1. Indicate the relationship between the two structures.

(a)

(b)

(c)

(d)

(e)
2. (a) Label each of the stereogenic centers below as R or S. Is the molecule chiral? If it is chiral, draw the enantiomer of the compound. If it is not chiral, indicate any symmetry elements present.

(b) Label each of the stereogenic centers below as R or S. Is the molecule chiral? If it is chiral, draw the enantiomer of the compound. If it is not chiral, indicate any symmetry elements present.

3. Write the major organic reactant(s) or product(s) of the following reactions. Clearly show the stereochemistry of the reactant(s) or product(s) where isomers are possible. Indicate whether the starting material is **chiral or achiral by circling** the appropriate designation under the starting material. When more than one product is formed, clearly state whether **equal or unequal amounts** of the compounds are formed. Also indicate whether the product(s) is(are) optically active or optically inactive.

(a) 

(b) 

chiral     achiral

optically active  optically inactive
4. (a) When the optically active tosylate (A) shown below was reacted with CH₃SNa in CH₃OH, the reaction was observed to be second order and the substitution product shown was formed almost exclusively. Show the mechanism for this reaction and predict the stereochemistry of the product.

(b) If the solvent in part (a) was changed from methanol to dimethyl formamide [DMF, HCON(CH₃)₂], the same product was formed but at a much faster rate. Explain.

5. (b) Would you expect the following reaction to occur faster in DMF or in ethanol? Explain your answer.

   Br + NaCN → CN + NaBr
6. The reaction of B with NaCN in ethanol is much faster than the reaction of A with NaCN in ethanol. The rate of reaction of A with 0.2 M NaCN is twice as fast as with 0.1 M NaCN. The rate of reaction of B with either 0.1 M or 0.2 M NaCN is the same.

(a) A reacts with NaCN by a________ mechanism.

(b) The reaction of the R isomer of A would give:
    _____ the R isomer of C, _____ the S isomer of C, _____ a racemic mixture of C.

(c) B reacts with NaCN by a________ mechanism.

(d) The reaction of the R isomer of B would give:
    _____ the R isomer of D, _____ the S isomer of D, _____ a racemic mixture of D.

(e) Explain why B reacts faster than A.

(f) Explain why two products are formed from B.
7. How the following syntheses can be efficiently accomplished. More than one step may be required. Show any intermediate products that would be isolated in the course of the synthesis.

8. Write an electron pushing reaction mechanism for the acid catalyzed equilibration of 3-ethyl-1-pentene and 3-ethyl-2-pentene. Which isomer is more stable?

9. Depending on the reaction conditions and reagents employed, 3,3-dimethyl-1-butene (t-butyl ethylene) can be converted into three different alcohols. Reactions of 3,3-dimethyl-1-butene with H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O produces 2,3-dimethyl-2-butanol. Draw a detailed mechanism for its formation. Use electron pushing arrows (curved arrows) to show how each intermediate is converted to the next intermediate in the sequence.
10. *trans*-2-Methylcyclohexanol is subjected to acid-catalyzed dehydration. Provide the structure of the major product with a reasonably detailed reaction mechanism to explain the product formation.

\[ \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{SO}_4 \text{, } 20 \% \text{ H}_2\text{SO}_4 \rightarrow \text{80 °C} \]

11. *trans*-1-Bromo-2-methylcyclohexane is subjected to dehydrohalogenation reaction. Provide the major product with a reasonably detailed reaction mechanism to explain the product formation.

\[ \text{CH}_3\text{Br} \rightarrow \text{NaOEt} \text{, } \text{EtOH} \rightarrow 60^\circ \text{C} \]

12. For each pair of reactions, circle the reaction that is faster. Convincingly explain your choice.

(a) \[ \text{Br}_2/\text{H}_2\text{O} \text{ versus } \]

\[ \text{HO} \text{ Br} \]

\[ \text{Br} \text{ OH} \]
13. Write an electron pushing reaction mechanism for the following acid catalyzed rearrangement. Comment on the change in ring strain energy for steps involving change in ring size.

14. Write the two major organic products of the bromination of (S)-3-methyl-1-methylenecyclohexane, clearly showing their stereochemistry. Indicate whether each product is optically active or optically inactive. Will the amounts of the two products be equal or unequal? What is the stereochemical relationship between the two different products (i.e. structural isomers, diastereomers, enantiomers, etc)? Draw the most stable chair form of one of the products.
15. Write an electron pushing mechanism for the following reaction. Show all intermediates and use the curved arrow notation to indicate how one intermediate is converted to the next. Draw the most stable chair conformation of the product.

\[
\begin{align*}
\text{Br}_2 & \quad \text{CH}_3\text{OH} \\
\text{Br} & \quad \text{H} \\
\text{H} & \quad \text{OCH}_3 \\
\end{align*}
\]

16. The following scheme involves a strategy for a stereospecific synthesis of Z and E alkenes. Provide appropriate reaction conditions and structures A and B.

\[
\begin{align*}
\text{Li/EtNH}_2 & \quad \text{H}_2, \text{Lindlar catalyst} \\
\end{align*}
\]

A (C\textsubscript{6}H\textsubscript{12})  
B (C\textsubscript{6}H\textsubscript{12})
17. The following scheme involves a strategy for a stereospecific synthesis of vicinal dibromides

(a) Provide appropriate reaction conditions and structures A–D in the boxes. (The reaction conditions and correct structures of A and B can be deduced from the reaction conditions and reagents as well as from the structures of C and D respectively).

(b) Provide the mechanistic rationale for the above bromination reactions to generate C and D.
18. Write the **appropriate intermediate(s) and product(s)** for the following reactions. Clearly show the stereochemistry of the intermediate(s) and product(s) where isomers are possible.

(a) \( \text{Cyclopentene} \xrightarrow{\text{Hg(OAc)}_2, \text{THF, H}_2\text{O}} \) \( \text{NaBH}_4 \xrightarrow{\cdot \text{OH}} \)

(b) \( \text{Cyclopentene} \xrightarrow{\text{BH}_3: \text{THF}} \) \( \text{H}_2\text{O}_2 \xrightarrow{\cdot \text{OH}} \)

(c) \( \text{Cyclopentene} \xrightarrow{\text{OsO}_4, \text{pyridine}} \) \( \text{NaHSO}_3 \xrightarrow{\text{H}_2\text{O}} \)

(d) \( \text{Cyclopentene} \xrightarrow{\text{Br}_2} \) \( \text{C}_6\text{H}_10\text{Br} \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_11\text{OBr} \)

(d) \( \text{Cyclopentene} \xrightarrow{\text{O}_3} \) \( \text{ozonide} \xrightarrow{\text{Zn/ AcOH}} \text{C}_6\text{H}_11\text{O}_2 \)
19. Spodoptol is the sex attractant produced by the female fall armyworm moth to attract male moths. The formula of spodoptol is $\text{C}_{14}\text{H}_{28}\text{O}$. Hydrogenation of spodoptol with $\text{H}_2$ and Pt produced the straight chain primary alcohol 1-tetradecanol, $\text{C}_{14}\text{H}_{30}\text{O}$, $\text{H}_3\text{C}-(\text{CH}_2)_{12}-\text{CH}_2\text{OH}$. Ozonolysis of spodoptol followed by work-up with Zn and acid produced a mixture of two aldehydes $\text{A}$, $\text{C}_5\text{H}_{10}\text{O}$ and $\text{B}$, $\text{C}_9\text{H}_{18}\text{O}_2$.

\[ \text{Spodoptol} \xrightarrow{\text{H}_2, \text{Pt}} \xrightarrow{1) \text{O}_3} \xrightarrow{2) \text{Zn, H}^+} \text{C}_5\text{H}_{10}\text{O} + \text{C}_9\text{H}_{18}\text{O}_2 \]

(a) What are the structures of $\text{A}$, $\text{C}_5\text{H}_{10}\text{O}$ and $\text{B}$, $\text{C}_9\text{H}_{18}\text{O}_2$?

$\text{A} =$ \\
$\text{B} =$ 

(b) Draw two possible structures for spodoptol. Both of these compounds were synthesized and only one of them attracted male fall armyworm moths.

20. Starting from 1-methyl-1-cyclopentene, a tertiary alcohol, a secondary alcohol, and a diol can be synthesized. Indicate specific reagents and the reaction mechanism involved in each of the following transformation. Specify unambiguously the stereochemistry of the intermediates and the products if relevant (Don’t use acidic hydration conditions for the first transformation).
21. What reagents would you use to accomplish the following transformations?

(a) \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Cl} \\
\text{Cl} \\
\text{H} \\
\text{H} \\
\end{array}
\]  
\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Cl} \\
\text{Cl} \\
\text{H} \\
\text{H} \\
\end{array}
\]

(b) \[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{OH} \\
\text{OH} \\
\text{H} \\
\text{H} \\
\end{array}
\]

(c) \[
\begin{array}{c}
\text{CHO} \\
\text{CHO} \\
\end{array}
\]

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

22. Methylcyclopentene can be transformed to two different ethers as shown. Provide appropriate reagents and conditions for each reaction. Use ethyl alcohol in the first reaction and ethyl chloride in the second.