CHM 228 Exam 1b Summer 2013

Multiple Choice
Identify the choice that best completes the statement or answers the question.

Instructions: Select the most reasonable formula for the compounds with the following mass spectral data.

1. Refer to instructions. M+ at m/z = 101
   a. C₅H₆Br
   b. C₄H₂N₂
   c. C₆H₅N
   d. C₅H₁₂O

   Instructions: Refer to the structure of 3-methylbutan-2-one below to answer the following question(s).

   ![Structure of 3-methylbutan-2-one]

   2. Refer to instructions. What is the splitting pattern for the hydrogens in 3-methylbutan-2-one labeled A, B, and C, respectively?
      a. singlet, singlet, singlet
      b. singlet, septet, quartet
      c. singlet, septet, doublet
      d. singlet, septet, doublet, doublet

   3. Refer to instructions. What is the ratio of peak areas upon integration of the spectrum for A, B, and C respectively?
      a. 3:1:3:3
      b. 1:1:6
      c. 1:1:6
      d. 3:1:6
Problem

4. Below is the mass spectrum of an unknown hydrocarbon. In addition, this hydrocarbon shows characteristic absorption at 2100 cm\(^{-1}\) in its IR spectrum. Give the structure of this unknown.

(Spectrum obtained from: SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/)

5. Cyclohexene and hex-2-yne both have the molecular formula, C\(_6\)H\(_{10}\).

a) How would you use infrared spectroscopy to distinguish between the two compounds?

b) How could the mass spectrum be used to distinguish between the two compounds?

IR yne has 2100
ene has 3090 + 1640
mass - same M\(^+\)
fragmentation would be different
yne CH\(_3\)C=CC=CH\(_2\)
ene C\(_6\)H\(_5\) = 57
allylic like
Instructions: For each of the compounds below tell how many signals you would expect the molecule to have in its normal, broadband decoupled $^{13}$C NMR spectra.

6. Number of signals:

7. Number of signals:

8. Treatment of tert-butyl alcohol with hydrogen chloride yields a mixture of tert-butyl chloride and 2-methylpropene.

$\text{(CH}_3\text{)}_3\text{COH} \xrightarrow{\text{HCl}} \text{(CH}_3\text{)}_3\text{CCl} + \text{(CH}_3\text{)}_2\text{C}==\text{CH}_2$

a) After chromatographic separation, how would you use $^1$H NMR to help you decide which was which?

b) How would the $^{13}$C NMR for the two compounds differ?

$^1$H NMR ENE 2 SIGNALS
ONE AT 5-6 ppm
ONE AT 1.7 ppm
HALIDE 1 SIGNAL $\approx$ 1.5

$^{13}$C ENE 2 PEAKS 100-140 ppm
HALIDE 1 PEAK $\approx$ 40 ppm
1 PEAK $\approx$ 20 ppm
Matching

**Instructions:** Match a structure from the list below to the following IR spectra.

A. \[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array}
\]

B. \[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array}
\]

C. \[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array}
\]

D. \[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array}
\]

E. \[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array}
\]

F. \[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array}
\]

(Spectrum obtained from: SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/)
Which has a stronger (more intense) characteristic stretching frequency in the IR spectrum, C=C or C=O? Briefly explain why.

\[ C=O \text{ larger dipole} \]

Describe (using the 4 types of information available in an NMR spectrum), the proton spectrum of the reactant and the product when 1, 3-butadiene reacts with Hydrogen gas (H₂) and a catalyst to form butane.

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{CH}=&\text{CH}_2 \\
1) & \text{ 2 signals} \\
2) & \text{ 2:1 integration} \\
3) & \text{ 5-6 ppm} \\
4) & \text{ doublet + triplet}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
1) & \text{ 2 signals} \\
2) & \text{ 3:2 integration} \\
3) & \text{ 1.3-0.9 ppm} \\
4) & \text{ triplet + quartet}
\end{align*}
\]

4) Also acceptable \( \rightarrow \) \text{doublet, quartet} \quad \text{but not correct}

Use the spectra on the following pages to identify the compound. Partial credit for any fact that you can establish, such as D.U., Molecular mass, etc.
ISO PROPYL ALCOHOL

No significant UV absorption above 220 nm
Problem 69

IR Spectrum (liquid film)

Mass Spectrum

$C_4H_8O_2$

$^{13}C$ NMR Spectrum
(50.0 MHz, CDCl$_3$ solution)

DEPT

proton decoupled

 solvent

$^1H$ NMR Spectrum
(200 MHz, CDCl$_3$ solution)

expansions

exchanges with D$_2$O

TMS

No strong UV absorption above 220 nm
**IR Spectrum**

(liquid film)

- Wavenumber: 3500 - 2200 cm⁻¹
- peak at 1709 cm⁻¹

**Mass Spectrum**

- Mass: M⁺ 116 < 1%
- Structure: C₆H₁₂O₂

**13C NMR Spectrum**

(100 MHz, CDCl₃ solution)

- DEPT: CH₂, CH₃, CH
- Solvent
- Proton decoupled

**1H NMR Spectrum**

(400 MHz, CDCl₃ solution)

- Exchanges with D₂O
- Offset
- TMS

**No significant UV absorption above 220 nm**

**Formula**

`CH₃-C=C-C-OH`
CH₃CH₂-O-CH₂-CH₃

No significant UV absorption above 220 nm
Problem

Instructions: Consider the pair of reactions below to answer the following question(s).

a. \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{-\text{OH}, \text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Br}^- \]

or

b. \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{-\text{SH}, \text{RSH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{SH} + \text{Br}^- \]

1. Consider the reactions above.
   a) Which reaction would be predicted to be faster? B
   b) Classify the reactions as S_N1 or S_N2.
   c) Explain your answers to the questions above.

2. Consider the following compound:

   ![Chemical Structure]

   a) What is the IUPAC name of the compound?
   a. (R)-1-chloro-3-methyl-2-cyclohexene
   b. (S)-1-chloro-3-methyl-2-cyclohexene
   c. (R)-3-chloro-1-methylcyclohexene
   d. (S)-3-chloro-1-methylcyclohexene

   b) How could this compound be used to produce a conjugated diene?
   a. substitution
   b. elimination
   c. allylic free radical formation
   d. either b or c
Multiple Choice
Identify the choice that best completes the statement or answers the question.

**Instructions:** Consider the reaction below to answer the following question.

![Chemical structure](image)

3. Refer to instructions. The mechanism for this reaction is:
   a. $S_n2$
   b. E2
   c. $S_n1$
   d. E1

**Instructions:** Consider the reaction below to answer the following question(s).

![Chemical structures](image)

4. Refer to instructions. Compound B is the:
   a. $S_n2$ product
   b. $S_n1$ product
   c. E2 product
   d. E1 product

5. Refer to instructions. Compound C is the:
   a. $S_n2$ product
   b. $S_n1$ product
   c. E2 product
   d. E1 product

6. Which conditions favor an efficient (fast, high yield) $S_n2$ reaction between an appropriate alkyl halide and a nucleophile with a charge?
   a. high concentration of a strong nucleophile, polar protic solvent
   b. high concentration of a weak nucleophile, nonpolar solvent
   c. low concentration of a strong nucleophile, polar aprotic solvent
   d. low concentration of a weak nucleophile, nonpolar solvent
   e. high concentration of a strong nucleophile, polar aprotic solvent
7. Which of the following represents the transition state of the $S_{N2}$ reaction between methyl iodide and ammonia?

- a.

- b.

- c.

- d.

Short Answer

8. Order these compounds with respect to $S_{N2}$ reactivity. (1 = most reactive, 3 = least).

2-chloro-2-methylpropane 1-chloropropane 2-chlorobutane

- 3

- 1

- 2
9. Solvolysis (in methanol) of 2-bromo-3-methylbutane gives several products. Draw structures of all E1 and SN1 products.

\[
\begin{align*}
\text{SN1} & : \quad \text{C=CH}_2 + \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3 \\
\text{E1} & : \quad \text{C=CH}_2 + \text{CH}_3 \text{CH}_2 \text{CH}_3
\end{align*}
\]

10. Draw a complete SN2 mechanism for the reaction of cyclohexanol with HBr.

\[
\begin{align*}
\text{SN2} & : \quad \text{O-H} + \text{H-Br} \rightarrow \text{Br}^{-} + \text{H}_2\text{O}
\end{align*}
\]

2-bromo-2-methylbutane or 2-bromo-3-methylbutane.

12. 3-bromocyclohexene undergoes $S_N1$ reaction rapidly in methanol. Draw a complete mechanism.

13. Show the reagents required to convert 1-chlorobutane into:

1-hexyne

1-butanol

14. Which is the strongest nucleophile? Choose one from each pair. Briefly explain your choice.

Iodide or chloride

CH$_3$CH$_2$CH$_2$O$^-$ or CH$_3$CHCH$_3$
15. Make a **stereochemical** drawing of the product.

(S)-1-bromo-1-fluoroethane reacts with NaOH.

16. Draw the structure of the product.

17. Draw the structure of an alkylhalide that will produce only 2,4-diphenylpent-2-ene in an E2 reaction.

For extra credit, make a stereochemical drawing of the halide that will produce the E isomer.