Alkenes: Reactions and Synthesis

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Based on McMurry’s Organic Chemistry, 7th edition
Alkenes react with many electrophiles to give useful products by addition (often through special reagents).
Why this chapter?

To begin a systematic description of major functional groups

Begin to focus on general principles and patterns of reactivity that tie organic chemistry
7.1 Preparation of Alkenes: A Preview of Elimination Reactions

- Alkenes are commonly made by
  - Elimination of HX from alkyl halide (dehydrohalogenation)

- Uses heat and KOH

- Elimination of H-OH from an alcohol (dehydration)
  - require strong acids (sulfuric acid, 50 ºC)
Bromine and chlorine add to alkenes to give 1,2-dihalides, an industrially important process.
- $\text{F}_2$ is too reactive and $\text{I}_2$ does not add.
- $\text{Cl}_2$ reacts as $\text{Cl}^+ \text{Cl}^-$.

**Ethylene** + **Cl$_2$** $\rightarrow$ **1,2-Dichloroethane (ethylene dichloride)**

- $\text{Br}_2$ is similar.
Addition of Br₂ to Cyclopentene

- Addition is exclusively trans

Cyclopentene → trans-1,2-Dibromo-cyclopentane (sole product)

cis-1,2-Dibromo-cyclopentane (NOT formed)

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Mechanism of Bromine Addition

- $\text{Br}^+$ adds to an alkene producing a cyclic ion
- Bromonium ion, bromine shares charge with carbon
  - Gives trans addition

George Andrew Olah
(May 22, 1927 – March 8, 2017)

The Nobel Prize in Chemistry 1994
Bromonium Ion Mechanism

- Electrophilic addition of bromine to give a cation is followed by cyclization to give a bromonium ion
- This bromonium ion is a reactive electrophile and bromide ion is a good nucleophile
- Stereospecific anti addition
### 7.3 Addition of Hypohalous Acids to Alkenes: Halohydrin Formation

- This is formally the addition of HO-X to an alkene to give a 1,2-halo alcohol, called a halohydrin.
- The actual reagent is the dihalogen (Br$_2$ or Cl$_2$ in water in an organic solvent).

![Chemical reaction diagram](image-url)
Mechanism of Formation of a Bromohydrin

- $\text{Br}_2$ forms bromonium ion, then water adds.
- Orientation toward stable $\text{C}^+$ species.

3-Bromo-2-butanol (a bromohydrin)
An Alternative to Bromine

- Bromine is a difficult reagent to use for this reaction
- **N-Bromosuccinimide (NBS)** produces bromine in organic solvents and is a safer source
- Aromatic rings do not react
7.4 Addition of Water to Alkenes: Oxymercuration

- **Hydration of an alkene** is the addition of H-OH to give an alcohol.

- Acid catalysts are used in high temperature industrial processes: ethylene is converted to ethanol.

\[
\text{H}_2\text{C} = \text{C} - \text{H} + \text{H}_2\text{O} \xrightarrow{\text{H}_3\text{PO}_4\text{ catalyst}} 250 \degree\text{C} \quad \text{CH}_3\text{CH}_2\text{OH} \\
\text{Ethylene} \quad \text{Ethanol}
\]
Oxymercuration Intermediates

- For laboratory-scale hydration of an alkene
- Use mercuric acetate in THF followed by sodium borohydride
- Markovnikov orientation
  - via mercurinium ion
MECHANISM FOR REACTION OF ALKENES WITH Hg(OAc)$_2$ / H$_2$O

**Step 1:**
The $p$ electrons act as the nucleophile with the electrophilic Hg and loss of an acetate ion as a leaving group, forming the mercurinium ion.

**Step 2:**
Water functions as a nucleophile and attacks one of the mercury substituted carbons resulting in cleavage of the C-Hg bond.

**Step 3:**
The acetate ion functions as a base deprotonating the oxonium ion to give the alcohol. This completes the oxymercuration part of the reaction.

**Step 4:** (mechanism not shown)
The hydride reduces the Hg off, creating a C-H bond while breaking the C-Hg bond. This is the demercuration part of the process.
7.5 Addition of Water to Alkenes: Hydroboration

- Herbert Brown (HB) invented hydroboration (HB)
- Borane ($BH_3$) is electron deficient and is a Lewis acid
- Borane adds to an alkene to give an organoborane

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

\[
\begin{align*}
\text{BH}_3 & \quad \text{THF solvent} \quad \text{BH}_3 \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{H} \quad \text{CH}_2\text{CH}_3
\end{align*}
\]

2-Methyl-2-pentene $\rightarrow$ Organoborane intermediate $\rightarrow$ 2-Methyl-3-pentanol

The Nobel Prize in Chemistry 1979

Herbert Charles Brown
United States (1912-2004)
Addition of H-BH₂ (from BH₃-THF complex) to three alkenes gives a trialkylborane.

Oxidation with alkaline hydrogen peroxide in water produces the alcohol derived from the alkene.
Orientation in Hydration via Hydroboration

- Regiochemistry is opposite to Markovnikov orientation
  - OH is added to carbon with most H’s
- H and OH add with syn stereochemistry to the same face of the alkene (opposite of anti addition)
- STEREOSPECIFIC
Borane is a Lewis acid
Alkene is Lewis base
Transition state involves anionic development on B
The components of BH$_3$ are added across C=C
More stable carbocation is also consistent with steric preferences
MECHANISM FOR REACTION OF ALKENES WITH BH₃

Step 1:
A concerted reaction. The π electrons act as the nucleophile with the electrophilic B and the H is transferred to the C with syn stereochemistry.

Step 2:
First step repeats twice more so that all of the B-H bonds react with C=C

Step 3:
Peroxide ion reacts as the nucleophile with the electrophilic B atom.

Step 4:
Migration of C-B bond to form a C-O bond and displace hydroxide. Stereochemistry of C center is retained.

Step 5:
Attack of hydroxide as a nucleophile with the electrophilic B displacing the alkoxide.

Step 6:
An acid/base reaction to form the alcohol.
7.6 Addition of Carbenes to Alkenes

- The **carbene** functional group is “half of an alkene”
- Carbenes are electrically neutral with six electrons in the outer shell (carbocations also have six electrons)
- They add symmetrically across double bonds to form cyclopropanes

![Chemical structure diagram](http://www.chemtube3d.com/Carbenes-Reactions(AlkeneInsertionSinglet).html)
"Will you children stop talking? I must have quiet if I am to use my vast mental powers!"

"You talk like a stranger, unca Donald! Don't you feel good?"

"Of course I feel good! In fact, I feel like a super man!"

"I have changed! I have become professor Donald Duck, mightiest chemist in the universe!"

"That bump on the head was even unca Donald brain fever!"

"We'll have to humor him along till we can get a doctor!"

"Eureka! There it is—duckmite! The most ghastly explosive ever cooked up by man!"

"Hop in the car with me, little boys! I'm taking these cans of duckmite to an open place where I can test its colossal power!"
Evidence of early (1944) research on methylene. $CH_2$ by D. Duck. (As unearthed by Professors P. P. Caspar and G. S. Hammond of the California Institute of Technology.)
Formation of Dichlorocarbene

- Base removes proton from chloroform
- Stabilized carbanion remains
- Unimolecular elimination of \( \text{Cl}^- \) gives electron deficient species, dichlorocarbene
- Orbital picture for the carbene is similar to that of a carbocation
Reaction of Dichlorocarbene

- Addition of dichlorocarbene is stereospecific
- *cis* alkenes give *cis* cyclopropanes
- *trans* alkenes give *trans* cyclopropanes

\[
\begin{align*}
\text{ cis-2-Pentene: } & \quad \text{CH}_3\text{CH}_2\text{C}==\text{C}-\text{CH}_3 + \text{CHCl}_3 \xrightarrow{\text{KOH}} \text{CH}_3\text{CH}_2\text{C}==\text{C}-\text{CH}_3 + \text{KCl} \\
\text{ Cyclohexene: } & \quad \text{(structure) + CHCl}_3 \xrightarrow{\text{KOH}} \text{(structure)} + \text{KCl}
\end{align*}
\]
Simmons-Smith Reaction

- Equivalent of addition of CH₂:
- Reaction of diiodomethane with zinc-copper alloy produces a carbenoid species
- Forms cyclopropanes by cycloaddition

\[
\text{Diiodomethane} \quad + \quad \text{Zn(Cu)} \quad \rightarrow \quad \text{ICH}_2\text{ZnI} \quad \text{["CH₂"]}
\]

\[
\begin{align*}
\text{Cyclohexene} & \quad + \quad \text{CH}_2\text{I}_2 \quad \frac{\text{Zn(Cu)}}{\text{Ether}} \quad \rightarrow \quad \text{Bicyclo[4.1.0]heptane} \\
& \quad \text{(92%)}
\end{align*}
\]
7.7 Reduction of Alkenes: Hydrogenation

- Addition of H-H across C=C
- Reduction in general is addition of H₂ or its equivalent, or a loss of O from the molecule
- Requires Pt or Pd as powders on carbon and H₂
- Hydrogen is first adsorbed on catalyst
- Reaction is heterogeneous (process is not in solution)

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
\]

\[
\text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{CH}_3
\]

\[
\text{H}_2, \text{PtO}_2 \quad \text{CH}_3\text{CO}_2\text{H} \quad \text{solvent}
\]

1,2-Dimethyl-cyclohexene \textit{cis}-1,2-Dimethyl-cyclohexane (82%)
Hydrogen Addition - Selectivity

- Selective for C=C. No reaction with C=O, C=N
- Polyunsaturated liquid oils become solids
- If one side is blocked, hydrogen adds to other
- STEREOSELECTIVE
Catalytic Hydrogenation Mechanism

- Heterogeneous – reaction between phases

- Addition of H-H is syn

1. Molecular hydrogen adsorbs to the catalyst surface and dissociates into hydrogen atoms.

2. The alkene adsorbs to the catalyst surface, using its \( \pi \) bond to complex to the metal atoms.

3. A hydrogen atom is transferred from the metal to one of the alkene carbon atoms, forming a partially reduced intermediate with a C-H bond and carbon-metal \( \sigma \) bond.

4. A second hydrogen is transferred from the metal to the second carbon, giving the alkane product and regenerating the catalyst. Because both hydrogens are transferred to the same face of the alkene, the reduction has syn stereochemistry.
Oxidation of Alkenes: Epoxidation and Hydroxylation

- Oxidation is addition of O, or loss of H
- Epoxidation results in a cyclic ether with an oxygen atom
- Stereochemistry of addition is syn
- MCPBA in CH₂Cl₂ are the usual conditions

Addition of acid results in a trans-1,2-diol
- Treatment of the epoxide with aqueous acid give a trans diol
Osmium Tetroxide Catalyzed Formation of Diols

- **Hydroxylation** - converts to syn-diol
- Osmium tetroxide, then sodium bisulfate
- Via cyclic osmate di-ester
- Osmium is toxic, so catalytic amount and NMO are used

![Chemical structures and reaction diagrams](image-url)
Oxidation of Alkenes: Cleavage to Carbonyl Compounds

- **Ozone**, $O_3$, adds to alkenes to form molozonide
- Reduce molozonide to obtain ketones and/or aldehydes

**Chemical Equations**:

1. $3O_2 \xrightarrow{Electric\ discharge} 2O_3$
2. $CH_2Cl_2, -78^\circ C \xrightarrow{O_3} \xrightarrow{Zn, CH_3CO_2H/H_2O}$
3. $O_3 \xrightarrow{1.} \xrightarrow{2.\ Zn, H_3O^+} (tetrasubstituted)$
4. $CH_3(CH_2)_7CH=CH(CH_2)_7COCH_3 \xrightarrow{1.\ O_3} \xrightarrow{2.\ Zn, H_3O^+} (disubstituted)$

**Chemical Structures**:

- An alkene
- A molozonide
- An ozonide
- Isopropylidenecyclohexane
- Cyclohexanone and Acetone
- Methyl 9-octadecenoate and Nonanal and Methyl 9-oxononanoate

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Permanganate Oxidation of Alkenes

- Oxidizing reagents other than ozone also cleave alkenes

- Potassium permanganate (KMnO$_4$) can produce carboxylic acids and carbon dioxide if H’s are present on C=C

$$\text{3,7-Dimethyl-1-octene} \xrightarrow{\text{KMnO}_4 / \text{H}_3\text{O}^+} \text{2,6-Dimethylheptanoic acid (45\%)}$$
Cleavage of 1,2-diols

- Reaction of a 1,2-diol with periodic (per-iodic) acid, HIO₄, cleaves the diol into two carbonyl compounds.
- Sequence of diol formation with OsO₄ followed by diol cleavage is a good alternative to ozonolysis.
Addition of Radicals to Alkenes: Polymers

- A polymer is a very large molecule consisting of repeating units of simpler molecules, formed by polymerization.
- Alkenes react with radical catalysts to undergo radical polymerization.
- Ethylene is polymerized to polyethylene, for example.
Free Radical Polymerization: Initiation

- **Initiation** - a few radicals are generated by the reaction of a molecule that readily forms radicals from a nonradical molecule
- A bond is broken homolytically

### Polyethylene—a synthetic alkene polymer

- **Ethylene**
- **Polyethylene**

### Benzoyl peroxide

- **Heat**
- **Benzoyloxy radical**
Polymerization: Propagation

- Radical from initiation adds to alkene to generate alkene radical
- This radical adds to another alkene, and so on many times

Chain propagation ends when two radical chains combine
- Not controlled specifically but affected by reactivity and concentration

Termination
Other Polymers

- Other alkenes give other common polymers

\[ \text{Propylene} \quad \rightarrow \quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\end{array} \]

\[ \text{Polypropylene} \]

\[ \text{Styrene} \quad \rightarrow \quad \begin{array}{c}
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \text{CH} \\
\end{array} \]

\[ \text{Polystyrene} \]

- Radical stability: \(3^\circ > 2^\circ > 1^\circ\) (just like with carbocations)
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Formula</th>
<th>Trade or common name of polymer</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>$H_2C=CH_2$</td>
<td>Polyethylene</td>
<td>Packaging, bottles</td>
</tr>
<tr>
<td>Propene (propylene)</td>
<td>$H_2C=CHCH_3$</td>
<td>Polypropylene</td>
<td>Moldings, rope, carpets</td>
</tr>
<tr>
<td>Chloroethylene (vinyl chloride)</td>
<td>$H_2C=CHCl$</td>
<td>Poly(vinyl chloride) Tedlar</td>
<td>Insulation, films, pipes</td>
</tr>
<tr>
<td>Styrene</td>
<td>$H_2C=CHC_6H_5$</td>
<td>Polystyrene</td>
<td>Foam, moldings</td>
</tr>
<tr>
<td>Tetrafluoroethylene</td>
<td>$F_2C=CF_2$</td>
<td>Teflon</td>
<td>Gaskets, nonstick coatings</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>$H_2C=CHCN$</td>
<td>Orlon, Acrilan</td>
<td>Fibers</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>$H_2C=C=CO_2CH_3$</td>
<td>Plexiglas, Lucite</td>
<td>Paint, sheets, moldings</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>$H_2C=CHOCOCH_3$</td>
<td>Poly(vinyl acetate)</td>
<td>Paint, adhesives, foams</td>
</tr>
</tbody>
</table>
9.10 Stereochemistry of Reactions: Addition of H₂O to Alkenes

- Many reactions can produce new chiral centers from compounds without them
- What is the stereochemistry of the chiral product?
- What relative amounts of stereoisomers form?
- Example addition of H₂O to 1-butene

\[ \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2\text{O} \text{ Acid catalyst}} \text{CH}_3\text{CH}_2\text{C} - \text{CH} - \text{CH}_3 + \text{H} - \text{C} - \text{CH}_2\text{CH}_2\text{H} \]

1-Butene (achiral)  \( \rightarrow \)  \((S)-2\)-Butanol (50%)  +  \((R)-2\)-Butanol (50%)
Achiral Intermediate Gives Racemic Product

- Addition via carbocation
- Top and bottom are equally accessible
- Achiral reactant + Achiral reactant = Optically Inactive Product
- Optical Activity doesn’t come from nowhere

فعالیت نوری از ناکجا آباد نمی‌آید
Addition of $\text{H}_2\text{O}$ to a Chiral Alkene

- What is the stereochemical result of the addition of $\text{H}_2\text{O}$ to a chiral alkene $R$-4-methyl-1-hexene?

- Product has 2 chiral centers

- Chiral + Achiral = Optically Active

- Chiral Intermediate has different top and bottom sides

- Amounts of the two products will be different

- Product will have optical activity