Chemistry 344: Spectroscopy and Spectrometry Problem Set 3

Name (print): ____________________________

TA Name (print): __________________________

I. The NMR spectra of p-nitrobenzyl alcohol are provided below.

A. In the $^{13}$C-NMR spectrum, assign the hybridization of the $^{13}$C-atoms responsible for each signal. Identify any key functional group signals.

B. Predict the $^1$H-NMR chemical shift for each $^1$H-atom in the molecule using empirical (Curphy-Morrison) parameters.
C. Assign the $^1$H-atoms in the molecule to their corresponding signals in the $^1$H-NMR spectrum.

D. How well do the Curphy-Morrison parameters predict the observed $^1$H-NMR chemical shifts?

<table>
<thead>
<tr>
<th>Predicted</th>
<th>Observed</th>
<th>The agreement is excellent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.16 ppm</td>
<td>8.23 ppm</td>
</tr>
<tr>
<td>B</td>
<td>7.49 ppm</td>
<td>7.54 ppm</td>
</tr>
<tr>
<td>C</td>
<td>4.95 ppm</td>
<td>4.84 ppm</td>
</tr>
</tbody>
</table>

E. Rationalize the intense deshielding and resultant downfield shift of the $^1$H-atoms attached ortho to the nitro group by providing a series of resonance structures.

- $\text{NO}_2$ groups are EWW. and deshield their ortho $^1$H-atom neighbors.
II. The three $^3$H-NMR spectra below from 7.0 – 7.7 ppm correspond to three bromochlorobenzenes; identify each molecule and assign the $^1$H-atoms to their corresponding signals.
III. For the IR, $^1$H-NMR and $^{13}$C-NMR spectra shown below for C$_7$H$_4$BrN, analyze the structure and each of the spectra as instructed.

A. What is the unsaturation number (U) or index of hydrogen deficiency (IHD)? What does this indicate about which functional groups are possible for this molecule?

$$U = IHD = \frac{2C + 2 + N - H - X}{2}$$

* lost of rings and/or $\pi$ bonds *

B. The IR spectrum of C$_7$H$_4$BrN is provided below; identify any key absorptions that will assist in the determination of its structure.
C. The $^{13}$C-NMR spectrum of C$_7$H$_4$BrN is provided below; identify the hybridization and likely functional group identity of each $^{13}$C-atom signal. Explain why the signals at 133.61 and 132.86 ppm are so intense and what that indicates about the structure.

D. The $^1$H-NMR spectrum of C$_7$H$_4$BrN is provided below; determine the structure. Assign each of the H-atoms in the molecule to a signal on the spectrum using the key provided.
IV. Determine the structure of the molecule with formula $C_{10}H_{14}O$ that corresponds to the spectra shown below. Fully analyze each spectrum.
* Without additional spectra, it is very difficult to distinguish from (wrong, but worth full credit in a quiz/exam problem)
V. Determine the structure of the molecule with formula C_{12}H_{12}O_2 that corresponds to the spectra shown below. Fully analyze each spectrum.
VI. The subsequent IR, EI-Mass, $^1H$-NMR and $^{13}C$-NMR spectra were obtained from the product of an $SN_2$ reaction of 4-hydroxybenzaldehyde and methyl bromoacetate. Predict the product, determine its structure and fully analyze the spectra.

A. Predict the structure of the product and the $^1H$-NMR chemical shifts of its $^1H$-atoms using empirical parameters.
B. The $^1$H-NMR spectrum contains a number of impurities. What evidence is present of an ethyl ester or propyl ester impurity?

$$R\text{COOCH}_2\text{CH}_3 \quad \delta \approx 4.15 \text{ ppm}$$

$$R\text{COOC}\text{H}_3 \quad \delta \approx 1.30 \text{ ppm}$$

$$S_{ex.} \approx 1.65 \text{ ppm}$$
The image shows a 1D NMR spectrum with peaks labeled for different functional groups:

- A peak labeled as $^{13}$C (sp²) is observed around 100 ppm.
- A peak labeled as $^{13}$C (sp³) is observed around 40 ppm.
- An impurity peak is indicated near 70 ppm.
- The region from 110 ppm to 120 ppm is highlighted, possibly indicating a specific compound or impurity.

The 2D IR spectrum shows absorption bands at:

- 3500 cm⁻¹ for C-H.
- 1750 cm⁻¹ for C=O.
- 1500 cm⁻¹ for C=C.

The spectra are detailed with specific wavenumbers marked for analysis.
VII. Vanillin and acetone were reacted in basic conditions. Reactions such as these can lead to aldol addition or condensation products depending on the aldehyde and ketone chosen, the concentration of the base used, and the temperature of the reaction. Use the subsequent spectra to determine the outcome of the reaction.

* Aldol condensation product as there are only two $^{13}\text{C}(sp^3)$ atoms.
accidental overlap.

Peak: 1 R.Time: 3.7 (Scan #: 200) MassPeak: 84

m/z = 197

m/z = 177

m/z = 149
VIII. Determine the structure of the molecule with formula $\text{C}_{12}\text{H}_{12}\text{O}_2$ that corresponds to the spectra shown below. Fully analyze each spectrum.
$\text{H} \text{C} \text{O} \text{H}$

$m/z = 148$
IX. In an electrophilic aromatic substitution, 4-methoxyphenylacetic acid reacts with bromine without the need for a catalyst. The $^1$H-NMR spectrum in $\text{C}_6\text{D}_6$ below shows the product mixture of the reaction.

A. Identify the structure of the product and assign its $^1$H-NMR spectrum.

B. Three $^1$H-NMR signals are easily discernable in the aromatic region of the spectrum which represent two impurities one of which is the starting material. Identify the other impurity and determine the ratio between product and reactant.

\[
\frac{1.07 \text{ prod.}}{0.02 \text{ s.m.}} = 0.02 \text{ s.m.}
\]

$\text{C}_6\text{D}_6 \text{ with an H.}$
C. Rationalize the $^1$H-NMR chemical shifts of each $^1$H-atom attached to the aromatic ring of the product using a series of resonance structures. Clearly state how the resonance structures impact the chemical shift of the $^1$H-atoms.

Two electron-donating substituents ortho- to one another result in increased electron density at all ring positions relative to benzene, shielding all three H-atoms, resulting in their signals appearing upfield relative to that of benzene.
X. An aldol condensation used in the organic laboratory at Madison College produced the stereoisomeric product mixture shown below.

\[
\begin{array}{c}
\text{Ar} \quad \text{H} \\
\text{CH} = \text{CH} \quad \text{CH} \\
\end{array}
\begin{array}{c}
\text{Ar} \\
\text{H} \\
\text{CH} = \text{CH} \\
\end{array}
\text{NaOEt} \quad \text{EtOH} \quad \text{Ar} \quad \text{H} \quad \text{Ar}
\]

A. For each of the stereoisomers, estimate the expected coupling constant (\(J_{\alpha\beta}\)) for \(H_\alpha - H_\beta\) for each of the molecules.

\[
\begin{array}{c}
\text{A} \\
\text{Ar} \quad \text{H} \quad \text{Ar} \\
\text{H} \quad \text{Ar} \quad \text{H} \\
\end{array}
\begin{array}{c}
\text{B} \\
\text{Ar} \quad \text{H} \quad \text{Ar} \\
\text{H} \quad \text{Ar} \quad \text{H} \\
\end{array}
\]

\[
\sim 15 \text{ Hz} \quad \sim 15 \text{ Hz} \quad \sim 10 \text{ Hz}
\]

B. Unfortunately, only five of the six possible vinyl \(^1\text{H}\)-atom signals (labeled 1 – 5) are observable in the aromatic and vinyl regions of the product mixture. These integrals, however, are sufficient to determine the product ratio of this reaction. Use the coupling constants and integrals of the identified signals to estimate the product ratio. Use the most isolated signal integrals for each molecule.

\[
\frac{1.00 \text{ major } 2H}{0.38 \text{ minor } 2H} \approx \frac{2.6 \text{ major to minor}}{}
\]
XI. An electrophilic aromatic substitution, the sulfuric acid-catalyzed nitration of methyl benzoate, was carried out in the Organic Chemistry Bootcamp at UW-Waukesha. The spectra presented below are from authentic student samples. Analyze the spectra to understand the outcome of this reaction.

\[
\text{methyl benzoate} \quad \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \quad \text{potential nitrated products}
\]

A. Estimate the \(^1\text{H}-\text{NMR}\) chemical shifts of the \(^1\text{H}\)-atoms in methyl benzoate by analysis of the \(\pi\) conjugation using a series of resonance structures and by empirical (Curphy-Morison) parameters.

B. Predict the expected fragmentation pattern of the molecular ion of methyl benzoate in an EI-Mass Spectrometer and provide a complete electron-pushing mechanism.
C. The authentic $^1$H-NMR spectrum of methyl benzoate is provided below from the Aldrich database. Assign each of the signals to its corresponding $^1$H-atom in methyl benzoate. Comment on how well the resonance structures and empirical parameters predicted the $^1$H-NMR spectrum.

* Very good agreement with C-N parameters
D. The major product of the EAS nitration of methyl benzoate was obtained after recrystallization in methanol; its $^1$H-NMR spectrum is shown below.

i. Assign the methanol, CHCl$_3$ and TMS signals.

ii. Determine the major product of the reaction and assign each of the $^1$H-NMR signals to its corresponding $^1$H-atom(s) in the major product.

iii. Justify the assignments with use of empirical (Curphy-Morrison) parameters.
F. Based upon their EI-Mass spectra, propose the identity of the components of the mixture responsible for the GC trace peaks 2 and 3. Use Curphy-Morrison parameters to predict the $^1$H-NMR chemical shift of each of the $^1$H-atoms in the proposed components 2 and 3. From the GC-MS alone, it is not possible for you to distinguish between these two components.

For C-M parameters, see previous page.

G. Use the GC-trace to determine the ratio of components in the product mixture in order of relative abundance in the form of X:Y:Z:1.

1 2.86 %  
2 13.43 %  
3 1.48 %  
4 82.23 %  

55.6 : 9.1 : 1.9 : 1.0  

Major Product  
Starting Material
E. Prior to recrystallization, the crude product mixture was analyzed by GC-MS and the data are presented below. Determine the identity of the components of the mixture responsible for GC trace peaks 1 and 4. Provide a fragmentation mechanism to rationalize the major signals observed in the EI-Mass spectrum of component 4.

![GC-MS spectra with annotations]

- **Peak 1**: Rt 4.2 min, Mass peaks 27, labeled as *Starting Material*.
- **Peak 2**: Rt 6.8 min, Mass peaks 59, labeled as *Racemomers of Major Product*.
- **Peak 3**: Rt 7.1 min, Mass peaks 47, labeled as *Major Product*.
- **Peak 4**: Rt 7.2 min, Mass peaks 87, labeled as *Major Product*.

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H. The $^1$H-NMR spectrum of the crude mixture is shown below. Assign the $^1$H-atoms for all of the integrated signals in the aromatic region of the $^1$H-NMR spectrum.

I. Based upon the experimental data, comment on the regioselectivity of the nitration of methyl benzoate. Which product(s) are favored and which are disfavored?

The nitration of methyl benzoate is highly selective for the meta regioisomer, but ortho and para products are generated.

55.6 : 9.1 : 1.0
meta ortho para
J. The Curphy-Morrison predictions of the $^1$H-NMR chemical shifts of which component matches the most poorly to its experimental spectrum? Explain why the parameters do not predict the $^1$H-NMR chemical shifts of the $^1$H-atoms in this molecule to the same degree of accuracy as in the other molecules.

All of the C-M predictions work well for methyl benzoate, meta methyl nitrobenzoate, para methyl nitrobenzoate. But for the ortho product they predict less well. This occurs due to a sterically induced twist of the $-\text{NO}_2$ and ester substituents out of the plane. This changes the conjugation, $\sigma$ bond lengths, and the orientation of the magnetic field generated by the substituents. The structural change makes the empirical parameters less reliable.