6.10
Acid-Catalyzed Hydration of Alkenes
**Acid-Catalyzed Hydration of Alkenes**

\[ C═C \quad + \quad H―OH \quad \rightarrow \quad H―C―C―OH \]

reaction is acid catalyzed; typical hydration medium is 50% $H_2SO_4$-50% $H_2O$
Follows Markovnikov's Rule

\[\text{H}_3\text{C} \quad \text{C} = \text{C} \quad \text{H} \quad \text{CH}_3 \quad \xrightarrow{50\% \text{ H}_2\text{SO}_4} \quad \xrightarrow{50\% \text{ H}_2\text{O}} \quad \text{CH}_3 \quad \text{C} \quad \text{CH}_3\text{CH}_2\text{CH}_3 \quad \text{CH}_3 \quad \text{OH} \quad (90\%)\]
Follows Markovnikov's Rule

\[
\text{CH}_2 = \quad 50\% \text{ H}_2\text{SO}_4 \\ 50\% \text{ H}_2\text{O} \quad \rightarrow \\
\text{CH}_3 \\ \text{OH} \\
\] (80%)
involves a carbocation intermediate

is the reverse of acid-catalyzed dehydration of alcohols to alkenes

\[ \text{CH}_3\text{C} \equiv \text{CH}_2 + \text{H}_2\text{O} \xrightleftharpoons{\text{H}^+} \text{CH}_3\text{C} \equiv \text{CH}_3 \text{CH}_3 \text{C} \equiv \text{CH}_3 \]
Step (1) Protonation of double bond

Mechanism
Step (2) Capture of carbocation by water

Mechanism
Step (3) Deprotonation of oxonium ion

Mechanism

\[
\begin{align*}
\text{CH}_3\text{C} & \rightarrow \text{O}^+ : + \quad \text{O}^+ : \\
\text{CH}_3\text{H} & \rightarrow \quad \text{H} \\
\text{fast} & \\
\text{CH}_3\text{C} & \rightarrow \text{O}^- : + \quad \text{H} + \quad \text{O}^+ : \\
\text{CH}_3\text{H} & \rightarrow \quad \text{H} 
\end{align*}
\]
The more stable the carbocation, the faster it is formed, and the faster the reaction rate.
In an equilibrium process, the same intermediates and transition states are encountered in the forward direction and the reverse, but in the opposite order.
6.11 Hydroboration-Oxidation of Alkenes
Suppose you wanted to prepare 1-decanol from 1-decene?
Suppose you wanted to prepare 1-decanol from 1-decene?

Needed: a method for hydration of alkenes with a regioselectivity opposite to Markovnikov's rule.
Two-step reaction sequence called hydroboration-oxidation converts alkenes to alcohols with a regiochemistry opposite to Markovnikov's rule.

1. hydroboration
2. oxidation

Synthesis
Hydroboration can be viewed as the addition of borane (BH₃) to the double bond. But BH₃ is not the reagent actually used.
Hydroboration reagents:

Diborane ($\text{B}_2\text{H}_6$) normally used in an ether-like solvent called "diglyme".
Hydroboration reagents:

\[ \text{Hydroboration Step} \]

\[ \text{C} = \text{C} + \text{H-BH}_2 \rightarrow \text{H-C-C-BH}_2 \]

Borane-tetrahydrofuran complex (H\(_3\)B-THF)
Organoborane formed in the hydroboration step is oxidized with hydrogen peroxide.
Example

1. $\text{B}_2\text{H}_6$, diglyme
2. $\text{H}_2\text{O}_2$, $\text{HO}^-$

(93%)
Example

1. H₃B-THF
2. H₂O₂, HO⁻

(98%)
Features of Hydroboration-Oxidation

- hydration of alkenes
- regioselectivity opposite to Markovnikov's rule
- no rearrangement
- stereospecific syn addition
Example

1. $\text{B}_2\text{H}_6$, diglyme
2. $\text{H}_2\text{O}_2$, $\text{HO}^-$

(82%)
6.12
Stereochemistry of Hydroboration-Oxidation
Features of Hydroboration-Oxidation

- hydration of alkenes
- regioselectivity opposite to Markovnikov's rule
- no rearrangement
- stereospecific syn addition
H and OH become attached to same face of double bond

only product is \textit{trans}-2-methylcyclopentanol (86\%) yield
6.13
Mechanism of Hydroboration-Oxidation
1-Methylcyclopentene + BH$_3$

- **syn addition of H and B to double bond**
- **B adds to less substituted carbon**
Organoborane intermediate
Add hydrogen peroxide

OH replaces B on same side
trans-2-Methylcyclopentanol