Basic Lab Procedure

S343 Handout 2

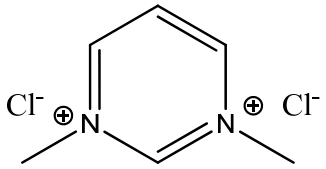
Questions from "Techniques in Organic Chemistry".

Chapter 10: Questions 1-5
Chapter 11: Questions 1-4
Chapter 12: Questions 3, 4
Chapter 14: Questions 1-2
Chapter 15: Questions 1-3
Chapter 18: Questions 1-3
Chapter 19: Questions 1-5
Chapter 20: Questions 1-6,8

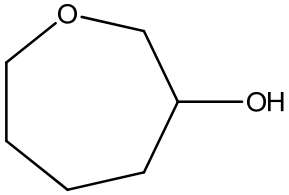
Problems:

1. You have obtained a mixture of the following compounds. Rank them from "most water soluble" to "least water soluble".

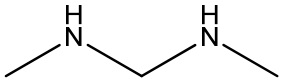
Compound A



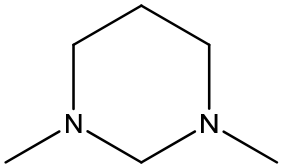
Compound B



Compound C



Compound D



Most water soluble _____ > _____ > _____ > _____ Least water soluble

2. If you performed an extraction with the mixture from problem 1, which compounds would you expect to be predominately in the organic layer in each of the following cases?

A. Extraction between ether and water
B. Extraction between ether and aqueous acid

3. True or false

_____ If too much recrystallization solvent is used, little or no recrystallization may occur even if the solution is cooled slowly and allowed to sit for a long period of time.

_____ In recrystallization, rapid crystal formation increases purity of the sample by not allowing impurities as much time to be trapped in the growing crystal lattice.

_____ The melting point of a pure, solid compound with weaker intermolecular interactions would be expected to have a relatively lower, but sharp and not depressed, melting point.

_____ If a mixed melting point between an unknown and known compound is conducted, it is reasonably safe to conclude that the two compounds are not identical if there is a melting point depression or the melting range is expanded by a number of degrees.

_____ Heating a melting point sample too quickly can lead to an inaccurate melting point, either higher or lower than the actual melting point, depending on the apparatus.

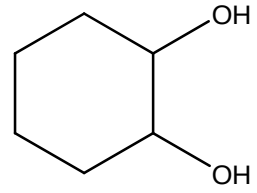
_____ Either drying agents or a rotovap are used to remove leftover solvent from the target compound.

4. The solubility of a compound is 59 g/100mL in boiling methanol and 30 g/100mL in cold methanol, whereas its solubility in water is 7.2 g/100 mL at 95°C and 0.22 g/100mL at 2°C. In this case, which would be a better recrystallization solvent, methanol or water?

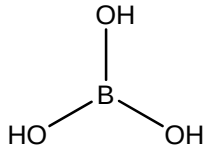
5. You have about 0.10g of naphthol impurity and your target compound dissolved in 200 mL of water. Knowing your target compound is very water soluble, but not very soluble in ether, you perform one extraction with 50 mL of ether. Will this be enough to extract most (90%) the naphthol into the ether? Show all calculations. (The partition coefficient is about 6.)

6. A student tried to synthesize 1,2-cyclohexanediol and ended up with boric acid as a byproduct of the reaction. In an attempt to separate the 1,2-cyclohexanediol, the student performed an extraction with water and ether. It didn't work. Explain.

1,2-cyclohexanediol



boric acid



7. What is the problem with using too much recrystallizing solvent? What is the problem with using too little recrystallizing solvent?

8. To determine the identity of a compound using melting points, a student thought it might be just as effective to make a sample of the unknown and a separate sample of the authentic and watch them melt right next to each other, rather than going through the hassle of making a mixed melting point sample. Is he right or wrong? Explain.

9. A student conducted an experiment transforming cyclohexanone into cyclohexanol. Halfway through the reaction, the student checked the progress with TLC using 2:1 hexanes:ethyl acetate. She saw two spots with $R_f = 0.4$ and $R_f = 0.6$.

a. Which spot is higher on the plate, $R_f = 0.4$ or $R_f = 0.6$?

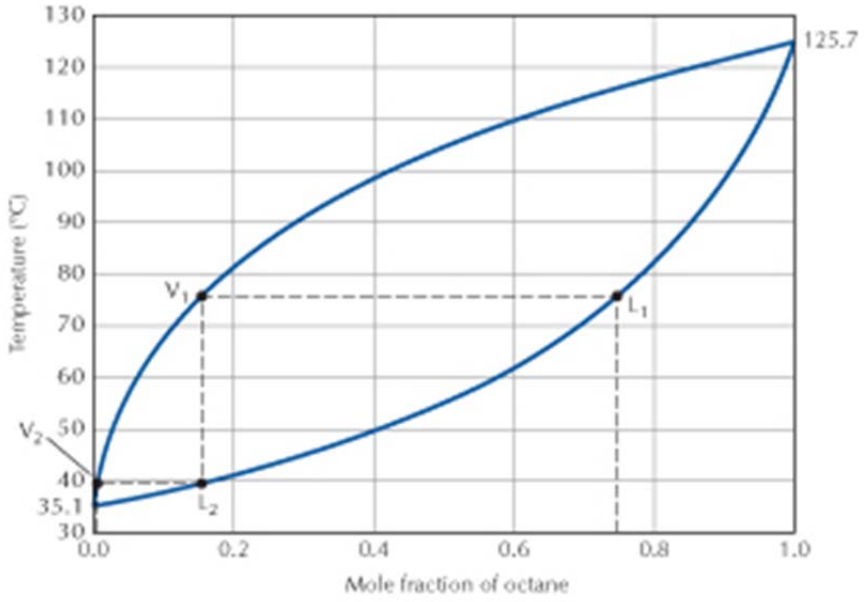
b. Which compound, the alcohol or the ketone, is more likely to be the compound with $R_f = 0.4$? Explain using physical principles.

c. If she wanted to move the spots just a little further up on the plate, which solvent should she use: 100% hexanes, 3:1 hexanes:EtOAc, 1:1 hex:EtOAc, 1:3 hex: EtOac, or 100% EtOAc?

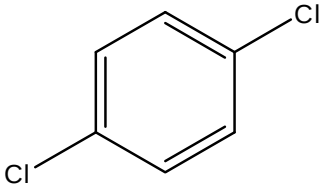
10. What are the advantages and disadvantages of fractional distillation versus simple distillation? When would you use each one?

11. Draw the apparatus used in simple distillation. Label all pieces and give their purpose.

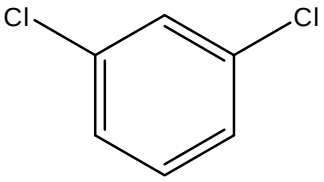
12. Explain in a paragraph what is physically happening in the distillation of a 75%/25% octane/pentane mixture starting at point L1. (Refer to Figure 12.6.)



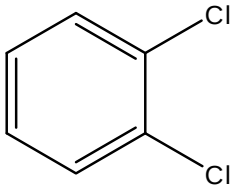
13. A student performed a reaction in organic laboratory that was designed to make about 2 grams of Product A. The reaction is also known to produce small quantities of Products B and C.



Product A
boiling point: 173 °C
melting point: 52 °C



Product B
boiling point: 173 °C
melting point: -25 °C



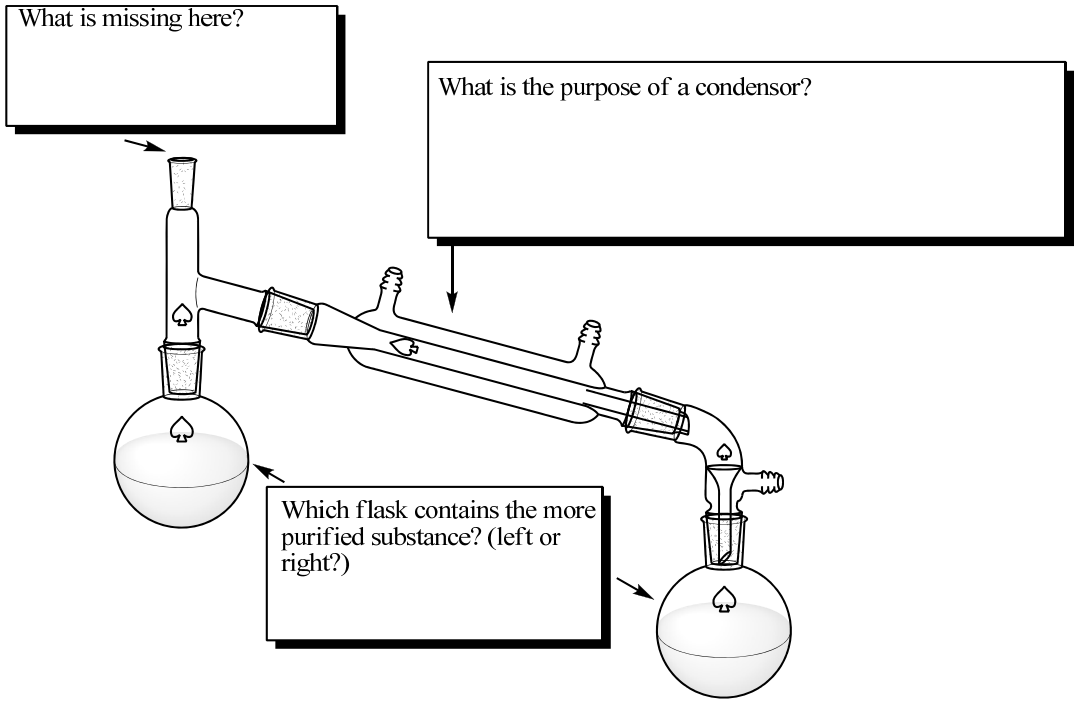
Product C
boiling point: 178 °C
melting point: -18 °C

a. Upon isolating the solid unpurified product, the student took a melting point, which was 41-49 °C. What does this data suggest about the purity of Product A? Explain the physical basis of depressed, broad melting points.

b. The student took a TLC of the crude product mix. How many spots would you expect to see if the product were purely Compound A? How many spots would you expect to see on a well resolved TLC plate if Compound A contains both Compound B and C as impurities?

c. Would fractional distillation be an effective way to purify this material? Explain.

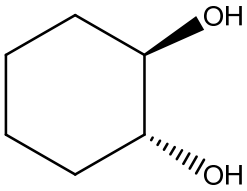
14. Refer to the drawing of a simple distillation:



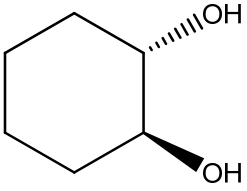
15. You performed a dihydroxylation reaction on cyclohexene, and you want to determine the stereochemical outcome of the reaction. You take a small amount of your crude product and dissolve it in pentane. You then inject 5 μL of the solution into a GC.

A. A giant peak comes out of the GC at a low retention time. What is the most likely identity of the compound that produces this peak?

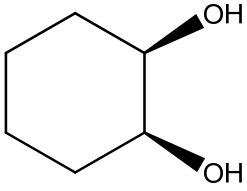
B. What are the stereochemical relationships between these products: same, enantiomer, diastereomer, or no relationship?



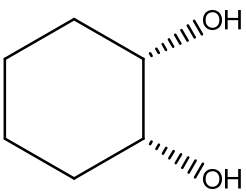
compound A



compound B



compound C



compound D

Compound A and B_____ Compound A and C_____

Compound B and C_____ Compound C and D _____

C. If the reaction produced all possible dihydroxylated products, how many peaks do you expect to see in your GC? Explain.

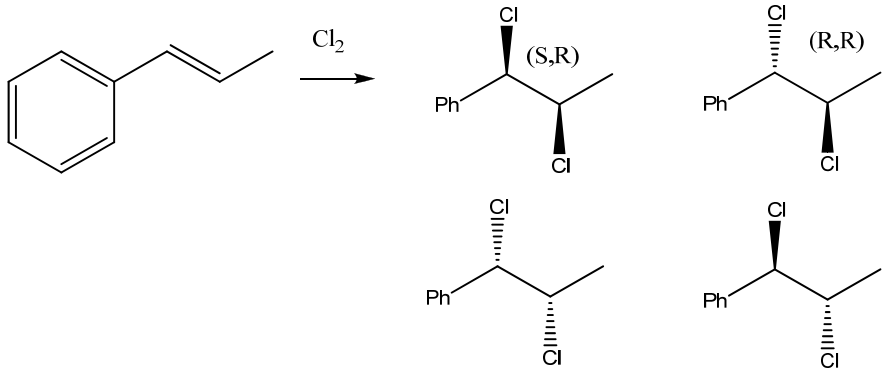
D. Can you get any information from GC data that you can't get from TLC that would make it worth the extra work to perform this procedure?

16. What is meant by a theoretical plate, and which has the most: GC, fractional distillation, or simple distillation?

17. Label these statements as “true” or “false”.

_____ Under a definite set of experimental conditions, a compound always travels through GC column in a fixed amount of time, called the response factor.
_____ In GC, the stationary phase consists of a column coated with a non-volatile liquid, usually a polymer, with a high boiling point.
_____GC is more limited than TLC in the sense that one is generally unable to analyze solid compounds by GC, whereas solid samples can be analyzed by TLC.
_____ In GC, the identity of a compound can be determined directly from the retention time even if no authentic sample is available.

18. A student carried out the following experiment to determine the stereochemical outcome of the addition. There are 4 possible products.



A student carried out a GC analysis of the reaction mixture and saw two peaks at retention times 1.34 minutes (area = 120) and 1.78 minutes (area = 80). In a second experiment, the sample was spiked with authentic (S,R) compound, and the GC scan showed that the peak at 1.34 minutes increased. In a third experiment, the sample was spiked with authentic (R,R) compound, and the peak at 1.78 min increased. According to this data, what is the product distribution for each of these compounds in the mixture. (If there is none detected, write 0%.) Show all work.