

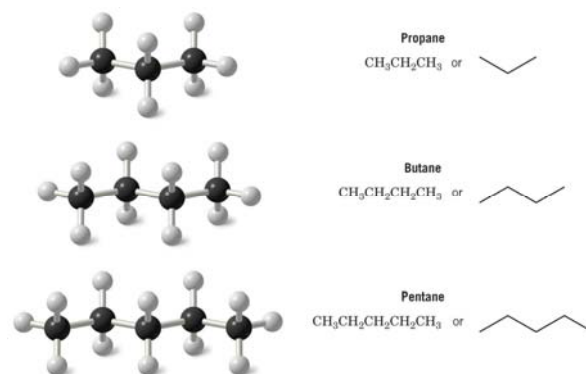
# Chapter 4

## Alkanes: Nomenclature, Conformational Analysis, and an Introduction to Synthesis

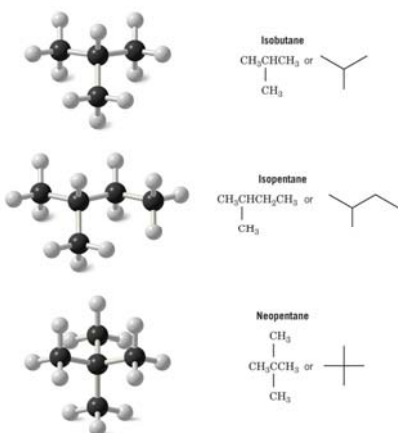
### ◆ Shapes of Alkanes

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

⌘ Straight chain alkanes are also called unbranched alkanes



→ Branched alkanes have at least one carbon which is attached to more than two other carbons



Chapter 4

3

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

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

Molecular Formula	Structural Formula	mp (°C)	bp (°C) <sup>a</sup> (1 atm)	Density <sup>b</sup> (g mL <sup>-1</sup> )	Index of Refraction <sup>c</sup> ( $n_D$ , 20° C)
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-95	68.7	0.6594 <sup>20</sup>	1.3748
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>   CH <sub>3</sub>	-153.7	60.3	0.6532 <sup>20</sup>	1.3714
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>2</sub> CH <sub>3</sub>   CH <sub>3</sub>	-118	63.3	0.6643 <sup>20</sup>	1.3765
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> CH—CHCH <sub>3</sub>         CH <sub>3</sub> CH <sub>3</sub>	-128.8	58	0.6616 <sup>20</sup>	1.3750
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> —C—CH <sub>2</sub> CH <sub>3</sub>   CH <sub>3</sub>	-98	49.7	0.6492 <sup>20</sup>	1.3688

<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 ( $n_D$ ).

Chapter 4

4

→ The number of constitutional isomers possible for a given molecular formula increases rapidly with the number of carbons

Molecular Formula	Possible Number of Constitutional Isomers
C <sub>4</sub> H <sub>10</sub>	2
C <sub>5</sub> H <sub>12</sub>	3
C <sub>6</sub> H <sub>14</sub>	5
C <sub>7</sub> H <sub>16</sub>	9
C <sub>8</sub> H <sub>18</sub>	18
C <sub>9</sub> H <sub>20</sub>	35
C <sub>10</sub> H <sub>22</sub>	75
C <sub>15</sub> H <sub>32</sub>	4,347
C <sub>20</sub> H <sub>42</sub>	366,319
C <sub>30</sub> H <sub>62</sub>	4,111,846,763
C <sub>40</sub> H <sub>82</sub>	62,481,801,147,341

### ◆ 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**

Name	Number of Carbon Atoms	Structure	Name	Number of Carbon Atoms	Structure
Methane	1	CH <sub>4</sub>	Heptadecane	17	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub>
Ethane	2	CH <sub>3</sub> CH <sub>3</sub>	Octadecane	18	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>3</sub>
Propane	3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	Nonadecane	19	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> CH <sub>3</sub>
Butane	4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	Eicosane	20	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> CH <sub>3</sub>
Pentane	5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	Heneicosane	21	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>19</sub> CH <sub>3</sub>
Hexane	6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	Docosane	22	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>20</sub> CH <sub>3</sub>
Heptane	7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	Tricosane	23	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>21</sub> CH <sub>3</sub>
Octane	8	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	Triacontane	30	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>28</sub> CH <sub>3</sub>
Nonane	9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	hentriacontane	31	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>29</sub> CH <sub>3</sub>
Decane	10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	Tetracontane	40	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>38</sub> CH <sub>3</sub>
Undecane	11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>	Pentacontane	50	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>48</sub> CH <sub>3</sub>
Dodecane	12	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	Hexacontane	60	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>58</sub> CH <sub>3</sub>
Tridecane	13	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub>	Heptacontane	70	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>68</sub> CH <sub>3</sub>
Tetradecane	14	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CH <sub>3</sub>	Octacontane	80	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>78</sub> CH <sub>3</sub>
Pentadecane	15	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> CH <sub>3</sub>	Nonacontane	90	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>88</sub> CH <sub>3</sub>
Hexadecane	16	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CH <sub>3</sub>	Hectane	100	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>98</sub> CH <sub>3</sub>

● **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

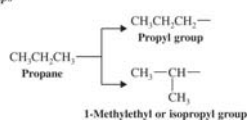
ALKANE		ALKYL GROUP	ABBREVIATION
CH <sub>3</sub> -H Methane	becomes	CH <sub>3</sub> - Methyl	Me-
CH <sub>3</sub> CH <sub>2</sub> -H Ethane	becomes	CH <sub>3</sub> CH <sub>2</sub> - Ethyl	Et-
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -H Propane	becomes	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> - Propyl	Pr-
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -H Butane	becomes	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> - Butyl	Bu-



- **Nomenclature of Branched Alkyl Chains**

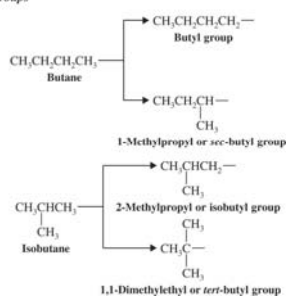
→ Two alkyl groups can be derived from propane

*Three-Carbon Groups*



→ Four groups can be derived from the butane isomers

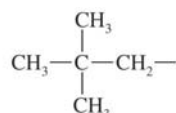
*Four-Carbon Groups*



Chapter 4

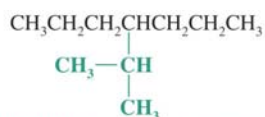
11

→ The neopentyl group is a common branched alkyl group

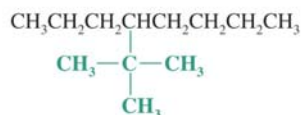


2,2-Dimethylpropyl or neopentyl group

→ Examples



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



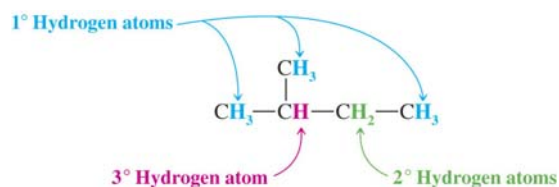
4-(1,1-Dimethylethyl)octane or 4-*tert*-butyloctane

Chapter 4

12

## ◆ Classification of Hydrogen Atoms

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



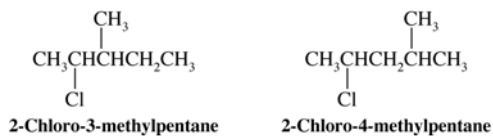
Chapter 4

13

## ● 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



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

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



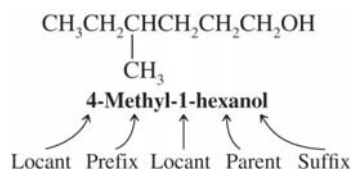
Chapter 4

14

- **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



- **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

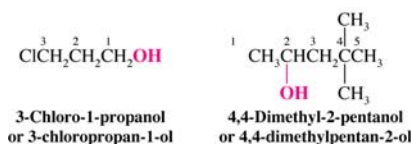
- Number the parent to give the hydroxyl the lowest possible number

- The other substituents take their locations accordingly

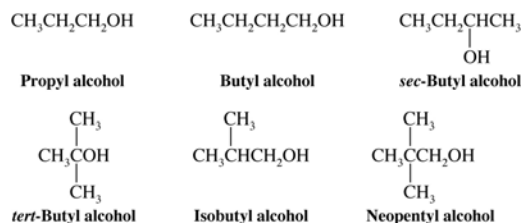
Chapter 4

15

- **Examples**



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

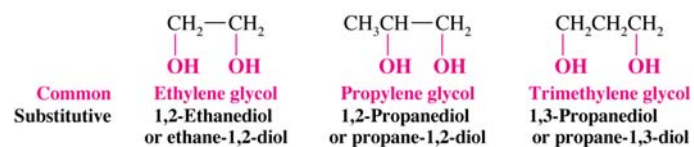


Chapter 4

16

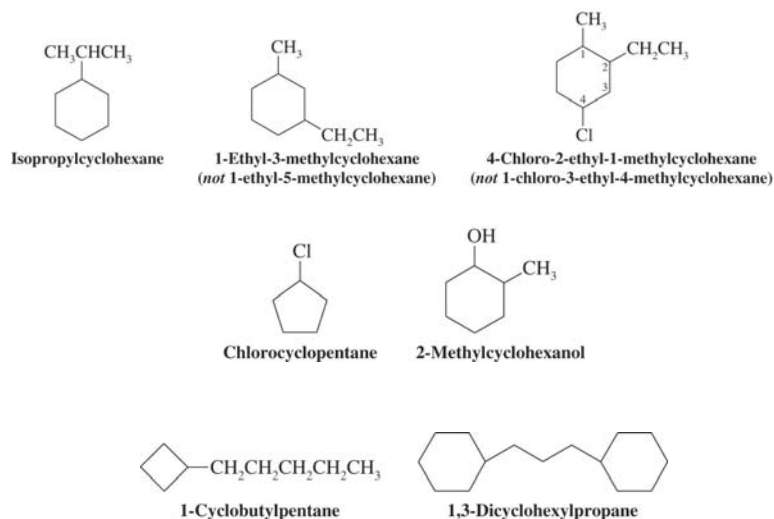


→ Alcohols with two hydroxyls are called diols in IUPAC nomenclature and glycols in common nomenclature



### ◆ 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

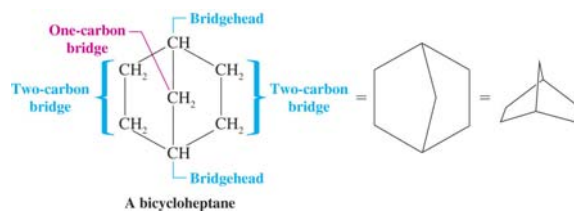


Chapter 4

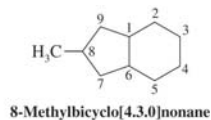
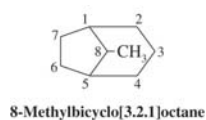
19

## ◆ 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



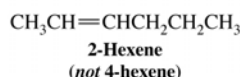
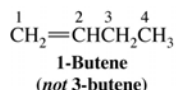
Chapter 4

20

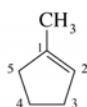
## ◆ Nomenclature of Alkenes and Cycloalkenes

→ 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

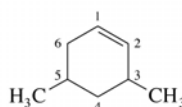
→ The compound is numbered to give one of the alkene carbons the lowest number



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



1-Methylcyclopentene  
(not 2-methylcyclopentene)



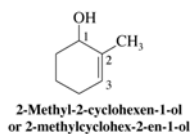
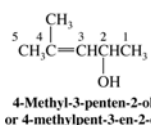
3,5-Dimethylcyclohexene  
(not 4,6-dimethylcyclohexene)

Chapter 4

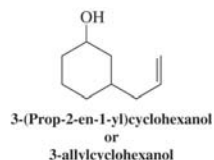
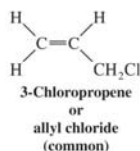
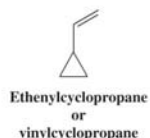
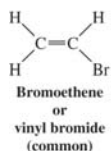
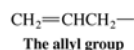
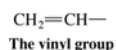
21

→ 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



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

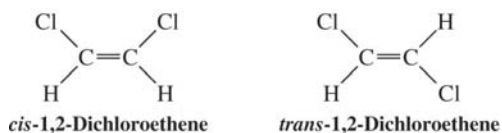


Chapter 4

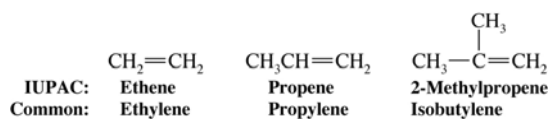
22

→ 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

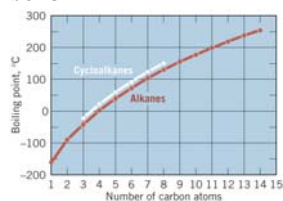


Chapter 4

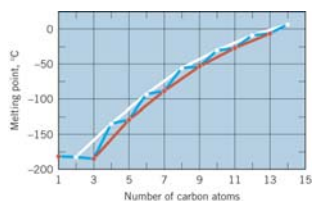
23

## ◆ 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



Chapter 4

24

## ◆ Sigma Bonds and Bond Rotation

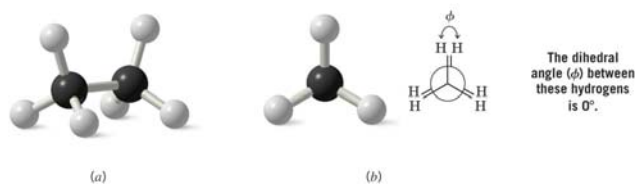
→ Ethane has relatively free rotation around the carbon-carbon bond

→ 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



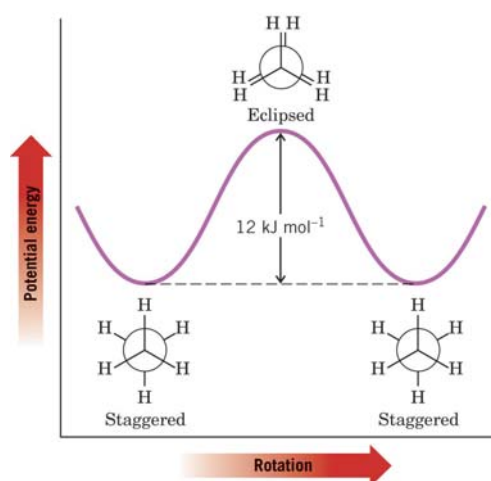
→ The eclipsed conformation has all C-H bonds on adjacent carbons directly on top of each other



Chapter 4

25

→ The potential energy diagram of the conformations of ethane shows that the staggered conformation is more stable than eclipsed by  $12 \text{ kJ mol}^{-1}$



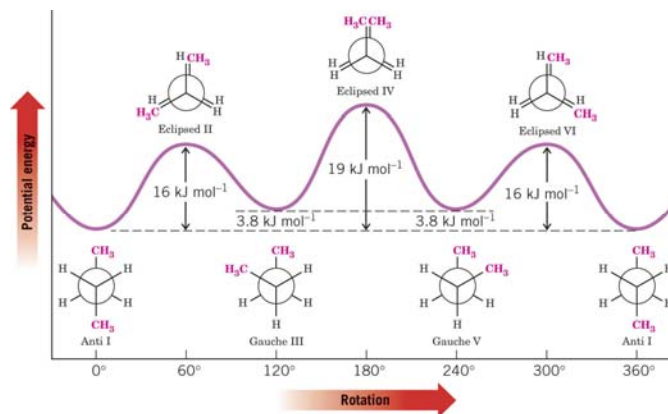
Chapter 4

26

## ◆ Conformational Analysis of Butane

→ Rotation around C<sub>2</sub>-C<sub>3</sub> of butane gives six important conformations

⌘ The gauche conformation is less stable than the anti conformation by 3.8 kJ mol<sup>-1</sup> because of repulsive van der Waals forces between the two methyls



Chapter 4

27

## ◆ The Relative Stabilities of Cycloalkanes: Ring Strain

→ Heats of combustion per CH<sub>2</sub> unit reveal cyclohexane has no ring strain and other cycloalkanes have some ring strain

Cycloalkane (CH <sub>2</sub> ) <sub>n</sub>	n	Heat of Combustion (kJ mol <sup>-1</sup> )	Heat of Combustion per CH <sub>2</sub> Group (kJ mol <sup>-1</sup> )	Ring Strain (kJ mol <sup>-1</sup> )
Cyclopropane	3	2091	697.0	115
Cyclobutane	4	2744	686.0	109
Cyclopentane	5	3320	664.0	27
Cyclohexane	6	3952	658.7	0
Cycloheptane	7	4637	662.4	27
Cyclooctane	8	5310	663.8	42
Cyclononane	9	5981	664.6	54
Cyclodecane	10	6636	663.6	50
Cyclopentadecane	15	9885	659.0	6
Unbranched alkane	—	—	658.6	—

Chapter 4

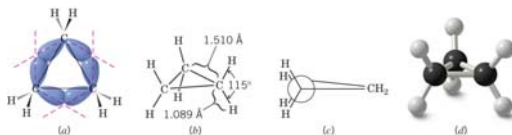
28

## ◆ The Origin of Ring Strain in Cyclopropane and Cyclobutane : Angle Strain and Torsional Strain

→ *Angle strain* is caused by bond angles different from  $109.5^\circ$

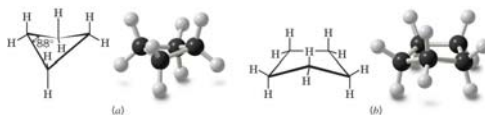
→ *Torsional strain* is caused by eclipsing C-H bonds on adjacent carbons

→ Cyclopropane has both high angle and torsional strain



→ Cyclobutane has considerable angle strain

↳ It bends to relieve some torsional strain



→ Cyclopentane has little angle strain in the planar form but bends to relieve some torsional strain

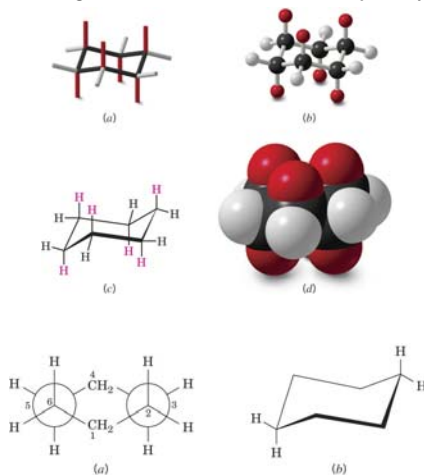
Chapter 4

29

## ◆ Conformations of Cyclohexane

→ The chair conformation has no ring strain

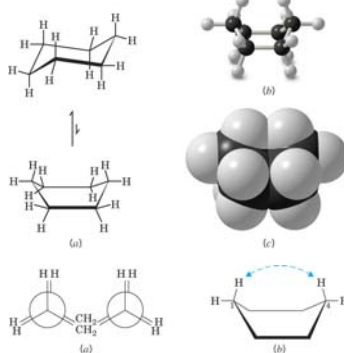
↳ All bond angles are  $109.5^\circ$  and all C-H bonds are perfectly staggered



Chapter 4

30

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



→ The twist conformation is intermediate in stability between the boat and the chair conformation

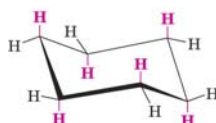


Chapter 4

31

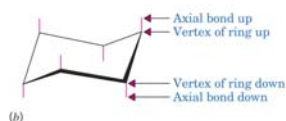
## ◆ Substituted Cyclohexanes: Axial and Equatorial Hydrogen Atoms

- 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



Chapter 4

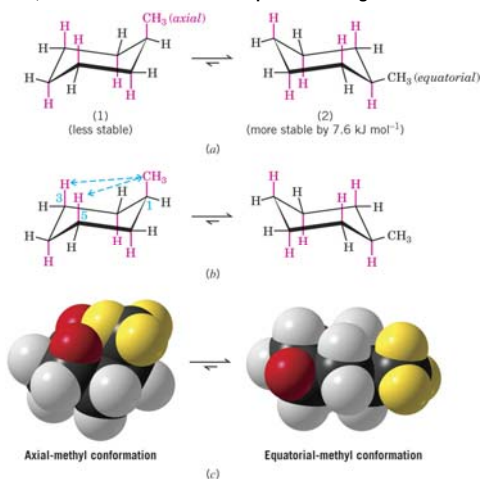
32



→ 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



Chapter 4

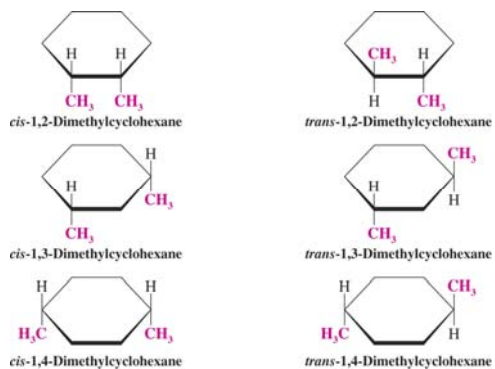
33

◆ Disubstituted Cycloalkanes

→ Can exist as pairs of cis-trans stereoisomers

⌘ Cis: groups on same side of ring

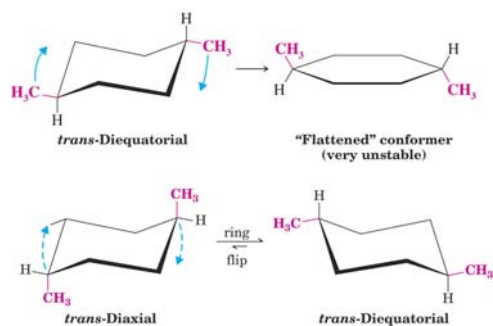
⌘ Trans: groups on opposite side of ring



Chapter 4

34

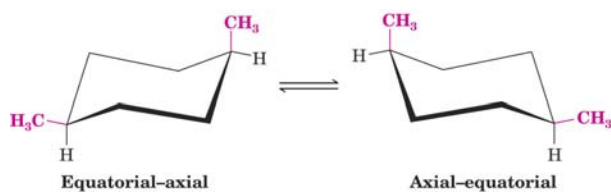
- **Trans-1,4-dimethylcyclohexane prefers a *trans*-diequatorial conformation**



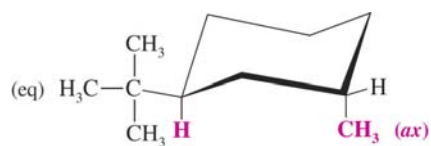
Chapter 4

35

- **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**

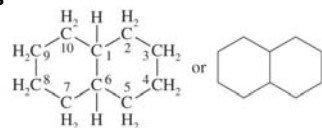


Chapter 4

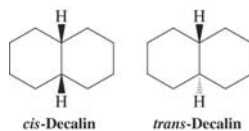
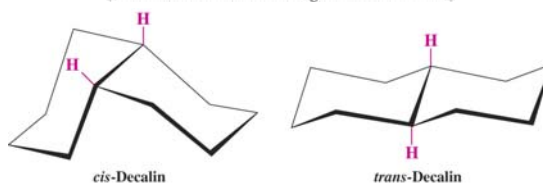
36

## ◆ 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)



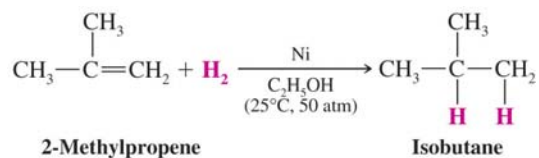
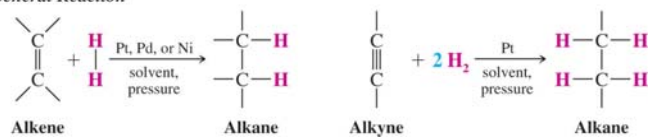
Chapter 4

37

## ◆ Synthesis of Alkanes and Cycloalkanes

### ● Hydrogenation of Alkenes and Alkynes

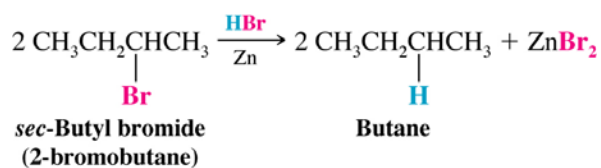
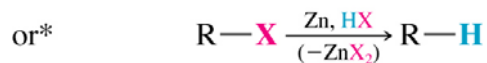
General Reaction



Chapter 4

38

• Reduction of Alkyl Halides

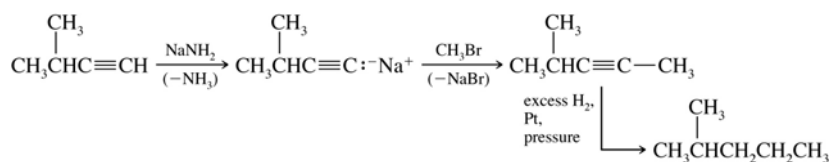
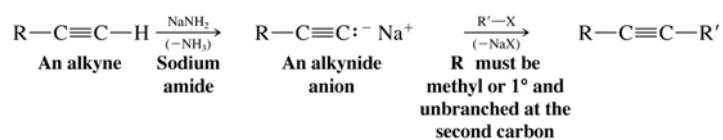


Chapter 4

39

• Alkylation of Terminal Alkynes

→ Alkynes can be subsequently hydrogenated to alkanes



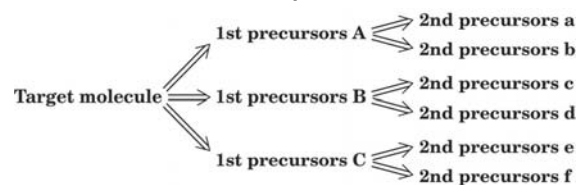
Chapter 4

40

## ◆ 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*

