Chem 21 Problem Set – Exam III

A. Spectroscopy

1. Review the following terms:
   a) wavelength: \( \lambda \) distance between crests of a wave
   b) frequency: \( f \) # of waves passing through a given point/sec
   c) wavenumber: \( \tilde{\nu} \) in cm\(^{-1}\)
   d) absorption: \[ \log \text{ of transmittance} \]
   e) transmittance: \[ \frac{I}{I_0} = \text{transmittance} \]
   f) bond stretching vs. bending vibrations

2. What characteristics of a sample determine absorption band position in IR spectroscopy?
   • mass of atoms in bond in question:
   • strength of bond in question: \( \tilde{\nu} \) Hooke's Law

3. What characteristics of a sample determine absorption band intensity?
   • bond polarity: \( \tilde{\nu} \) intensity
   • number of bonds
   • sample concentration
   • type of bond

4. Match each of the IR spectra shown below with the class of organic compounds that is represented by the spectrum. Choose from the following list: alkane, alkene, alcohol, ether, amine, carboxylic acid, ester, amide.
5. What characteristics must a sample have to absorb UV and/or visible light? How does conjugation affect UV/VIS absorption?

- ππ* and/or non-bonding π–π
- Conjugation lowers energy needed for LUMO → HOMO
- π and π* are inversely proportional

6. How might a molecule undergo a “red shift” or “blue shift?” Give examples.

- Conditions that add or subtract from delocalization of π–π such as protonation/deprotonation

7. What is the Beer’s Law equation; how can it be used?

\[ A = \varepsilon L c \]  

Beer’s Law provides a mathematical correlation between A and c

8. Consider the UV/VIS spectra shown below for NAD⁺ and NADH. How might one measure the rate of a reaction that consumes NAD⁺ and generates NADH?

- NADH absorbs light of \( \lambda = 340 \text{ nm} \)
- NAD⁺ does not absorb light of \( \lambda = 340 \text{ nm} \)
- A sample composed of reactants which generates NADH and consumes NAD⁺ will absorb \( \lambda = 340 \text{ nm} \) at a rate that reflects rate at which NADH is made.

9. What is the molecular ion that is produced in mass spectrometry?

Molecular ion = molecule from which a \( e^- \) has been removed and therefore carries a net \( +\) charge

10. How can one use the molecular ion and the M+1 peaks to determine the number of C in a molecule? How can one use the “rule of 13” to find a “base formula” for a sample? What is suggested by the presence of an M+2 peak?

\[ \frac{\text{intensity of M+1}}{\text{intensity of M}} = \# \text{ of } C \]

\[ \frac{m/2}{13} = \text{integer} + \# C \]

\[ \text{remainder} = R + 2 = \# H \]

M+2 usually means if a Cl or Br is present
11. a) The mass spectrum of an alkyl halide is shown below:

   i. What is the molecular mass of the alkyl halide $m/z = 139$
   ii. What halide is present? $\text{Br}$
   iii. Given that the peak at $m/z = 55$ represents the heterolytic cleavage product of this alkyl halide, what is the molecular formula of the compound and suggest a few possible structures.

b) Identify 2 different “homolytic cleavage products” on the mass spectrum generated from 1-ethoxybutane shown:

c) The mass spectrum for 2,6-dimethyl-4-heptanone is shown. Which peak represents the McLafferty rearrangement product?
12. Match the following $^{13}$C-NMR with the compounds listed here:

- **p-xylene**
  - Chemical structure:
  - NMR spectrum:

- **2-methylbutanal**
  - Chemical structure:
  - NMR spectrum:

- **Toluene**
  - Chemical structure:
  - NMR spectrum:

- **dipropyl ether**
  - Chemical structure:
  - NMR spectrum:

- **2,2,4-trimethylpentane**
  - Chemical structure:
  - NMR spectrum:
13. $^1$H-NMR
a) 2-pentanone or 2-butanol?

b) 2-pentanol or 3-pentanol
c) IR and 1H-NMR data are shown below for a compound with a molecular formula of $C_5H_{10}O$. Determine the structure of the compound. Explain the splitting pattern for the peaks at $\sim 2.2$ ppm

![IR and 1H-NMR spectra with annotations](image)

- $CH_2$ split by $CH$
- $CH_3$ split by $CH$ with different $J$ values
- $CH - (CH_3)_2$
- $(CH_3)_2 - CH$

I = 1, 2, 6

I = 1

9.0 2.0 1.0 ppm from TMS

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d) IR and 1H-NMR data are shown below for a compound with a molecular formula of $C_5H_{10}O$. Determine the structure of the compound.

![IR and 1H-NMR spectra with annotations](image)

- $\text{no } C = O$
- $\text{no } O - H$
- aromatic

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B. Alkynes

1. Name this compound:

2. What are the major products when 2-hexyne is treated with the following reagents? 1-hexyne?
   a. H₂ with Pt/C
   b. H₂ with Lindlar catalyst
   c. sodium metal in liquid ammonia
   d. sodium amide, NaNH₂
   e. aqueous H₂SO₄ (1 eq.)
   f. 1 eq. of HCl

C. Delocalized Electrons

1. Draw two additional resonance structures of the species shown below. Include formal charges and curved arrows to show electron movement. Circle the most stable structure of the three.

2. Draw the structures of the 1,2- and 1,4-addition products that result from the reaction below. Label the kinetic product and the thermodynamic product.

3. Predict the product of the reaction shown.
D. Organic Synthesis

1. Show how each of the following compounds could be prepared using the given organic starting materials, organic reagents with no more than 4 C and any necessary inorganic reagents.

a) \[ \text{H}_3\text{C}-\text{C}≡\text{CH} \]

\[ \text{NaNH}_2 \]

\[ \text{Pb Br}_2 \]

\[ \text{Br}_2/\text{CH}_2\text{Cl}_2 \]

Lindlar's catalyst

b) \[ \text{cis-4,5-dimethylcyclohexene} \]