Problem Set 5 Answers

Smith Text: See solutions manual

Techniques in Organic Chemistry:

1. The calculated chemical shift values are in the parentheses.
   a. \( \text{C}_5\text{H}_11\text{Cl} \) is 1-chloro-2,2-dimethylpropane.
   \[
   \begin{array}{c}
   \text{Cl} \\
   3.33 \\
   (3.4)
   \end{array}
   \]

   b. \( \text{C}_5\text{H}_{10}\text{O}_2 \) is 3-hydroxy-3-methyl-2-butanone.
   \[
   \begin{array}{c}
   \text{OH} \\
   3.88 \\
   2.25 \\
   (2.2)
   \end{array}
   \]

   c. \( \text{C}_6\text{H}_{12}\text{O}_2 \) is 4-hydroxy-4-methyl-2-pentanone.
   \[
   \begin{array}{c}
   \text{OH} \\
   3.83 \\
   1.26 \\
   (1.2)
   \end{array}
   \]

   d. \( \text{C}_5\text{H}_{10}\text{O} \) is 3-methyl-butanal.
   \[
   \begin{array}{c}
   2.31 \\
   2.21 \\
   0.98 \\
   \end{array}
   \]
   \[9.77 \text{ (9.5-10.5, from Table 19.2)}
   \]
   \[2.31 \text{ (2.3)}
   \]
   \[0.98 \text{ (1.0)}
   \]
   \[2.21 \text{ (1.9)}
   \]
e. C₆H₄O is 3-buten-2-ol. The assignments of the 5.19 ppm and 5.06 ppm protons cannot be made on the basis of calculated chemical shifts; however, the relative sizes of the cis- and trans-proton-proton coupling constants allow the assignments (see Table 19.6).

\[
\begin{array}{c}
\text{OH} \\
\text{4.30 (4.6)} \\
\text{2.50} \\
\text{1.27 (1.4)} \\
\text{5.19 (5.27)} \\
\text{5.06 (5.26)} \\
\end{array}
\]

2.

dq, 7.0 ppm

\[
\begin{array}{c}
\text{H} \\
\text{H₃C} \\
\text{s, 3.7} \\
\end{array}
\]

dd, 1.9 ppm

dq, 5.85 ppm

3.

\[
\begin{array}{c}
\text{H₃C} \\
\text{H} \\
\text{CH₃} \\
\text{HO} \\
\end{array}
\]

6H, d, 1.2 ppm

1H, s, 2.0 ppm

1H, sp, 4.0 ppm

The \(^1\)H NMR signal at 2.0 ppm, which exchanges with D₂O to form HOD at 4.6 ppm, is the O–H of 2-propanol. This proton at oxygen splits with the methine proton at C-2 if chemical exchange of the O–H becomes slow. An increasing concentration of 2-propanol leads to greater intermolecular hydrogen bonding and a downfield shift of the proton on oxygen. The two methyl groups comprise the doublet at 1.2 ppm, while the septet at 4.04 ppm is the methine proton at C-2.

7. The molecular formula indicates two Double Bond Equivalents; because one double-bond equivalent is a carbonyl group, the other one may be a C=C. That assignment would be consistent with the vinyl signal (1H) at 5.06 ppm. C₈H₂₃₃O also has three singlet methyl groups; the chemical shift of one methyl group (2.10 ppm) suggests that it is attached to the carbonyl carbon. The chemical shifts of the other two methyl groups are consistent with their being allylic; there is a small allylic splitting in the 1.65 ppm methyl
peak, which suggests that it is trans to the vinyl proton (Table 19.6). Two methylene groups appear at 2.25 ppm and 2.45 ppm. The C₈H₁₄O compound is 6-methyl-5-heptene-2-one.

Additional Problems:

1. The two methyl groups are actually not equivalent because they are diastereotopic. They have very similar chemical shifts, so they nearly overlap.
2. The following spectrum is a proton NMR of allyl ethyl ether. Assign the protons to the matching signals and explain the splitting based on these coupling constants: $J_{ab} = 0 \text{ Hz}$, $J_{ac} = 10 \text{ Hz}$, $J_{bc} = 18 \text{ Hz}$, $J_{cd} = 5 \text{ Hz}$.

![Diagram of allyl ethyl ether structure with NMR spectrum]
3. The following spectrum is a proton NMR of 3-methylstyrene. Match the signals at 5.2 ppm, 5.8 ppm, and 6.7 ppm with protons A, B, and C. Draw tree diagrams to explain the coupling of each of these protons. (coupling constants: \( J_{ab} = 10 \text{ Hz}, \ J_{ac} = 16 \text{ Hz}, \ J_{bc} = 0 \text{ Hz}. \)

4. Based on the IR, \(^1\text{H} \text{ NMR}, \) and \(^{13}\text{C} \text{ NMR} \) on the following page, predict the structure of the compound. Explain why no splitting is observed in signal A even though one might expect it be coupled to another set of equivalent protons.

\[
\begin{align*}
\text{O} \\
\text{H} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\
\text{J for aldehyde} = 0-2 \text{ Hz} \text{ so not observed}
\end{align*}
\]
The following spectrum represents one isomer of ethylphenol. Is it the 1,2-, 1,3-, or 1,4-isomer? Explain your answer based on the splitting and integration observed in the spectrum.

Integration - With 1.4 pdt, there are 2 sets of protons integrating to 2

Splitting - doublets observed because HA split by HB and vice versa
4. The following three spectra represent the aromatic protons of 1,2-, 1,3-, and 1,4-nitroaniline. Assign each spectrum to the appropriate compound and then match the appropriate protons with each signal. (Hint: the nitro group is a strong electron withdrawing group, which deshields adjacent atoms by induction.)
7. Based on ranges of coupling constants provided in class, estimate the expected splitting (in Hz) observed between the lettered hydrogen atoms. (Give values of $J_{ab}$, $J_{ac}$, $J_{bc}$, etc.)

A $J_{AB} = 0$
B $J_{AB} = 0 - 10$ Hz
C $J_{AB} = 0$
D $J_{AB} = 0 - 2$ Hz
E $J_{AB} = 0$
F $J_{AB} = 0 - 10$ Hz
G $J_{AB} = 0$
H $J_{AB} = 0$
I $J_{AB} = 0 - 10$ Hz
$J_{AC} = 11 - 18$ Hz
$J_{BC} = 0 - 2$ Hz
Graphically analyze the following spectrum of methyl vinyl thioether. Assign the peaks and determine approximate coupling constants for $J_{\text{bd}}$, $J_{\text{cd}}$, and $J_{\text{hc}}$. Each small square on the spectrum represents 5 Hz. (Hint: Watch out—there are two signals that are partially overlapping.)

$$60 \text{ MHz} = \frac{60 \text{ Hz}}{1 \text{ ppm}}$$

\[ \text{MM} \quad J = 2 \text{ blocks} = 10 \text{ Hz} \]

\[ \text{MM} \quad J = 3+ \text{ blocks} = 18 \text{ Hz} \]

$H_B = 3+ \text{ blocks} = 18 \text{ Hz}$ for $J_{\text{bd}}$

$H_C = 2 \text{ blocks} = 10 \text{ Hz}$ for $J_{\text{cd}}$

$H_d = \text{ doublet of doublets}$
Determine the structure of the following aromatic compound with formula C₆H₅BrO. The peak at about 5.6 ppm disappears when the sample is washed with D₂O.
19. Determine the structure of the following compound with formula $\text{C}_3\text{H}_7\text{BrO}$.
$J_{AB} = 7.6 \text{ Hz}$

$J_{BC} = 1.6 \text{ Hz}$

$J_{AC} = 0 \text{ Hz}$

(2-3 Hz)

(0-1 Hz)

$400 \text{ MHz instrument}$
$\text{C}_6\text{H}_{11}\text{ClO}$

$^1\text{H NMR}$

Int: 1 1 3 1 3
Split: $\ddd$ $\dd$ $s$ $p$ $t$

$^{13}\text{C NMR}$

Answer:

[Chemical structures with chemical shifts]
\[ \text{C}_5\text{H}_9\text{BrO}_2 \]

\[ \text{H} \text{ NMR} \]

\[ \text{ppm} \]

Int: 1 1 1
Split: dd dd p

\[ \text{C} \text{ NMR} \]

\[ \text{ppm} \]

Answers:

\[ \text{Br} \]

1.78 4.20 4.67 4.42

2.21

19.7 67.6 20.7 49.5
\[ \text{C}_7\text{H}_{14}\text{O}_3 \]

**\(^1H\) NMR**

- Int: 1 1 2 1 1 2 2 3
- Split: s s sx t dd dd t p d

**\(^{13}\text{C}\) NMR**

**Answers:**

- OH: 52.6
- CO: 210.6
- OH: 35.9
- OH: 25.4
- CO: 62.3
- CH: 22.6
- CH: 3.9
- CH: 3.62
- CH: 2.45
- CH: 3.0
- CH: 1.86
- CH: 1.18