**Exam 3  Chem 3045x  Friday, December 3, 1999**

**Instructions:** This is a closed book examination. You may not use any notes, books or external materials during the course of the examination. Please **print** your name and social security number below. Print your name on the top of each page of the exam.

Be sure to allot your time in a manner that is related to the point value of the question. Be sure to show your reasoning wherever possible for partial credit.

**Correlation tables for IR, 1H NMR and 13C NMR are attached to the last page of the exam.**

All material to be graded must be on one of the pages of the exam. If you need more space than is available on the page with the questions, use the back page of the previous page and label the number of the question on that page.

**Your Name:** ________________________________

**Your Soc. Sec. Number:** ________________________________

**Time of the exam:** 50 minutes (10:00 AM to 10:50 AM).

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<th>Question</th>
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**Total:** 100 Points
(1) 10 Points.

When butadiene is treated with one equivalent of HCl, the products 1 and 2 are formed, but in different amounts depending on temperature.

\[
\text{CH}_2\text{=CH} \text{CH} = \text{CH}_2 + \text{HCl} \rightarrow \text{H}_2\text{C} \equiv \text{C} \text{CH} = \text{CH}_2 + \text{CH}_2 \text{CH} = \text{CH} \text{CH}_2
\]

If the reaction is performed at -80\(^\circ\text{C}\) the ratio of products is 80\% 1 and 20\% 2. If the reaction is performed at 40\(^\circ\text{C}\) the product ratio is (20\% 1 and 80\% 2). Suggest an explanation for these observations.

(2) 10 Points.

Arrange the isomers of molecular formula C\(_4\)H\(_9\)Cl in order of decreasing rate of reaction with sodium iodide in acetone. Explain your reasoning.
(3) 10 Points.

Which do you expect to possess a higher frequency CH stretching frequency, acetylene or ethylene? Explain your reasoning.

Which do expect to possess a higher frequency, a CH vibration or a CD vibration? Explain your reasoning.

(4) 10 Points

Consider the structures A and B as being synthesized though a Diels-Alder cycloaddition. Draw the structure of the diene and the dienophile that could be employed to produce the structure of A and B.

Structure of Diene  Structure of Dieneophile

![Diagram of structures A and B]
(5) 10 Points.

Consider the following cycloaddition reaction of two 1,3-butadiene molecules. Use the theory of HOMO-LUMO interactions to determine whether this reaction is expected to be allowed with respect to the phase at the reacting centers. Indicate your reasoning and be clear in labeling the phasing in any orbital diagrams.
(6) 10 Points

Draw the structures of the products expected from the indicated reaction conditions:

\[
\begin{align*}
\text{heat, } \text{CCl}_4 & & \text{?} \\
\text{CH}_3\text{CH}_2\text{C}≡\text{C}−\text{H} & & \text{H}_3\text{O}^+ \rightarrow \text{?} & \text{Hg}^+ \\
\end{align*}
\]
(7) 10 Points

Suggest a synthesis of the indicated products using the indicated starting material and any other reagents, organic or inorganic, required.

\[
\text{CHBr}_2\text{CH}_2\text{CH}_3 \xrightarrow{?} \text{CH}_3\text{CCl}_2\text{CH}_3
\]

\[
\text{?} \xrightarrow{?} \text{HO}
\]
(8) 10 Points. Assume that the structures A, B, C and D, below are planar. Which structures, if any, are aromatic? Explain your reasoning.
(9) (20 Points. 10 Points for each spectrum) Suggest a structure that is consistent with the IR, 1H NMR and 13C NMR spectra shown on the following pages for the molecular compositions $A = C_5H_{10}O$ and $B = C_6H_{10}O$. Indicate briefly how each structure is consistent with each spectra. The number of protons responsible for each signal is indicated under or next to the signal on the spectrum.

The suggested structure for $A$ is

![Structure for A]

My reasoning for suggesting the structure for $A$: [Explain reasoning here]
The suggested structure for B is

My reasoning for suggesting the structure for B: