CHAPTER 03: ALKANES

Classification of Hydrocarbons:

- **Saturated**: Contains the maximum number of hydrogen atoms possible (no double or triple bonds present).

- **Unsaturated**: Does not contain the maximum number of hydrogen atoms possible (has double or triple bonds present).

### Molecular Formulas

- All C-C single bonds.
- Saturated with hydrogen atoms.
- Ratio: ________________
- Alkane homologs: ________________

Notice that some molecular formulas can have different structures (ISOMERS!!!!)
Nomenclature of Organic Compounds

A. Two Types of Chemical Names:

1. Common Names: common names are the older names.

Examples

<table>
<thead>
<tr>
<th>Number of Carbon Atoms</th>
<th>Number of Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>12</td>
<td>355</td>
</tr>
<tr>
<td>15</td>
<td>4,347</td>
</tr>
<tr>
<td>20</td>
<td>366,319</td>
</tr>
</tbody>
</table>

2. IUPAC Names: (International Union of Pure and Applied Chemistry)

  o IUPAC names are considered the “official” names. They are systematic which means that they follow a system of rules.

  • IUPAC system has two goals:

    1. All compounds should ___________________________.

    2. The name should be based on _____________________ of the compound.
IUPAC System for Naming

1) **Parent name**: A prefix that indicates the number of carbons in the longest carbon chain.

2) **Suffix**: An ending that indicates the most important functional group in the compound. (alkANE, alkENE, alkYNE, alkOXIDE, etc…).

- **Some Important Base Names for 1 to 10 Carbons**
  (MEMORIZE THIS TABLE):

<table>
<thead>
<tr>
<th># of Carbons</th>
<th>Base Name</th>
<th>Simple Alkane Name (base + ane)</th>
<th>Structure</th>
<th>Alkyl Group Name (base + yl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>meth</td>
<td>methane</td>
<td>H-CH₂-H</td>
<td>Methyl</td>
</tr>
<tr>
<td>2</td>
<td>eth</td>
<td>ethane</td>
<td>H-(CH₂)₂-H</td>
<td>Ethyl</td>
</tr>
<tr>
<td>3</td>
<td>prop</td>
<td>propane</td>
<td>H-(CH₂)₃-H</td>
<td>Propyl</td>
</tr>
<tr>
<td>4</td>
<td>but</td>
<td>butane</td>
<td>H-(CH₂)₄-H</td>
<td>Butyl</td>
</tr>
<tr>
<td>5</td>
<td>pent</td>
<td>pentane</td>
<td>H-(CH₂)₅-H</td>
<td>Pentyl</td>
</tr>
<tr>
<td>6</td>
<td>hex</td>
<td>hexane</td>
<td>H-(CH₂)₆-H</td>
<td>Hexyl</td>
</tr>
<tr>
<td>7</td>
<td>hept</td>
<td>heptane</td>
<td>H-(CH₂)₇-H</td>
<td>Heptyl</td>
</tr>
<tr>
<td>8</td>
<td>oct</td>
<td>octane</td>
<td>H-(CH₂)₈-H</td>
<td>Octyl</td>
</tr>
<tr>
<td>9</td>
<td>non</td>
<td>nonane</td>
<td>H-(CH₂)₉-H</td>
<td>Nonyl</td>
</tr>
<tr>
<td>10</td>
<td>dec</td>
<td>decane</td>
<td>H-(CH₂)₁₀-H</td>
<td>Decyl</td>
</tr>
</tbody>
</table>

**Carbon Branches Are Named as Alkyl Groups:**
- An alkyl group is a chain of carbons with an empty bond that can be attached to another atom or group of atoms.

- Alkyl groups are named like the corresponding alkane, but the –ane suffix is changed to –yl.

- Branches are on carbon chain are called ____________________________.
Naming Alkanes With Substituents:

1) Find the longest continuous chain of carbons and count the number of carbons to get the base name, then add the correct suffix to get the parent compound name.

2) Number the longest chain starting from the end with the nearest substituent. 
   The goal is to put the substituents at the lowest numbers possible.

3) Add the substituent names in alphabetical order in front of the parent name using a number and a dash to indicate the carbon where the substituent is attached (for example, 2-methyl).

4) If two or more substituents are identical, put all the numbers together, separated by commas, and use the prefixes di- (2), tri- (3), or tetra- (4) in front of the substituent name (for example: 2,2,3-trimethyl).

IMPORTANT: These prefixes do NOT COUNT FOR ALPHABETIZING PURPOSES.
Example

Check Point
Sometimes in naming a compound we need to know subrules...

Subrules (RULE #1): Chain Length
- If there is a tie, ______________________________

Subrules (RULE #2): Substituent Location Tie
- If there are different substituents at equivalent positions on the chain, the substituent of __________ alphabetical order is given the lowest number.

Subrules (RULE #3): Substituent Name Tie
- If the branches are the same and at the same location, then you have to keep stepping in toward the center until a difference is found. If no difference is found, then it doesn't matter which end you number from.
Naming Complicated Substituent Groups

The following procedure is used to name complicated substituents:

1) Find the longest carbon chain that starts from the point of attachment to the parent chain. Name that chain as the corresponding alkyl group (-yl ending).

2) Number the longest carbon chain starting from the point of attachment. The point of attachment is always carbon 1 of the substituent.

3) Identify and name the branches on the complicated substituent chain. List them in front of the parent name, in alphabetical order, with a number and a dash to indicate their position.

4) Once all the numbers for the branches are determined, the branches are named using -yl, and ordered alphabetically.

- If branches themselves are branched, then the complete name of the branch (with numbers) must be determined at this time. It is the complete name of the branch which is alphabetized.

- For example:
Special Common Names of Substituents (memorize):

Important: When these descriptors are used in an IUPAC name, iso is alphabetized normally; the hyphenated prefixes, however (sec- and tert-) are disregarded when alphabetizing.

- Straight chains are called normal groups, and the word “normal-” or “n-” is used in front of their name:

- Chains with a forked methyl branch at the end are called “iso-“ groups:

- Two other special butyl groups:

- Other special groups to know:
Nomenclature of Alkyl Halides (Haloalkanes)

Classes of Alkyl Halides

- Alkyl halides are classified based on the type of carbon to which the halogen (-X) is attached:

IUPAC Nomenclature of Alkyl Halides

1) Find the longest carbon chain and name as an alkane.

2) Add the name of the halogen substituents in front of the alkane name: fluoro, chloro, bromo, or iodo. Do not put a space between the substituent name and the alkane name.

3) Use a number and dash in front to indicate the number of the carbon where the halogen is attached.

4) Use di-, tri-, tetra-, etc. for multiple halogens. There must be a number in front for each halogen (for example, 2,2-dichloro not 2-dichloro).

Example:

A few Common Names of Alkyl Halides (memorize).
Cycloalkanes and Bicycloalkanes

A. Monocyclic (one ring) Alkanes

1) Count the number of carbons in the ring and determine the name of the alkane with the same number of carbons.

2) Add the prefix “___________________–” in front of the alkane name.

3) Number the ring starting from the carbon and in the direction that gives the substituents the lowest numbers possible.

4) When the ring has fewer carbons than an attached chain, use the attached chain as the parent and name the ring as a “cycloalkyl” substituent group.
B. Bicycloalkanes (two rings)

1) Count the total number of carbons in the bicyclic rings, and determine the name of the alkane with the same number of carbons.

2) Find the two bridgehead carbons. These carbons will have three bridges attached.

3) Count the number of carbons in each bridge, excluding the bridgehead carbons.

4) Arrange the numbers from highest to lowest out them in front of the alkane name, in brackets, separated by periods.

5) Put the prefix “bicyclo” in front of the name.

Example(s)
Conformations of Carbon Chains

A. Conformations of Ethane

- Look at the rotation around carbon atoms in ethane…

- These are $\rightarrow$ stereoisomers that interconvert by rotation around single bonds.

- We can use to help us look at conformations.

- The two conformations of ethane have different potential energies. We can draw an energy profile to show how the energy changes as the bond rotates:
B. Conformations of Butane

- There are two important trends:

  1) The staggered conformations are always _________ in energy than the eclipsed types.

  2) Largest groups farther apart from each other have the lowest energy.

*These principles generally apply to the conformations of other molecules.*
Ring Conformations

- Cyclic alkanes have the general formula ___________

- **Definition:** Ring Strain = ______________ + ______________

Cyclopropane:

- Very little angle strain.
- Can twist to almost eliminate torsional strain.

Cyclobutane

Cyclopentane

- Very little angle strain.
- Can twist to almost eliminate torsional strain.

Cyclohexane

- No angle strain
- Can twist to almost eliminate all torsional strain.
B. Heats of Combustion of Cyclic Alkanes

- A higher ΔH of combustion per CH₂ =

- We can determine the relative stability of cyclic carbon compounds by comparing the amount of heat energy given off during combustion:

\[
2C_nH_{2n} + 3O_2 \rightarrow 2nCO_2 + 2nH_2O + \text{Heat}
\]

Cycloalkane Heats of Combustion

<table>
<thead>
<tr>
<th>Ring Size</th>
<th>Cycloalkane</th>
<th>Molar Heat of Combustion (kJ)</th>
<th>Heat of Combustion per CH₂ Group (kJ)</th>
<th>Ring Strain per CH₂ Group (kJ)</th>
<th>Total Ring Strain (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Cyclopropane</td>
<td>2091</td>
<td>697</td>
<td>39</td>
<td>117</td>
</tr>
<tr>
<td>4</td>
<td>Cyclobutane</td>
<td>2744</td>
<td>686</td>
<td>28</td>
<td>112</td>
</tr>
<tr>
<td>5</td>
<td>Cyclopentane</td>
<td>3320</td>
<td>664</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>Cyclohexane</td>
<td>3951</td>
<td>658</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Cycloheptane</td>
<td>4637</td>
<td>662</td>
<td>4</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>Cyclooctane</td>
<td>5309</td>
<td>663</td>
<td>5</td>
<td>40</td>
</tr>
</tbody>
</table>

Reference: Long Chain Alkane

658 0 0
Cyclohexane

A. Conformations of Cyclohexane

1. The chair conformation has ___________________. This makes it more stable than the boat, which has eclipsing along the middle two bonds. These can be seen in Newman projections along the middle bonds of the two conformations:

2. The boat conformation is destabilized by interaction between two hydrogens at the top of the left most and right most atoms. This is called the _______________ ____________:

3. Twist boat (Permutation of boat)

4. Half-Chair
B. Energy Profile Cyclohexane

C. Axial and Equatorial Hydrogens on the Chair and Conformational Rotation

- There are two different types of hydrogens on the chair conformation:
  1) Axial
     - 6 positions
     - More sterically hindered
  2) Equitorial
     - 6 positions
     - less sterically hindered
     - larger substituents prefer this position
Monosubstituted Cycloalkanes

- The chair conformation can *ring flip* to form the opposite chair in order to accommodate the more stable conformation:

<table>
<thead>
<tr>
<th>Substituent</th>
<th>dG (kcal/mol)</th>
<th>% Equitorial</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.2</td>
<td>58.385</td>
<td>0.7127</td>
</tr>
<tr>
<td>Br</td>
<td>0.6</td>
<td>73.416</td>
<td>0.36209</td>
</tr>
<tr>
<td>CH₃</td>
<td>1.8</td>
<td>95.467</td>
<td>0.04747</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>5.4</td>
<td>99.989</td>
<td>1.07E-4</td>
</tr>
</tbody>
</table>
Disubstituted cyclohexanes
A) Let’s look at trans-1,3-dimethylcyclohexane.

B) Let’s look at cis-1,3-dimethylcyclohexane.

- Bulky Substituents
  - Groups like t-butyl cause a large energy difference between the axial and equatorial conformer.
  - Most stable conformer puts t-butyl ________________ regardless of other substituents.
• Occasionally, we can not get the t-butyl groups into equatorial positions.
  
  o In these cases we have to adopt the _twist boat_ conformation.
Physical Properties of Alkanes

1. Unbranched Alkanes
   - BP
   - MP

<table>
<thead>
<tr>
<th>Molecule</th>
<th>BP (°C)</th>
<th>MP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Branched Alkanes:
   - BP
   - MP

<table>
<thead>
<tr>
<th>Molecule</th>
<th>BP (°C)</th>
<th>MP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
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Basic Reactions of Alkanes:
1.

2.