Systematic nomenclature of alkenes:
The C=C bond is a priority group

- sulfonic acids > carboxylic acids > esters > amides > nitriles > aldehydes > ketones > alcohols > thiols > amines > \textit{alkenes (benzenes) > alkynes}

When the C=C bond is outranked by another priority group

- If the C=C bond is part of the parent, immediately before the priority group marker use \textit{...en(e)...} to indicate the presence of the C=C and a position number to indicate its location

- If the C=C bond is not part of the parent, the chain having the C=C is treated as a substituent ending in \textit{...enyl}

Write the systematic name

```
\begin{center}
\includegraphics[width=0.3\textwidth]{santolinatriene.png}
\end{center}
```

“santolinatriene” constituent of Artemesia source of absinthe and wormwood

Write the systematic name

```
\begin{center}
\includegraphics[width=0.3\textwidth]{pheromone.png}
\end{center}
```

pheromone of California red scale \textit{Aonidiella aurantii}
Write the systematic name

H₃CO
\[\begin{array}{c}
\text{HO}
\end{array}\]
“eugenol”

Topical anesthetic

Major constituent of clove oil

11-1
Alkenes can exist as configurational stereoisomers

Stereoisomers are possible when neither alkene carbon has two identical substituents

\[A \neq B \quad \{\begin{array}{c}
A
\quad B
\quad Y
\quad Z
\end{array}\} \quad Y \neq Z\]

11-2
C=C bonds don’t rotate freely
\[(\Delta H^\ddagger = 65 \text{ kcal/mol, } k_{25 \degree C} = 10^{-35} \text{ s}^{-1})\]

11-1
Alkene stereoisomers are specified by the cis,trans system or…

Use cis or trans when both alkene carbons have a substituent in common

\[
\text{trans-2-pentene}\]

\[
\text{cis-2,3-dichloro-2-pentene}\]

11-1
… by the E,Z system if cis or trans is not appropriate

\[
\begin{array}{c}
\text{F} \\
\text{H₃C} \\
\text{Cl}
\end{array}\]

\[\text{(E)-1-chloro-2-fluoropropene}\]

11-1
Divide C=C bond perpendicular to bond axis and rank groups by CIP system

\[
\begin{array}{c}
1 \\
\text{F} \\
\text{H₃C} \\
2 \\
\text{Cl} \\
1
\end{array}\]
Assign E or Z based on the location of the higher ranking groups

**E**: cross C=C bond to connect higher ranking groups

(E)-1-chloro-2-fluoropropene

**Z**: don’t cross C=C bond to connect higher ranking groups

(Z)-1-chloro-2-fluoropropene

Write the systematic name

antifungal from alga Plocamium cartilagineum

Alkene carbons and the atoms directly attached to them must lie in a plane

Double bonds at small-ring “bridgeheads” can’t attain planarity

These alkenes have never been isolated: $E_{\text{strain}} \sim 38$ kcal/mol

Alkyl substituents stabilize C=C bonds

<table>
<thead>
<tr>
<th>Substitution</th>
<th>$\Delta H^\circ_f$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monosubstituted</td>
<td>$-10.5$</td>
</tr>
<tr>
<td>Disubstituted</td>
<td>$-12.3$</td>
</tr>
<tr>
<td>Trisubstituted</td>
<td>$-14.0$</td>
</tr>
<tr>
<td>Tetrasubstituted</td>
<td>$-14.2$</td>
</tr>
</tbody>
</table>

Trans alkenes are frequently more stable than their cis stereoisomers, but...

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ_f$ (kcal/ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis</td>
<td>$-1.6$</td>
</tr>
<tr>
<td>trans</td>
<td>$-2.7$</td>
</tr>
</tbody>
</table>
small-ring cis cycloalkenes are more stable than their trans stereoisomers

\[
\Delta H^\circ (\text{cis} \rightarrow \text{trans}) \quad \text{[kcal/mol]}
\]

- calculated; trans never observed
- trans never isolated

Alkenes are prepared by β-elimination (E1 or E2) of alkyl halides

\[
\begin{align*}
\text{Br} & \quad \beta \\
\alpha & \quad \beta \\
\text{NaOEt} & \\
51\% & + \\
18\% & + \\
\text{disubstituted} & + \\
\text{monosubstituted} & \\
\end{align*}
\]

Base removes the β-H anti to the leaving group in the E2† reaction.

Epoxidation of alkenes by peroxo acids yields oxacyclopropanes (epoxides)

Epoxide usually forms on the least hindered side.

Common peroxo acids

- meta-chloro-peroxybenzoic acid (mCPBA)
- magnesium monoperoxyphthalate (MMPP)

Epoxidation: Mechanism
Concerted mechanism results in retention of the geometry about the C=C bond

\[
\text{Et} \quad \text{Et} \\
\text{H} \\
\text{CH}_2\text{CO}_3\text{H} \quad \text{CH}_2\text{Cl}_2 \\
\text{Et} \quad \text{H}
\]

ethyl groups remain trans

Epoxides are ubiquitous in nature

![Periplanone-B](image)

Aromatic hydrocarbons are detoxified by conversion to arene oxides

\[
\text{benzo[a]pyrene} \quad \text{an arene oxide}
\]

Nucleophiles open epoxides regioselectively

- Nucs attack more substituted epoxide carbon under acidic conditions
- basic Nucs attack less substituted epoxide carbon

Nucleophiles open epoxides stereospecifically: Back-side attack

\[
\text{basic nucleophile (1) MeONa} \\
\text{(2) } H^+ \\
\text{acidic conditions MeOH} \\
\text{H}^+
\]

Predict the product; show stereochemistry

\[
\begin{align*}
\text{H} & \quad \text{mCPBA} \\
\text{Et} & \quad \text{H} \\
\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]
Basic nucleophiles react with epoxides via $S_N2$

Nucleophiles open epoxides in acid via a hybrid mechanism

Transition state has partial carbocationic character

Predict the product; show stereochemistry

Electrophilic addition: E-Nu type molecules add across the C=C bond
E-Nu type molecules

Electrophilic and nucleophilic ends are identified by electronegativity difference

<table>
<thead>
<tr>
<th>E-Nu</th>
<th>E-Nu</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-X (X = Cl, Br, I)</td>
<td>X-N₃ (X = Br, I)</td>
</tr>
<tr>
<td>X-Cl (X = Br, I)</td>
<td>I-Br</td>
</tr>
<tr>
<td>PhSe-X (X = Cl, Br)</td>
<td>I-NCO</td>
</tr>
</tbody>
</table>

E-Nu molecule equivalents

"E-Nu" Method of generation

- "H-OH" H₃O⁺
  - (1) BH₃
  - (2) H₂O₂, NaOH(aq)
- "X-OH" X₂, H₂O (X = Cl, Br)
- "X-OR" X₂, ROH (X = Cl, Br)
Reaction Coordinate

X– rapidly traps the carbocation to yield the Markovnikov product

Less stable carbocation intermediates are formed less rapidly

Predict the major product

Stereochemistry of hydrohalogenation depends on conditions

Rearrangements can occur due to intermediacy of a carbocation

Write a detailed mechanism
Halogenation of alkenes with $X_2$ yields a trans-1,2-dihalide

Anti stereospecificity
Markovnikov regioselectivity

Mechanism of halogenation

Cyclic halonium cations are opened by nucleophiles in a backside manner and with Markovnikov regioselectivity

Predict the major product; show stereochemistry

Syn addition increases if an “open” cation can compete with the “bridged” cation
Nucleophiles (H₂O, ROH) present in the reaction mixture can react with halonium

Anti stereospecificity
Markovnikov regioselectivity

Mechanism of halohydrin formation: Why can water compete with chloride?

Cl₂
H₂O
“Cl−OH”

73%

a halohydrin

Predict the products;
Show stereochemistry

Predict the product

Acid-catalyzed hydration: Addition of H₂O

Industrially important
Markovnikov regioselectivity; reversible

50% H₂SO₄(aq)

50%
**Acid-catalyzed hydration: Mechanism**

![Mechanism diagram](image)

**Rearrangements and polymerization limit the use of acid-catalyzed hydration**

Write a mechanism

![Mechanism diagram](image)

**A better way of making alcohols from alkenes: Use epoxides**

![Reaction pathway](image)

**Propose a synthesis**

![Synthesis reaction](image)

**Hydroboration-oxidation: Counter-Markovnikov alcohols from alkenes**

Syn stereospecificity

![Reaction pathway](image)
Hydroboration–oxidation:
Mechanism of hydroboration step

H adds to more substituted carbon.—Why?

Hydroboration–oxidation:
Mechanism of oxidation step

\[ \text{HOOH} + \text{OH}^- \rightarrow \text{HOO}^- + \text{H}_2\text{O} \]

\[ K_{eq} = 10^{3.7} = 5000 \]

Hydroboration–oxidation:
Mechanism of oxidation step

1,2 alkyl shift from boron to oxygen

Hydroboration–oxidation:
Mechanism of oxidation step

B undergoes attack and rearrangement twice more

Hydroboration–oxidation:
Mechanism of oxidation step

Alkylborane continues to react until all Hs are transferred
BH₃ prefers the less hindered face of the alkene

\[ \text{(1) BH₃, ether} \quad \rightarrow \quad \text{78\%} \]
\[ \text{(2) H₂O₂, NaOH(aq)} \quad \rightarrow \quad \text{22\%} \]

Osmium tetroxide (OsO₄) converts alkenes to cis-1,2-diols

Syn stereospecificity

\[ \text{(1) OsO₄ (0.001 eq.), ether} \quad \rightarrow \quad \text{85 °C, 5 h} \]
\[ \text{(2) H₂O₂(aq)*} \quad \rightarrow \quad \text{OH} \quad \text{OH} \]

* Other oxidizing agents: R₂NO, H₂S, NaHSO₃, etc.

Osmylation: Mechanism

\[ \text{OsO₄ \quad \rightarrow \quad 2H₂O \quad \rightarrow \quad \text{H₂O₂ \quad -2H₂O}} \]

OsO₄ prefers the less hindered face of the alkene: Predict the product

\[ \text{(1) OsO₄ \quad \rightarrow \quad \text{Me}} \]
\[ \text{(2) H₂O₂, ROOH} \quad \rightarrow \quad ? \]
Suggest a synthesis of the antitussive guaifenesin (Organidin™)

\[
\begin{align*}
\text{OMe} & \quad \text{OH} \\
\text{?} & \quad \text{OMe} \quad \text{O} \quad \text{OH} \quad \text{OH} \\
\text{guaifenesin}
\end{align*}
\]

Ozonolysis: Mechanism

\[
\text{electric discharge} \quad 3\text{O}_2 \rightarrow 2\text{O}_3 \quad \Delta H^\circ = +64 \text{ kcal}
\]

\[
\text{Ozonolysis: Mechanism}
\]

Ozonolysis: “Solvolytic” work-up

Mild reducing agents (Zn, Me₂S, SO₃²⁻) deoxygenate the ozonide to afford carbonyl compounds

\[
\begin{align*}
\text{H} & \quad \text{O} \quad \text{O} \quad \text{H} \\
\text{C(+1)} & \quad \text{C(+2)} & \quad \text{mild [H]} & \quad \text{C(+1)} & \quad \text{C(+2)}
\end{align*}
\]

Ozonolysis: Reductive work-up

NaBH₄ further reduces carbonyl compounds to alcohols

\[
\begin{align*}
\text{NaBH}_4 & \quad \text{H} \quad \text{OH} \quad \text{H} \\
\text{C(+1)} & \quad \text{C(+2)} & \quad \text{NaBH}_4 & \quad \text{C(-1)} & \quad \text{C(0)}
\end{align*}
\]
Ozonolysis: Oxidative work-up

H₂O₂ oxidizes C–H bonds in the ozonide to afford carboxylic acids

Predict the products

Rubber is a hydrocarbon polymer of repeating units; Deduce its structure

Problem

When C₁₀H₁₆ is treated with ozone followed by reductive work-up with NaBH₄, the sole organic product is cyclopentanol. What is the structure of C₁₀H₁₆?

Catalytic hydrogenation: Alkanes from alkenes

Syn stereospecificity
H₂ adds to the least hindered side of alkene
Catalytic hydrogenation: Mechanism

Propose a structure of humulene, a major flavor component of beer

Total hydrogenation of aromatics: Predict the product

Radical counter-Markovnikov hydrobromination of alkenes
Counter-Markovnikov hydrobromination: Mechanism

**Initiation**

\[ \text{RO–OR} \rightarrow \text{RO}^* + \text{OR} \]
\[ \Delta H^o \text{O–O} = 35 \text{ kcal/mol} \]

\[ \text{RO}^* + \text{H–Br} \rightarrow \text{RO–H} + \text{•Br} \]

**Propagation**

\[ \text{Br}^* + \text{H–Br} \rightarrow \text{H} + \text{Br} \]
\[ \Delta H^o = -7 \text{ kcal/mol} \]

\[ \text{Br}^* + \text{Br} + \text{H–Br} \rightarrow \text{Br} + \text{H–Br} \]
\[ \Delta H^o = -10 \text{ kcal/mol} \]

**Abstraction of an allylic hydrogen**

is a less favorable 1st propagation step

\[ \text{Br}^* + \text{H}_2\text{C} = \text{C} = \text{C} = \text{H} \rightarrow \text{•Br} + \text{H–Br} \]
\[ \Delta H^o = -2 \text{ kcal/mol} \]

\[ \text{Br}^* + \text{H}_2\text{C} = \text{C} = \text{C} = \text{H} \rightarrow \text{•Br} + \text{H–Br} \]
\[ \Delta H^o = -7 \text{ kcal/mol} \]

**Predict the product**

\[ \text{Ph} \]

12-12