Chapter 3
The Nature of Organic Reactions: Alkenes and Alkynes

- Unsaturated hydrocarbon: contains one or more carbon-carbon double or triple bonds
- Alkene: contains a carbon-carbon double bond, C=C, and has the general formula C_\text{n}H_{2\text{n}}
- Alkyne: contains a carbon-carbon triple bond and has the general formula C_\text{n}H_{2\text{n}-2}
- Arenes: benzene and its derivatives (Ch 5)

Naming Alkenes and Alkynes

IUPAC system of nomenclature
(International Union of Pure and Applied Chemistry)

Prefix — Parent — Locant — Suffix

Where and what are the substituents? How many carbons? Where is the primary functional group? What is the primary functional group?

-ane
-ene
-yne

Naming Alkenes

- Step 1: Name the parent hydrocarbon
  - Find the longest carbon chain that contains the double bond
  - Name the compound using the suffix -ene

Named as a pentene NOT as a hexene, since the double bond is not contained in the six-carbon chain
Naming Alkenes

• Step 1: Name the parent hydrocarbon
• Step 2: Number the atoms in the chain
  – Number the parent chain to give the first carbon of the double bond the lower number
  – If the double bond is equidistant from the two ends, begin at the end nearer the first branch point

Before 1993

Naming Alkenes

• Step 1: Name the parent hydrocarbon
• Step 2: Number the atoms in the chain
• Step 3: Write the full name
  – Follow IUPAC rules for numbering and naming substituents
  – If more than one double bond is present, give the position of each and use one of the suffixes – diene, -triene, and so on
  – For a cycloalkene, the double bond must be numbered 1,2

New naming system: 2,5-Dimethylhept-3-ene 3-Propylhexa-1,4-diene
(Old naming system: 2,5-Dimethyl-3-heptene 3-Propyl-1,4-hexadiene)

Before 1993
Table 3.1  Common Names of Some Alkenes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Systematic name</th>
<th>Common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{C}==\text{CH}_2$</td>
<td>Ethene</td>
<td>Ethylene</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}==\text{CH}_2$</td>
<td>Propene</td>
<td>Propylene</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>2-Methylpropene</td>
<td>Isobutylene</td>
</tr>
<tr>
<td>$\text{CH}_3\text{C}==\text{CH}_2$</td>
<td>2-Methylbuta-1,3-diene</td>
<td>Isoprene</td>
</tr>
</tbody>
</table>

Electronic Structure of Alkenes

- Three equivalent $sp^2$ hybrid orbitals lie in a plane at angles of $120^\circ$ to one another
- The fourth carbon orbital is an unhybridized $p$ orbital perpendicular to the $sp^2$ plane
- When two such carbon atoms approach each other, they form a $\sigma$ bond by head-on overlap of $sp^2$ orbitals and a $\pi$ bond by sideway overlap of $p$ orbitals

Naming Alkynes

Begin numbering at the end nearer the triple bond.

6-Methyloct-3-yne
(Old name: 6-Methyl-3-octyne)
Cis-Trans Isomers of Alkenes

- Because of restricted rotation about a C=C double bond, groups on adjacent carbons are either cis or trans to each other.
- The cis-trans system: configuration is determined by the orientation of atoms of the main chain.
Trans alkenes are more stable than cis alkenes because of nonbonded interaction strain between alkyl substituents of the same side of the double bond.

Sequence Rules: The E, Z Designation

- The cis-trans naming system works only with two disubstituted alkenes.
- With trisubstituted and tetrasubstituted double bonds, the E, Z system is needed for describing double-bond geometry.
Sequence Rules: The $E$, $Z$ Designation

- The $E$, $Z$ system uses the priority rules of the $R$, $S$ system to assign to the groups on each carbon of a carbon-carbon double bond
  1. Each atom bonded to the $C=\text{C}$ double bond is assigned a priority
  2. If groups of higher priority are on the same side, configuration is $Z$ (German, zusammen)
  3. If groups of higher priority are on opposite sides, configuration is $E$ (German, entgegen)

- Rule 1:
  Taking the double-bond carbons separately, look at the atoms directly attached to each carbon and rank them according to atomic number

- Rule 2:
  If a decision can’t be reached by ranking the first atoms in the substituents, look at the second, third, or fourth atoms away from the double-bond carbons until the first difference is found
• Rule 3: Multiple-bonded atoms are equivalent to the same number of single-bonded atoms

![Diagram showing equivalent structures with multiple and single bonds]

Kinds of Organic Reactions

1. Addition reactions
2. Elimination reactions
3. Substitution reactions
4. Rearrangement reactions
• Addition reactions
  Two reactants add together to form a single new product with no atoms “left over”

• Elimination reactions
  A single reactant splits into two products

• Substitution reactions
  Two reactants exchange parts to give two new products

• Rearrangement reactions
  A single reactant undergoes a reorganization of bonds and atoms to yield a single isomeric product
**How Reactions Occur: Mechanisms**

- **Reaction mechanism:** describes how a reaction occurs
  - which bonds are broken and which new ones are formed
  - the order in which bond-breaking and bond-forming steps take place
  - the role of the catalyst (if any is present)
  - the energy of the entire system during the reaction

- A covalent two-electron bond can break in two ways
  1. A bond can break in an electronically symmetrical way so that one electron remains with each product fragment (homolytic)
  2. A bond can break in an electronically unsymmetrical way so that both electrons remain with one product fragment, leaving the other fragment with a vacant orbital (heterolytic)

- A covalent two-electron bond can form in two ways
  1. A bond can form in an electronically symmetrical (homogenic) way when one electron is donated to the new bond by each reactant
  2. A bond can form in an electronically unsymmetrical (heterogenic) way when both bonding electrons are donated to the new bond by one reactant

1. The reaction involves symmetrical bond breaking and making are called radical reactions
2. A radical (often called a “free radical”) is a chemical species that contains an odd number of valence electrons and thus has an orbital that contains only one electron

1. The reaction involve unsymmetrical bond breaking and making are called polar reactions
2. A polar reactions involve species that contains an even number of valence electrons and have only electron pair in their orbitals
The fundamental characteristic of all polar reactions is that electron-rich sites in one molecule react with electron-poor site in another.

A nucleophile is a substance that is “nucleus loving” and thus attracted to a positive charge, and has an electron-rich atom and can form a bond by donating an electron pair to an electron-poor atom.

A electrophile is a substance that is “electron loving” and thus attracted to a negative charge, and has an electron-poor atom and can form a bond by accepting an electron pair from a nucleophile.

The Mechanism of an Organic Reaction: Addition of HCl to Ethylene

A electrophilic addition reaction

A carbon-carbon double bond is electron-rich (nucleophile), and its π electrons are relatively accessible to reaction with external electron-poor reagents (electrophile).

The chemistry of alkenes should involve reaction of the electron-rich double bond with electron-poor reagents.
The mechanism of the electrophilic addition of HCl to ethylene

1. A hydrogen atom on the electrophile HCl is attacked by σ electrons from the nucleophilic double bond, forming a new C-H bond. This leaves the other carbon atom with a positive charge and a vacant p orbital. Simultaneously, two electrons from the H-Cl bond move onto chlorine, giving chloride anion.

2. Chloride ion donates an electron pair to the positively charged carbon atom, forming a C-Cl bond and yielding the neutral addition product.

Reaction energy diagram:
- A graph showing the changes in energy that occur during a chemical reaction.

Reaction progress:
- A measure of the change in position of atoms during a reaction.

# Describing a Reaction: Transition States and Intermediates

Transition state:
- An energy maximum on a reaction energy diagram.
- Represents the highest-energy structure involved in this step of the reaction and can't be isolated or directly observed.

Activation energy, $E_{\text{act}}$:
- The energy difference between reactants and the transition state.
- Measure how rapidly a reaction occurs.
- If activation energy is large, only a few molecular collisions occur with sufficient energy to reach the transition state, and the reaction is slow.
- Range 40 to 125 kJ/mol (10-30 kcal/mol).
- Less than 80 kJ/mol take place spontaneously at or below room temperature.
**Reaction intermediate:**
A substance formed transiently during the course of a multistep reaction

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**Describing a Reaction:**

**Catalysis**

**Catalyst:**
A substance that increases the rate of a chemical reaction by providing an alternative mechanism
Does not take part in the reaction