EXAM #1

Name: Practice Exam
ID#: 

Check your exam to be sure it is complete. There are nine questions in this exam. It is worth 100 points. To receive full credit for your submissions, make sure you do your own work. Read each question carefully, and answer in clearly legible and coherent English. Use the back of the page for additional space if needed. Partial credit will be given, so show your work. Don't fall in love with individual problems. Do the ones first which you can do easily. Pace yourself. Good luck!

N. Totah

NOTE: This exam includes questions on Mass Spec, radical chemistry, and conjugated systems and so does not overlap completely with material than we have discussed this semester. I left this exam intact so you could get a feel for what to expect overall. To facilitate your studies, I have added a few additional questions at the end relevant to this year's exam.

1. ___________ (of 9)
2. ___________ (of 6)
3. ___________ (of 6)
4. ___________ (of 14)
5. ___________ (of 12)
6. ___________ (of 15)
7. ___________ (of 20)
8. ___________ (of 10)
9. ___________ (of 8)

Total: ___________ (100)
1. (9 points) Give IUPAC names for the following compounds:

a. 

b. 

c. 

Name: ______________________


2. (6 points) Write a complete, stepwise mechanism for the following transformation. Use curved arrows to denote electron flow. Show only one possible termination step.

\[ \text{CH}_4 + \text{Br}_2 \xrightarrow{\text{hv}} \text{CH}_3\text{-Br} + \text{HBr} \]
a. What information can be gained about this compound by looking at the mass spectrum?

A. not aromatic  
B. contains chlorine  
C. contains bromine  
D. none of the above  

Answer: _____

b. The peak at m/z = 169 represents the loss of what fragment from the molecule?

A. $^1\text{CH}_3$  
B. $^2\text{CH}_3$  
C. $^3\text{OH}$  
D. $^4\text{OH}$  

Answer: _____

c. The base peak appears at the following location:

A. m/z = 186  
B. m/z = 184  
C. m/z = 105  
D. m/z = 51  

Answer: _____
4a. (8 points) Label the following structures as aromatic, antiaromatic, or nonaromatic.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>[diagram]</td>
<td></td>
</tr>
</tbody>
</table>

4b. (6 points) Draw an orbital picture for the compound shown below that clearly supports your conclusion in part 4a (e.g. that this compound is aromatic, antiaromatic, or nonaromatic). Clearly show the disposition of all lone pairs. Briefly explain your reasoning.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>[diagram]</td>
<td></td>
</tr>
</tbody>
</table>
x 5a. (4 points) Rank the following compounds in order of decreasing reactivity in the Diels-Alder reaction. Rank the most reactive compound 1, and the least reactive compound 4.

[diagram of compounds]

x 5b. (4 points) Rank the following compounds in order of increasing stability. Rank the least stable compound 1, and the most stable compound 4.

[diagram of compounds]

x 5c. (4 points) Rank the following compounds in order of decreasing value of $\lambda_{\text{max}}$ by UV spectroscopy. Rank the compound with the largest value of $\lambda_{\text{max}}$ 1, and the compound with the smallest value of $\lambda_{\text{max}}$ 4.

[diagram of compounds]
x 6. (15 points) 1,3,5-hexatriene reacts with one molar equivalent of Br₂ to give only 1,2- and 1,6- addition products.

a. Draw the structures of these products (one in each box).

b. Why is no 1,4-addition product observed? Clearly explain.

c. If the reaction is run at 80°C, which of these products (1,2- vs. 1,6-) would you expect to be major? Clearly explain. For full credit, draw a reaction coordinate (energy diagram) that depicts formation of the 1,2- and 1,6-addition products.
Name: ___________________________

7. (20 points) Predict the major product(s) for the following reactions. Assume reagents are present in equimolar amounts unless otherwise indicated. Clearly depict any stereochemistry. "No Reaction" is a possible answer. CAUTION! Don't confuse reactions that will occur slowly with those that will not occur!

x a. 

\[
\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \xrightarrow{\Delta} \]

x b. 

\[
\text{product(s) of step 1} \xrightarrow{\Delta} \]

x c. 

\[
\text{MeO}_2\text{C} \xrightarrow{\Delta} \text{CO}_2\text{Me} \]

\[
\text{HBr} \xrightarrow{\text{ROOR}}
\]
Name: ______________________

x d.  
\[
\text{CH}_3\text{CH}_2-\text{C}^*\text{H} + \text{Br}_2 \xrightarrow{\text{hv}} 
\]

x e.  
\[
\text{Cl}_2 \xrightarrow{\text{ether, -80°C}} 
\]

x f.  
\[
\text{CH}_3 + \text{C}=\text{C} + \xrightarrow{\Delta} 
\]

x g.  
\[
\text{hv, CCl}_4 
\]
8. (10 points) Propose a structure that is consistent with the spectral data provided. For full credit, briefly explain your reasoning.

F.W.: C$_3$H$_{12}$O
IR: 690, 798, 880 cm$^{-1}$
$^1$H NMR: integral values are listed above each peak
9. (8 points) An unknown isomer of $\text{C}_4\text{H}_9\text{Cl}$ has the $^{13}\text{C}$ NMR and DEPT-135 spectra shown below:

Circle the compound that is represented by these spectra. Clearly explain your reasoning. For full credit, you will need to explain how each of the other three isomers was eliminated from consideration.
Additional practice problems for Exam 1 Material:

2a. (4 points) Rank the following compounds in order of decreasing reactivity to Electrophilic Aromatic Substitution. Rank the most reactive compound 1, and the least reactive compound 4. Place the number corresponding to the relative reactivity of each compound in the blank below it.

![Compounds](image)

3. (10 points) Write a complete, stepwise mechanism to account for each of the following transformations. Use curved arrows to denote electron flow.

![Mechanism](image)
4. (6 points) Nitrosobenzene reacts readily with Cl₂/FeCl₃ to give the monochlorination product(s). Using your knowledge of Electrophilic Aromatic Substitution reactions, answer the questions below. Clearly explain your reasoning. Use diagrams to support your arguments.

(a) Predict whether the nitroso group (-N=O) is ortho/para or meta directing.

(b) The nitroso group is slightly deactivating (e.g. nitrosobenzene will react more slowly than benzene). Explain.
5. (10 points) Predict the major product(s) for the following reactions. Assume reagents are present in excess amounts unless otherwise indicated. Clearly depict any stereochemistry. "No Reaction" is a possible answer. CAUTION! Don't confuse reactions that will occur slowly with those that will not occur!

a. 

\[
\text{Cl-} \begin{array}{c} \text{O-CH}_2 \text{Cl} \\ \text{Cl} \end{array} \xrightarrow{\text{HNO}_3} \text{H}_2\text{SO}_4 \xrightarrow{1 \text{ equiv}}
\]

d. 

\[
\text{CH}_3 \xrightarrow{\text{NBS}} \text{CCl}_4 \xrightarrow{(\text{PhCO})_2\text{O}}
\]

i. 

\[
\text{CO}_2\text{H} \xrightarrow{\text{Br}_2} \text{FeBr}_3 \xrightarrow{\text{(step 1)}}
\]

product(s) of step 1: 
1. \text{SnCl}_2, \text{H}_3\text{O}^+ \\
2. \text{NaOH}

(step 2)

l. 

\[
\text{CO}_2\text{H} \xrightarrow{\text{CH}_3\text{CH}_2\text{Cl}} \text{AlCl}_3
\]
8. (5 points) Show how you would following transformations. Use any organic or inorganic reagents that you need. Avoiding product mixtures if possible, but assume that ortho and para products can be separated. Clearly indicate at what stage (if any) such separations are needed.

a.

\[
\text{benzene or toluene} \quad \rightarrow \quad \begin{array}{c}
\text{Cl} \\
\text{SO}_3\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{CO}_2\text{H}
\end{array}
\]