

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^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:

$\text{CH}_2\text{CH}_2 < \text{RCHCH}_2 < \text{RCHCHR} = \text{R}_2\text{CCH}_2 < \text{R}_2\text{CCHR} < \text{R}_2\text{CCR}_2$ (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:

2.5 Alkadienes (or Dienes)

Alkadienes: Compounds containing two double bond

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 bonds

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*
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- ⇒ *Preparation of Alkenes and Alkynes*
- ⇒ *Additions to Alkenes and Alkynes*
 - *Electrophilic Additions*
 - *Hydration*
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 - *Halogenation*
 - *Mechanisms and Stereochemistry*
 - *Polymerization*
- ⇒ *Oxidations of Alkenes and Alkynes*
- ⇒ *Dienes*
 - *Reactions of Dienes*
 - *Terpenes and Rubber*