8.13
Substitution and Elimination
as Competing Reactions
Alkyl halides can react with Lewis bases in two different ways; nucleophilic substitution or elimination.

**Two Reaction Types**

- **β-elimination**
  - Chemical reaction: $\text{H} - \text{Y} + \text{C} = \text{C} \to \text{H} + \text{C} = \text{C} + \text{Y}^-$

- **nucleophilic substitution**
  - Chemical reaction: $\text{H} - \text{Y} + \text{X}^- \to \text{H} + \text{X}^- + \text{C} = \text{C}$
How can we tell which reaction pathway is followed for a particular alkyl halide?

**Two Reaction Types**

- **β-elimination**

  \[
  \text{H} \quad \text{C} \quad \text{C} \quad \text{X} + \text{:Y}^- \quad \text{C} \equiv \text{C} \quad + \quad \text{H-Y} \quad + \quad \text{:X}^- \\
  \]

- **nucleophilic substitution**

  \[
  \text{H} \quad \text{C} \quad \text{C} \quad \text{Y} \quad + \quad \text{:X}^- \quad \text{C} \quad \text{C} \quad \text{X} \\
  \]
A systematic approach is to choose as a reference point the reaction followed by a typical alkyl halide (secondary) with a typical Lewis base (an alkoxide ion).

The major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism.
Example

\[
\begin{align*}
\text{CH}_3\text{CHCHCH}_3 & \quad \xrightarrow{\text{Br}} \quad \text{NaOCH}_2\text{CH}_3 \\
& \quad \xrightarrow{\text{ethanol, 55°C}} \\
\text{CH}_3\text{CHCHCH}_3 & \quad + \quad \text{CH}_3\text{CH=CH}_2 \\
\text{OCH}_2\text{CH}_3 & \quad (13\%) \quad \text{and} \quad (87\%)
\end{align*}
\]
Figure 8.11

E2

\[ \text{CH}_3\text{CH}_2\text{-O-} \]

[Diagram of a molecule with a bromine (Br) atom and the notation E2]
Figure 8.11

\[ S_{N2} \]

\[
\text{CH}_3\text{CH}_2\text{O}^\cdot
\]

\[ \text{Br} \]
Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

1) decreased crowding at the carbon that bears the leaving group
Decreased crowding at carbon that bears the leaving group increases substitution relative to elimination.

*Uncrowded Alkyl Halides*

**primary alkyl halide**

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \quad \xrightarrow{\text{NaOCH}_2\text{CH}_3} \quad \text{ethanol, 55°C} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{CH}_3\text{CH}=\text{CH}_2 \\
(91\%) \quad + \quad (9\%)
\]
But a crowded alkoxide base can favor elimination even with a primary alkyl halide.

**primary alkyl halide + bulky base**

\[
\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{CH}_2\text{Br} \\
\text{KOC(CH}_3)_3 \\
\text{tert-butyl alcohol, 40°C} \\
\]

\[
\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{CH}_2\text{OC(CH}_3)_3 + \text{CH}_3(\text{CH}_2)_{15}\text{CH=CH}_2 \\
(13\%) \quad (87\%) 
\]
Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

1) decreased crowding at the carbon that bears the leaving group
2) decreased basicity of the nucleophile

When is substitution favored?
Weakly Basic Nucleophile

Weakly basic nucleophile increases substitution relative to elimination

secondary alkyl halide + weakly basic nucleophile

\[ \text{CH}_3\text{CH(CH}_2\text{)}_5\text{CH}_3 \]

Cl

KCN

DMSO

\[ \text{CH}_3\text{CH(CH}_2\text{)}_5\text{CH}_3 \]

CN

pK\textsubscript{a} (HCN) = 9.1

(70%)
Weakly basic nucleophile increases substitution relative to elimination.

Secondary alkyl halide + weakly basic nucleophile

\[ \text{NaN}_3 \]

\[ pK_a (\text{HN}_3) = 4.6 \]

(75%)
Tertiary alkyl halides are so sterically hindered that elimination is the major reaction with all anionic nucleophiles. Only in solvolysis reactions does substitution predominate over elimination with tertiary alkyl halides.
**Example**

\[ (\text{CH}_3)_2\text{CCH}_2\text{CH}_3 \xrightarrow{\text{Br}} \text{CH}_3 \text{CH}=\text{C}=\text{CH} \text{CH}_3 \]

\[ \text{CH}_3\text{CCH}_2\text{CH}_3 + \text{CH}_2=\text{C}=\text{CCH}_2\text{CH}_3 + \text{CH}_3\text{C}=\text{CHCH}_3 \]

**Reaction Conditions:**
- Ethanol, 25°C
- 64% yield
- 2M sodium ethoxide in ethanol, 25°C
- 1% yield
- 99% yield