

Chemistry 334

Second Hour Examination

October 27, 1995

Professor Charonnat

Name: _____

Be certain that your examination has six (6) pages including this one.

Put your name on **each** page of this examination booklet.

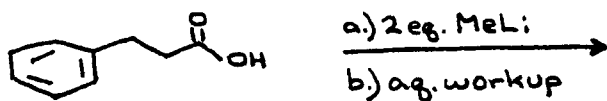
By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Name: _____

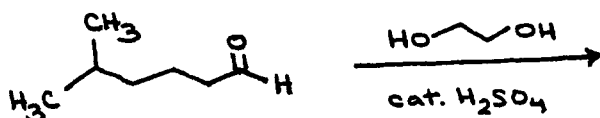
1. (25 points)

For each of the following five (5) questions draw the structure of the expected major organic product. If relevant, **clearly** specify absolute and/or relative stereochemistry.

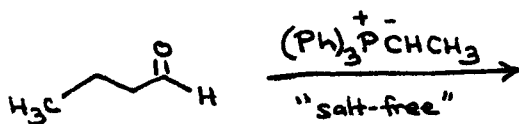
A.



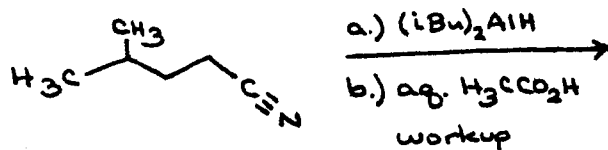
B.



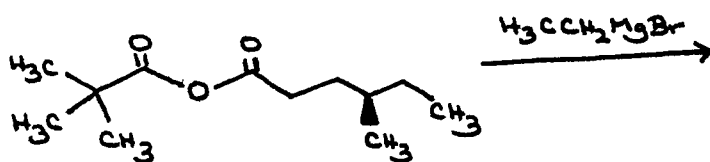
C.



D.



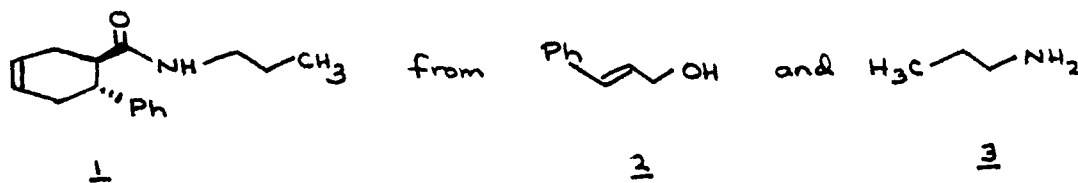
E.



Name: _____

2. (25 points)

Design a synthesis of a racemic mixture of the amide 1 from the primary alcohol 2, the primary amine 3, mono- or difunctional organic compounds of six carbons or less, and any inorganic reagents that are necessary. Draw clearly **all** reagents and isolable synthetic intermediate products. (**N.B.** Do **not** draw mechanisms for each synthetic transformation!)



3. (25 points)

Answer the following three (3) questions precisely, succinctly and with correct grammar.

A. Why is trifluoroacetic acid much more acidic than acetic acid?

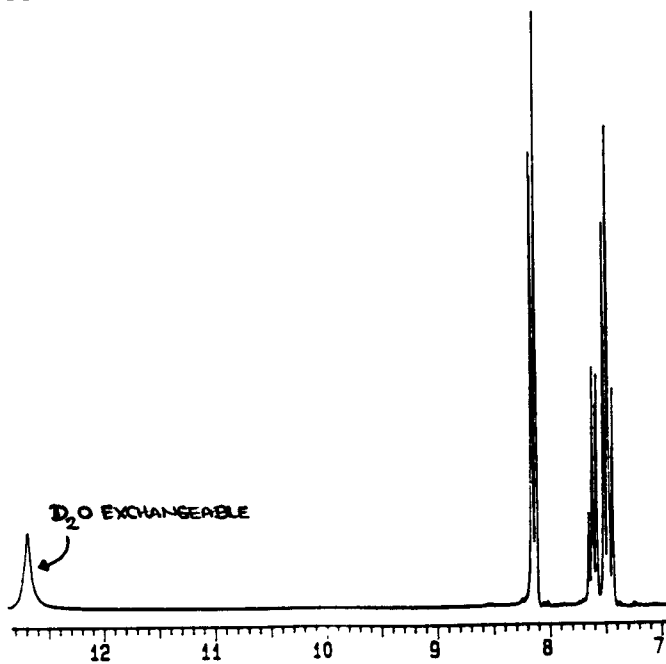
Draw annotated structures to illustrate your answer.

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3. (cont.)

B. Why is an amide more stable towards hydrolysis than the corresponding ester?
Draw annotated structures to illustrate your answer.

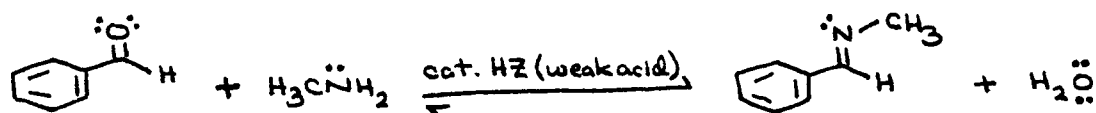
C. A sample is known to be either benzaldehyde (PhCHO) or benzoic acid (PhCO_2H). The ^1H NMR spectrum of the compound is shown below. What is the identity of this sample? State the ^1H NMR evidence that supports your reasoning.



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4. (25 points)

Draw the mechanism of the following imine preparation, using the curved-arrow notation to indicate the reorganization of electron density. Show **all** intermediates and denote **all** lone pairs, formal charges and countercharges where appropriate.



Congratulations!

1	/25
2	/25
3	/25
4	/25
<hr/>	
Total:	/100

SELECTED ¹H NMR CORRELATIONS

structural type	chemical shift range (ppm)
cyclopropyl	0.0 - 0.9
RNH ₂ R ₂ NH	0.5 - 5.0 ^a
-CH ₃ (saturated)	0.7 - 1.3
$\text{H}_3\text{C}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{X}$ (X = halogen, O, N, carbonyl)	0.9 - 1.2
$-\overset{\text{I}}{\text{C}}\text{H}_2$ (saturated)	1.2 - 1.3
$-\overset{\text{I}}{\text{C}}\text{H}$ (saturated)	1.4 - 1.6
$\text{H}_3\text{C}-\overset{\text{I}}{\text{C}}-\text{X}$ (X = halogen, O, N, carbonyl)	1.0 - 2.0
ROH	1.0 - 5.0 ^a
$\text{H}_3\text{C}-\text{C}=\text{C}$	1.6 - 1.9
$\text{H}_3\text{C}-\text{C}\equiv\text{C}-$	1.8 - 2.2
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-$	1.9 - 2.6
H ₃ C-Ar	2.1 - 2.6
$\text{H}_3\text{C}-\text{N}$	2.1 - 3.0
$-\text{C}\equiv\text{C}-\text{H}$ (nonconjugated)	2.0 - 2.6
$-\text{C}\equiv\text{C}-\text{H}$ (conjugated)	2.8 - 3.1
$\text{H}_3\text{C}-\text{X}$ (X = halogen, O)	2.6 - 4.4
Ar-NH ₂ Ar ₂ NH	3.0 - 5.0 ^a
$\text{H}_3\text{C}-\text{O}-$	3.3 - 4.2
ArOH	4.0 - 10.0 ^a
$\text{H}_2\text{C}=\overset{\text{I}}{\text{C}}$ (nonconjugated)	4.6 - 5.0
$\overset{\text{H}}{\text{C}}=\overset{\text{I}}{\text{C}}$ (nonconjugated)	5.1 - 5.9
$\text{H}_2\text{C}=\overset{\text{I}}{\text{C}}$ (conjugated)	5.3 - 6.3
$\overset{\text{H}}{\text{C}}=\overset{\text{I}}{\text{C}}$ (conjugated)	5.3 - 7.7
ArH	6.0 - 9.5
$\overset{\text{O}}{\parallel}{\text{R}-\text{C}-\text{H}}$ $\overset{\text{O}}{\parallel}{\text{Ar}-\text{C}-\text{H}}$	9.5 - 10.5
$\overset{\text{O}}{\parallel}{\text{R}-\text{C}-\text{OH}}$ $\overset{\text{O}}{\parallel}{\text{Ar}-\text{C}-\text{OH}}$	9.7 - 13.2