

Chemistry 334

Final Examination

May 26, 1999

Professor Charonnat

Name: _____

Be certain that your examination has eleven (11) 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. (20 points)

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

A. Hofmann elimination of a tetraalkylammonium hydroxide affords

1. predominantly the most substituted alkene
2. predominantly the least substituted alkene
3. equal amounts of all possible alkenes

B. All peptides contain

1. carbohydrates
2. fatty acids
3. α -amino acids

C. Which of the following is an example of nonrepetitive secondary peptide structure?

1. an α -helix
2. an omega loop
3. a β -pleated sheet

D. Feedback inhibition of an enzyme involves the final product of a biosynthetic pathway inhibiting the catalytic action of

1. the last enzyme in the pathway
2. the second enzyme in the pathway
3. the first enzyme in the pathway

E. Terpenes are composed of a multiple of

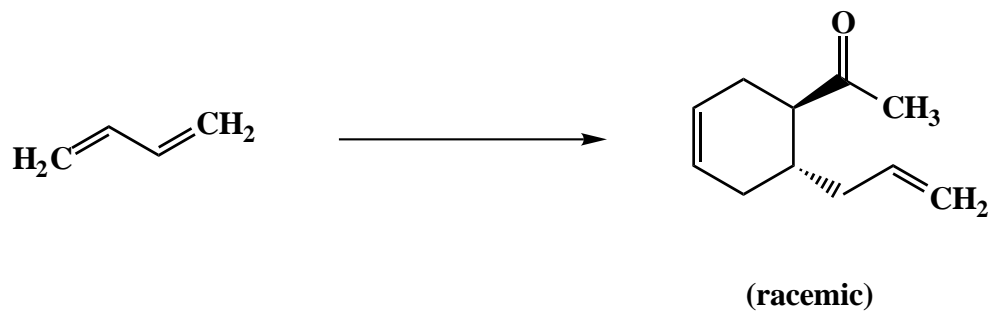
1. two carbons
2. three carbons
3. five carbons

Name: _____

2. (25 points)

For each of the following five (5) questions draw the specific reagent(s) necessary to effect the transformation shown.

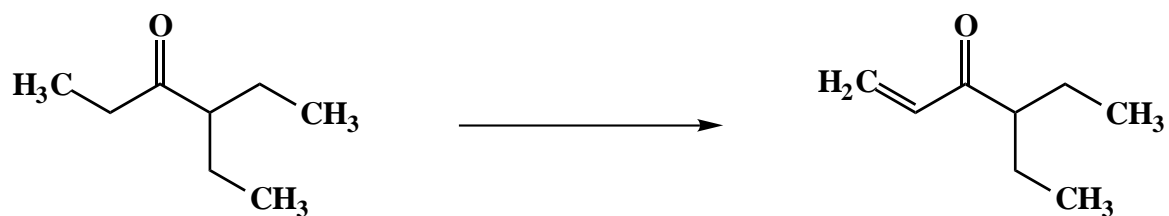
A.



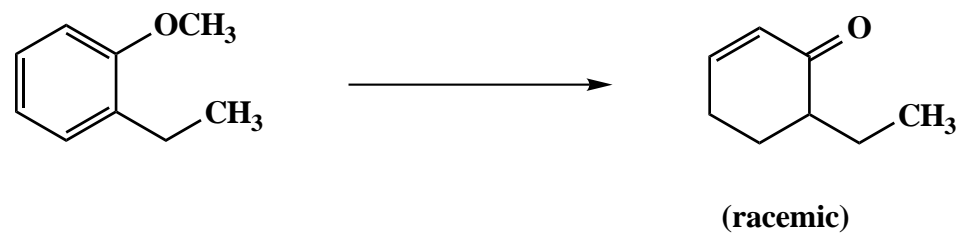
B.



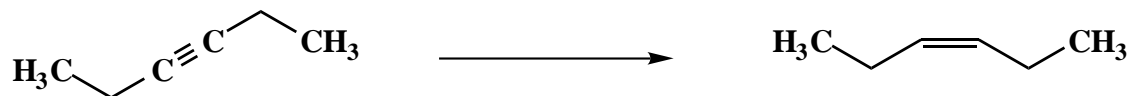
C.



D.



E.

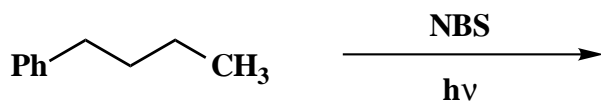


Name: _____

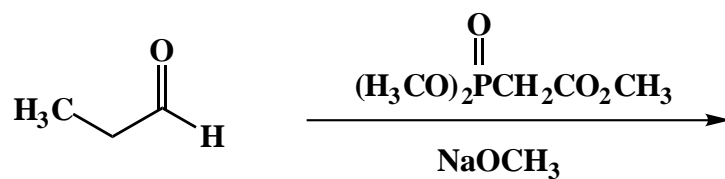
3. (25 points)

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.

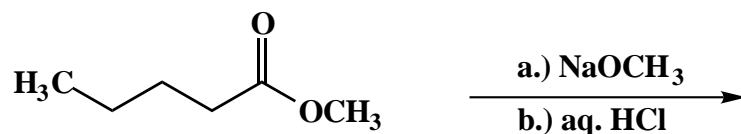
A.



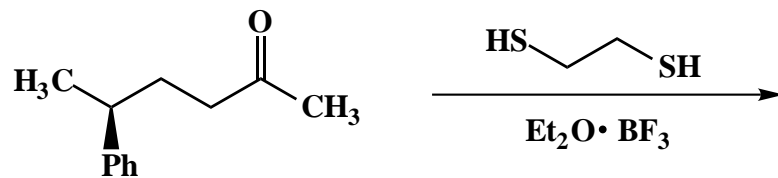
B.



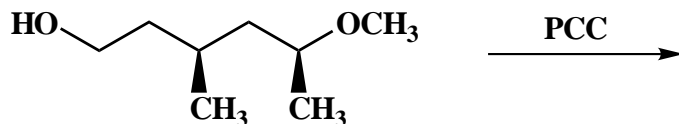
C.



D.



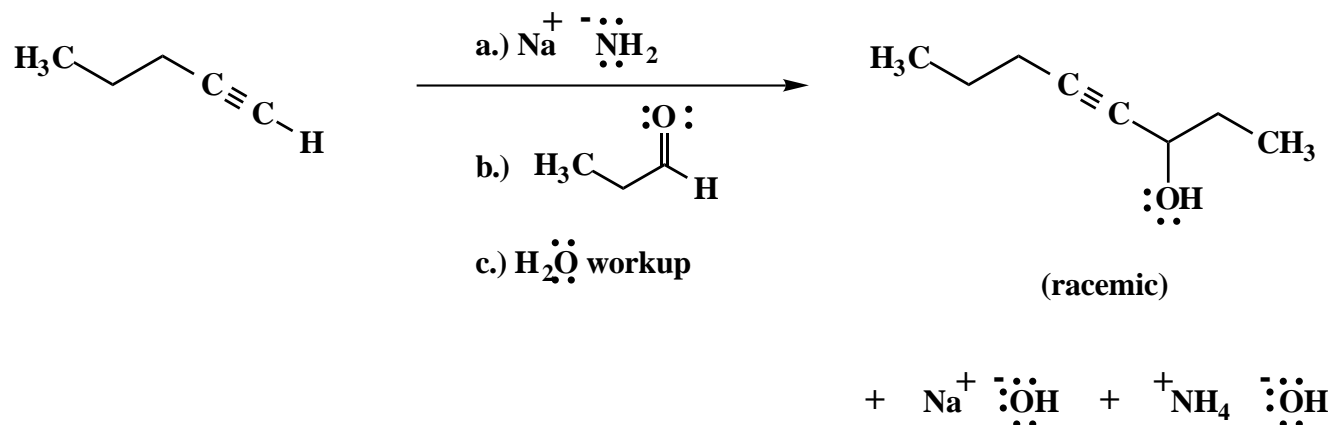
E.



Name: _____

4. (20 points)

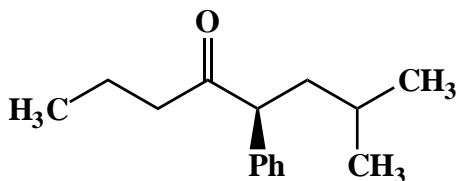
Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show all intermediates and denote all unshared electrons, formal charges and countercharges where appropriate. Explain briefly why a racemic mixture is obtained.



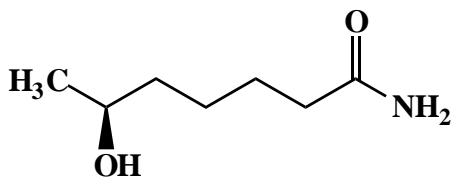
5. (20 points)

Use IUPAC nomenclature to write the systematic name for both of the following two (2) compounds.

A.



B.

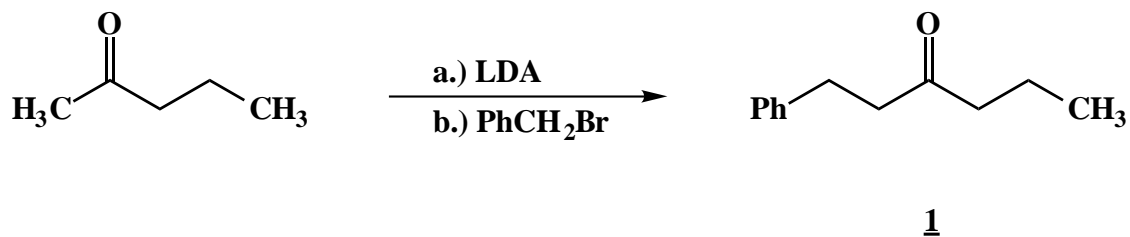


Name: _____

6. (20 points)

Answer the following two (2) questions precisely, succinctly and with correct grammar.

A. Why does the following reaction afford the α -substituted product **1** and essentially none of the corresponding regioisomer?

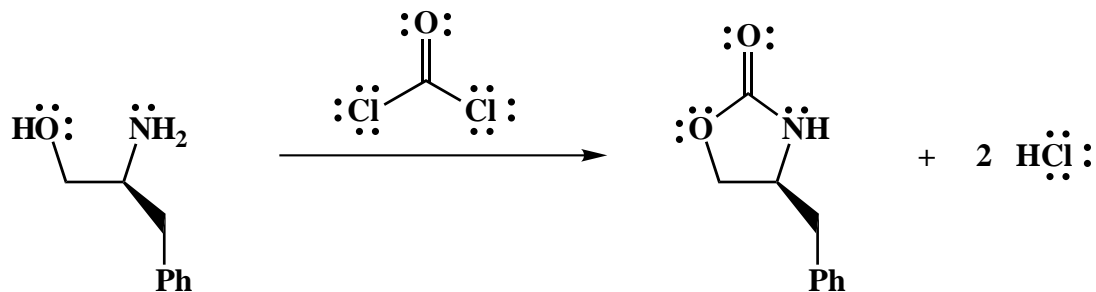


B. The biosynthesis of steroids involves a cyclization of squalene oxide in which the newly formed B ring is fixed in a boat conformation. Explain the mechanistic basis for this unusual result.

Name: _____

7. (25 points)

The following reaction gives the benzyloxazolidinone used in Evans' enantioselective synthesis of α -amino acids. Draw the mechanism of this transformation, using the curved-arrow notation to indicate the reorganization of electron density. Show all intermediates and denote all unshared electrons, formal charges and countercharges where appropriate.



Name: _____

8. (25 points)

Draw the structure of a specific example for each of the following twelve (12) categories.

A. any naturally-occurring wax:

B. any naturally-occurring phospholipid:

C. any isolated diene:

D. any conjugated diene:

E. any polymer that can be formed under acidic conditions:

F. any polymer that can be formed under basic conditions:

G. any α -amino acid:

H. any β -amino acid:

I. any D-ketose:

J. any L-triose:

K. any terpene:

L. any steroid:

Name: _____

9. (20 points)

The ^1H NMR spectrum of compound A ($\text{C}_4\text{H}_{11}\text{N}$) is shown below. Clearly assign all the resonances that you can identify with certainty and draw the structure of compound A.

The spectrum is unavailable due to copyright considerations.

Name: _____

9. (continued)

¹H NMR assignments:

chemical shift (ppm)

assignment

explanation of multiplicity

structure of compound A:

Congratulations!

1	/20
2	/25
3	/25
4	/20
5	/20
6	/20
7	/25
8	/25
9	/20
<hr/> Total:	<hr/> /200

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
-C≡C-H (nonconjugated)	2.0 - 2.6
-C≡C-H (conjugated)	2.8 - 3.1
H ₃ C-X (X = halogen, O)	2.6 - 4.4
Ar-NH ₂ Ar ₂ NH	3.0 - 5.0 ^a
H ₃ C-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