Instructions: This is a closed book examination. Please print your name and social security number on the front page of the examination. 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.

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

Your Name (Print): ________________________________

Your Soc. Sec. Number: ____________________________

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

Points for each question:

Question 1: 10 points ________________
Question 2: 10 points ________________
Question 3: 10 points ________________
Question 4: 10 points ________________
Question 5: 10 points ________________
Question 6: 10 Points ________________
Question 7: 10 Points ________________
Question 8: 10 Points ________________
Question 9: 5 Points ________________
Question 10: 15 Points _______________

Total: 100 Points ________________
(1) 10 Points. Draw the structures of the three alkyne isomers of composition C₅H₈. Which of the isomer(s) can be prepared in good yield by alkylation (or dialkylation) of acetylene and also draw the structures of isomer(s) which cannot be prepared in good yield by this method?

Structures of isomer(s) that can be prepared in good yield by alkylation (or dialkylation) of acetylene.

The reaction is $S_N^2$

 Structures of isomer(s) that cannot be prepared in good yield by alkylation (or dialkylation) of acetylene.

Explanation:

Elimination favored with strong base

(2) 10 Points. Treatment of 2-butyne with an acidic solution containing Hg(II) yield an unstable intermediate which is not isolated, but that is transformed under the reaction
conditions to an isolated product that absorbs strongly at 1720 cm$^{-1}$ in the infrared. Suggest a structure for the unstable intermediate and the isolated product. Show your reasoning for complete credit.

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{CH}_3 \quad \xrightarrow{\text{Hg}^{(II)} / \text{H}_3\text{O}^+} \\
\text{H}_3\text{C} & \equiv \text{CH}_3 + \text{H}_3\text{C} = \text{C} = \text{O} & \text{H}_3\text{C} & \equiv \text{CH}_3
\end{align*}
\]

Unstable enol intermediate

Tautomerization

Ketone $1720 \text{ cm}^{-1}$

Isolated product
(3) **10 Points.** The alkane formed by catalytic hydrogenation treatment of (S)-4-methyl-1-hexyne is optically active, but the product formed by the catalytic hydrogenation of (S)-3-methyl-1-pentyne is not optically active. Draw the structures of the products of each catalytic hydrogenation and explain why one is optically active and the other is not optically active.

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{CH}_2\text{CH}_3 & \quad \text{H} \\
\text{(S)-3-Methyl-1-pentyne} & \quad \text{H}_2/\text{cat.} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CH}_3 & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 \\
\text{(S)-4-Methyl-1-hexyne} & \quad \text{H}_2/\text{cat.} \\
\end{align*}
\]

\[
\begin{align*}
\text{achiral} & \quad \text{plane of symmetry} \\
\text{chiral} & \quad \text{optically active}
\end{align*}
\]
(4) **10 Points.** Which 1,3-diene and which dienophile would you choose to synthesize the following compounds? Be sure to indicate stereochemistry if appropriate.

Diene + Dienophile

Work backwards
(5) **10 Points.** An acidic solution of initially pure A upon standing for several weeks is found to contain both A and B. Suggest an explanation of this observation.
(6)  **10 Points.** A solution of 1,3-cyclobutadiene (A) reacts to form the product B at low temperatures in the absence of acids, bases or catalysts. Suggest a mechanism for the formation of B from A.

\[
\text{A} \quad \rightarrow \quad \text{B}
\]

**Diels-Alder**
(7) **10 Points.** The chloride A undergoes $S_N^1$ solvolysis in water at a very slow rate compared to the chloride B. Give an explanation for this result based on the structure of the carbonium ion involved in each reaction.

[Diagram showing the reaction of chloride A and chloride B with water, indicating very slow and very fast rates, respectively, and the structures of the carbonium ions involved.]
(8) **10 Points.** Draw a Lewis structure consistent with the following NMR spectra and molecular compositions.

(a) Molecular composition $\text{C}_8\text{H}_{18}$; $^1\text{H} \text{NMR}$ consists of a singlet at $\delta = 0.9 \text{ ppm}$

(b) Molecular composition $\text{C}_8\text{H}_8$; $^1\text{H} \text{NMR}$ consists of a singlet at $\delta = 5.8 \text{ ppm}$

(c) Molecular composition $\text{C}_2\text{H}_3\text{Cl}_3$; $^1\text{H} \text{NMR}$ consists of a singlet at $\delta = 2.7$

$$\text{H}_3\text{C} - \text{CCl}_3$$

(d) Molecular composition $\text{C}_3\text{H}_5\text{Br}$; $^{13}\text{C} \text{NMR}$ consists of three signals at $\delta = 33 \text{ ppm}$ (triplet), $\delta = 118 \text{ ppm}$ (triplet) and $\delta = 134 \text{ ppm}$ (doublet).

$$\text{Br}$$
(9)  5 Points. Draw a sketch of the HOMO and the LUMO of 1,3-butadiene.

\[
\begin{array}{cc}
\text{HOMO} & \text{LUMO} \\
\end{array}
\]

(10)  15 Points. Consider three pure compounds, A, B and C, each of which has the molecular composition $\text{C}_8\text{H}_{10}$. Suggest a structure that is consistent with the $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra shown on the following pages for A, B and C. Indicate briefly how each structure is consistent with each spectrum.

\[
\text{The suggested structure for A is}
\]

My reasoning for suggesting the structure for A:

SODAR = 4
Simple proton NMR
$^{13}\text{C}$ NMR 4 different carbons, lots of symmetry

\[
\text{The suggested structure for B is}
\]

My reasoning for suggesting the structure for B:

SODAR = 4
$^{13}\text{C}$ NMR 3 different carbons, lots of symmetry
The suggested structure for C is

My reasoning for suggesting the structure for C:
SODAR = 4
$^{13}$C NMR 5 different carbons