. . . with cyanide anion affords a . . . .

\[
\text{K}^+ \cdot \text{CN}^- + \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br} \rightarrow \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CN} + \text{KBr}
\]

. . . with azide anion affords alkyl azides

\[
\text{Na}^- \cdot \text{Br}^- + \text{Na}^+ \cdot \text{N}_3^- \rightarrow \text{N}_3 + \text{NaBr}
\]

. . . with an thiols or thiolate ions affords a . . . .

\[
\text{R}^- \cdot \text{S}^- + \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl} \rightarrow \text{CH}_2-\text{S}^- + \text{S}^- \cdot \text{R}^- + \text{KCl}
\]

Chapter 8: Alkenes: Structure and Preparation via Elimination Reactions

8.1 Introduction to Elimination Reactions – Nucleophiles are Lewis bases. They can also promote elimination reactions of alkyl halides or sulfonates rather than substitution.
8.2 Alkenes in Nature and in Industry (please read)
8.3 Nomenclature of Alkenes (please read and understand)

Prefix-Parent-Suffix

Suffix for alkenes: -ene
Many of the same rules for alkanes apply to alkenes

1. Name the parent hydrocarbon by locating the longest carbon chain that contains the double bond and name it according to the number of carbons with the suffix -ene.

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

Parent = pentene

not hexene (does not contain double bond)

2a. Number the carbons of the parent chain so the double bond carbons have the lowest possible numbers. Indicate the double bond by the number of the first alkene carbon.

\[
\begin{align*}
&\text{H}_2\text{C} = \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \\
&\quad \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \quad \text{6} \\
\end{align*}
\]

2-hexene

2b. If the double bond is equidistant from each end, number so the first substituent has the lowest number.

\[
\begin{align*}
&\text{H}_2\text{C} = \text{CH}_3 \\
&\quad \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \quad \text{6} \\
\end{align*}
\]

2-methyl-3-hexene

3. Write out the full name, numbering the substituents according to their position in the chain and list them in alphabetical order.

4. If more than one double bond is present, indicate their position by using the number of the first carbon of each double bond and use the suffix -diene (for 2 double bonds), -triene (for 3 double bonds), -tetraene (for 4 double bonds), etc.

\[
\begin{align*}
&\text{H}_2\text{C} = \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}_2 \\
&\quad \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\
&\text{1,4-pentadiene} \\
&\text{H}_2\text{C} = \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}_3 \\
&\quad \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\
&\text{1,3-pentadiene} \\
\end{align*}
\]
5a. Cycloalkenes are named in a similar way. Number the cycloalkene so the double bond carbons get numbers 1 and 2, and the first substituent is the lowest possible number.

5b. If there is a substituent on one of the double bond carbons, it gets number 1.

Alkenes as substituents:

- ethenyl or vinyl (vinylcyclohexane)
- 2-propenyl or allyl (allylcyclohexane)
- methylene (methylene cyclohexane)
- ethylene (ethylene cyclohexane)

Non-IUPAC (non-systematic) Alkenes

- ethylene (ethene)
- propylene (propene)
- isobutylene (2-methylpropene)
- isoprene (2-methyl-1,3-butadiene)

Double bonds are classified according to the number of substituents attached to C=C

- monosubstituted
- disubstituted
- trisubstituted
- tetrasubstituted

8.4 Stereoisomerism in Alkenes

Using cis and trans designations

C₄H₈: four isomeric butenes

- 1-butene
- 2-methylpropene
- cis-2-butene
- trans-2-butene
recall cycloalkane stereoisomers: substituents are either on the same side of the ring (cis) or on opposite sides (trans).

Substituents on an alkene can also be either cis (on the same side of the double bond) or trans (on opposite sides of the double bond). Cis/trans isomers of alkenes are stereoisomers, they have the same connectivity but different three-dimensional arrangements of groups. Cis/trans alkene stereoisomers does not normally interconvert as this would require breaking the $\pi$-bond.

Using the $E$ and $Z$ designations – cis and trans can be ambiguous for tri- and tetra-substituted alkenes

\[
\begin{align*}
&\text{trans-1,2-dimethylcyclopropane} & \text{cis-1,2-dimethylcyclopropane} & \text{trans-2-butene} & \text{cis-2-butene} \\
\end{align*}
\]

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

\[\text{E/Z System: } \text{For each carbon of the double bond, the groups are assign a priority (high or low) according to the Cahn-Ingold-Prelog system. Thus, the high priority groups can be on the same side or on opposite side of the double bond.}

If the high priority groups are on opposite sides then the double bond is designated as E (entgegen- across)

If the high priority groups are on the same side then the double bond is designated as Z (zusammen- together)
8.5 Alkene Stability – In general, *cis*-disubstituted alkenes are less stable than *trans*-disubstituted alkenes.

\[
\begin{align*}
\text{cis-2-butene} & \quad \Delta H^\circ_{\text{combustion}}: -2686 \text{ KJ/mol} \\
\text{trans-2-butene} & \quad -2682 \text{ KJ/mol}
\end{align*}
\]

*trans* isomer is ~4 KJ/mol more stable than the *cis*.

* cis-alkenes are destabilized by steric strain

More highly substituted double bonds are generally more stable than less highly substituted ones.

<table>
<thead>
<tr>
<th>tetrasubstituted</th>
<th>trisubstituted</th>
<th>disubstituted</th>
<th>monosubstituted</th>
</tr>
</thead>
</table>
| \[\begin{array}{c}
R \quad R \\
R \quad R \\
R \quad R
\end{array}\] | \[\begin{array}{c}
R \quad H \\
R \quad H \\
R \quad H
\end{array}\] | \[\begin{array}{c}
R \quad R \\
R \quad H \\
H \quad R
\end{array}\] | \[\begin{array}{c}
R \quad H \\
H \quad R \\
H \quad H
\end{array}\] |

Hyperconjugation: stabilizing effect due to “bonding” interactions between a filled C-H orbital and a vacant neighboring orbital.

Increasing the substitution of an alkene increases the number of possible hyperconjugation interactions.
8.6 Possible Mechanisms for Elimination

\[
\text{Br} - \overset{\text{H}}{\text{C}} - \text{C}^{-} \quad \xrightarrow{} \quad \text{C} = \overset{\text{C}}{\text{C}} \quad + \quad \text{H} - \text{Br}
\]

8.7 The E2 Mechanism

\[
\text{rate} = k[\text{alkyl halide}][\text{base}]
\]

2nd-order (bimolecular) kinetics implies that both base and alkyl halide are involved in the rate-determining step.

Mechanism is a concerted (one-step) bimolecular process with a single transition state: C—H bond breaks, π-bond forms, and C—X bond breaks at the same time.
Alkyl halide substrate: 1°, 2° and 3° alkyl halides are all potential substrates for the E2 reaction.

The reactivity of an alkyl halides toward the E2 reaction is more reflective of the stability of the alkene formed.

Regioselectivity of E2 Reactions – In some cases, E2 reactions may potentially give isomeric alkenes

*Zaitsev Rule* – When more than one alkene product is possible from an elimination reaction, the most highly substituted (most stable) alkene is usually the major product.

*Hofmann* Elimination Product – The less substituted alkene product from an elimination reaction.
Stereoselectivity of E2 Reactions – the *trans*-alkene product will usually favored.

Geometric requirements for E2 reactions

**Syn planar:**
the H and X are eclipsed
\[
\text{dihedral angle} = 0 ^\circ
\]

**Anti periplanar:**
the H and X are anti staggered
\[
\text{dihedral angle} = 180 ^\circ
\]

Generally, the anti periplanar (coplanar) geometry is energetically preferred (staggered conformation vs eclipsed)

In the periplanar conformation, the orbitals are pre-aligned for \( \pi \)-bond formation.
8.9 The $E_1$ Mechanism

Kinetics:
rate $= k \ [R-X]$

1st-order (unimolecular) kinetics implies a two step reaction with the first step being rate-determining.
Reactivity of the substrate toward the E₁ elimination reaction correlates with the stability of the intermediate carbocation.

<table>
<thead>
<tr>
<th>Least Reactive</th>
<th>Most Reactive</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{C}^-\text{C}^-\text{X}$</td>
<td>$\text{H}_3\text{C}^-\text{C}^-\text{X}$</td>
</tr>
<tr>
<td>$\text{H}^+\text{C}^-\text{C}^-\text{X}$</td>
<td>$\text{H}_3\text{C}^-\text{C}^-\text{X}$</td>
</tr>
<tr>
<td>1° halide</td>
<td>3° halide</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Least Stable</th>
<th>Most Stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{C}^-\text{C}^-\text{H}$</td>
<td>$\text{H}_3\text{C}^-\text{C}^-\text{CH}_3$</td>
</tr>
<tr>
<td>$\text{H}^+\text{C}^-\text{C}^-\text{H}$</td>
<td>$\text{H}_3\text{C}^-\text{C}^-\text{CH}_3$</td>
</tr>
<tr>
<td>1°</td>
<td>3°</td>
</tr>
</tbody>
</table>

Regioselectivity of the E₁ elimination – E₁ elimination usually follows Zaitsev’s rule.

\[ \text{Br} + \text{H}_2\text{CH}_2\text{COH, } \Delta \rightarrow (75\%) + (25\%) \]

Stereoselectivity of the E₁ elimination – the trans alkene is generally preferred
8.10 Drawing the Complete Mechanism of an E₁ Process.
Dehydration of an alcohol

8.11 Drawing a Complete Mechanism of an E₂ Processes
8.12 Substitution vs. Elimination: Identifying the Reagents

Nucleophilic substitution (S_N1 or S_N2) and elimination (E1 or E2) are competing processes.

\[
\begin{align*}
\text{E}_1 & \quad \text{H}_3\text{CO}^- & \quad \text{H}_2\text{COH} \\
\text{S}_\text{N}1 & \quad \text{CH}_3 & \quad \text{H}_3\text{COOH}
\end{align*}
\]

Nucleophilicity vs Basicity:

- Methanol or methoxide act as a nucleophile = substitution reaction
- Methanol or methoxide act as a base = elimination reaction

- Nucleophiles are Lewis bases – pKa of the corresponding acid
- Neutral vs charged (anionic) nucleophiles/bases
- Polarizability (increases down the periodic chart)

8.13 Substitution vs Elimination Identifying the Mechanism(s)

- Reagents that only act as nucleophiles (X^-, RS^-, RSH, N_3^-, NC^-)
- Reagents that only act as bases (H^-, R_2N^-)
- Reagents that are strong nucleophiles and strong bases (RO^-)
- Reagents that are weak nucleophiles and weak bases (ROH)
8.14 Substitution vs. Elimination: Predicting the Products

S\textsubscript{N}2 – nucleophile replaces the LG with inversion (backside attack) of stereochemistry (stereospecific).

S\textsubscript{N}1 – nucleophile replaces the LG, unless the intermediate carbocation undergoes rearrangement. The S\textsubscript{N}1 reaction is not stereospecific.

E2 – The more substituted alkene is usually favored (Zaitsev rule), unless bulky bases (e.g., t-butoxide) are used. The alkene geometry (E vs Z) is determined by the anti-periplanar conformation. In the case of a disubstituted alkene product, the trans geometry is favored.

E1 – The more thermodynamically favored alkene is favored. This will be the more substituted alkene product (Zaitsev rule), with the most sterically demanding groups trans.

Chapter 9. Addition Reactions of Alkenes
9.1 Introduction to Addition Reactions

Substitution Reactions: two reactants exchange parts to give new products (Chapter 7)

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H-Br} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{Br} + \text{H-OH}
\]

Elimination Reaction: a single reactant is split into two (or more) products. Opposite of an addition reaction (Chapter 8)

\[
\text{BrCH} = \text{CH}_2 + \text{NaOH} \quad \rightarrow \quad \text{C} = \text{C} + \text{H-OH} + \text{Na-Br}
\]

Addition Reaction: two reactants add to form a product with no (or few) atoms are left over (Chapter 9)

\[
\text{C} = \text{C} + \text{H-Br} \quad \rightarrow \quad \text{BrCH} = \text{CH}_2
\]