Chapter 4
Alkanes: Nomenclature,
Conformational Analysis, and an
Introduction to Synthesis
Shapes of Alkanes

“Straight-chain” alkanes have a zig-zag orientation when they are in their most straight orientation.

Straight chain alkanes are also called unbranched alkanes.

- **Propane**
  - $\text{CH}_3\text{CH}_2\text{CH}_3 \text{ or } \ \backslash\backslash$

- **Butane**
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \text{ or } \ \backslash\ldash\backslash$

- **Pentane**
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \text{ or } \ \backslash\backslash\backslash$

Chapter 4 2
Branched alkanes have at least one carbon which is attached to more than two other carbons.
Constitutional isomers have different physical properties (melting point, boiling point, densities etc.)

- Constitutional isomers have the same molecular formula but different connectivity of atoms

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Structural Formula</th>
<th>mp (°C)</th>
<th>bp (°C)&lt;sup&gt;a&lt;/sup&gt; (1 atm)</th>
<th>Density&lt;sup&gt;b&lt;/sup&gt; (g mL&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Index of Refraction&lt;sup&gt;c&lt;/sup&gt; (n&lt;sub&gt;D&lt;/sub&gt; 20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>−95</td>
<td>68.7</td>
<td>0.6594&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.3748</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>−153.7</td>
<td>60.3</td>
<td>0.6532&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.3714</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH(CH&lt;sub&gt;3&lt;/sub&gt;)CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>−118</td>
<td>63.3</td>
<td>0.6643&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.3765</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH—CHCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>−126.8</td>
<td>58</td>
<td>0.6616&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.3750</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;—CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>−98</td>
<td>49.7</td>
<td>0.6492&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.3688</td>
</tr>
</tbody>
</table>

<sup>a</sup>Unless otherwise indicated, all boiling points given in this book are at 1 atm or 760 torr.

<sup>b</sup>The superscript indicates the temperature at which the density was measured.

<sup>c</sup>The index of refraction is a measure of the ability of the alkane to bend (refract) light rays. The values reported are for light of the D line of the sodium spectrum (n<sub>D</sub>).
The number of constitutional isomers possible for a given molecular formula increases rapidly with the number of carbons.

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Possible Number of Constitutional Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>4\text{H}</em>{10}$</td>
<td>2</td>
</tr>
<tr>
<td>$\text{C}<em>5\text{H}</em>{12}$</td>
<td>3</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{14}$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{C}<em>7\text{H}</em>{16}$</td>
<td>9</td>
</tr>
<tr>
<td>$\text{C}<em>8\text{H}</em>{18}$</td>
<td>18</td>
</tr>
<tr>
<td>$\text{C}<em>9\text{H}</em>{20}$</td>
<td>35</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{22}$</td>
<td>75</td>
</tr>
<tr>
<td>$\text{C}<em>{15}\text{H}</em>{32}$</td>
<td>4,347</td>
</tr>
<tr>
<td>$\text{C}<em>{20}\text{H}</em>{42}$</td>
<td>366,319</td>
</tr>
<tr>
<td>$\text{C}<em>{30}\text{H}</em>{62}$</td>
<td>4,111,846,763</td>
</tr>
<tr>
<td>$\text{C}<em>{40}\text{H}</em>{82}$</td>
<td>62,481,801,147,341</td>
</tr>
</tbody>
</table>
IUPAC Nomenclature of Alkanes, Alkyl Halides and Alcohols

- Before the end of the 19th century compounds were named using nonsystematic nomenclature
- These “common” or “trivial” names were often based on the source of the compound or a physical property
- The International Union of Pure and Applied Chemistry (IUPAC) started devising a systematic approach to nomenclature in 1892
- The fundamental principle in devising the system was that each different compound should have a unique unambiguous name
- The basis for all IUPAC nomenclature is the set of rules used for naming alkanes
## Nomenclature of Unbranched Alkanes

<table>
<thead>
<tr>
<th>Name</th>
<th>Number of Carbon Atoms</th>
<th>Structure</th>
<th>Name</th>
<th>Number of Carbon Atoms</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1</td>
<td>CH$_4$</td>
<td>Heptadecane</td>
<td>17</td>
<td>CH$_{17}$CH$_3$</td>
</tr>
<tr>
<td>Ethane</td>
<td>2</td>
<td>CH$_3$CH$_3$</td>
<td>Octadecane</td>
<td>18</td>
<td>CH$_{18}$CH$_3$</td>
</tr>
<tr>
<td>Propane</td>
<td>3</td>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>Nonadecane</td>
<td>19</td>
<td>CH$_{19}$CH$_3$</td>
</tr>
<tr>
<td>Butane</td>
<td>4</td>
<td>CH$_3$(CH$_2$)$_2$CH$_3$</td>
<td>Eicosane</td>
<td>20</td>
<td>CH$_{20}$CH$_3$</td>
</tr>
<tr>
<td>Pentane</td>
<td>5</td>
<td>CH$_3$(CH$_2$)$_3$CH$_3$</td>
<td>Heneicosane</td>
<td>21</td>
<td>CH$_{21}$CH$_3$</td>
</tr>
<tr>
<td>Hexane</td>
<td>6</td>
<td>CH$_3$(CH$_2$)$_4$CH$_3$</td>
<td>Docosane</td>
<td>22</td>
<td>CH$_{22}$CH$_3$</td>
</tr>
<tr>
<td>Heptane</td>
<td>7</td>
<td>CH$_3$(CH$_2$)$_5$CH$_3$</td>
<td>Tricosane</td>
<td>23</td>
<td>CH$_{23}$CH$_3$</td>
</tr>
<tr>
<td>Octane</td>
<td>8</td>
<td>CH$_3$(CH$_2$)$_6$CH$_3$</td>
<td>Triacontane</td>
<td>30</td>
<td>CH$_{30}$CH$_3$</td>
</tr>
<tr>
<td>Nonane</td>
<td>9</td>
<td>CH$_3$(CH$_2$)$_7$CH$_3$</td>
<td>Hentriacontane</td>
<td>31</td>
<td>CH$_{31}$CH$_3$</td>
</tr>
<tr>
<td>Decane</td>
<td>10</td>
<td>CH$_3$(CH$_2$)$_8$CH$_3$</td>
<td>Tetracontane</td>
<td>40</td>
<td>CH$_{40}$CH$_3$</td>
</tr>
<tr>
<td>Undecane</td>
<td>11</td>
<td>CH$_3$(CH$_2$)$_9$CH$_3$</td>
<td>Pentacontane</td>
<td>50</td>
<td>CH$_{50}$CH$_3$</td>
</tr>
<tr>
<td>Dodecane</td>
<td>12</td>
<td>CH$_3$(CH$<em>2$)$</em>{10}$CH$_3$</td>
<td>Hexacontane</td>
<td>60</td>
<td>CH$_{60}$CH$_3$</td>
</tr>
<tr>
<td>Tridecane</td>
<td>13</td>
<td>CH$_3$(CH$<em>2$)$</em>{11}$CH$_3$</td>
<td>Heptacontane</td>
<td>70</td>
<td>CH$_{70}$CH$_3$</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>14</td>
<td>CH$_3$(CH$<em>2$)$</em>{12}$CH$_3$</td>
<td>Octacontane</td>
<td>80</td>
<td>CH$_{80}$CH$_3$</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>15</td>
<td>CH$_3$(CH$<em>2$)$</em>{13}$CH$_3$</td>
<td>Nonacontane</td>
<td>90</td>
<td>CH$_{90}$CH$_3$</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>16</td>
<td>CH$_3$(CH$<em>2$)$</em>{14}$CH$_3$</td>
<td>Hectane</td>
<td>100</td>
<td>CH$_{100}$CH$_3$</td>
</tr>
</tbody>
</table>
**Nomenclature of Unbranched Alkyl groups**

The unbranched alkyl groups are obtained by removing one hydrogen from the alkane and named by replacing the -ane of the corresponding alkane with -yl.

<table>
<thead>
<tr>
<th>ALKANE</th>
<th>ALKYL GROUP</th>
<th>ABBREVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃—H</td>
<td>CH₃—</td>
<td>Me—</td>
</tr>
<tr>
<td>Methane</td>
<td>Methyl</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂—H</td>
<td>CH₃CH₂—</td>
<td>Et—</td>
</tr>
<tr>
<td>Ethane</td>
<td>Ethyl</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂CH₂—H</td>
<td>CH₃CH₂CH₂—</td>
<td>Pr—</td>
</tr>
<tr>
<td>Propane</td>
<td>Propyl</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂—H</td>
<td>CH₃CH₂CH₂CH₂—</td>
<td>Bu—</td>
</tr>
<tr>
<td>Butane</td>
<td>Butyl</td>
<td></td>
</tr>
</tbody>
</table>
- **Nomenclature of Branched-Chain Alkanes (IUPAC)**

  - Locate the longest continuous chain of carbons; this is the parent chain and determines the parent name.
  
  \[
  \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3
  \]

  - Number the longest chain beginning with the end of the chain nearer the substituent.

  - Designate the location of the substituent.

  - When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain.

  - Substituents are listed alphabetically.

  - 2-Methylhexane

  - 3-Methylheptane

  - Substituents are listed alphabetically.
When two or more substituents are identical, use the prefixes *di-*-, *tri-*-, *tetra-* etc.

- Commas are used to separate numbers from each other
- The prefixes are used in alphabetical prioritization

When two chains of equal length compete to be parent, choose the chain with the greatest number of substituents

\[\text{2,3,5-Trimethyl-4-propylheptane (four substituents)}\]

When branching first occurs at an equal distance from either end of the parent chain, choose the name that gives the lower number at the first point of difference

\[\text{2,3,5-Trimethylhexane (not 2,4,5-trimethylhexane)}\]
Nomenclature of Branched Alkyl Chains

Two alkyl groups can be derived from propane

*Three-Carbon Groups*

\[ \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \begin{cases} \text{CH}_3\text{CH}_2\text{CH}_2- \\
\text{CH}_3- \text{CH} - \\
\text{CH}_3 \\
1\text{-Methylethyl or isopropyl group} \end{cases} \]

Four groups can be derived from the butane isomers

*Four-Carbon Groups*

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \begin{cases} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2- \\
\text{CH}_3\text{CH}- \\
\text{CH}_3 \\
1\text{-Methylpropyl or sec-butyl group} \end{cases} \]

\[ \text{CH}_3\text{CHCH}_3 \rightarrow \begin{cases} \text{CH}_3\text{CHCH}_2- \\
\text{CH}_3 \end{cases} \]

\[ \text{CH}_3\text{CHCH}_3 \rightarrow \begin{cases} \text{CH}_3\text{C}- \\
\text{CH}_3 \end{cases} \]

1,1-Dimethylethyl or tert-butyl group
The neopentyl group is a common branched alkyl group

\[
\text{CH}_3 \\
\text{CH}_3 \quad \text{C} \quad \text{CH}_2 \\
\text{CH}_3
\]

2,2-Dimethylpropyl or neopentyl group

Examples

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3 \quad \text{CH} \\
\text{CH}_3
\]

4-(1-Methylethyl)heptane or 4-isopropylheptane

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3 \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3
\]

4-(1,1-Dimethylethyl)octane or 4-tert-butyl octane
 Classification of Hydrogen Atoms

Hydrogens take their classification from the carbon they are attached to.

- $1^\circ$ Hydrogen atoms
- $3^\circ$ Hydrogen atom
- $2^\circ$ Hydrogen atoms
Nomenclature of Alkyl Halides

In IUPAC nomenclature halides are named as substituents on the parent chain.

- Halo and alkyl substituents are considered to be of equal ranking.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CHCHCH}_2\text{CH}_3 & \quad \text{CH}_3\text{CHCH}_2\text{CHCH}_3 \\
\text{Cl} & \quad \text{Cl} \\
2\text{-Chloro-3-methylpentane} & \quad 2\text{-Chloro-4-methylpentane}
\end{align*}
\]

In common nomenclature the simple haloalkanes are named as alkyl halides.

- Common nomenclature of simple alkyl halides is accepted by IUPAC and still used.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{Cl} & \quad \text{CH}_3\text{CHCH}_3 & \quad (\text{CH}_3)_3\text{CBr} & \quad \text{CH}_3\text{CHCH}_2\text{Cl} & \quad \text{CH}_3\text{CCH}_2\text{Br} \\
\text{Ethyl chloride} & \quad \text{Isopropyl bromide} & \quad \text{tert-Butyl bromide} & \quad \text{Isobutyl chloride} & \quad \text{Neopentyl bromide}
\end{align*}
\]
**IUPAC Substitutive Nomenclature**

- An IUPAC name may have up to 4 features: locants, prefixes, parent compound and suffixes.
- Numbering generally starts from the end of the chain which is closest to the group named in the suffix.

\[
\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

- 4-Methyl-1-hexanol

**Locant**  **Prefix**  **Locant**  **Parent**  **Suffix**

**IUPAC Nomenclature of Alcohols**

- Select the longest chain containing the hydroxyl and change the suffix name of the corresponding parent alkane from -ane to -ol.
- Number the parent to give the hydroxyl the lowest possible number.
- The other substituents take their locations accordingly.
Examples

\[ \text{3-Chloro-1-propanol or 3-chloropropan-1-ol} \]

\[ \begin{align*}
\text{3-ClCH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_3\text{CHCH}_2\text{CCH}_3
\end{align*} \]

\[ \text{4,4-Dimethyl-2-pentanol or 4,4-dimethylpentan-2-ol} \]

Common Names of simple alcohols are still often used and are approved by IUPAC

\[ \begin{align*}
\text{Propyl alcohol} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{Butyl alcohol} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{sec-Butyl alcohol} & : \text{CH}_3\text{CH}_2\text{CHCH}_3
\end{align*} \]

\[ \begin{align*}
\text{tert-Butyl alcohol} & : \text{CH}_3\text{CH}_2\text{COH} \\
\text{Isobutyl alcohol} & : \text{CH}_3\text{CHCH}_2\text{OH} \\
\text{Neopentyl alcohol} & : \text{CH}_3\text{CCH}_2\text{OH}
\end{align*} \]
Alcohols with two hydroxyls are called diols in IUPAC nomenclature and glycols in common nomenclature.

<table>
<thead>
<tr>
<th>Common Substitutive</th>
<th>Ethylene glycol 1,2-Ethanediol or ethane-1,2-diol</th>
<th>Propylene glycol 1,2-Propanediol or propane-1,2-diol</th>
<th>Trimethylene glycol 1,3-Propanediol or propane-1,3-diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂—CH₂</td>
<td>OH</td>
<td>OH</td>
<td>CH₃CH—CH₂</td>
</tr>
</tbody>
</table>

Chapter 4
Nomenclature of Cycloalkanes

- The prefix cyclo- is added to the name of the alkane with the same number of carbons
  - When one substituent is present it is assumed to be at position one and is not numbered
  - When two alkyl substituents are present the one with alphabetical priority is given position 1
  - Numbering continues to give the other substituent the lowest number
  - Hydroxyl has higher priority than alkyl and is given position 1
  - If a long chain is attached to a ring with fewer carbons, the cycloalkane is considered the substituent
Isopropylocyclohexane

1-Ethyl-3-methylcyclohexane *not* 1-ethyl-5-methylcyclohexane

4-Chloro-2-ethyl-1-methylcyclohexane *not* 1-chloro-3-ethyl-4-methylcyclohexane

Chlorocyclopentane

2-Methylcyclohexanol

1-Cyclobutylpentane

1,3-Dicyclohexylpropane
Bicyclic compounds

- Bicycloalkanes contain 2 fused or bridged rings
- The alkane with the same number of total carbons is used as the parent and the prefix bicyclo- is used

The number of carbons in each bridge is included in the middle of the name in square brackets

8-Methylbicyclo[3.2.1]octane
8-Methylbicyclo[4.3.0]nonane
Nomenclature of Alkenes and Cycloalkenes

- Alkenes are named by finding the longest chain containing the double bond and changing the name of the corresponding parent alkane from -ane to -ene.
- The compound is numbered to give one of the alkene carbons the lowest number.

\[
\begin{align*}
1\text{-Butene} & : CH_2=CHCH_2CH_3 \\
2\text{-Hexene} & : CH_3CH=CHCH_2CH_2CH_3 \\
\end{align*}
\]

- The double bond of a cycloalkene must be in position 1 and 2.

\[
\begin{align*}
\text{1-Methylcyclopentene} & : \begin{array}{c}
\text{CH}_3 \\
\text{1} \\
\text{5} \\
\text{4} \\
\text{2} \\
\text{3} \\
\end{array} \\
\text{(not 2-methylcyclopentene)} \\
\text{3,5-Dimethylcyclohexene} & : \begin{array}{c}
\text{H}_3\text{C} \\
\text{5} \\
\text{6} \\
\text{4} \\
\text{2} \\
\text{3} \\
\text{CH}_3 \\
\end{array} \\
\text{(not 4,6-dimethylcyclohexene)} \\
\end{align*}
\]
Compounds with double bonds and alcohol hydroxyl groups are called alkenols

The hydroxyl is the group with higher priority and must be given the lowest possible number

\[ \text{OH} \]

4-Methyl-3-penten-2-ol or 4-methylpent-3-en-2-ol

2-Methyl-2-cyclohexen-1-ol or 2-methycyclohex-2-en-1-ol

Two groups which contain double bonds are the vinyl and the allyl groups

\[
\begin{align*}
\text{CH}_2\text{═CH—} & \quad \text{The vinyl group} \\
\text{CH}_2\text{═CHCH}_2— & \quad \text{The allyl group}
\end{align*}
\]

Bromoethene or vinyl bromide (common)

Ethenylecyclopropane or vinylcyclopropane

3-Chloropropene or allyl chloride (common)

3-(Prop-2-en-1-yl)cyclohexanol or 3-allylcyclohexanol
If two identical groups occur on the same side of the double bond the compound is cis.

If they are on opposite sides the compound is trans.

Several alkenes have common names which are recognized by IUPAC.
Physical Properties of Alkanes and Cycloalkanes

- Boiling points of unbranched alkanes increase smoothly with number of carbons.

- Melting points increase in an alternating pattern according to whether the number of carbon atoms in the chain is even or odd.
**Sigma Bonds and Bond Rotation**

- Ethane has relatively free rotation around the carbon-carbon bond.
- The staggered conformation has C-H bonds on adjacent carbons as far apart from each other as possible.
  - The drawing to the right is called a Newman projection.
  - The dihedral angle (φ) between these hydrogens is 180°.

- The eclipsed conformation has all C-H bonds on adjacent carbons directly on top of each other.
  - The dihedral angle (φ) between these hydrogens is 0°.
The potential energy diagram of the conformations of ethane shows that the staggered conformation is more stable than eclipsed by 12 kJ mol⁻¹.
Conformational Analysis of Butane

Rotation around C₂-C₃ of butane gives six important conformations:

- The gauche conformation is less stable than the anti conformation by 3.8 kJ mol⁻¹ because of repulsive van der Waals forces between the two methyls.
The Relative Stabilities of Cycloalkanes: Ring Strain

Heats of combustion per CH₂ unit reveal cyclohexane has no ring strain and other cycloalkanes have some ring strain

<table>
<thead>
<tr>
<th>Cycloalkane (CH₂)_n</th>
<th>n</th>
<th>Heat of Combustion (kJ mol⁻¹)</th>
<th>Heat of Combustion per CH₂ Group (kJ mol⁻¹)</th>
<th>Ring Strain (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropane</td>
<td>3</td>
<td>2091</td>
<td>697.0</td>
<td>115</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>4</td>
<td>2744</td>
<td>686.0</td>
<td>109</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>5</td>
<td>3320</td>
<td>664.0</td>
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<td>9885</td>
<td>659.0</td>
<td>6</td>
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<td>Unbranched alkane</td>
<td>—</td>
<td>—</td>
<td>658.6</td>
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The Origin of Ring Strain in Cyclopropane and Cyclobutane: Angle Strain and Tortional Strain

- **Angle strain** is caused by bond angles different from 109.5°
- **Tortional strain** is caused by eclipsing C-H bonds on adjacent carbons
- Cyclopropane has both high angle and tortional strain

- Cyclobutane has considerable angle strain
  - It bends to relieve some tortional strain

- Cyclopentane has little angle strain in the planar form but bends to relieve some tortional strain
Conformations of Cyclohexane

- The chair conformation has no ring strain
  - All bond angles are 109.5° and all C-H bonds are perfectly staggered
The boat conformation is less stable because of flagpole interactions and tortional strain along the bottom of the boat.

The twist conformation is intermediate in stability between the boat and the chair conformation.
Substituted Cyclohexanes: Axial and Equatorial Hydrogen Atoms

- Axial hydrogens are perpendicular to the average plane of the ring
- Equatorial hydrogens lie around the perimeter of the ring

- The C-C bonds and equatorial C-H bonds are all drawn in sets of parallel lines
  - The axial hydrogens are drawn straight up and down

(a) Axial bond up
(b) Vertex of ring up
(c) Vertex of ring down
(d) Axial bond down
Methyl cyclohexane is more stable with the methyl equatorial

- An axial methyl has an unfavorable 1,3-diaxial interaction with axial C-H bonds 2 carbons away
- A 1,3-diaxial interaction is the equivalent of 2 gauche butane interactions
Disubstituted Cycloalkanes

- Can exist as pairs of cis-trans stereoisomers
  - Cis: groups on same side of ring
  - Trans: groups on opposite side of ring

- [Diagrams of cis-trans isomers for cis-1,2-Dimethylcyclohexane, cis-1,3-Dimethylcyclohexane, cis-1,4-Dimethylcyclohexane, trans-1,2-Dimethylcyclohexane, trans-1,3-Dimethylcyclohexane, trans-1,4-Dimethylcyclohexane]
**Trans-1,4-dimethylcylohexane prefers a trans-diequatorial conformation**
Cis-1,4-dimethylcyclohexane exists in an axial-equatorial conformation

A very large tert-butyl group is required to be in the more stable equatorial position
Bicyclic and Polycyclic Alkanes

The bicyclic decalin system exists in non-interconvertible cis and trans forms

Decalin (bicyclo[4.4.0]decane)
(carbon atoms 1 and 6 are bridgehead carbon atoms)
Synthesis of Alkanes and Cycloalkanes

- Hydrogenation of Alkenes and Alkynes

**General Reaction**

\[
\text{Alkene} + \text{H}_2 \xrightarrow{\text{Pt, Pd, or Ni, solvent, pressure}} \text{Alkane} \quad \text{Alkyne} + 2\text{H}_2 \xrightarrow{\text{Pt, solvent, pressure}} \text{Alkanes}
\]

2-Methylpropene + \( \text{H}_2 \) \( \xrightarrow{\text{Ni, } \text{C}_2\text{H}_5\text{OH}, 25^\circ\text{C, 50 atm}} \) Isobutane
Reduction of Alkyl Halides

\[ R-X + Zn + HX \longrightarrow R-H + ZnX_2 \]

or*

\[ R-X \xrightarrow{Zn, HX} R-H \]

\[ 2 \text{CH}_3\text{CH}_2\text{CHCH}_3 \xrightarrow{\text{HBr}} \text{Zn} \rightarrow 2 \text{CH}_3\text{CH}_2\text{CHCH}_3 + \text{ZnBr}_2 \]

/sec-Butyl bromide (2-bromobutane) Butane/
Alkylation of Terminal Alkynes

Alkynes can be subsequently hydrogenated to alkanes

\[ \text{An alkyne} \quad \text{Sodium amide} \quad \text{An alkynide anion} \quad \text{R must be methyl or 1° and unbranched at the second carbon} \]

\[ R-\text{C}≡\text{C}-\text{H} \xrightarrow{\text{NaNH}_2, \text{(-NH}_3\text{)}} \quad \text{R-\text{C}≡\text{C}-\text{Na}^+} \quad \text{R-\text{C}≡\text{C}-\text{R'}} \]

\[ \text{CH}_3\text{CHC≡CH} \xrightarrow{\text{NaNH}_2, \text{(-NH}_3\text{)}} \text{CH}_3\text{CHC≡C}^-\text{Na}^+ \xrightarrow{\text{CH}_3\text{Br, (-NaBr)}} \text{CH}_3\text{CHC≡C}^-\text{CH}_3 \]

excess H\text{, Pt, pressure} \quad \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3

Chapter 4
Retrosynthetic Analysis-Planning Organic Synthesis

- The synthetic scheme is formulated working backward from the target molecule to a simple starting material.
- Often several schemes are possible.

Retrosynthetic Analysis

\[
\begin{align*}
\text{Target molecule} & \rightarrow 1\text{st precursors B} \rightarrow 2\text{nd precursors c} \\
& \rightarrow 1\text{st precursors C} \rightarrow 2\text{nd precursors e} \\
& \rightarrow 2\text{nd precursors a} \\
& \rightarrow 2\text{nd precursors b} \\
& \rightarrow 2\text{nd precursors d} \\
& \rightarrow 2\text{nd precursors f}
\end{align*}
\]