B.Sc.(H) Chemistry
Semester - II
Core Course - III (CC-III)
Organic Chemistry - I

# III. Chemistry of Aliphatic Hydrocarbons
## A. Carbon-Carbon sigma bonds

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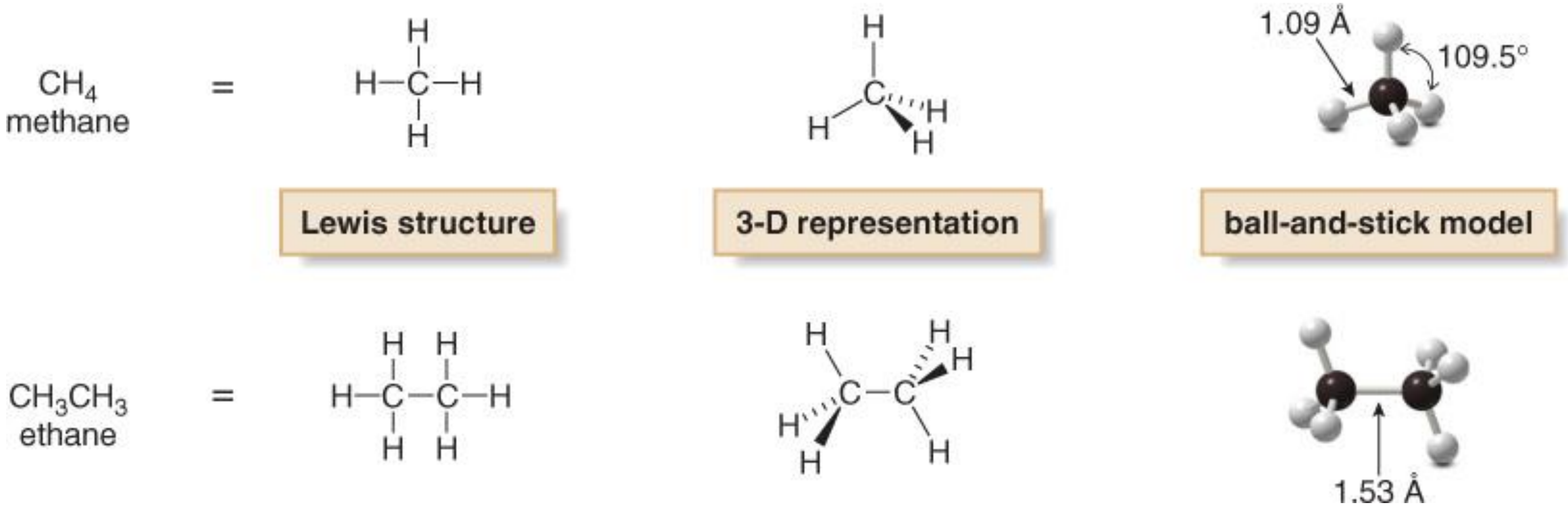
# Alkanes

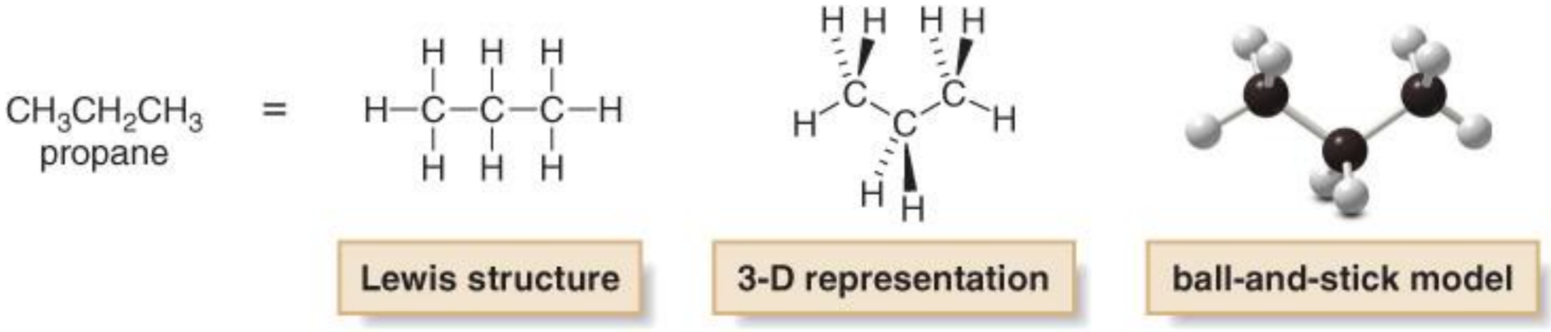
## Introduction

- **Recall that alkanes are aliphatic hydrocarbons having C—C and C—H σ bonds. They can be categorized as acyclic or cyclic.**
- **Acyclic alkanes have the molecular formula $C_nH_{2n+2}$ (where n = an integer) and contain only linear and branched chains of carbon atoms. They are also called saturated hydrocarbons because they have the maximum number of hydrogen atoms per carbon.**
- **Cycloalkanes contain carbons joined in one or more rings. Because their general formula is $C_nH_{2n}$, they have two fewer H atoms than an acyclic alkane with the same number of carbons.**

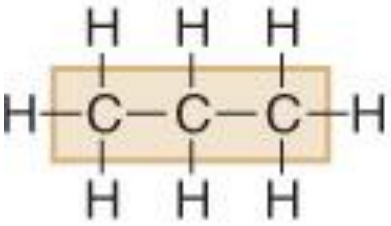
- **All C atoms in an alkane are surrounded by four groups, making them *sp*$^3$ hybridized and tetrahedral, and all bond angles are 109.5°.**
- **The 3-D representations and ball-and-stick models for these alkanes indicate the tetrahedral geometry around each C atom. In contrast, the Lewis structures are not meant to imply any 3-D arrangement. Additionally, in propane and higher molecular weight alkanes, the carbon skeleton can be drawn in a variety of ways and still represent the same molecule.**



- **The three-carbon alkane $CH_3CH_2CH_3$, called propane, has a molecular formula $C_3H_8$. Note in the 3-D drawing that each C atom has two bonds in the plane (solid lines), one bond in front (on a wedge) and one bond behind the plane (on a dashed line).**



- **Additionally, in propane and higher molecular weight alkanes, the carbon skeleton can be drawn in a variety of ways and still represent the same molecule. For example, the three carbons of propane can be drawn in a horizontal row or with a bend. These representations are equivalent.**
- **In a Lewis structure, the bends in a carbon chain don’t matter.**



3 C’s in a row

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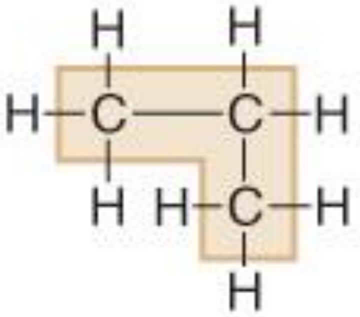
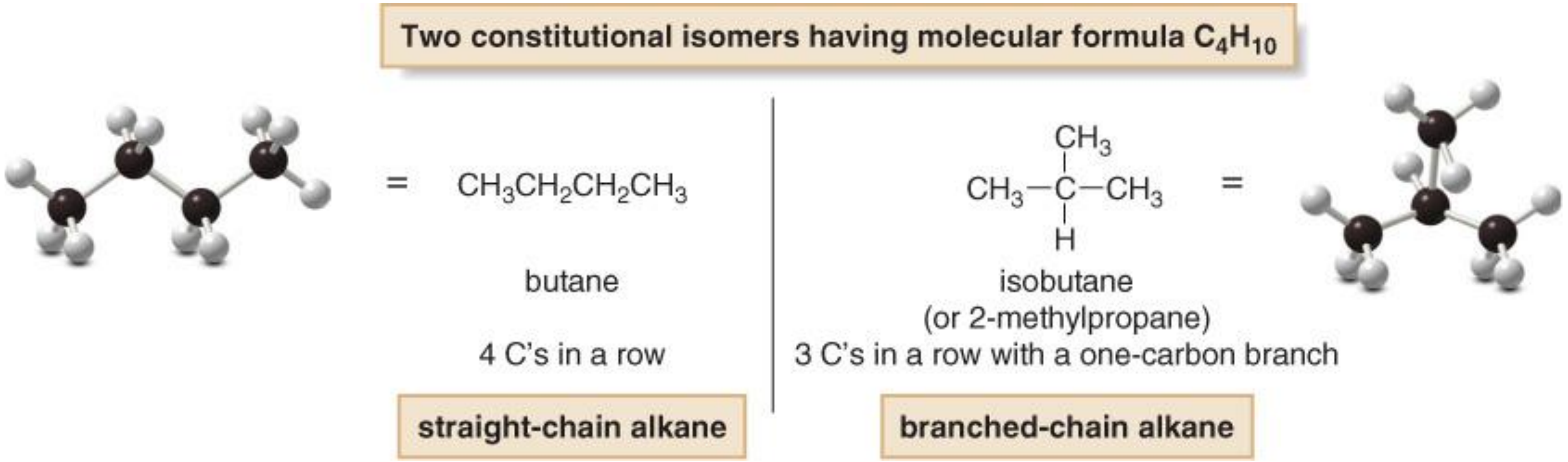


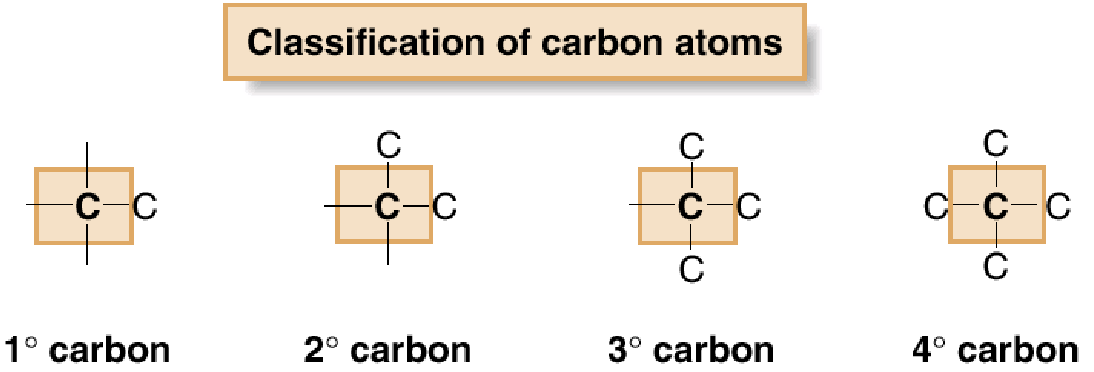
3 C’s with a bend

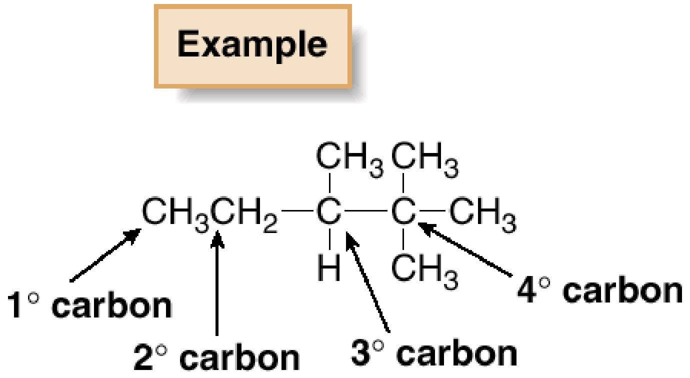
- **There are two different ways to arrange four carbons, giving two compounds with molecular formula $C_4H_{10}$, named butane and isobutane.**
- **Butane and isobutane are isomers—two different compounds with the same molecular formula. Specifically, they are constitutional or structural isomers.**
- **Constitutional isomers differ in the way the atoms are connected to each other.**



- **Carbon atoms in alkanes and other organic compounds are classified by the number of other carbons directly bonded to them.**

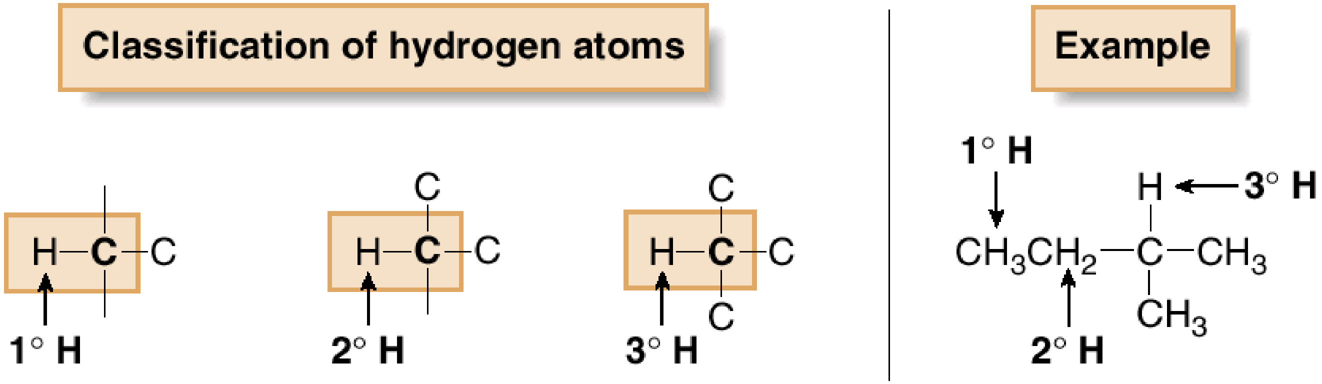
- A *primary carbon* (1° carbon) is bonded to *one* other C atom.
- A *secondary carbon* (2° carbon) is bonded to *two* other C atoms.
- A *tertiary carbon* (3° carbon) is bonded to *three* other C atoms.
- A *quaternary carbon* (4° carbon) is bonded to *four* other C atoms.





- **Hydrogen atoms are classified as primary (1°), secondary (2°), or tertiary (3°) depending on the type of carbon atom to which they are bonded.**

- A *primary hydrogen* (1° H) is on a C bonded to one other C atom.
- A *secondary hydrogen* (2° H) is on a C bonded to two other C atoms.
- A *tertiary hydrogen* (3° H) is on a C bonded to three other C atoms.



$$CH_3CH_2-\overset{H}{\underset{CH_3}{C}}-CH_3$$

- **The maximum number of possible constitutional isomers increases dramatically as the number of carbon atoms in the alkane increases. For example, there are 75 possible isomers for an alkane having 10 carbon atoms, but 366,319 possible isomers for one having 20 carbons.**
- **The suffix “ane” identifies a molecule as an alkane.**
- **By increasing the number of carbons in an alkane by a $CH_2$ group, one obtains a “homologous series” of alkanes, as shown in Table 4.1. The $CH_2$ group is called “methylene.”**

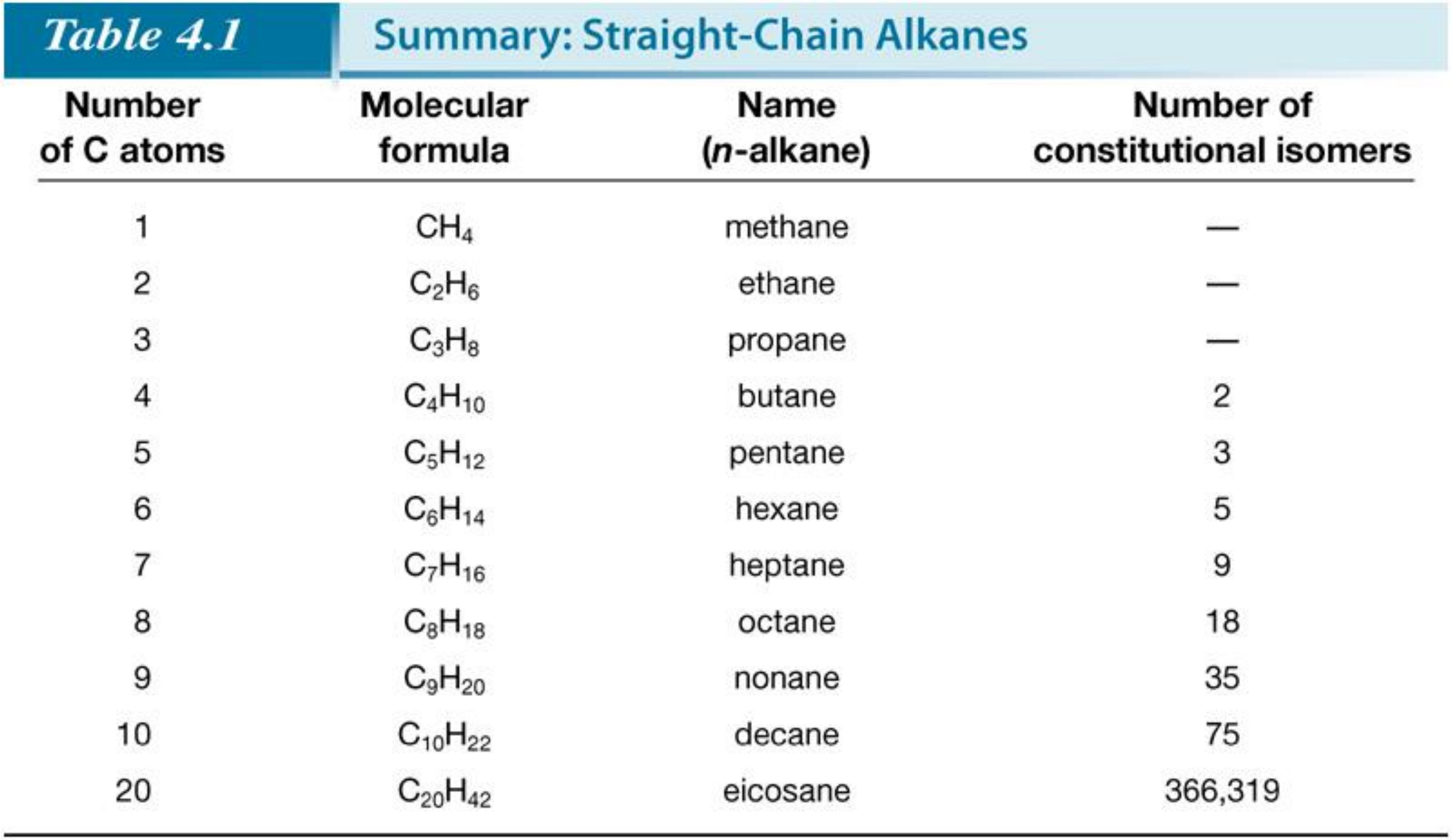


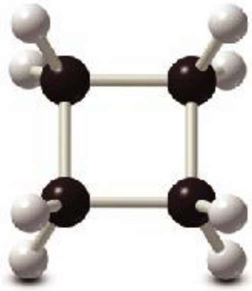
**Table 4.1** Summary: Straight-Chain Alkanes

| Number of C atoms | Molecular formula | Name (*n*-alkane) | Number of constitutional isomers |
|---|---|---|---|
| 1 | $CH_4$ | methane | — |
| 2 | $C_2H_6$ | ethane | — |
| 3 | $C_3H_8$ | propane | — |
| 4 | $C_4H_{10}$ | butane | 2 |
| 5 | $C_5H_{12}$ | pentane | 3 |
| 6 | $C_6H_{14}$ | hexane | 5 |
| 7 | $C_7H_{16}$ | heptane | 9 |
| 8 | $C_8H_{18}$ | octane | 18 |
| 9 | $C_9H_{20}$ | nonane | 35 |
| 10 | $C_{10}H_{22}$ | decane | 75 |
| 20 | $C_{20}H_{42}$ | eicosane | 366,319 |

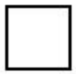
## Cycloalkanes

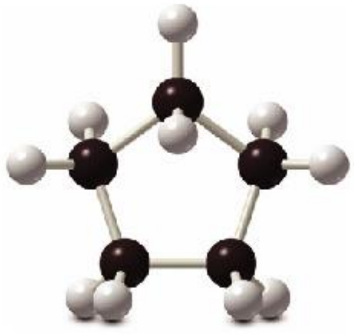
**Cycloalkanes have molecular formula $C_nH_{2n}$ and contain carbon atoms arranged in a ring. Simple cycloalkanes are named by adding the prefix *cyclo-* to the name of the acyclic alkane having the same number of carbons.**

cyclopropane
$C_3H_6$

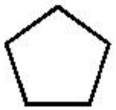


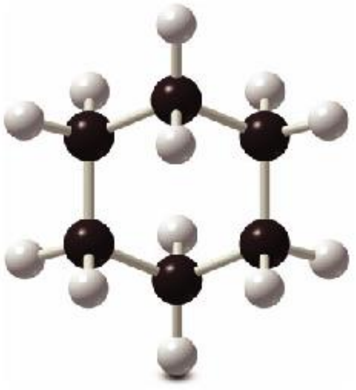
cyclobutane
$C_4H_8$



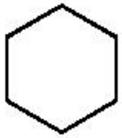


cyclopentane
$C_5H_{10}$





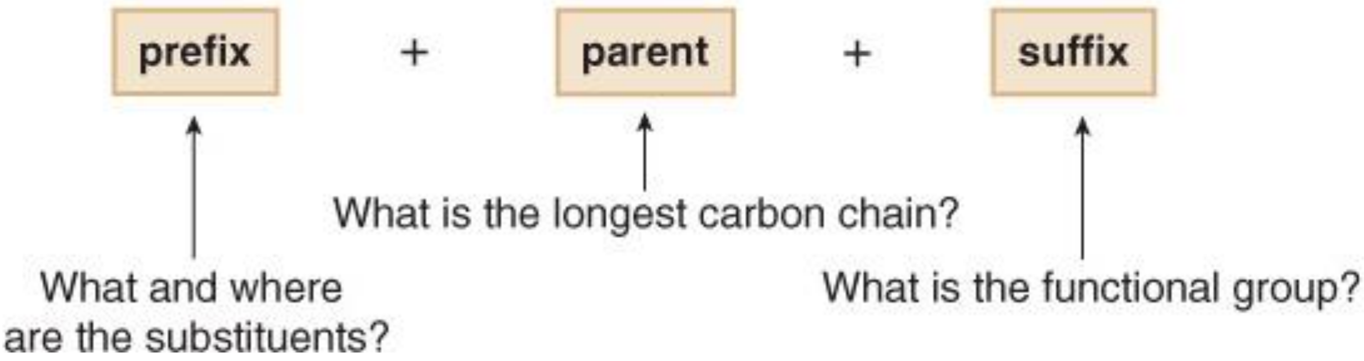
cyclohexane
$C_6H_{12}$



# Nomenclature

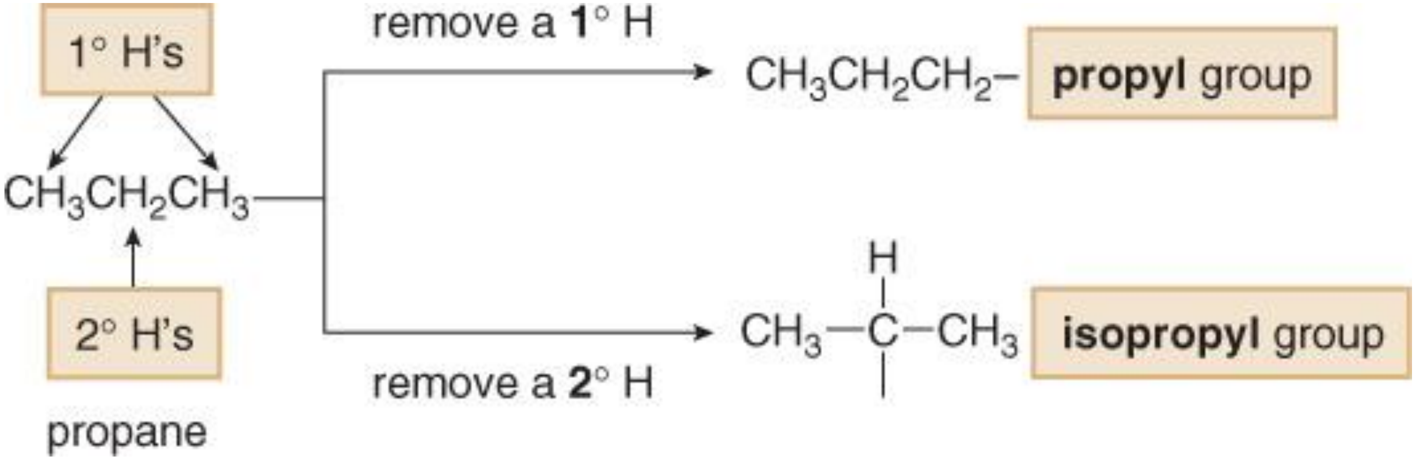
The name of every organic molecule has 3 parts:

1. The parent name indicates the number of carbons in the longest continuous chain.
2. The suffix indicates what functional group is present.
3. The prefix tells us the identity, location, and number of substituents attached to the carbon chain.

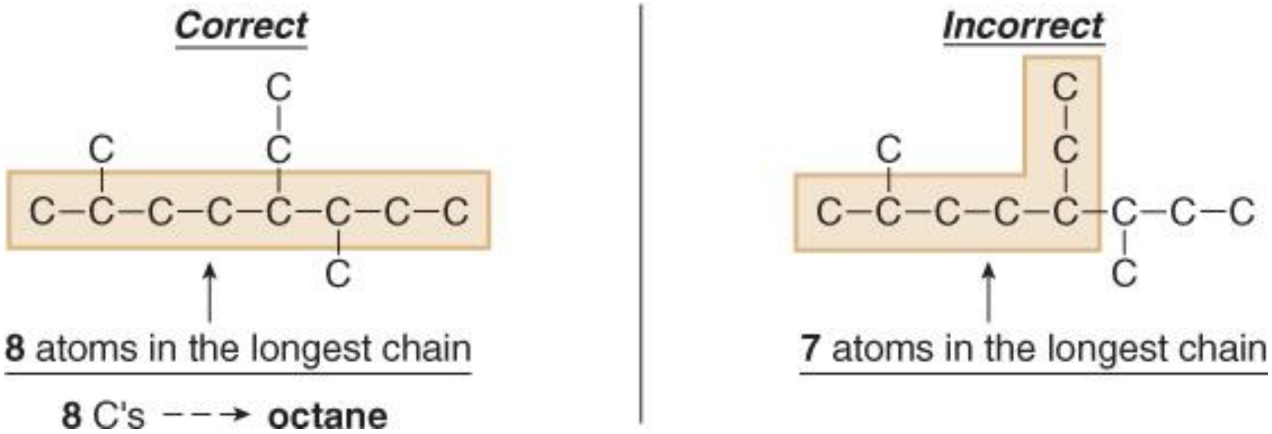


- **Carbon substituents bonded to a long carbon chain are called alkyl groups.**
- **An alkyl group is formed by removing one H atom from an alkane.**
- **To name an alkyl group, change the –*ane* ending of the parent alkane to –*yl*. Thus, methane ($CH_4$) becomes methyl ($CH_3$-) and ethane ($CH_3CH_3$) becomes ethyl ($CH_3CH_2$-).**

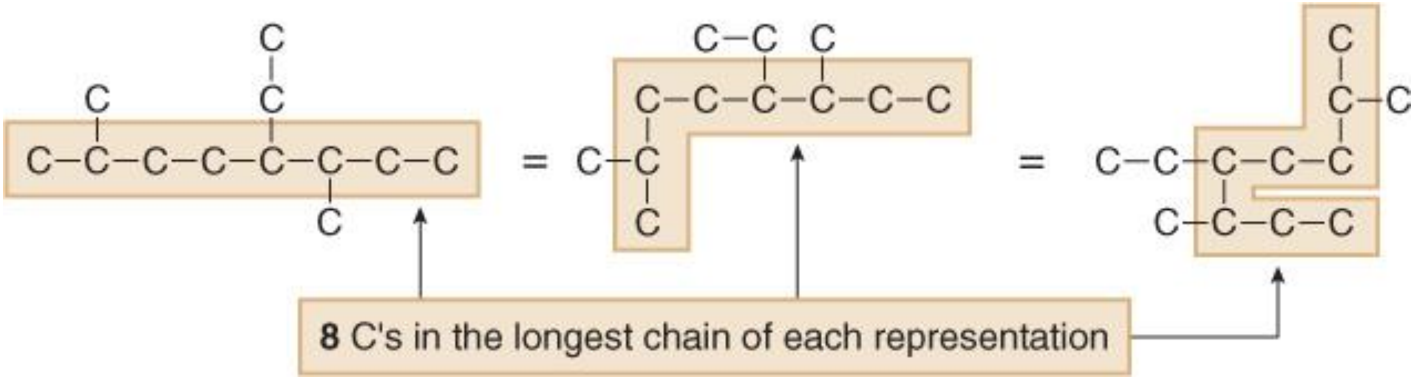
**Naming three- or four-carbon alkyl groups is more complicated because the parent hydrocarbons have more than one type of hydrogen atom. For example, propane has both 1° and 2° H atoms, and removal of each of these H atoms forms a different alkyl group with a different name, propyl or isopropyl.**



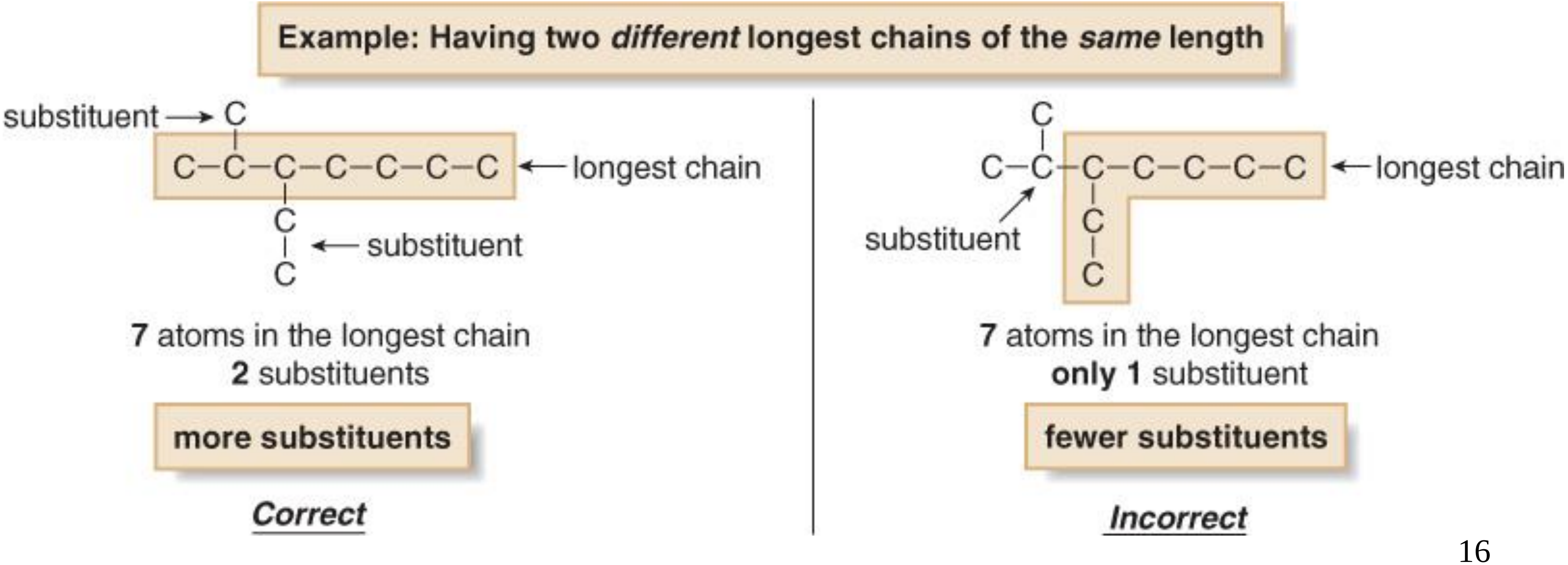
## 1. Find the parent carbon chain and add the suffix.



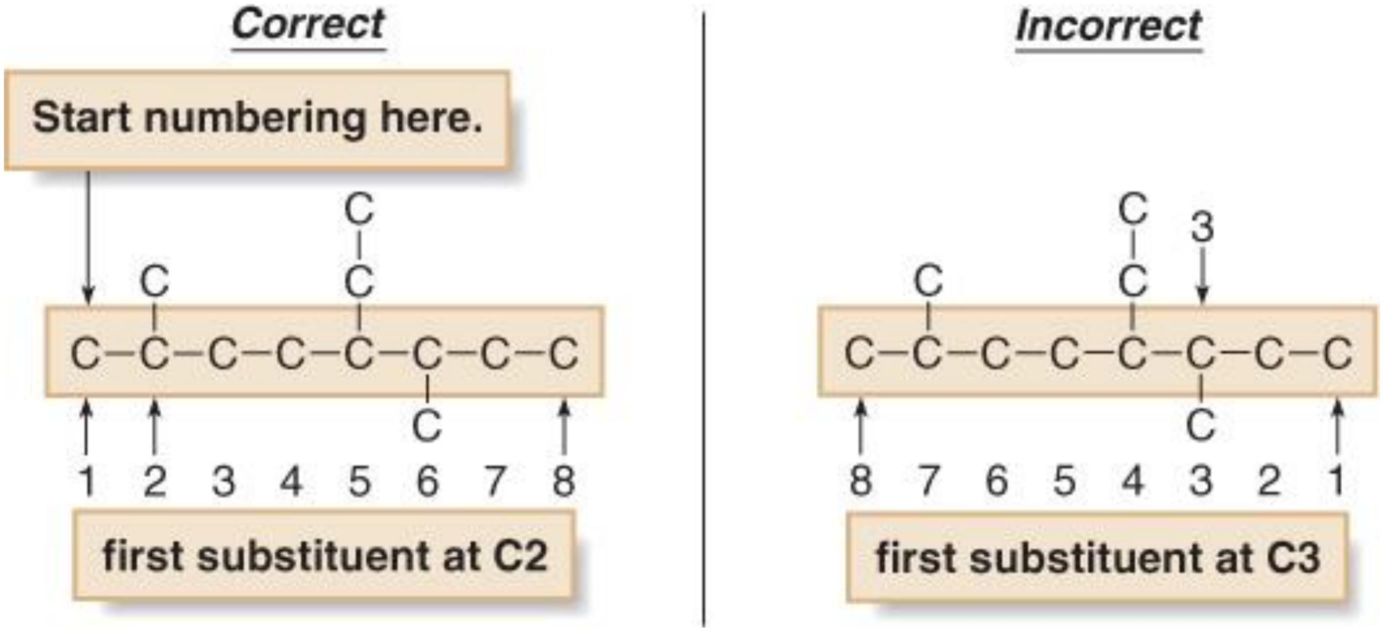
## Note that it does not matter if the chain is straight or it bends.



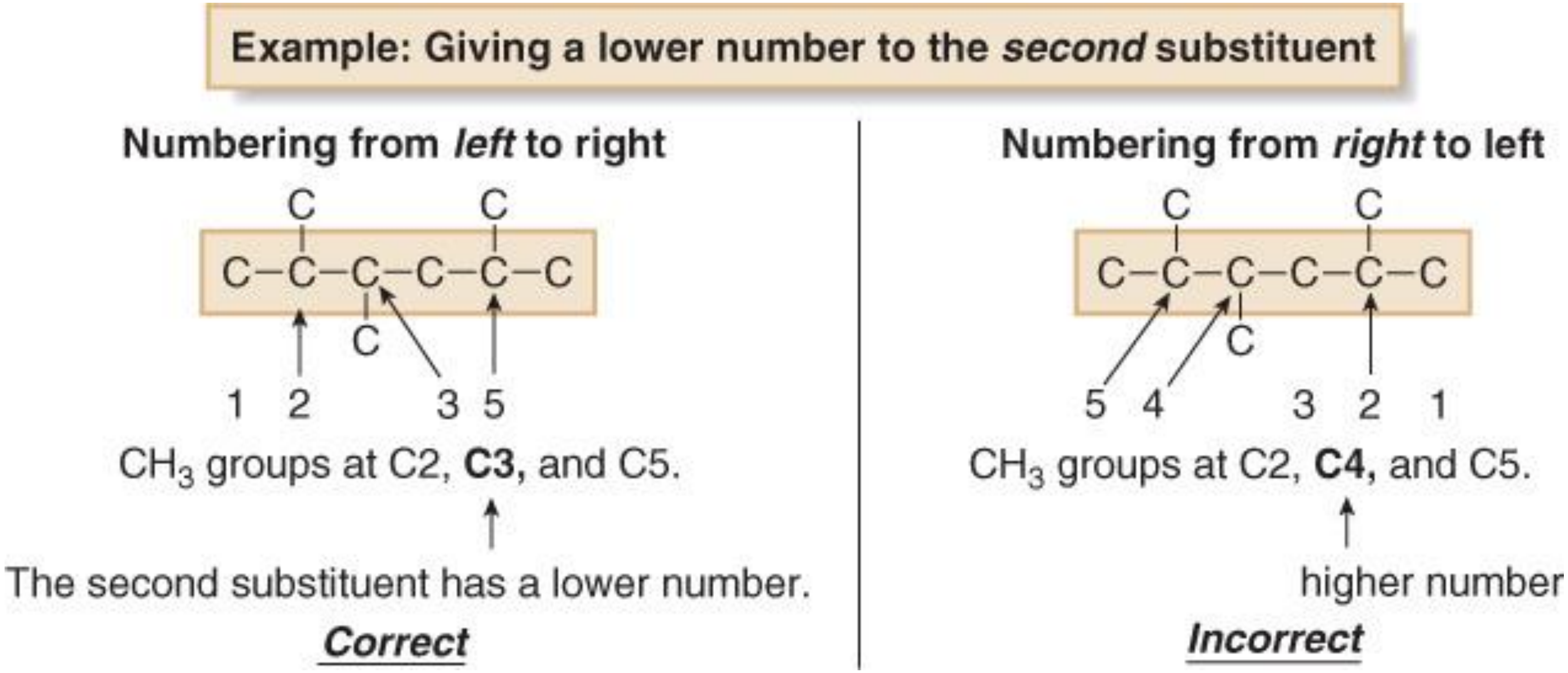
**Also note that if there are two chains of equal length, pick the chain with more substituents. In the following example, two different chains in the same alkane have seven C atoms. We circle the longest continuous chain as shown in the diagram on the left, since this results in the greater number of substituents.**



2. **Number the atoms in the carbon chain to give the first substituent the lowest number.**



**If the first substituent is the same distance from both ends, number the chain to give the second substituent the lower number.**

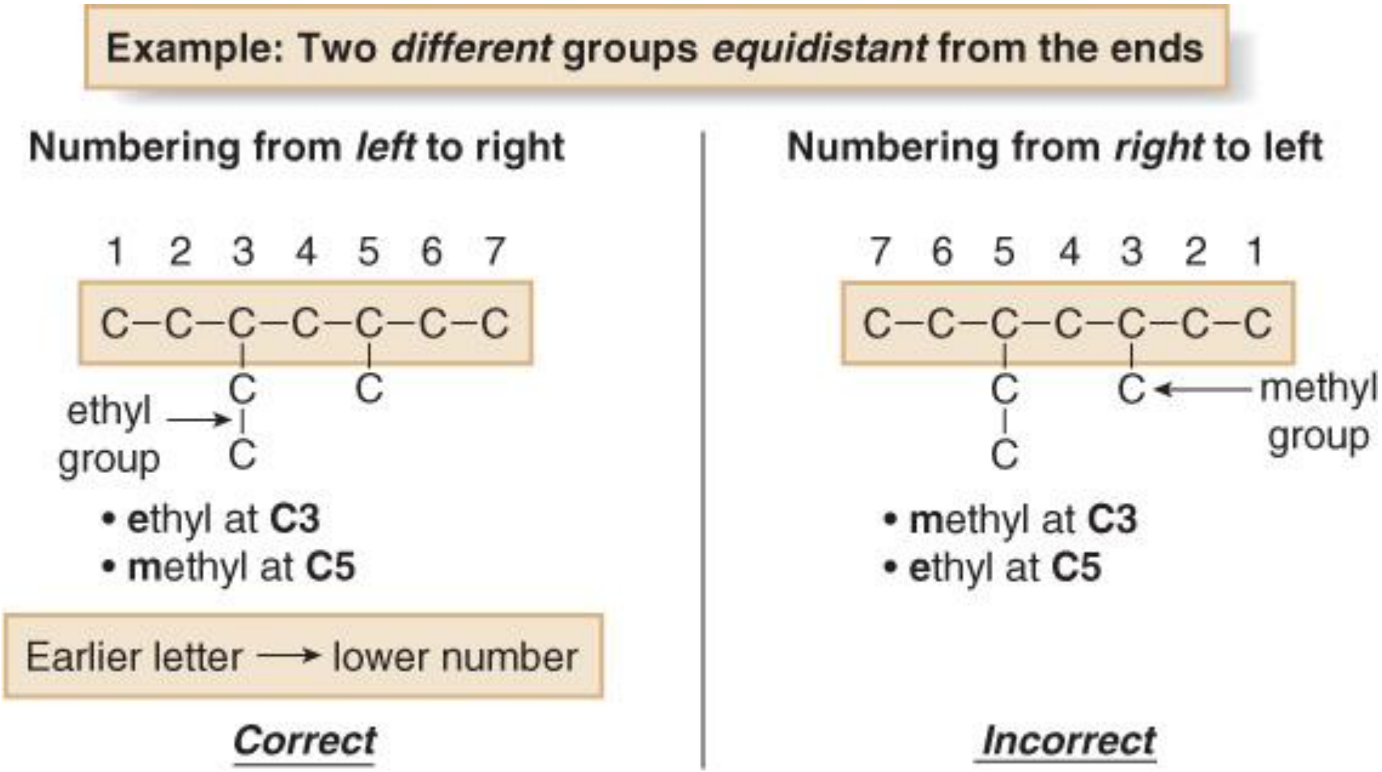


$CH_3$ groups at C2, **C3,** and C5.

The second substituent has a lower number.

$CH_3$ groups at C2, **C4,** and C5.

**When numbering a carbon chain results in the same numbers from either end of the chain, assign the lower number alphabetically to the first substituent.**


Example: Two *different* groups *equidistant* from the ends

Numbering from *left* to right

- ethyl at **C3**
- methyl at **C5**

Earlier letter → lower number

*Correct*

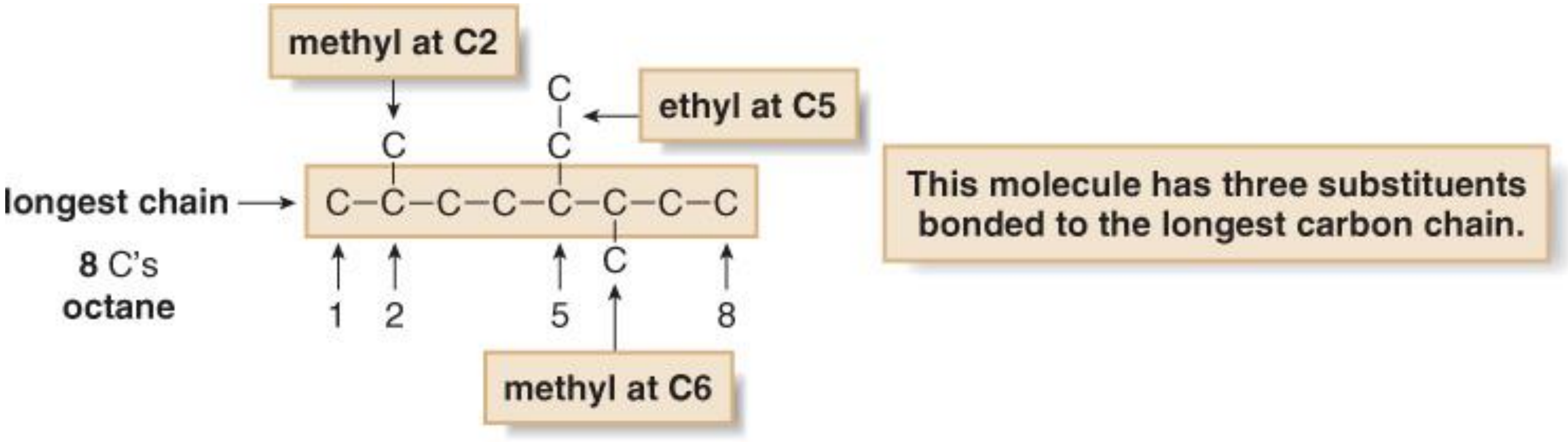
Numbering from *right* to left

- methyl at **C3**
- ethyl at **C5**

*Incorrect*

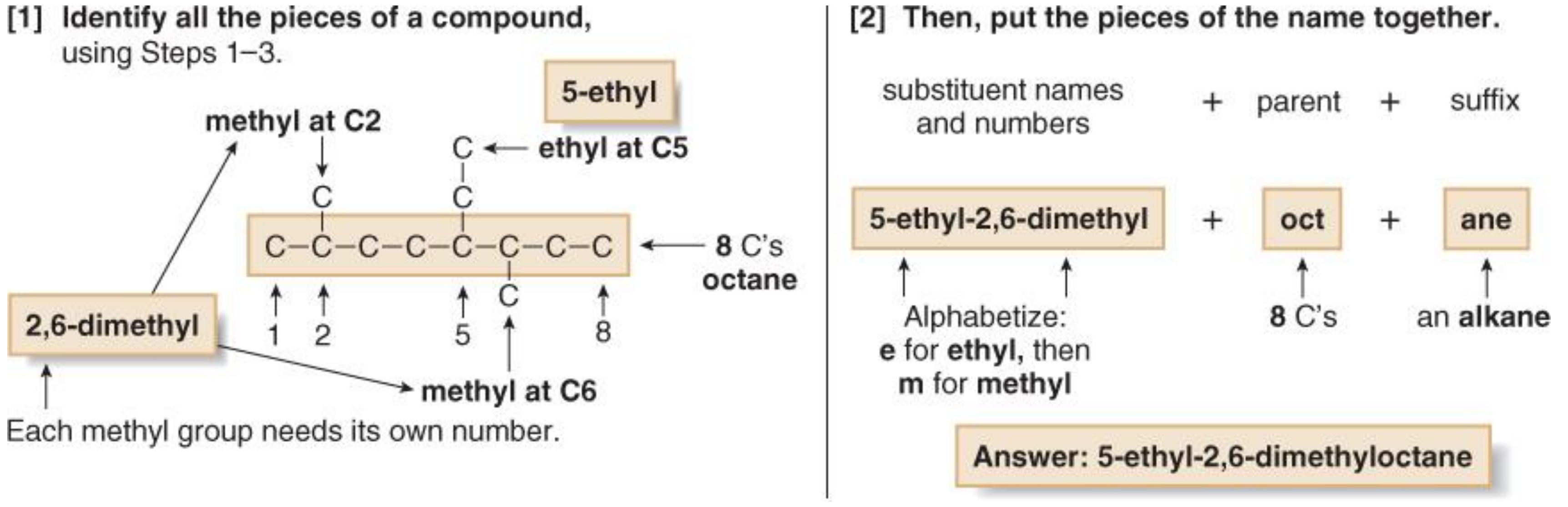
# 3. Name and number the substituents.

- **Name the substituents as alkyl groups.**
- **Every carbon belongs to either the longest chain or a substituent, not both.**
- **Each substituent needs its own number.**
- **If two or more identical substituents are bonded to the longest chain, use prefixes to indicate how many: di- for two groups, tri- for three groups, tetra- for four groups, and so forth.**



## 4. Combine substituent names and numbers + parent and suffix.

- **Precede the name of the parent by the names of the substituents.**
- **Alphabetize the names of the substituents, ignoring all prefixes except iso, as in isopropyl and isobutyl.**
- **Precede the name of each substituent by the number that indicates its location.**
- **Separate numbers by commas and separate numbers from letters by hyphens. The name of an alkane is a single word, with no spaces after hyphens and commas.**

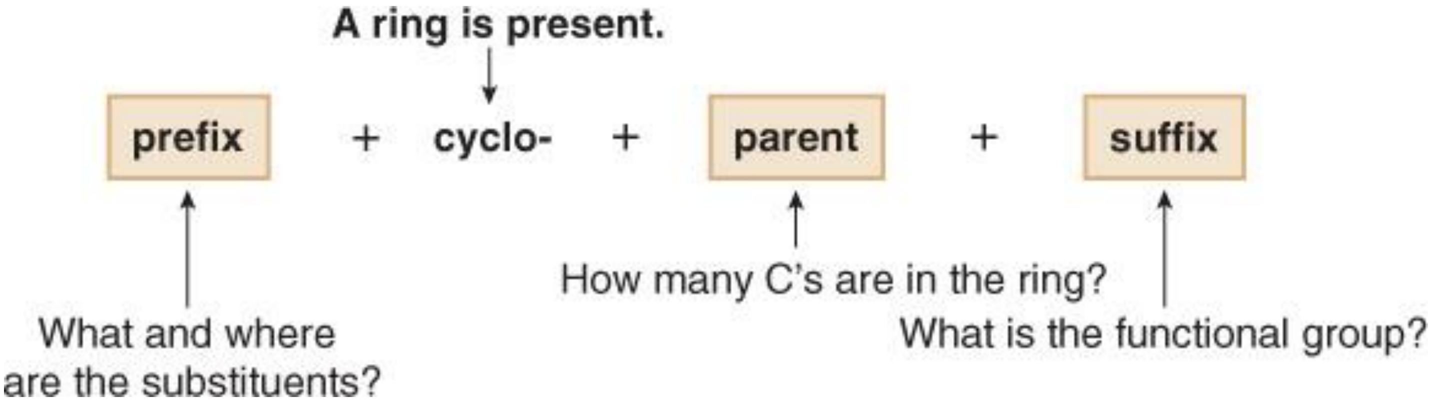


**[1] Identify all the pieces of a compound,** using Steps 1–3.

**[2] Then, put the pieces of the name together.**

**Answer: 5-ethyl-2,6-dimethyloctane**

**Cycloalkanes are named by using similar rules, but the prefix cyclo- immediately precedes the name of the parent.**



A ring is present.

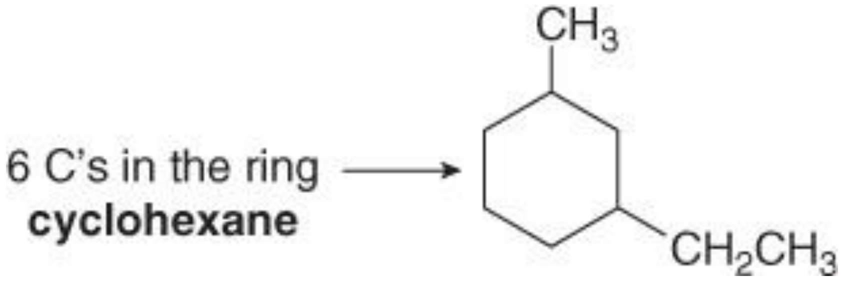
prefix + cyclo- + parent + suffix

What and where are the substituents?

How many C's are in the ring?

What is the functional group?

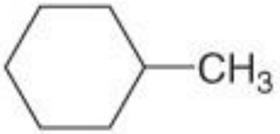
## 1. Find the parent cycloalkane.



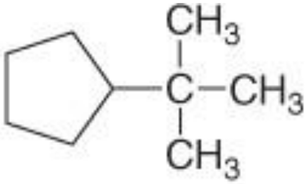
6 C's in the ring

**cyclohexane**

**2. Name and number the substituents. No number is needed to indicate the location of a single substituent.**



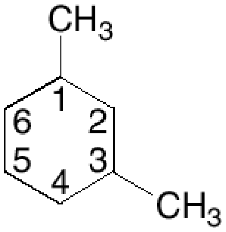
methylcyclohexane



*tert*-butylcyclopentane

**For rings with more than one substituent, begin numbering at one substituent and proceed around the ring to give the second substituent the lowest number.**

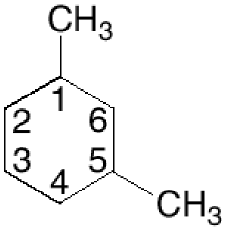
**numbering clockwise**



$CH_3$ groups at C1 and **C3**
The 2nd substituent has a lower number.

***Correct:*** **1,3-dimethylcyclohexane**

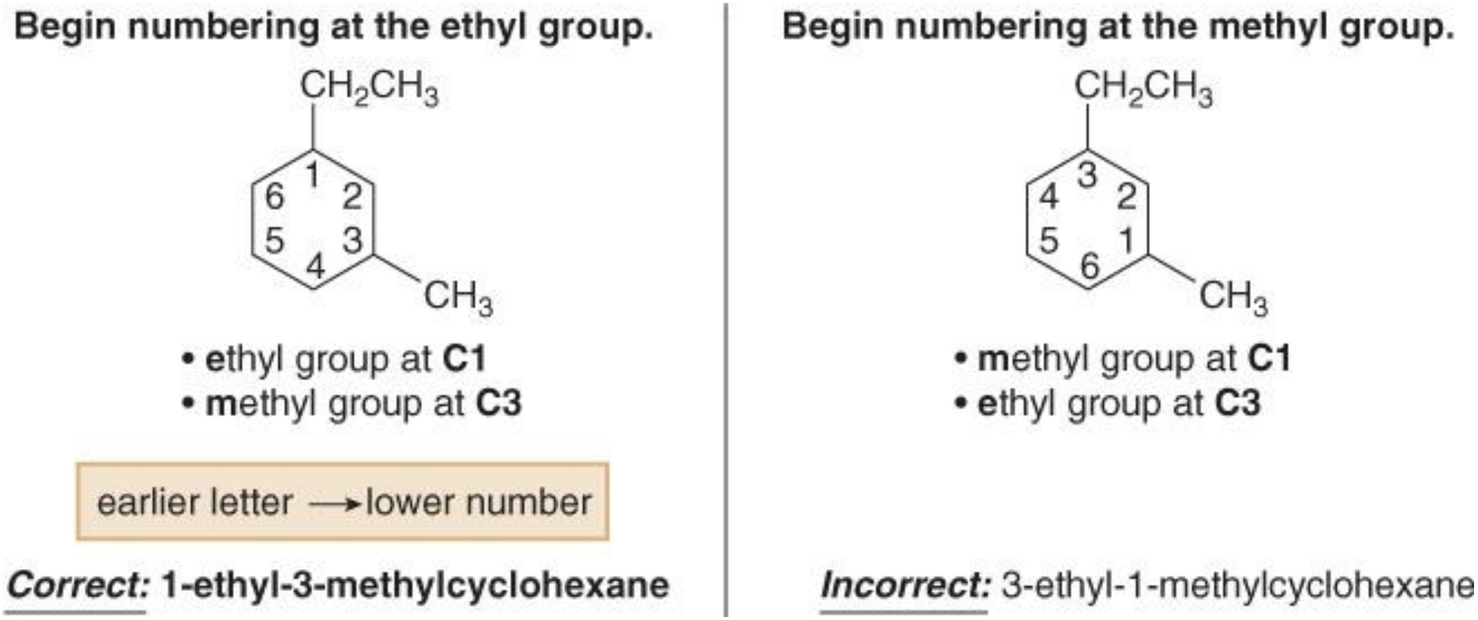
**numbering counterclockwise**



$CH_3$ groups at C1 and **C5**

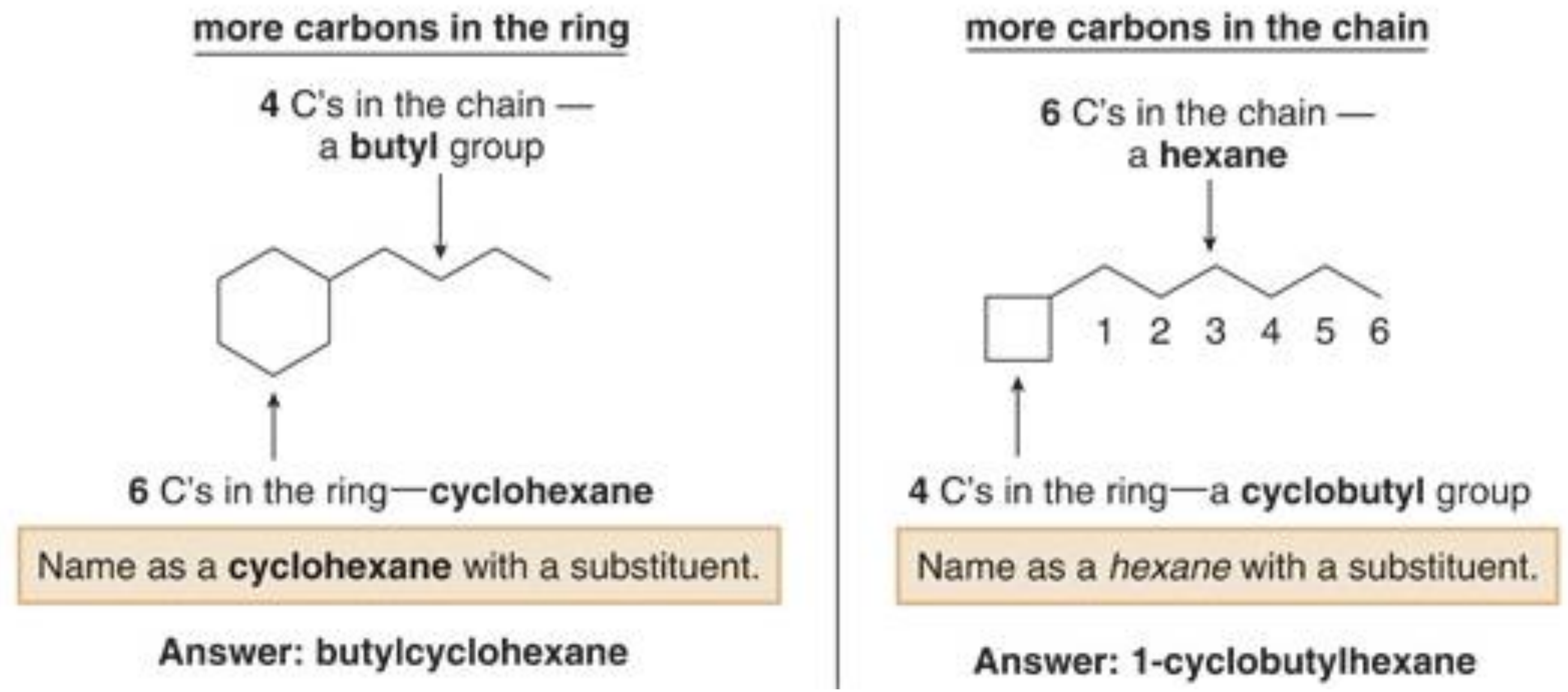
***Incorrect:*** 1,5-dimethylcyclohexane

With two different substituents, number the ring to assign the lower number to the substituents alphabetically.



Note the special case of an alkane composed of both a ring and a long chain. If the number of carbons in the ring is greater than or equal to the number of carbons in the longest chain, the compound is named as a cycloalkane.

Figure 4.2
Two contrasting examples—
Naming compounds containing both a ring
and a long chain
of carbon atoms



**more carbons in the ring**

**4** C's in the chain —
a **butyl** group

**6** C's in the ring—**cyclohexane**

Name as a **cyclohexane** with a substituent.

**Answer: butylcyclohexane**

**more carbons in the chain**

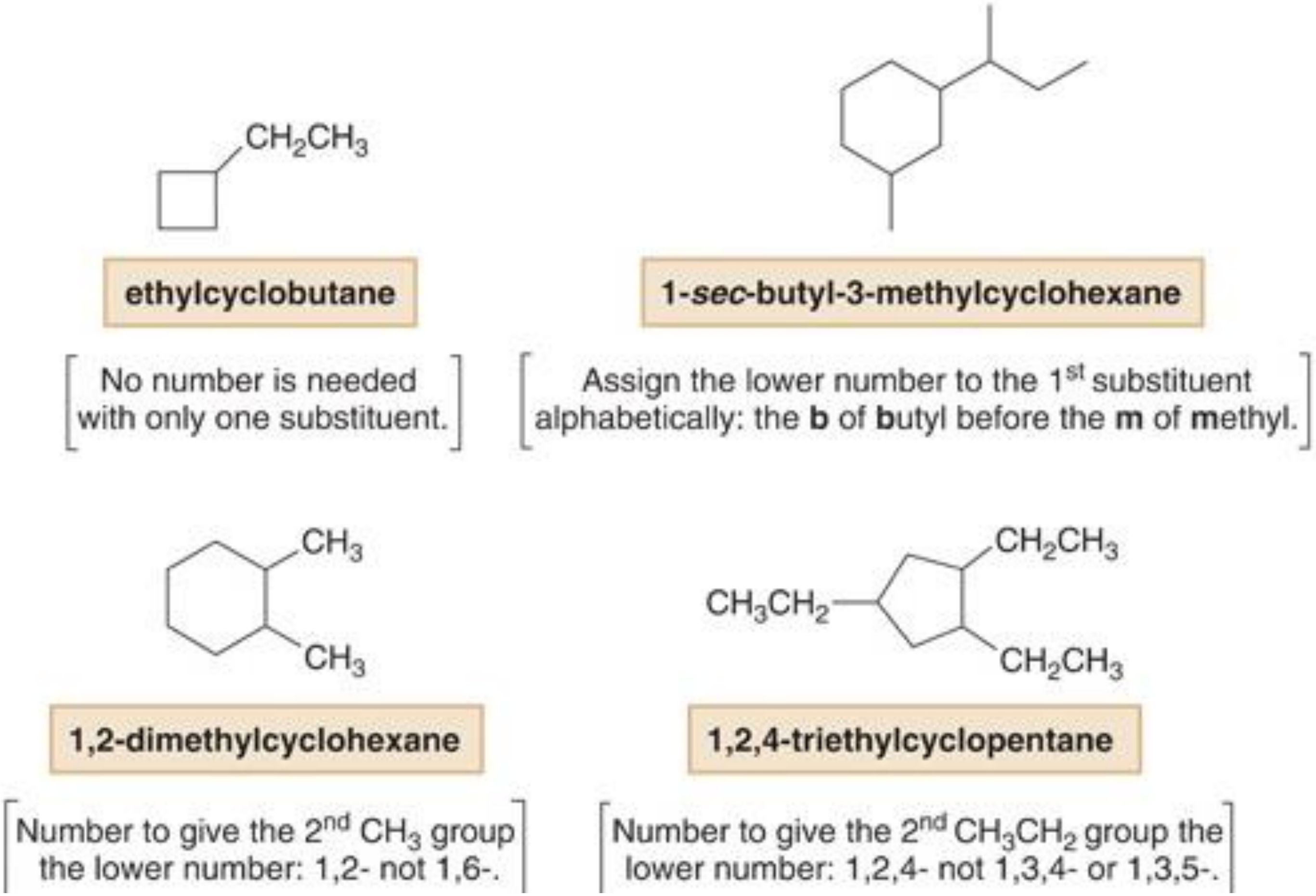
**6** C's in the chain —
a **hexane**

**4** C's in the ring—a **cyclobutyl** group

Name as a *hexane* with a substituent.

**Answer: 1-cyclobutylhexane**

Figure 4.3
Examples of cycloalkane nomenclature



**ethylcyclobutane**

No number is needed with only one substituent.

**1-*sec*-butyl-3-methylcyclohexane**

Assign the lower number to the 1st substituent alphabetically: the **b** of **butyl** before the **m** of **methyl**.

**1,2-dimethylcyclohexane**

Number to give the 2nd $CH_3$ group the lower number: 1,2- not 1,6-.

**1,2,4-triethylcyclopentane**

Number to give the 2nd $CH_3CH_2$ group the lower number: 1,2,4- not 1,3,4- or 1,3,5-.

# Nomenclature—Common Names

Some organic compounds are identified using common names that do not follow the IUPAC system of nomenclature. Many of these names were given long ago before the IUPAC system was adopted, and are still widely used. Additionally, some names are descriptive of shape and structure, like those below:

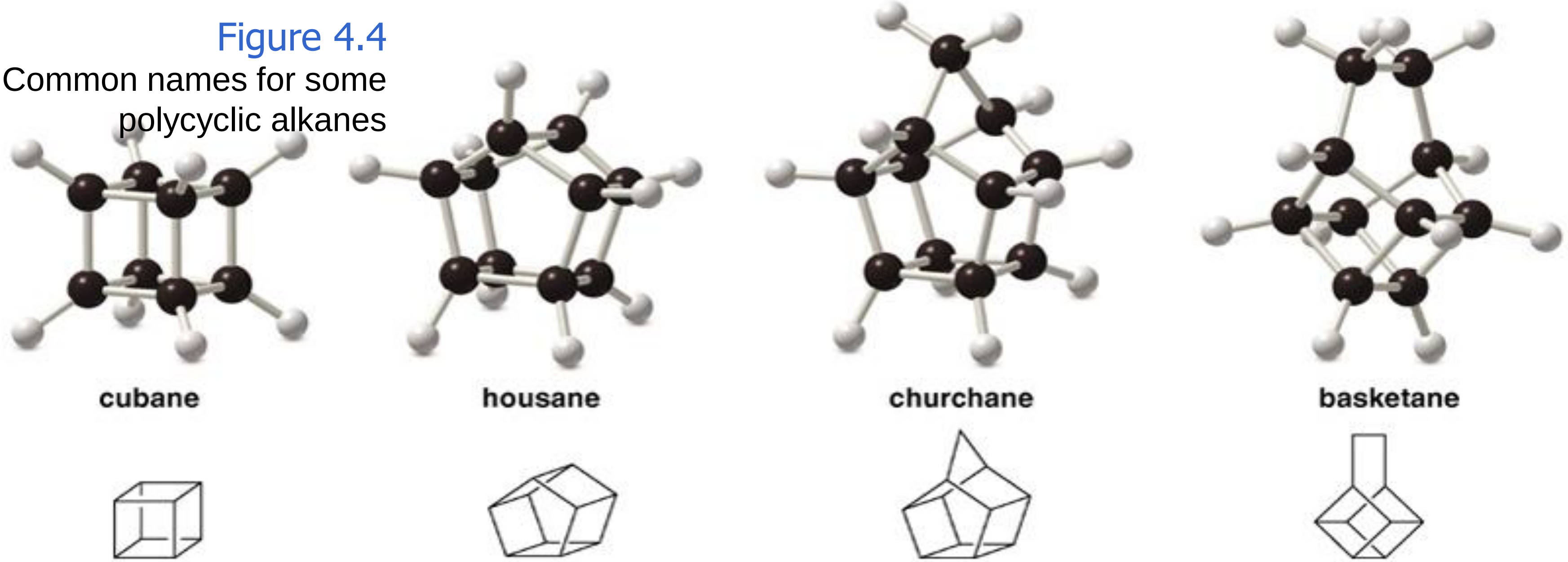


Figure 4.4
Common names for some polycyclic alkanes

# Physical Properties of Alkanes

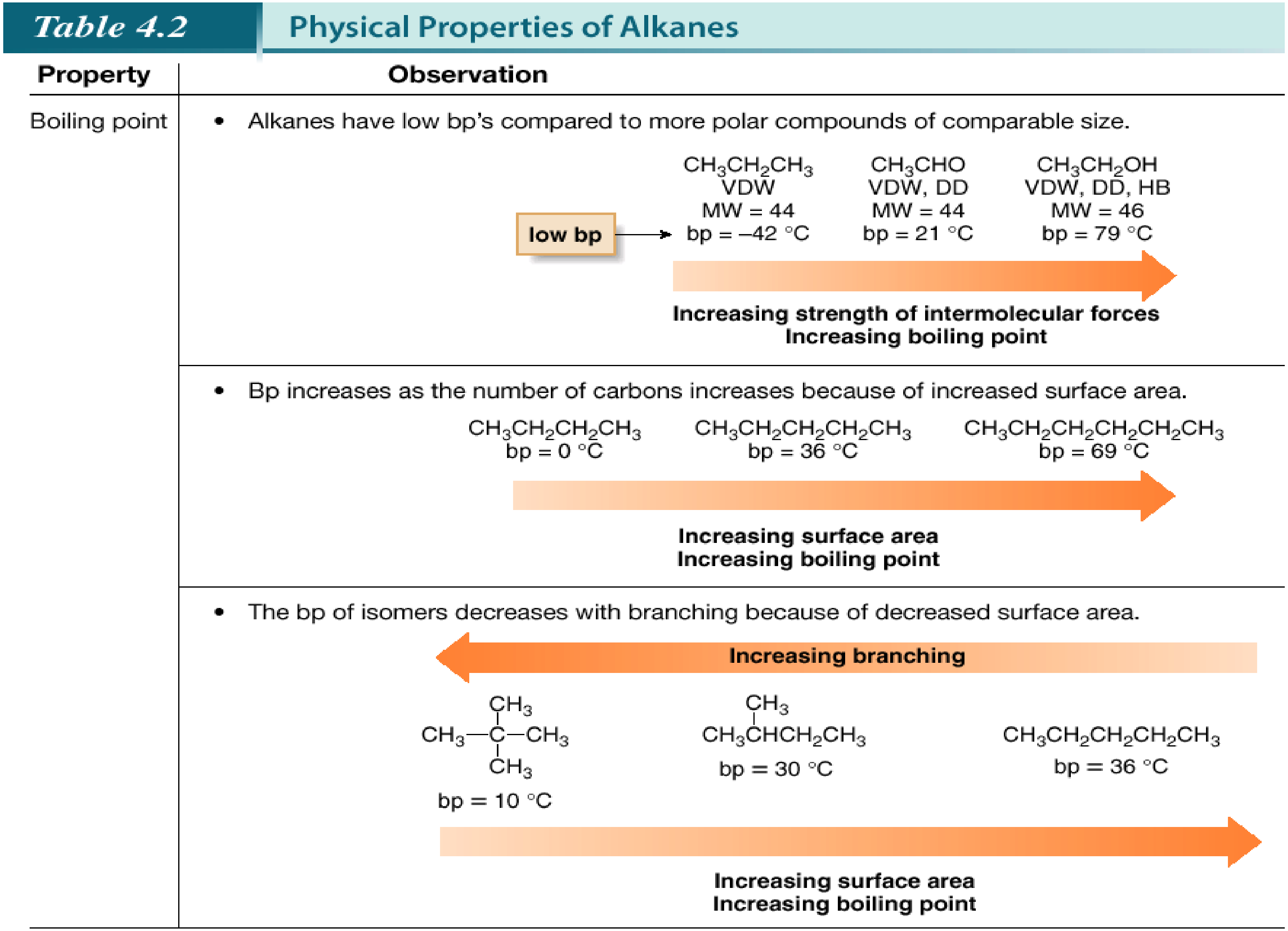


**Table 4.2** **Physical Properties of Alkanes**

| Property | Observation |
|---|---|
| Boiling point | • Alkanes have low bp's compared to more polar compounds of comparable size.<br>**low bp** → $CH_3CH_2CH_3$ VDW MW = 44 bp = –42 °C<br>$CH_3CHO$ VDW, DD MW = 44 bp = 21 °C<br>$CH_3CH_2OH$ VDW, DD, HB MW = 46 bp = 79 °C<br>**Increasing strength of intermolecular forces**<br>**Increasing boiling point** |
|  | • Bp increases as the number of carbons increases because of increased surface area.<br>$CH_3CH_2CH_2CH_3$ bp = 0 °C<br>$CH_3CH_2CH_2CH_2CH_3$ bp = 36 °C<br>$CH_3CH_2CH_2CH_2CH_2CH_3$ bp = 69 °C<br>**Increasing surface area**<br>**Increasing boiling point** |
|  | • The bp of isomers decreases with branching because of decreased surface area.<br>**Increasing branching**<br>$CH_3-C(CH_3)_2-CH_3$ bp = 10 °C<br>$CH_3CH(CH_3)CH_2CH_3$ bp = 30 °C<br>$CH_3CH_2CH_2CH_2CH_3$ bp = 36 °C<br>**Increasing surface area**<br>**Increasing boiling point** |

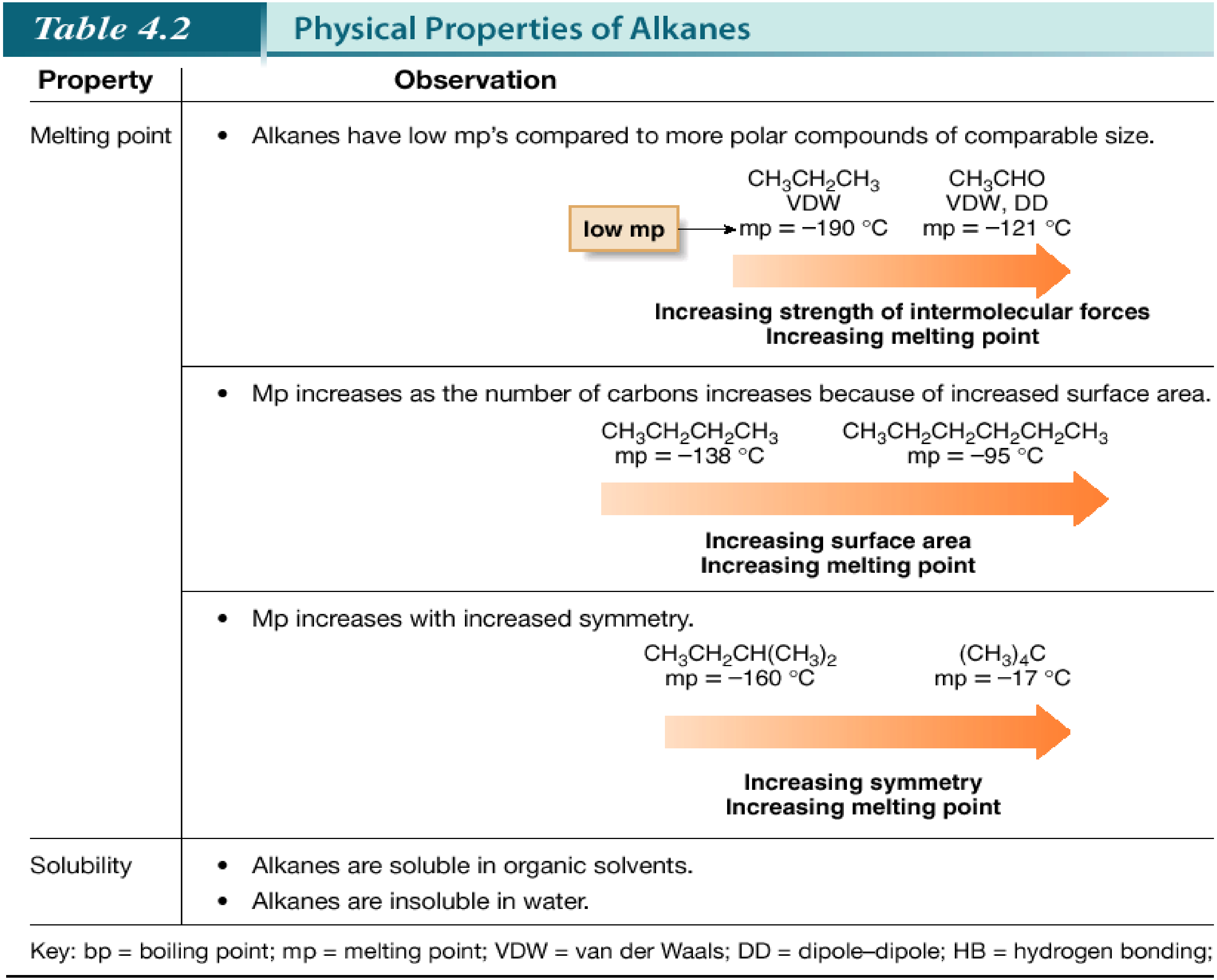


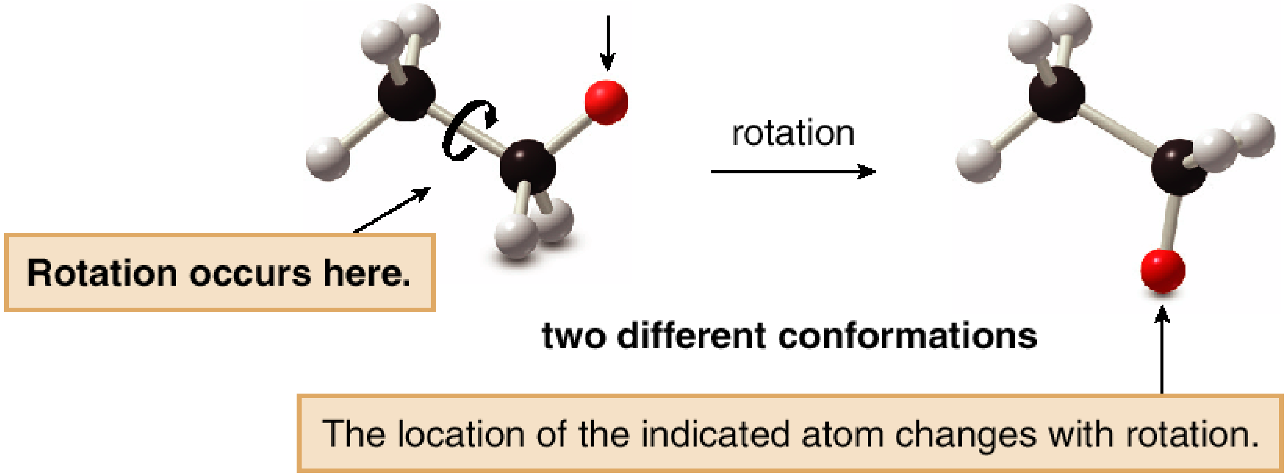
**Table 4.2** Physical Properties of Alkanes

| Property | Observation |
|---|---|
| Melting point | • Alkanes have low mp's compared to more polar compounds of comparable size.<br>**low mp** → $CH_3CH_2CH_3$ VDW mp = −190 °C<br>$CH_3CHO$ VDW, DD mp = −121 °C<br>**Increasing strength of intermolecular forces**<br>**Increasing melting point** |
| | • Mp increases as the number of carbons increases because of increased surface area.<br>$CH_3CH_2CH_2CH_3$ mp = −138 °C<br>$CH_3CH_2CH_2CH_2CH_2CH_3$ mp = −95 °C<br>**Increasing surface area**<br>**Increasing melting point** |
| | • Mp increases with increased symmetry.<br>$CH_3CH_2CH(CH_3)_2$ mp = −160 °C<br>$(CH_3)_4C$ mp = −17 °C<br>**Increasing symmetry**<br>**Increasing melting point** |
| Solubility | • Alkanes are soluble in organic solvents.<br>• Alkanes are insoluble in water. |

Key: bp = boiling point; mp = melting point; VDW = van der Waals; DD = dipole–dipole; HB = hydrogen bonding;

# Conformations of Acyclic Alkanes :

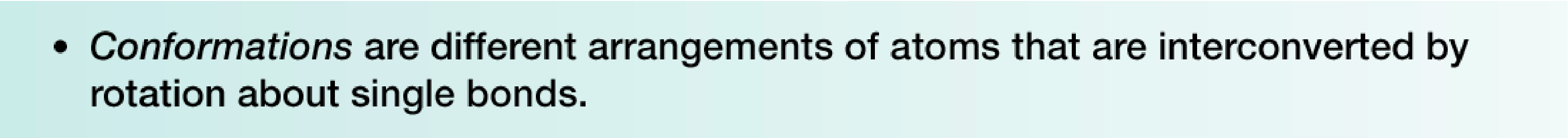
**Conformations** are different arrangements of atoms that are interconverted by rotation about single bonds.



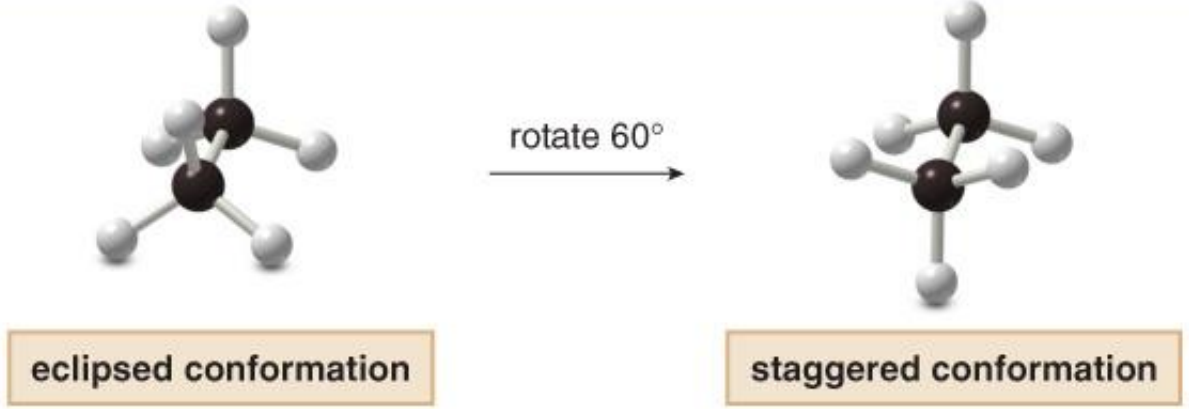
Rotation occurs here.

two different conformations

The location of the indicated atom changes with rotation.


- *Conformations* are different arrangements of atoms that are interconverted by rotation about single bonds.

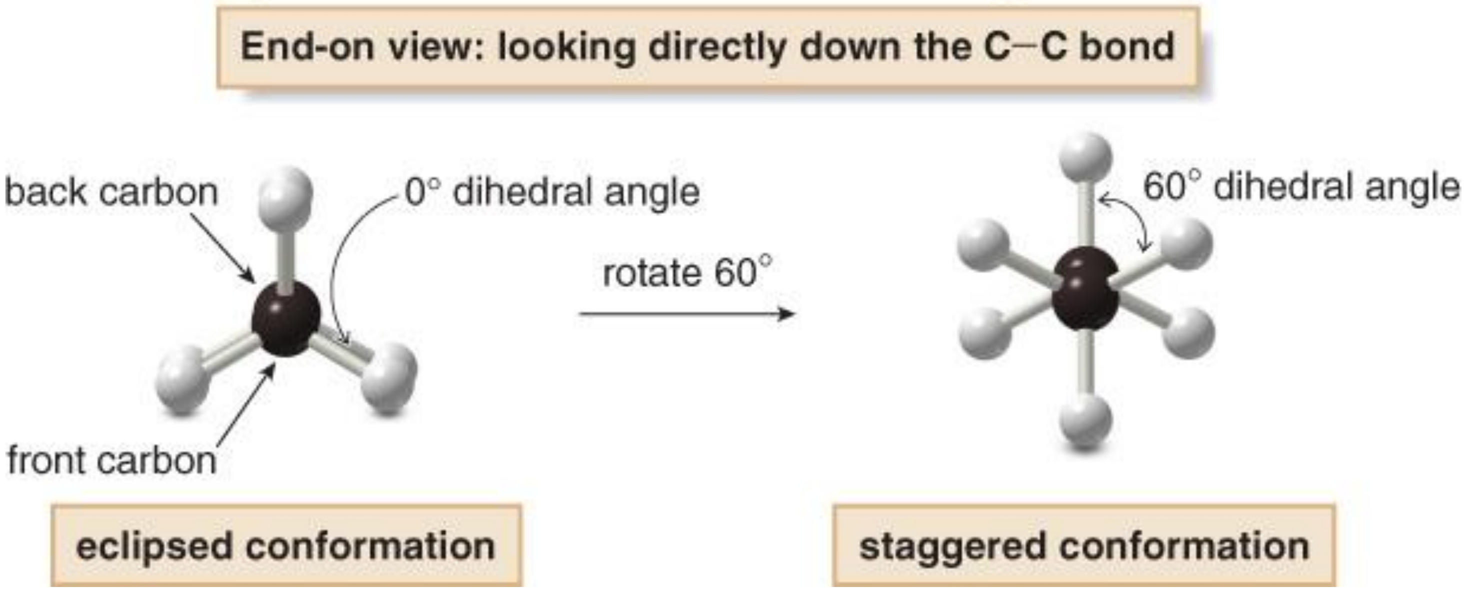
- **Names are given to two different conformations.**
- **In the eclipsed conformation, the C—H bonds on one carbon are directly aligned with the C—H bonds on the adjacent carbon.**
- **In the staggered conformation, the C—H bonds on one carbon bisect the H—C—H bond angle on the adjacent carbon.**



The C–H bonds are all **aligned.**

The C–H bonds in front
**bisect** the H–C–H bond angles in back.

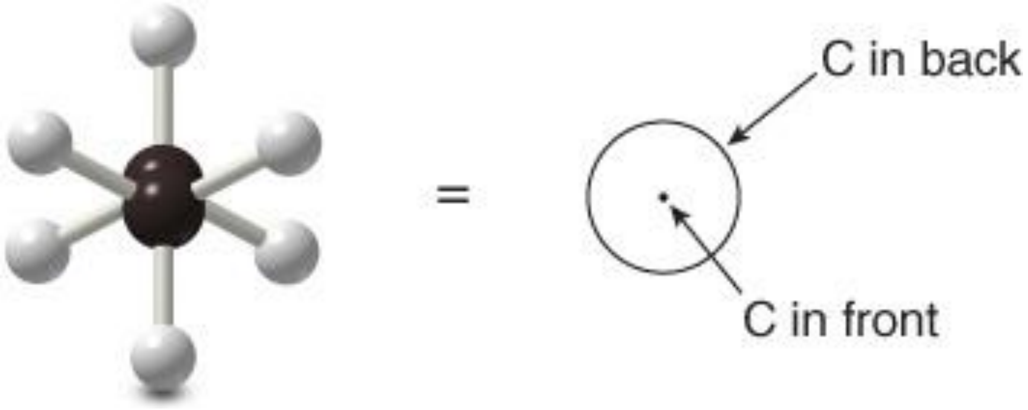
- **Rotating the atoms on one carbon by 60° converts an eclipsed conformation into a staggered conformation, and vice versa.**
- **The angle that separates a bond on one atom from a bond on an adjacent atom is called a dihedral angle. For ethane in the staggered conformation, the dihedral angle for the C—H bonds is 60°. For eclipsed ethane, it is 0°.**



- **End-on representations for conformations are commonly drawn using a convention called a Newman projection.**

## How to Draw a Newman Projection:

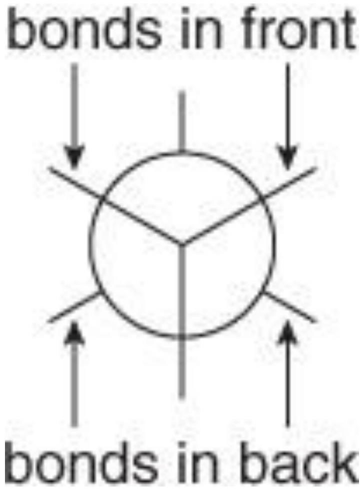
**Step 1. Look directly down the C—C bond (end-on), and draw a circle with a dot in the center to represent the carbons of the C—C bond.**



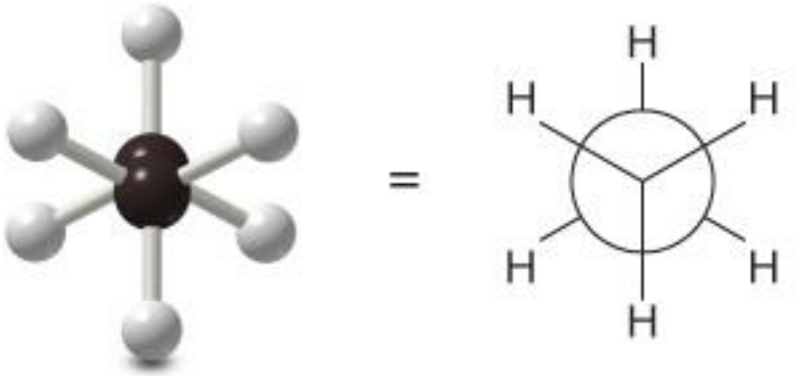
**Step 2.** **Draw in the bonds.**

**Draw the bonds on the front C as three lines meeting at the center of the circle.**

**Draw the bonds on the back C as three lines coming out of the edge of the circle.**



## Step 3. Add the atoms on each bond.



Each C has 3 H's in ethane.

Figure 4.6

Newman projections for the staggered and eclipsed conformations of ethane

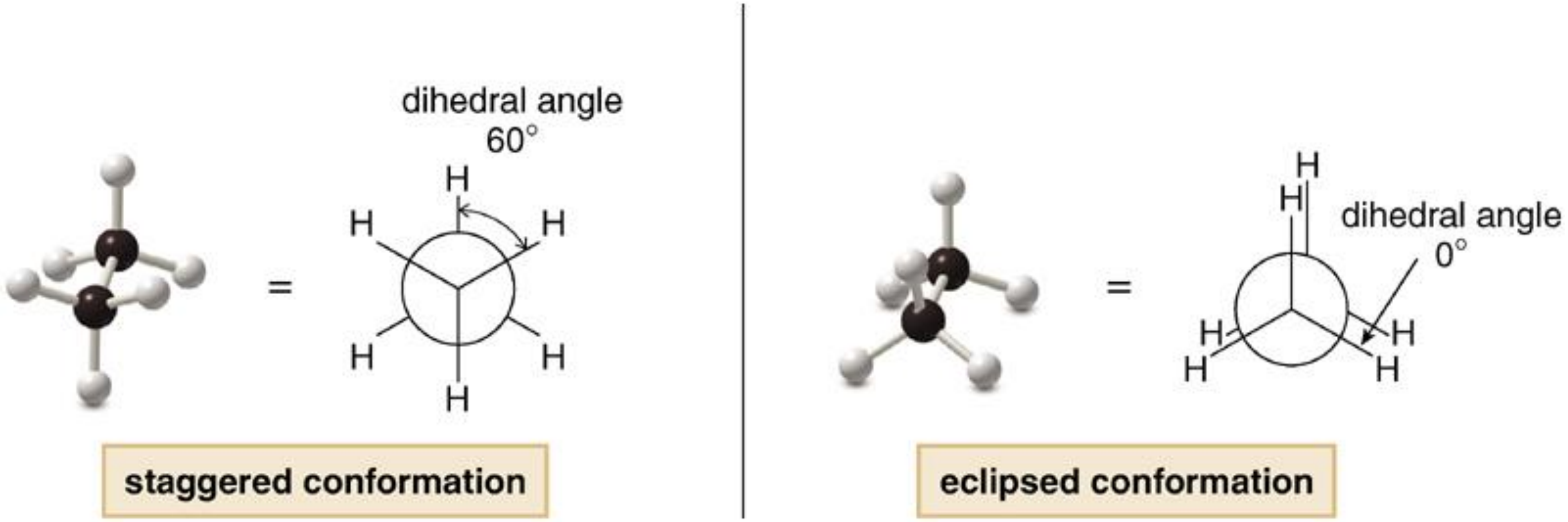
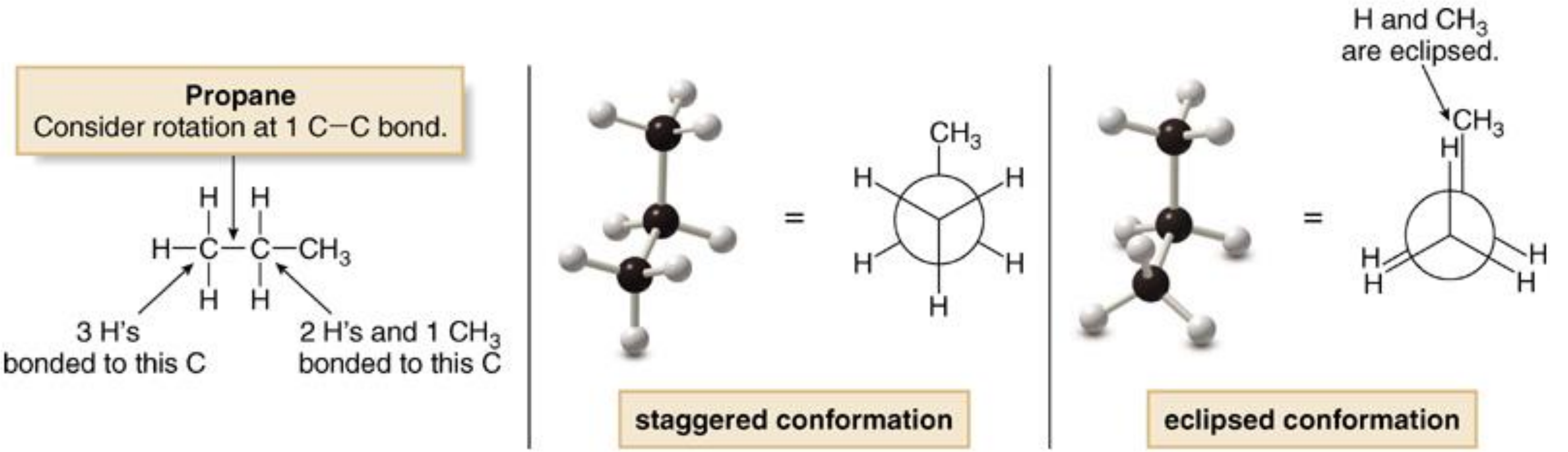
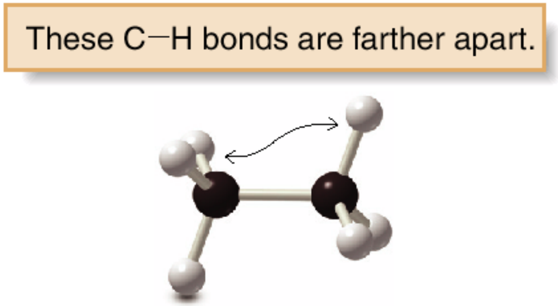


Figure 4.7 Newman projections for the staggered and eclipsed conformations of propane

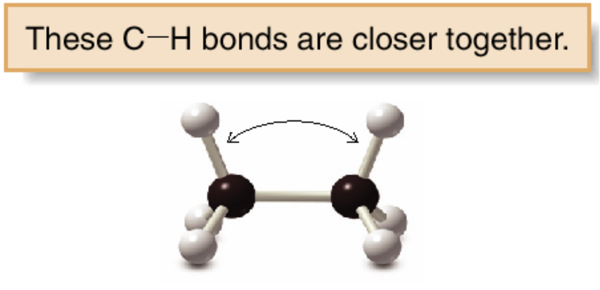


- The staggered and eclipsed conformations of ethane interconvert at room temperature, but each conformer is not equally stable.
- The staggered conformations are more stable (lower in energy) than the eclipsed conformations.
- Electron-electron repulsion between bonds in the eclipsed conformation increases its energy compared with the staggered conformation, where the bonding electrons are farther apart.



**staggered conformation**
side view

**more stable**



**eclipsed conformation**
side view

**less stable**

- **The difference in energy between staggered and eclipsed conformers is ~3 kcal/mol, with each eclipsed C—H bond contributing 1 kcal/mol. The energy difference between staggered and eclipsed conformers is called torsional energy.**
- **Torsional strain is an increase in energy caused by eclipsing interactions.**

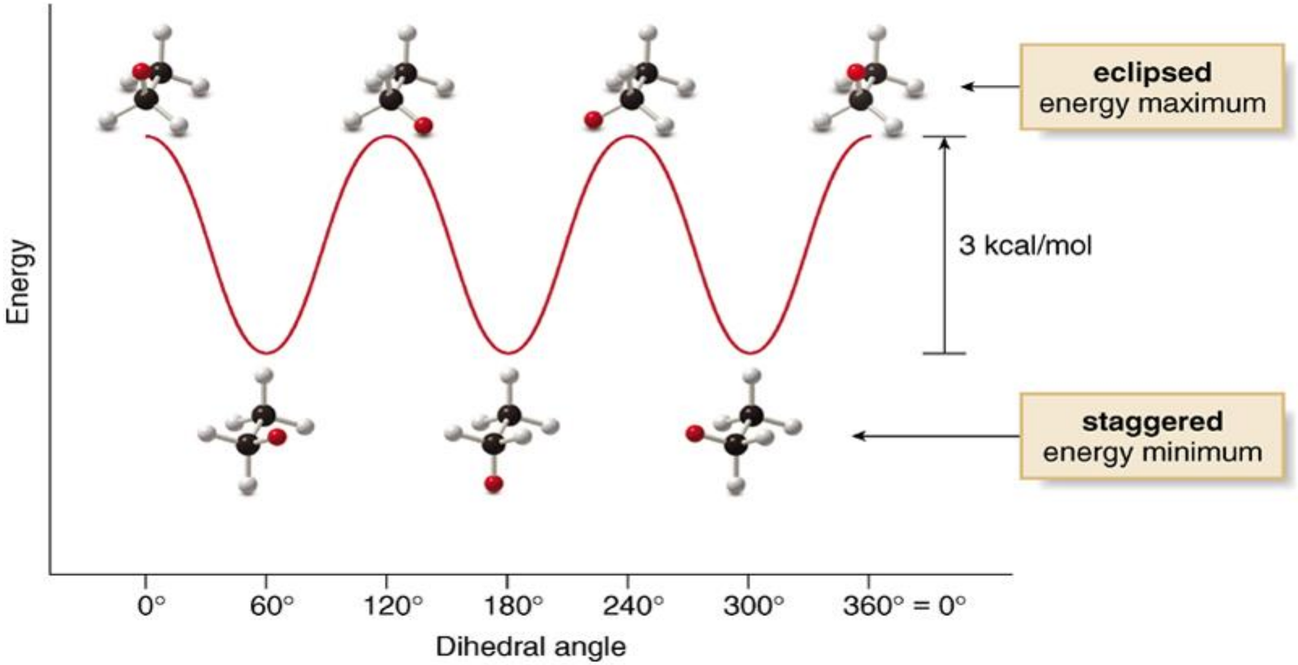


Figure 4.8
Graph: Energy versus dihedral angle for ethane

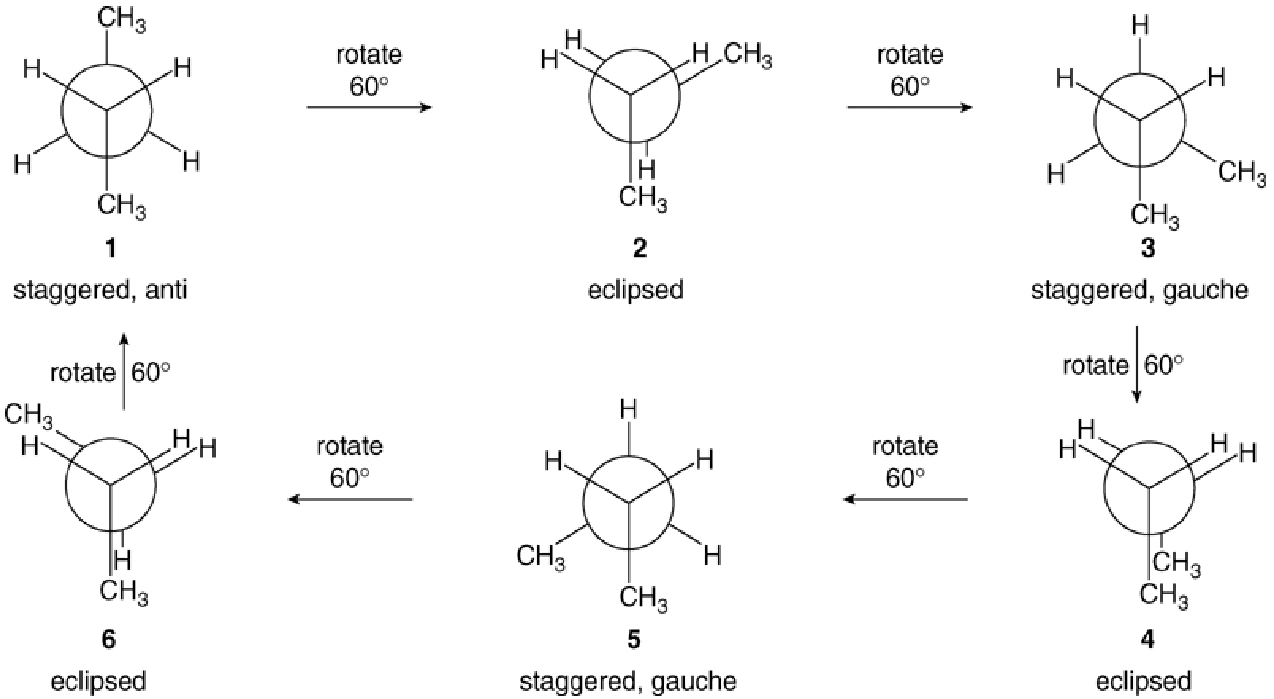
At any given moment, all ethane molecules do not exist in the more stable staggered conformation; rather, a higher percentage of molecules is present in the more stable staggered conformation than any other possible arrangement.

Each H,H eclipsing interaction contributes 1 kcal/mol of destabilization to the eclipsed conformation.

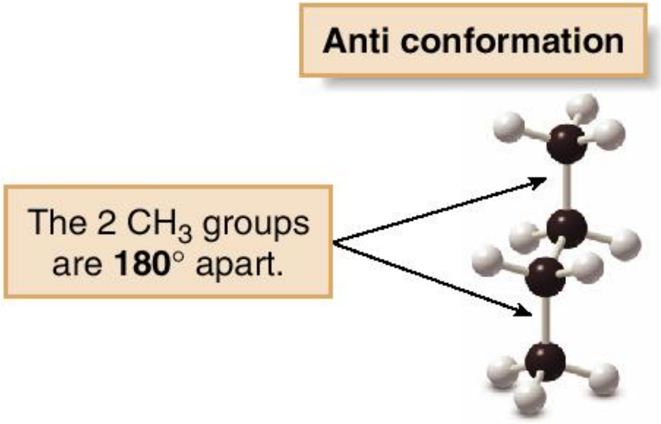
- Note the position of the labeled H atom after each 60° rotation. All three staggered conformations are identical (except for the position of the label), and the same is true for all three eclipsed conformations.

- **An energy minimum and maximum occur every 60° as the conformation changes from staggered to eclipsed. Conformations that are neither staggered nor eclipsed are intermediate in energy.**
- **Butane and higher molecular weight alkanes have several C—C bonds, all capable of rotation. It takes six 60° rotations to return to the original conformation.**

Figure 4.9
Six different conformations of butane



- **A staggered conformation with two larger groups 180° from each other is called anti.**
- **A staggered conformation with two larger groups 60° from each other is called gauche.**
- **The staggered conformations are lower in energy than the eclipsed conformations.**
- **The relative energies of the individual staggered conformations depend on their steric strain.**
- **Steric strain is an increase in energy resulting when atoms are forced too close to one another.**
- **Gauche conformations are generally higher in energy than anti conformations because of steric strain.**

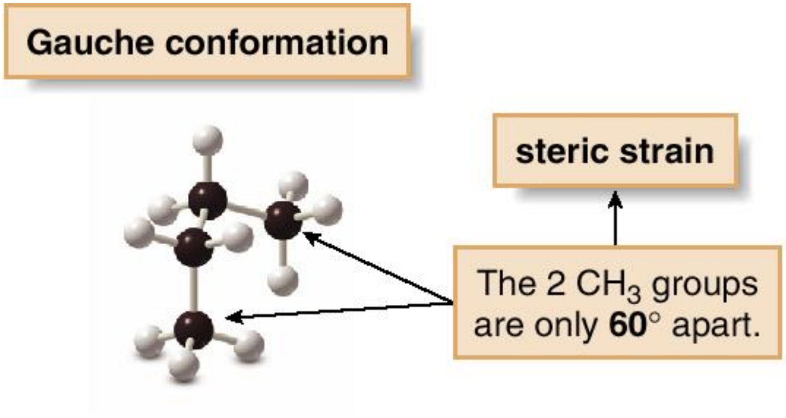


**Anti conformation**

The 2 $CH_3$ groups are **180**° apart.

**lower in energy**

**1**



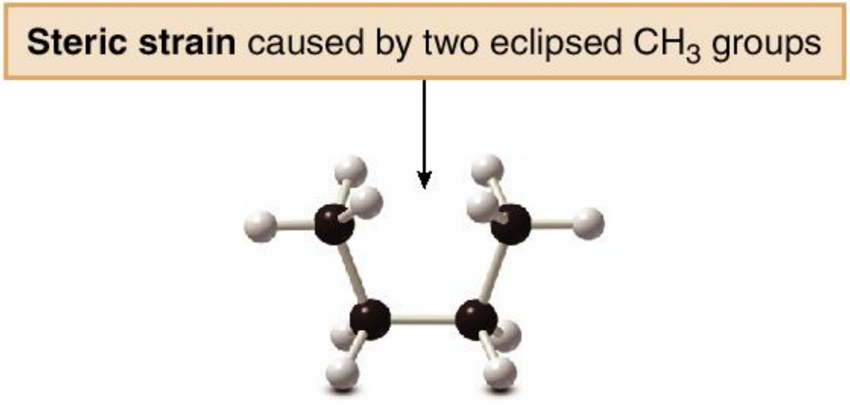
**Gauche conformation**

**steric strain**

The 2 $CH_3$ groups are only **60**° apart.

**higher in energy**

**3**



**Steric strain** caused by two eclipsed $CH_3$ groups

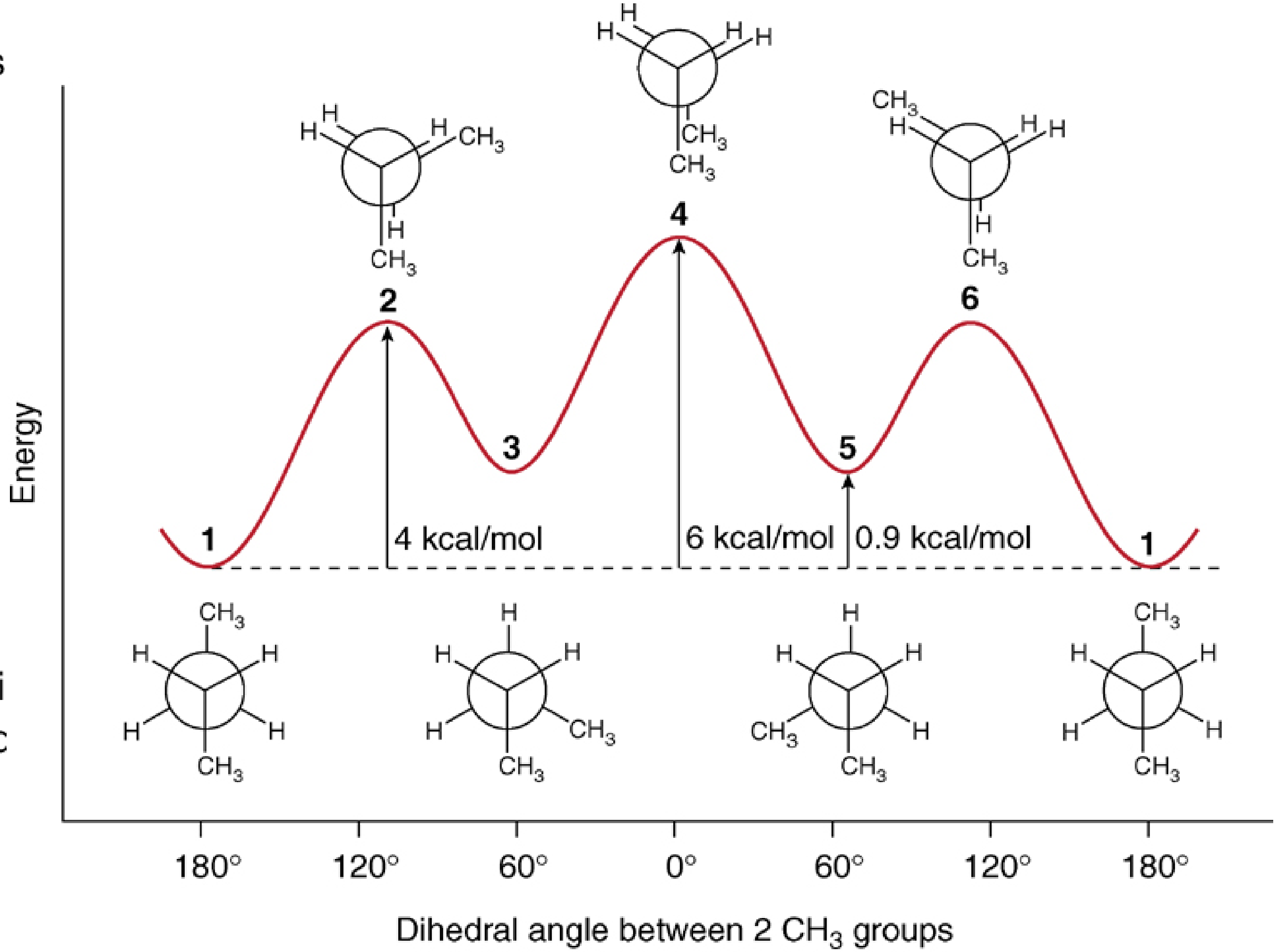
side view

**4**

## Figure 4.10

Graph: Energy versus dihedral angle for butane

- Staggered conformations **1, 3,** and **5** are at energy minima.
- Anti conformation **1** is lower in energy than gauche conformations **3** and **5,** which possess steric strain.
- Eclipsed conformations **2, 4,** and **6** are at energy maxima.
- Eclipsed conformation **4,** which has additional steri strain due to two eclipsec $CH_3$ groups, is highest in energy.



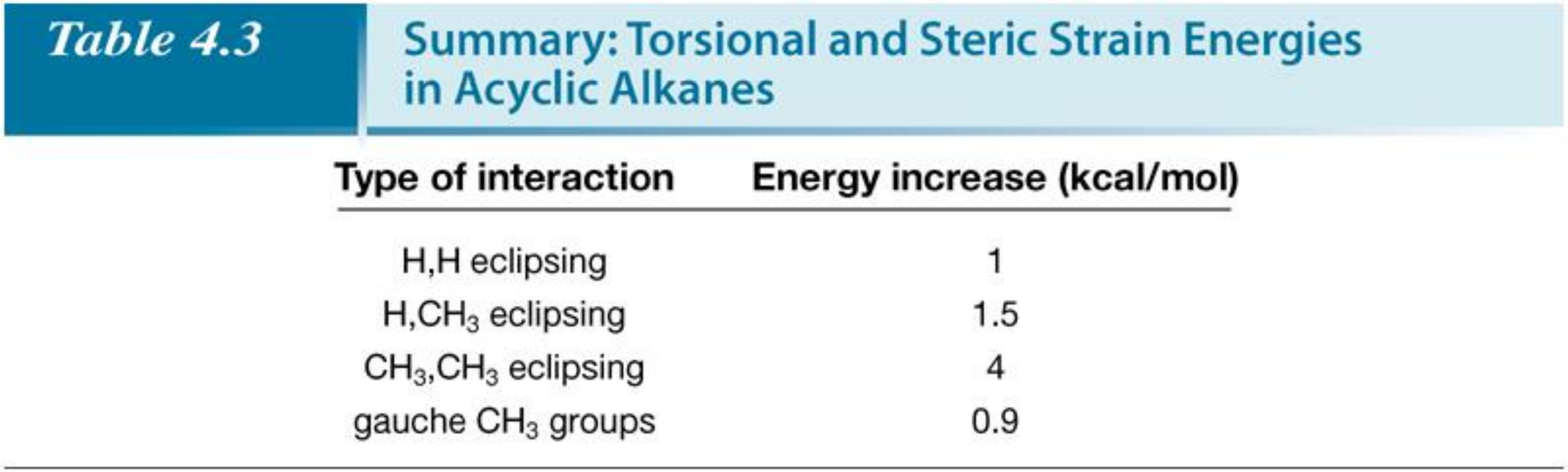


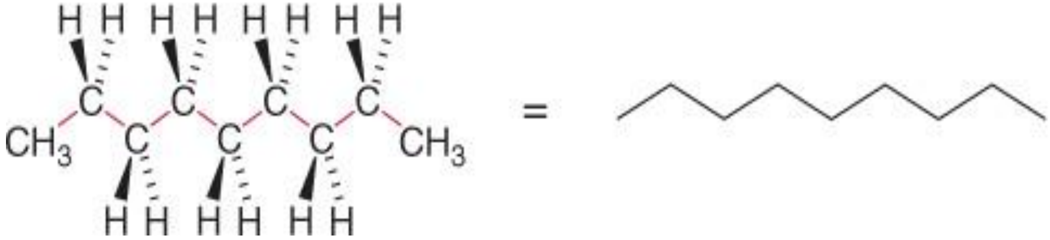
**Table 4.3** Summary: Torsional and Steric Strain Energies in Acyclic Alkanes

| Type of interaction | Energy increase (kcal/mol) |
|---|---|
| H,H eclipsing | 1 |
| H,$CH_3$ eclipsing | 1.5 |
| $CH_3$,$CH_3$ eclipsing | 4 |
| gauche $CH_3$ groups | 0.9 |

- **The energy difference between the lowest and highest energy conformations is called a barrier to rotation.**

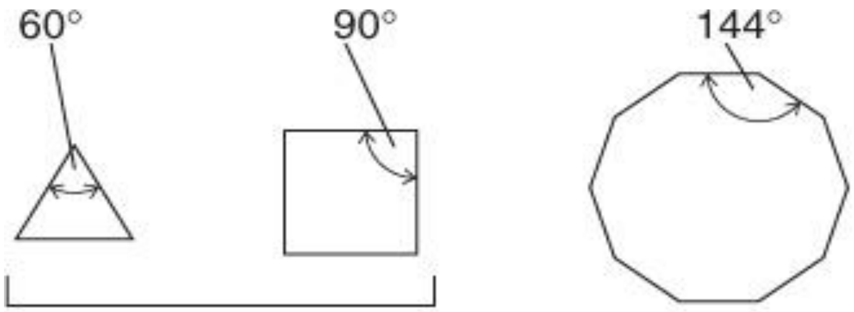
- **Since the lowest energy conformation has all bonds staggered and all large groups anti, alkanes are often drawn in zigzag skeletal structures to indicate this.**

A zigzag arrangement keeps all carbons **staggered** and **anti.**



# Introduction to Cycloalkanes

- **Besides torsional strain and steric strain, the conformations of cycloalkanes are also affected by angle strain.**
- **Angle strain is an increase in energy when bond angles deviate from the optimum tetrahedral angle of 109.5°.**
- **The Baeyer strain theory was formulated when it was thought that rings were flat. It states that larger rings would be very highly strained, as their bond angles would be very different from the optimum 109.5°.**
- **It turns out that cycloalkanes with more than three C atoms in the ring are not flat molecules. They are puckered to reduce strain.**

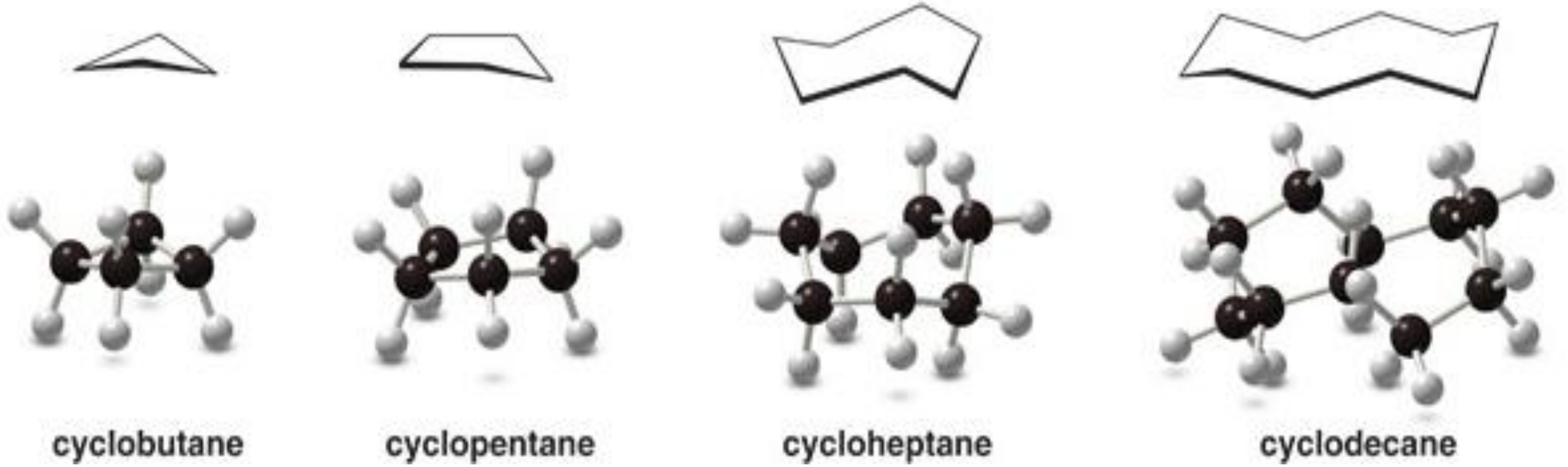


small internal angles
**angle strain**

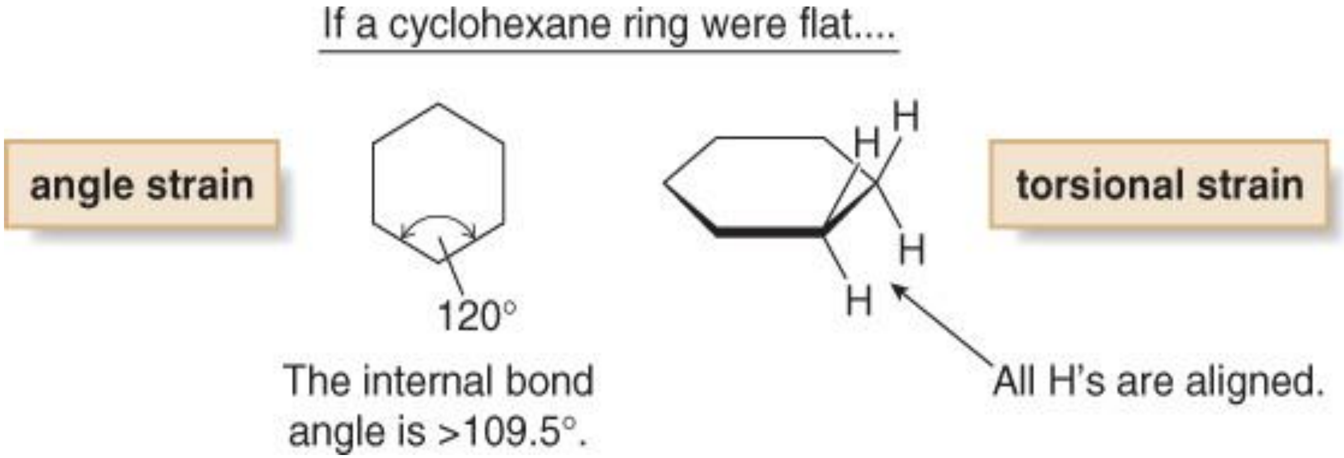
large internal angles
**angle strain**

---

Figure 4.11
Three-dimensional structure
of some cycloalkanes



# Cyclohexane


If a cyclohexane ring were flat....

**angle strain**

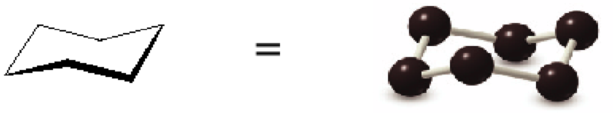
**torsional strain**

The internal bond angle is >109.5°.

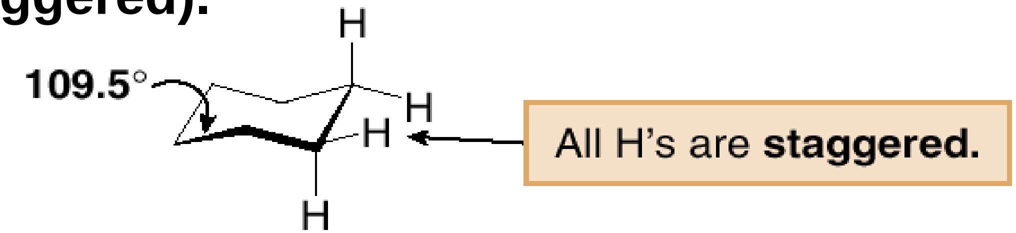
All H's are aligned.

**In reality, cyclohexane adopts a puckered “chair” conformation, which is more stable than any possible other conformation.**

**The carbon skeleton of chair cyclohexane**

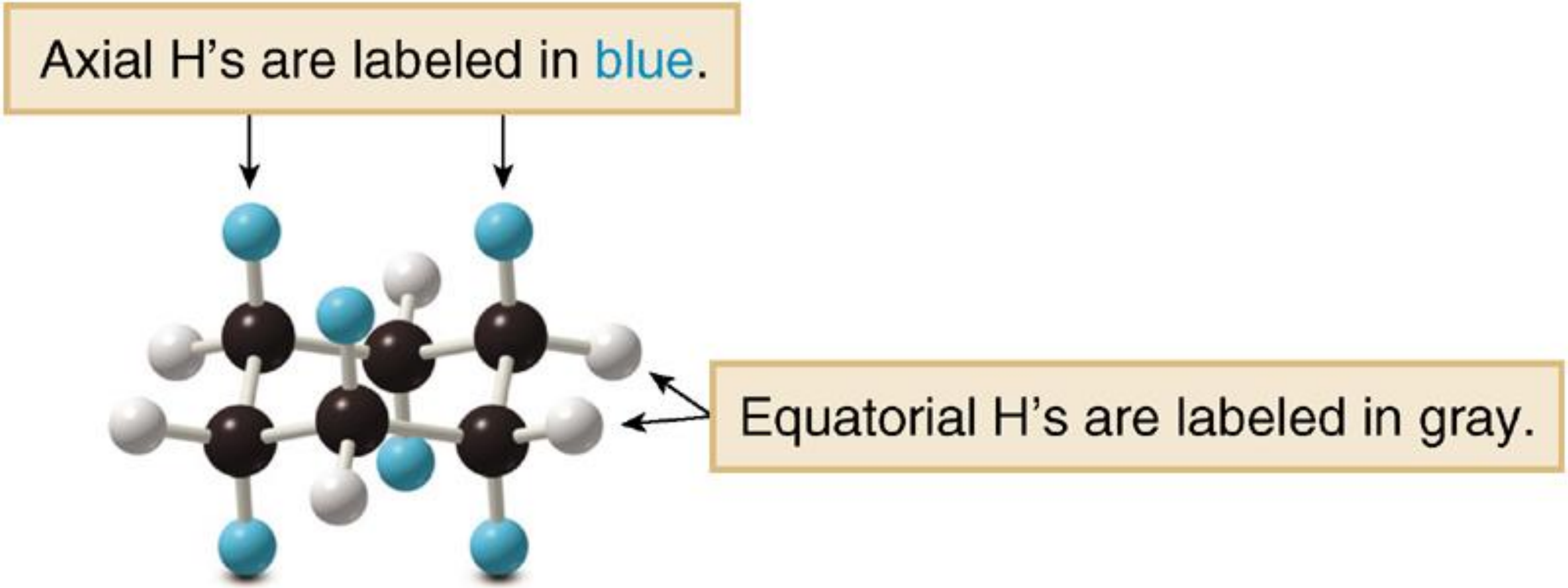


**The chair conformation is so stable because it eliminates angle strain (all C—C—C angles are 109.5°), and torsional strain (all hydrogens on adjacent C atoms are staggered).**



All H's are **staggered.**

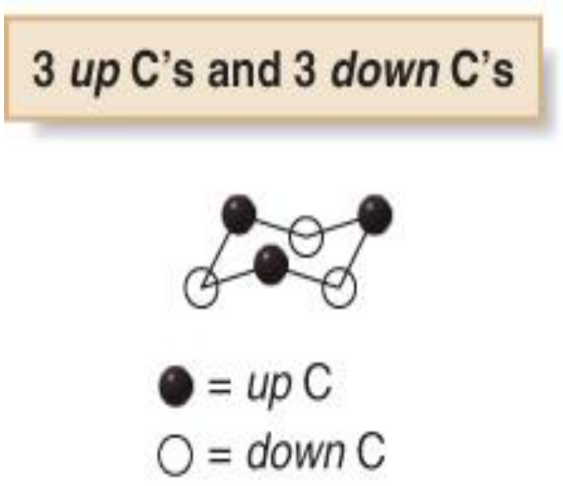
Figure 4.12
A three-dimensional model of the chair form of cyclohexane with all H atoms drawn

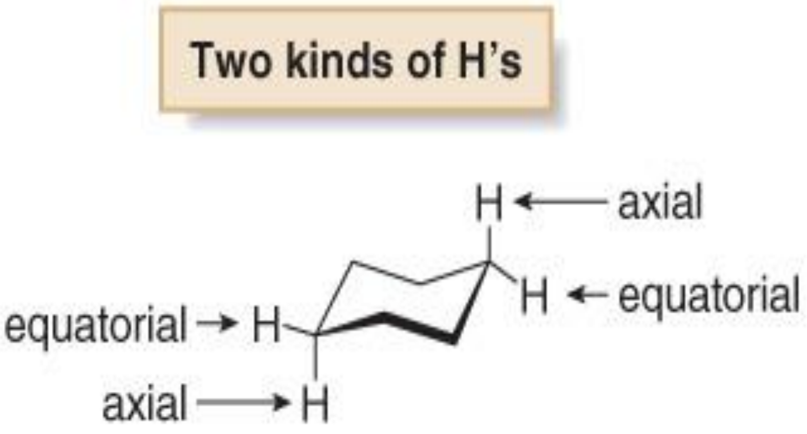


Axial H's are labeled in blue.

Equatorial H's are labeled in gray.

- **In cyclohexane, three C atoms pucker up and three C atoms pucker down, alternating around the ring.**
- **Each C in cyclohexane has two different kinds of hydrogens: (1) axial hydrogens are located above and below the ring (along a perpendicular axis); (2) equatorial hydrogens are located in the plane of the ring (around the equator).**

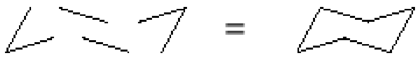


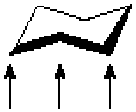


- **Axial** bonds are oriented **above** and **below**.
- **Equatorial** bonds are oriented around the **equator**.

## *How To* Draw the Chair Form of Cyclohexane

**Step [1]** **Draw the carbon skeleton.**



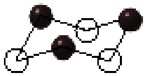


These atoms are in front.

- Draw three parts of the chair: **a wedge, a set of parallel lines,** and **another wedge.**
- Then, join them together.
- The bottom 3 C's come out of the page, and for this reason, bonds to them are often highlighted in bold.

---

**Step [2]** **Label the *up* C's and *down* C's on the ring.**



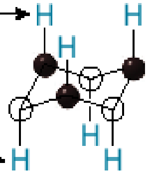
● = *up* C ○ = *down* C

- There are 3 *up* and 3 *down* C's, and they alternate around the ring.

---

**Step [3]** **Draw in the axial H atoms.**

**3** axial H's **above** the ring →



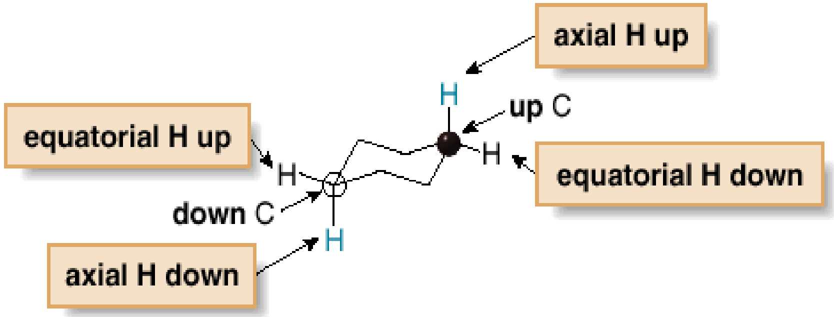
**3** axial H's **below** the ring →

- On an *up* C the axial H is *up.*
- On a *down* C the axial H is *down.*

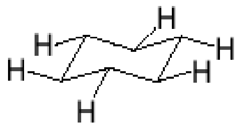
## *How To, continued . . .*

**Step [4]** Draw in the equatorial H atoms.

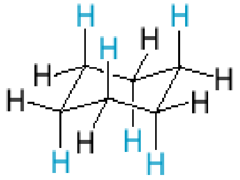
- The axial H is **down** on a down C, so the equatorial H must be up.
- The axial H is **up** on an up C, so the equatorial H must be down.



All equatorial H's drawn in.

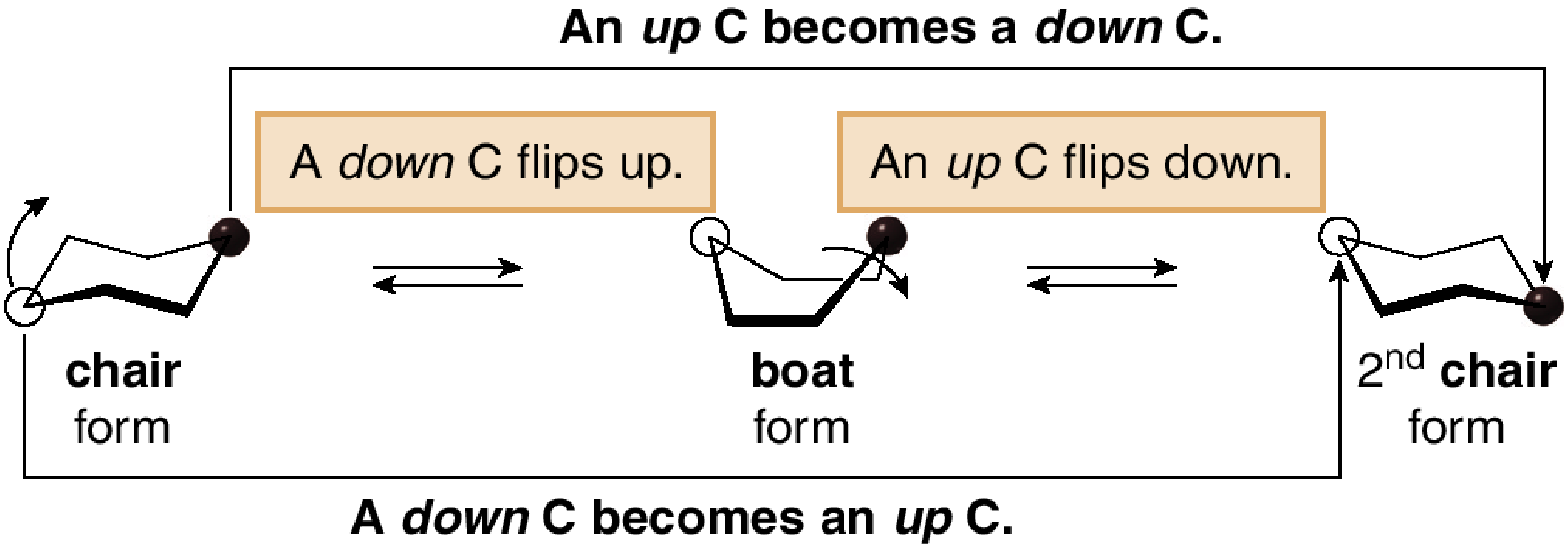


All H's drawn in.



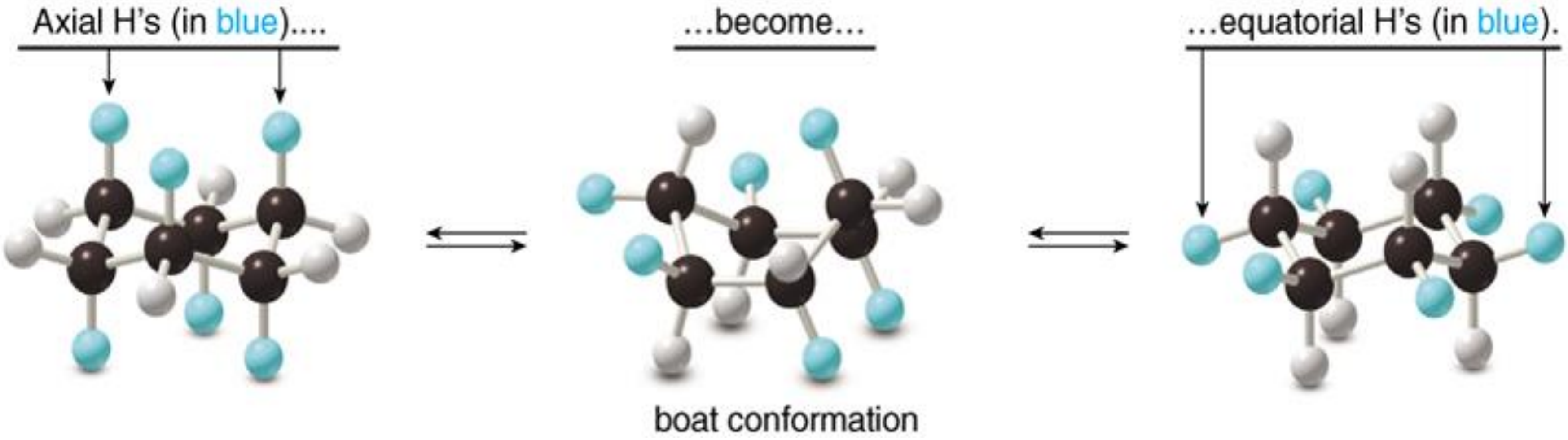
Axial H's are drawn in blue.

- **An important conformational change in cyclohexane involves "ring-flipping." Ring-flipping is a two-step process.**
- **As a result of a ring flip, the up carbons become down carbons, and the down carbons become up carbons.**
- **Axial and equatorial H atoms are also interconverted during a ring-flip. Axial H atoms become equatorial H atoms, and equatorial H atoms become axial H atoms.**



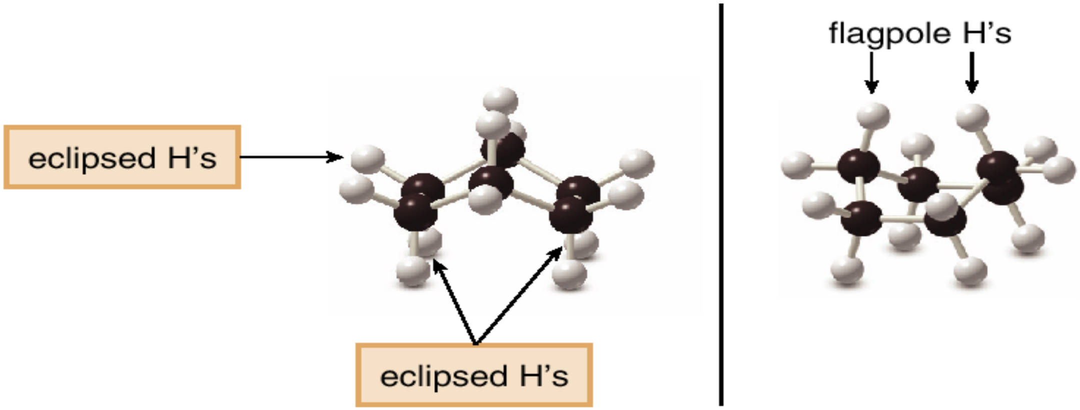
# Figure 4.13

Ring-flipping interconverts axial and equatorial hydrogens in cyclohexane



- **The chair forms of cyclohexane are 7 kcal/mol more stable than the boat forms.**
- **The boat conformation is destabilized by torsional strain because the hydrogens on the four carbon atoms in the plane are eclipsed.**
- **Additionally, there is steric strain because two hydrogens at either end of the boat, the “flag pole” hydrogens, are forced close to each other.**

Figure 4.14
Two views of the boat conformation of cyclohexane



The boat form of cyclohexane is less stable than the chair forms for two reasons.

- Eclipsing interactions between H’s cause torsional strain.
- The proximity of the flagpole H’s causes steric strain.

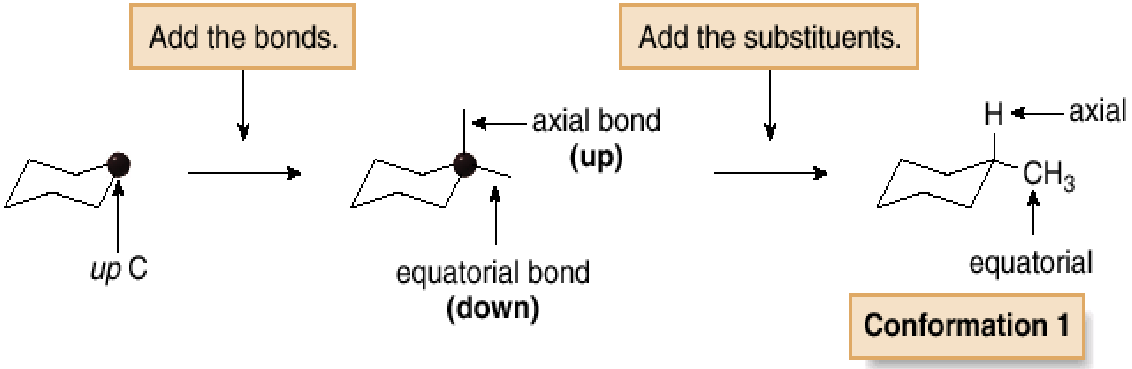
- **Note that the equatorial position has more room than the axial position, so larger substituents are more stable in the equatorial position.**
- **There are two possible chair conformations of a monosubstituted cyclohexane, such as methyl cyclohexane.**

# How to draw the two conformations of a substituted cyclohexane:

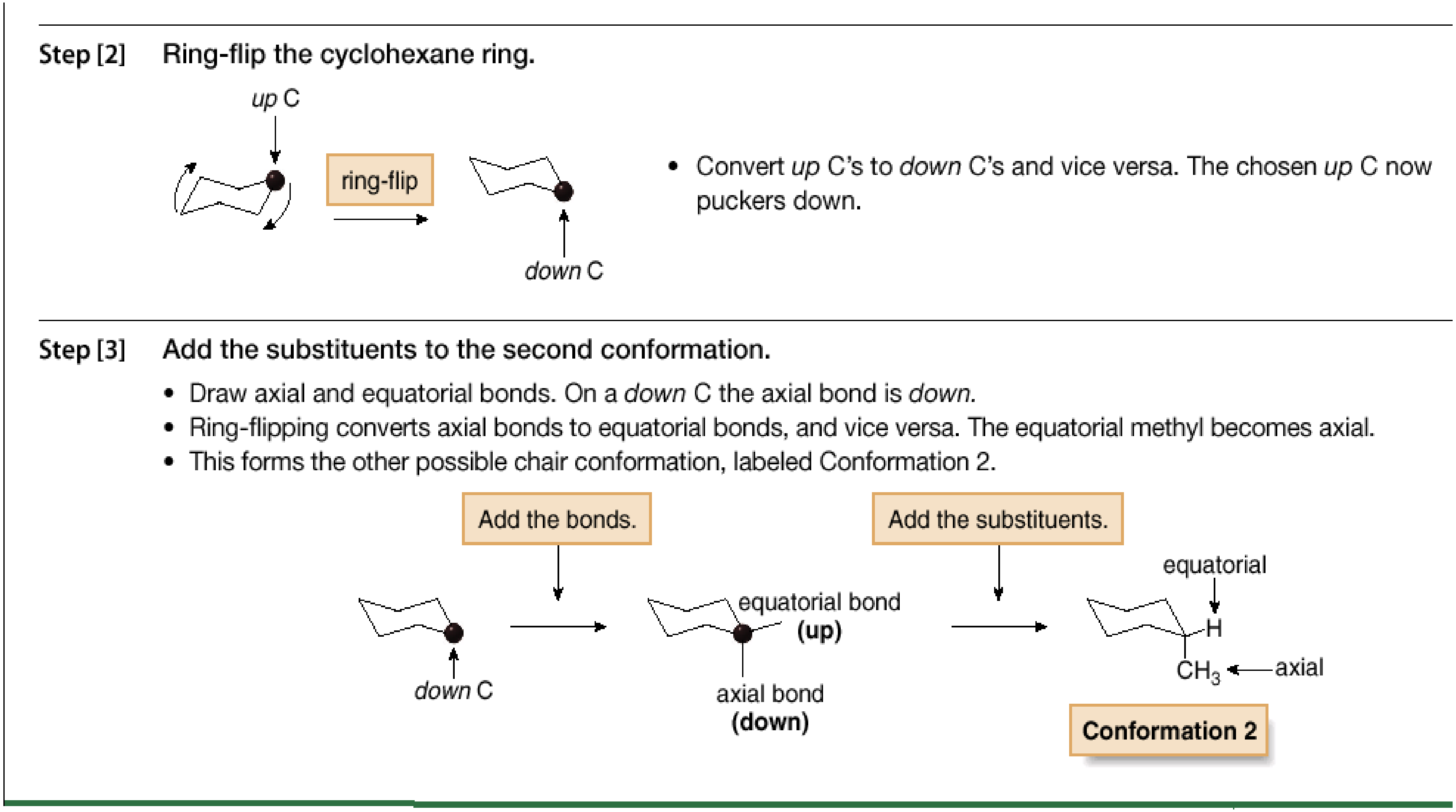
**How To** Draw the Two Conformations for a Substituted Cyclohexane

**Step [1]** **Draw one chair form and add the substituents.**

- Arbitrarily pick a ring carbon, classify it as an *up* or *down* carbon, and draw the bonds. Each C has one axial and one equatorial bond.
- Add the substituents, in this case H and $CH_3$, arbitrarily placing one axial and one equatorial. In this example, the $CH_3$ group is drawn equatorial.
- This forms one of the two possible chair conformations, labeled Conformation 1.



# How to draw the two conformations of a substituted cyclohexane:



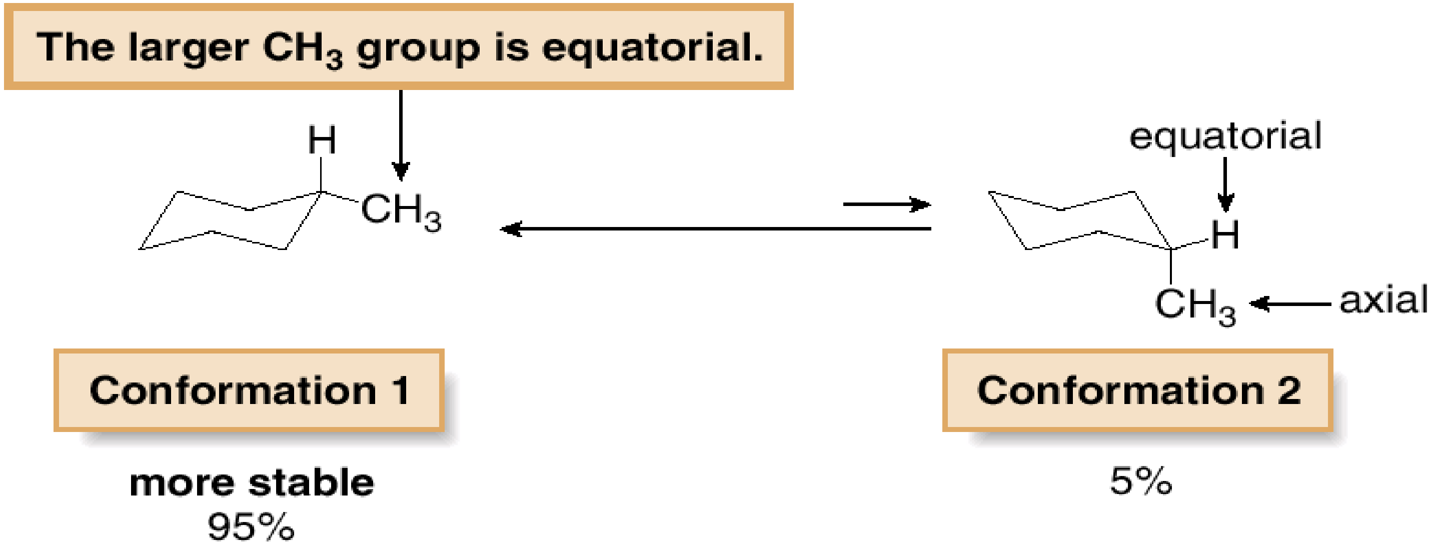
**Step [2]** Ring-flip the cyclohexane ring.

- Convert *up* C's to *down* C's and vice versa. The chosen *up* C now puckers down.

**Step [3]** Add the substituents to the second conformation.

- Draw axial and equatorial bonds. On a *down* C the axial bond is *down*.
- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The equatorial methyl becomes axial.
- This forms the other possible chair conformation, labeled Conformation 2.

- Note that the two conformations of cyclohexane are different, so they are not equally stable.
- Larger axial substituents create destabilizing (and thus unfavorable) 1,3-diaxial interactions.
- In methylcyclohexane, each unfavorable H,$CH_3$ interaction destabilizes the conformation by 0.9 kcal/mol, so Conformation 2 is 1.8 kcal/mol less stable than Conformation 1.


**The larger $CH_3$ group is equatorial.**

**Conformation 1**

**more stable**
95%

**Conformation 2**

5%

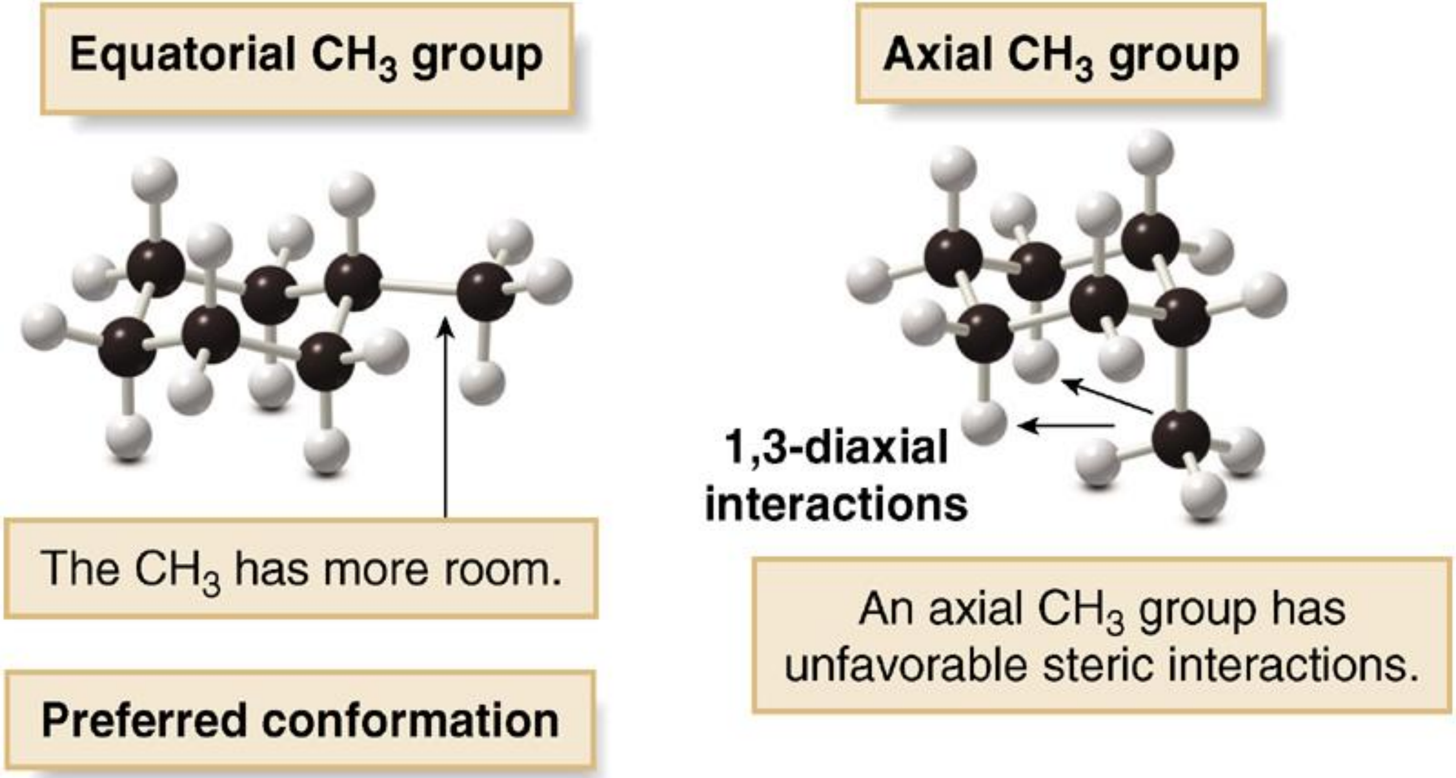
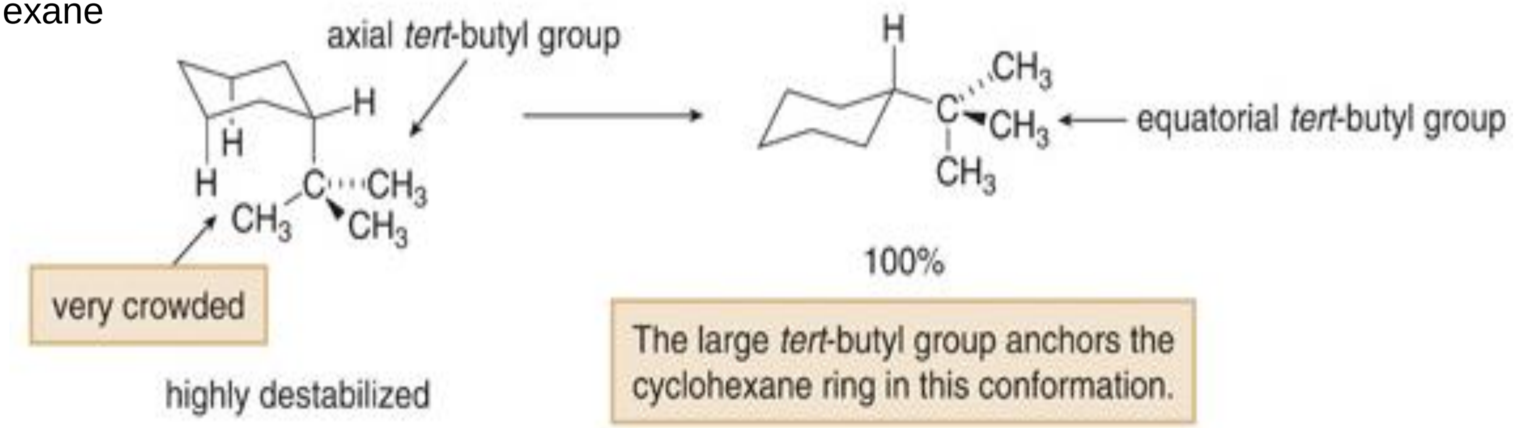


Figure 4.15
Three-dimensional representations for the two conformations of methylcyclohexane

# Substituted Cyclohexane

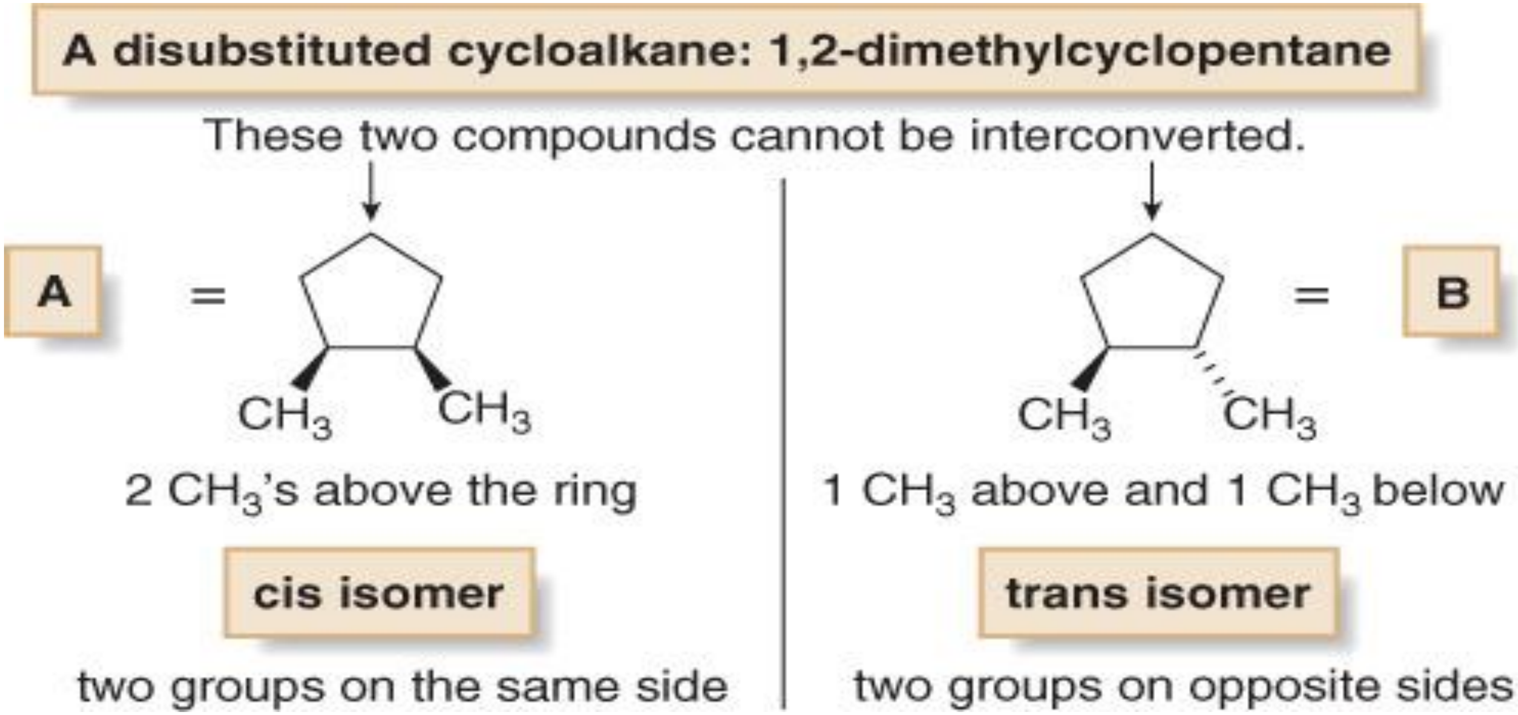
- **Note that the larger the substituent on the six-membered ring, the higher the percentage of the conformation containing the equatorial substituent at equilibrium.**
- **With a very large substituent like *tert*-butyl [$(CH_3)_3C$-], essentially none of the conformation containing an axial *tert*-butyl group is present at room temperature, so the ring is essentially anchored in a single conformation having an equatorial *tert*-butyl group.**

Figure 4.16
The two conformations of *tert*-butylcyclohexane



## Disubstituted Cycloalkanes

- **There are two different 1,2-dimethylcyclopentanes—one having two $CH_3$ groups on the same side of the ring and one having them on opposite sides of the ring.**



**A disubstituted cycloalkane: 1,2-dimethylcyclopentane**

These two compounds cannot be interconverted.

2 $CH_3$'s above the ring

**cis isomer**

two groups on the same side

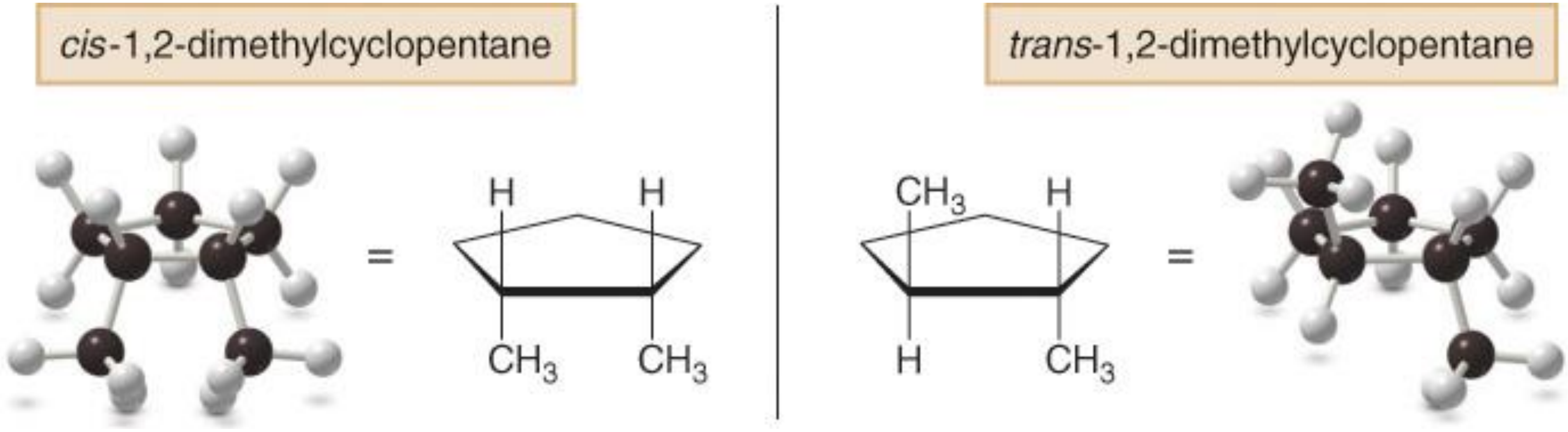
1 $CH_3$ above and 1 $CH_3$ below

**trans isomer**

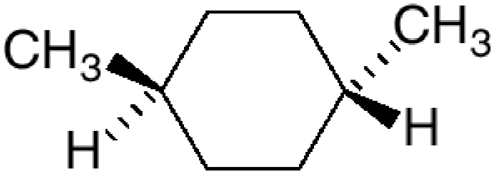
two groups on opposite sides

- **A and B are isomers. Specifically, they are stereoisomers.**

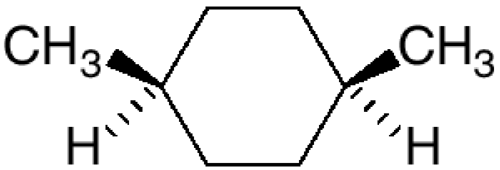
- Stereoisomers are isomers that differ only in the way the atoms are oriented in space.
- The prefixes cis and trans are used to distinguish these isomers.
- The cis isomer has two groups on the same side of the ring.
- The trans isomer has two groups on opposite sides of the ring.



- **A disubstituted cyclohexane, such as 1,4-dimethylcyclohexane, also has cis and trans stereoisomers. In addition, each of these stereoisomers has two possible chair conformations.**



***trans*-1,4-dimethylcyclohexane**



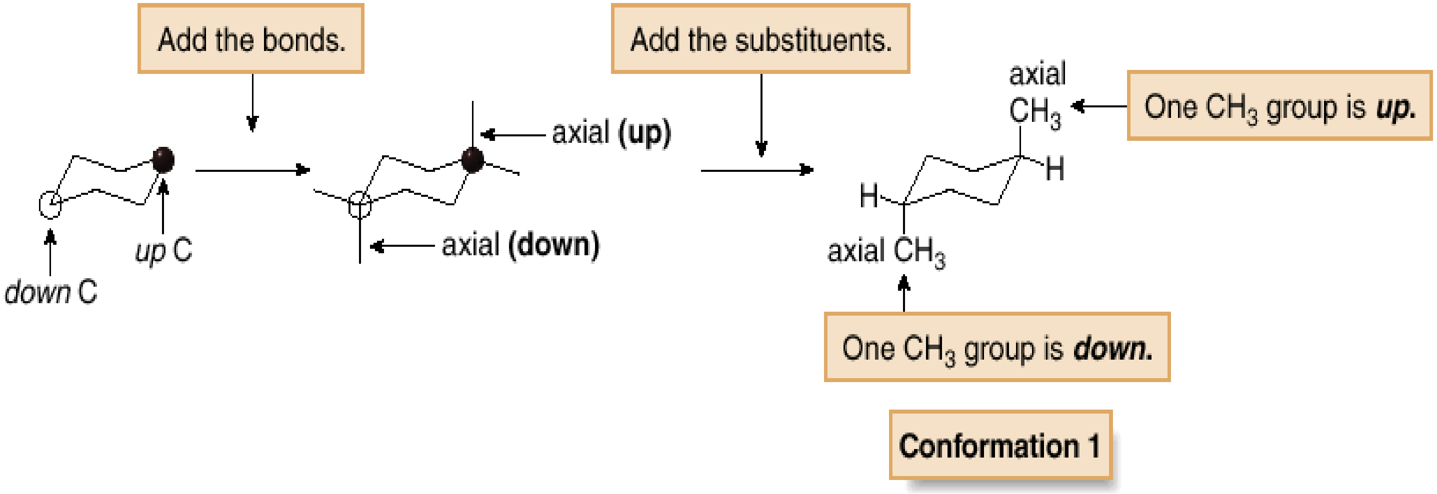
***cis*-1,4-dimethylcyclohexane**

- **Cis and trans isomers are named by adding the prefixes cis and trans to the name of the cycloalkane. Thus, the cis isomer would be named *cis*-1,4-dimethylcyclohexane, and the trans isomer would be named *trans*-1,4-dimethylcyclohexane.**
- **All disubstituted cycloalkanes with two groups bonded to different atoms have cis and trans isomers.**

## *How To* Draw Two Conformations for a Disubstituted Cyclohexane

**Step [1]** **Draw one chair form and add the substituents.**

- For *trans*-1,4-dimethylcyclohexane, arbitrarily pick two C's located 1,4- to each other, classify them as *up* or *down* C's, and draw in the substituents.
- The trans isomer must have one group *above* the ring (on an *up* bond) and one group *below* the ring (on a *down* bond). The substituents can be either axial or equatorial, as long as one is up and one is down. The easiest trans isomer to visualize has two axial $CH_3$ groups. This arrangement is said to be **diaxial.**
- This forms one of the two possible chair conformations, labeled Conformation 1.



Add the bonds.

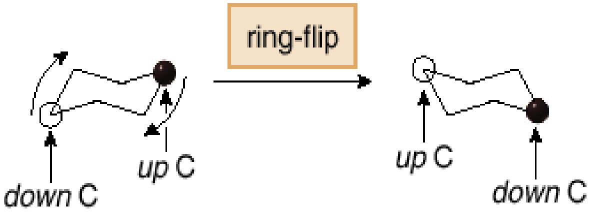
Add the substituents.

One $CH_3$ group is ***up.***

One $CH_3$ group is ***down.***

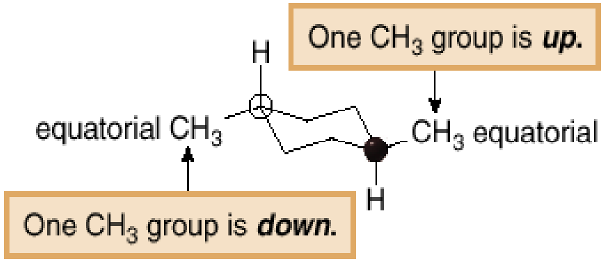
**Conformation 1**

**Step [2]** Ring-flip the cyclohexane ring.



- The *up* C flips down, and the *down* C flips up.

**Step [3]** Add the substituents to the second conformation.



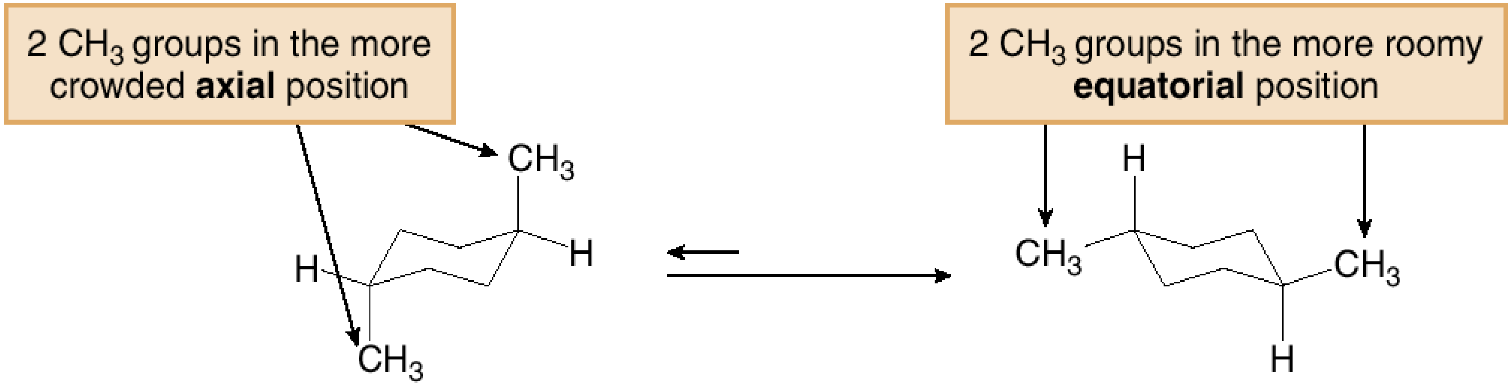
One $CH_3$ group is ***up.***

One $CH_3$ group is ***down.***

**Conformation 2**

- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The diaxial $CH_3$ groups become diequatorial. This trans conformation is less obvious to visualize. It is still trans, because one $CH_3$ group is above the ring (on an *up* bond), and one is below (on a *down* bond).

- **Conformations 1 and 2 are not equally stable. Because conformation 2 has both larger $CH_3$ groups in the roomier equatorial position, it is lower in energy.**
- **The cis isomer has two substituents on the same side, either both on up bonds or both on down bonds.**
- **A trans isomer has two substituents on opposite sides, one up and one down.**
- **Whether substituents are axial or equatorial depends on the relative location of the two substituents (on carbons 1,2-, 1,3-, or 1,4-).**


2 $CH_3$ groups in the more crowded **axial** position

2 $CH_3$ groups in the more roomy **equatorial** position

**1**
**diaxial conformation**

**2**
**diequatorial conformation**
**more stable**

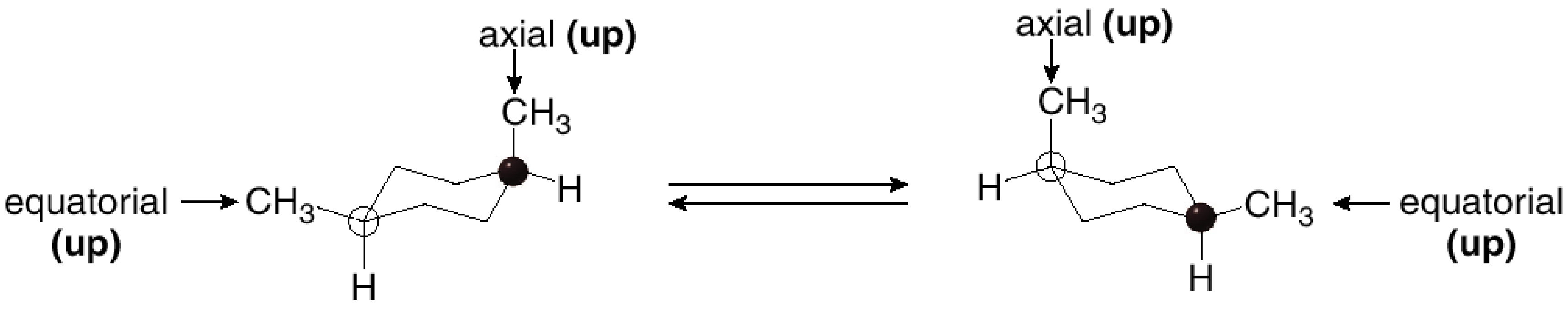


Figure 4.17
The two conformations of
*cis*-1,4-dimethylcyclohexane

**Conformation 1**
50%

**Conformation 2**
50%

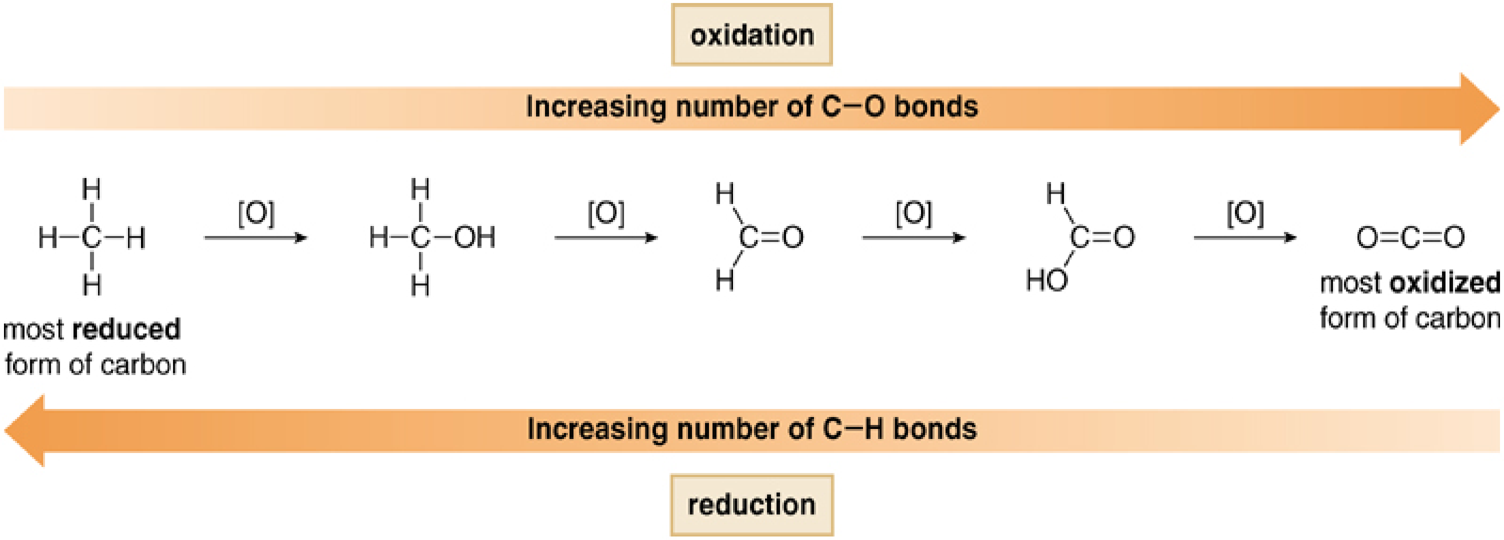
- A cis isomer has two groups on the same side of the ring, either both *up* or both *down*. In this example, Conformations **1** and **2** have two $CH_3$ groups drawn up.
- Both conformations have one $CH_3$ group axial and one equatorial, making them equally stable.

# Oxidation of Alkanes

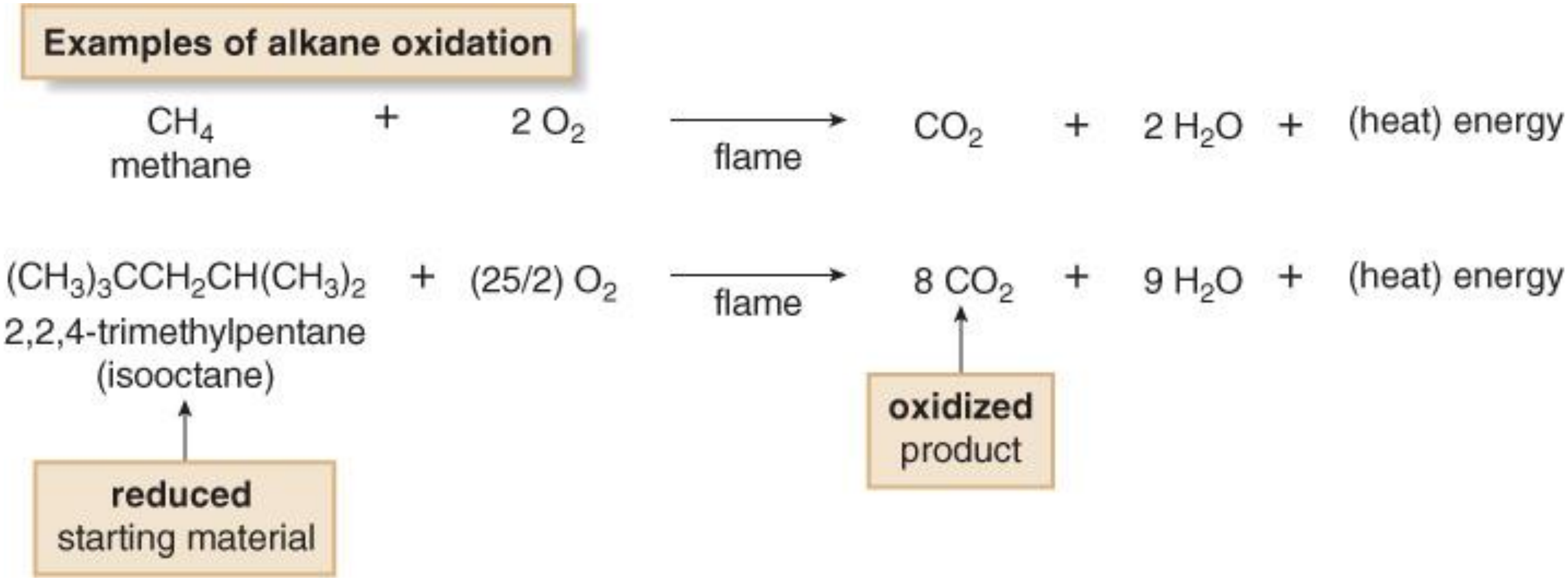
- Alkanes are the only family of organic molecules that have no functional group. Consequently, they undergo very few reactions.
- One reaction that alkanes undergo is combustion.
- Combustion is an oxidation-reduction reaction.
- Recall that oxidation is the loss of electrons and reduction is the gain of electrons.
- To determine if an organic compound undergoes oxidation or reduction, we concentrate on the carbon atoms of the starting material and the product, and compare the relative number of C—H and C—Z bonds, where Z = an element more electronegative than carbon (usually O, N, or X).

- Oxidation results in an increase in the number of C—Z bonds; or
- Oxidation results in a decrease in the number of C—H bonds.
- Reduction results in a decrease in the number of C—Z bonds; or
- Reduction results in an increase in the number of C—H bonds.

Figure 4.18
The oxidation and reduction of a carbon compound



- **Alkanes undergo combustion—that is, they burn in the presence of oxygen to form carbon dioxide and water.**
- **This is an example of oxidation. Every C—H and C—C bond in the starting material is converted to a C—O bond in the product.**



**Examples of alkane oxidation**

$$\underset{\text{methane}}{CH_4} + 2\,O_2 \xrightarrow[\text{flame}]{} CO_2 + 2\,H_2O + \text{(heat) energy}$$

$$\underset{\text{2,2,4-trimethylpentane (isooctane)}}{(CH_3)_3CCH_2CH(CH_3)_2} + (25/2)\,O_2 \xrightarrow[\text{flame}]{} 8\,CO_2 + 9\,H_2O + \text{(heat) energy}$$

# Thank You

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