CHM 1321
Sample Final Exam
ANSWERS

April 1390 Alison Flynn

Time: 3 hours

Name: _____

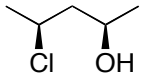
Student Number: _____

Notes:

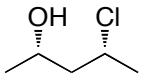
- Attempt all questions
- The marks are given as a guide and are subject to minor changes
- A calculator and molecular models are permitted
- When key ideas such as "resonance" are used in explanations, draw structures to prove your point
- Show relative stereochemistry where applicable
- Total number of pages: 16
- Approximate number of points:

1. Identify the stereochemical relationship between the following molecules (enantiomers, diastereomers, constitutional isomers, same molecule, other). (**4 points**)

a.



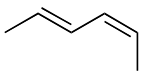
and



Relationship: _____

Enantiomers

b.



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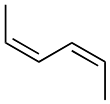
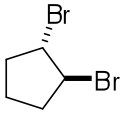


Relationship: _____

Diastereomers

c.



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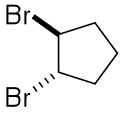
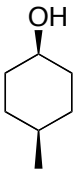


Relationship: ___same molecule____

d.



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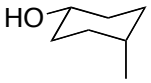


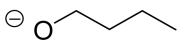
Relationship: _____

Same molecule

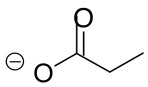
2.

a. Arrange the following molecules in order of **increasing nucleophilic ability** in an $\mathbf{S_N2}$ reaction. (**1 point**)

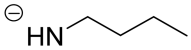
A



B



C



D

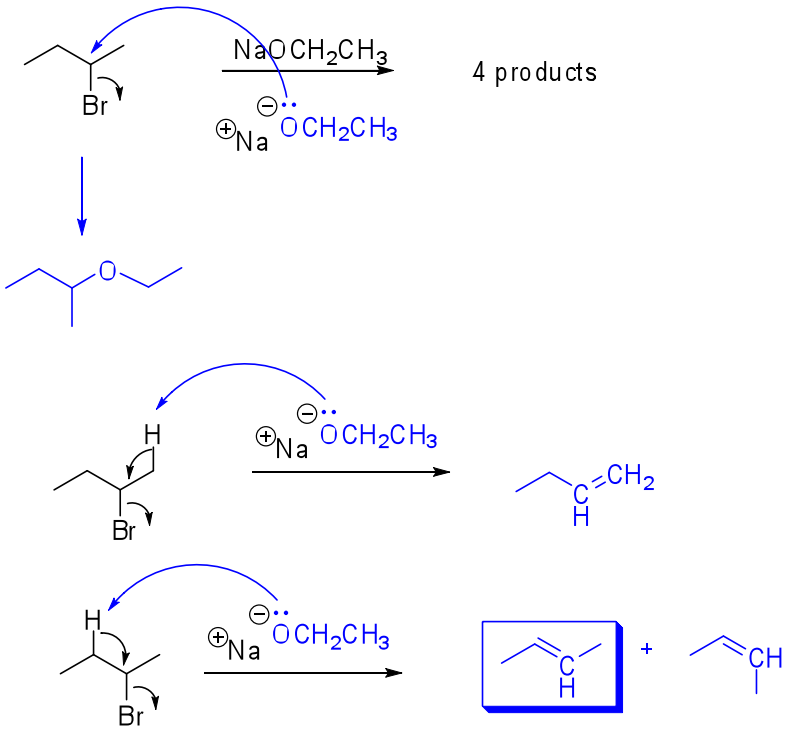
A < C < B < D

b. Explain the difference in nucleophilic ability between **B** and **D**. (**3 points**)

D is less electronegative than **B** and is therefore better able to donate its electrons.

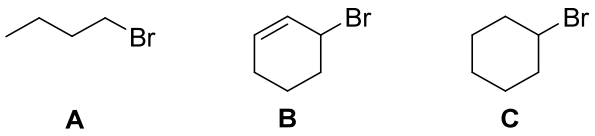
3. The following reaction gives four (4) possible products.

   a. Draw mechanisms to account for the formation of each product. (**14 points**)
   b. Circle the major alkene product. (**1 point**)



4. Arrange the following electrophiles in order of increasing reactivity in an $\mathbf{S_N1}$ reaction. (**1 point**)

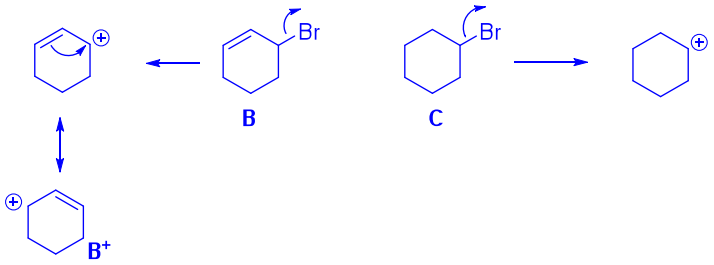
a.



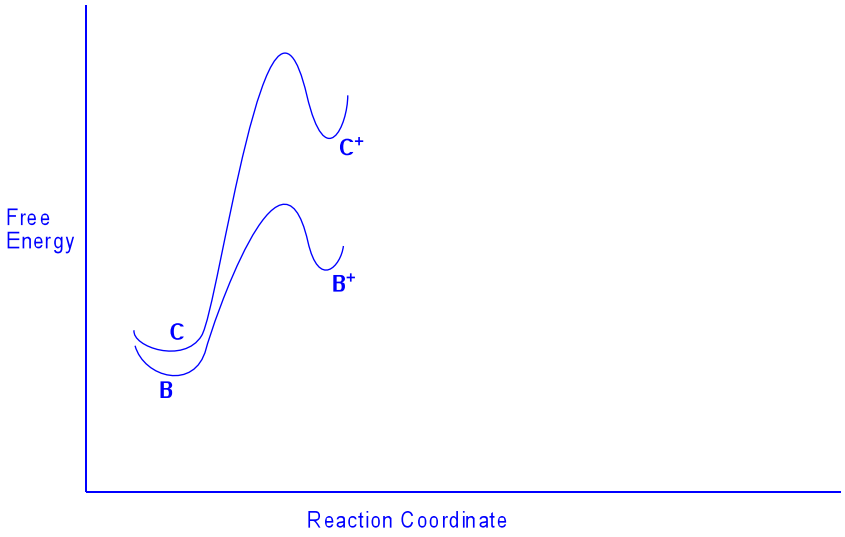
A < C < B

b. Clearly explain the difference in reactivity between **B** and **C**. Your answer should include a reaction coordinate diagram. (**10 points**)

Note: in 2011, Hammond postulate was not covered in 1321, but the rest of the explanation applies.

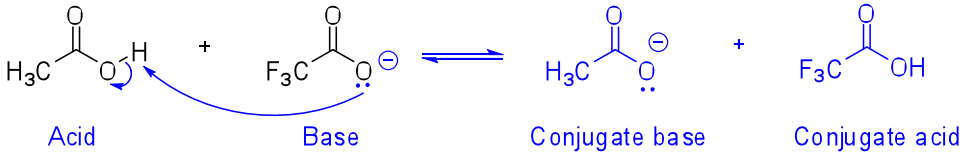


The carbocation derived from **B** is resonance-stabilized and is therefore more stable than the carbocation derived from **C** which is not resonance-stabilized (only 2°). According to the Hammond postulate, the transition state most closely resembles the species closest to it in energy, the carbocation in this case. Consequently, the more stable carbocation has the lowest energy transition state leading to its formation allowing it to form more quickly and easily, and so **B** reacts faster than **C**.



5.

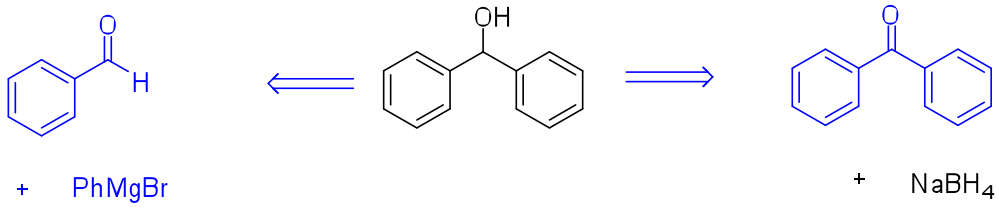
a. Draw a mechanism for the acid/base reaction shown below. (**5 points**)
b. Does the equilibrium favor the starting materials or the products?(**1 point**)
c. Explain your answer in part b. (**4 points**)



Compare bases:

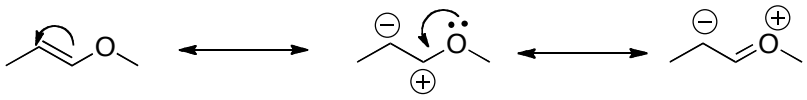
The 3 fluorines in the base help to disperse the negative charge via the inductive effect. The stabilization of the negative charge cannot be done in the way in the conjugate base. The equilibrium lies to the left, toward the more stable base.`

6. Suggest **two** different ways to synthesize the following alcohol from a carbonyl-containing compound. Mechanisms are not required. (**5 points**)



7.

a. Draw the resonance structures for the following ether, including arrows showing the movement of electrons. (**5 points**)



Major

- All atoms Have full octets
- no charges

Minor

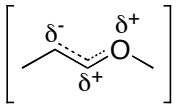
- C+ lacks an octet

Intermediate

- All atoms have a full octet
- 2 charges

b. Identify the major, minor, and intermediate (if applicable) structures and explain your choices. (**7 points**)

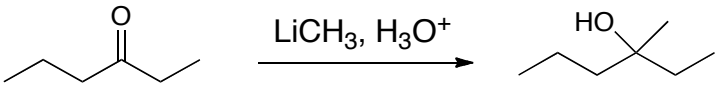
c. Draw the resonance hybrid structure. (**3 points**)



d. What is the physical significance of the resonance hybrid structure? (**2 points**)

The resonance hybrid is the true representation of the molecule. Molecules are not interconverting between resonance structures; they are a mix of all the resonance contributors.

8. The following reaction will **not** give the product shown:



a. Explain why not by showing the reaction that would take place. (**2 points**)

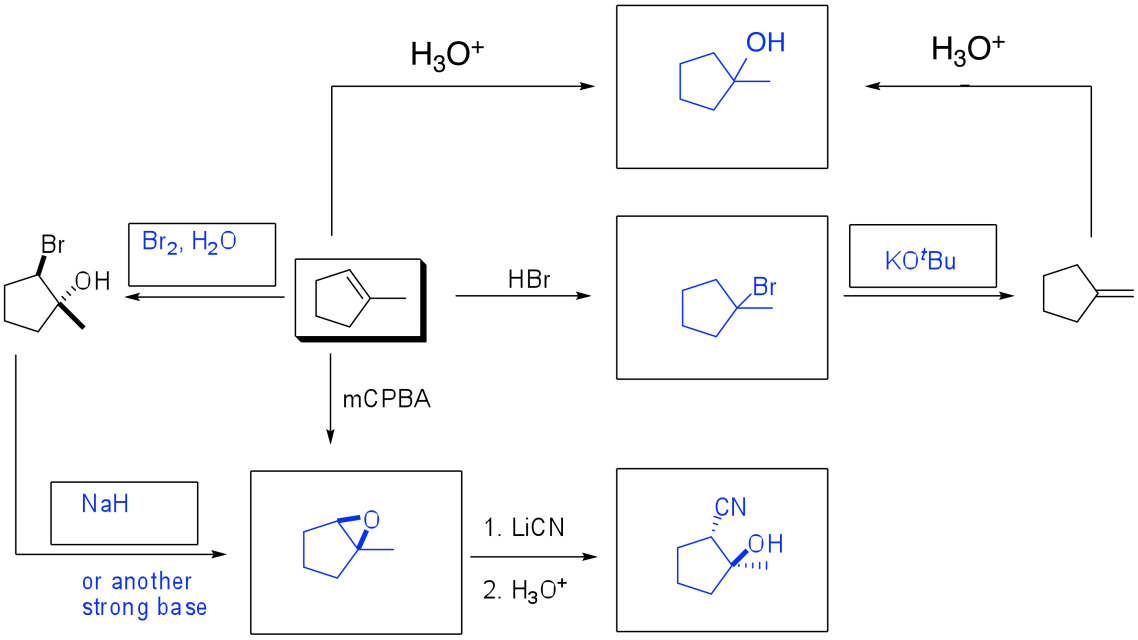
$LiCH_3 + H_3O^+ \longrightarrow CH_4 + H_2O + Li^+$

(acid/base reaction)

b. Suggest a solution to this problem in order to obtain the desired product. (**2 points**)

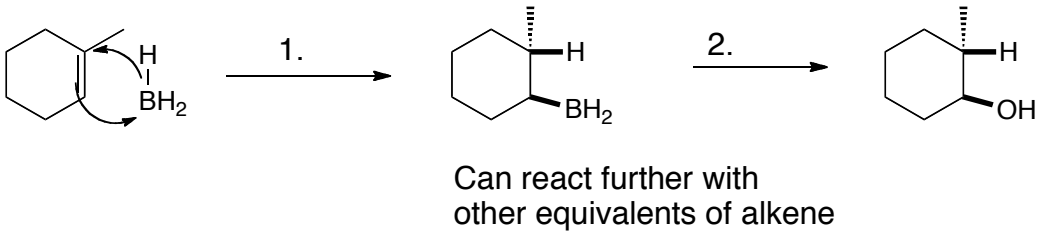
Separate the steps: 1. LiCH3
2. H3O+

9. Fill in the boxes with the missing reagents, starting materials, or products as required. Be sure to show relative stereochemistry where applicable. (**10 points**)



10.

a. Give a mechanism for the following reaction: (**9 points**)



Can react further with other equivalents of alkene

b. Explain the regiochemistry of the reaction. (**2 points**)

This reaction results in anti-Markovnikov addition of OH to an alkene. The more electronegative H of the BH_3 bonded to the more electropositive carbon of the alkene in the first step of the reaction.

c. Explain the stereochemistry of the reaction. (**2 points**)

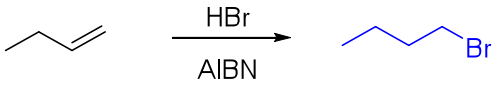
The addition of H and BH_2 to the alkene occurs simultaneously, installing the H and the B on the same side of the molecule (syn addition).

11. Give the products of the following transformations. (**14 points**)

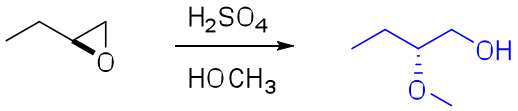
Note: - "No reaction" is **not** a possible answer.
- Mechanisms are not required but part marks might be given for an incorrect answer with a reasonable mechanism.

Note: The OsO_4 reaction can proceed with or without NMO (with NMO, a co-oxidant, only small amounts of OsO_4 are required. Without NMO, a stoichiometric amount of OsO_4 is required—i.e. one mole of starting material would require one mole of OsO_4)

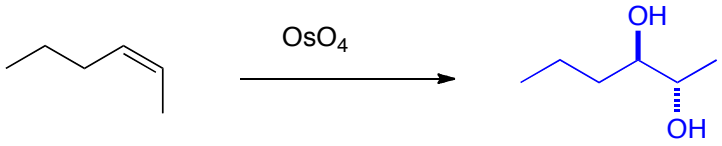
a.



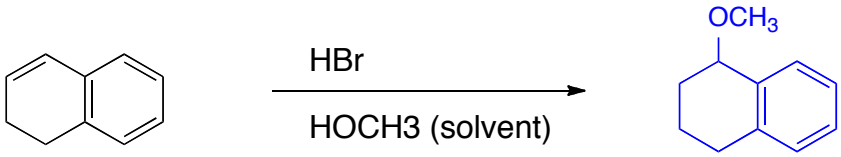
b.



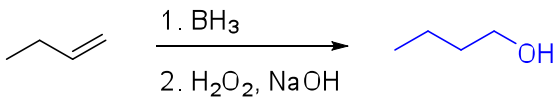
c.



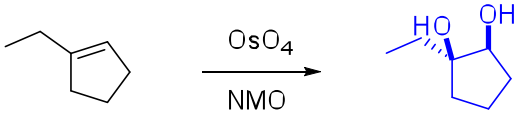
d.



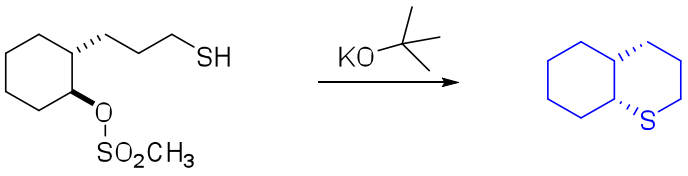
e.



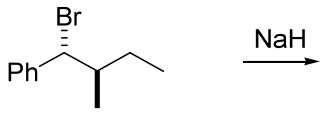
f.



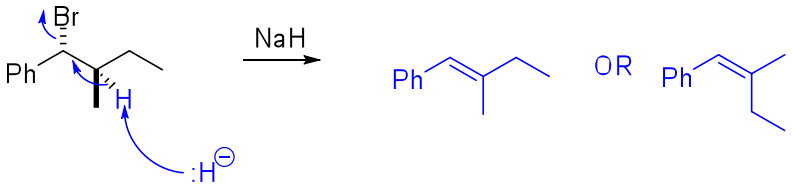
g.



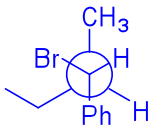
12.



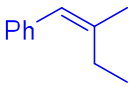
a. Draw a mechanism in **2D** for the elimination reaction shown above, ignoring stereochemistry. (**4 points**)



b. Draw a Newman projection of the starting material in its reactive conformation. (**2 points**)

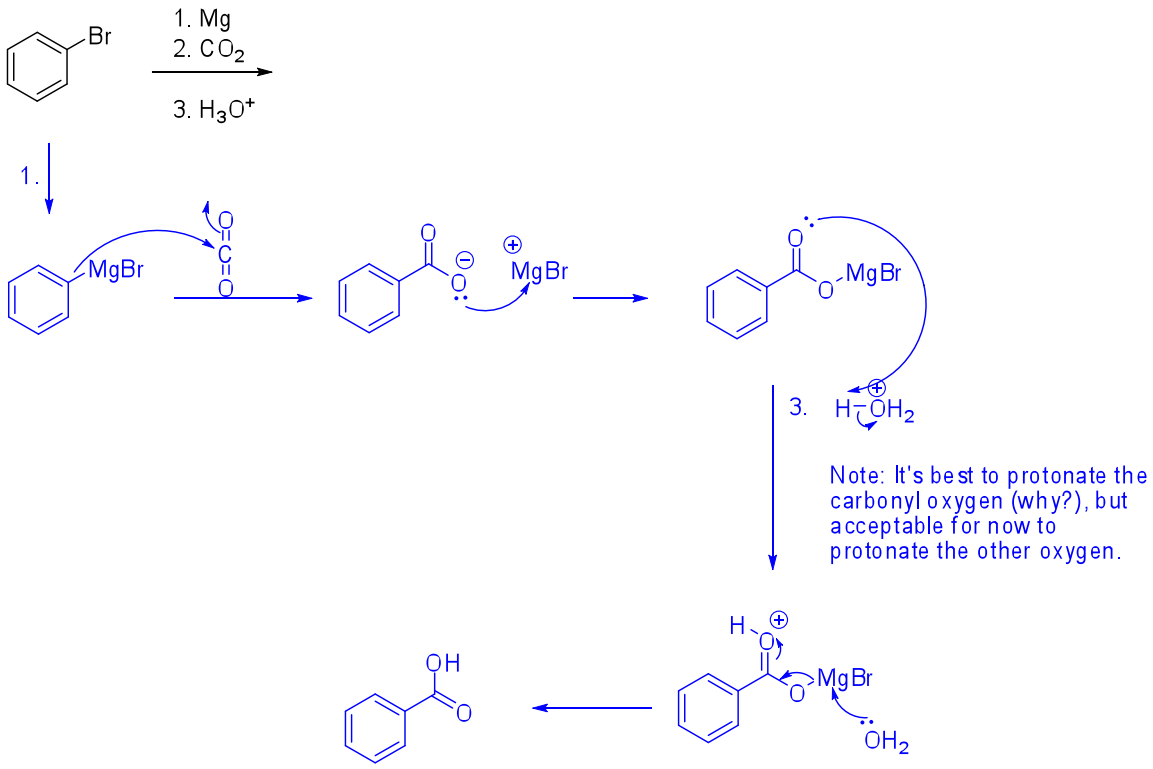


c. Draw the final product of this reaction with the correct stereochemistry. (**2 points**)



13.

a. Give a mechanism for the following reaction. (**11 points**)



b. Why was it important to use obtain dry ice **immediately before** using it in the laboratory? (**2 points**)

Condensation (water from the air) surrounds the dry ice if left out in the air. This reacts with the Grignard reagent (acid/base), destroying the nucleophile.

c. Calculate the yield if a student began the experiment with 3.0 mL of bromobenzene (density = 1.5 g/mL, molar mass = 157 g/mol) and obtained 2.9 g of white crystals at the end of the reaction (molar mass of product = 122 g/mol). Please clearly show your calculations. (**3 points**)

n (PhBr) = 3.0 mL × 1.5 g/mL × mol/157g = 0.029 mol or 29 mmol

n (product) = 2.9 g × mol/122 g = 0.024 mol or 24 mmol

Yield = (24 mmol / 29 mmol) * 100
= 83%

d. How could you verify that the white crystals were the desired product? (**1 point**) Melting point (better would be to mix the product with a known sample of the product—if the melting point range is correct and narrow, it is likely the correct compound)

14. Describe how you would separate a mixture of benzyl amine and benzophenone. Both compounds are soluble in EtOAc. (**10 points**)
Be specific – a first year student should be able perform the separation by following your instructions.

$R\text{-}NH_2$ and a ketone (the actual structures are not required to solve the problem, only the key functional groups must be known)

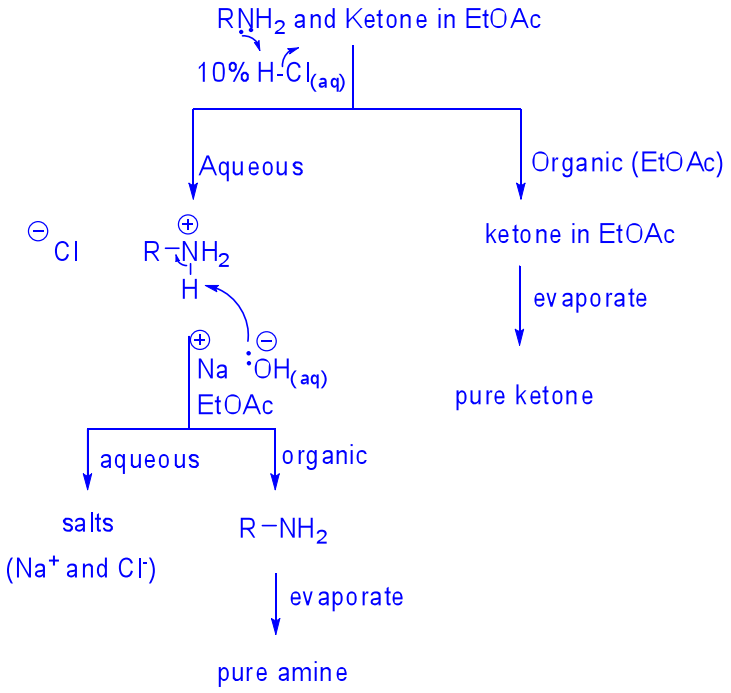
Dissolve both in EtOAc.

Add 10% HCl (aqueous), shake and separate the layers.

Evaporate the organic layer – get pure ketone

To the aqueous layer, add EtOAc (solvent) and 1M NaOH (aqueous), shake and separate the layers.

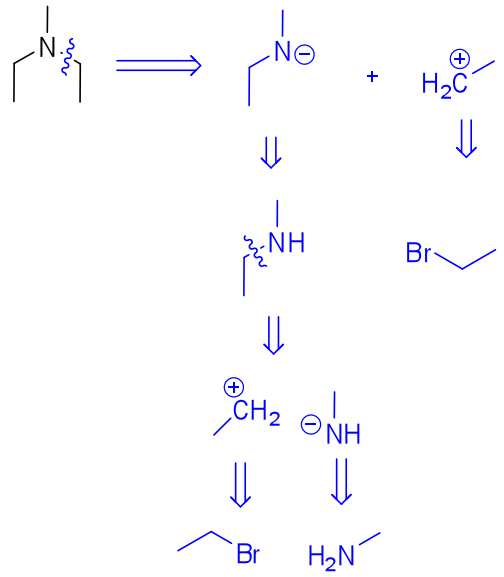
Evaporate the organic layer – get pure amine.



15. Suggest a synthesis of the following molecule from starting materials that possess two carbons or less. (**12 points**)

Notes:
- Your answer must include a retrosynthetic analysis and a synthesis.
- Mechanisms are not required.

RETROSYNTHESIS:



SYNTHESIS: