Before you begin this exam: First: You are allowed to have a simple model set at your seat. Please put away all other materials. Second: Place your student identification on your desk. A proctor will come around to check everyone's ID. Third: Read through the entire exam. Do not waste time on problems that you can’t do if there are others that look easy. Fourth: It is critically important that your answers be written in a clear, unambiguous manner. Answers in which your intentions are unclear will not receive credit. Fifth: Read the instructions for each problem. You will have until 9:50 to complete this exam. There will be no extensions, so budget your time carefully.

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A. (10x4=40) Complete **TEN** of the following reactions with the major organic product(s). Write **NO** at the three reactions you do not want graded. If you do more than ten and the others are not clearly marked, only the first ten will be graded.

1. \[ \text{Cyclohexene} + \text{H}_2 \xrightarrow{\text{Lindlar catalyst}} \text{Cyclohexane} \]

2. \[ \text{Cyclohexene} + \text{Br}_2 \xrightarrow{\text{(one equivalent)}} \text{(two products)} \]

3. \[ \text{Cyclohexene} \xrightarrow{1) \text{Hg(OAc)}_2} \text{Cyclohexane} \]
\[ \xrightarrow{2) \text{NaBH}_4, \text{HO}^{-}} \]

4. \[ \text{1,3-Pentadiene} + \text{CF}_3\text{CO}_2\text{H} \xrightarrow{} \text{Product} \]

5. \[ \text{1-Methylcyclopropene} + \text{H}_2 \xrightarrow{\text{PtO}} \text{1-Methylcyclohexane} \]

6. \[ \text{1-Butene} \xrightarrow{\text{H}_2\text{O}} \text{2-Methyl-1-butene} \]

7. \[ \text{Cyclopentadiene} + \text{Br}_2 \xrightarrow{\text{(one equivalent)}} \text{Cyclohexene} \]
8. $\text{H}_3\text{C}-\text{C}-\text{C}==\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{H}

9. $\text{Br} + \text{CH}_3\text{C}-\text{CH}_2\text{O}^\bullet + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C}-\text{CH}_2\text{CH}_3

10. $\text{C}≡\text{C} - \text{CH}_3$
   1) $\text{NaNH}_2/\text{NH}_3$
   2) $\text{CH}_3\text{I}$

11. $\text{H}_2\text{C}==\text{C}-\text{CH}_3 + \text{CH}_3\text{COBr} \xrightarrow{\text{hv}} \text{CH}_2==\text{CH}-\text{CH}_2\text{Br}$

12. $\text{HC}≡\text{C}-\text{CH}_2\text{CH}_3$
   1) $\text{R}_2\text{BH}$
   2) $\text{H}_2\text{O}_2, \text{HO}^-$

13. $\text{Br}_2 + \text{C}_8\text{H}_8 + \text{CH}_3\text{OH} \rightarrow \text{C}_8\text{H}_8\text{C}-\text{O}-\text{CH}_3$

B. (3x4=12) In each box provided, supply the reagents needed to change the starting material on the left into the product shown on the right. Complete THREE of these problems. Write NO at the two problems you do not want graded. If you do more than three and the others are not clearly marked, only the first three will be graded.

1. $\text{HBr}$, $\text{R}_2\text{Br}, \Delta$

C. (2x4=8) In each case below the product and reagents are given. Draw the structure of the starting material that will lead to the product(s) shown. Complete TWO of these problems. Write NO at the one problem you do not want graded. If you do more than two and the others are not clearly marked, only the first two will be graded.

1. 

2. 

[Ph means \( \bullet \bullet \bullet \) ]

In-In is a generic initiator
D. (8) Draw the reactions needed to prepare the product from the starting material and additional reagents you may need. There is no single reaction that will do the job. Do only ONE of the problems below. Clearly mark the one that you don’t want graded with a NO. If you do both or don’t clearly mark one of them, only the first will be graded.

1. Prepare from

\[
\text{HC≡CH} \xrightarrow{\text{NH}_2^+ \text{NH}_2^-} \text{HC≡CH} + \text{CH}<_{2CH}_3 \xrightleftharpoons{\text{H}_2, \text{H}_{\text{Lindlar catalyst}}} \text{HC≡C} - \text{CH}_2\text{CH}_3
\]

2. Prepare from 1,3-butadiene

\[
\text{HO} - \text{C} - \text{HO} \xrightarrow{\text{OsO}_4, \text{Na}_2 \text{SO}_3, \text{H}_2\text{O}} \xrightarrow{\triangle} \bigcirc + \bigcirc
\]

E. (2x8=16) Write a mechanism for each reaction below. Use the curved arrow convention. Clearly show the intermediates and the correct number of steps.

1. Write a four-step chain mechanism for the following reaction. Do not include termination steps.

\[
\text{H}_3\text{C} - \text{C}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{RO-OR, heat}} \text{H}_3\text{C} - \text{C}=\text{CH}_2 + \text{Br}^-
\]

\[
\text{RO} \cdot + \text{H}_2\text{Br} \rightarrow \text{ROH} + \text{Br}^-
\]

\[
\text{CH}_3\text{CH} - \text{CH} = \text{CH}_2 + \text{Br}^- \rightarrow \text{CH}_3\text{CH} - \text{CH} - \text{CH}_2\text{Br}
\]

\[
\text{CH}_3\text{CH} - \text{CH} = \text{CH}_2 + \text{Br}^- \rightarrow \text{CH}_3\text{CH} - \text{CH} = \text{CH}_2 + \text{Br}^- + \text{Br}^-
\]
2. A key step in the formation of β-carotene from lycopene is a reaction like the simplified version shown below. Write a three-step ionic mechanism for this reaction. Use the curved arrow convention, show all the intermediates clearly and use the correct number of steps.

F. (6) When the product of the Diels-Alder reaction between 2,3-dimethyl-1,3-butadiene and cis-2-butene is treated with hydrogen over a platinum catalyst, a cyclic hydrocarbon, C₁₀H₂₀, is formed. Draw this product in its most stable conformation.

G. (2x5=10) Provide a very brief explanation for each of the following observations.

1. The \( \lambda_{\text{max}} \) of 1,3-butadiene lies at longer wavelengths than the \( \lambda_{\text{max}} \) for ethylene.

   The more conjugation, the smaller is the energy gap between highest occupied molecular orbital (HOMO) and the lowest unoccupied (LUMO) MO. A smaller energy difference means a longer wavelength of absorption.

2. Predict the sign of \( \Delta S \) for the (forward) Diels-Alder reaction. Explain why the Diels-Alder reaction tends to go in reverse at higher temperatures.

   Because two molecules join to make one molecular, disorder is decreased and \( \Delta S \) is negative.

   For the forward reaction, \( \Delta H \) is negative. In the following expression for \( \Delta G \), \( T \) is always positive. If \( \Delta S \) is negative, the second term, -T\( \Delta S \), is positive. When \( T \) is large, this second positive term dominates, and \( \Delta G \) is positive. A positive \( \Delta G \) means that the reverse reaction is favored.

\[
\Delta G = \Delta H - T \Delta S
\]