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

Alkanes = saturated hydrocarbons

Simplest alkane = methane \( \text{CH}_4 \)

We can build additional alkanes by adding \(- \text{CH}_2-\) units

\( \text{C}_n\text{H}_{2n+2} = \) saturated = no double bonds, no rings

Shapes of Alkanes

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

There is no limit on length of chain

Polyethylene = an “infinite” alkane

Branched alkanes

At least one carbon attached to more than two others

Many constitutional isomers are possible

Same molecular formula but different connectivity of atoms

Constitutional isomers have different physical properties (melting point, boiling point, densities etc.)

<table>
<thead>
<tr>
<th>Structural Formula</th>
<th>mp (°C)</th>
<th>bp (°C/1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>-85</td>
<td>60.3</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>-153.7</td>
<td>60.3</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>-118</td>
<td>63.3</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}(-\text{CH}_3)_n\text{CH}_3 )</td>
<td>-128.8</td>
<td>98</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}(-\text{CH}_3)_n\text{CH}_3 )</td>
<td>-98</td>
<td>49.7</td>
</tr>
</tbody>
</table>

“hexanes” \( \text{C}_6\text{H}_{14} \)
The number of constitutional isomers possible for a given molecular formula rise 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>C₂H₆</td>
<td>2</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>3</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>5</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>9</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>18</td>
</tr>
<tr>
<td>C₇H₁₆</td>
<td>35</td>
</tr>
<tr>
<td>C₈H₁₈</td>
<td>75</td>
</tr>
<tr>
<td>C₉H₂₀</td>
<td>4,347</td>
</tr>
<tr>
<td>C₁₀H₂₂</td>
<td>306,319</td>
</tr>
<tr>
<td>C₁₂H₂₆</td>
<td>4,111,846,763</td>
</tr>
<tr>
<td>C₁₈H₃₄</td>
<td>62,481,801,147,341</td>
</tr>
</tbody>
</table>

A complex mixture of organic compounds, largely alkanes
US uses 17 M barrels/day, 75% for energy, 8% chemicals
Refineries not only separate the compounds, but “reform” the molecules by catalytic cracking and rearrangements

A reaction of alkanes - Combustion

All hydrocarbons are combustible
Combine with oxygen and release energy
Heat of combustion is very high

\[ 2\text{C}_4\text{H}_{10} + 25\text{O}_2 \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O} \]

\[ \Delta H_{\text{comb}} = -5452 \text{ kJ/mol} \text{ (or } -47.8 \text{ kJ/g}) \]

Octane boosters (anti-knock additives)

Smother engine performance if combustion is slowed
For decades, used Tetraethyl lead, now banned
For past decade, MTBE was used, now also banned

Examples of “reforming” to raise octane

Some Octane Ratings of Hydrocarbons and Additives

<table>
<thead>
<tr>
<th>Octane Rating</th>
<th>Hydrocarbon/Aditive</th>
<th>Octane Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>heptane</td>
<td>0</td>
</tr>
<tr>
<td>91</td>
<td>heptane</td>
<td>0</td>
</tr>
<tr>
<td>99</td>
<td>2,2,4-trimethylpentane</td>
<td>100</td>
</tr>
<tr>
<td>95</td>
<td>benzene</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>methyl</td>
<td>0</td>
</tr>
<tr>
<td>87</td>
<td>ethanol</td>
<td>0</td>
</tr>
<tr>
<td>85</td>
<td>n-amyl-1-butyl ether</td>
<td>106</td>
</tr>
<tr>
<td>85</td>
<td>isooctane</td>
<td>100</td>
</tr>
</tbody>
</table>

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2 \text{SiO}_2 \text{ silica-alumina catalyst, } 500^\circ \text{C} \]

\[ 2\text{C}_7\text{H}_{16} + 4\text{H}_2 \rightarrow 2\text{C}_7\text{H}_{18} \]

\[ 2\text{C}_7\text{H}_{16} + 4\text{H}_2 \rightarrow 2\text{C}_7\text{H}_{18} \]

isooctane = 100
(2,2,5-trimethylpentane)
(vs heptane = 0)

For past decade, MTBE was used, now also banned

Examples of “reforming” to raise octane
Early chemicals were given “common” or “trivial” names 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.

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### IUPAC Nomenclature

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### Nomenclature of Unbranched Alkanes – Learn the first ten!

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<tr>
<th>Name</th>
<th>Number of Carbon Atoms</th>
<th>Structure</th>
</tr>
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<tbody>
<tr>
<td>Methane</td>
<td>1</td>
<td>CH₄</td>
</tr>
<tr>
<td>Ethane</td>
<td>2</td>
<td>CH₂CH₃</td>
</tr>
<tr>
<td>Propane</td>
<td>3</td>
<td>CH₃CH₂CH₃</td>
</tr>
<tr>
<td>Butane</td>
<td>4</td>
<td>CH₃CH₂CH₂CH₃</td>
</tr>
<tr>
<td>Pentane</td>
<td>5</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>Hexane</td>
<td>6</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>Heptane</td>
<td>7</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>Octane</td>
<td>8</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>Nonane</td>
<td>9</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>Decane</td>
<td>10</td>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃</td>
</tr>
</tbody>
</table>

### Nomenclature of Branched-Chain Alkanes (IUPAC)

1. Locate the longest continuous chain of carbons; this is the parent chain and determines the parent name.

   \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]
   \( 7 \text{ carbons} = \text{heptane} \)

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

3. Designate the location of the substituent.

   \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]
   \( 3\)-Methylheptane

### Nomenclature of Branched-Chain Alkanes (IUPAC) – cont.

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

   - Substituents are listed alphabetically.

   \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]
   \( 4\)-ethyl-3-methylheptane
5. When two or more substituents are identical, use the prefixes di-, tri-, tetra- etc.
   a) Commas are used to separate numbers from each other
   b) Repeat the number if two substituents on same carbon
   c) The prefixes are used in alphabetical prioritization

4-ethyl-2,3,3-trimethylheptane

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

7. 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

Two alkyl groups can be derived from propane

4-isopropylheptane

The neopentyl group is a common branched alkyl group

2,2-Dimethylpropyl or neopentyl group

4-(1,1-Dimethylethyl)octane or 4-tert-butyl octane

How many butyl groups are possible?

Classification of Hydrogen Atoms

Hydrogens take their classification from the carbon they are attached to
What type of hydrogens in neopentane?

CH₃
CH₂CH₂CH₃
CH₃

Nomenclature of Aliphatic Halides

- In IUPAC nomenclature halides are named as substituents on the parent chain
- Halo and alkyl substituents are considered to be of equal ranking

<table>
<thead>
<tr>
<th>CH₂Cl₂CH₂Cl</th>
<th>CH₂Cl₂CH₃</th>
<th>CH₂Cl₂CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
</tr>
<tr>
<td>2-Chloro-3-methylpentane</td>
<td>2-Chloro-4-methylpentane</td>
<td></td>
</tr>
</tbody>
</table>

- In common nomenclature the simple haloalkanes are named as alkyl halides
- Common nomenclature of simple alkyl halides is accepted by IUPAC and still used

<table>
<thead>
<tr>
<th>CH₂Cl₂Cl</th>
<th>CH₂CH₂Cl</th>
<th>CH₂CH₂Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>Br</td>
<td>Br</td>
</tr>
<tr>
<td>Ethyl chloride</td>
<td>Isopropyl chloride</td>
<td>Isobutyl chloride</td>
</tr>
</tbody>
</table>

Nomenclature of Alcohols

In the IUPAC naming system, there may be as many as four components to the name:

- Locant indicates the position of a substituent.
- Prefix names the substituent group.
- Parent is the parent alkane.
- Suffix names a key function.

Examples:

CH₃CH₂CH₂CH₂CH₂OH

- Parent: CH₃
- Suffix: OH
- Prefix: 2-butanol
- Locant: 3

IUPAC Nomenclature of Alcohols

1. Select the longest chain containing the hydroxyl and change the suffix ending of the parent alkane from -e to -ol
2. Number the parent to give the hydroxyl the lowest possible number
3. The other substituents take their locations accordingly

CH₃CH₂CH₂CH₂CH₂CH₂OH

4-methyl-3-hexanol

- Parent: CH₃
- Suffix: OH
- Prefix: 4-methyl-3-butanol
- Locant: 3

Alcohols with two hydroxyls are called diols in IUPAC nomenclature and glycols in common nomenclature

<table>
<thead>
<tr>
<th>CH₂OH</th>
<th>CH₃OH</th>
<th>CH₃CH₂OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>OH</td>
<td>OH</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>CH₃CH₂OH</th>
<th>CH₃CH₂CH₂OH</th>
<th>CH₃CH₂CH₂CH₂OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propyl alcohol</td>
<td>Butyl alcohol</td>
<td>sec-Butyl alcohol</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>CH₃CH₂OH</td>
<td>CH₃CH₂CH₂OH</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃CH₂OH</td>
<td>CH₃CH₂CH₂OH</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
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<td>CH₃CH₂OH</td>
<td>CH₃CH₂CH₂OH</td>
</tr>
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<td>CH₃CH₂CH₂OH</td>
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<tr>
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<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃CH₂OH</td>
<td>CH₃CH₂CH₂OH</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
</tbody>
</table>
Nomenclature of cycloalkanes

- Ring compounds are very common
- Named as cyclo + base name for number of C in ring

![Cycloalkanes](image)

- Chlorocyclopentane

Nomenclature of Substituted Cycloalkanes

- 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 = position 1

![Chlorocyclopentane](image)

Cycloalkyl group

- If other parts of the molecule are dominant or if a long chain is attached to a ring with fewer carbons, the cycloalkane is considered the substituent

![Cycloalkyl group](image)

Bicyclic Compounds – the Playground of Organic Chemists

- 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

![Bicyclic Compounds](image)

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

Bicyclic Compounds – the Playground of Organic Chemists

Beginning at bridgehead position, number around largest ring first, then second largest ring

![Bicyclic Compounds](image)
Alkenes are named by finding the longest chain containing the double bond and changing the name of the parent alkane from -ane to -ene.

The compound is numbered to give one of the alkene carbons the lowest number.

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

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

Double bonds plus alcohol hydroxyl groups = alkenols

Note that positions of both the C=C and the OH must be indicated.

The vinyl and allyl groups are common names that need to be readily recognized:

- Vinyl: CH2=CH-
- Allyl: CH2=CHCH3

Several alkenes have common names which are recognized by IUPAC:

- Ethene: CH2=CH-
- Propene: CH3=CHCH3
- 2-Methylpropene: CH3=CHCH2CH3

Alkynes = named similarly to alkenes

(1) The name of the parent alkane is modified by dropping the "ane" ending and adding "yne."

(2) The parent chain is numbered to give the carbons of the alkyne lower numbers.

(3) The location of the triple bond is given by the lower positional number of the alkyne carbons.

- 1-pentyne: CH3C≡CH
- 2-butyne: CH2=CHC≡CH

Alkene nomenclature – cis and trans

- 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:

- Ethene: CH2=CH-
- Propene: CH3=CHCH3
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Terminal alkynes have an acidic H

R—C≡CH pKa = 25
**Physical Properties of Alkanes**

The unbranched alkanes (CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₄, etc.) form a regular series where each member differs from the next in order by -CH₂-. Such a regular series is called a homologous series.

The boiling points of the unbranched alkanes increase more or less regularly with increasing size reflecting the increasing van der Waals attractions.

- Form a regular series where each member differs from the next in order by -CH₂-

### Table: Melting Points of Alkanes

<table>
<thead>
<tr>
<th></th>
<th>Pentane</th>
<th>Hexane</th>
<th>Heptane</th>
<th>Octane</th>
</tr>
</thead>
<tbody>
<tr>
<td>mp (°C)</td>
<td>-130</td>
<td>-95</td>
<td>-91</td>
<td>-57</td>
</tr>
</tbody>
</table>

### Graph: Boiling Points of Alkanes

**Other physical properties of hydrocarbons**

- Less dense than water
- Immiscible with water and other highly polar solvents
- Solvent for non-polar organic compounds

**How to draw a Newman projection**

- Sight down the C-C bond (sigma bond is symmetric)
- Groups on front carbon intersect in center
- Groups on back carbon end at circle

**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 potential energy diagram of the conformations of ethane

The staggered conformation is more stable than eclipsed by 12 kJ mol⁻¹

**Melting points reflect size, but also packing factors**

- Propane: -188°C
- Ethane: -183°C
- Methane: -182°C

**Potential Energy Diagram**

- Rotation rate: 10¹³/sec
- Energy barrier called torsional strain
The conformational features are the same for the two C-C bonds.

Consider as ethane with 1 H replaced by a CH₃

Barrier = 14 kJ/mol

Conclusion: eclipsing of methyl with H adds very little to energy barrier.

During one complete rotation around the internal bond in butane, the three staggered conformations include two called “gauche” and one called “anti.”

The staggered anti is more stable than the two equivalent staggered gauche conformations. In the anti conformation, the two CH₃ groups are on opposite sides of the structure. In the gauche conformations, the two groups are within van der Waals repulsive interaction distance, and 3.8 kJ/mol of steric strain energy is introduced.

Rotation around C₁-C₃ of butane gives three energy minima.

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 Newman projection formulas as viewed from the left are:

The anti gauche gauche conformation is 3.8 kJ mol⁻¹ more stable than the two equivalent staggered gauche conformations. In the anti conformation, the two CH₃ groups are on opposite sides of the structure. In the gauche conformations, the two groups are within van der Waals repulsive interaction distance, 3.8 kJ/mol of steric strain energy is introduced.

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The Origin of Ring Strain in Cyclopropane: Angle Strain and Torsional Strain

Angle strain is caused by bond angles different from 109.5°

C-C angle of 60° means orbital overlap is reduced

Torsional strain is caused by eclipsing C-H bonds on adjacent C's

Cyclopropane has both high angle and torsional strain.

Normal bond length $sp^3-C-C = 1.54\,\text{Å}$

Normal $sp^3-C-H = 1.10\,\text{Å}$ $sp^3-C-H = 1.09\,\text{Å}$
Cyclobutane: Angle Strain and Torsional Strain

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

Cyclopentane

The internal angles of a regular pentagon are 108°, close to the idealized tetrahedral bond angles. Thus, a planar cyclopentane would have very little angle strain. But a planar geometry would have very severe torsional strain (10 eclipsed H). Consequently, the geometry of cyclopentane is bent.

Cyclopentane: Angle Strain and Torsional Strain

Cyclohexane: the perfect ring

- Not 120°, the angle of simple hexagon
- Adopts a chair conformation with no ring strain!
- All bond angles are 109.5° and all C-H bonds are perfectly staggered

Two types of H in chair cyclohexane

- 6 H are axial (up and down)
- 6 H are equatorial (close to plane of ring)

Rotation about single bonds flips the ring to a boat form

- The boat conformation is less stable because of flagpole interactions and torsional strain along the bottom of the boat

Ring flipping leads to a second chair

Proceeds via boat (or slightly twisted boat)

Every axial position becomes equatorial, and vice versa

Ring flipping occurs rapidly at room temperature
Conformational Energy Diagram for cyclohexane

Energy and Equilibrium

Another view of energy barrier

Drawing Cyclohexanes

Cyclohexane structure can be elaborated

To draw chair cyclohexanes, follow these steps:
1.) Draw the carbon chair. 2.) Add the axial hydrogens.
3.) Draw the C1 and C4 equatorial hydrogens.
4.) Draw the remaining equatorial hydrogens.

Note: kcal/mol x 4.2 = kJ/mol
Diamond = “infinite” cyclohexane rings

Substituted cyclohexanes
Methyl cyclohexane is more stable with the methyl equatorial
- An axial methyl has an unfavorable 1,3-diaxial interaction with
taxial C-H bonds 2 carbons away

More stable by
7.6 kJ/mol
95% eq
at R.T.

Destabilization of axial groups due to steric interactions
In axial methylcyclohexane there are two gauche interactions

Each gauche interaction introduces 3.75 kJ/mol of steric strain

Equatorial groups are free of torsional strain
Equivalent to a staggered butane

Disubstituted cycloalkanes
With two substituents on the ring in different positions, configurational isomers arise
Cis: groups on same side of ring
Trans: groups on opposite side of ring
e.g.: 1,2-dichlorocyclobutane

cis isomer
trans isomer
For 3, 4, or 5 membered rings, can treat as if planar

1,3-dimethylcyclopentane

```
CH3
CH3
H  H
CH   CH
H  H
```

**Preferred conformations**

Trans-1,4-dimethylcyclohexane prefers trans diequatorial conformation

```
H  H
CH3  CH3
```

Cis-1,4-dimethylcyclohexane exists in an axial-equatorial conformation

```
H  H
CH3  CH3
```

Note methyls on opposite sides of ring

**Confirming whether cis or trans**

Test one: identify each substituent as on the upper or lower side of ring

Test Two: Flatten the Ring

```
CH3
H  
CH
H
```

Since the two bonds to the CH3 groups are "upper", meaning same side, they are "cis."

```
CH3
H  
CH
H
```

Since the CH3 groups are on the same side, they are "cis."

**Is diequatorial always trans?**

Diequatorial isomer

```
trans
```

```
cis
```

```
trans
```

```
cis
```
**Trans 1,2 dimethylcyclohexane: an energy analysis**

1,2-dimethylcyclohexane

1,2-dienitol

1,2-dienoic acid

Each axial methyl group generates 2 x 3.75 kJ/mol of strain energy, for a total of 7.5 kJ/mol.

But the energy difference between the 1,2-axial and the 1,2-diequatorial conformations is only 3 gauche interactions or 3 x 3.75 kJ/mol.

There is one gauche interaction from the interacting CH₃ groups.

**Synthesis of Alkanes and Cycloalkanes**

2. Reduction of Alkyl Halides

R−X + Zn + HX → R−H + ZnX₂

or

R−X − ZnX₂ (ZnX₂)

2 CH₃CH₂CH₂CH₃ + Br₂ → 2 CH₃CH₂CH₂CH₂Br + H₂

See: Butyl bromide (2-bromobutane)

**Steroid backbone**

Cholesterol

**Bicyclic and Polycyclic Alkanes**

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

**Synthesis of Alkanes and Cycloalkanes**

1. Hydrogenation of Alkenes and Alkynes

General Reaction

Alkene + H₂ → Alkane

CH₃CH₃→ CH₃CH₂H₂

2-Methylpropane

Isobutane

3. Alkylation of Terminal Alkynes

- Alkynes can be subsequently hydrogenated to alkanes

R−C≡C−H + Na⁺[Br⁻] −→ R−C≡C−Br

R−C≡C−H + Na⁺[Cl⁻] −→ R−C≡C−Cl

R−C≡C−H + Na⁺[Br⁻] −→ R−C≡C−Br

R−C≡C−H + Na⁺[Cl⁻] −→ R−C≡C−Cl

CH₃CH₃CH₃→ CH₃CH₃CH₃

Butane

Butane

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2. Reduction of Alkyl Halides

R−X + Zn + HX → R−H + ZnX₂

or

R−X + ZnX₂ −→ R−H

2 CH₃CH₂CH₂CH₃ + Br₂ → 2 CH₃CH₂CH₂CH₂Br + H₂

See: Butyl bromide (2-bromobutane)
The synthetic scheme is formulated working backward from the target molecule to a simple starting material. Often several schemes are possible.