Chapter 6: Organic Halogen Compounds; Substitution and Elimination Reactions
• Halogen compounds are important for several reasons. Simple alkyl and aryl halides, especially chlorides and bromides, are versatile reagents in syntheses.

• Through substitution reactions, which we will discuss in this chapter, halogens can be replaced by many other functional groups. Organic halides can be converted to unsaturated compounds through dehydrohalogenation.
6.1 Nucleophilic Substitution

Alkyl halides undergo nucleophilic substitution reactions, in which a nucleophile displaces the halide leaving group from the alkyl halide substrate. Hydroxide ion is the nucleophile. It reacts with the substrate (ethyl bromide) and displaces bromide ion. The bromide ion is called the leaving group.
These ideas are generalized in the following equations for a nucleophilic substitution reaction:

\[
\begin{align*}
\text{Nu}\,\text{(neutral)} & + R:L \rightarrow R:\text{Nu}^{+} + :L^{-} \\
\text{Nu}\,\text{(anion)} & + R:L \rightarrow R:\text{Nu} + :L^{-}
\end{align*}
\]
6.2 Examples of Nucleophilic Substitution

- Nucleophiles can be classified according to the kind of atom that forms a new covalent bond. For example, the hydroxide ion is an oxygen nucleophile. In the product, a new carbon–oxygen bond is formed.
- The most common nucleophiles are oxygen, nitrogen, sulfur, halogen, and carbon nucleophiles.
- Table 6.1 shows some examples of nucleophiles and the products that they form when they react with an alkyl halide.
Table 6.1  Reactions of Common Nucleophiles with Alkyl Halides (Eqs. 6.2 and 6.3)

<table>
<thead>
<tr>
<th>Nu</th>
<th>R–Nu</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxygen nucleophiles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. ( \text{HO}^- ) hydroxide</td>
<td>R–OH alcohol</td>
<td></td>
</tr>
<tr>
<td>2. ( \text{RO}^- ) alkoxide</td>
<td>R–OR ether</td>
<td></td>
</tr>
<tr>
<td>3. ( \text{HOH} ) water</td>
<td>R–( \text{O}^- )H alklyloxonium ion</td>
<td>These ions lose a proton and the products are alcohols and ethers.</td>
</tr>
<tr>
<td>4. ( \text{ROH} ) alcohol</td>
<td>R–( \text{O}^- )H dialkyloxonium ion</td>
<td></td>
</tr>
<tr>
<td>5. ( \text{R–C}^- \text{O}^- ) carboxylate</td>
<td>R–OC–R ester</td>
<td></td>
</tr>
<tr>
<td><strong>Nitrogen nucleophiles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. ( \text{NH}_3 ) ammonia</td>
<td>R–( \text{NH}_3 ) alkylammonium ion</td>
<td>With a base, these ions readily lose a proton to give amines.</td>
</tr>
<tr>
<td>7. ( \text{RNH}_2 ) primary amine</td>
<td>R–( \text{NH}_2 \text{R} ) dialkylammonium ion</td>
<td></td>
</tr>
<tr>
<td>8. ( \text{R}_2\text{NH} ) secondary amine</td>
<td>R–( \text{NR}_2 ) trialkylammonium ion</td>
<td></td>
</tr>
<tr>
<td>9. ( \text{R}_3\text{N} ) tertiary amine</td>
<td>R–( \text{NR}_3 ) tetraalkylammonium ion</td>
<td></td>
</tr>
</tbody>
</table>
Sulfur nucleophiles

10. $\text{HS}^-$: hydrosulfide $\text{R-SH}$ thiol
11. $\text{RS}^-$: mercaptide $\text{R-SR}$ thioether (sulfide)
12. $\text{R}_2\text{S}$: thioether $\text{R-SR}_2$ trialkylsulfonium ion

Halogen nucleophiles

13. $\text{I}^-$: iodide $\text{R-I}$ alkyl iodide

Carbon nucleophiles

14. $-\text{C≡N}$: cyanide $\text{R-C≡N}$ alkyl cyanide (nitrile)
15. $-\text{C≡CR}$: acetylide $\text{R-C≡CR}$ alkyne

The usual solvent is acetone. Sodium iodide is soluble in acetone, but sodium bromide and sodium chloride are not.

Sometimes the isonitrile, $\text{R-N≡C}$, is formed.
PROBLEM 6.1 Using Table 6.1, write complete equations for the following nucleophilic substitution reactions:

a. $\text{Na}^+\text{-OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

b. $(\text{CH}_3\text{CH}_2)_3\text{N}^\equiv + \text{CH}_3\text{CH}_2\text{Br}$

c. $\text{Na}^+\text{-SH} + \begin{array}{c} \text{CH}_2\text{Br} \\
\end{array}$

\[
\begin{align*}
\text{a. } & \quad \text{NaOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Na}^+\text{Br}^- \\
\text{b. } & \quad (\text{CH}_3\text{CH}_2)_3\text{N} + \text{CH}_3\text{CH}_2\text{Br} \quad \rightarrow \quad (\text{CH}_3\text{CH}_2)_4\text{N}^+ \text{ Br}^- \\
\text{c. } & \quad \text{NaSH} + \begin{array}{c} \text{CH}_2\text{Br} \\
\end{array} \quad \rightarrow \quad \begin{array}{c} \text{CH}_2\text{SH} \\
\end{array} + \text{Na}^+\text{Br}^- 
\end{align*}
\]
PROBLEM 6.2 Write an equation for the preparation of each of the following compounds, using a nucleophilic substitution reaction. In each case, label the nucleophile, the substrate, and the leaving group.

a. \((\text{CH}_3\text{CH}_2\text{)}_3\text{N}\)  
   b. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\)  
   c. \((\text{CH}_3\text{)}_2\text{CHCH}_2\text{CN}\)  
   d. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3\)  
   e. \((\text{CH}_3\text{CH}_2\text{)}_3\text{S}^+\text{Br}^-\)  
   f. \(\text{CH}_2=\text{CHCH}_2\text{I}\)

---

6.2

a. \[(\text{CH}_3\text{CH}_2\text{)}_2\text{NH} + \text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{CH}_3\text{CH}_2\text{)}_2\text{NH}^+ + \text{Br}^-\]
   
   (nucleophile) \quad (substrate) \quad (leaving group)

   (item 8, Table 6.1) This reaction is followed by the acid-base equilibrium:

   \[(\text{CH}_3\text{CH}_2\text{)}_2\text{NH} + (\text{CH}_3\text{CH}_2\text{)}_2\text{NH}^+ \rightleftharpoons (\text{CH}_3\text{CH}_2\text{)}_2\text{NH}_2 + (\text{CH}_3\text{CH}_2\text{)}_3\text{N}\]

b. \[\text{HO}^- + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{Br}^-\]
   
   (nucleophile) \quad (substrate) \quad (leaving group)

   (item 1, Table 6.1)

c. \[-\text{C}=\text{N} + (\text{CH}_3\text{)}_2\text{CHCH}_2\text{Br} \rightarrow (\text{CH}_3\text{)}_2\text{CHCH}_2\text{CN} + \text{Br}^-\]
   
   (nucleophile) \quad (substrate) \quad (leaving group)

   (item 14, Table 6.1)
d. \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3 + \text{Br}^- \]

nucleophile substrate leaving group

or

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

nucleophile substrate leaving group

(item 2, Table 6.1) Iodides or chlorides could also be used as substrates.

e. \[ \text{(CH}_3\text{CH}_2)_2\text{S}^- + \text{CH}_3\text{CH}_2\text{Br} \rightarrow \text{(CH}_3\text{CH}_2)_3\text{S}^- + \text{Br}^- \]

nucleophile substrate leaving group

(item 12, Table 6.1)

f. \[ \text{I}^- + \text{CH}_2=\text{CHCH}_2\text{Br} \rightarrow \text{CH}_2=\text{CHCH}_2\text{I} + \text{Br}^- \]

nucleophile substrate leaving group

(item 13, Table 6.1)
The substitution reactions have some limitations with respect to the structure of the $R$ group in the alkyl halide.

-These are reactions of alkyl halides. Aryl halides and vinyl halides, do not undergo this type of nucleophilic substitution reaction.

-Elimination rather than substitution occurs when the nucleophile is an anion or a base or both.
H₂O + CH₃—C—CH₃ → CH₃—C—CH₃ + H⁺ + Br⁻  
(about 80%; some methylpropene is also formed)

but

-CH₃ + CH₃—C—CH₃ → CH₃—C—CH₃ + H₂O + Br⁻  
(methylpropene)
6.3 Nucleophilic Substitution Mechanisms

- There are two main nucleophilic substitution mechanisms. These are described by the symbols $S_N2$ and $S_N1$, respectively.
- The $S_N$ part of each symbol stands for “substitution, nucleophilic.”
- The meaning of the numbers 2 and 1 will become clear as we discuss each mechanism.
6.4 The $S_N2$ Mechanism

The $S_N2$ mechanism is a one-step process in which the bond to the leaving group begins to break as the bond to the nucleophile begins to form. It can be represented by the following equation:

$$\text{nucleophile} + \text{substrate} \rightarrow [\text{transition state}]^{\text{TS}} \rightarrow \text{product} + \text{leaving group}$$
How can we recognize when a particular nucleophile and substrate react by the $S_N2$ mechanism?

1. *The rate of the reaction depends on both the nucleophile and the substrate concentrations.*

2. Every $S_N2$ displacement occurs with inversion of configuration.

\[
\begin{align*}
\text{HO}^- &+ \text{C} - \text{Br} \quad \text{CH}_3 \quad \text{CH}_2\text{CH}_3 \\
\text{H} \quad \text{CH}_2\text{CH}_3 &\rightarrow \text{HO} - \text{C} \quad \text{CH}_3 \\
&\quad \text{CH}_2\text{CH}_3 \quad + \text{Br}^-
\end{align*}
\]

(R)-2-bromobutane \quad \text{(S)-2-butanol}
3. The reaction is fastest when the alkyl group of the substrate is methyl or primary and slowest when it is tertiary. Secondary alkyl halides react at an intermediate rate.
PROBLEM 6.4  Predict the product from the $S_{N}2$ reaction of

a. \textit{trans}-4-methylcyclohexyl bromide with cyanide ion.
b. (\textit{S})-2-bromopentane with cyanide ion.
c. (\textit{R})-2-chlorobutane with NaSH.
PROBLEM 6.5  Arrange the following compounds in order of decreasing $S_{N2}$ reactivity toward sodium ethoxide:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CHBr} & \quad \text{CH}_3\text{CHCH}_2\text{Br} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}
\end{align*}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHCH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}
\]

The more crowded the carbon where displacement occurs, the slower the reaction rate.
Summary
-The $S_N2$ mechanism is a one-step process favored for methyl and primary halides.
-It occurs more slowly with secondary halides and usually not at all with tertiary halides.
- An $S_N2$ reaction occurs with inversion of configuration.
- Its rate depends on the concentration of both the nucleophile and the substrate (the alkyl halide).
6.5 The $S_N1$ Mechanism

The $S_N1$ mechanism is a two step process:

The bond between the carbon and the leaving group breaks first then the resulting carbocation combines with the nucleophile.

$\text{substrate} \xrightarrow{\text{slow}} \text{carbocation} + -:L$

Resulting carbocation combines with the nucleophile.

$\text{carbocation} + :\text{Nu} \xrightarrow{\text{fast}} \text{Nu}$ and $\text{Nu}$
The diagram illustrates the reaction coordinate for the bromination of tert-butanol. The reaction pathway involves the formation of a carbocation intermediate, which then leads to the formation of a protonated alcohol. The initial reactants are water and tert-butyl bromide, and the final products are tert-butanol and hydrogen bromide.

- **Reactants**: \( \text{H}_2\text{O} + (\text{CH}_3)_3\text{C} - \text{Br} \)
- **Carbocation intermediate**: \( (\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O} + \text{Br}^- \)
- **Protonated alcohol**: \( (\text{CH}_3)_3\text{C} - \text{OH}_2^+ + \text{Br}^- \)
- **Products**: \( (\text{CH}_3)_3\text{C} - \text{OH} + \text{H} - \text{Br} \)
How can we recognize when a particular nucleophile and substrate react by the $S_N^1$ mechanism?

1. The rate of the reaction does not depend on the concentration of the nucleophile.

2. If the carbon bearing the leaving group is stereogenic, the reaction occurs mainly with loss of optical activity (that is, with racemization).
(R)-3-bromo-3-methylhexane 

\[
\begin{align*}
\text{Br} & \quad \text{aqueous acetone} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{Br}^- & \\
\end{align*}
\]

Carbocation intermediate

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

50% S

(product from attack on the bottom face of the carbocation)

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

50% R

(product from attack on the top face of the carbocation)

\[
\begin{align*}
\text{H}_2\text{O} & \quad -\text{H}^+ \\
\end{align*}
\]
3. The reaction is fastest when the alkyl group of the substrate is tertiary and slowest when it is primary.

• The reason is that $S_N1$ reactions proceed via carbocations, so the reactivity order corresponds to that of carbocation stability ($3^\circ > 2^\circ > 1^\circ$).
<table>
<thead>
<tr>
<th>Variables</th>
<th>$S_{N2}$</th>
<th>$S_{N1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Halide structure</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary or CH$_3$</td>
<td>Common</td>
<td>Rarely*</td>
</tr>
<tr>
<td>Secondary</td>
<td>Sometimes</td>
<td>Sometimes</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Rarely</td>
<td>Common</td>
</tr>
<tr>
<td><strong>Stereochemistry</strong></td>
<td>Inversion</td>
<td>Racemization</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td>Rate is retarded by polar protic solvents and increased by polar aprotic solvents</td>
<td>Because the intermediates are ions, the rate is increased by polar solvents</td>
</tr>
<tr>
<td><strong>Nucleophile</strong></td>
<td>Rate depends on nucleophile concentration; mechanism is favored when the nucleophile is an anion</td>
<td>Rate is independent of nucleophile concentration; mechanism is more likely with neutral nucleophiles</td>
</tr>
</tbody>
</table>

*Allyl and benzyl substrates are the common exceptions (see Problem 6.7b).*
How can we tell whether a nucleophile is strong or weak, or whether one nucleophile is stronger than another? Here are a few useful generalizations:

1. Negative ions are more nucleophilic, or better suppliers, than the corresponding neutral molecules.

   \[
   \text{HO}^- > \text{HOH} \quad \text{RS}^- > \text{RSH} \quad \text{RO}^- > \text{ROH}
   \]

2. Elements low in the periodic table tend to be more nucleophilic than elements above them in the same column.

   \[
   \text{HS}^- > \text{HO}^- \quad \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-
   \]

3. Across a row in the periodic table, more electronegative elements (the more tightly an element holds electron to itself) tend to be less nucleophilic.

   \[
   \text{R}^- \quad > \quad \text{N}^- \quad > \quad \text{R}^-\text{O}^- \quad > \quad \text{F}^- \quad \text{and} \quad \text{H}_3\text{N}: \quad > \quad \text{H}_2\text{O}: \quad > \quad \text{HF}:
   \]
6.8 Which mechanism, $S_N1$ or $S_N2$, would you predict for each of the following reactions?

\[
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 + \text{Na}^+\text{SH} \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 + \text{NaBr}
\]

\[
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 + \text{HBr}
\]
6.7 Dehydrohalogenation, and Elimination Reaction; The E2 and E1 Mechanisms

In elimination (or dehydrohalogenation) reactions of alkyl halides, a hydrogen atom and a halogen atom from adjacent carbons are eliminated and a carbon–carbon double bond is formed.
There are two main mechanisms for elimination reactions, designated E2 and E1.

- **E2 mechanism** is a process in which HX is eliminated and a C=C bond is formed in the same step.

• The preferred conformation for the substrate in an E2 reaction is: The H-C-C-L atoms lie in a single plane, with H and L in an *anti* arrangement.
• **E1 mechanism** is a two-step process with the same first step as an $S_{N1}$ reaction.

\[
\begin{align*}
\text{substrate} & \quad \text{slow} \quad \text{carbocation} \\
\begin{array}{c}
\text{C} \quad \text{C} \quad \text{L} \\
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{C} \\
\text{C}^+ \\
\end{array} \quad + \quad \begin{array}{c}
\text{L}^- \\
\end{array}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{carbocation} & \quad \text{Nu} \quad \text{SN1} \\
\begin{array}{c}
\text{C} \quad \text{C}^+ \\
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{C} \quad \text{C} \quad \text{Nu} \\
\end{array} \quad \begin{array}{c}
\text{C} \quad \text{C} \\
\text{C} \quad \text{C} \\
\end{array}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{E1} & \quad \text{SN1} \\
\begin{array}{c}
\text{C} \quad \text{C}^+ \\
\end{array} \quad \begin{array}{c}
\text{C} \quad \text{C} \quad \text{C} \\
\end{array} \quad + \quad \begin{array}{c}
\text{H}^+ \\
\end{array}
\end{align*}
\]
6.8 Substitution and Elimination in Competition

• Tertiary Halides
  Substitution can only occur by the $S_N1$ mechanism, but elimination can occur by either the E1 or the E2 mechanism.

With weak nucleophiles and polar solvents, the $S_N1$ and E1 mechanisms compete with each other.

\[
\text{t-butyl bromide} \quad \xrightarrow{H_2O} \quad \text{(CH}_3\text{)}_3\text{C}^+ + \text{Br}^- \\
\text{H}_2\text{O, } S_N1 \quad \rightarrow \quad \text{(CH}_3\text{)}_3\text{COH} \quad \text{(about 80%)} \\
\text{E1} \quad \rightarrow \quad \text{(CH}_3\text{)}_2\text{C} \equiv \text{CH}_2 + \text{H}^+ \quad \text{(about 20%)}
\]
• With a strong nucleophile (which can act as a base), elimination by the E2 mechanism is favored.

With OH\(^-\) or CN\(^-\) as nucleophiles, only elimination occurs with alkene as the exclusive product.

\[
\text{HO}^- + \text{C}(-\text{Br})\text{C}(-\text{CH}_3)\text{CH}_3 \xrightarrow{\text{E2}} \text{H}_2\text{C}(-\text{C}(-\text{CH}_3)\text{CH}_3)\text{H} + \text{H}_2\text{O} + \text{Br}^- \\

t\text{-butyl bromide} \quad \text{methylpropene (100%)}
\]
Primary Halides

With most nucleophiles, primary halides give mainly substitution products ($S_N$2). Only with very bulky, strongly basic nucleophiles do we see that the E2 process is favored. For example,

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} & \quad \text{1-bromobutane} \\
\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+ \quad \text{in ethanol} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 \\
& \quad \text{butyl ethyl ether} \quad \text{(S_N2; 90\%)} \\
& \quad \text{1-butene} \quad \text{(E2; 10\%)} \\
\text{CH}_3\text{C}\text{O}^- \text{K}^+ \quad \text{in t-butyl alcohol} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OC(CH}_3\text{)}_3 + \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 \\
& \quad \text{butyl t-butyl ether} \quad \text{(S_N2; 15\%)} \\
& \quad \text{1-butene} \quad \text{(E2; 85\%)}
\end{align*}
\]
t-butoxide

Ethoxide
Secondary Halides

All four mechanisms, $S_{N2}$ and $E2$ as well as $S_{N1}$ and $E1$, are possible. The product composition is sensitive to the nucleophile (its strength as a nucleophile and as a base) and to the reaction conditions (solvent, temperature).

Substitution is favored with stronger nucleophiles that are not strong bases ($S_{N2}$) or by weaker nucleophiles in polar solvents ($S_{N1}$), but elimination is favored by strong bases ($E2$).
2-bromopropane (Br)

- Reaction with strong nucleophile ($\text{CH}_3\text{CH}_2\text{S}^- \text{Na}^+$):
  - Product: $\text{CH}_3\text{CHCH}_3$ (S$_\text{N2}$) $\text{SCH}_2\text{CH}_3$

- Reaction with weak nucleophile ($\text{CH}_3\text{CH}_2\text{OH}$):
  - Product: $\text{CH}_3\text{CHCH}_3$ + $\text{CH}_3\text{CH}=$=$\text{CH}_2$ $\text{OCH}_2\text{CH}_3$
  - $\text{S}_\text{N1}$; major
  - $\text{E}_1$; minor

- Reaction with strong base ($\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+$):
  - Product: $\text{CH}_3\text{CHCH}_3$ + $\text{CH}_3\text{CH}=$=$\text{CH}_2$ $\text{OCH}_2\text{CH}_3$
  - $\text{S}_\text{N2}$; minor
  - $\text{E}_2$; major
<table>
<thead>
<tr>
<th>Halide type</th>
<th>$S_{N1}$</th>
<th>$S_{N2}$</th>
<th>E1</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1CH_2X$</td>
<td>Does not occur</td>
<td>Highly favored</td>
<td>Does not occur</td>
<td>Occurs when strong bases are used</td>
</tr>
<tr>
<td>(primary)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_2CHX$</td>
<td>Can occur with benzylic and allylic halides</td>
<td>Occurs in competition with E2 reaction</td>
<td>Can occur with benzylic and allylic halides</td>
<td>Favored when strong bases are used</td>
</tr>
<tr>
<td>(secondary)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_3CX$</td>
<td>Favored in hydroxylic solvents</td>
<td>Does not occur</td>
<td>Occurs in competition with $S_{N1}$ reaction</td>
<td>Favored when bases are used</td>
</tr>
<tr>
<td>(tertiary)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Homework
13, 14, 22, 24, 25, 28, 29