

Chemistry 334

Hour Examination #2

April 7, 1999

Professor Charonnat

Name: _____

Be certain that your examination has seven (7) pages including this one.

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

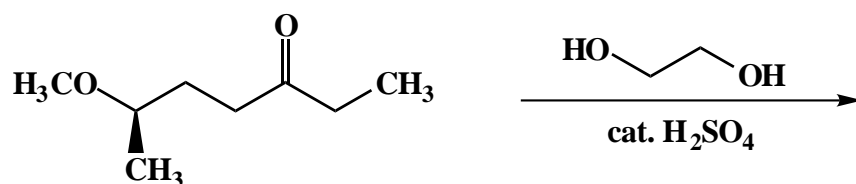
By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Name: _____

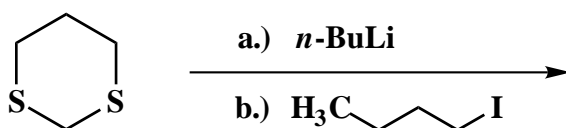
1. (25 points)

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

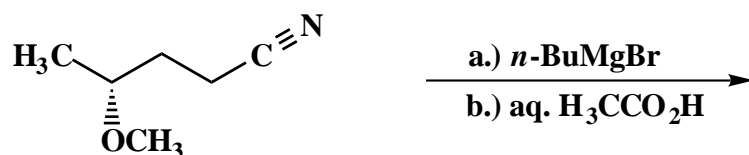
A.



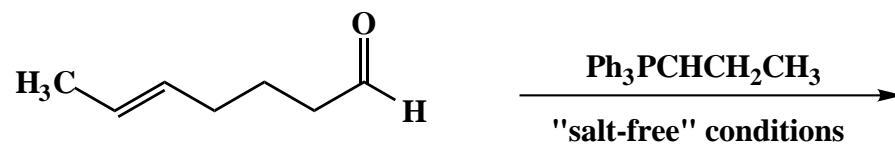
B.



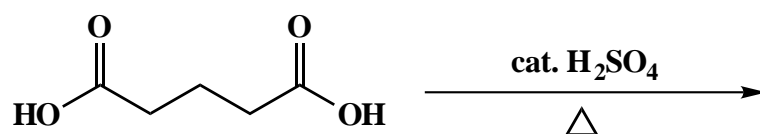
C.



D.



E.



Name: _____

2. (20 points)

For each of the following five (5) questions, circle the number that corresponds to the correct answer.

A. Reaction of propionic acid with excess methyllithium, followed by aqueous workup yields:

1. an ester
2. a ketone
3. a secondary alcohol

B. It is possible to drive a Fischer esterification reaction towards completion by:

1. increasing water concentration
2. increasing alcohol concentration
3. decreasing alcohol concentration

C. Most reactions of carboxylic acid derivatives with nucleophiles proceed via:

1. an S_N1 mechanism
2. an S_N2 mechanism
3. an addition-elimination mechanism

D. The bond that is formed to crosslink polysaccharide chains in bacterial cell walls is an:

1. amide
2. ester
3. ether

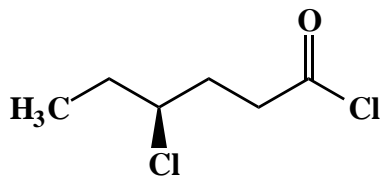
E. Carboxylic acids have higher boiling points than the corresponding aldehydes primarily due to:

1. increased molecular weight
2. hydrogen bonding
3. sterics

Name: _____

3. (10 points)

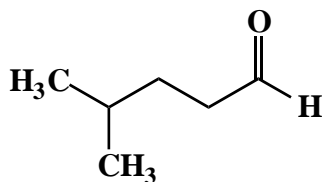
Use IUPAC nomenclature to write the systematic name of the following acid chloride.



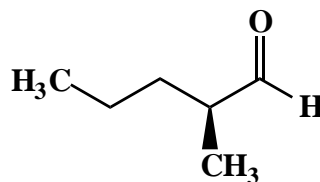
4. (10 points)

Answer the following question precisely, succinctly and with correct grammar.

How could one use ^1H NMR spectroscopy to distinguish between the following carbonyl compounds? State specifically which resonances one would look for. Do so for both carbonyl compounds.



1

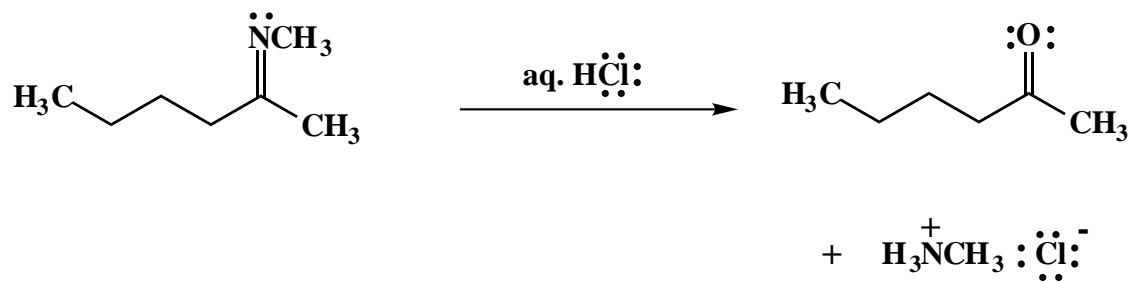


2

Name: _____

5. (20 points)

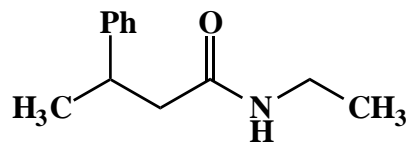
Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show **all** intermediates and denote **all** lone pair electrons, formal charges and countercharges where appropriate. Clearly designate reversibility or irreversibility for each primary mechanistic step.



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6. (15 points)

Design a synthesis of a racemic mixture of the amide **3** from *trans*-2-butenal. Use any inorganic and organic reagents that are necessary. Show all reagents and stable synthetic intermediate compounds. (**N.B.** Do **not** draw mechanisms for each synthetic transformation!)



Congratulations!

1	/25
2	/20
3	/10
4	/10
5	/20
6	/15
<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
$\text{H}_3\text{C}-\overset{\text{ }}{\underset{\text{ }}{\text{C}}}-\overset{\text{ }}{\underset{\text{ }}{\text{C}}}-\text{X}$ (X = halogen, O, N, carbonyl)	0.9 - 1.2
$-\overset{\text{ }}{\text{CH}_2}$ (saturated)	1.2 - 1.3
$-\overset{\text{ }}{\text{CH}}$ (saturated)	1.4 - 1.6
$\text{H}_3\text{C}-\overset{\text{ }}{\text{C}}-\text{X}$ (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
$\text{H}_2\text{C}=\text{C}$ (nonconjugated)	4.6 - 5.0
$\overset{\text{H}}{\text{C}}=\text{C}$ (nonconjugated)	5.1 - 5.9
$\text{H}_2\text{C}=\text{C}$ (conjugated)	5.3 - 6.3
$\overset{\text{H}}{\text{C}}=\text{C}$ (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