E2: Bi-molecular Elimination Reaction
aka β-elimination
aka 1,2-elimination
Rate = \[
[\text{alkyl halide}] \cdot [\text{Base}]
\]
Mechanism:
\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH}_2 \quad \rightarrow \quad \text{CH}_2 = \text{C} - \text{CH}_3 + \text{H}_2\text{O} + \text{Br}^- \\
\end{align*}
\]
1. **Concerted Rxn**
Regioselectivity:
\[
\begin{align*}
\text{H}_3\text{C} \quad \rightarrow \quad \text{Ig} & \quad \text{EI} > \text{RBr} > \text{RCI} > \text{RF} \quad \text{* Weaker the Base the Better the Ig.}\n\text{CH}_2 \quad \rightarrow \quad \text{CH}_2 = \text{C} - \text{CH}_3 \quad \text{Major} \quad \text{→ Alkene Like TS}
\end{align*}
\]
Zaitsev's Rule
More substituted alkene product is obtained when \( \text{H}^+ \) ( proton) is removed from \( \text{C} \) bounded to fewest \( \text{H} \).

Exceptions to Zaitsev:
* Conjugated dienes and delocalized electrons!!

\[
\begin{align*}
\text{CH}_2 &= \text{CH} - \text{CH}_2 - \text{C} - \text{CH} - \text{CH}_3 \\
\end{align*}
\]

* Bulky Bases

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

F as the leaving group....
\[
0^\circ > 10^\circ > 20^\circ > 30^\circ \quad \text{Carbocation TS}
\]

EI:
\[
\text{Unimolecular Elimination Rxn}
\]
Rate = \[
[\text{alkyl halide}]
\]
Depends on:
- ease of C\textsuperscript{+} formation
  \(2^\circ > 1^\circ > \text{aryl} > 1^\circ \text{ vinyl} > 2^\circ > 1^\circ \)
- leaving group
- Watch out for C\textsuperscript{+} rearrangements.

Mechanism:
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 - C - CH_3 + H_2O & \rightarrow \text{CH}_3 - C - CH_3 \\
& \rightarrow \text{CH}_3 - C - CH_3 \\
& \quad \text{CH}_3 \\
\end{align*}
\]

- 2 step Rxn
  - 1st: Rate determining. Heterolytic break of alkyl halide \(\rightarrow\) form C\textsuperscript{+}
  - 2nd: Base rules Half B C

More substituted alkyl Halide formed.

More 

11.4 Competition Between E2 and E1

<table>
<thead>
<tr>
<th>3°</th>
<th>E1</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2°</td>
<td>E1</td>
<td>E2</td>
</tr>
<tr>
<td>1°</td>
<td>No primary form</td>
<td>E2</td>
</tr>
</tbody>
</table>

Protic polar sol.
- abprotic polar

Low concentration
- high concentration

11.5 Stereochemistry of Elimination Rxn

**E2**

Elimination
<table>
<thead>
<tr>
<th>Syn - same side</th>
<th>Anti - opposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>- eclipsed</td>
<td>Staggered - faster, less stereocent</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Front side attack</th>
<th>Back side attack</th>
</tr>
</thead>
<tbody>
<tr>
<td>e - move to backside of C bonded to X</td>
<td>best overlap of interacting orbitals</td>
</tr>
<tr>
<td>- no repulsion of electron density</td>
<td>Base and X lig</td>
</tr>
</tbody>
</table>

\[
\text{H}_3\text{C} - \text{CH} - \text{CH}_2\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2 = \text{CH} - \text{CH}_2\text{CH}_3 + \text{CH}_3\text{C} = \text{C}^\equiv\text{H} \quad \text{E}\text{yr} \quad \text{X}^+ \quad \text{Z} \\
\text{CH}_3 < \text{CH} = \text{CH} - \text{CH}_3 < \text{CH}_3< \text{C} = \text{C}^\equiv\text{H} \quad \text{X}^+ \quad \text{Z}
\]

- Regioselective: more of 1 constitutional isomer
- Stereoselective: more of 1 stereoisomer.

- If 2 H are attached to the β Carbon will get a mixture of E and Z.
- Major product will be bulky groups opposite single bonds.

- If 1 H is attached to the β Carbon will get one conformer E or Z... depends on stereochemical reactivity.
E1:

C+ $\text{sp}^2 \Rightarrow \text{flat (planar)}$ both syn/anti $\Rightarrow \text{E or Z}$

Major Product $+$ bulky on opposite sides.

11.6 Cyclic Compounds

E2

Anti Elimination:
X and H must be trans to each other

6 Membered rings:
X and H must be axial

Rate: faster if X $+$ H in axial but most stable chair

H not always removed from $\beta$ C bond-to-quest $+$ must be in axial position.

E1 - Because C$=$O formed - mechanism in 2 steps.

Follows Zaitsev's - doesn't need to be in axial. * Watch for C$=$S shifts.

11.7 Kinetic Isotope Effect

Deuterium Kinetic Isotope Effect $= \frac{k_{\text{H}}}{k_{\text{D}}} = \frac{\text{rate constant C-H}}{\text{rate constant C-D}}$

Proton $\frac{1}{P}$ in rate
determines step of E2

In stronger bond $\Rightarrow$ harder to break.

Back
11.8 Competition Between Substitution and Elimination

<table>
<thead>
<tr>
<th>SN2/E2</th>
<th>SN1/E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>good strong nuc/base</td>
<td>weak nuc/base</td>
</tr>
<tr>
<td>High conc.</td>
<td>low concentration</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>SN2</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°</td>
<td>Observed</td>
<td>wins</td>
</tr>
<tr>
<td>Bulky Alkyl halide or Bulky Nuc/Base</td>
<td>çu</td>
<td>win</td>
</tr>
<tr>
<td>Bulk Alkyl halide or Bulky Nuc/Base</td>
<td></td>
<td>can't get into due backside attack</td>
</tr>
<tr>
<td>2°</td>
<td>both → stronger base</td>
<td>2°</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{C}^\text{II}$ vs $\text{CH}_3\text{C}^\text{II}$ at $180^\circ\text{C}$ back</td>
<td>$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{C}^-$ at 15.9</td>
</tr>
<tr>
<td>3°</td>
<td>X</td>
<td>wins</td>
</tr>
</tbody>
</table>

E1 vs SN1

No 1°

2°/3° => Both
11.9 Substitution And Elimination Reaction in Synthesis

Williamson Ether synthesis \[ R'-Br + RO^- \rightarrow R-O-R \]

SN2 Rxn: need alkyl halid alkoide ion \[ \text{from alcohol } ROH+Na^+ \rightarrow RO^- \]

\[ CH_3O^- + CH_3CH_2Br \rightarrow CH_3O-CH_2CH_3 \]

\[ CH_3CH_2Br + CH_3C=O \rightarrow CH_3CH_2O-CH_2CH_3 \]

\[ \text{Cyclic structure} \]

11. 10 Consecutive E2

\[ CH_3-CH CH=CH_2 \overset{\text{OH}}{\rightarrow} CH_3CH=CH=CH=CH \text{ conjugated diene} \]

\[ CH_3CH=CH\overset{\text{OH}}{\rightarrow} CH_3CH=CH=CH \text{ alkene} \]

11.11 Intermolecular vs Intramolecular Reaction

\[ \text{B, 6 membered ring} \]

\[ \text{Cyclic structure} \]