Chapter 7
Alkenes and Alkynes I:
Properties and Synthesis
Elimination Reactions of Alkyl Halides
The (E)-(Z) System for Designating Alkene Diastereomers

The Cahn-Ingold-Prelog convention is used to assign the groups of highest priority on each carbon.

- If the group of highest priority on one carbon is on the same side as the group of highest priority on the other carbon the double bond is Z (zusammen).
- If the highest priority groups are on opposite sides the alkene is E (entgegen).

![Chemical structures demonstrating the (E)-(Z) system for designating alkene diastereomers.](image-url)
Relative Stabilities of Alkenes

- Generally cis alkenes are less stable than trans alkenes because of steric hindrance.

Heat of Hydrogenation

- The relative stabilities of alkenes can be measured using the exothermic heats of hydrogenation.
  - The same alkane product must be obtained to get accurate results.
Heats of hydrogenation of three butene isomers:

- The greater the number of attached alkyl groups \( (i.e. \) the more highly substituted the carbon atoms of the double bond), the greater the alkene’s stability.

### Overall Relative Stabilities of Alkenes

- The greater the number of attached alkyl groups \( (i.e. \) the more highly substituted the carbon atoms of the double bond), the greater the alkene’s stability.

**Relative Stabilities of Alkenes**

- Tetrasubstituted
- Trisubstituted
- Disubstituted
- Monosubstituted
- Unsubstituted
Synthesis of Alkenes via Elimination Reactions

- Dehydrohalogenation
  - Reactions by an E2 mechanism are most useful
    - E1 reactions can be problematic
  - E2 reaction are favored by:
    - Secondary or tertiary alkyl halides
    - Alkoxide bases such as sodium ethoxide or potassium tert-butoxide
  - Bulky bases such as potassium tert-butoxide should be used for E2 reactions of primary alkyl halides
• Zaitsev’s Rule: Formation of the Most Substituted Alkene is Favored with a Small Base

- Some hydrogen halides can eliminate to give two different alkene products

\[ \text{CH}_3\text{CH} = \text{C} - \text{CH}_3 + \text{H} - \text{B} + :\text{Br}^- \]

\[ \text{CH}_3\text{CH} = \text{C} - \text{CH}_3 + \text{H} - \text{B} + :\text{Br}^- \]

- Zaitzev’s Rule: when two different alkene products are possible in an elimination, the most highly substituted (most stable) alkene will be the major product

- This is true only if a small base such as ethoxide is used

\[ \text{CH}_3\text{CH}_2\text{O}^- + \text{CH}_3\text{CH}_2\text{C} - \text{CH}_3 \xrightarrow{70^\circ C/\text{CH}_3\text{CH}_2\text{OH}} \text{CH}_3\text{CH} = \text{C} - \text{CH}_3 + \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \]

2-Methyl-2-butene (69\%) (more stable)

2-Methyl-1-butene (31\%) (less stable)
The transition state in this E2 reaction has double bond character.

The trisubstituted alkene-like transition state will be most stable and have the lowest $\Delta G^\ddagger$.

Kinetic control of product formation: When one of two products is formed because its free energy of activation is lower and therefore the rate of its formation is higher.

This reaction is said to be under kinetic control.
Formation of the Least Substituted Alkene Using a Bulky Base

- Bulky bases such as potassium tert-butoxide have difficulty removing sterically hindered hydrogens and generally only react with more accessible hydrogens (e.g. primary hydrogens)

\[
\text{CH}_3\text{CH}_2\text{CBr} + \text{K}^+\text{(CH}_3\text{)}_3\text{O}^- \xrightarrow{75^\circ\text{C}} \text{CH}_3\text{CH} = \text{CCH}_3 + \text{CH}_3\text{CH}_2\text{C} = \text{CCH}_3
\]

2-Methyl-2-butene (27.5%) (more substituted) 2-Methyl-1-butene (72.5%) (less substituted)
The Stereochemistry of E2 Reactions: The Orientation of Groups in the Transition State

- All four atoms involved must be in the same plane
  - Anti coplanar orientation is preferred because all atoms are staggered

\[
\text{Anti coplanar transition state (preferred)} \quad \text{Syn coplanar transition state (only with certain rigid molecules)}
\]

- In a cyclohexane ring the eliminating substituents must be diaxial to be anti coplanar

\[
\text{Here the } \beta\text{-hydrogen and the chlorine are both axial. This allows an anti coplanar transition state.} \quad \text{A Newman projection formula shows that the } \beta \text{ hydrogen and the chlorine are anti coplanar when they are both axial.}
\]
Neomenthyl chloride and menthyl chloride give different elimination products because of this requirement.

In neomenthyl chloride, the chloride is in the axial position in the most stable conformation.

- Two axial hydrogens anti to chlorine can eliminate; the Zaitzev product is major.

Both green hydrogens are anti to the chlorine in this the more stable conformation. Elimination by path (a) leads to 1-menthene; by path (b) to 2-menthene.
In menthyll chloride the molecule must first change to a less stable conformer to produce an axial chloride.

Elimination is slow and can yield only the least substituted (Hoffman) product from anti elimination.

Menthyll chloride (more stable conformation)
Elimination is not possible for this conformation because no hydrogen is anti to the leaving group.

Menthyll chloride (less stable conformation)
Elimination is possible from this conformation because the green hydrogen is anti to the chlorine.

2-Menthene (100%)
Acid Catalyzed Dehydration of Alcohols

Recall that elimination is favored over substitution at higher temperatures.

Typical acids used in dehydration are sulfuric acid and phosphoric acid.

The temperature and concentration of acid required to dehydrate depends on the structure of the alcohol.

Primary alcohols are most difficult to dehydrate, tertiary are the easiest.

Rearrangements of the carbon skeleton can occur.
Mechanism for Dehydration of Secondary and Tertiary Alcohols: An E1 Reaction

Only a catalytic amount of acid is required since it is regenerated in the final step of the reaction.

\[ \text{Step 1} \]

2° or 3° Alcohol (R’ may be H) + Strong acid (typically sulfuric or phosphoric acid) \[ \rightleftharpoons \text{Protonated alcohol} + \text{Conjugate base} \]

The alcohol accepts a proton from the acid in a fast step.

\[ \text{Step 2} \]

The protonated alcohol loses a molecule of water to become a carbocation. This step is slow and rate determining.
Recall the stability of carbocations is:

\[
\begin{align*}
R - C^+ & > R - C^+ \quad (3^\circ) \\
R - C^+ & > R - C^+ \quad (2^\circ) \\
R - C^+ & > R - C^+ \quad (1^\circ) \\
\text{Methyl} & > R - C^+
\end{align*}
\]

- The second step of the E1 mechanism in which the carbocation forms is rate determining.
- The transition state for this reaction has carbocation character.
- Tertiary alcohols react the fastest because they have the most stable tertiary carbocation-like transition state in the second step.
The relative heights of $\Delta G^\ddagger$ for the second step of E1 dehydration indicate that primary alcohols have a prohibitively large energy barrier.
A Mechanism for Dehydration of Primary Alcohols: An E2 Reaction

- Primary alcohols cannot undergo E1 dehydration because of the instability of the carbocation-like transition state in the 2nd step.
- In the E2 dehydration, the first step is again protonation of the hydroxyl to yield the good leaving group (water).

**Diagram:**

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Primary alcohol + Strong acid → Protonated alcohol + Conjugate base

The alcohol accepts a proton from the acid in a fast step.
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A base removes a hydrogen from the β carbon as the double bond forms and the protonated hydroxyl group departs. (The base may be another molecule of the alcohol or the conjugate base of the acid.)
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Carbocation Stability and the Occurrence of Molecular Rearrangements

- **Rearrangements During Dehydration of Secondary Alcohols**
  - Rearrangements of carbocations occur if a more stable carbocation can be obtained
  - **Example**

  \[
  \text{CH}_3\text{C}-\text{CH}-\text{CH}_3 + 85\% \text{H}_3\text{PO}_4 \xrightarrow{\text{heat}} \text{CH}_3\text{C}=\text{C}-\text{CH}_3 + \text{CH}_2=\text{C}-\text{CH}-\text{CH}_3
  \]

  - 3,3-Dimethyl-2-butanol
  - 2,3-Dimethyl-2-butene (major product)
  - 2,3-Dimethyl-1-butene (minor product)
  - The first two steps are the same as for any E1 dehydration

  **Step 1**

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

  Protonated alcohol

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In the third step the less stable 2° carbocation rearranges by shift of a methyl group with its electrons (a methanide). This is called a 1,2 shift.

The removal of a proton to form the alkene occurs to give the Zaitzev (most substituted) product as the major one.
A hydride shift (migration of a hydrogen with its electrons) can also occur to yield the most stable carbocation.

Carbocation rearrangements can lead to formation of different ring sizes.
Synthesis of Alkynes by Elimination Reactions

→ Alkynes can be obtained by two consecutive dehydrohalogenation reactions of a vicinal dihalide.

\[
\text{R—C—C—R + 2 NH}_2^- \rightarrow \text{R—C≡C—R + 2 NH}_3 + 2 \text{ Br}^- 
\]

**Step 1**

Amide ion \( \text{vic-Dibromide} \)

The strongly basic amide ion brings about an E2 reaction.

**Step 2**

Bromoalkene \( \text{Amide ion} \)

A second E2 reaction produces the alkyne.

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Alkenes can be converted to alkynes by bromination and two consecutive dehydrohalogenation reactions

\[
\text{CH}_3\text{CH}_2\text{CH} \equiv \text{CH}_2 + \text{Br}_2 \text{ (CCl}_4\text{)} \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_2\text{Br} \rightarrow \text{Br} \rightarrow \text{NaNH}_2 \text{ (mineral oil, 110–160°C)}
\]

\[
\left[\text{CH}_3\text{CH}_2\text{CH} \equiv \text{CHBr}\right] + \text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}_2 \rightarrow [\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}] \rightarrow \text{NaNH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C} \equiv \text{C}^- \text{Na}^+ \rightarrow \text{CH}_3\text{CH}_2\text{C} \equiv \text{CH} + \text{NH}_3 + \text{NaCl}
\]

Geminal dihalides can also undergo consecutive dehydrohalogenation reactions to yield the alkyne

\[
\text{Cyclohexyl methyl ketone} \xrightarrow{\text{PCl}_5 \text{ (0°C)}} \text{A gem-dichloride (70–80%)} \xrightarrow{(1) 3 \text{NaNH}_2\text{, mineral oil, heat \text{(2) HA}}} \text{Cyclohexylacetylene (46%)}
\]
The Acidity of Terminal Alkynes

Recall that acetylenic hydrogens have a pKa of about 25 and are much more acidic than most other C-H bonds.

\[ \text{H–C≡C–H} \quad \text{pK}_a = 25 \]
\[ \text{H–C≡C–H} \quad \text{pK}_a = 44 \]
\[ \text{H–C≡C–H} \quad \text{pK}_a = 50 \]

The relative acidity of acetylenic hydrogens in solution is:

\[ \text{H–OH} > \text{H–OR} > \text{H–C≡CR} > \text{H–NH}_2 > \text{H–CH=CH}_2 > \text{H–CH}_2\text{CH}_3 \]

\[ \text{pK}_a \quad 15.7 \quad 16–17 \quad 25 \quad 38 \quad 44 \quad 50 \]

Acetylenic hydrogens can be deprotonated with relatively strong bases (sodium amide is typical).

The products are called alkyndes.

\[ \text{H–C≡C–H} + \text{NaNH}_2 \overset{\text{liq. NH}_3}{\rightarrow} \text{H–C≡C} : \text{Na}^+ + \text{NH}_3 \]
\[ \text{CH}_3\text{C≡C–H} + \text{NaNH}_2 \overset{\text{liq. NH}_3}{\rightarrow} \text{CH}_3\text{C≡C} : \text{Na}^+ + \text{NH}_3 \]
Replacement of the Acetylenic Hydrogen Atom of Terminal Alkynes

Sodium alkynides can be used as nucleophiles in $S_N2$ reactions

- New carbon-carbon bonds are the result
- Only primary alkyl halides can be used or else elimination reactions predominate

\[
\text{RC} \equiv \text{C}^- + \text{CBr}^- \rightarrow \text{RC} \equiv \text{C}^- \text{CH}_2\text{R}' + \text{NaBr}
\]

Sodium alkynide $\rightarrow$ $1^\circ$ Alkyl halide

\[
\text{RC} \equiv \text{C}^- + \text{CBr}^- \rightarrow \text{RC} \equiv \text{CH} + \text{R'}\text{CH} = \text{CHR}'' + \text{Br}^-
\]

2$^\circ$ Alkyl halide
Hydrogenation of Alkenes

- Hydrogen adds to alkenes in the presence of metal catalysts
- Heterogeneous catalysts: finely divided insoluble platinum, palladium or nickel catalysts
- Homogeneous catalysts: catalyst (typically rhodium or ruthenium based) is soluble in the reaction medium
  - Wilkinson’s catalyst is $\text{Rh}[(C_6H_5)_3P]_3\text{Cl}$
- This process is called a reduction or hydrogenation
  - An unsaturated compound becomes a saturated (with hydrogen) compound

$$\text{CH}_2\text{=CH}_2 + \text{H}_2 \xrightarrow{\text{Ni,Pd, or Pt, 25 C}} \text{CH}_3\text{—CH}_3$$

$$\text{CH}_3\text{CH=CH}_2 + \text{H}_2 \xrightarrow{\text{Ni,Pd, or Pt, 25 C}} \text{CH}_3\text{CH}_2\text{—CH}_3$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH=CH}_2 + \text{H}_2 \xrightarrow{\text{Rh[(C}_6\text{H}_5)_3\text{P]}_3\text{Cl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$
Hydrogenation: The Function of the Catalyst

The catalyst provides a new reaction pathway with lower $\Delta G^\ddagger$ values.

$\Delta H^\circ = -120 \text{ kJ mol}^{-1}$

$\Delta G^\ddagger_{(1)} \gg \Delta G^\ddagger_{(2)}$
In heterogeneous catalysis the hydrogen and alkene adsorb to the catalyst surface and then a step-wise formation of C-H bonds occur.

Both hydrogens add to the same face of the alkene (a syn addition).

Addition to opposite faces of the double bond is called anti addition.

Catalytic hydrogenation is a syn addition.
Hydrogenation of Alkynes

- Reaction of hydrogen using regular metal catalysts results in formation of the alkane

\[
\text{CH}_3\text{C≡CCH}_3 \xrightarrow{\text{Pt} \quad \text{H}_2} [\text{CH}_3\text{CH≡CHCH}_3] \xrightarrow{\text{Pt} \quad \text{H}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

- Syn Addition of Hydrogen: Synthesis of cis-Alkenes

- The P-2 catalyst nickel boride results in syn addition of one equivalent of hydrogen to a triple bond

- An internal alkyne will yield a cis double bond

\[
\text{Ni}\left(\begin{array}{c} O \\ \text{OCCH}_3 \end{array}\right)_2 \xrightarrow{\text{NaBH}_4 \quad \text{C}_2\text{H}_5\text{OH}} \text{Ni}_2\text{B}_{\text{P-2}}
\]

\[
\text{CH}_3\text{CH}_2\text{C≡CCH}_2\text{CH}_3 \xrightarrow{\text{H}_2/\text{Ni}_2\text{B}(\text{P-2}) \quad \text{(syn addition)}} \text{(Z)-3-Hexene (cis-3-hexene) (97%)}
\]
Lindlar’s catalyst also produces cis-alkenes from alkynes

\[ \text{R} = \text{C} = \text{C} = \text{R} \quad \xrightarrow{\text{H}_2, \text{Pd/CaCO}_3, \text{quinoline} (\text{syn addition})} \quad \text{R} \quad \text{C} = \text{C} \quad \text{R} \]

- Anti Addition of Hydrogen: Synthesis of trans-Alkenes
- A dissolving metal reaction which uses lithium or sodium metal in low temperature ammonia or amine solvent produces trans-alkenes
- Net anti addition occurs by formal addition of hydrogen to the opposite faces of the double bond

\[ \text{CH}_3(\text{CH}_2)_2 = \text{C} = \text{C} = (\text{CH}_2)_2\text{CH}_3 \quad \xrightarrow{(1) \text{ Li, C}_2\text{H}_5\text{NH}_2, -78^\circ\text{C}} \quad \xrightarrow{(2) \text{ NH}_4\text{Cl}} \quad \text{CH}_3(\text{CH}_2)_2 = \text{C} = \text{C} \quad \text{H} \]

4-Octyne

\[ (E)-4-\text{Octene} \quad (\text{trans-4-octene}) \quad (52\%) \]
The mechanism is a free radical reaction with two electron transfer reactions from the metal.

The vinylic anion prefers to be trans and this determines the trans stereochemistry of the product.

\[
\text{Li}^+ + R\text{-C}≡\text{C-R} \rightarrow \begin{array}{c}
\text{C}≡\text{C} \\
\text{R} \\
\end{array} \begin{array}{c}
\text{H} \\
\text{R} \\
\end{array} 
\text{Radical anion} \quad \begin{array}{c}
\text{C}≡\text{C} \\
\text{R} \\
\end{array} \begin{array}{c}
\text{H} \\
\text{R} \\
\end{array} \text{Vinylic radical}
\]

A lithium atom donates an electron to the π bond of the alkyn. An electron pair shifts to one carbon as the hybridization states change to \(sp^2\).

The radical anion acts as a base and removes a proton from a molecule of the ethylamine.

\[
\text{R} \quad \begin{array}{c}
\text{C}≡\text{C} \\
\text{H} \\
\text{R} \\
\end{array} \begin{array}{c}
\text{Li}^+ \\
\end{array} \begin{array}{c}
\text{C}≡\text{C} \\
\text{R} \\
\end{array} \begin{array}{c}
\text{H} \\
\text{R} \\
\end{array} \begin{array}{c}
\text{trans-Vinylic anion} \\
\text{Vinylic radical} \\
\end{array}
\]

A second lithium atom donates an electron to the vinylic radical.

The anion acts as a base and removes a proton from a second molecule of ethylamine.
Structural Information from Molecular Formulas and the Index of Hydrogen Deficiency (IHD)

- Unsaturated and Cyclic Compounds
  - A compound with the general molecular formula $C_nH_{2n}$ will have either a double bond or a ring
    
    \[
    \text{CH}_2\text{=CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3
    \]
    
    1-Hexene \hspace{1cm} \text{(C}_6\text{H}_{12})
    
    \[
    \text{Cyclohexane}
    \]
    
    \text{(C}_6\text{H}_{12})

  - A compound with general formula $C_nH_{2n-2}$ can have a triple bond, two double bonds, a double bond and a ring or two rings

  - Index of Hydrogen Deficiency: the number of pairs of hydrogen atoms that must be subtracted from the molecular formula of the corresponding alkane to give the molecular formula of the compound under consideration
Example: A compound with molecular formula \( \text{C}_6\text{H}_{12} \)

\[
\begin{align*}
\text{C}_6\text{H}_{14} &= \text{formula of corresponding alkane (hexane)} \\
\text{C}_6\text{H}_{12} &= \text{formula of compound (1-hexene or cyclohexane)} \\
\text{H}_2 &= \text{difference} = 1 \text{ pair of hydrogen atoms} \\
\text{Index of hydrogen deficiency} &= 1
\end{align*}
\]

Hydrogenation allows one to distinguish a compound with a double bond from one with a ring

\[
\begin{align*}
\text{CH}_2&\text{CH(\text{CH}_2)_3\text{CH}_3} + \text{H}_2 & \frac{\text{Pt}}{25^\circ\text{C}} & \text{CH}_3(\text{\text{CH}_2})_4\text{CH}_3 \\
\text{+ H}_2 & \frac{\text{Pt}}{25^\circ\text{C}} & \text{no reaction}
\end{align*}
\]

- Compounds Containing Halogens, Oxygen, or Nitrogen
  - For compounds containing halogen atoms, the halogen atoms are counted as if they were hydrogen atoms
  - Example: A compound with formula \( \text{C}_4\text{H}_6\text{Cl}_2 \)
    - This is equivalent to a compound with molecular formula \( \text{C}_4\text{H}_8 \) which has IHD=1
For compounds containing oxygen, the oxygen is ignored and IHD is calculated based on the rest of the formula.

Example: A compound with formula C₄H₈O has IHD = 1

For compounds containing nitrogen, one hydrogen is subtracted for each nitrogen and the nitrogen is ignored in the calculation.

Example: A compound with formula C₄H₉N is treated as if it has formula C₄H₈ and has IHD = 1.