

Chemistry 334

Examination #2

August 11, 2000

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.

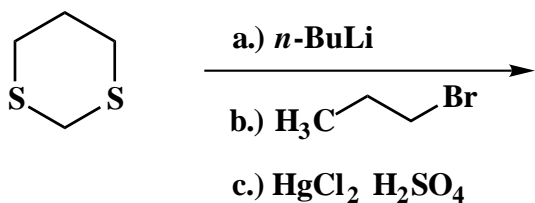
By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Name: _____

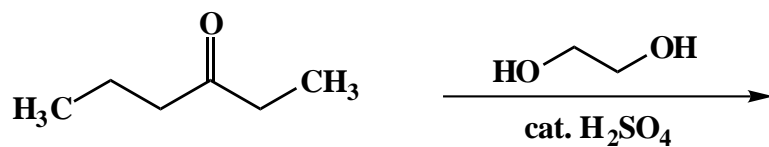
1. (25 points)

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.



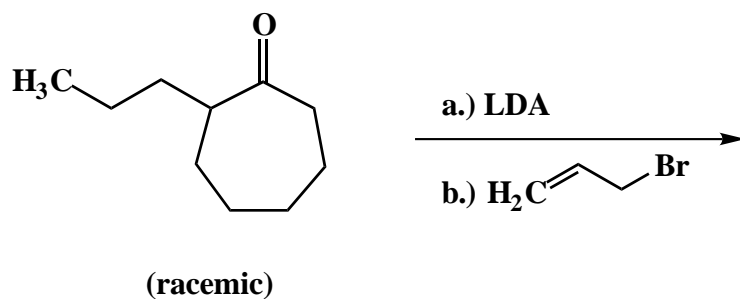
B.



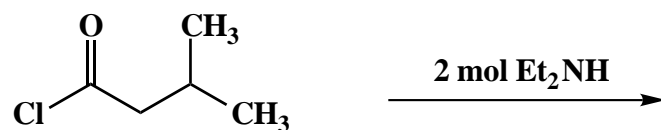
C.



D.



E.

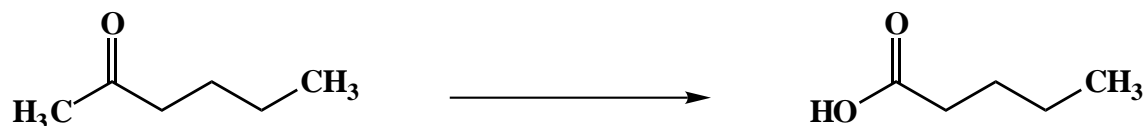


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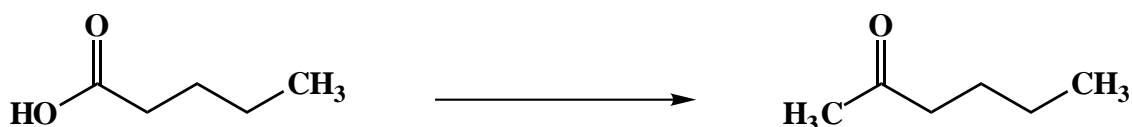
2. (25 points)

For each of the following five (5) questions, draw the specific reagent(s) necessary to effect the transformation shown. If more than one reaction is involved in an answer, be certain to distinguish the individual steps clearly.

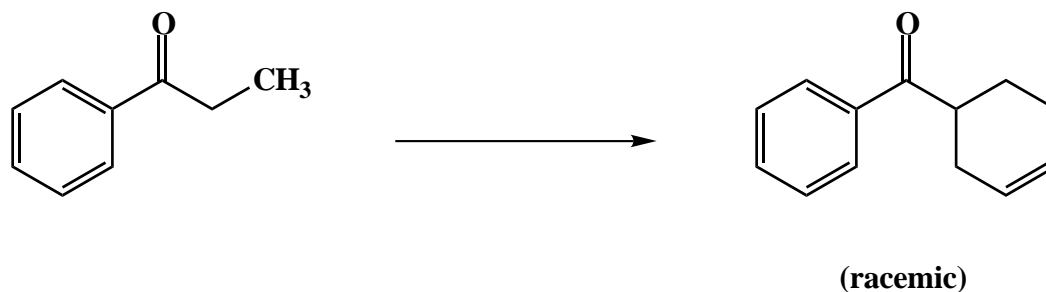
A.



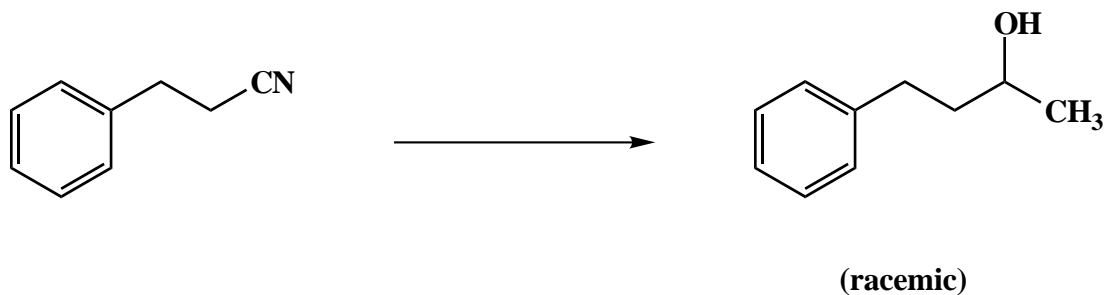
B.



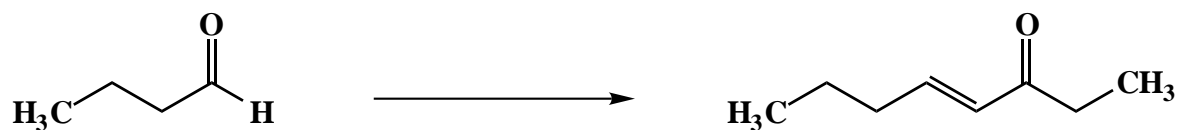
C.



D.



E.



Name: _____

3. (25 points)

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

A. The ^1H NMR resonance of the aldehyde proton of 2-methylheptanal is a:

1. singlet
2. doublet
3. triplet
4. quartet

B. Rank the following compounds from least to most acidic.

1. ester, ketone, β -ketoester
2. ketone, β -ketoester, ester
3. β -ketoester, ketone, ester

C. β -Ketoacids decarboxylate upon heating due to:

1. decreased sterics
2. increased enthalpy
3. increased entropy

D. The Claisen condensation requires:

1. a catalytic amount of base for the reaction to go to completion
2. one equivalent of base for the reaction to go to completion
3. two equivalents of base for the reaction to go to completion

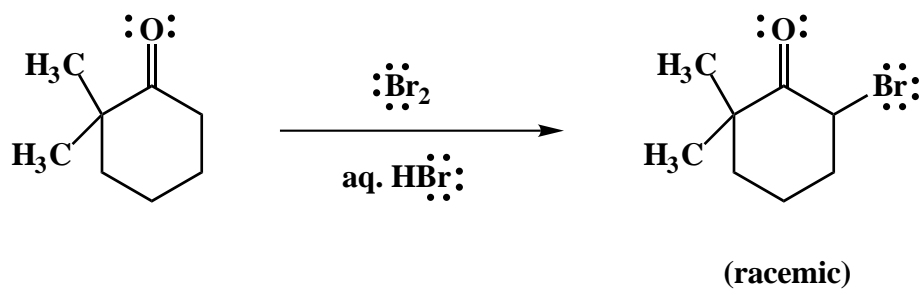
E. The Robinson annulation is:

1. a Michael addition, then an aldol condensation, and finally a dehydration
2. an aldol condensation, then a Michael addition, and finally a dehydration
3. a Michael addition, then a dehydration, and finally an aldol condensation

Name: _____

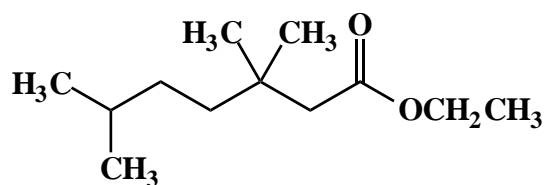
4. (20 points)

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.



5. (10 points)

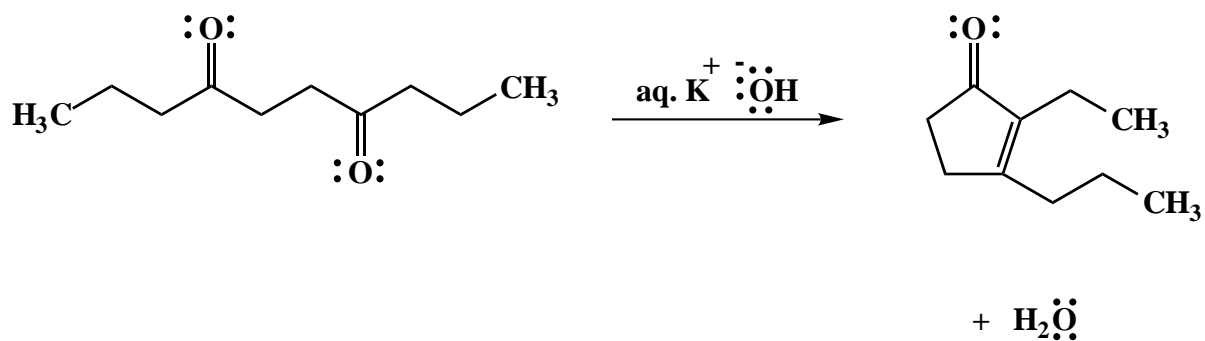
Use IUPAC nomenclature to write the systematic name of the following ester.



Name: _____

6. (25 points)

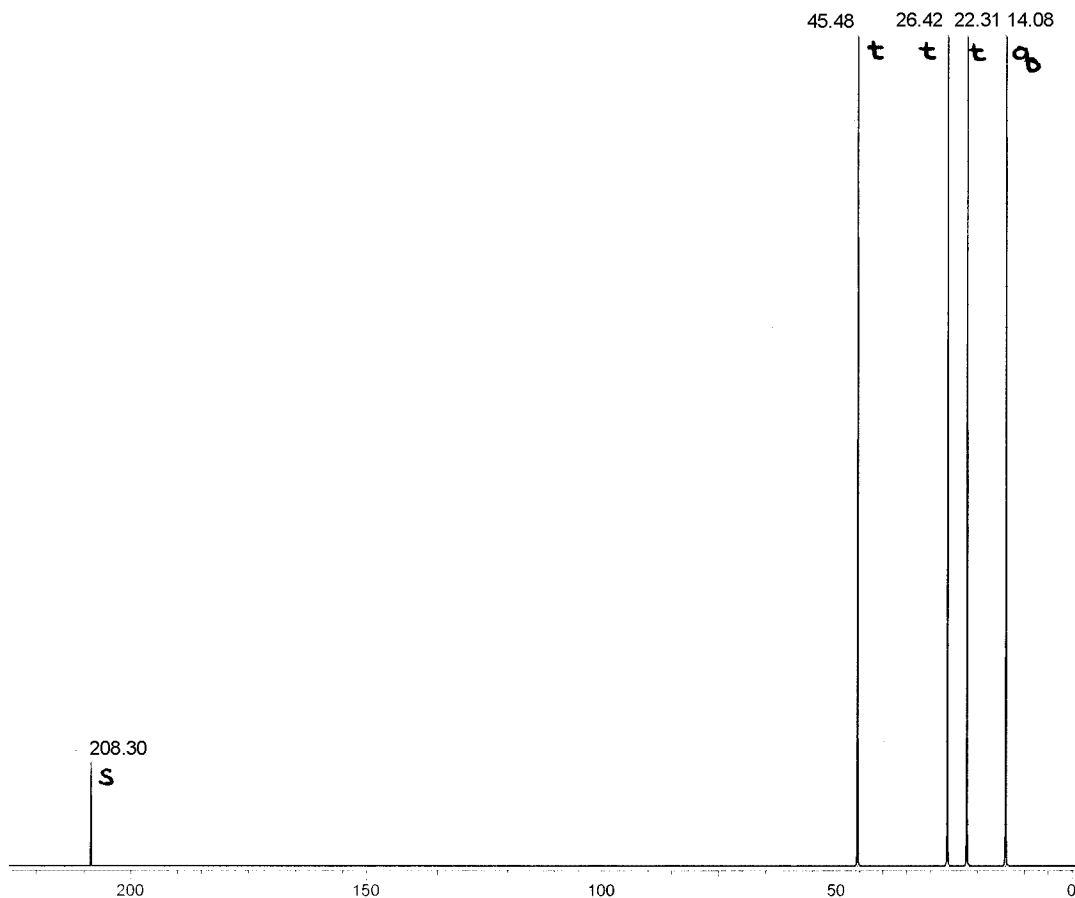
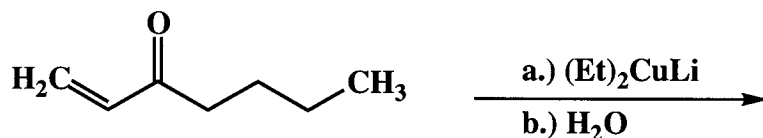
Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show all intermediates and denote all unshared electrons, formal charges and countercharges where appropriate.



Name: _____

7. (20 points)

The following reaction affords a high yield of a single product. The broadband proton-decoupled ^{13}C NMR spectrum of this product is shown below. The ^{13}C NMR multiplicities (s = singlet, t = triplet, q = quartet) are the multiplicities in the corresponding off-resonance proton-decoupled ^{13}C NMR spectrum. Draw all mechanistically reasonable possible products for this reaction. Then circle the actual product. On the next page, clearly assign all the resonances of the ^{13}C NMR spectrum to support your answer. Explain why the alternate possible products can be ruled out due to the spectroscopic data. (A ^{13}C NMR correlation table is included on page 9.)



Name: _____

7. (continued)

¹³C NMR assignments:

chemical shift (ppm)

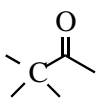

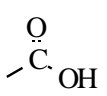



assignment

explanation of multiplicity

Congratulations!

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

SELECTED ^{13}C NMR CORRELATIONS

structural type	chemical shift range (ppm)
cyclopropyl	- 10 - 10
$-\text{CH}_3$ (saturated)	10 - 30
$-\overset{\text{I}}{\text{CH}_2}$ (saturated)	10 - 55
$-\overset{\text{I}}{\text{CH}}$ (saturated)	25 - 55
$-\overset{\text{I}}{\text{C}}$ (saturated)	30 - 55
$-\overset{\text{I}}{\text{C}}-\text{I}$	- 10 - 45
$-\overset{\text{I}}{\text{C}}-\text{Br}$	25 - 65
$-\overset{\text{I}}{\text{C}}-\text{Cl}$	35 - 80
	20 - 50
$-\text{C}-\overset{\text{I}}{\text{N}}$	30 - 70
$-\overset{\text{I}}{\text{C}}-\text{O}-$	40 - 80
$-\text{C}\equiv\text{C}-$	65 - 85
	100 - 150
$-\text{C}\equiv\text{N}$	110 - 125
ArH	110 - 160
 	155 - 185
 	190 - 210