II Alkanes, Alkenes, and Alkynes

**Hydrocarbon:** Compound composed of only carbon and hydrogen

**Saturated Hydrocarbons:** Compound with only single bonds

**Unsaturated Hydrocarbons:** Compounds with AT LEAST one double or triple bond

2.1 Alkanes

**Alkane:** Compound composed of only carbon and hydrogen and single bonds

**Acyclic Alkanes:** Compound composed of only carbon and hydrogen in a 'chain-like' conformation

*Example:*

**Cycloalkane:** cyclic compound containing only carbon and hydrogen

*Example:*

In a molecule, atoms that are not carbon or hydrogen are called **Heteroatoms** (such as N, O). Cyclic structure containing heteroatoms are called heterocyclic.

*Example:*
2.1.1 Isomers, Nomenclature, and Conformations of Alkanes

Basic Alkanes ⇒ chain like molecules based on C and H with NO branch

Branched Alkanes: Alkanes that have carbons that are bonded to more than 2 carbons (these are skeletal isomers)

*Example Butane:*

**Primary Carbon:** Carbon bonded to only ONE other carbon (1°)

**Secondary Carbon:** Carbon bonded to TWO other carbons (2°)

**Tertiary Carbon:** Carbon bonded to THREE other carbons (3°)

**Quaternary Carbon:** Carbon bonded to FOUR other carbons (4°)

Nomenclature:
⇒ parent: longest alkyl chain of the molecules

→ if two possible chains have the same # of carbons, the one with the more branch points wins

⇒ suffix: If only alkane, ending is -ane; if molecule has functional groups, they determine the suffix

**Alkyl Group:** Hydrocarbon chain with one open point of attachment

often R is used to describe a generic alkyl group

*Example:*
Alkyl Groups:

*Examples of Nomenclature:*
**Conformational Isomers:** Isomers that differ as a result of the degree of rotation around a carbon-carbon single bond

Let us take Ethane as an example to describe alkane conformation:

Conformation or orientations of alkanes can be expressed using several different methods:

A) **Sawhorse Diagram:** A way of representing conformational isomers with stick drawings

B) **Newman Projection:** A way of representing conformational isomers using an end-on projection of a carbon-carbon bond

**Eclipsed:** Conformation around a carbon-carbon single bond in which attached atoms are as close together as possible

**Staggered:** Conformation around a carbon-carbon single bond in which attached atoms are as far apart as possible

**Torsional or Dihedral Angle:** Angle between the bonds in the Newman Projection
Example 1,2-Dibromoethane:

Q1: Which of these structures is the most stable and why:

Example Butane:

- Staggered most stable.
- Two possibilities, Anti and Gauche
2.1.2 Cycloalkanes

- Cyclic structure based on Carbon-Carbon single bonds

**Fused Ring Systems:** Several cycles (or rings) share two common atoms and the bond between them

**Spiro Compound:** Two Rings share ONE carbon

**Bridged Ring Compounds:** Two rings share two non-connected atoms, thereby building a bridgehead with bridgehead atoms

*Examples:*

*Nomenclature:*
Conformation of Cycloalkanes:

**Boat Confirmation:** An unstable conformation of cyclohexane with 109.5° bond angles but in which most bonds are eclipsed

*Example:*

**Chair Confirmation:** The most stable conformation of cyclohexane in which all bonds are staggered and the bond angles are 109.5°

*Example:*

⇒ The hydrogens are either above and below the ring or to the side of the ring

**Axial Bond:** Bond on cyclohexane chain perpendicular to the ring with three up and three down on alternating carbons

**Equatorial Bonds:** Bonds on cyclohexane chair parallel to the ring

*Cycloalkanes are not restricted to one confirmation but can **FLIP** between different conformations. This is called **Ring Flip.**
Substituted Cycloalkanes

Bulky substituents prefer to be in equatorial position and NOT axial

*Example Methylcyclohexane:*

**Geometric Isomers:** *Cis* and *trans* isomers; a type of stereoisomers in which atoms or groups display orientation differences around a double bond or ring

**Cis Isomer:** Geometric isomer in which groups are on the same side of a ring or double bond

**Trans Isomer:** Geometric Isomer in which groups are on the opposite sides of a ring or double bond

*Example:*
2.1.3 Properties of Alkanes

- Melting and boiling points increase with increased molecular weight (Methane bp. -164°C, decane bp. 174°C)
- Boiling point decrease with chain branching (decrease in surface area) but melting points increase
- Non-polar substances ⇒ not water soluble
- Alkanes are less dense than water and swim on top of water

2.1.4 Reactions of Alkanes

- In general very un-reactive ⇒ you need a lot of driving force

A) Oxidation

Example Methane:

B) Halogenation

Halogenation (a substitution reaction): Introduction of a halogen into a molecule (chlorination, bromination)

General Reaction:

• You need heat or light
Example Methane:

*How to control the degree of halogenation?*

**Mechanism:**
- same as free radical polymerization

*Where does halogenation takes place?*
Properties and nomenclature of haloalkanes

- Toxic and cause cancer
- Major component of free radicals in ozone layer
- Polar bond (partial charges)
- Nomenclature same as basic alkane nomenclature

Examples:
2.2 Alkenes and Alkynes

- **Alkene**: Hydrocarbon with at least one carbon-carbon double bond (olefins)
- **Alkynes**: Hydrocarbon with at least one carbon-carbon triple bond

**Nomenclature:**

*Examples:*

*Classification based on substitution patterns:*

Monosubstituted:

Disubstituted:

Trisubstituted:

Tetrasubstituted:
**Properties of Alkenes and Alkynes**

- NO rotation around double and triple bonds
- Similar to Alkanes (bp and mp)

**Isomerism**

* cis and trans:*

If you have four different substituents around a double bond cis/trans does not work

**E/Z Nomenclature:**

- Each substituent is assigned a priority
- The substituent with the highest priority on each carbon is determined
- If these substituents are on the same side of the molecule, the configuration is Z (zusammen (meaning together))
- If these substituents are opposite from each other, the configuration is E (entgegen (meaning opposite))
Examples:

How to determine the group priorities?

1) The greater the atomic number the higher the priority
2) If the two substituents on an sp\textsuperscript{2} carbon have the same atomic number (there is a tie), the atomic numbers of the atoms that are attached to the "tied" atoms must be considered
3) If an atom is doubly bonded to another atom, the priority system treats it as if it were a singly bonded to two of these atoms
4) In the case of isotopes, the mass number is used to determine the priority

Examples:
2.2.1 Preparation of Alkenes and Alkynes

- Elimination Reactions:

**Dehydrohalogenation**: A reaction in which hydrogen and halogen are eliminated from a molecule

*Examples:*

**Dehydration**: A reaction in which the elements of water (H and OH) are eliminated from a molecule

*Examples:*
Mechanism:

What about the orientation of the double bond?

Example:

**Zaitsev's Rule:** In applicable elimination reactions, the most substituted alkene (with alkyl groups) will predominate

Stability:

\[
\text{CH}_2\text{CH}_2 < \text{RCHCH}_2 < \text{RCHCHR} = \text{R}_2\text{CCH}_2 < \text{R}_2\text{CCHR} < \text{R}_2\text{CCR}_2 \text{ (most stable)}
\]
2.3 Reactions of Alkenes and Alkynes

⇒ Additions are the most common reactions using alkenes and alkynes

Addition to:

| Alkene | Alkyne |

Four major additions:

1) Addition of **hydrogen halides**

2) **Halogenation**: Reaction in which halogen is introduced into a molecule

3) **Hydration**: Reaction in which the elements of water (H and OH) are introduced into a molecule

4) **Hydrogenation**: Reaction in which hydrogen is introduced into a molecule
Examples:
2.3.1 Mechanism

**Electrophilic Addition**: Addition reaction initiated by an electron-deficient species (electrophile)

- Generic Mechanism:

- Mechanism of Addition of Hydrogen Halides:
• Mechanism for the Addition of Halogen

• Mechanism for the Addition of Water:
• Orientation of Addition:
The more alkyl groups attached to carbocation, the more stable ($3^\circ > 2^\circ > 1^\circ$)

**Markovnikov’s Rule:** When an unsymmetrical reagent adds to an unsymmetrical alkene, the positive portion of the reagent adds to the carbon that results in the formation of the more stable carbocation

**Regioselective:** In addition reactions, a reaction in which one of two possible positional isomers predominates

**Regiospecific:** In addition reactions, a reaction in which one of two possible positional isomers is formed exclusively

*Examples:*
• Addition reactions in Polymer Chemistry

**Polymer:** A giant molecule composed of a repeating structural unit  
**Monomer:** Compound(s) from which a polymer is made

*Examples of Addition Polymers:*
- Polyethylene:
- Polypropylene:
- Polystyrene:
- Polymethylmethacrylate (PMMA):
- Orlon:
- Teflon:
- Polyvinylchloride

- Polyvinylidene chloride

Mechanism of the **Cationic Polymerization**:
2.4 Oxidation Reactions of Alkenes and Alkynes

1) Hydroxylation with Potassium Permanganate (KMnO$_2$)

*Example:*

2) Ozonolysis

*Example:*
Alkadienes: Compounds containing two double bonds

Conjugation: Alternating double and single bonds in a molecule

Isolated or Non-Conjugated Double Bond: Two double bonds separated by more than one single bond

Additions:

Allylic Carbocation: Carbocation in which a positive carbon is adjacent to a carbon-carbon double bond
Orbital considerations of allylic carbocations:

- Important Dienes:
  1) Terpenes
2) Rubber
Summary of Chapter 2:

⇒ Alkenes
  → Nomenclature
  → Isomers
  → Conformation
⇒ Cycloalkanes
⇒ Reactivity of Alkanes
⇒ Properties of Alkanes
⇒ Alkenes and Alkynes
  → Nomenclature
  → Isomers
⇒ Preparation of Alkenes and Alkynes
⇒ Additions to Alkenes and Alkynes
  → Electrophilic Additions
  → Hydration
  → Hydrogenation
  → Halogenation
  → Mechanisms and Stereochemistry
  → Polymerization
⇒ Oxidations of Alkenes and Alkynes
⇒ Dienes
  → Reactions of Dienes
  → Terpenes and Rubber