

+2
each

1. (20pts) Fill in the blanks below with one of the following words or phrases: extraction, IR spectroscopy, gas chromatography, recrystallization, mass spectrometry, melting point, fractional distillation, simple distillation, thin layer chromatography. Each phrase may be used more than once or not at all.

A. The best way to isolate a nonpolar liquid compound from a nonpolar solid would be

simple distillation. (+1 fractional)

B. TLC would be an effective, inexpensive way to determine the number of products formed in a reaction, but GC would serve the same purpose while also giving data to determine a product distribution.

C. MS and IR are techniques that can be linked to database libraries to help in identification of compounds.

D. Of all these techniques, GC has the most theoretical plates, and therefore the best separation of compound mixtures.

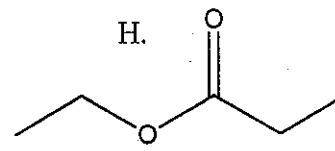
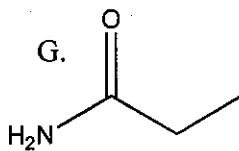
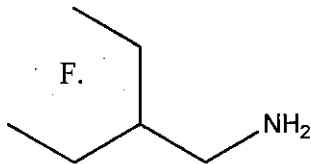
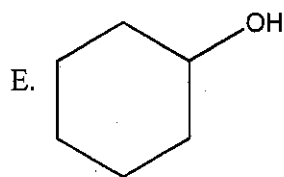
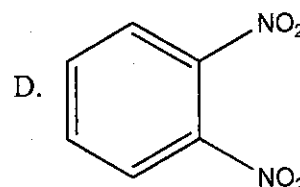
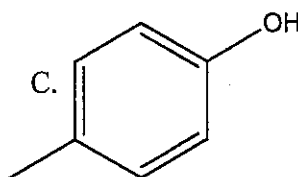
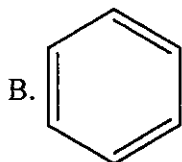
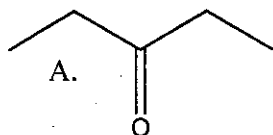
E. If an ~90% pure solid compound needs to be purified, the most effective means would be

recrystallization. Two techniques to analyze the success of your purification would be

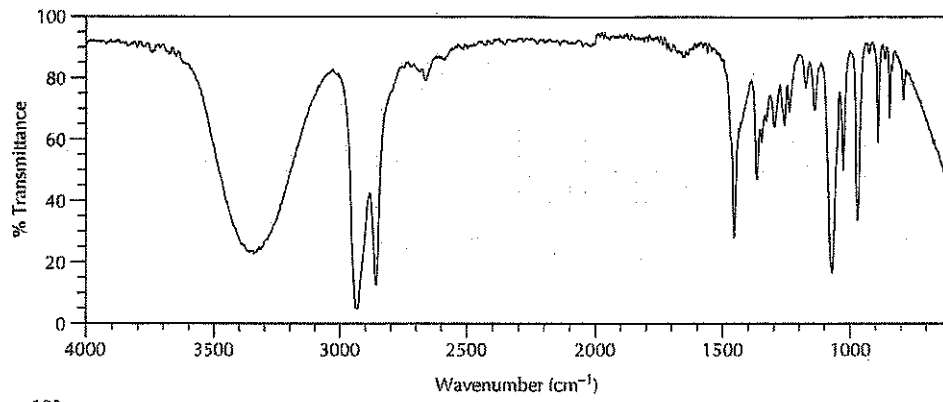
GC acceptable melting point and TLC.

F. In a reaction workup, the most effective crude purification would be extraction because you can often separate most of the solvents, starting materials, and byproducts from your intended product, especially if they are different in polarity from your target compound.

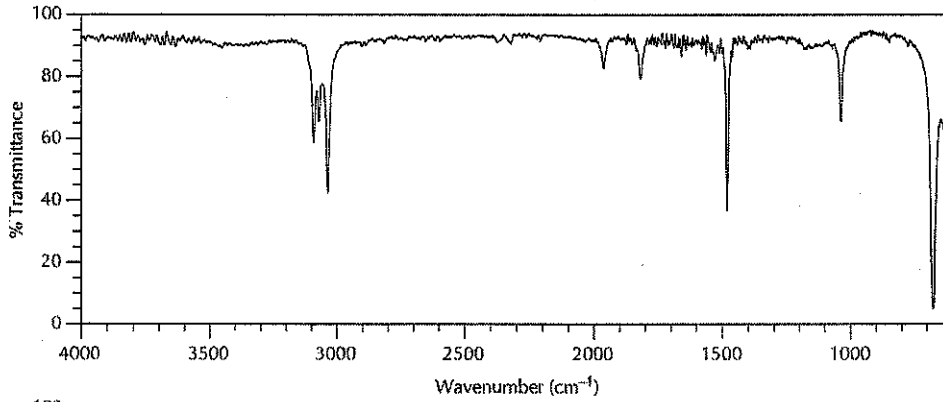
2. (15pts) On the next page are a number of IR spectra. Match the letter of the compound below with the IR spectrum that is most consistent.



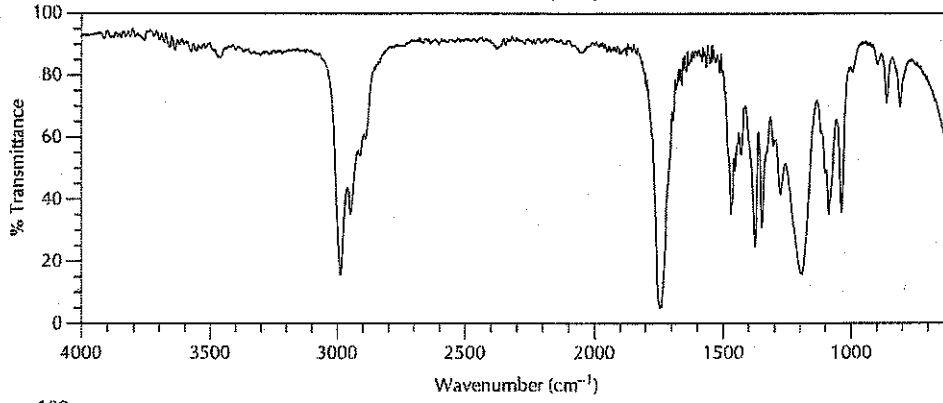
Answer: +3



E

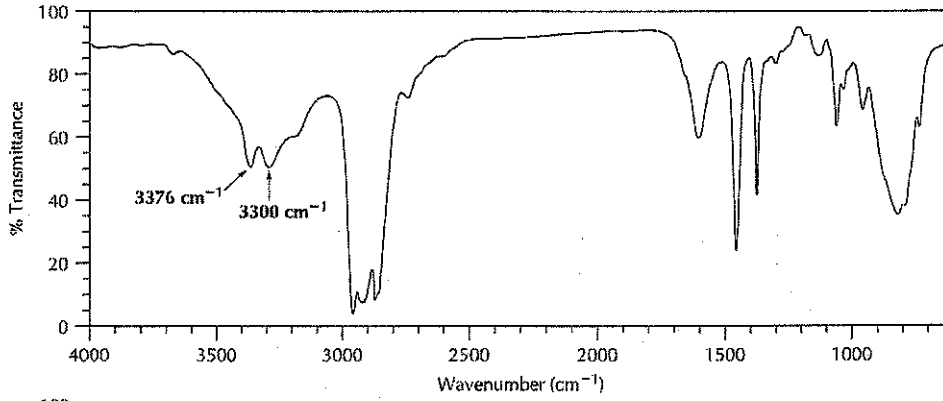


B

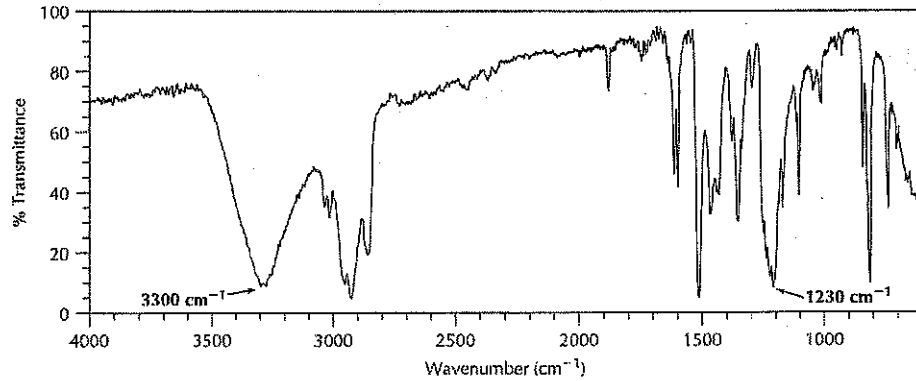


H

+2
A



F



C

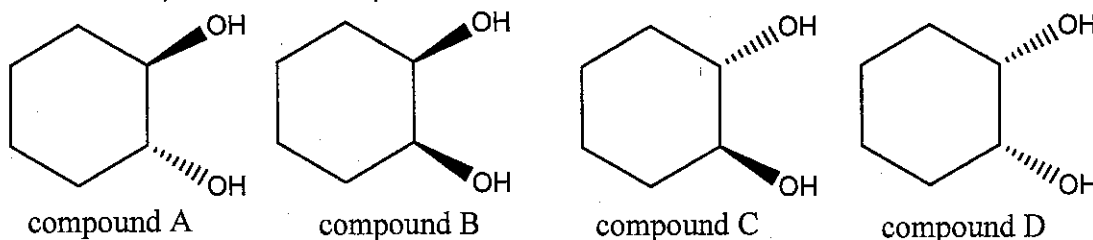
3. (20pts) The dihydroxylation lab that you performed was altered in the following way to obtain GC data: "After the reaction is complete, use a separatory funnel to extract the 1,2-cyclohexanediol with 1-butanol. Combine the 1-butanol extractions, dry the organic layer with magnesium sulfate, and filter the magnesium sulfate. Inject a 0.5 μ L sample of the extraction solution onto the GC, fitted with a polar column."

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?

+3

1-butanol

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



Compound A and B diastereomers Compound A and C enantiomers

Compound B and C diastereomers Compound C and D diastereomers

+1
each

C. An authentic sample of Compound A was run in the GC, giving a signal at a retention time of 2.145 minutes. An authentic sample of Compound B was run in the GC, giving a signal at retention time of 2.677 minutes. The GC of your reaction mixture gave these data: a peak with area 4501 at 0.732 minutes and a peak of area 499 at 2.144 minutes. Based on these data, give the product distribution of the reaction.

50 % Compound A 0 % Compound B 50 % Compound C 0 % Compound D

+2
each

D. Based on what you learned in the lab, these data are most consistent with which of the following:

Oxone reaction Permanganate Reaction Both reactions
 Neither reaction Can't be determined from these data

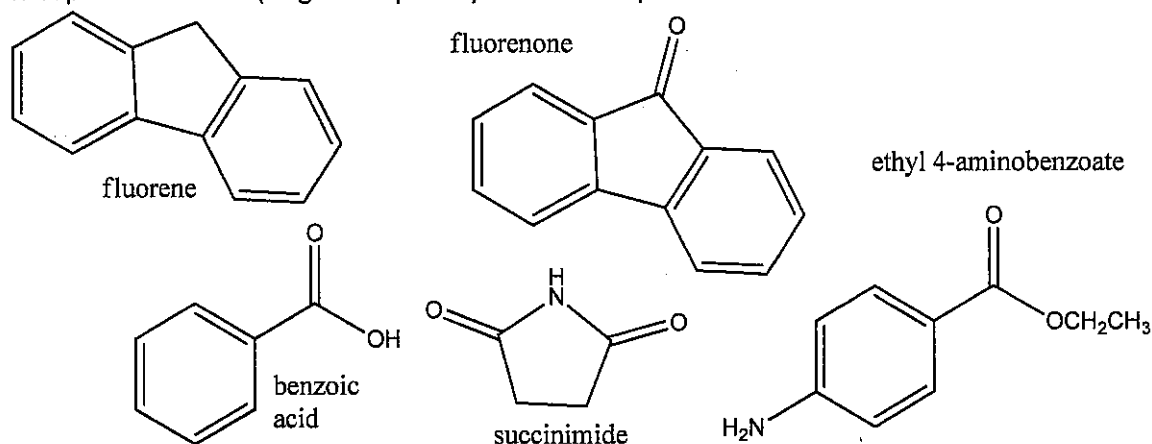
+2

Explain:

According to the data, the mechanism produces trans products. (In other words, this is an anti-addition.) That is consistent with Oxone.

+3

4. (32pts) A student conducted an extraction experiment just like yours, examining the best solutions to separate fluorene (target compound) from four impurities:



He also looked up these melting point data: benzoic acid, 122°C; ethyl 4-aminobenzoate, 88-90 °C; fluorene, 113-115 °C; fluorenone, 82-84 °C; succinimide 125-127 °C.

These are the melting point data he collected for each compound after extracting each 50/50 mixture of fluorene and impurity with dilute aqueous acid, dilute aqueous base, and neutral water.

	Ethyl aminobenzoate	Benzoic acid	fluorenone	Succinimide
Neutral	88-90 °C	88-90 °C	80-84 °C	112-114 °C
Acid	110-113 °C	88-95 °C	79-82 °C	112-114 °C
base	75-92 °C	111-114 °C	80-85 °C	113-115 °C

one point each

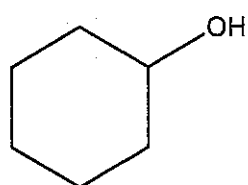
Based on these data, MARK WITH AN "X" ALL CORRECT ANSWERS that indicate which solvents were effective in extracting the impurity from fluorene, giving a predominately pure target compound.

- A. fluorenone: ___ Aq. HCl ___ Aq. NaOH ___ Water None
- B. benzoic acid: ___ Aq. HCl Aq. NaOH ___ Water ___ None
- C. Succinimide: Aq. HCl Aq. NaOH Water ___ None
- D. Ethyl 4-aminobenzoate Aq. HCl ___ Aq. NaOH ___ Water ___ None

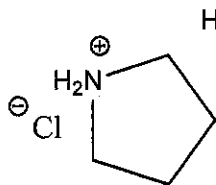
Based on these conclusions, indicate all solvents that you would expect to be effective in separating fluorene from these impurities:

- E. Compound 1 ___ Aq. HCl ___ Aq. NaOH ___ Water None
- F. Compound 2 Aq. HCl Aq. NaOH Water ___ None
- G. Compound 3 Aq. HCl Aq. NaOH Water ___ None
- H. Compound 4: ___ Aq. HCl ___ Aq. NaOH ___ Water None

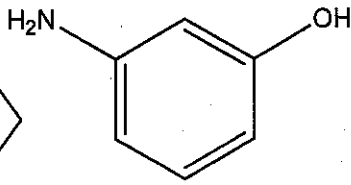
(X) = either acceptable



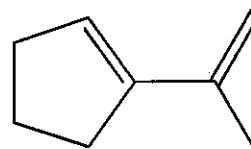
Compound 1



Compound 2

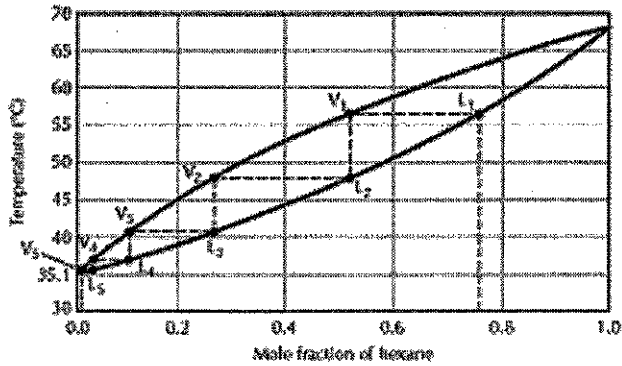


Compound 3



Compound 4

5. (16pts) Answer these questions based on the figure below, which describes the distillation of a 75% hexane/25% pentane mixture.



- +2 A. What is the boiling point of pure hexane? 67-68°C pure pentane? 35°C
 +2 B. According to these data, how many theoretical plates are necessary to separate (99%) a 75%/25% hexane/pentane mixture?

Five

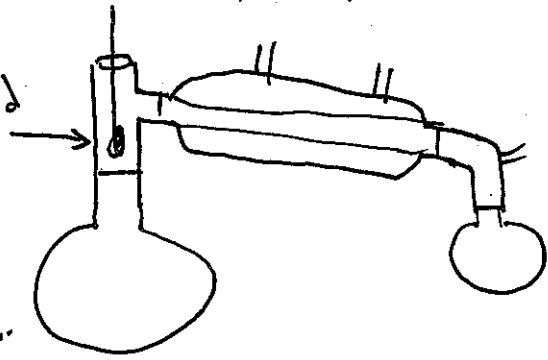
- +2 C. In the transition from point L₃ to point V₃ on this graph:
 a. The % composition of the mixture remains unchanged
 b. The liquid solution is vaporized to a gas phase of more purified pentane
 c. The temperature of the mixture increases as it vaporizes
 d. The solution condenses into a more pure pentane mixture
 e. all of the above are true

- +2 D. In our elimination experiment, we used simple distillation even though the boiling points of 2-methyl-2-butene and 2-methyl-1-butene are separated by one 6 °C. How was this effective?

The goal was not to separate the alkenes from each other, but rather from solvent. The goal was to distill the mixture (without separation) for further analysis.

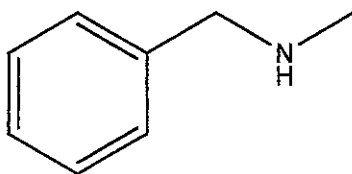
- E. A student conducted a distillation of 2-chloro-2-methylbutane and was supposed to see a boiling point on the range of 81-86 °C, but the distillation occurred from 73-77 °C. She confirmed that the thermometer was accurate, and further analysis showed that the compound's identity was correct. What was likely wrong with the experiment that gave incorrect data? Draw a distillation setup (with glassware labeled with names) that emphasizes the most likely problem.

+3
 Thermometer should be placed below bend in distillation head - This student had it too high.

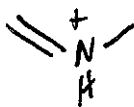


- Labels on
 distillation pot (Flask)
 distillation head
 +5 Condenser
 vacuum adapter
 receiving Flask

6. (12pts) The compound below has the following peaks on a mass spectrum. Explain why each one is observed.



+3 A. $m/z = 44$



common fragmentation for amines

+3 B. $m/z = 91$



→ tropylium ion

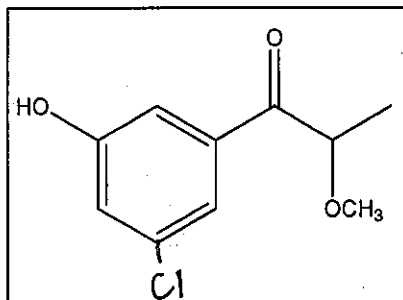
+3 C. $m/z = 121$ This is the molecular ion.

+3 D. $m/z = 122$ This is $M^+ + 1$ from isotope (probably ^{13}C)

7. (12pts) An unknown compound was determined to have a molecular formula of $C_{10}H_9ClO_3$. How many degrees of unsaturation in this compound?

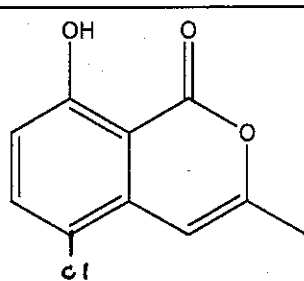
+3 $C_{10}H_9ClO_3 \equiv C_{10}H_{10}$ saturated = $C_{10}H_{22}$ or **SIX** DU

This compound has characteristic IR peaks at 3300 cm^{-1} (broad, smooth), above/below 3000 cm^{-1} , 1710 cm^{-1} (intense), and 1599 cm^{-1} (sharp.) Mark each compound as "consistent" or "inconsistent" with the data. If inconsistent, explain how.



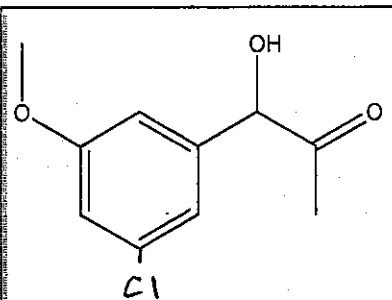
inconsistent

- C=O IR stretch
- wrong MF



inconsistent

- IR matches
- wrong MF

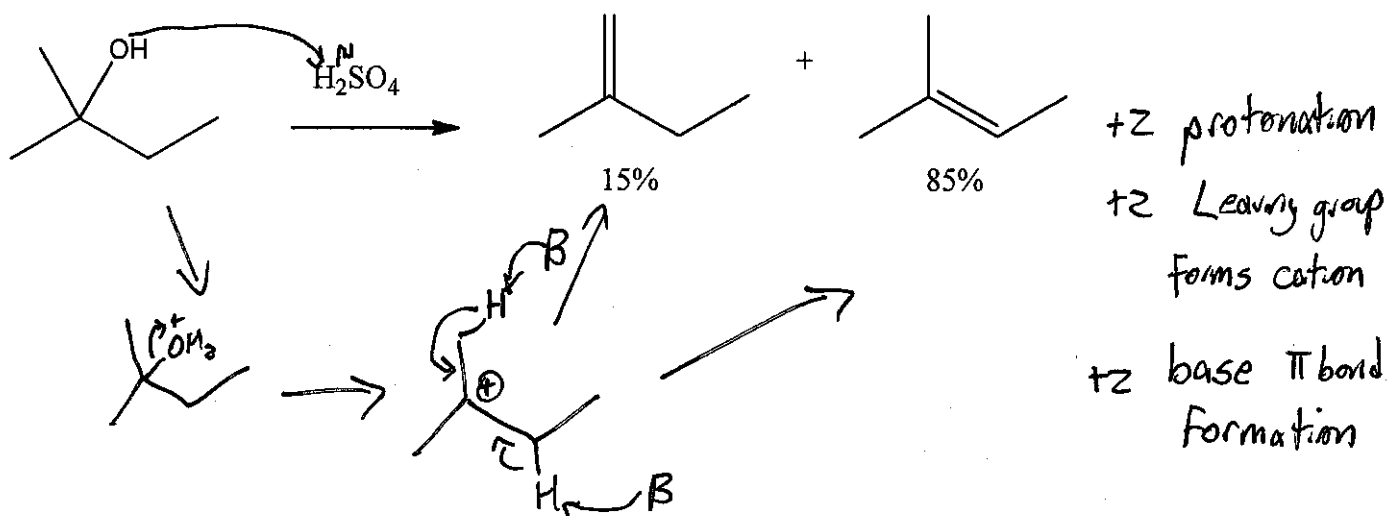
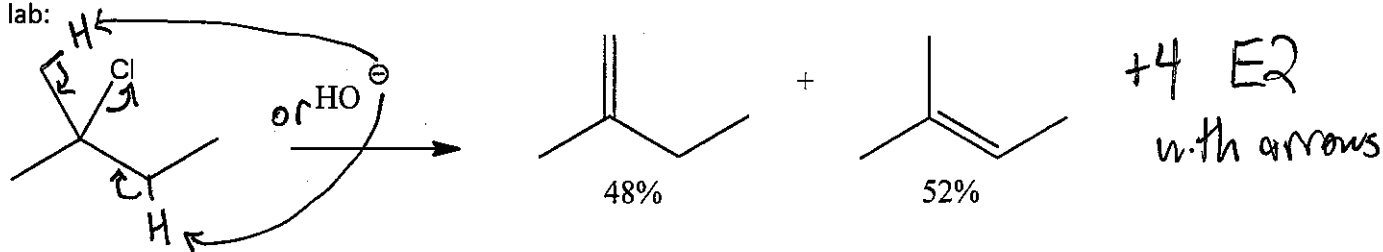


Inconsistent

- IR matches
- wrong MF

+1
+1
+1

8. (20pts) Draw acceptable mechanisms for each of these elimination products that you performed in lab:



If the stability of the product were the only factor in this product distribution, we would expect the two reactions to give the same product distribution. Explain why the product distribution for the basic elimination is closer to 50/50.

+3 The basic elimination is E2, and therefore sterics play a role.

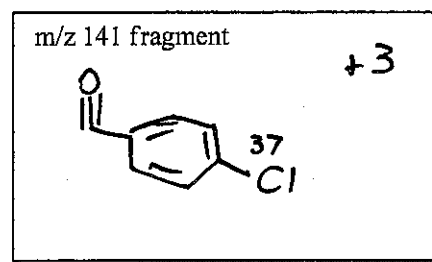
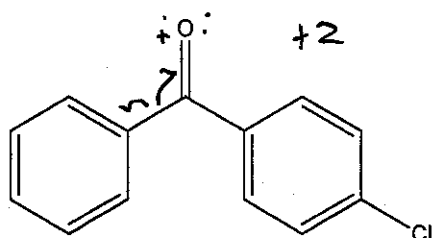
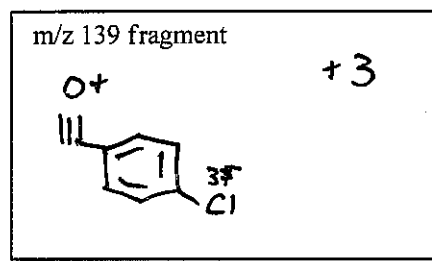
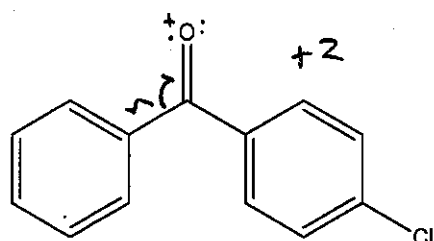
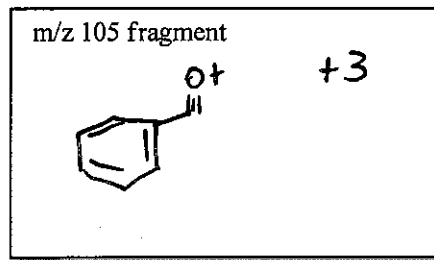
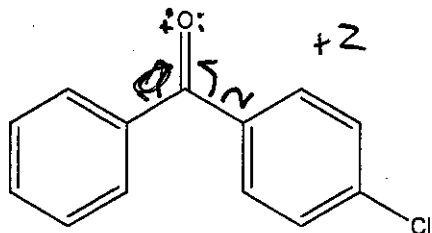
+2 The primary H's are more accessible to be removed by the base (more stable TS argument.)

TLC is also able to separate isomers like these alkene products. TLC is faster and cheaper than GC—so why was GC necessary for this experiment (two reasons.)

+3 ① TLC is qualitative - can't determine pdt distribution %

+2 } ② These pdts are volatile - evaporate from TLC
or { ③ Too similar to separate by TLC

9. (15pts) Similar types of cleavages give rise to two peaks for 4-chlorobenzophenone, one at $m/z = 105$ (the base peak) and one at $m/z = 139$ (70% of the base peak). A clue to the fragments' identities is the fact that the $m/z = 139$ peak is accompanied by a peak at $m/z = 141$ that is about one-third of the $m/z = 139$ peak intensity. The $m/z = 105$ peak has no such partner. What structures correspond to these peaks? Draw mechanisms of fragmentation to support your answers.



10. (16pts) You conducted an oxidation reaction in which benzaldehyde, a liquid, was made into benzoic acid, a solid. You conducted a TLC analysis of the unpurified reaction and concluded that the benzoic acid had been formed, but that there was still a small amount of benzaldehyde impurity. You conducted a recrystallization and then took a TLC of the recrystallized benzoic acid and the recrystallization solvent.

A. Initially, you ran your TLC of the impure benzoic acid in a 3:1 hexane/ethyl acetate mixture and saw only one spot with $R_f = 0.05$ even though there was an impurity. Explain

+1 The solvent was too nonpolar - neither compound moved,
+1 so they overlapped.

B. You tried a new TLC solvent, and authentic benzoic acid had an R_f of 0.35. The new solvent was

- +2
a. 3:1 hexane/ether
b. water
c. 5:1 hexane/ethyl acetate
d. 1:1 hexane/ethyl acetate

C. In the new TLC solvent, the impurity most likely had an R_f of

- +2
a. zero
b. 0.05
c. less than 0.35
d. 0.35
e. greater than 0.35
f. great than 1.0

C. For your recrystallization, would you choose water (solubility 0.35g benzoic acid/100 mL water at 0 °C; 10.4 g benzoic acid/100 mL of water, boiling) or would you choose hexanes (solubility 0.05g benzoic acid/100 mL hexanes at 0 °C; 0.15 g hexanes/100 mL of hexanes, boiling)? Explain.

+1 water - You want to choose a solvent with large
+1 differential solubility between hot and cold solvent.

+2 D. True or false: To maximize the effectiveness of your recrystallization, it is important to let the hot solution cool slowly so that the impurities are not trapped in the re-forming crystal lattice.

+2 E. True or false: Recrystallization is generally successful at purifying a solid compound from a small amount of solid or liquid impurity.

F. How could you use TLC to determine if your recrystallization was successful? Be specific.

A TLC of the recrystallized compound should show only one spot with R_f of 0.35 (match authentic.)

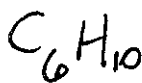
+2

+2

11. 10pts You analyzed an unknown compound by MS, elemental analysis and IR. According to elemental analysis, the compound is 87.8% C and 13.2% H. The molecular ion peak is at $m/z = 82$, and the only characteristic IR peak is a stretch below 3000 cm^{-1} .

4 A. Using the Rule of 13 and the data above, determine all consistent molecular formula for this compound.

$$\frac{82}{13} = 6 \text{ remainder } 4 =$$



(+2)

No others - hydrocarbon

(+2)

2 B. Based on the molecular formula(s) above, how many degrees of unsaturation does this compound have?

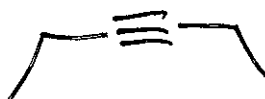
two (+2)

4 C. Propose a structure that is consistent with all these data, and explain why it is consistent.



Partial credit

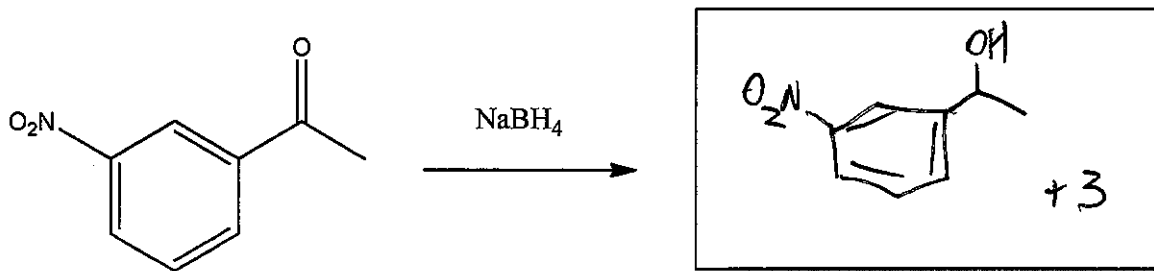
(+4)



or other bicyclic compounds

12. (12pts) In lab, you conducted an reduction in which you used IR to determine reagent selectivity.

A. What was the product of the reaction you conducted?



B. What specific IR data did you see to conclude that you obtained the product you drew in part A?

+1
each

C=O stretch disappeared
O-H stretch appeared

NO₂ stretches remained

C. You could use the same strategy to determine the selectivity of these reduction reagents. Given the IR data with each reaction, predict the product of these reductions. (s=strong, sh=sharp, br=broad)

