5.8
Preparation of Alkenes:
Elimination Reactions
**β-Elimination Reactions Overview**

- **dehydrogenation of alkanes:**
  \[ X = Y = H \]

- **dehydration of alcohols:**
  \[ X = H; \quad Y = \text{OH} \]

- **dehydrohalogenation of alkyl halides:**
  \[ X = H; \quad Y = \text{Br, etc.} \]

---

**Chemical Structures:**

- **Dehydrogenation:**
  \[ X\_C\_C\_Y \rightarrow \text{C≡C} + X\_Y \]

- **Dehydration:**
  \[ X\_C\_C\_Y \rightarrow \text{C≡C} + X\_Y \]

- **Dehydrohalogenation:**
  \[ X\_C\_C\_Y \rightarrow \text{C≡C} + X\_Y \]
Dehydrogenation

limited to industrial syntheses of ethylene, propene, 1,3-butadiene, and styrene

important economically, but rarely used in laboratory-scale syntheses

\[ \text{CH}_3\text{CH}_3 \xrightarrow{750^\circ C} \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \]

\[ \text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{750^\circ C} \text{H}_2\text{C}=\text{CHCH}_3 + \text{H}_2 \]
5.9
Dehydration of Alcohols
**Dehydration of Alcohols**

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 160^\circ\text{C}} \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2\text{O}
\]

\[
\text{CH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2\text{SO}_4, 140^\circ\text{C}} \text{C}_2\text{H}_4 + \text{H}_2\text{O}
\]

(79-87%)

\[
\text{H}_3\text{C} - \text{C} - \text{OH} \xrightarrow{\text{H}_2\text{SO}_4, \text{heat}} \text{C} = \text{C} = \text{CH}_2 + \text{H}_2\text{O}
\]

\[
\text{H}_3\text{C} \quad \text{C} = \text{C} = \text{CH}_2 + \text{H}_2\text{O}
\]

(82%)
Relative Reactivity

- **tertiary**: most reactive
- **primary**: least reactive
5.10 Regioselectivity in Alcohol Dehydration: The Zaitsev Rule
Regioselectivity

A reaction that can proceed in more than one direction, but in which one direction predominates, is said to be regioselective.
A reaction that can proceed in more than one direction, but in which one direction predominates, is said to be regioselective.

![Chemical Diagram]
When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.

The Zaitsev Rule

R OH
R C C CH₂R
H CH₃

three protons on this β carbon
When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the \( \beta \) carbon having the fewest hydrogens.

The Zaitsev Rule

two protons on this \( \beta \) carbon
When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.

The Zaitsev Rule

only one proton on this β carbon
When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.

The Zaitsev Rule

![Diagram of the Zaitsev Rule]

- Only one proton on this β carbon
5.11

Stereoselectivity in Alcohol Dehydration
A stereoselective reaction is one in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amounts than any other.
5.12
The Mechanism of Acid-Catalyzed Dehydration of Alcohols
The dehydration of alcohols and the reaction of alcohols with hydrogen halides share the following common features:

1) Both reactions are promoted by acids

2) The relative reactivity decreases in the order tertiary > secondary > primary

These similarities suggest that carbocations are intermediates in the acid-catalyzed dehydration of alcohols, just as they are in the reaction of alcohols with hydrogen halides.
first two steps of mechanism are identical to those for the reaction of tert-butyl alcohol with hydrogen halides
Step 1: Proton transfer to tert-butyl alcohol

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

fast, bimolecular

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

tert-Butyloxonium ion
Step 2: Dissociation of \( \text{tert}-\text{butyloxonium ion} \) to carbocation

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C}^+ & + :\text{O}^- \\
\text{tert-Butyl cation} & + \text{H} \\
\end{align*}
\]

Mechanism
Step 3: Deprotonation of *tert*-butyl cation.

Mechanism

[Diagram of the step showing the reaction mechanism]
Carbocations

are intermediates in the acid-catalyzed dehydration of tertiary and secondary alcohols

carbocations can:

react with nucleophiles
lose a $\beta$-proton to form an alkene
Dehydration of Primary Alcohols

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 160^\circ\text{C}} \text{H}_2\text{C}\equiv\text{CH}_2 + \text{H}_2\text{O}
\]

avoids carbocation because primary carbocations are too unstable

oxonium ion loses water and a proton in a bimolecular step
Step 1: Proton transfer from acid to ethanol

CH₃CH₂−O− + H−O→ H\text{H}\text{H} \quad \text{fast, bimolecular}

CH₃CH₂−O− + :O− → CH₃CH₂−O− + :O−

Ethyloxonium ion
Step 2: Oxonium ion loses both a proton and a water molecule in the same step.

Mechanism

H

:O: + H—CH₂—CH₂—O:

H

 slow, bimolecular

H

:O—H + H₂C═CH₂ + :O:
Sometimes the alkene product does not have the same carbon skeleton as the starting alcohol.
Example

\[
\text{OH} \xrightarrow{\text{H}_3\text{PO}_4, \text{heat}} \text{3\%} \quad + \quad \text{64\%} \quad + \quad \text{33\%}
\]
Rearrangement involves alkyl group migration

Carbocation can lose a proton as shown or it can undergo a methyl migration. The $\text{CH}_3$ group migrates with its pair of electrons to adjacent positively charged carbon.
Rearrangement involves alkyl group migration.

\[ \text{CH}_3\text{C-CHCH}_3 \xrightarrow{97\%} \text{CH}_3\text{C}^+\text{CHCH}_3 \]

3% tertiary carbocation; more stable

tertiary carbocation; more stable
Rearrangement involves alkyl group migration

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{CHCH}_3 \\
\text{CH}_3 & \quad + \quad \text{CHCH}_3
\end{align*}
\]
Another rearrangement

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{H}_3\text{PO}_4, \text{heat}} \text{CH}_3\text{CH}_2\text{CH}\equiv\text{CH}_2 + \text{CH}_3\text{CH}\equiv\text{CHCH}_3
\]

12% mixture of cis (32%) and trans-2-butene (56%)
oxonium ion can lose water and a proton (from C-2) to give 1-butene

doesn't give a carbocation directly because primary carbocations are too unstable
Rearrangement involves hydride shift

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{+}{\text{O}}: \xrightarrow{\text{H}} \text{CH}_3\text{CH}_2\text{CHCHCH}_3
\]

hydrogen migrates with its pair of electrons from C-2 to C-1 as water is lost

\[
\text{CH}_3\text{CH}_2\text{CH}\equiv\text{CH}_2
\]

carbocation formed by hydride shift is secondary
Rearrangement involves hydride shift

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \xrightarrow{+\text{H}} \text{CH}_3\text{CH}_2\text{CHCHCH}_3 \]

\[ \downarrow \]

\[ \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \quad \text{CH}_3\text{CH}=\text{CHCHCH}_3 \]

mixture of \textit{cis} and \textit{trans}-2-butene
Hydride Shift

\[ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CHO}: \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CHCH}_2^+ \]
Carbocations can...

- react with nucleophiles
- lose a proton from the $\beta$-carbon to form an alkene
- rearrange (less stable to more stable)