

Chemistry 334

Examination #2

August 12, 1999

Professor Charonnat

Name: _____

Be certain that your examination has nine (9) pages including this one.

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

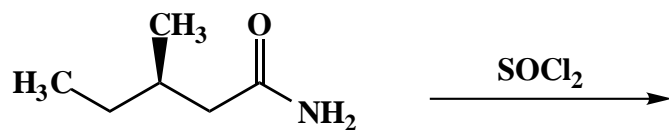
By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Name: _____

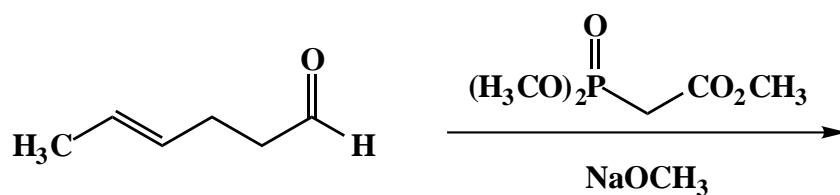
1. (25 points)

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.

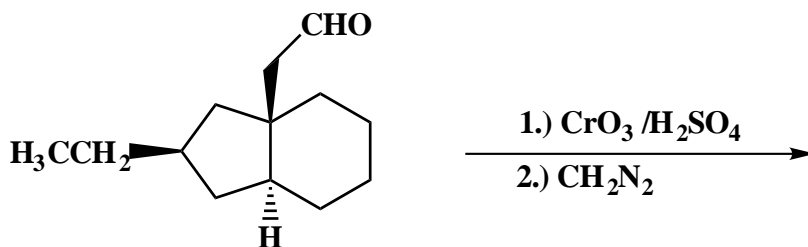
A.



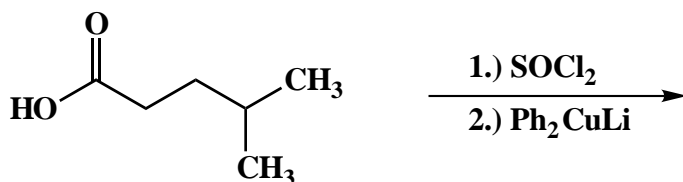
B.



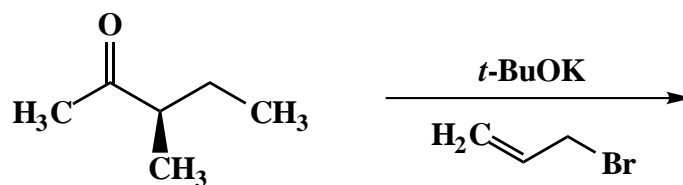
C.



D.



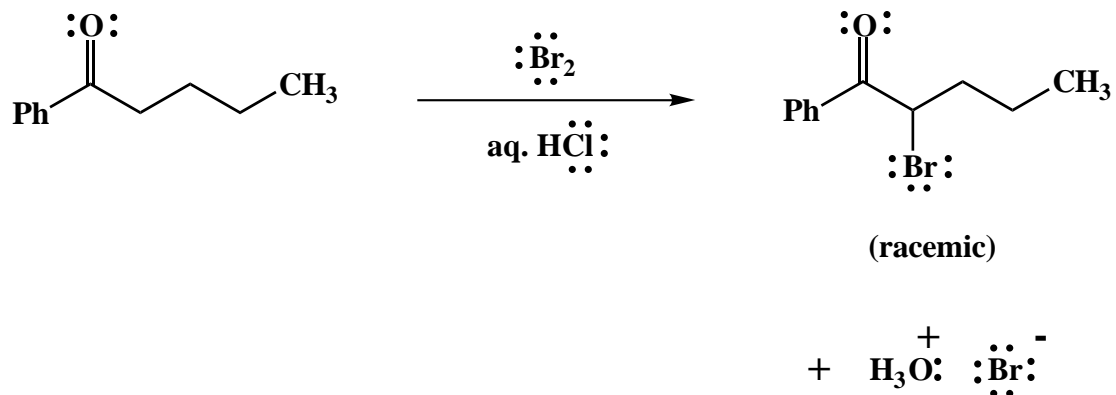
E.



Name: _____

2. (25 points)

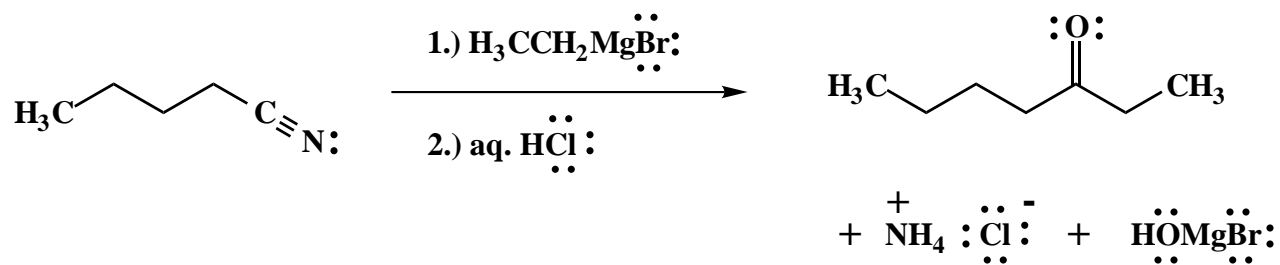
Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show **all** intermediates and denote **all** lone pair electrons, formal charges and countercharges where appropriate. How much HCl is required for the reaction to proceed to completion? State your reasoning succinctly and clearly.



Name: _____

3. (25 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.



Name: _____

4. (20 points)

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

A. When 3,3-dimethyl-2-butanone is deprotonated by LDA, an enolate is formed that is:

1. a monomer
2. a dimer
3. a tetramer

B. Bender's work shows that basic hydrolysis of esters occurs via:

1. an S_N1 mechanism
2. an S_N2 mechanism
3. a nucleophilic addition/elimination mechanism

C. Treatment of a 1,5-diketone with sodium ethoxide can afford a:

1. cyclopentenone derivative
2. cyclohexenone derivative
3. cycloheptenone derivative

D. Robinson annulation involves:

1. a Michael addition followed by an aldol condensation
2. a Michael addition followed by a Claisen condensation
3. an aldol condensation followed by a Michael addition

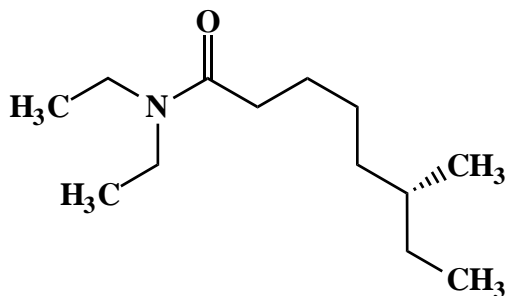
E. An enol is:

1. more nucleophilic than the corresponding enolate
2. equally nucleophilic as the corresponding enolate
3. less nucleophilic than the corresponding enolate

Name: _____

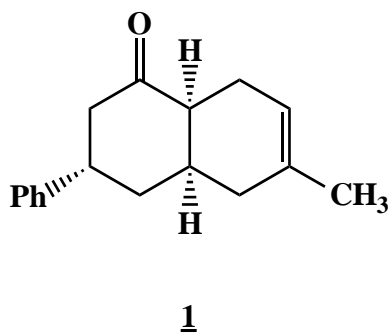
5. (10 points)

Use IUPAC nomenclature to write the systematic name of the following amide.



6. (25 points)

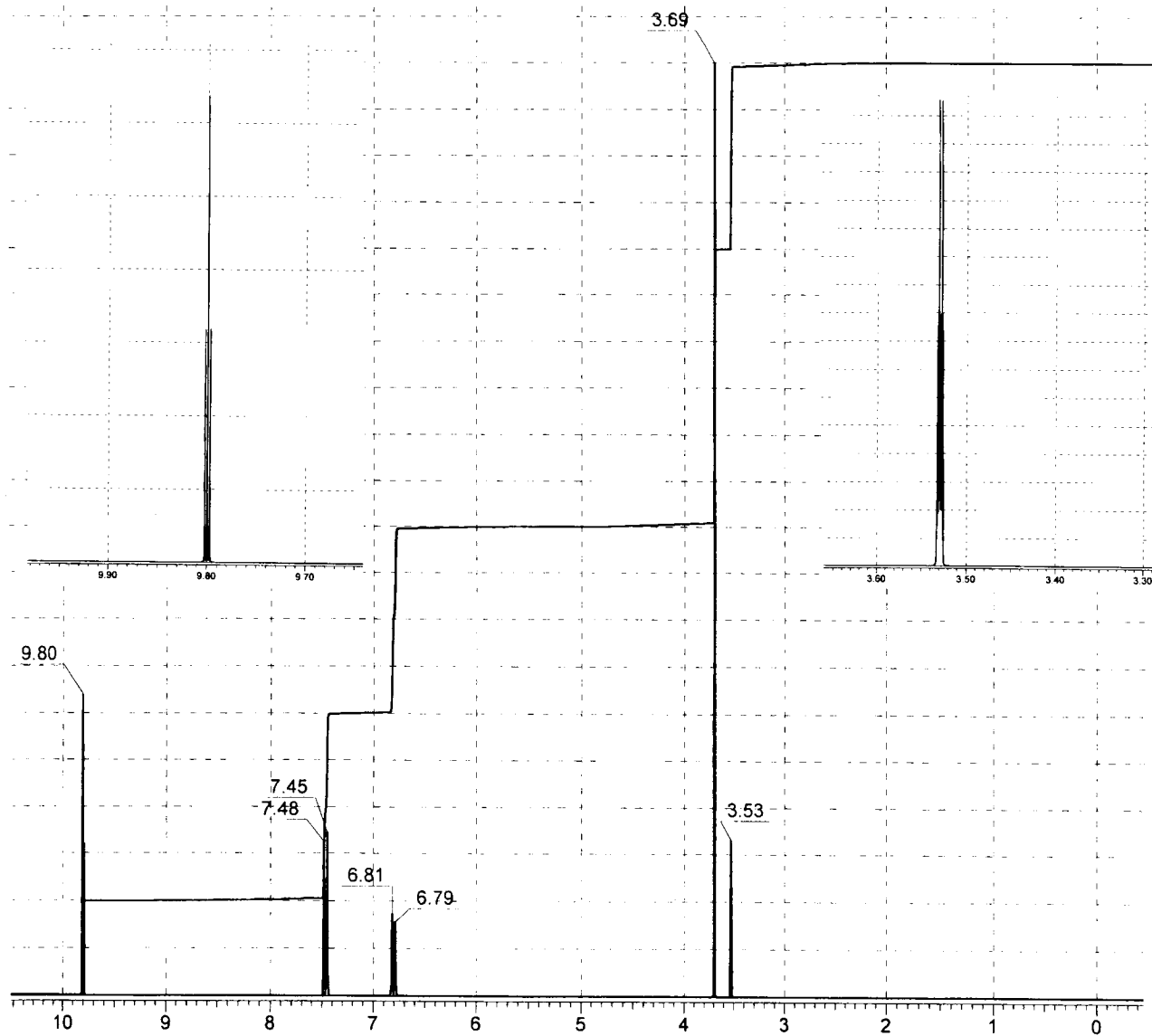
Design a synthesis of a racemic mixture of the ketone **1** from cyclohexanone, isoprene and phenyllithium. Use any additional inorganic and organic reagents that are necessary. Show all reagents and stable synthetic intermediate compounds. (**N.B.** Do not draw mechanisms for each synthetic transformation!)



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7. (20 points)

The ^1H NMR spectrum of compound A ($\text{C}_9\text{H}_{10}\text{O}_2$) is shown below. Clearly assign all the resonances and draw the structure of compound A.



Name: _____

7. (cont.)

¹H NMR assignments:

chemical shift (ppm)

assignment

explanation of multiplicity

structure of compound A:

Congratulations!

1	/25
2	/25
3	/25
4	/20
5	/10
6	/25
7	/20
<hr/> Total:	<hr/> /150

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