

Chemistry 333

Final Examination

May 19, 2003

Professor Charonnat

Name: _____

Be certain that your examination has thirteen (13) 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.

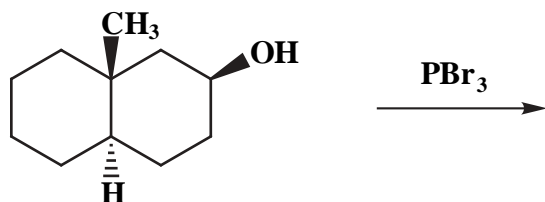
Molecular models are allowed for this examination. Calculators are unnecessary and are not allowed.

Name: _____

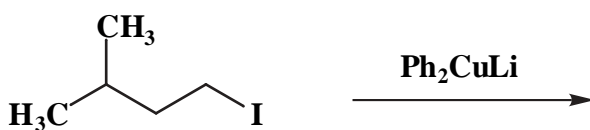
1. (50 points)

For each of the following ten (10) questions draw the structure of the expected major organic product. Clearly specify stereochemistry, if relevant.

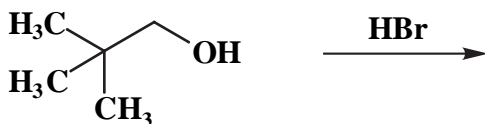
A.



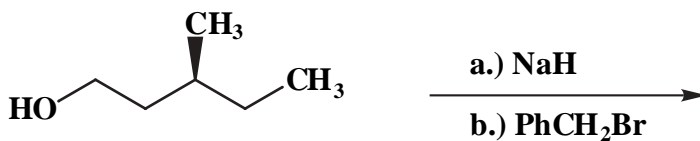
B.



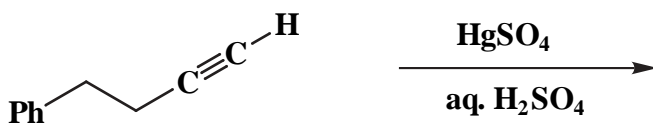
C.



D.



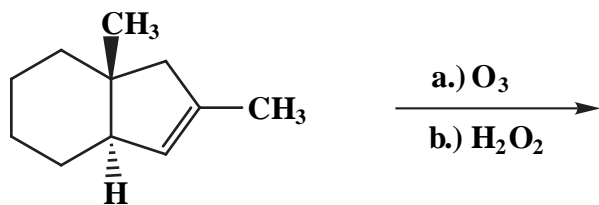
E.



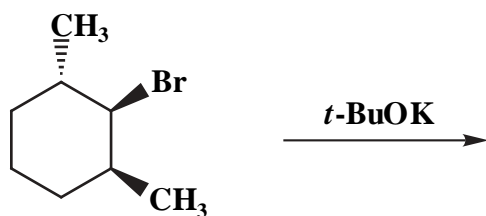
Name: _____

1. (cont.)

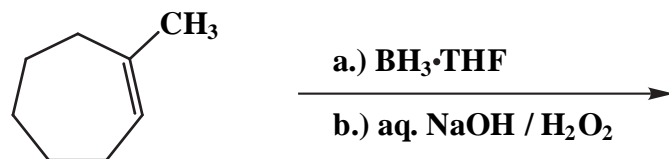
F.



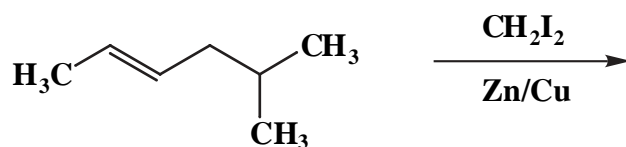
G.



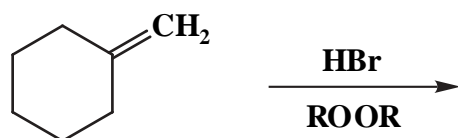
H.



I.



J.



Name: _____

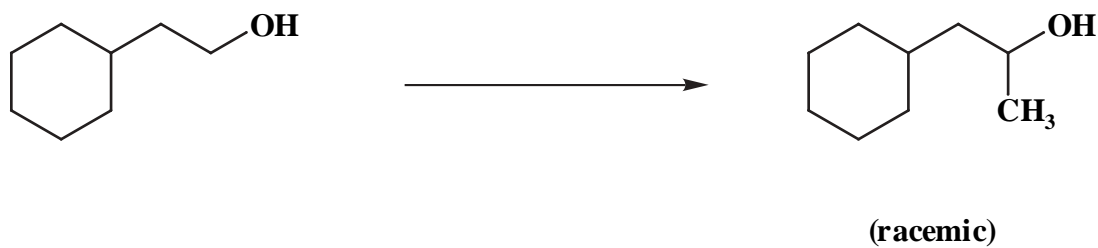
2. (25 points)

For both of the following two (2) 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.

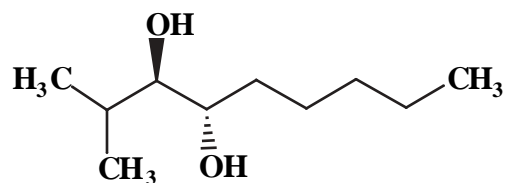


B.



3. (10 points)

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



Name: _____

4. (25 points)

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

A. The rate constant of an S_N1 reaction depends upon:

1. the nucleophile concentration only
2. the substrate concentration only
3. both the nucleophile and substrate concentrations

B. Which of the following alkanes is the least stable?

1. *cis*-1,3-dimethylcyclohexane
2. 1,1,3,3-tetramethylcyclohexane
3. *cis*-1,1,3,5-tetramethylcyclohexane

C. Infrared absorptions are used to probe:

1. electronic transitions
2. vibrational transitions
3. rotational transitions

D. Infrared spectroscopy is used predominantly to determine:

1. molecular weight
2. molecular connectivity
3. functional groups

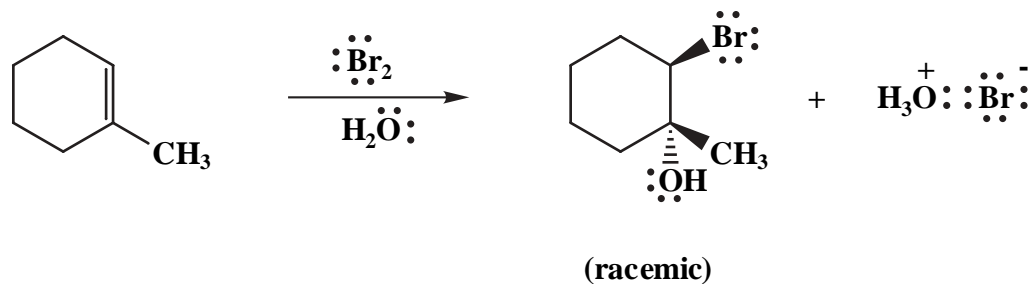
E. Other factors being equal, increased mass causes the vibrational frequency to be:

1. higher
2. the same
3. lower

Name: _____

5. (15 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.



Name: _____

6. (25 points)

The mass spectrum of an unknown organic compound is shown below. What is the identity of the compound? State your reasoning clearly. Analyze as many labeled signals as possible in the mass spectrum.

mass spectral assignments:

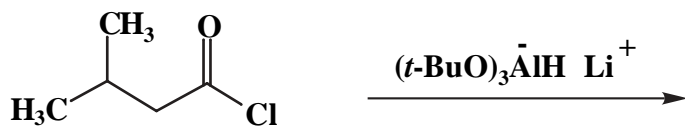
m/z	assignment
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structure :

Name: _____

7. (25 points)

When the following reaction was run, a major product was formed in modest (65%) yield. The ^1H NMR spectrum of the product is shown below (t = triplet, dd = doublet of doublets, t•sept = triplet of septets, d = doublet). Use this spectroscopic evidence to determine the identity of the product. Make clear assignments of all resonances to explain your reasoning. (A ^1H NMR correlation table is included on page 12.)



Name: _____

7. (continued)

¹H NMR assignments:

chemical shift (ppm)

assignment

explanation of multiplicity

structure:

Name: _____

8. (25 points)

The broadband proton-decoupled ^{13}C NMR spectrum of an unknown compound ($\text{C}_{10}\text{H}_{14}$) is shown below. The labels next to each of the resonances signify the multiplicities observed in the corresponding off-resonance proton-decoupled ^{13}C NMR spectrum (s = singlet, d = doublet, t = triplet, q = quartet). Use this spectroscopic evidence to determine the identity of the compound. Make clear assignments of all resonances to explain your reasoning. (A ^{13}C NMR correlation table is included on page 13.)

Name: _____

8. (continued)

¹³C NMR assignments:

chemical shift (ppm)

assignment

explanation of multiplicity

structure:

Congratulations!

1	/50
2	/25
3	/10
4	/25
5	/15
6	/25
7	/25
8	/25
Total:	<hr/> /200

course grade: _____

SELECTED ^1H NMR CORRELATIONS

structural type	chemical shift range (ppm)
cyclopropyl	0.0 - 0.9
RNH_2 R_2NH	0.5 - 5.0 ^a
$-\text{CH}_3$ (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
$-\overset{\text{I}}{\text{CH}_2}$ (saturated)	1.2 - 1.3
$-\overset{\text{I}}{\text{CH}}$ (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
$\text{H}_3\text{C}-\text{Ar}$	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
$\text{Ar}-\text{NH}_2$ Ar_2NH	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
$\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \diagup \end{array}$	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
$\begin{array}{c} \diagdown \text{C} \diagup \\ // \\ \diagdown \text{C} \diagup \end{array}$	100 - 150
$-\text{C}\equiv\text{N}$	110 - 125
ArH	110 - 160
$\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \text{OH} \end{array}$ $\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \text{X} \end{array}$	155 - 185
$\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \text{H} \end{array}$ $\begin{array}{c} \text{O} \\ // \\ \diagdown \text{C} \diagup \end{array}$	190 - 210