1. There are 8 isomeric alcohols with the formula C₅H₁₂O. Draw these and determine if they are 1°, 2° or 3°.

2. Each of the following is an example of a substitution reaction. Label the leaving group (in the substrate) and the nucleophile.

\[ \text{(a) } \text{ClCH}_2-\text{C}-\text{OC(CH}_3)_3 \xrightarrow{\text{NaN}_3} \text{N}_3\text{CH}_2-\text{C}-\text{OC(CH}_3)_3 \]

\[ \text{(b) } \text{NC}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl} \xrightarrow{\text{OH}^+ / \text{H}_2\text{O}} \text{NC}-\text{C}_6\text{H}_4-\text{CH}_2\text{OH} \]

\[ \text{(c) } \text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaCN}} \text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{CN} \]

\[ \text{(d) } \text{TsOCH}_2 \xrightarrow{\text{HC≡CNa}} \text{HC≡C-C\text{CH}_2} \]

3. Show how to synthesize the following from 1-bromopropan by a substitution reaction.

(a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{N}_3 \)

(b) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 \)

(c) \( \text{CH}_3-\text{C}-\text{OCH}_2\text{CH}_2\text{CH}_3 \)

4. Predict the products of these following substitution reactions.

(a) \[ \text{BrCH}_2-\text{C}-\text{OCH}_2\text{CH}_3 \xrightarrow{\text{NaI / acetone}} \]
5. Which of the following substrates (if any) in each pair below would you expect to react more rapidly by SN2? Why?

(a) CH₃CH₂CH₂CH₂Br or (CH₃)₂CHBr
(b) CH₃CH₂CH₂Cl or CH₃CH₂CH₂I
(c) (CH₃CH₂)₂CHOTf + EtOH or (CH₃CH₂)₂CHOTf + NaOEt
(d) CH₃CH₂CH₂OTs + NaI

6. Show the mechanisms and products of your choices in Problem 6 (c) and (d).

7. Show the products and their stereochemistry in the following SN₂ reactions.
8. Write an equation, clearly showing the stereochemistry of the starting material and the product, for the reaction of (S)-1-bromo-2-methylbutane with sodium iodide in acetone. What is the configuration (R or S) of the product?

9. Which of the following substrates (if any) in each pair below would you expect to react more rapidly by $S_N1$? Why?

(a) (CH$_3$)$_3$CBr or (CH$_3$)$_3$COTs

(b) (CH$_3$)$_3$CBr or (CH$_3$)$_2$CHBr

(c) (CH$_3$)$_3$CBr + NaOCH$_3$ or (CH$_3$)$_3$CBr + NaOH

(d) (CH$_3$)$_2$CHBr + NaN$_3$ $\xrightarrow{\text{EtOH}}$

or

(CH$_3$)$_2$CHBr + NaN$_3$ $\xrightarrow{\text{CH$_3$CN}}$
10. Show the products and their stereochemistry for the following SN1 reactions.

(a) \[
\text{CH}_3\text{OTf} + \text{CH}_3\text{CO}_2\text{Na} \rightarrow \]

(b) \[
\text{(CH}_3\text{)}_3\text{C} + \text{I}^- \rightarrow \]

(c) \[
\text{CH}_3\text{CH}_2\text{Cl} + \text{CH}_3\text{OH} \rightarrow \]

11. Show the mechanism that explains how the following reactions could occur.

(a) \[
\text{(CH}_3\text{)}_3\text{C} \rightarrow \text{Na}_3 \rightarrow \text{(CH}_3\text{)}_3\text{C} + \text{(CH}_3\text{)}_3\text{C} \]

(b) \[
\text{CH}_2\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{OH} \rightarrow \]

12. Arrange the isomers of molecular formula C4H9Cl in order of decreasing rate of reaction with sodium iodide in acetone (hint: Would NaI in acetone favor SN1 or SN2 mechanism?).
13. Secondary alkyl halides can undergo S_N1 or S_N2 reactions. Solvent is one factor that may exert an influence. (a) For each of the reactions below, suggest which mechanism is more likely. Justify your answer. (b) Suggest two experimental methods by which you might verify your predictions. Explain what you expect to observe.

\[
\text{CH}_3\text{CH}_2\text{CH}-\text{Br} + \text{NaN}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}-\text{N}_3 \quad \text{(rxn 1)}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}-\text{Br} + \text{NaN}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}-\text{N}_3 \quad \text{(rxn 2)}
\]

14. Identify the products of the following reactions.

(a) \[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \rightarrow \text{C}_5\text{H}_10\text{ClI}
\]

(b) \[
\text{BrCH}_2\text{CH}_2\text{Br} + \text{NaSCH}_2\text{CH}_2\text{SNa} \rightarrow \text{C}_4\text{H}_8\text{S}_2
\]

(c) \[
\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{Na}_2\text{S} \rightarrow \text{C}_4\text{H}_8\text{S}
\]

15. Show the mechanism and products of reaction for the following. Label the rate-limiting step.

(a)

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}
\]

(b) \[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{NaBr, H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}
\]

16. The reaction of 2,2-dimethyl-1-propanol with HBr is very slow and gives 2-bromo-2-methylbutane as the major product. Give a mechanistic explanation for these observations.
17. Show two methods by which each of the following reactions could be achieved. Explain which would be the best method and why.

(a) \[ \text{CH}_3\text{CHCH}_3\text{OH} \rightarrow \text{CH}_3\text{CHCH}_3\text{Br} \]

(b) \[ \text{CH}_2\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{CH}_3\text{Cl} \]

(c) \[ \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{Cl} \]

18. Outline an efficient synthesis of each of the following compounds from the indicated starting material and any necessary organic or inorganic reagents.

(a) cyanocyclopentane from cyclopentane

(b) cyanocyclopentane from cyclopentanol

(c) iodoisobutane from isobutanol

(d) 2-iodo-2-methylpropane from 2-chloro-2-methylpropane

19. Something is wrong with each of the following reactions. Identify the error and suggest a better route to achieve the same result.

(a) \[ \text{CH}_3\text{C} \rightarrow \text{CH}_3\text{I} \]

(b) \[ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \]