TOPIC 9. STRUCTURE DETERMINATION
(chapter 9 and part of chapter 2)

OBJECTIVES

1. Use combustion analysis to determine empirical formula.
2. Determine molecular weight (and molecular formula) from mass spectrometry.
3. Calculate number of rings and double bonds from molecular formula.
4. Use $^1$H and $^{13}$C NMR spectroscopy to identify other structural features.
5. Combine conclusions from individual techniques to determine the structure of organic compounds.

Problems in this section will be restricted to the following classes of aliphatic and aromatic compounds:

Alkanes, alkenes, alkynes, alkyl halides, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, acyl chlorides, anhydrides, amides, amines, nitriles
COMBUSTION ANALYSIS

\[ C_xH_yO_z + O_2 \rightarrow xCO_2 + (\frac{y}{2})H_2O \]

Measure mass of CO\(_2\) and H\(_2\)O formed from a known mass of compound; data cited as mass % of each element present.

e.g.,

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass%</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>55.7</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>37.3</td>
<td></td>
</tr>
</tbody>
</table>

Mole% =

Ratio =

Be careful when rounding. Do not round by more than 0.05 to 0.1

EMPIRICAL AND MOLECULAR FORMULAS; DETERMINATION OF “SODAR”

Molecular formula is an integral number of times the empirical formula.

\[ C_2H_3O \]

Sum of double bonds or rings (“SODAR”)

For C, H, O:

\[ \frac{(2\#C + 2 - \#H)}{2} \]

For C, H, O, N, Hal:

\[ \frac{(2\#C + 2 - \#H - \#Hal + \#N)}{2} \]

Each Hal replaces a H
Each N adds an extra H
S, O: no effect on calculation

If SODAR calculated from empirical formula is not a positive integral (or 0), this cannot be the molecular formula.

\[ C_2H_3O \]
Problem: Determine the value of SODAR for the following molecular formulas.

SODAR

CH$_3$Br

CH$_5$N

C$_3$H$_8$N

C$_6$H$_6$

MASS SPECTROMETRY

Theory and Experiment

$M + e^- (70 \text{ eV}) \rightarrow M^+ + 2e^-$

$M^+ \rightarrow$ lower mass ions
Data Available
e.g., mass spectrum of ethane, CH₃CH₃

![Graph showing mass spectrum data]

Ions also fragment, which can give further clues about the structure (beyond scope of this course).

Knowledge of molecular weight (from mass spec) and empirical formula (from combustion analysis) allows determination of molecular formula.

---

[SPECTROSCOPY: THE INTERACTION OF LIGHT AND MATTER]

High energy - kills life

<table>
<thead>
<tr>
<th>Highest energy</th>
<th>Very dangerous</th>
<th>Tanning rays</th>
<th>What we see</th>
<th>IR - bonds vibrating</th>
<th>Microwave oven, rotation of molecules</th>
<th>Lowest energy</th>
<th>Radio/TV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cosmic rays</td>
<td>X-rays</td>
<td>Visible</td>
<td>Microwave</td>
<td>NMR</td>
<td>Microwave</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10^{19} Hz</td>
<td>10^{16} Hz</td>
<td>10^{13} Hz</td>
<td>10^{11} Hz</td>
<td>10^{9} Hz</td>
<td>10^{7} Hz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 nm</td>
<td>200 nm</td>
<td>400 nm</td>
<td>800 nm</td>
<td>2 μm</td>
<td>50 μm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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INFRARED SPECTROSCOPY

See Chapter 2; Table 2.7

Problem: Determine the structure of the compound with the following empirical formula and IR spectrum.

Empirical formula: C₄H₈O

IR; peak at 1720 cm⁻¹; no broad peak at 3300, no strong peaks at 1000 to 1200 cm⁻¹, no strong peaks at 1600-1650 cm⁻¹
HYDROGEN (PROTON) NUCLEAR MAGNETIC RESONANCE (\(^{1}H\) NMR) SPECTROSCOPY

Nuclear Spin (\(^{1}H, ^{13}C, ^{19}F, ^{31}P\))

The Energy of the Spin States of Hydrogen Nuclei in a Magnetic Field
An early $^1$H NMR spectrum

...not much chemical information

A modern $^1$H NMR spectrum

...lots of chemical information

If the applied magnetic field is held constant, the protons $H_a$ and $H_b$ absorb irradiation with different frequencies.
Preview: Types of Information available from a $^1$H NMR spectrum

A $^1$H nuclear magnetic resonance spectrum contains information about the:

(a) number of different types of proton

(b) relative number of each type of proton

(c) proximity to functional groups

(d) the number of adjacent protons

(a) The number of signals in the spectrum is the number of types of proton.

$^1$H NMR spectrum of methane $\text{CH}_4$

\[ E \quad \text{one peak} \Rightarrow \text{one type of proton} \]

$^1$H NMR spectrum of ethane $\text{CH}_3\text{CH}_3$

\[ E \quad \text{one peak} \Rightarrow \text{one type of proton} \]
$^1$H nuclear magnetic resonance spectrum of methanol...

\[ \text{CH}_3\text{–OH} \]

\[ \text{two peaks} \Rightarrow \text{two types of proton} \]

(b) The relative area of each peak (the integration) corresponds to the relative number of each type of proton

$^1$H NMR spectrum of methanol

\[ \text{H}_3\text{C–OH} \]

integral ratio \( \frac{\_}{\_} \Rightarrow \text{ratio of types of proton} \)

$^1$H NMR spectrum of $p$-xylene

\[ \text{H}_3\text{C–CH}_3 \]

integral ratio \( \frac{\_}{\_} \Rightarrow \text{ratio of types of proton} \)
(c) The chemical shift indicates the environment of the proton

$^1$H NMR spectrum of methanol

Shielding and Deshielding
**The δ-scale**

The frequency at which a proton resonates is measured relative to the frequency for the protons of tetramethylsilane, TMS (which resonates at a relatively low frequency), and cited on the δ (delta) scale in parts per million of the frequency at which TMS resonates.

\[
\delta = \frac{v_{\text{proton}} - v_{\text{TMS}}}{v_{\text{TMS}}} \times 10^6 \quad \text{[ppm]}
\]

---

**Effect of Structure on Chemical Shift (δ scale, ppm)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-CH₃</td>
<td>0.9</td>
</tr>
<tr>
<td>CH₃-N(CH₃)₂</td>
<td>2.2</td>
</tr>
<tr>
<td>CH₃-OCH₃</td>
<td>3.2</td>
</tr>
<tr>
<td>CH₃-F</td>
<td>4.3</td>
</tr>
<tr>
<td>CH₃-Cl</td>
<td>3.1</td>
</tr>
<tr>
<td>CH₃-Br</td>
<td>2.7</td>
</tr>
<tr>
<td>CH₃-I</td>
<td>2.2</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>7.3</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>5.3</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Approximate $^1H$-NMR chemical shifts for various substituent groups

<table>
<thead>
<tr>
<th>Type of proton</th>
<th>Expected range</th>
<th>Typical value</th>
<th>$\Delta$ (Change in chemical shift)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3$-$\text{C}$-$\text{R}$ (sp$^3$)</td>
<td>0.9 - 1.8</td>
<td>1.0</td>
<td>-- (methyl standard position)</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{R}$ (sp$^3$)</td>
<td>1.1 - 2.0</td>
<td>1.2</td>
<td>0.2 (methylene)</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{C}$-$\text{R}$ (sp$^3$)</td>
<td>1.3 - 2.1</td>
<td>1.4</td>
<td>0.4 (methylene)</td>
</tr>
<tr>
<td>$\text{CH}$-$\text{C}$-$\text{R}$ (sp$^3$)</td>
<td>2.2 - 2.8</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{O}$</td>
<td>3.3 - 3.7</td>
<td>3.5</td>
<td>2.5</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{Br}$</td>
<td>3.1 - 4.1</td>
<td>3.2</td>
<td>2.2</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{C}$-$\text{O}$</td>
<td>2.7 - 4.1</td>
<td>2.8</td>
<td>1.8</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{C}$-$\text{N}$</td>
<td>1.6 - 2.6</td>
<td>1.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{C}$-$\text{Cl}$</td>
<td>2.3 - 2.9</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{C}$-$\text{Br}$</td>
<td>9 - 10</td>
<td>9.5</td>
<td>--</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{C}$-$\text{O}$</td>
<td>4.5 - 6.0</td>
<td>5.5</td>
<td>--</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{N}$-$\text{R}$</td>
<td>6.5 - 8.5</td>
<td>7.0</td>
<td>--</td>
</tr>
<tr>
<td>$\text{H}$-$\text{C}$-$\text{N}$-$\text{N}$</td>
<td>2.5</td>
<td>2.5</td>
<td>--</td>
</tr>
<tr>
<td>$\text{H}$-$\text{OH}$ (alcohol)</td>
<td>1 - 3*</td>
<td>1 - 3*</td>
<td>--</td>
</tr>
<tr>
<td>$\text{H}$-$\text{OH}$ (phenol)</td>
<td>5 - 8*</td>
<td>5 - 8*</td>
<td>--</td>
</tr>
</tbody>
</table>

Note that the $\Delta$ (change in chemical shift) values are additive. For example:

- $\text{Ar}$-$\text{CH}_2$-$\text{N}$-$\text{R}$, Chemical shift of $\text{CH}_2$-$\text{N}$-$\text{R}$ group = $1.5 (\text{Ar}) + 1.5 (\text{N}) + 0.2 (\text{m}) + 4.2 \text{ ppm}$
- $\text{Ar}$-$\text{CH}_2$-$\text{OH}$, Chemical shift of $\text{CH}_2$-$\text{OH}$ group = $1.5 (\text{Ar}) + 2.5 (\text{O}) + 0.2 (\text{m}) + 5.2 \text{ ppm}$

Approximate $^{13}$C-NMR chemical shifts for various carbon atoms

Aliphatic, 0 to 40 ppm; aliphatic with electronegative substituent, 30 to 60 ppm; triple bond, 65-90; double bond, 100-150 ppm; aromatic, 110-175 ppm; carbonyl, 170 to 220 ppm

You will be provided with a copy of Table 9.1 on exams. This provides approximate ranges for values of chemical shifts for particular types of protons. Remember that protons adjacent to two (or more) electron withdrawing groups will appear further downfield than a proton adjacent to only one.

(d) The multiplicity of a signal indicates the number of adjacent protons

$^1H$ NMR spectrum of ethanol
Spin-Spin Coupling

The magnetic field experienced by a proton is effected by the magnetic field generated by each adjacent proton.

If \( H_b \) spin \( \uparrow \), need to apply larger \( E (=h\nu) \) to achieve resonance of \( H_a \).

If \( H_b \) spin \( \downarrow \), need to apply smaller \( E (=h\nu) \) to achieve resonance of \( H_a \).

If \( H_a \) spins \( \uparrow + \uparrow \), need to apply larger \( E (=h\nu) \) to achieve resonance of \( H_b \).

If \( H_a \) spins \( \uparrow + \downarrow \), or, \( \downarrow + \uparrow \) need to apply \( E \) achieve resonance of \( H_b \).

If \( H_a \) spins \( \downarrow + \downarrow \), need to apply smaller \( E (=h\nu) \) to achieve resonance of \( H_b \).
Coupling is only observed between non-equivalent protons.

The signal for proton a proton with $N$ adjacent equivalent protons will be split into a multiplet consisting of $N+1$ lines.

The relative area of each peak within a multiplet can be determined from Pascal's triangle.
Problems: How can you get a pentet?

Problems: What is the multiplicity of the signal for the following protons?
   (a) the protons of 1,2-dichloroethane
   (b) the protons of C-2 of 1,4-dichlorobutane
**Multiplets of Multiplets**

\[ J_{ab} > J_{bc} \quad J_{ab} = J_{bc} \]

---

**Geminal protons**

- Rings
- Vinyl groups
Summary: Types of information available from $^1$H NMR spectrum

<table>
<thead>
<tr>
<th>Number of signals</th>
<th>Number of types of proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integral of signals</td>
<td>Relative number of each type of proton</td>
</tr>
<tr>
<td>Chemical Shift</td>
<td>Electronic environment</td>
</tr>
<tr>
<td>Multiplicity</td>
<td>Number of adjacent protons</td>
</tr>
</tbody>
</table>

Problems: Predict the appearance (chemical shift, integral and multiplicity) of the $^1$H NMR signals of the following compounds.

(a) 2-butanone, CH$_3$COCH$_2$CH$_3$

(b) methyl 3-chloropropanoate, CICH$_2$CH$_2$CO$_2$CH$_3$
Problems: Provide structures consistent with the following data.

(a) Compound A: C₂H₄Cl₂, one singlet in ¹H NMR spectrum

(b) Compound B: C₅H₁₂O₂, two singlets in ¹H NMR spectrum

1³C NMR SPECTROMETRY

Introduction

¹³C (not ¹²C) has nuclear spin

However, ¹³C is only present at 1.1% abundance

- Signals are weak
- Spectra usually acquired without multiplicity information

- Larger range of chemical shifts (0 to >200 ppm)
Types of Information available from a $^{13}$C NMR spectrum

A $^{13}$C nuclear magnetic resonance spectrum contains information about the:

(a) number of different types of carbon
   - Each peak corresponds to a different type of carbon
(b) type of carbons and proximity to functional groups
   - Chemical shift provides information about the type of carbon present

Unlike $^1$H NMR spectra, simple $^{13}$C NMR spectra do not provide information about the:

relative number of each type of proton
or
number of adjacent protons or carbons
USING DATA TO DETERMINE STRUCTURE

1. Write down conclusions from each individual technique
   - Use combustion analysis to determine empirical formula, and mass spectrometry to give molecular weight (and molecular formula)
   - Calculate number of rings and double bonds from molecular formula (SODAR)
   - Determine presence of functional groups present from infrared spectroscopy.
   - Use $^1$H and $^{13}$C NMR spectroscopy to identify other structural features.
2. Use these conclusions to determine the structure
3. Check your answer (predict the spectra; do your predicted spectra match the data provided?)

WORK PROBLEMS!!

In the remaining lectures we will cover problem solving approaches for determining organic structures from spectral (and other) information.

Additional problem appear in the following sources:

Solomons 9.29-38
www.nd.edu/~smithgrp/structure/workbook.html

(just do the “easy” problems from this site. The answers to these problems are NOT available from this site; do not bother Prof. Smith. The answers to the easy problems, along with answers to the problems in these notes are posted on the “Notes and HWebs” page of the course web site)
USING SPECTRAL INFORMATION AND OTHER DATA TO DETERMINE THE STRUCTURE OF AN UNKNOWN COMPOUND

Elemental Analysis: C, 54.51; H, 9.09

Mass spectrometry: m/e M⁺, 88

A. If you are provided with the elemental analysis (%C, H, O...), determine the empirical formula i.e., ratio of elements, C : H : O : ... = %C/12 : %H/1 : %O/16 : ...

| empirical formula: ____________ |

REMEMBER: The molecular formula might be an integral times the empirical formula

If you are provided with the molecular weight (from mass spectrometry), determine the molecular formula and determine the number of multiple bonds and rings (i.e., SODAR):

for C, H, O, N, Hal: SODAR = (2#C + 2 - #H - #Hal + #N) / 2 ; SODAR= ____________

Infrared Spectrum

<table>
<thead>
<tr>
<th>absorbance - %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>frequency – cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
</tr>
<tr>
<td>3000</td>
</tr>
<tr>
<td>2000</td>
</tr>
<tr>
<td>1500</td>
</tr>
<tr>
<td>1000</td>
</tr>
<tr>
<td>500</td>
</tr>
</tbody>
</table>

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B. Bonds vibrate at certain frequencies. Determine the bonds present (and hence the functional groups) by considering the infrared spectrum

i. Does your compound contain oxygen? Y N If there is no oxygen, go to part Bii.

(a) C=O bonds vibrate at approximately 1700 cm\(^{-1}\), usually giving rise to a strong absorption. Is there a strong absorption around 1700 cm\(^{-1}\)? Some tables list frequencies for specific carbonyl-containing functional groups.

Y ? N Conclusion: ______________________ |

(b) C-O bonds vibrate at approximately 1200-1000 cm\(^{-1}\); these peaks are usually strong. Is there a strong absorption at 1000-1200 cm\(^{-1}\)?

Y ? N Conclusion: ______________________ |

(c) O-H bonds give rise to a broad vibration band; in alcohols this appears at approximately 3300 cm\(^{-1}\), but in carboxylic acids this band is very broad and might also appear between 2800 and 3200 cm\(^{-1}\) (which overlaps with sharp C-H bond vibrational bands). If nitrogen is present, remember that N-H bonds also vibrate at 3000-3500 cm\(^{-1}\). Is there a broad absorption in the 3500-3000 cm\(^{-1}\) range?

Y ? N Conclusion: ______________________ |

(d) Based on the presence or absence of vibrational bands arising from covalent bonds to oxygen, you should be able to predict the functional groups present in the molecule. Circle the combination of bonds present and the corresponding functional group:

<table>
<thead>
<tr>
<th>Bonds Present</th>
<th>Absent</th>
<th>Functional Group</th>
<th>Bonds Present</th>
<th>Absent</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O, O-H, C-O</td>
<td>-</td>
<td>acid</td>
<td>C=O</td>
<td>O-H, O-H</td>
<td>ether</td>
</tr>
<tr>
<td>C=O, C-O</td>
<td>O-H</td>
<td>ester</td>
<td>C=O</td>
<td>O-H, C-O</td>
<td>aldehyde or ketone</td>
</tr>
<tr>
<td>O-H, C-O</td>
<td>C=O</td>
<td>alcohol</td>
<td>C=O, N-H</td>
<td>O-H, C-O</td>
<td>1° or 2° amide</td>
</tr>
</tbody>
</table>

ii. Other common vibration bands to look for are those for C C and C=C. If nitrogen is present, look for C N and N-H vibration bands. Are any of these bands present?

Y ? N Conclusion: ______________________ |

iii. sp\(^2\) C-H bonds (in arenes and alkenes) give rise to a sharp vibrational band at 3100-3000 cm\(^{-1}\). Is there a sharp absorption at 3100-3000 cm\(^{-1}\)?

Y ? N Conclusion: ______________________ |

iv. Draw the functional groups indicated by the infrared spectrum (i.e., structures from i(d), ii and iii)
C. Consider the $^{13}$C NMR spectrum...

i. Each type of carbon gives rise to a separate singlet. How many types are carbon are there?

ii. The $^{13}$C chemical shift gives you a clue about the type of carbon (i.e., carbonyl, aromatic, alkenes) and the presence of electronegative substituents.

Conclusion: ______________________________

$^{1}$H NMR Spectrum

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D. Certain common features give rise to recognizable patterns in the \( ^1H \) NMR spectrum...

i. Ethyl groups always give rise to a quartet (2H) downfield from a triplet (3H). Is there a quartet downfield from a triplet?

<table>
<thead>
<tr>
<th>Y</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conclusion: ____________________</td>
<td></td>
</tr>
</tbody>
</table>

ii. iso-Propyl groups always give a septet (1H) downfield from a doublet (6H). Remember, you might not see the weak outside peaks in the septet. Is there a septet downfield from a doublet?

<table>
<thead>
<tr>
<th>Y</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conclusion: ____________________</td>
<td></td>
</tr>
</tbody>
</table>

iii. tert-Butyl groups always give a singlet (9H) at ca. \( \delta 1.2 \). Is there a singlet at ca. \( \delta 1.2 \)?

<table>
<thead>
<tr>
<th>Y</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conclusion: ____________________</td>
<td></td>
</tr>
</tbody>
</table>

iv. If there are ethyl or isopropyl groups: consider the chemical shift of the downfield signal, it gives you a clue about the substituent (i.e., “X” in \( CH_3CH_2-X \) or \( (CH_3)_2CH-X \)).

   Conclusion: ____________________  

v. Aromatic protons appear at \( \delta 6.5-8.5 \). Is there a signal at \( \delta 6.5-8.5 \)?

<table>
<thead>
<tr>
<th>Y</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conclusion: ____________________</td>
<td></td>
</tr>
</tbody>
</table>

vi. If there are aromatic protons: consider the multiplicity and integration, they give you clues about the substitution pattern?

   Conclusion: ____________________  

vii. Certain functional groups that you have already identified by infrared give rise to specific signals in the \( ^1H \) NMR, such as acid (\(-CO_2H\)), aldehyde (\(-CHO\)), alcohol (\(-OH\)), amine (\(-NH\)). Do signals corresponding to these functional groups appear in the \( ^1H \) NMR spectrum?

<table>
<thead>
<tr>
<th>Y</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conclusion: ____________________</td>
<td></td>
</tr>
</tbody>
</table>

viii. Are there any other singlets or multiplets which you have not assigned? If so, consider the multiplicity and integration. Here is a list of common isolated structural features (i.e., without neighboring protons) and their corresponding signals (multiplicity and integration). Do any of these appear in the spectrum? (Circle the combination of peaks and the structural subunit).

   You will also have to consider vinylic protons in D(x).

   \[
   \begin{align*}
   \text{CH-CH} & \quad \text{d}(1) \quad \text{d}(1) \quad \text{CH}_2-\text{CH}_2 \quad \text{t}(2) \quad \text{t}(2) \quad \text{CH-CH}_3 \quad \text{q}(1) \quad \text{d}(3) \\
   \text{CH-CH}_2 & \quad \text{t}(1) \quad \text{d}(2) \quad \text{CH}_3 \quad \text{s}(3)
   \end{align*}
   \]
ix. If any of these multiplets appear: consider the chemical shift of the downfield signal, it gives you a clue about the substituents on the fragment (Remember that substituent effects are cumulative).

Conclusion: _______________________________________

x. Vinylic protons appear at 4.5-6.5. Are there signals at 4.5-6.5 which you have not yet accounted for?

Y  N  Conclusion: ________________________________

xi. If there are vinylic protons: consider the multiplicity and integration, they give you clues about the substitution pattern.

Conclusion: _______________________________________

xii. Draw the substructures derived from the appearance of the $^1$H NMR spectrum (i-xi).

Bringing it all together....

E. If you are provided with the molecular formula: do you need to account for any other atoms in the molecule other than those determined in parts B,C and D?

Y  N  Remaining atoms: ________________________________

F. ...Bring it all together

Draw the functional groups derived from IR (B), substructures derived from NMR (C and D), and any other atoms left over in the molecular formula (E).
G. FINAL STRUCTURE
Combine these fragments in such a way that the valency of each atom (H=1, C=4, O=2, N=3) and the number of sites of unsaturation, and formula are satisfied. Remember to consider symmetrical structures.

Check your answer: predict the spectra of your final structure, it should be the same as those provided

WORK AS MANY PROBLEMS AS POSSIBLE...
Elemental Analysis: C, 54.51; H, 9.09

Elemental Analysis: C, 90.38; H, 9.47
Empirical Formula: C₅H₁₀O₂
Mass Spec: M⁺ m/e = 102

Empirical Formula: C₄H₁₀O
Mass Spec: M⁺ m/e = 74
Empirical Formula: C₆H₁₄O
Mass Spec: M⁺ m/e 102

Empirical Formula: C₃H₈O₂
Mass Spec: M⁺ m/e 76
Empirical Formula: C₈H₈Cl
Mass Spec: M⁺ m/e 140 and 142 (3:1 ratio)

Empirical Formula: C₇H₉N
Mass Spec: M⁺ m/e 107
Empirical Formula: C₇H₉N
Mass Spec: M⁺ m/e 107

Empirical Formula: C₄H₄O
Mass Spec: M⁺ m/e 136
Empirical Formula: C₄H₅Br
Mass Spec: M⁺ m/e= 184 and 186 (1:1 ratio)

IR

²¹²C NMR  ²¹²H NMR

Empirical Formula: C₂H₂O
Mass Spec: M⁺ m/e= 138
CHAPTER 9 ON EXAM 5

Types of Questions
- Use data from elemental analysis, infrared spectroscopy and nuclear magnetic resonance spectrometry ($^1$H and $^{13}$C) to determine the structure of organic compounds.
- In class assignment
- Take home assignment (more complex problems)

Preparing for Exam 4:
- Work as many problems as possible.
- Work in groups.
- Do the "Learning Group Problem" at the end of the chapter.
- Work through the practice exam