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**CHM 2123 ORGANIC CHEMISTRY LABORATORY**  
**YELLOW 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  
8 pages

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

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

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

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

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

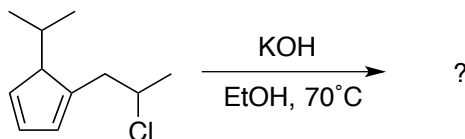
*Good luck!!!*

*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.*

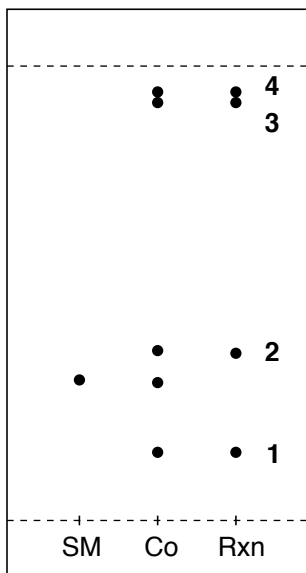
*By signing below, you acknowledge that you have ensured that you are complying with the above statement.*

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

1. A student performed the following reaction and observed their reaction mixture by TLC.

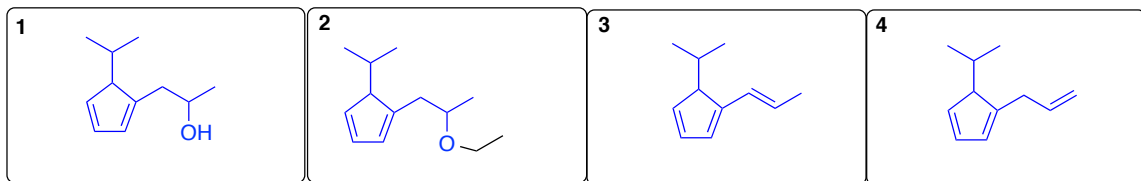


- a) a) They observed the following TLC plate. Determine the  $R_f$  values for spots 1 and 2. (1 point)



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

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



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

1. Is an  $S_N2$  product with  $-OH$  as a nucleophile.
2. Is an  $S_N2$  product with  $EtO^-$  as a nucleophile when  $EtOH$  undergoes acid/base equilibria with  $KOH$ .
3. The Zaitsev  $E2$  product, formed favorably. Mixture of *cis* and *trans* likely, indistinguishable by TLC.
4. The Hoffman  $E2$  product, likely the minor product with  $KOH$  as a base.

- d) d) With your knowledge of TLC theory, justify your assignment of compounds 1-4 to their placement on the TLC plate. (5 points)

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.

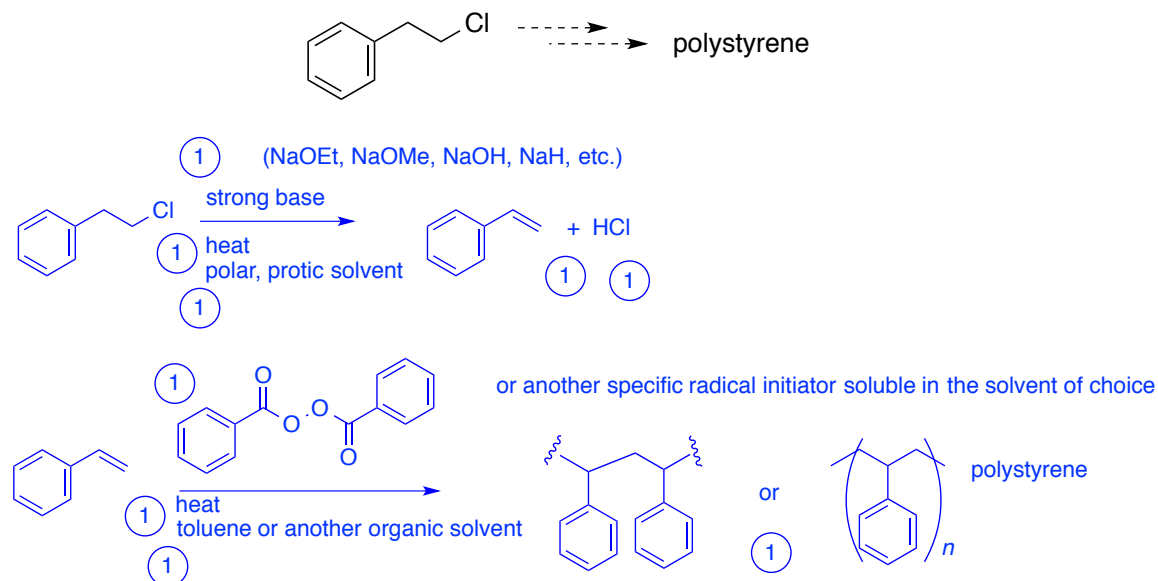
Less polar and less hydrogen bonding, for the ether oxygen can only participate as a hydrogen acceptor when interacting with the plate.

Significantly less polar, where no hydrogen bonding takes place.

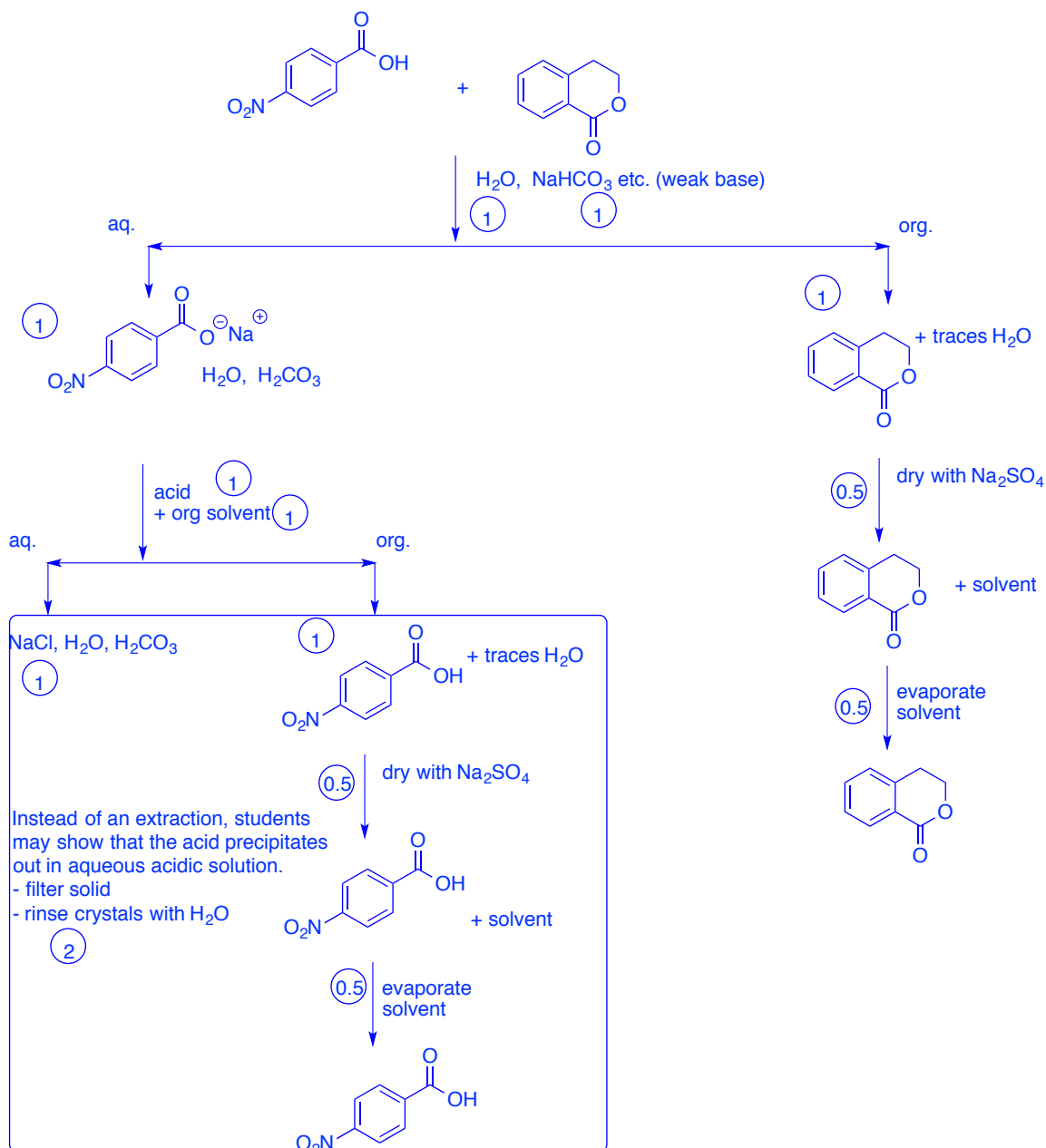
Least polar due to weakest dipole moment. No hydrogen bonding with the plate.

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.

2. **Polymerization. (6 points)** (This question was originally worth 9 points, but now has 3 bonus points). You are asked to synthesize polystyrene from 2-chloroethylbenzene. Provide a reaction scheme for your approach. Indicate all of the necessary reagents, solvents, reaction conditions, as well as intermediates formed in the transformation. A mechanism is not required.

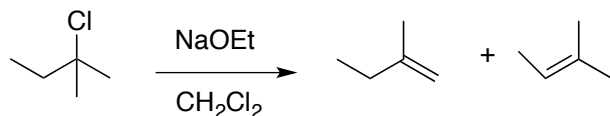


3. (10 points) **Separations.** Using a **flowchart**, provide a method for the separation of the following mixture of compounds in dichloromethane. Isolate each compound in their **crude form**. (Recrystallization not necessary).



4. (10 points) A student performed a reaction whereby she combined 0.9 mL of 2-chloro-2-methylbutane (106.59 g/mol, 0.87g/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 0.09 mL 2-methyl-1-butene (70.13 g/mol, 0.65 g/cm<sup>3</sup>) and 0.72 mL of 2-methyl-2-butene (70.13 g/mol, 0.66 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
2-chloro-2-methylbutane	106.59	0.87	1.0 mL	8.16	1.0
NaOEt	68.05	-----	1.3 g	19.1	2.34
CH <sub>2</sub> Cl <sub>2</sub>	84.93	1.33	12 mL	187.9	-----
		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 NaCl formed from the neutralization of the HCl formed in the reaction mixture.

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

$(0.09 \text{ mL} \times 0.65 \text{ g/mL}) / 70.13 \text{ g/mol} = 0.8 \text{ mmol 2-methyl-1-butene}$

$(0.72 \text{ mL} \times 0.66 \text{ g/mL}) / 70.13 \text{ g/mol} = 6.77 \text{ mmol 2-methyl-2-butene}$

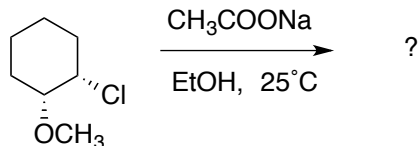
$6.77 + 0.8 = 7.57 \text{ mmol} / 8.16 \text{ mmol} = 93\% \text{ conversion}$

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

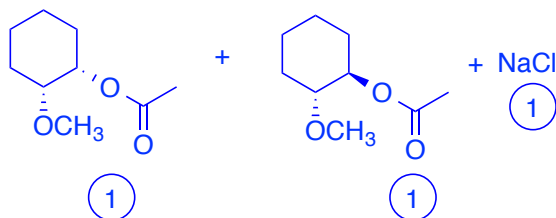
$0.8 / 7.57 = 10.6\% \text{ 2-methyl-1-butene}$

6.77 / 7.57 = 89.4 % 2-methyl-2-butene

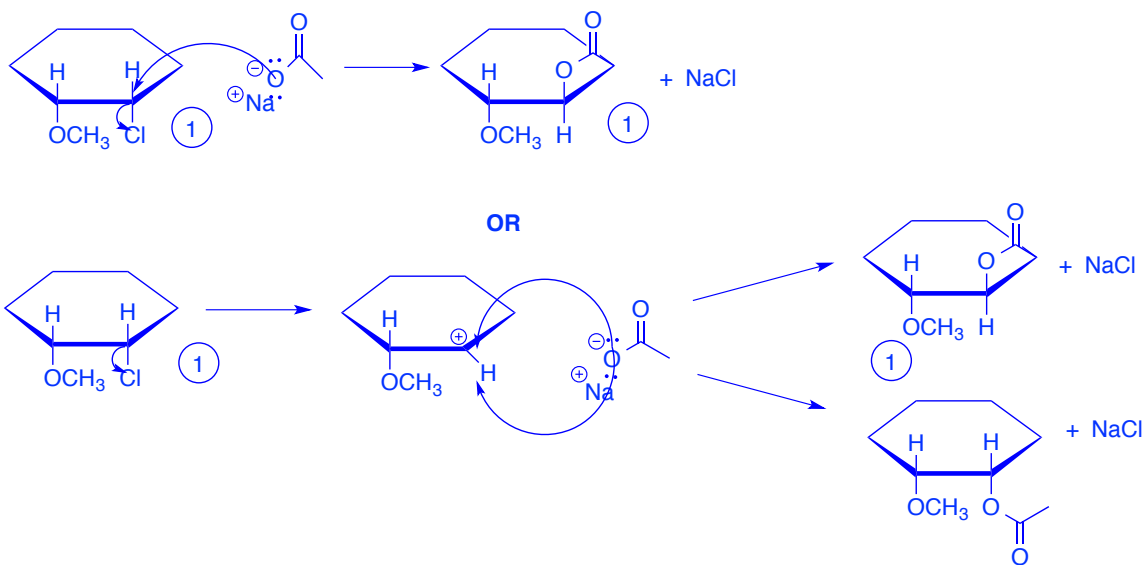
5. Mechanistic and kinetic analysis of reactions (11 points)



- 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 CH<sub>3</sub>COO<sup>-</sup> over time to determine kinetics

2. Set the experiment up with  $[R-Cl] = [CH_3COONa]$
3. Titrate aliquots with HCl at regular time intervals, OR set up 3-5 reactions of different concentration of acetate and NaOH and indicator to observe colour change at % completion
4. Plot data:
  - a)  $\ln[CH_3COO^-]$  vs.  $t = 1^{st}$  order (SN1)
  - b)  $1/[CH_3COO^-]$  vs.  $t = 2^{nd}$  order (SN2)
5. Line of best fit will indicate the reaction mechanism as SN1 or SN2.

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

Diastereomers will show two different peaks.

*(If the mechanism is SN1, two signals for the hydrogens bonded to the carbon bonded to the acetate for the two diastereomers.*

*If the mechanism is SN2, one single signal.)*

6. Short answer (**8 points**).

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

- Perform the reaction in acetone, a polar protic solvent. (A solvent must be specified) (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)

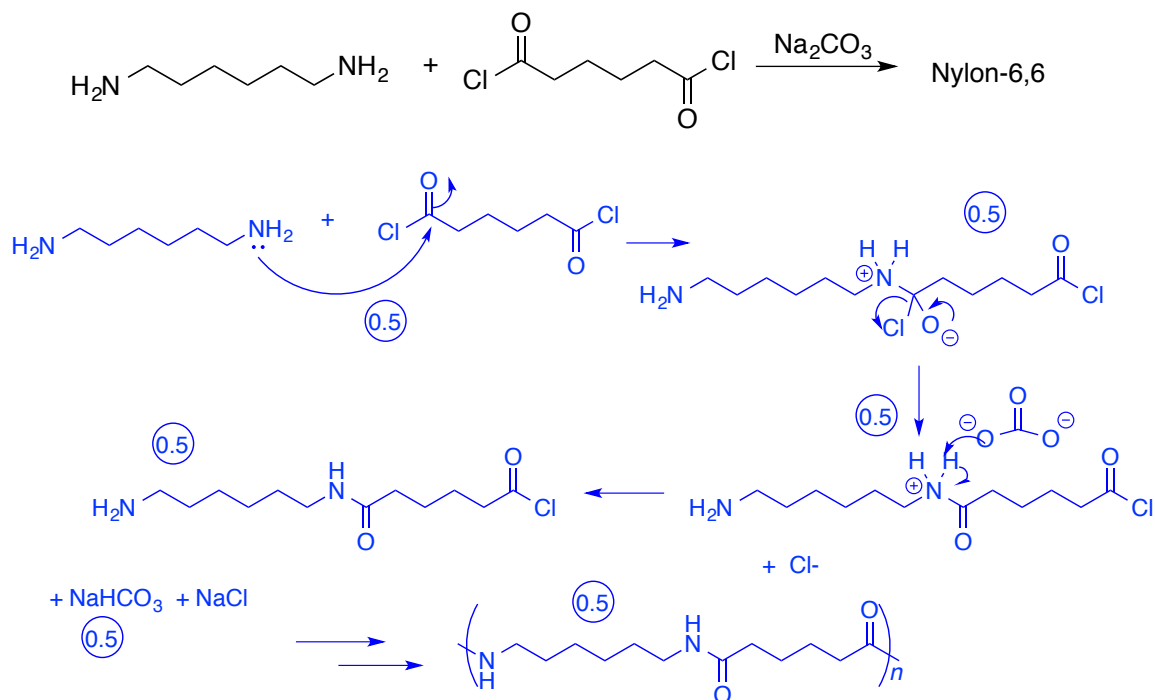
b) When determining if a compound can be purified by sublimation, what physical/chemical characteristic does the compound of interest need to possess? (**1 point**)

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  $Na_2CO_3$  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).