

Chemistry 334

First Hour Examination

September 29, 1995

Professor Charonnat

Name: _____

Be certain that your examination has eight (8) pages including this one.

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

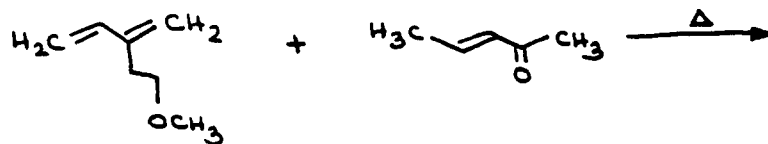
By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Name: _____

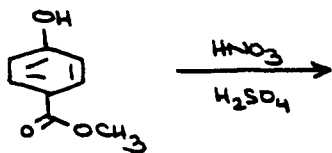
1. (25 points)

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

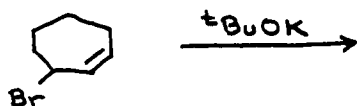
A.



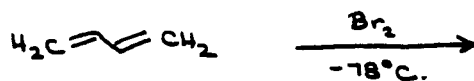
B.



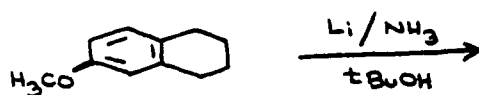
C.



D.



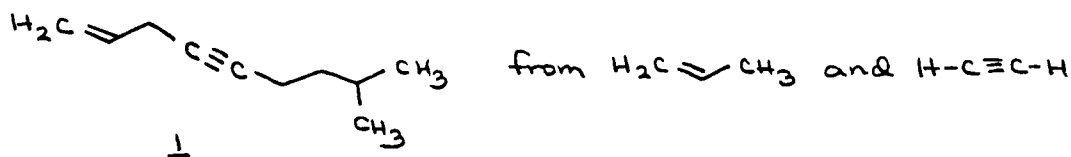
E.



Name: _____

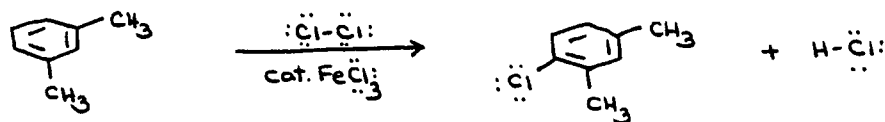
2. (25 points)

Design a synthesis of the following 1,4-enyne from propene, acetylene, mono- or difunctional organic compounds of six carbons or less, and any inorganic reagents that are necessary. Draw clearly **all** reagents and isolable synthetic intermediate products. (**N.B.** Do **not** draw mechanisms for each synthetic transformation!)



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 pairs, formal charges and countercharges where appropriate. Draw **all** important resonance structures that contribute to resonance-stabilized hybrids.



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4. (25 points)

The infrared, ^1H NMR and ^{13}C NMR (broadband ^1H decoupled) spectra of compound A ($\text{C}_8\text{H}_{14}\text{O}$) are shown below. Clearly assign all the resonances that you can identify with certainty and draw the structure of compound A. (Correlation tables follow on pages 6–8.)

The spectra are unavailable due to copyright considerations.

Name: _____

4. (cont.)

Infrared absorption assignments:

wave number (cm⁻¹)	functional group	type of vibration
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¹H NMR assignments:

chemical shift (ppm)	assignment	explanation of multiplicity
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¹³C NMR assignments:

chemical shift (ppm)	assignment	explanation of multiplicity
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structure of compound A:

Congratulations!

1	/25
2	/25
3	/25
4	/25
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Total:	/100

SELECTED INFRARED CORRELATIONS

Hydrocarbons

Alkyl C-H stretch	3000 - 2850 cm^{-1}	medium - strong
Aromatic C-H stretch	~ 3030 cm^{-1}	variable
Alkenyl C-H stretch	3100 - 3010 cm^{-1}	medium
Alkynyl C-H stretch	~ 3300 cm^{-1}	strong
Alkyl C-C stretch	~ 1200 cm^{-1}	weak
Aromatic C-C stretch	1600, 1580, 1500, 1450 cm^{-1}	variable
Isolated Alkenyl C=C stretch	1680 - 1640 cm^{-1}	medium
Conjugated Alkenyl C=C stretch	1640 - 1620 cm^{-1}	weak
Internal Alkynyl C≡C stretch	2260 - 2190 cm^{-1}	weak
Terminal Alkynyl C≡C stretch	2140 - 2100 cm^{-1}	medium

Alkyl Halides

C-F stretch	1400 - 1000 cm^{-1}	strong
C-Cl stretch	800 - 600 cm^{-1}	strong
C-Br stretch	600 - 500 cm^{-1}	strong
C-I stretch	~ 500 cm^{-1}	strong

Alcohols

O-H stretch	3650 - 3200 cm^{-1}	strong, broad
C-O stretch	1410 - 1260, 1200 - 1050 cm^{-1}	strong

Amines

N-H stretch (1° amine)	3500, 3400 cm^{-1}	medium
N-H stretch (2° amine)	3500 - 3310 cm^{-1}	medium
Aromatic C-N stretch	1360 - 1250 cm^{-1}	strong
Aliphatic C-N stretch	1410, 1220 - 1020 cm^{-1}	weak

Imines

C=N stretch	~ 1690 - 1630 cm^{-1}	variable
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Nitriles

C≡N stretch	2260 - 2220 cm^{-1}	medium
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Carbonyl Compounds

C=O stretch	1870 - 1630 cm^{-1}	strong
ketone	1750 - 1660 cm^{-1}	
aldehyde	1740 - 1660 cm^{-1}	
ester	1800 - 1720 cm^{-1}	
lactone	1820 - 1730 cm^{-1}	
carboxylic acid	1730 - 1680 cm^{-1}	
acid anhydride	1870 - 1780, 1830 - 1720 cm^{-1}	
acid chloride	1800 - 1720 cm^{-1}	
amide	1700 - 1630 cm^{-1}	
lactam	1780 - 1680 cm^{-1}	
C-H stretch (aldehyde)	2900 - 2820, 2780 - 2700 cm^{-1}	weak
O-H stretch (carboxylic acid)	~ 3000 cm^{-1}	very broad
N-H stretch (1° amide)	3500 - 3350, 3400 - 3180 cm^{-1}	medium
N-H stretch (2° amide)	3430 - 3140 cm^{-1}	medium

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

SELECTED ^{13}C NMR CORRELATIONS

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