

Chem 51LB

Practical Review

Answer Key

Organic Chemistry Peer Tutoring Department

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<https://sites.edu/ochemtutors>

PRACTICAL BREAKDOWN

WEEK 9

Week 9: A and B Level Grades

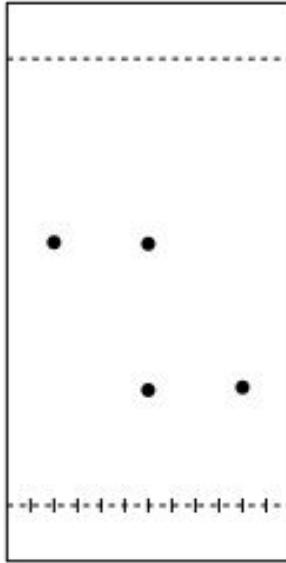
- Additional Techniques
 - TLC and Liquid/Liquid Extraction
 - Must complete both to get an A
 - Must complete 1 to get a B
- Mastery Final
 - Critical Thinking Questions

PRACTICAL BREAKDOWN

WEEK 10

Week 10: Everyone

- Knowledge Check - multiple choice high yield topics
 - Percent yield calculations, NMR and IR spectroscopy, etc
- Safety Scenario
 - know safety symbols
- Technique
 - Recrystallization
 - Know how to do calculate Percent Recovery

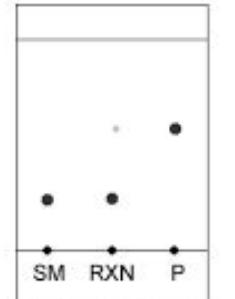


THIN LAYER CHROMATOGRAPHY

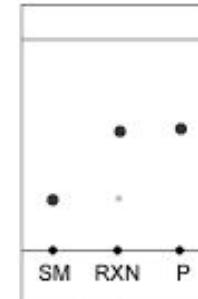
THIN LAYER CHROMATOGRAPHY: CONCEPTS

What is TLC?

- A visualisation technique using polarity of compounds to help us identify the components in an unknown sample
-



reaction just started;
little product has formed



reaction is done;
S.M. has been consumed

What information can you gather from TLC?

- The number of compounds present in a solution
 - Look at the number of spots in each lane
- Whether or not the reaction progressed to completion
 - Look for the presence of starting materials and products
- Determine the identity of an unknown compound ONLY by matching it to a known standard

HOW DOES TLC WORK?

TLC analysis separates compounds by their POLARITY

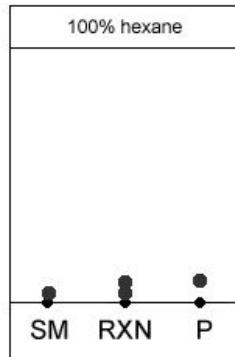
- Stationary phase: polar silica plate
- Mobile phase: the eluting solvent
- The mobile phase travels up the stationary state and carries the spotted compounds with it
- Because the stationary state is POLAR, the more POLAR compounds will interact more heavily with the plate than NONPOLAR compounds

So:

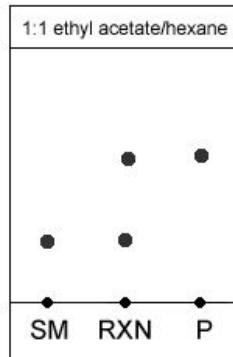
- Nonpolar compounds will usually travel farther up a plate than polar compounds
- Increasing the polarity of the solvent will cause all compounds to move up farther
 - For ex: increase the ratio of ethyl acetate:hexanes

TLC AND POLARITY

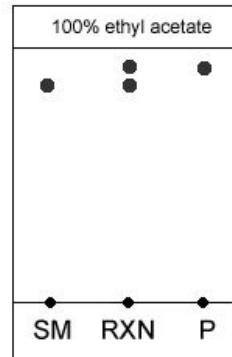
- Rf values of the spots should be between 0.2 and 0.8
- For a compounds that are more polar, using a more polar solvent such as 1:1 ethyl acetate:hexane will likely be the best option
- For compounds that are non-polar, using a more non-polar solvent such as 1:9 ethyl acetate: hexane or even 100% hexane may be the best option



too non-polar



just right



too polar

TLC PROCEDURE

1. Prepare an appropriate solvent and add about $\frac{1}{2}$ cm layer to the bottom of your chamber.
2. Mark your TLC plate with where you will spot the compounds and the origin about 1 cm above the bottom of the plate
 - a. Make sure to use pencil when marking TLC plates
3. Carefully spot your compounds with no more than 3 spots on 1 plate
 - a. Let the spot dry before spotting again
 - b. Careful not to make them too concentrated (1-2 spots should be good)
4. Place a piece of filter paper into the chamber
5. Put the plate into the chamber with tweezers, and make sure that your spots are not yet touching the solvent
 - a. Make sure the TLC plate is not touching the filter paper
6. Wait until the solvent has reached about 1 cm below the top of the plate
7. Carefully remove the plate and mark solvent front
8. Observe spotting and calculate Rf

Rf value = (distance spot traveled/height of solvent front)

TLC AND CO-SPOTTING

Co-spotting is a method used in which different solutions are spotted in the same lane to help determine the identity of the product

- Spot the standard for one possible compound in the unknown mixture in Lane A. In the same lane, spot the solution containing the unknown compound. If there is only one dark spot under the UV light, then you know that the standard spotted matches the identity of the compound.
- You can do the same with other standards in other lanes

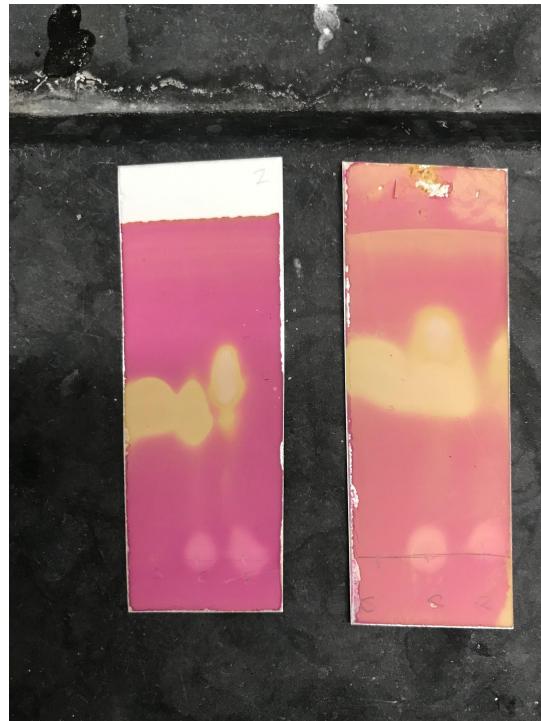
ON THE PRACTICAL

You will be given one of two possible tasks:

- (1) You will be given a solution containing two unknown compounds and will be provided with a set of 4-5 possible standards. Your job will be to determine the identity of the unknowns.
- (2) You will be given a set of known compounds and will be asked to determine what the best eluting solvent to visualize separated spots on a TLC plate would be.

A QUICK REVIEW

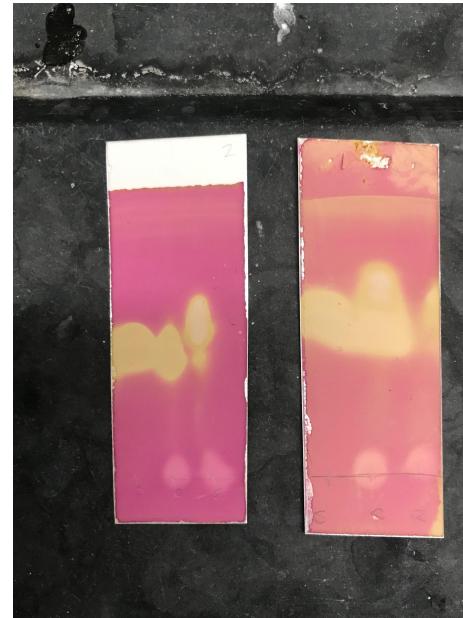
What can you conclude based on these plates? Do you notice any issues?



A QUICK REVIEW

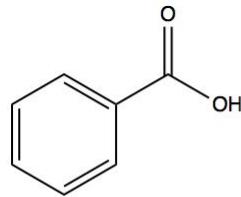
What can you conclude based on these plates?

1. The compounds seem to be very similar in polarity
2. They were spotted too close to each other
3. It is possible that the solvent moved too far up the second plate
4. The spots seem to be quite smeared, indicating that the solutions were spotted too many times or that the concentration of compound is too high

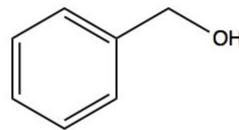


A QUICK REVIEW

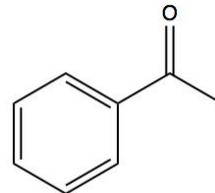
A TLC plate is spotted with the following compounds.



Compound 1



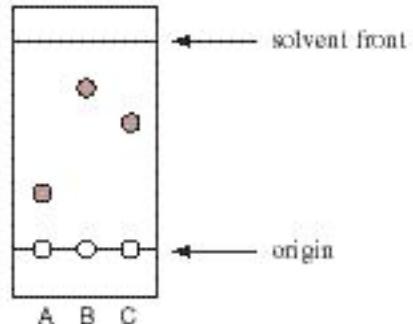
Compound 2



Compound 3

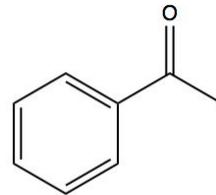
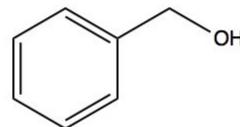
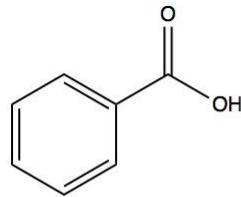
Determine which of the three compounds is spotted in lane C on the TLC plate:

- A) Compound 1
- B) Compound 2
- C) Compound 3



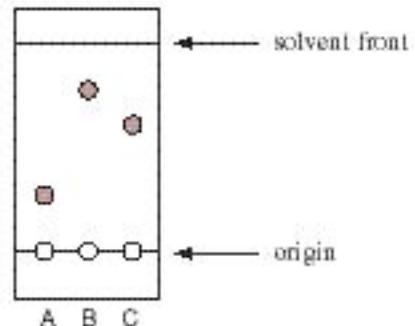
A QUICK REVIEW

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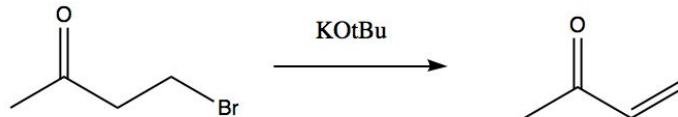
Determine which of the three compounds is spotted in lane C on the TLC plate:

- A) Compound 1
- B) Compound 2**
- C) Compound 3



CRITICAL THINKING PRACTICE

Chelsea and Jorge are analyzing the following reaction with TLC to determine if it has gone to completion.

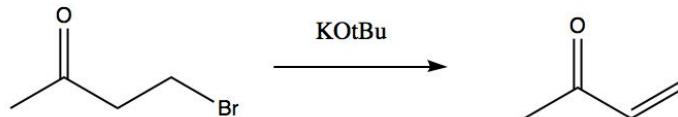


In their TLC analysis, they spotted lane 1 with reactant and lane 2 with their obtained product using a 1:1 hexanes:ethyl acetate solvent. Their plate showed that lane 2 had a noticeably higher spot than lane 1. Chelsea thinks that this means the reaction was successful because the product would be expected to elute higher. Jorge disagrees, saying that there must be significant unreacted starting material because polar compounds would move higher on a polar plate.

Who is correct, and why?

CRITICAL THINKING PRACTICE

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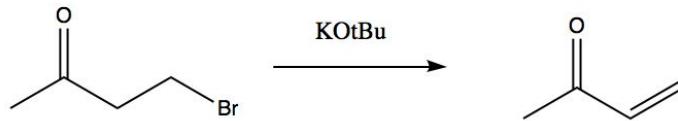


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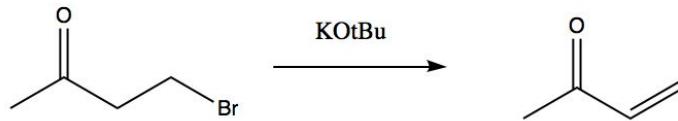
Chelsea is correct. The reaction's product is less polar than the reactant, so it would be expected to have a higher spot because it interacts less with the plate. Also, if lane 2 had unreacted starting material, the spot would be at the same level as in lane 1, not higher.

CRITICAL THINKING PRACTICE



What is one way to confirm that the reaction has gone to completion? (talk to your neighbor)

CRITICAL THINKING PRACTICE



What is one way to confirm that the reaction has gone to completion?
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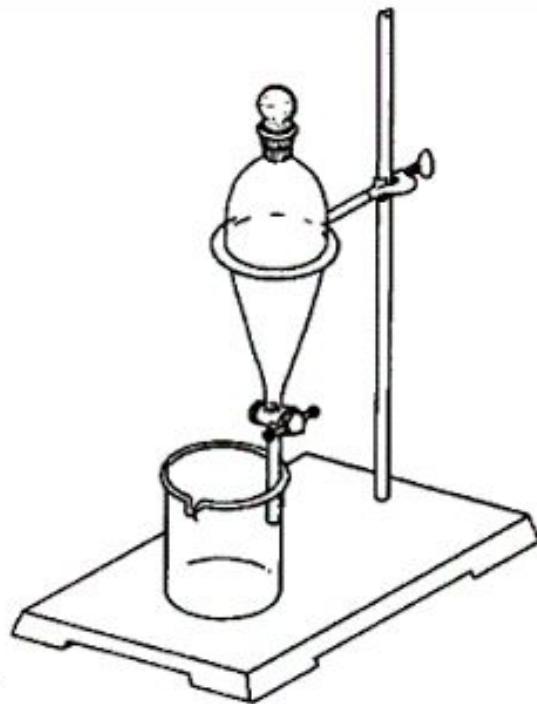
Spectroscopy Analysis

On H NMR look for:

- disappearance of 1 hydrogen next to a halogen
- Appearance of vinyl hydrogens (5-6 ppm)

On IR Spectrum look for:

- Appearance of an sp^2 C-H bond at $3000 - 3100 \text{ cm}^{-1}$



ACID-BASE EXTRACTION

ACID-BASE EXTRACTION CONCEPTS

What is it?

Acid-base extraction is a form of liquid-liquid extraction, a method of separation of two immiscible liquids based on different solubilities in organic and aqueous solvents.

- Organic Solvents: carbon-based
 - Diethyl ether, dichloromethane, etc
 - Usually nonpolar
- Aqueous Solvents: water-based solution
 - not carbon-based, and polar

What does it help you achieve?

- It helps you isolate compound(s)

HOW DOES ACID-BASE EXTRACTION WORK?

Extraction separates based on SOLUBILITY

Acid/Base Extraction

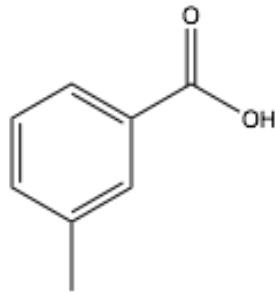
- When you have 2 compounds with similar solubility, you can add either an acid or a base to *selectively* deprotonate or protonate one of the compounds
- This will change that compound's solubility ONLY, allowing it to move into your other layer of solvent
- When you separate the layers of solvents, you will have both compounds isolated
- You can reverse the original acid-base reaction to precipitate your original compound

HOW DOES ACID-BASE EXTRACTION WORK? (CONT.)

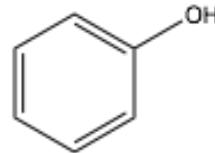
- When extracting with a base that will deprotonate an acid:
- The pKa of its conjugate acid must be higher than the pKa of one of the compounds (the one it will deprotonate) and lower than the pKa of the other compound (so it does not deprotonate that one).
- When extracting with an acid that will protonate a base:
- The pKa of the acid must again be between the pKas of the conjugate acids of the 2 bases you are trying to separate between.
- Only then will you be able to achieve selectivity.

A QUICK REVIEW

Which base is most appropriate to separate these 2 acids?



pKa ~ 5

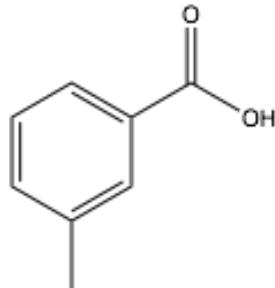


pKa ~ 10

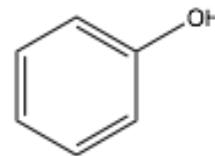
- a) OH^- (pKa~16)
- b) HCO_3^- (pKa~8)

A QUICK REVIEW

Which base is most appropriate to separate these 2 acids?



pKa ~ 5



pKa ~ 10

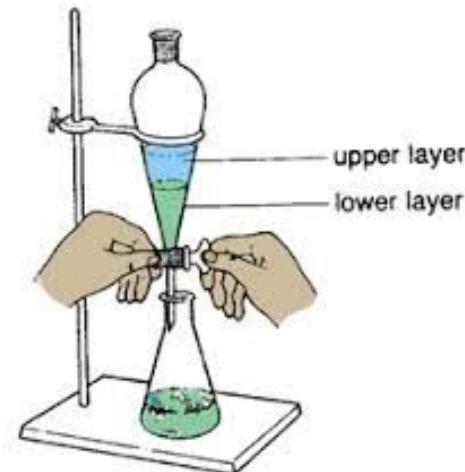
- a) OH^- (pKa~16)
- b) HCO_3^- (pKa~6.4)

Remember that the *pKa* of the base must be between the *pKa*'s of the 2 acids.

GENERAL PROCEDURES FOR ACID-BASE EXTRACTION

Separation

1. Dissolve mixture of compounds in organic solvent
2. Depending on the identity of the compounds, add either an acid or a base to the organic solvent
3. Pour the solution into a separatory funnel and turn the funnel several times. Wait until the solutions separate into distinct layers.
4. Pour out your aqueous layer into a labeled flask and your organic layer into another labeled flask



GENERAL PROCEDURES FOR ACID-BASE EXTRACTION (CONT.)

Recovery

1. For the organic solvent flask, add a drying agent. Then evaporate all of the solvent away to recover the compound you left dissolved in the organic solvent.
2. For the aqueous solvent flask, you need to reverse the acid-base reaction to isolate your original compound
 - a. If you added acid to the solution to separate the compounds, add a base this time to deprotonate the compound and cause precipitation
 - b. If you added a base to the solution to separate the compounds, add an acid this time to re-protonate the compound and cause precipitation
 - c. Allow crystallization to occur in an ice bath and do vacuum filtration to isolate crystals.

A QUICK REVIEW

Which layer will be on top when in the sep funnel with water?

1. Organic Solvent: dichloromethane (density = 1.33g/ml)
2. Organic solvent: diethyl ether (density = 0.706g/ml)

A QUICK REVIEW

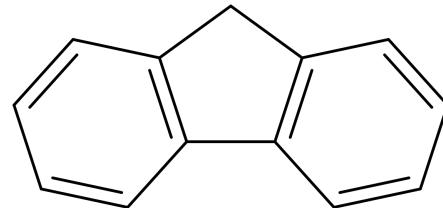
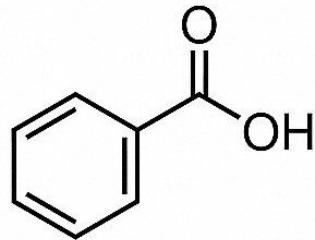
In each case, will the organic or aqueous layer be on the top in the sep funnel?

1. Organic Solvent: dichloromethane (density = 1.33g/ml) and water
2. Organic solvent: diethyl ether (density = 0.706g/ml) and water

Density of water is ~1.0g/ml. In case 1, the aqueous layer will be the top layer. In case 2, the organic layer will be the top layer.

ON THE PRACTICAL

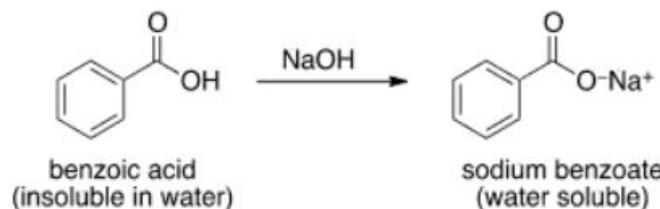
- You will start with benzoic acid and fluorene in an organic solvent (you have done this before!)
- Think about the solubility of benzoic acid and fluorene in an organic solvent or water



- Both compounds will be soluble in the organic layer, diethyl ether or dichloromethane

ON THE PRACTICAL (CONT.)

- Then add a strong base which will be able to deprotonate the acidic hydrogen on benzoic acid
 - Sodium hydroxide will be able to do this



- Deprotonated, benzoic acid is now a benzoate anion
 - Ions are very soluble in water!
- So, after mixing and venting, the benzoate ion should now be in the aqueous layer

ON THE PRACTICAL (CONT.)

At this point, you have two layers:

- (1) The organic layer containing fluorene
 - (a) Be sure to note the density of the organic layer and determine whether it is the top or bottom layer
- (2) The aqueous layer containing benzoate ion

Now, we need to bring back the benzoic acid!

After isolating the aqueous layer containing the benzoate ions, reprotoenate the compound using a lot of strong acid (likely HCl)

pH paper will be used to confirm the high acidity of the solution after adding HCl

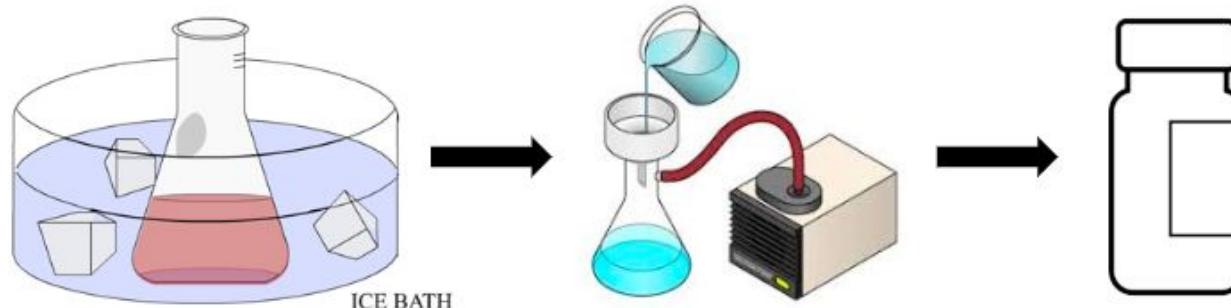
- Tip: use a pipette to drop a small amount of solution onto the pH paper as opposed to dipping the pH paper in the solution!



ON THE PRACTICAL (CONT.)

To obtain final product:

- Place the flask in an ice bath for 15 minutes (ideally) and wait for precipitate to form
- Once the precipitate has formed, isolate it using vacuum filtration
- Record the mass of the precipitate and place in scintillation vial and label the vial appropriately
 - Name, date, lab section, identification of product



QUICK REVIEW

How would you determine which layer is your aqueous layer and which is your organic layer in the sep funnel if you mix them up?

QUICK REVIEW

How would you determine which layer is your aqueous layer and which is your organic layer in the sep funnel if you mix them up?

Add 1 drop of water into the sep funnel and watch which layer it adds to. This is your aqueous layer.

QUICK REVIEW

What is the purpose of the drying agent?

- A) Add to the aqueous layer to remove any water contamination
- B) Add to the organic layer to remove any water contamination
- C) Add to the aqueous layer to remove contamination by organic product
- D) Add to both layers to remove excess acid or base

QUICK REVIEW

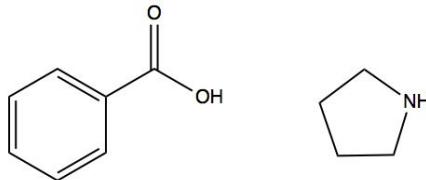
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LET'S LOOK AT AN EXAMPLE

Which of the following pairs of compounds can be separated by acid-base extraction; would you need to add acid or base?

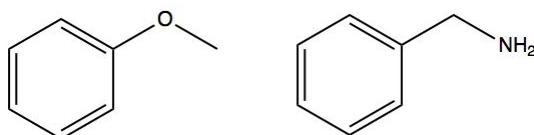
(A)



(B)



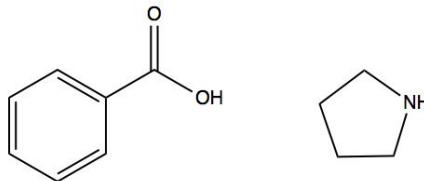
(C)



LET'S LOOK AT AN EXAMPLE

Which of the following pairs of compounds can be separated by acid-base extraction; would you need to add acid or base?

(A)



You can separate by adding a base to deprotonate the carboxylic acid on the first molecule.

LET'S LOOK AT AN EXAMPLE

Which of the following pairs of compounds can be separated by acid-base extraction; would you need to add acid or base?

(B)

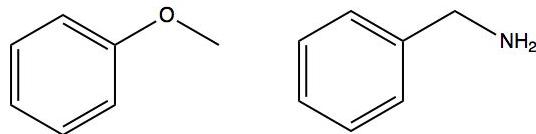


You cannot use acid-base extraction to separate these compounds. They are both alcohols and their pK_as are very similar. Additionally, using an acid in this case would protonate the alkene instead of the alcohol, and using a base would not be selective enough.

LET'S LOOK AT AN EXAMPLE

Which of the following pairs of compounds can be separated by acid-base extraction; would you need to add acid or base?

(C)



You can separate by adding an acid that would protonate the amine, which is highly basic.

CRITICAL THINKING PRACTICE

You are asked to determine the identity of a compound as compared to a set of standards during an organic chem practical. Seeing that you don't have much time left, you turn up the RAMP rate on the DigitMelt. The melting point of your product was 121 - 125 °C and the melting point of the final standard (Standard A) you are testing is 119 °C. You figure it is close enough, and claim that your product is the same compound as Standard A. Can you make this claim? Explain.

CRITICAL THINKING PRACTICE

You are asked to determine the identity of a compound as compared to a set of standards during an organic chem practical. Seeing that you don't have much time left, you turn up the RAMP rate on the DigitMelt. The observed melting point of your product was 121 - 125 °C and the melting point of the final standard (Standard A) you are testing for is 119 °C. You figure it is close enough, and claim that your product is the same compound as Standard A. Can you make this claim? Explain.

It is important to remember that the melting point of a product can never increase--an experimentally derived product will not be higher than its literature value. Melting point will never increase because the presence of any impurities in the product will disrupt the crystal lattice structure and less energy will be required to break the bonds of the structure (lower energy to break bonds = lower melting point). Thus, if the experiment was carried out at the proper RAMP rate and yielded these results, you could fairly confidently say that your product is NOT the same as Standard A. However, a faster than appropriate RAMP rate can cause the reading on the DigiMelt to be higher than the true value. So, because you do not have an accurate melting point measurement, you cannot make the claim that your product is the same as Standard A.

SAFETY REMINDERS

TLC

- Spotters go in glass waste
- Used plates go in solid waste

Extraction

- Put liquid waste in the correct container
- Label your glassware and clean it thoroughly

DONT BE NERVOUS

YOU GOT THIS