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**CHM 2123 ORGANIC CHEMISTRY LABORATORY
FINAL EXAM FALL 2015**

Professor: Katherine McGilvray

Date: Saturday, December 19th, 2015 14:00 - 17:00

Name: MARKING SCHEME Section: _____

Student #: _____ Your TA: _____

Check to see that
your exam contains
16 pages

QUESTION	POINTS	RESULT
1	10	
2	10	
3	10	
4	10	
5	10	
6 or 7	8	
8	12	
9	9	
10	15	
TOTAL	92	

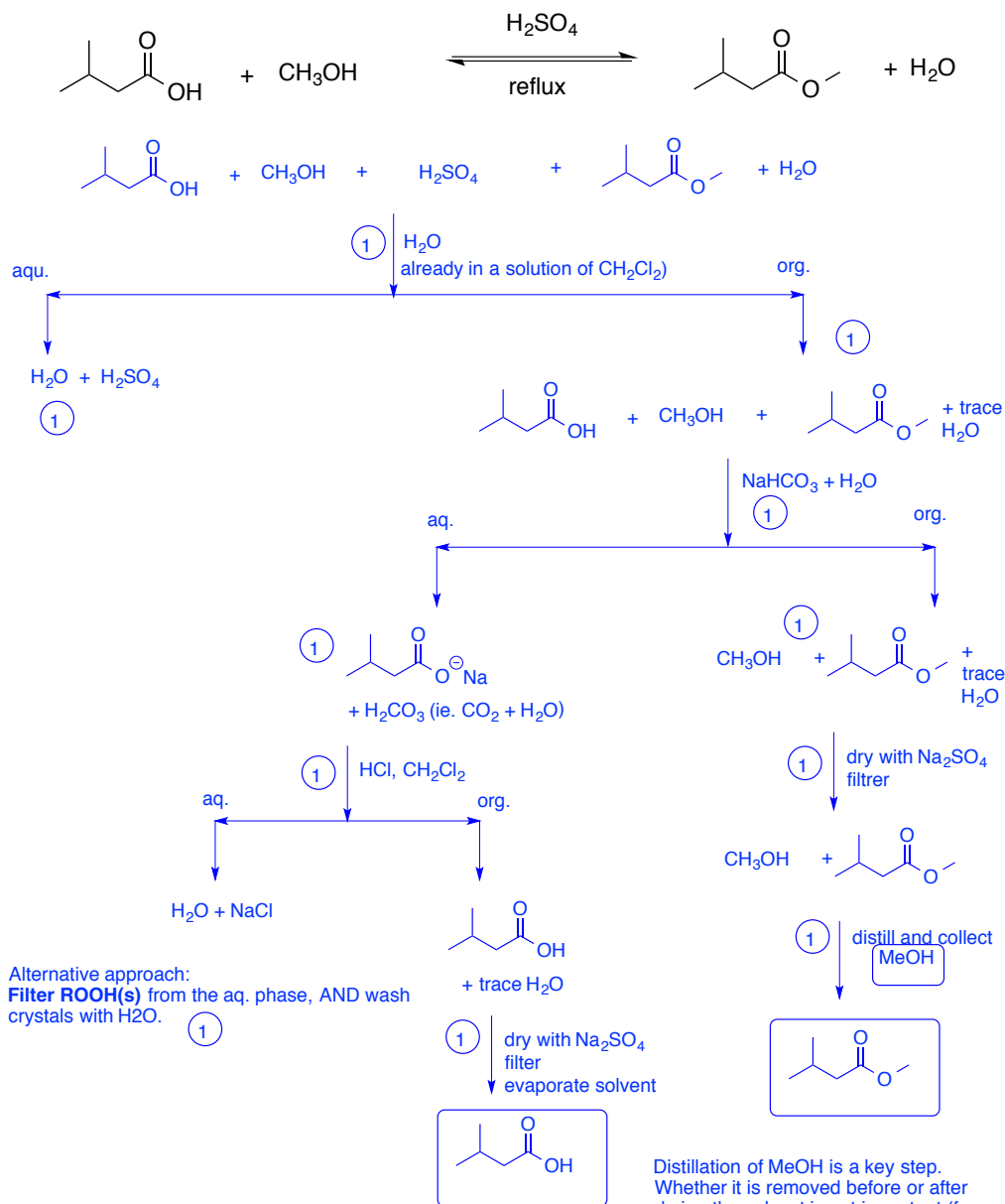
Question 10 contains two BONUS points! Good luck!!!

Cellular phones, unauthorized electronic devices or course notes are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: you will be asked to leave immediately, the exam and academic fraud allegations will be filed which may result in you obtaining a 0 (zero) for the exam.

By signing below, you acknowledge that you have ensured that you are complying with the above statement.

(Signature) _____

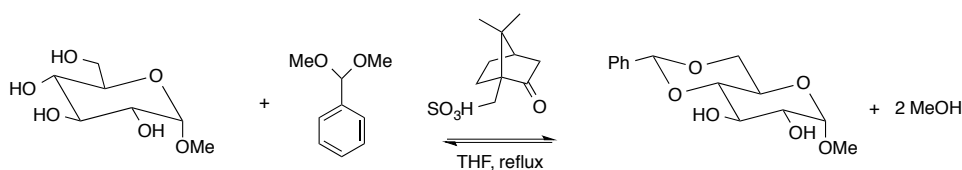
1. (10 points) **Separation and extraction.** A student performs the following esterification reaction for one hour and determines by TLC that the reaction did not go to completion. The student wishes to try again, and recovers the leftover starting materials as well as the ester from their reaction mixture. Starting with the reaction mixture diluted with dichloromethane at room temperature, use a **flowchart** and any necessary reagents from the **reagents box on p.15** and/or work-up techniques to provide a method for the separation of the following mixture of compounds. Isolate each of the three compounds as individual crude products. (Recrystallization not necessary).



- There will likely be confusion over where MeOH goes. This solvent is miscible in water, but is unlikely to be transferred if the aqueous phase is charged with acid, base, NaCl, etc.

- steps may be added to better reflect what was done in exp 8. Washing the organic phase with NaCl (satd) AFTER the H₂O wash, after the NaHCO₃ wash. Students thus might show this NaCl wash INSTEAD of drying with Na₂SO₄. We will accept this, and give them the point for the NaCl wash.

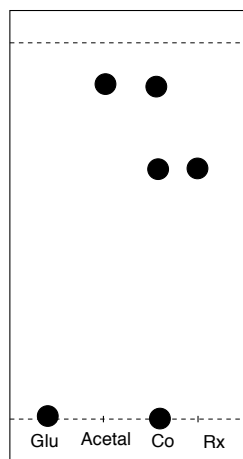
2. (10 points) In the preparation of a benzylidene acetal, a student arrived late in the lab. They quickly rinsed and dried their glassware with water and acetone, placed it in the oven for two minutes, and proceeded to start the reaction as illustrated below.



- a) 10-camphorsulfonic acid was used as an acid for this reaction. Why did the student use this instead of a more conventional acid such as HCl? (1 point)

*Need an **organic acid** under anhydrous conditions. HCl, even concentrated, is still an acid in aqueous solution.*

- b) After allowing the reaction to reflux for 45 minutes, they performed a TLC using 3:7 hexanes : ethyl acetate. They then visualized the plate using a UV lamp, followed by dipping the plate in a methanolic solution of 10% H_2SO_4 and heating the plate. Complete the anticipated TLC plate for this step of the experiment. (4 points)



1 pt per lane. Glu must be on the baseline. Co-spot can be Rx + one or two of the reagents. Rx needs have a smaller R_f than the acetal, but bigger R_f than Glu. If Rx shows the appearance of starting materials, this is ok.

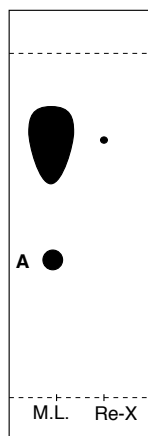
- c) Why was the methanolic H_2SO_4 treatment plus heating necessary in this reaction protocol? (1 point)

To visualize the starting sugar (Glu) and the final product on the TLC plate.

- d) The reaction mixture was cooled and a few drops of triethylamine were added. The contents of the reaction flask was transferred to a separatory funnel, diluted with 50 mL ethyl acetate, and washed three times with water. What purpose does the addition of triethylamine serve in this step of the experiment? (1 point)

- *To neutralize/deprotonate the acid catalyst in the reaction mixture so that it may be removed by extraction. (NOT to deprotonate a species in the mechanism, etc.)*

- e) Following recrystallization, the student performed a TLC to assess the purity of their crystals, and obtained the plate illustrated below, where M.L. and Re-X represent a spot of the mother liquor and the isolated crystals, respectively. A large streak appeared in the M.L. lane. What likely caused this, and what can you do to improve the resolution? (2 points)

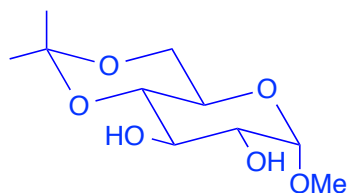


Streaking because **M.L. solution too concentrated** and/or too acidic. (1)

- *dilute solution and respot (1)*
- *(or neutralize acidic solution with a base, but this is unlikely at this point in the work-up. Nevertheless, I'll accept it based on theory) (1)*

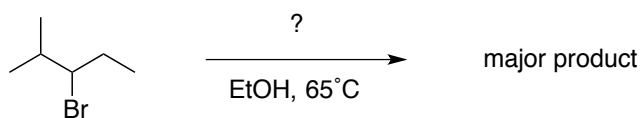
- f) There is an additional spot A whose R_f value does not correspond to any of the reagents in solution. This spot required visualization using the methanolic H_2SO_4 solution and heat. Propose a structure for this side-product. (1 point)

Structure of A:



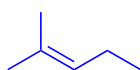
If there was residual acetone in the flask that had not evaporated prior to adding the reagents, acetone would react with the sugar (diol).

3. (10 points) A student carried out a synthesis in the undergrad lab, following the lab manual that instructed them to combine 0.5g of 3-bromo-2-methylpentane with 20 mL of ethanol, followed by the addition of NaOEt, and allowing the reaction to reflux for 45 minutes. Arriving 20 minutes late, the student rushed to set up the experiment. About 30 minutes into the reflux, the student panicked and questioned whether they may have accidentally added KOC(CH₃)₃ instead of NaOEt. Their TA told them to continue on with the experiment, and to characterize their final product by ¹H NMR.

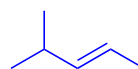


a) Identify the possible products that could form in the case of each reagent. (2 points)

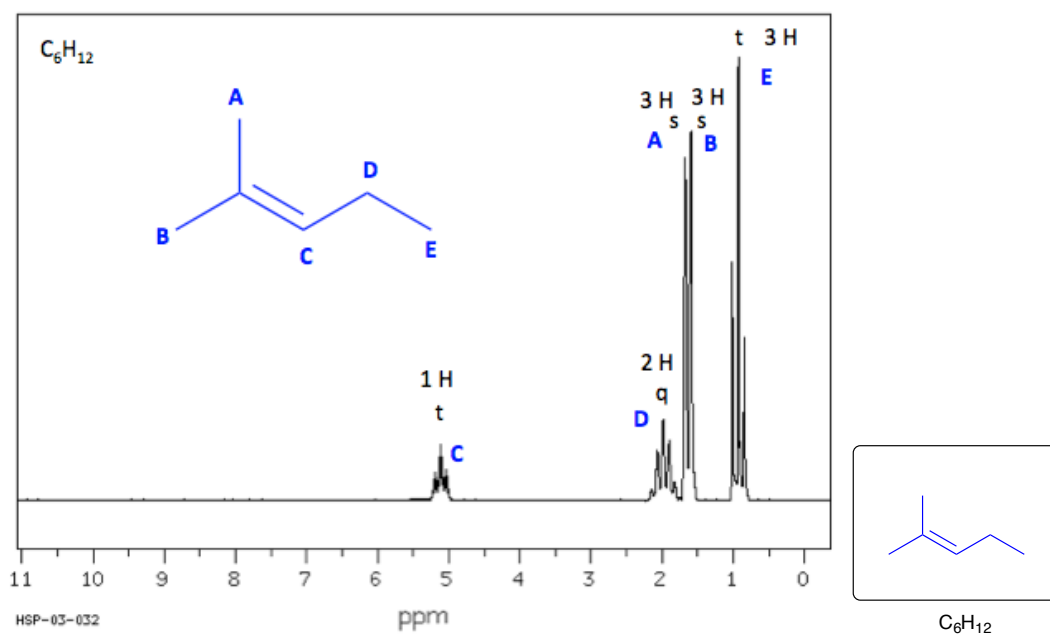
NaOEt:



KOC(CH₃)₃:



b) After workup and recrystallization, the ¹H NMR spectrum of the student's major product is below. Identify the compound, and indicate which peak corresponds to which proton. (5 points)



c) Did the student successfully add NaOEt to their reaction mixture? Explain your reasoning. (3 points)

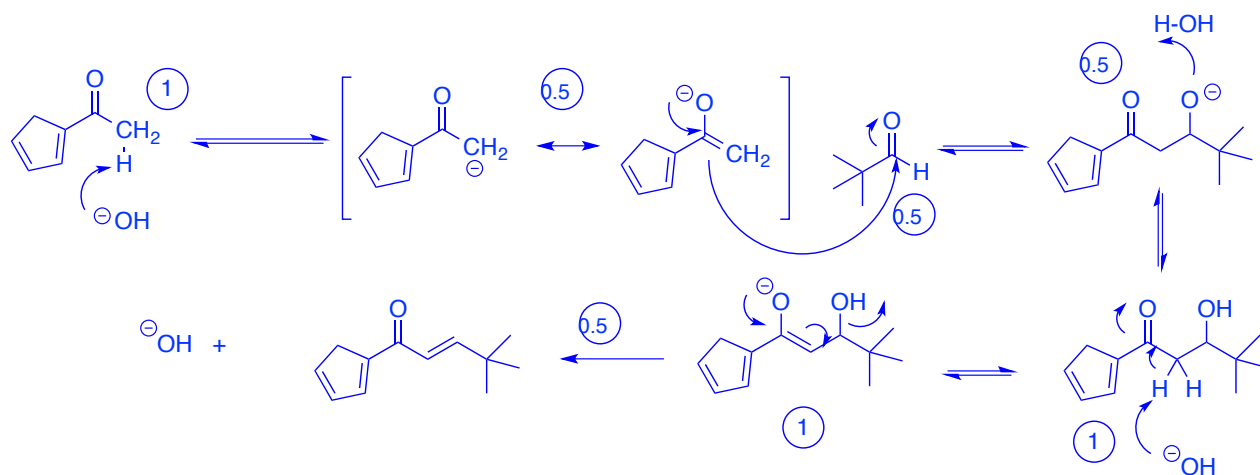
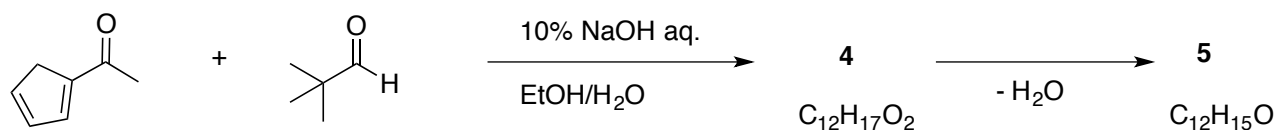
Yes, NaOEt was successfully added, based on:

*The spectrum: Peaks for A and B, for example, would have **been doublets**, and an additional peak would have appeared representing **a multiplet (1H)**, had KOCtBu been used instead. (2 pts)*

*The chemistry: Use of NaOEt, a small base, follows **Zaitzev's rule** to abstract the **most substituted beta-H**, whereas a bulky base such as KOCtBu would have abstracted the **most accessible beta-H**. (1 pt.)*

4. Reactions of carbonyl compounds. (10 points)

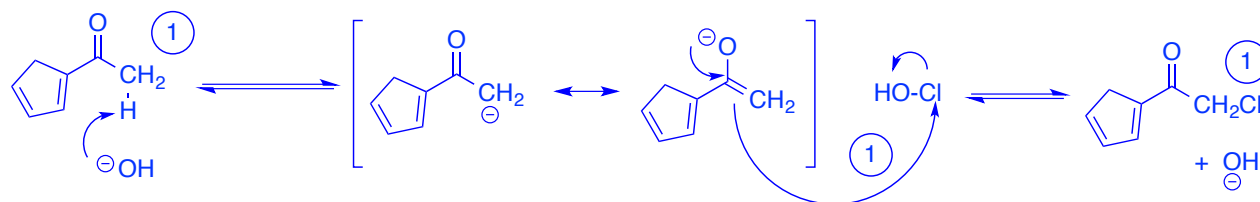
a) Provide a mechanism for the following reaction. Be sure to include key resonance structures. (5 points)



b) Provide a name for the reaction to yield product 5. (1 point)

Aldol condensation (0.5 if just Aldol).

c) How does an aqueous solution of bleach, NaOCl, serve as a reagent for the haloform reaction? Demonstrate with a mechanism showing a single mono-halogenation step using the methyl ketone in part a). (4 points)



If students simply show attack with NaOCl, this is also fine.

5. Ester hydrolysis (8 points) In an experiment to determine the molar mass of an unknown ester, a student dissolved 400 mg of the unknown ester into 35 mL of alcoholic NaOH. After the hydrolysis reaction was complete, 20.9 mL of 0.25 M H₂SO₄ was required to be neutralize the reaction mixture. In determining the concentration of the starting material, 20 mL of the NaOH alcoholic solution was neutralized with exactly 15.0 mL 0.25 M H₂SO₄.

a) Determine the concentration of NaOH used in this saponification reaction. (2 points).

$$0.25 \text{ M H}_2\text{SO}_4 \times 0.015 \text{ L} = 3.75 \text{ mmol} \times (2 \text{ mol NaOH}/1 \text{ mol H}_2\text{SO}_4) = (7.5 \text{ mmol } -\text{OH})/0.02 \text{ L}$$

$$[\text{NaOH}] = 0.375 \text{ M}$$

b) Determine the moles of unreacted NaOH after ester hydrolysis. (3 points)

$$[\text{NaOH}]_{\text{final}} = 0.25 \text{ M H}_2\text{SO}_4 \times 0.0209 \text{ L} = 5.225 \text{ mmol H}_2\text{SO}_4 \times (2 \text{ mol NaOH}/1 \text{ mol H}_2\text{SO}_4) = 10.45 \text{ mmol}$$

c) Determine the molar mass of the ester. (2 points)

$$[-\text{OH}] = [\text{NaOH}]_{\text{init}} - [\text{NaOH}]_{\text{final}}$$

$$[\text{NaOH}]_{\text{init}} = 0.375 \text{ M} \times 0.035 \text{ L} = 13.13 \text{ mmol } -\text{OH}$$

$$[-\text{OH}] = 13.13 \text{ mmol} - 10.45 \text{ mmol}$$

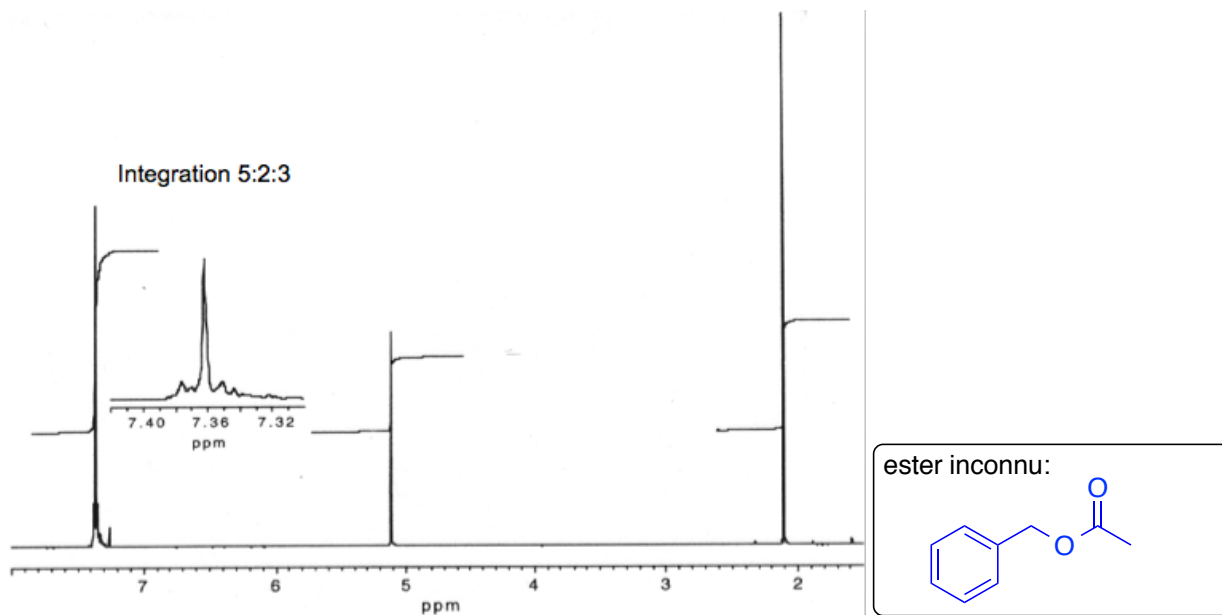
$$[-\text{OH}] = 2.66 \text{ mmol} \quad (1)$$

$$\text{Neutralization equivalent} = \text{mass of unknown ester} / \text{moles of base}$$

$$= 0.4 \text{ g} / 0.00266 \text{ mol}$$

$$= 150 \text{ g/mol} \quad (1)$$

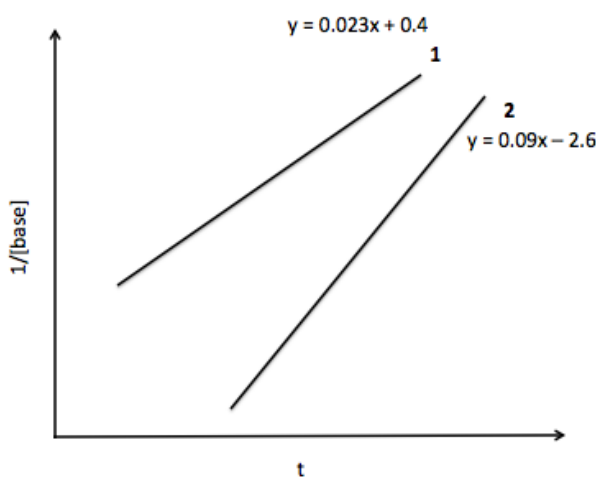
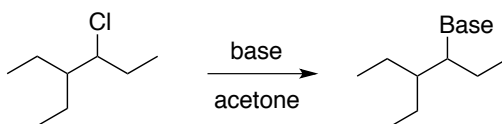
d) Based on the ¹H spectrum below, identify the structure of the unknown ester. (1 point)



This is the only possible ester. No other isomers match this spectrum.

You have the CHOICE to complete either question 6 OR 7. Clearly indicate your choice.

6. (8 points) **Kinetic Analysis.** A student was performing the following substitution reaction, where triethylamine and sodium acetate were employed to investigate the effect of base on the reaction rate under identical reaction conditions. The rate of the reaction was obtained by titrating aliquots of the reaction mixture against HCl to determine the concentration of base remaining in solution at different time points, and performing a linear analysis as shown below. The student shared their data with their lab partner, but unfortunately failed to label their trials.



a) Based on the trials 1 and 2 above, calculate the rate constants corresponding to each trial. What is the order of each reaction? (4 points)

1
 $k = 0.023 \text{ mol}^{-1}\text{Ls}^{-1}$

2
 $k = 0.09 \text{ mol}^{-1}\text{Ls}^{-1}$

(1 pt each, 0.5pt each if no units) Each rate is second order.(1)

b) Based on the analysis above, help the lab partner assign triethylamine and sodium acetate to trials 1 and 2. (2 points)

1
 NEt_3

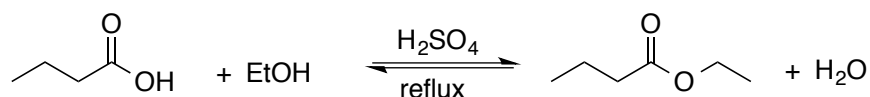
2
 CH_3COONa

d) Explain your rationale in part b). (2 points)

Even though triethylamine is the stronger base between the two, it is non-nucleophilic due to sterics and thus a weaker nucleophile compared to acetate.

You have the **CHOICE** to complete question 6 OR 7. Clearly indicate your choice.

7. (8 points) *Esterification*. A student was interested in synthesizing ethyl butyrate to add a pineapple scent to a soft soap that they had previously prepared. In this second experiment, the student added 3.0 mL of butyric acid (88.11 g/mol, 0.95 g/mL) to a 50 mL round bottom flask and followed by 15 mL ethanol (46.07 g/mol, 0.79 g/mL). Slowly, 1.0 mL H₂SO₄ (98.08 g/mol, 1.84 g/mL) was added while stirring, and the reaction was allowed to progress for 90 minutes under reflux conditions. Following workup, 0.7g of ethyl butyrate (116.16 g/mol, 0.88 g/mL) was isolated.



- a) Determine the number of equivalents of each reactant in this reaction. *A table of reagents is not necessary.* (3 points)

$$\text{RCOOH: } 3 \text{ mL} \times 0.95 \text{ g/mL} \times 1/88.11 \text{ g/mol} = 32.3 \text{ mmol (1.0 equiv)}$$

$$\text{EtOH: } 15 \text{ mL} \times 0.79 \text{ g/mL} \times 1/46.07 \text{ g/mol} = 257 \text{ mmol (~ 8.0 equiv.)}$$

$$\text{H}_2\text{SO}_4: 1.0 \text{ mL} \times 1.84 \text{ g/mL} \times 1/98.08 \text{ g/mol} = 18.7 \text{ mmol (0.6 equiv.)}$$

- b) Knowing that the reaction has an equilibrium constant of 4.0, determine the theoretical yield of ethyl butyrate. (4 points)

	ROOH	EtOH	↔	ROOR'	H ₂ O
i	32.3 (or 1.0)	257 (or 8.0)		0	0
c	-x	-x		+x	+x
e	(1-x)	(8-x)		x	x

$$K_{eq} = 4.0 = \frac{x^2}{(1-x)(8-x)}$$

$$4.0 = \frac{x^2}{8-9x+x^2}$$

$$32 - 36x + 3x^2 = 0$$

$$x = \frac{36 \pm \sqrt{(36)^2 - 4(3)(32)}}{2(3)}$$

$$x = \frac{36 \pm 32}{6}$$

$$x = 0.97$$

$$x = 11.0$$

$x = 0.97 \times 8$, or 7.76 mmol of ester at equilibrium (ie. theoretical yield)

c) Calculate the percent yield of this reaction. (1 point)

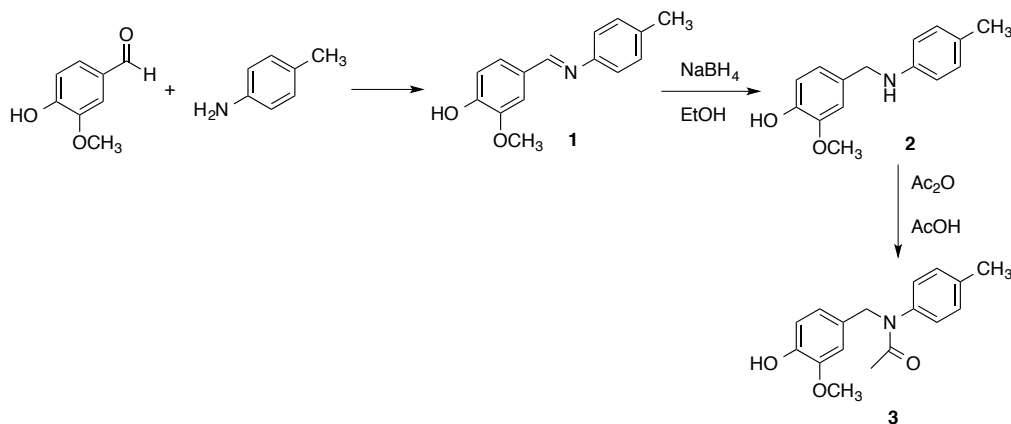
$$\% \text{ yield} = \text{actual/theoretical}$$

$$0.7\text{g}/116.16 \text{ g/mol} = 6.02 \text{ mmol}$$

$$\% \text{ yield} = 6.02 \text{ mmol}/7.76 \text{ mmol} \times 100$$

$$\% \text{ yield} = 77.6 \%$$

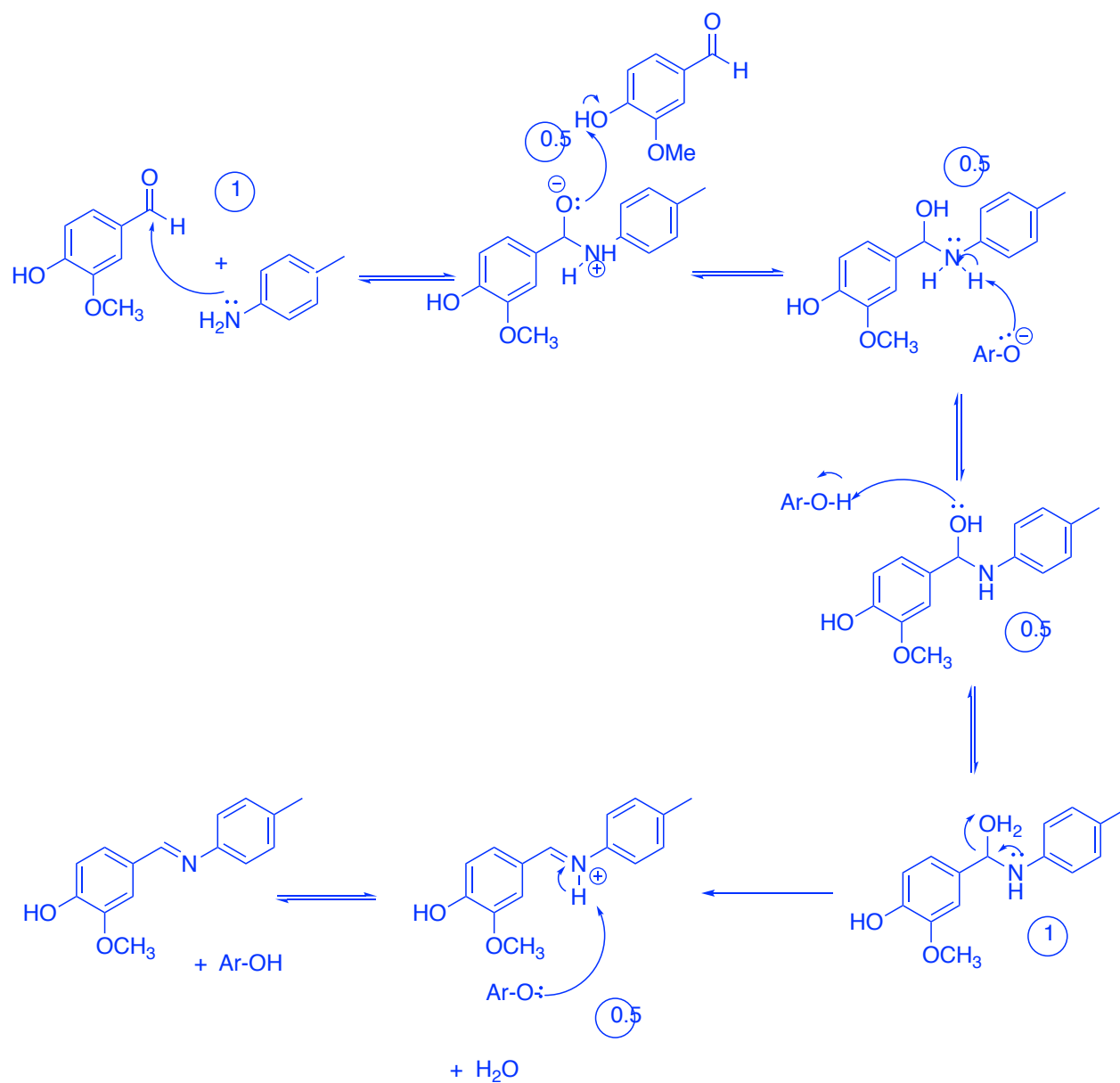
8. (12 points) **Reductive Amination.** You are asked to repeat the following experiment, as detailed from a research journal, for the preparation of an amide from an amine.



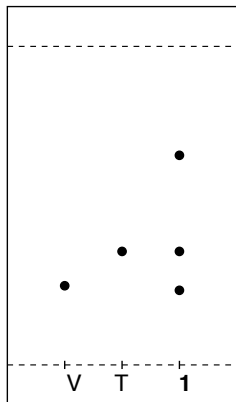
“Vanillin (0.58 g, 3.8 mmol) and para-toluidine (0.40 g, 3.8 mmol) are combined in a 250 mL beaker, and the solids are mixed with a Teflon stir rod to afford a dry, bright orange powder. (crude 90-95%, mp 102-103°C). The imine is subsequently reduced and then converted to the more stable amide by acetylation. The reduction is accomplished by the addition of 15 mL 95% ethanol to the beaker containing the imine, followed by the addition of NaBH₄ (0.1g, 2.7 mmol) in small increments to the stirred reaction mixture. The imine is only partially soluble in ethanol, but the product is quite soluble. Within 10 minutes, a colourless solution is an indication that the reaction is complete. Glacial acetic acid (2.0 mL) is added to the ethanoic solution followed by 2.0 mL acetic anhydride, and the reaction mixture is warmed on a steam bath for 5-10 minutes. The amide product precipitates out when 75mL of cold water is added slowly. White crystals are collected by vacuum filtration and analyzed by TLC and melting point. (crude 80-90%, mp 127-128°C.)”

a) Show a detailed mechanism for the formation of **1**, and be sure to show any proton transfer. (4 points)

Only intermolecular proton transfer will be accepted due to the geometry of the molecule.

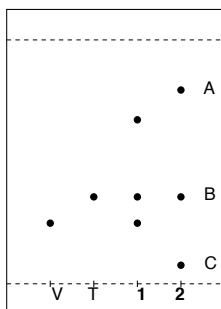


- b) After mixing the two starting materials for 15 minutes, you take the following TLC. What do these results indicate, and what should you do next? (2 points)

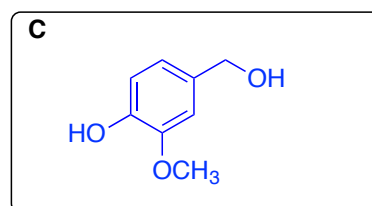
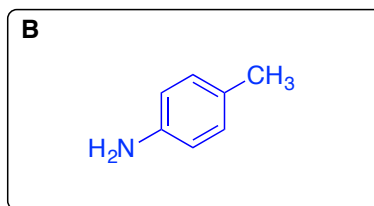
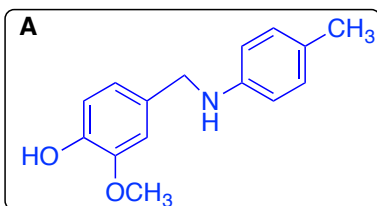


Starting material still remaining and **the reaction is not complete**. Leave reaction to proceed for **additional time**.

- c) Your lab partner doesn't agree, and insists you proceed to the reduction step of the experiment. Your ethanoic solution goes colourless after about 15 minutes following addition of NaBH_4 in ethanol, but you're worried that something went wrong. You take a TLC, as shown below.



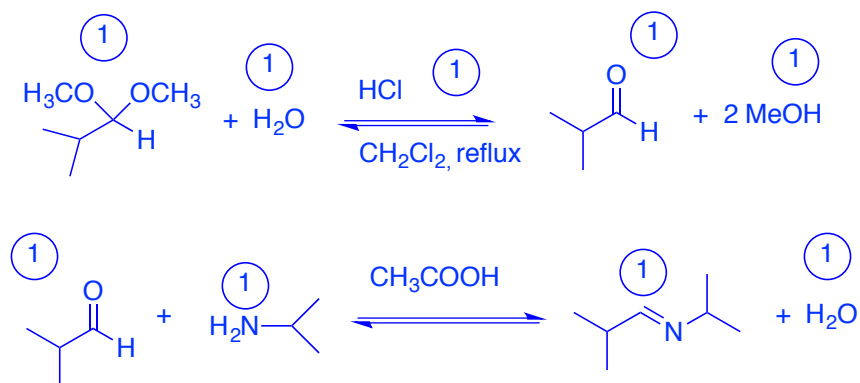
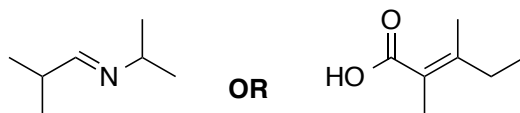
Unfortunately your instincts were right, and your reaction mixture shows impurities. Propose structures for the compounds responsible for spots A, B, and C. (3 points)



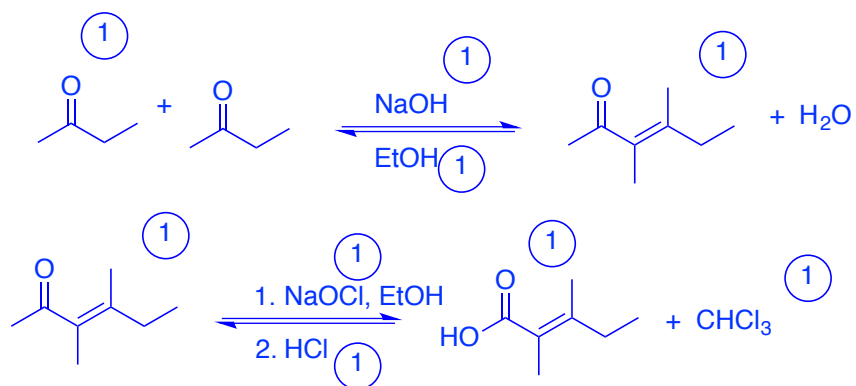
- d) Clearly you need to deviate from the protocol before you can proceed with the amidation step. You decide to purify your desired product by recrystallization. What are three key criteria to use when selecting a solvent system for recrystallization? (3 points)

- i. Dissolves compound when hot
- ii. Doesn't dissolve compound when cold
- iii. Dissolves impurities, or doesn't dissolve them at all.

9. (9 points) With access to **only** the chemicals listed in the **reagents box on p.15**, outline a synthetic approach (ie. reaction scheme) for **one** of the following two compounds. A mechanism is not necessary, but all reagents, solvents, intermediates and co-products, as well as reaction conditions, must be shown. Use reactions that you have seen in this course this semester.



OR

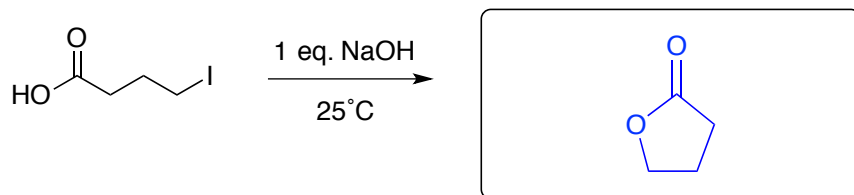


10. **Short answer questions. (15 points)**

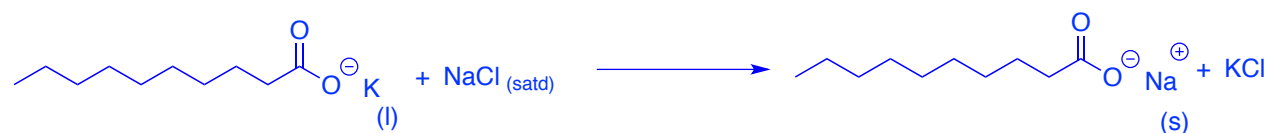
a) To what phase is Na_2SO_4 added during an extraction? (1 point)

The organic phase.

b) Determine the product of the following reaction. (1 point)

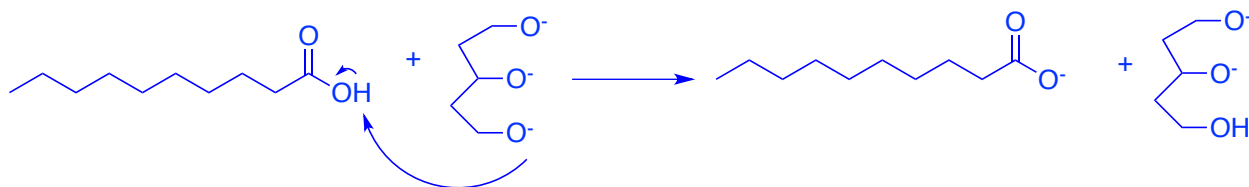


c) How can you convert a soft soap into a hard soap? Use an equation to illustrate the change that is occurring. (2 points)



The long alkyl chain should be shown, but we can accept R. No eqm arrow.

d) Why is saponification with NaOH considered an irreversible reaction? Show with an equation. (2 points)



Acid/base chemistry in the last step. Alkoxide RO^- is a much stronger base than the carboxylate, abstracting the proton and irreversibly forming the carboxylate and the alcohol.

e) Briefly explain how sublimation with a cold finger works to purify a compound. (2 points)

*Compound volatilizes to gas phase in a closed environment (Erlenmeyer) and **condenses on cold finger**, while impurities remain in solid or liquid phase at the bottom of the flask. Sublimation is effective when the **compound sublimates while impurities do not**.*

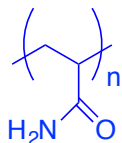
f) After dissolving your crude product in hot ethanol and allowing it to cool slowly at room temperature, no crystals have formed. Suggest three techniques to induce crystallization. (3 points)

- i. Place flask on ice
- ii. Scratch glassware with rod or add a seed crystal
- iii. Add a co-solvent

g) Between Br⁻ and I⁻, which ion performs as a better nucleophile in ethanol? Why? (1 point)

*I⁻ is more nucleophilic in polar solvents because nucleophilicity increases down the periodic table, and because larger ions **are solvated less strongly** than smaller ions.*

h) Give the structure of polyacrylamide. (1 point)



i) What does it mean when Benedict's reagent turns red? Give one example of a reactant that would cause this observation. (2 points)

*When the solution turns red, it means that a **reducible sugar is present**. Sugar with a hemi-acetal*

Ex. Glucose, lactose, galactose, fructose, ribose, maltose, starch, etc.

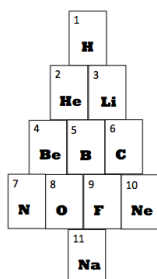
NOT sucrose.

j) What was your favorite experiment this semester and why? (1 point BONUS)

Any

k) What is **the best** holiday movie? (1 point BONUS)

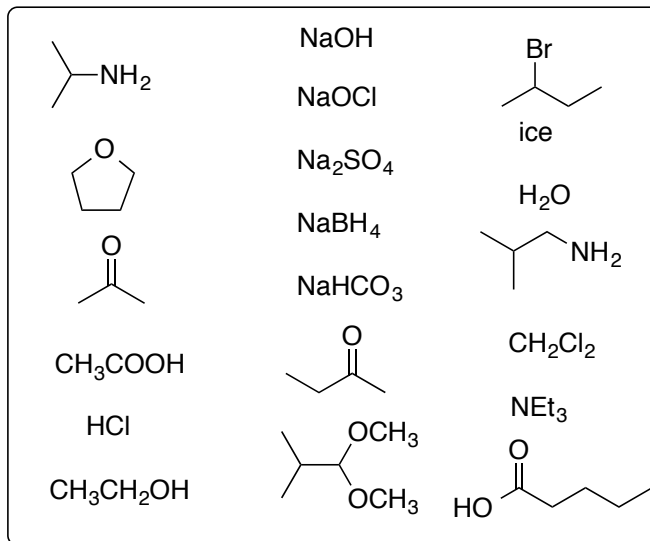
Any



O'Chemistry!

*Best wishes with all of your final exams.
Happy holidays and all the best in the new semester!*

Reagent Box



¹H NMR

