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**CHM 2123 ORGANIC CHEMISTRY LABORATORY**  
**WHITE COPY MIDTERM EXAM – NOVEMBER 2015**

Professor: Katherine McGilvray

Date: Saturday, November 14<sup>th</sup>, 2015 9:30 - 11:00

Check to see that  
your exam contains  
9 pages

Name: \_\_\_\_\_

Section: \_\_\_\_\_

Student #: \_\_\_\_\_

Your TA: \_\_\_\_\_

***Any sections written in PENCIL will NOT be eligible for re-correction.***

QUESTION	POINTS	RESULT
1	10	
2	3	
3	3	
4	11	
5	14	
6	10	
7	8	
<b>TOTAL</b>	<b>58</b>	

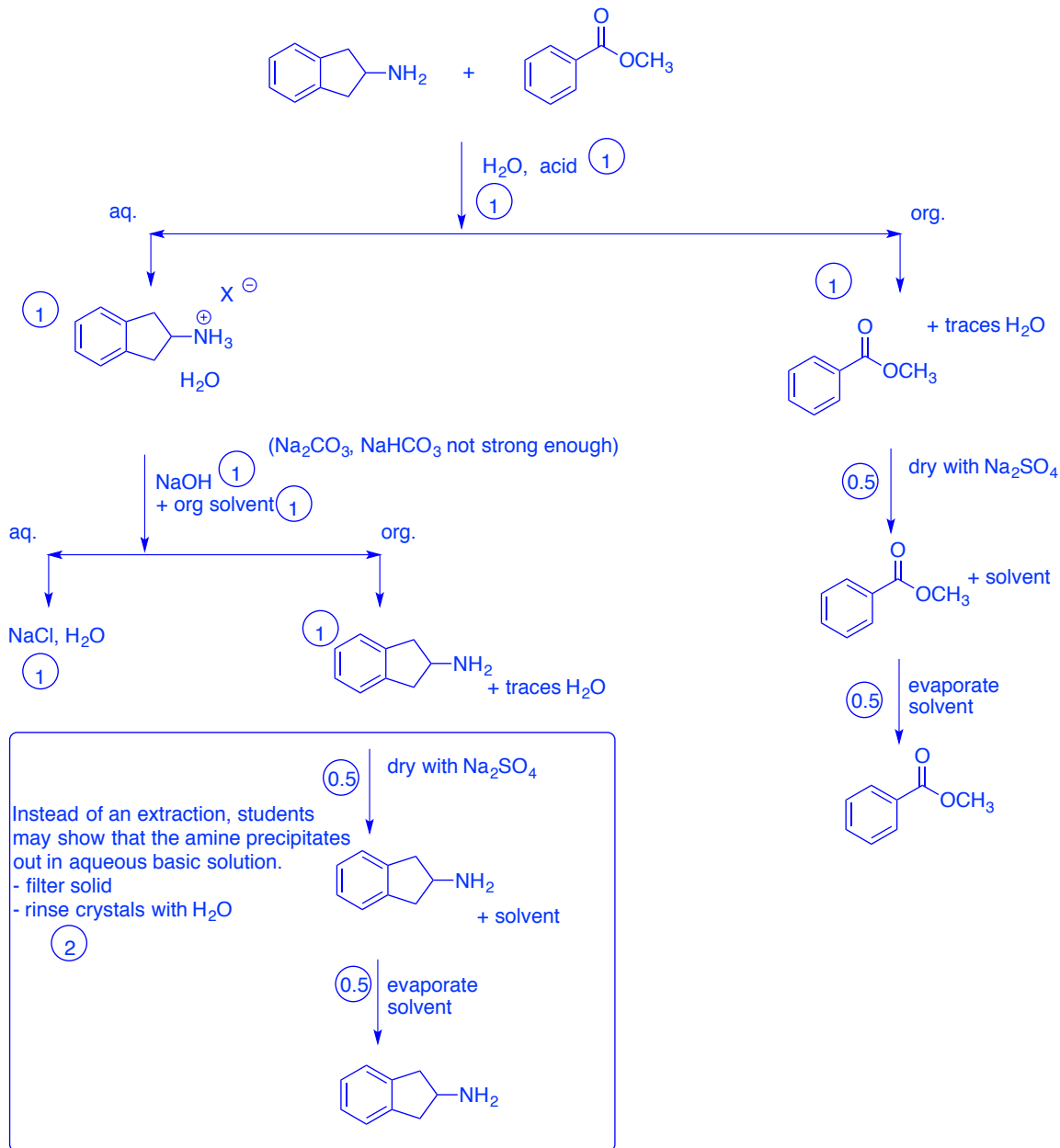
*Good luck!!!*

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

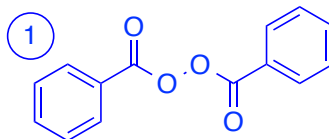
(Signature) \_\_\_\_\_

1. (10 points) Separations. Using a **flowchart**, provide a method for the separation of the following mixture of compounds in dichloromethane. Isolate each compound in their **crude form**. (Recrystallization not necessary).

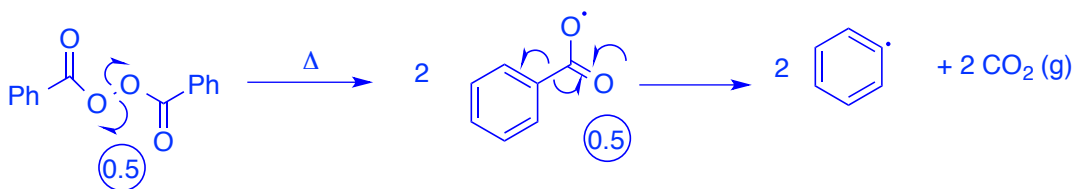


2. **Polymerization (3 points)**. In the synthesis of polystyrene-maleic anhydride, benzoyl peroxide was used to initiate the reaction.

a) What is the structure of benzoyl peroxide? (1 point)



b) Give the mechanism for the radical initiation of benzoyl peroxide. (1 point)

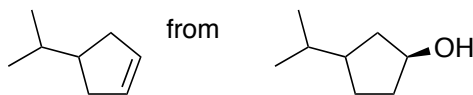


c) During the polymerization of acrylamide in water, a solution of ammonium persulfate was used as a radical initiator. Why could benzoyl peroxide not be used in that experiment? (1 point)

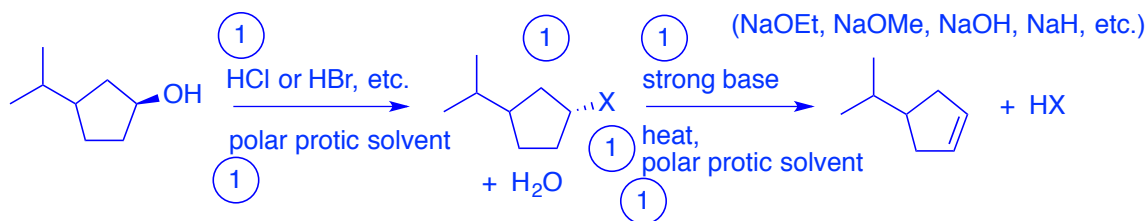
It is not soluble in aqueous media.

3. (3 points) (This question was meant to be worth 6 points. Now 3 BONUS points)

You are asked to synthesize

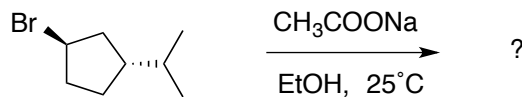


One technique involves using concentrated  $\text{H}_2\text{SO}_4$  and heat. Suggest an alternative approach. Provide a reaction scheme for your approach, which includes **all reagents, solvents, reaction conditions, and intermediates** formed in the transformation. A mechanism is NOT necessary. (6 points)

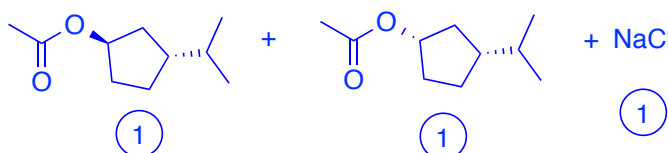


R-OH is a poor leaving group. It can be transformed into a better leaving group via acid,  $\text{TsOH}$ ,  $\text{POCl}_3$  in pyridine, etc.

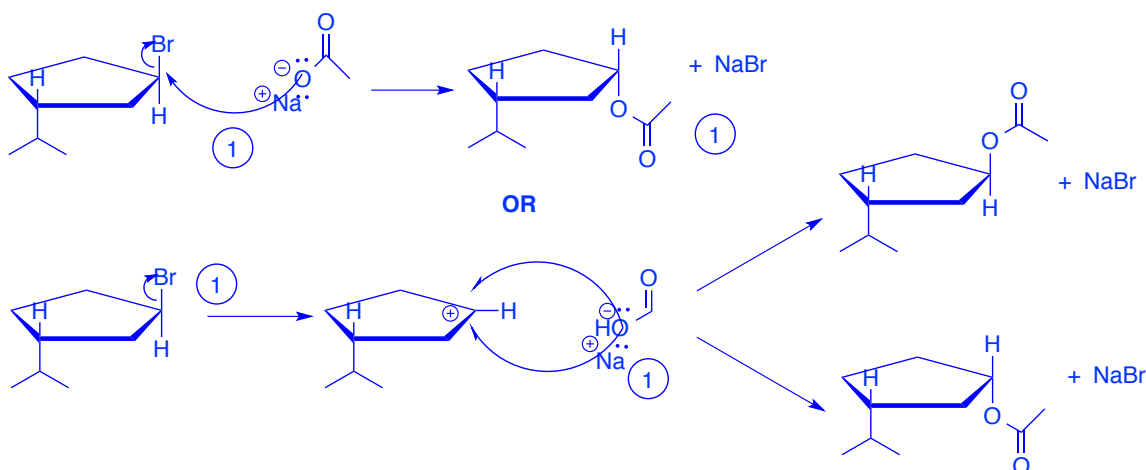
4. Mechanistic and kinetic analysis of reactions (11 points)



- a) Indicate the possible substitution product(s) and byproducts of the reaction illustrated above. (3 points)



- b) Provide one mechanism for the reaction listed above. (2 points)



- c) Based on what you have learned and performed in this course, briefly describe an experimental protocol (120 minutes max.) that could allow you to determine the mechanism of the reaction. (5 points)

1. Monitor the loss of  $\text{CH}_3\text{COO}^-$  over time to determine kinetics
2. Set the experiment up with  $[\text{R-Br}] = [\text{CH}_3\text{COONa}]$
3. Titrate aliquots with HCl at regular time intervals, OR set up 3-5 reactions of different concentration of acetate and HCl and indicator to observe colour change at % completion
4. Plot data:
  - a)  $\ln[\text{CH}_3\text{COO}^-]$  vs.  $t = 1^{\text{st}}$  order (SN1)
  - b)  $1/[\text{CH}_3\text{COO}^-]$  vs.  $t = 2^{\text{nd}}$  order (SN2)
5. Line of best fit will indicate the reaction mechanism as SN1 or SN2.

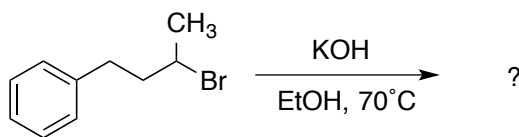
d) Explain how you could use  $^1\text{H}$  NMR spectroscopy to validate your mechanistic findings? (**BONUS point**)

Diastereomers will show two different peaks.

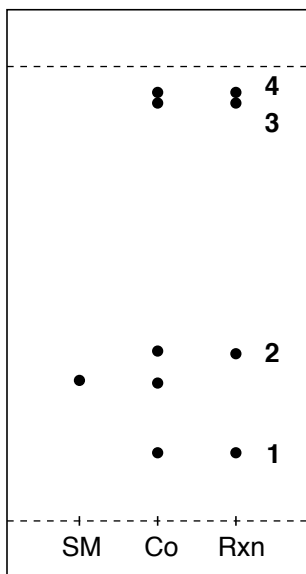
(If the mechanism is  $\text{SN}1$ , two signals for the hydrogens bonded to the carbon bonded to the acetate for the two diastereomers.

If the mechanism is  $\text{SN}2$ , one single signal.)

5. (**14 points**) A student performed the following experiment, and analyzed their reaction mixture by TLC.

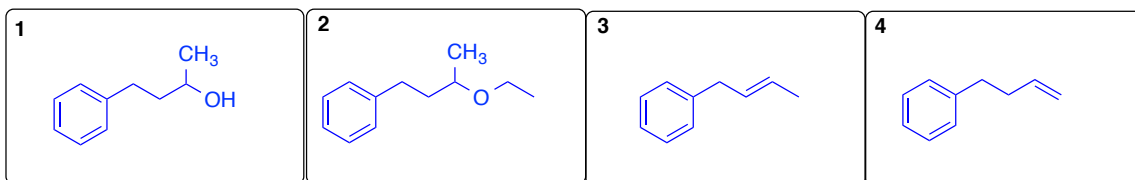


a) They observed the following TLC plate. Determine the  $R_f$  values for spots 1 and 2. (**1 point**)



**1:**  $1/6 = 0.17$  **2:**  $2.3/6 = 0.38$  (**0.5 each**)

b) Propose structures for compounds 1-4. (**4 points**)



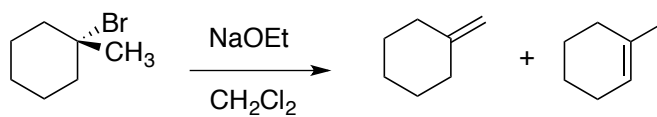
c) Explain your rationale behind products 1 – 4. (Do not discuss TLC theory here). ( **4 points**)

1. Is an SN2 product with –OH as a nucleophile.
2. Is an SN2 product with EtO<sup>-</sup> as a nucleophile when EtOH undergoes acid/base equilibria with KOH.
3. The Zaitsev E2 product, formed favorably. Cis and trans both possible, R<sub>f</sub> values essentially identical.
4. The Hoffman E2 product, likely the minor product with KOH as a base.

d) With your knowledge of TLC theory, rationalize the relative order and R<sub>f</sub> values of compounds **1 – 4** on the silica plate. ( **5 points**)

1. Most polar and most hydrogen bonding. Alcohol participates both as a hydrogen donor and a hydrogen acceptor when interacting with the silica on the plate.
2. Less polar and less hydrogen bonding, for the ether oxygen can only participate as a hydrogen acceptor when interacting with the plate.
3. Significantly less polar, where no hydrogen bonding takes place.
4. Least polar due to weakest dipole moment. No hydrogen bonding with the plate.
5. The more polar and the more hydrogen bonding a molecule can partake in with the plate, the smaller the R<sub>f</sub> value and the lower its position on the silica plate

6. ( **10 points**) A student performed a reaction whereby she combined 0.9 mL of 1-bromo-1-methylcyclohexane (132.63 g/mol, 1.30 g/cm<sup>3</sup>) in a 25 mL round bottom flask with 12 mL dichloromethane (84.93 g/mol, 1.33 g/cm<sup>3</sup>). The student then added 1.3 g sodium ethoxide (68.05 g/mol), added a stir bar, and proceeded to reflux the reaction for 45 minutes with rapid stirring. The reaction was then cooled to room temperature, at which point the mixture was transferred to a separatory funnel. The reaction mixture was washed three times with 10 mL of water (18.1 g/mol, 1.0 g/cm<sup>3</sup>). The organic phase was separated and 1.8 g Na<sub>2</sub>SO<sub>4</sub>(142.04 g/mol) was added and stirred. The mixture was filtered by gravity filtration. The products were isolated by distillation to afford 0.10 mL methylene cyclohexane (96.17 g/mol, 0.81 g/cm<sup>3</sup>) and 0.76 mL of 1-methyl-1-cyclohexene (96.17 g/mol, 0.80 g/cm<sup>3</sup>).



- a) Construct a table of reagents for this synthesis with the necessary materials. (4 points)

Compound	MW (g/mol)	Density (g/cm <sup>3</sup> )	Amount	mmoles	Equivalents
1-bromo-1-methylcyclohexane	132.63	1.30	0.9 mL	8.8	1.0
NaOEt	68.05	-----	1.3 g	19.1	2.2
CH <sub>2</sub> Cl <sub>2</sub>	84.93	1.33	12.0 mL	187.91	-----
		blank			
		blank			

(1 pt for each correct row, 0.5 pts for each blank row)

- b) Why was the mixture washed with water? (1 point)

To remove unreacted NaOEt as well as NaBr formed from the neutralization of the HBr formed in the reaction mixture.

- c) Determine the conversion of the reaction. (3 points)

$$(0.1 \text{ mL} \times 0.81 \text{ g/mL}) / 96.17 \text{ g/mol} = 0.84 \text{ mmol methylene cyclohexane}$$

$$(0.76 \text{ mL} \times 0.80 \text{ g/mL}) / 96.17 = 6.32 \text{ mmol 1-methyl-1-cyclohexene}$$

$$0.84 + 6.32 / 8.8 = 81.4\% \text{ conversion}$$

- d) Determine the selectivity of the reaction. (2 points)

$$0.84 + 6.32 = 7.16 \text{ mmol}$$

$$0.84 / 7.16 = 11.7\% \text{ methylene cyclohexane}$$

$$6.32 / 7.16 = 88.3\% \text{ 1-methyl-1-cyclohexene}$$

7. Short answer:

a) With the reaction of 1-bromobutane with KOH in Ethanol, provide an experimental modification that could significantly improve the yield of butanol relative to other products. Briefly justify your answer. (2 points)

- Perform the reaction in acetone, a polar aprotic solvent. (1) Reducing the interactions of base with the solvent increases the nucleophilicity of the base, favoring SN2 reaction. (1)

OR

- Perform the reaction at lower temperature to favor SN2 while disfavoring E2. (1) The energy barrier of a typical E2 reaction is higher than that for an SN2. (1)

etc.

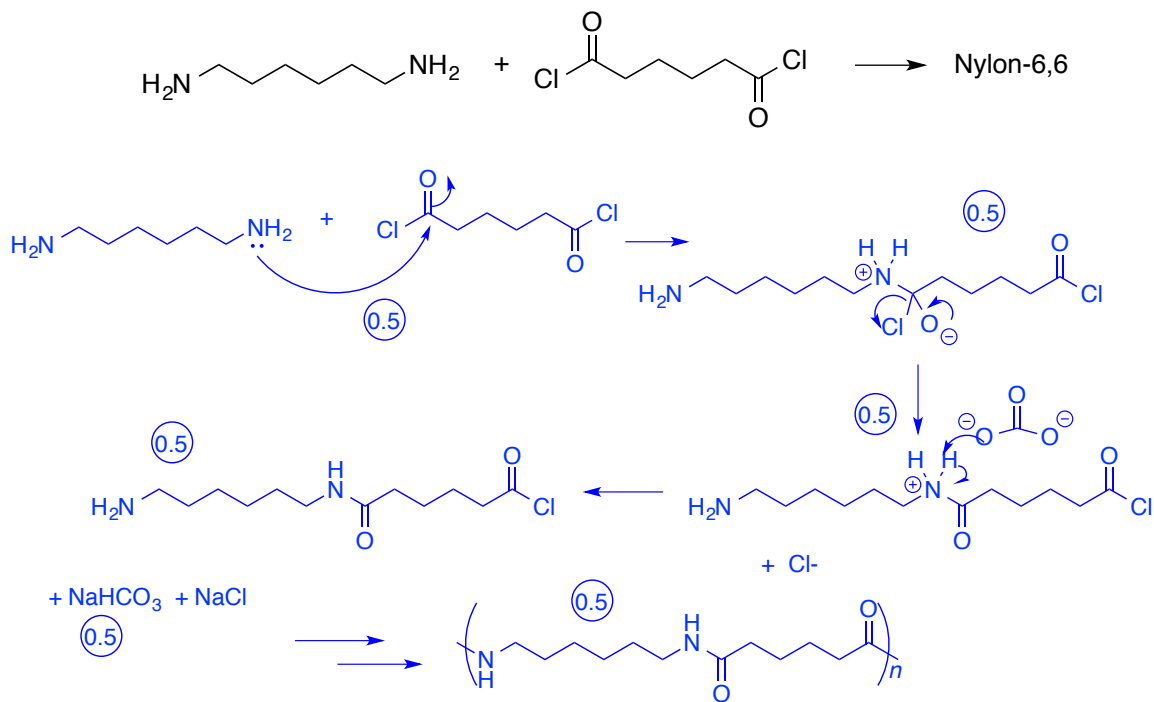
b) When determining if a compound can be purified by sublimation, what physical/chemical characteristic does the compound of interest need to possess? (1 point)

A substance with a **high vapour pressure** (ie. a substance that is volatile) will sublime easily at low temperatures.

c) In the isolation of caffeine from tea, what purpose did Na<sub>2</sub>CO<sub>3</sub> serve in the experiment? (1 point)

- deprotonate the polyphenols (0.5), and keep them in the aqueous phase (0.5)

d) Provide a mechanism for the condensation reaction of adipoyl chloride with hexamethylenediamine to produce Nylon-6,6. (3 points)



e) You run a TLC to assess the purity of caffeine before and after sublimation using 1:1 hexanes : ethyl acetate as your developing solvent, but you notice that your TLC shows both spots on the baseline. What can you do to improve the resolution? (1 point)

Increase the polarity of the mobile phase/ use a more polar solvent (solvent system).