Reactions to know

Substitution of Alcohols

\[ R-OH + HX \rightarrow R-X + HOH \]

**$S_N1$ Substitution**

\[ OH + HCl \rightarrow OH^+ + Cl^- \]

3° carbocation best
2° carbocation ok

1° will not form carbocation

**$S_N2$ Substitution**

\[ OH + HCl \rightarrow OH^+ + Cl^- \]

\[ R-OH + SOCl_2 \rightarrow R-Cl + SO_2 + HCl \]

$S_N2$ Substitution - will work with 1° and 2° alcohols, not 3° alcohols

\[ R-OH + PBr_3 \rightarrow R-Br + H_3PO_3 \]
Free Radical Halogenation

\[
\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{light or heat}} \text{CH}_3\text{Cl}
\]

Initiation

\[
\text{Cl} - \text{Cl} \rightarrow \text{Cl} \cdot + \text{Cl} \cdot
\]

Propagation

\[
\text{Cl} \cdot + \text{H-C-H} \rightarrow \text{Cl-H} + \text{C-H}
\]

\[
\text{H-C} \cdot + \text{Cl-Cl} \rightarrow \text{H-C-Cl} + \text{Cl} \cdot
\]

Termination

\[
\text{H-C} \cdot + \text{Cl} \cdot \rightarrow \text{H-C-Cl}
\]

Elimination of Alcohols

\[
\text{H-OH} \xrightarrow{\text{H}^+} \text{R}_2\text{C=CR}_2 + \text{HOH}
\]

E1 Elimination - proceeds through carbocation, 2° and 3° alcohols

E2 Elimination - 1° alcohols, requires anti-periplanar arrangement
Elimination of Halides

\[ R_2C\text{CR}_2H + RO^- \rightarrow R_2C\text{CR}_2 + HOR \]

**E2 Elimination** - 1°, 2° or 3° halides with strong base requires anti-periplanar arrangement

\[ \text{Cl}^- \rightarrow \text{KCl} + \text{HOCH}_3 \]

**E1 elimination** can occur under neutral conditions only with 3° halides

Electrophilic Addition to Alkenes

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<th>B(^-)</th>
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<td>( \text{H}_2\text{O} ) (H(^+) cat)</td>
<td>( \text{H}^+ )</td>
<td>( \text{HO}^- )</td>
<td>Markovnikov</td>
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<tr>
<td>( \text{BH}_3 ) then ( \text{H}_2\text{O}_2/\text{OH}^- )</td>
<td>( \text{OH}^+ )</td>
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<td>( \text{HX} )</td>
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<td>bridged, anti addn, Markovnikov</td>
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\[ \text{Most stable intermediate} \]
\[ \text{Lower energy pathway} \]
\[ \text{Markovnikov Addition} \]
Most stable intermediate
Lower energy pathway
Markovnikov Addition

Bromide can only come from the bottom and kick off the bromine on the top. This reaction forms the trans product selectively.

Markovnikov Addition even if there is no full carbocation

Hydroboration and Hydrogenation

1) BH₃

anti-Markovnikov hydration
syn addition

2) H₂O₂ / NaOH

syn addition of H₂