

Chemistry 334

Final Examination

May 24, 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.

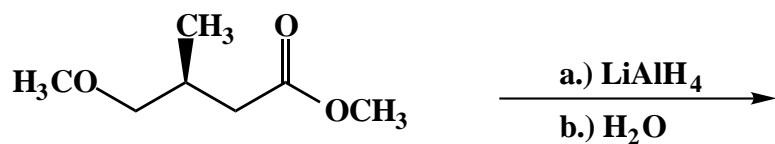
By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Name: _____

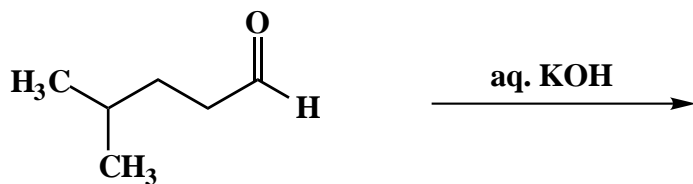
1. (25 points)

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.

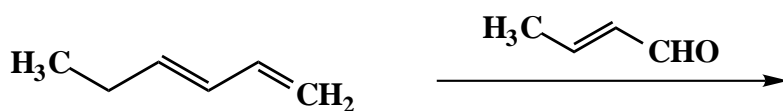
A.



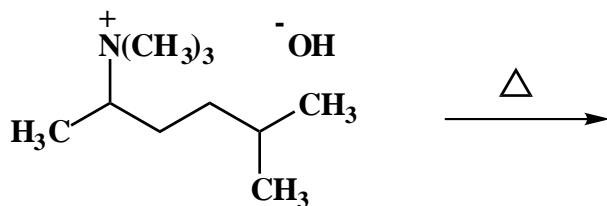
B.



C.



D.



E.

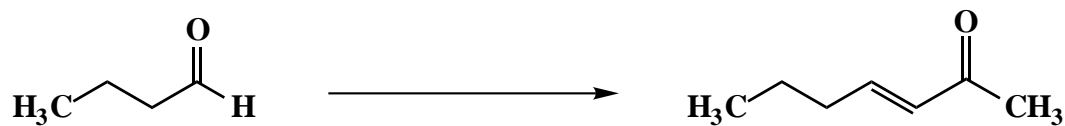


Name: _____

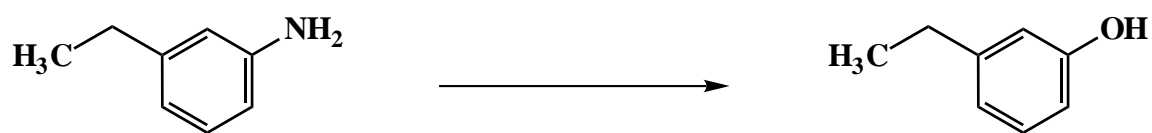
2. (25 points)

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

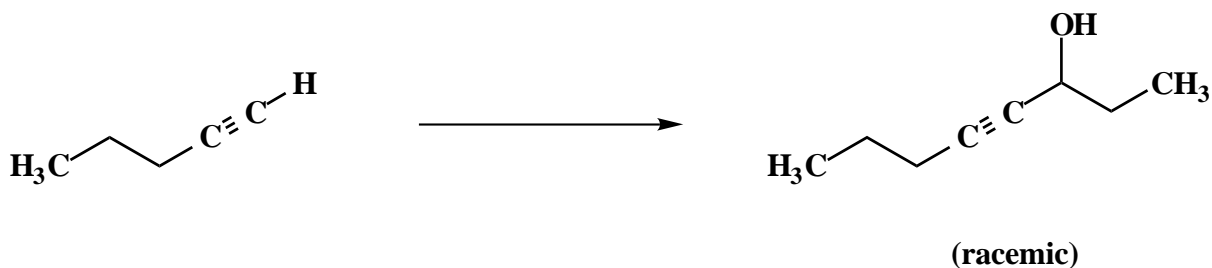
A.



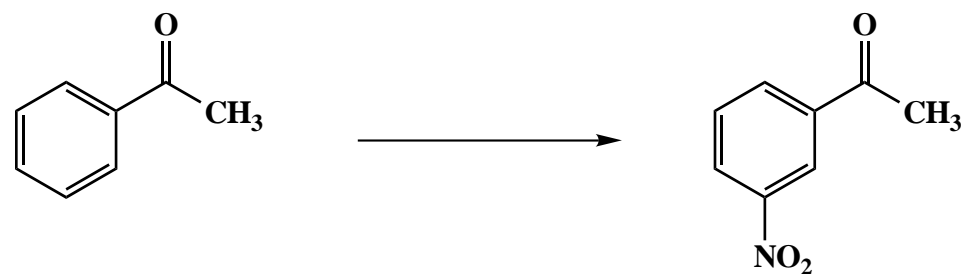
B.



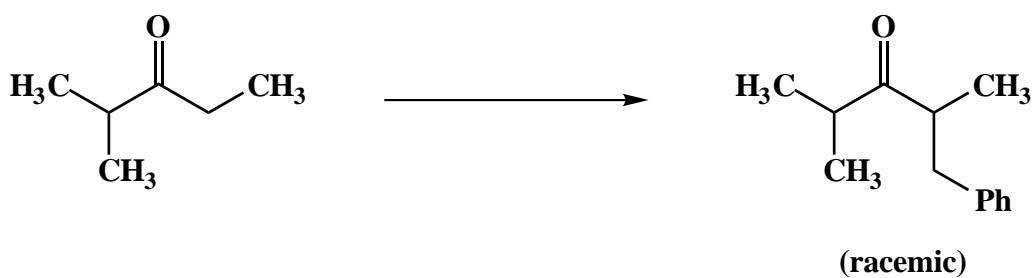
C.



D.



E.



Name: _____

3. (20 points)

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

A. The five-membered ring of prostaglandins is biosynthesized by

1. a carbocation cyclization
2. a carbanion cyclization
3. a radical cyclization

B. Enzymes enhance reaction rates by

1. lowering the energy of the transition state
2. maintaining the energy of the transition state
3. raising the energy of the transition state

C. The main problem with the Strecker synthesis of α -amino acids is that it affords a mixture of

1. regioisomers
2. enantiomers
3. diastereomers

D. Reductive amination of a ketone with a primary amine gives a

1. primary amine
2. secondary amine
3. tertiary amine

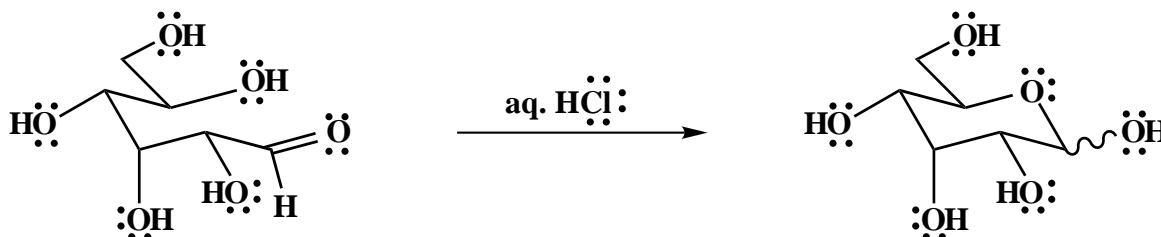
E. Fibrous proteins are soluble in

1. polar environments
2. nonpolar environments
3. both polar and nonpolar environments

Name: _____

4. (20 points)

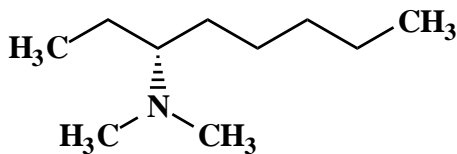
Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show all intermediates and denote all unshared electrons, formal charges and countercharges where appropriate. Clearly denote reversibility or irreversibility for each primary mechanistic step. Explain briefly why a mixture of α - and β -anomers is obtained.



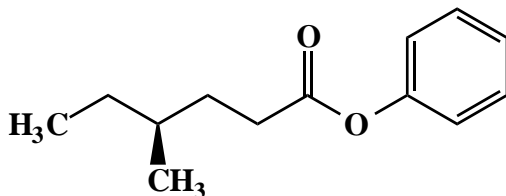
5. (20 points)

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

A.



B.

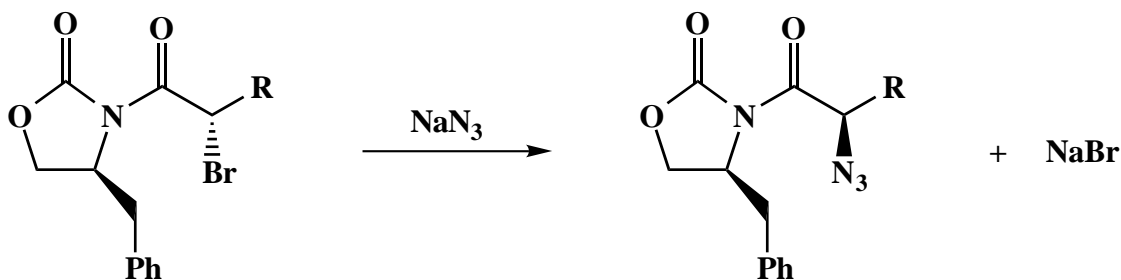


Name: _____

6. (20 points)

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

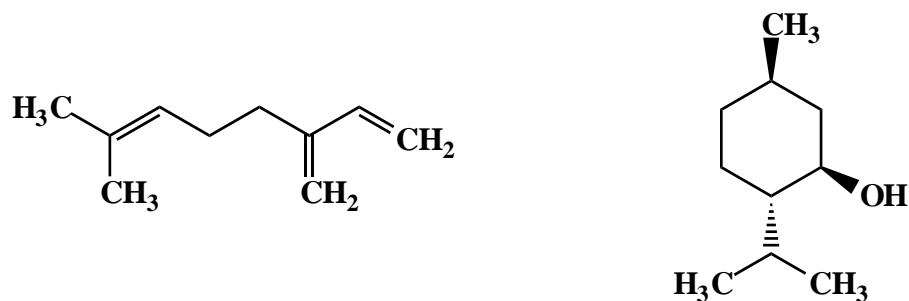
A. The following reaction is a critical step in Evans' enantioselective synthesis of α -amino acids. How does it occur, mechanistically? Why is the observed stereochemistry obtained?



B. What is meant by the term, "annulation"? Draw a specific example of an annulation reaction.

7. (10 points)

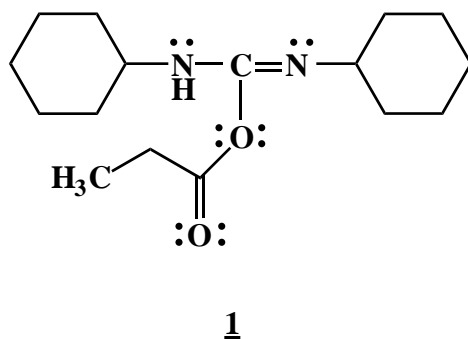
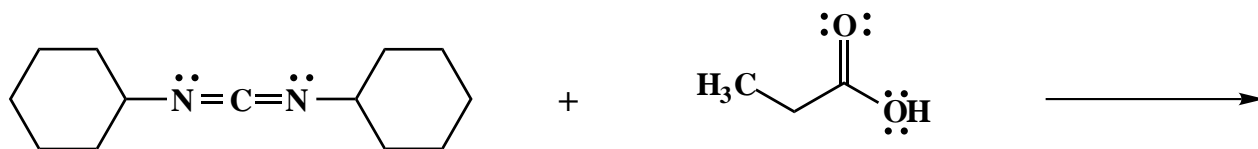
Circle the "isoprene" units in the following two (2) terpenes.



Name: _____

8. (15 points)

The following transformation is the first part of a DCC-facilitated coupling of a carboxylic acid to an amine. 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. Explain briefly why the intermediate 1 is so important for the coupling to occur. (Hint: What happens next?)



Name: _____

9. (25 points)

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

A. any naturally-occurring saturated fatty acid:

B. any naturally-occurring unsaturated fatty acid:

C. any allylic carbocation:

D. any dienophile:

E. any steroid:

F. any disaccharide:

G. any naturally-occurring acidic α -amino acid:

H. any naturally-occurring neutral α -amino acid:

I. any naturally-occurring phospholipid:

J. any naturally-occurring triacylglycerol:

K. any electrophile:

L. any nucleophile:

Name: _____

10. (20 points)

The ^1H NMR spectrum of compound A ($\text{C}_7\text{H}_9\text{N}$) 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: _____

10. (continued)

¹H NMR assignments:

chemical shift (ppm)

assignment

explanation of multiplicity

structure of compound A:

Congratulations!

| | |
|--------------|------------|
| 1 | /25 |
| 2 | /25 |
| 3 | /20 |
| 4 | /20 |
| 5 | /20 |
| 6 | /20 |
| 7 | /10 |
| 8 | /15 |
| 9 | /25 |
| 10 | /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 |