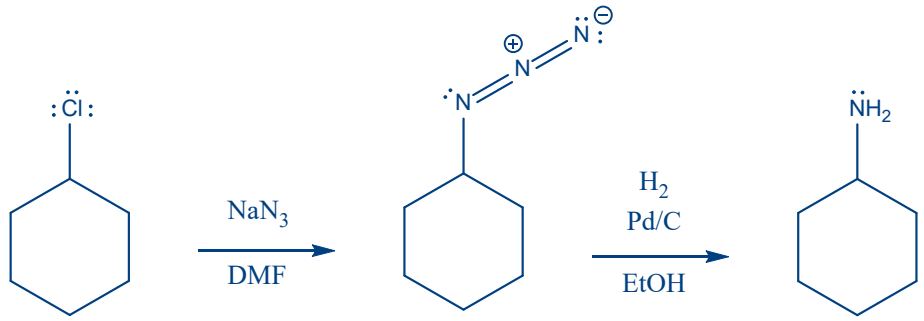
In cases where more than one reaction is required, please draw each reaction with its own arrow and draw the product of each reaction. We are NOT asking for mechanisms. But we are asking that if you react A and B to make C and then, in a later step, react C with D to make E, that there be two separate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

A $\xrightarrow{B}$ C $\xrightarrow{D}$ E *not* A $\xrightarrow[2.\ D]{1.\ B}$ E

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 answer above is representative; there are other valid answers.

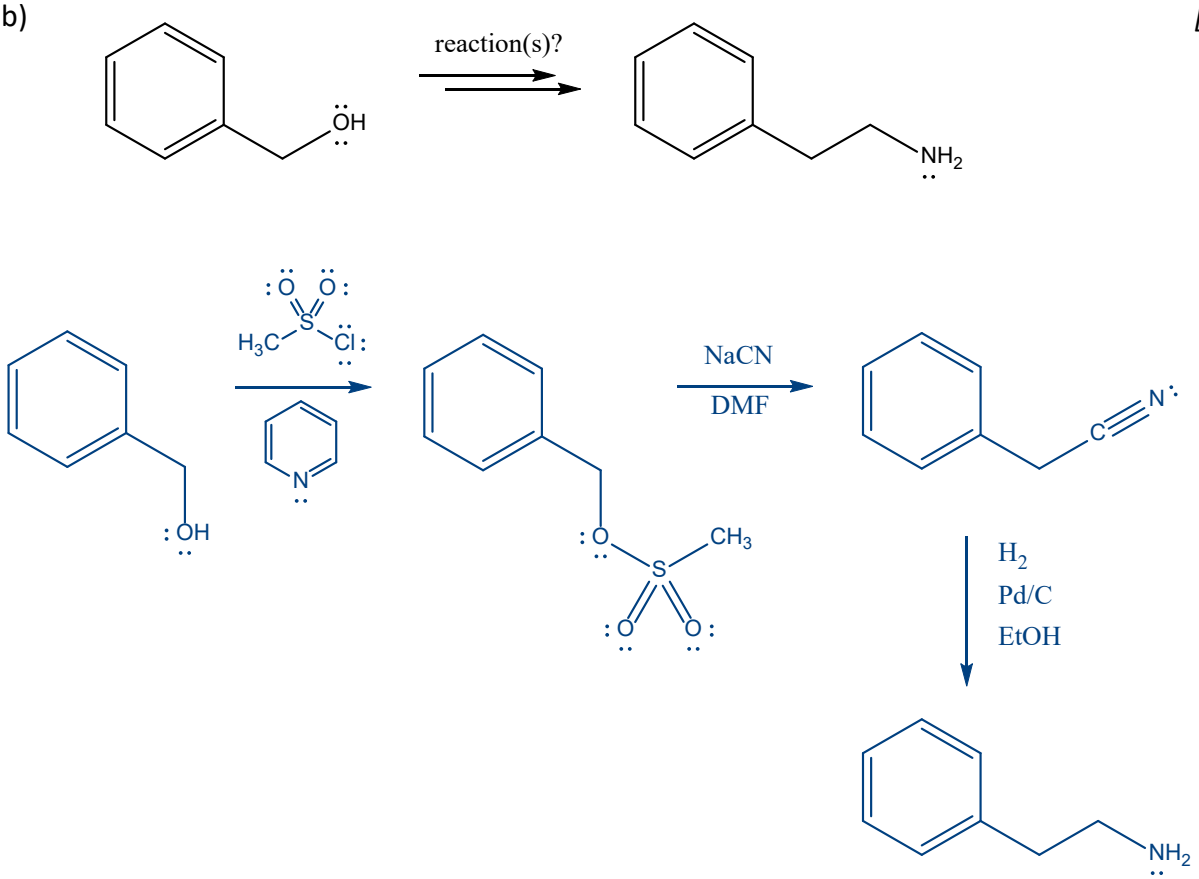
Important points to keep in mind for this question:

- *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.*

continued on next page…

6. *…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.)*
- *To get the correct length of carbon chain, cyanide (CN^-) is the best choice of nucleophile as it adds a carbon atom as well as a nitrogen atom. The resulting nitrile can be converted to the desired amine via either hydrogenation (shown above) or reduction with $LiAlH_4$ followed by aqueous workup.*